

SPECIALIST PERIODICAL REPORTS

**Organic Compounds  
of Sulphur,  
Selenium, and Tellurium  
VOLUME 6**

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Selenium, and Tellurium

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Volume 6



A Specialist Periodical Report

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# Organic Compounds of Sulphur, Selenium, and Tellurium

Volume 6

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A Review of the Literature Published between  
April 1978 and March 1980

Senior Reporter

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# *Preface*

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These Reports cover the period April 1978 to March 1980 inclusive, except in the case of Chapter 2 Part III, where the period ends in February 1980.

The major changes in the format and contents of this volume have been necessitated by economic considerations. Sulphur-containing heteroaromatic compounds which previously were included in these Reports and in the Reports on 'Aromatic and Heteroaromatic Chemistry' are now covered in detail only in the new Reports, 'Heterocyclic Chemistry'. The literature on these compounds has been reviewed up to March 1978 in Volume 5 of this series and thereafter in Volume 1 of the new series. Highlights of the literature of these compounds are given as Chapter 6 of this volume. The organization of the remainder of this volume is essentially the same as that of Volume 5 except that the section on the ylides and carbanionic compounds of selenium and tellurium has been considerably extended and the coverage of Chapter 3, Part III has been extended to include dithiocarbamates, xanthates, and trithiocarbonates.

I would like to take this opportunity of expressing my appreciation to the contributors to this volume for all the care and effort they have put into their Reports. This has, of course, made my own task much less onerous than it could have been.

DRH





# Contents

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Chapter 1	Aliphatic Organosulphur Compounds Compounds with Exocyclic Sulphur Functional Groups, and their Selenium and Tellurium Analogues	1
	<i>By G. C. Barrett</i>	
<b>1</b>	<b>Textbooks and Reviews</b>	<b>1</b>
<b>2</b>	<b>Spectroscopic and Other Physical Properties of Organosulphur, Organoselenium, and Organotellurium Compounds</b>	<b>2</b>
	Molecular Orbital Calculations and Conformational Analysis	2
	Ultraviolet Spectra, Circular Dichroism, and Optical Rotatory Dispersion	3
	Infrared, Raman, and Microwave Spectra	3
	Nuclear Magnetic Resonance Spectra	4
	Mass Spectra	6
	Photoelectron Spectra	7
	Electron Diffraction	7
	Dipole Moments and Studies of the Kerr Effect	7
	X-Ray Crystal Analysis	8
	Electron Spin Resonance Spectra	8
<b>3</b>	<b>Thiols, Selenols, and Telluroles</b>	<b>8</b>
	Preparation	8
	Reactions	10
	Thiyl and Related Selenium Radicals	13
<b>4</b>	<b>Thiolesters, Selenolesters, and Tellurolesters</b>	<b>13</b>
	Preparation	13
	Reactions of Thiolacids and Thiolesters, Selenolesters, and Tellurolesters	14
<b>5</b>	<b>Sulphides, Selenides, and Tellurides</b>	<b>15</b>
	Preparation from Thiols, Selenols, and Telluroles	15
	Preparation from Sulphenyl and Selenenyl Halides	17
	Preparation from Disulphides, Diselenides, and Ditellurides	20
	Preparation from Thiocyanates, Selenocyanates, and Tellurocyanates	21
	Preparation using Other Sulphenylation, Selenenylation, and Tellurenylation Reagents	22

- Preparation using the Elements Themselves, or Other Inorganic  
Sulphur, Selenium, and Tellurium Compounds 23
- Miscellaneous Methods of Preparation 23
- Reactions of Sulphides: Simple Reactions and Fundamental  
Properties 24
- Reactions of Sulphides, Selenides, and Tellurides: Rearrange-  
ments, and C–S, C–Se, and C–Te Bond Cleavage Reactions 25
- Reactions of Sulphides, Selenides, and Tellurides: Effects  
of Neighbouring Functional Groups 27
- Uses of Saturated Sulphides, Selenides, and Tellurides  
in Synthesis 28
- Vinyl Sulphides, Selenides, and Tellurides 31
- Allenic Sulphides 36
- Allyl Sulphides and Selenides 37
- Acetylenic Sulphides 38
- 6 Naturally Occurring Organosulphur Compounds 39**
- 7 Sulphonium Salts 39**
- Trialkyl- and Triaryl-sulphonium, -selenonium,  
and -telluronium Salts 39
- Halogeno-sulphonium Salts 41
- Amino-sulphonium Salts 42
- Alkoxy-sulphonium Salts 42
- Alkylthio-sulphonium Salts 43
- 8 Thioacetals [1-(Alkylthio)alkyl Sulphides] and their Selenium  
Analogues 44**
- Saturated Thioacetals and Selenoacetals 44
- Keten Dithioacetals 46
- 9 Trithio-orthoesters [1,1-Bis(alkylthio)alkyl Sulphides] 47**
- 10 Sulphuranes and Hypervalent Sulphur, Selenium, and Tellurium  
Compounds 48**
- 11 Sulphoxides, Selenoxides, and Telluroxides 49**
- Preparation 49
- Deoxygenation of Sulphoxides, Selenoxides, and Telluroxides 51
- Reactions of Saturated Sulphoxides and Selenoxides 51
- Reactions of Unsaturated Sulphoxides and Selenoxides 55
- Physical Properties and Stereochemistry of Sulphoxides 57
- 12 Sulphones 57**
- Preparation of Saturated Sulphones 57
- Reactions of Saturated Sulphones 58
- Unsaturated Sulphones 59
- Sulphones Used in Synthesis 60
- 13 Sulphenic and Selenenic Acids, and their Derivatives 61**
- Sulphenic and Selenenic Acids 61

- Sulphenate Esters 62
- Sulphenyl and Selenenyl Halides 62
- Sulphenamides and Selenenamides 63
- Thionitrites and Thionitrates 64
- 14 Thiocyanates and Isothiocyanates, and their Selenium and Tellurium Analogues 64**
  - Thiocyanates 64
  - Isothiocyanates 66
- 15 Sulphinic and Seleninic Acids, and their Derivatives 67**
  - Sulphinic and Seleninic Acids 67
  - Sulphinyl and Seleninyl Halides 68
  - Sulphinates Esters 68
  - Sulphinamides 69
- 16 Sulphonic and Selenonic Acids, and their Derivatives 69**
  - Preparation of Sulphonic Acids 69
  - Reactions of Sulphonic and Selenonic Acids 70
  - Sulphonyl Halides 71
  - Sulphonate Esters 72
  - Sulphonyl Hypochlorites 73
  - Sulphonamides 73
  - Sulphonyl Azides, Azosulphones, and Sulphonyl Isocyanates 74
- 17 Disulphides, Diselenides, and Ditellurides 75**
  - Preparation 75
  - Reactions 76
- 18 Thiolsulphinates 76**
- 19  $\alpha$ -Disulphoxides 77**
- 20 Thiolsulphonates 77**

Chapter 2 Ylides of Sulphur, Selenium, and Tellurium, and Related Structures 79  
*By E. Block, D. L. J. Clive, N. Furukawa, and S. Oae*

Part I Ylides and Carbanionic Compounds of Sulphur 79  
*By E. Block*

- 1 Introduction 79**
- 2 Sulphonium Ylides 80**
  - Synthesis and Properties 80
  - Reactions 81
- 3 Oxosulphonium and Amino-oxosulphonium Ylides 84**
  - Synthesis and Properties 84
  - Reactions 84

- 4 Oxy- and Aza-sulphonium Ylides** 85  
 Oxysulphonium Ylides 85  
 Azasulphonium Ylides 87
- 5 Thiocarbonyl Ylides** 87
- 6 Sulphenyl Carbanions** 89  
 Synthesis and Properties 89  
 Reactions 90  
   1,3-Dithianyl Anions 90  
   Acyclic Thioacetal and Orthothioformate Anions 94  
   Thioallyl and Related Anions 97  
    $\alpha$ -Thiovinyl Anions 98  
   Miscellaneous  $\alpha$ -Thiocarbanions 100
- 7 Sulphinyl and Sulphiliminyll Carbanions** 102  
 Synthesis and Properties 102  
 Reactions 103
- 8 Sulphonyl and Sulphonimidoyl Carbanions** 106  
 Synthesis and Properties 106  
 Reactions 106

Part II Ylides and Carbanionic Compounds of Selenium  
 and Tellurium

112

*By D. L. J. Clive*

Reviews 112

- 1 Ylides** 112
- 2 Selenium-stabilized Carbanions** 112  
 Methods of Preparation 112  
   Deprotonation of Aryl Alkyl Selenides 113  
   Deprotonation of Selenoketals and Seleno-  
     orthoesters 114  
   Deprotonation of Benzyl Selenides 115  
   Deprotonation of Vinyl Selenides 115  
   Deprotonation of Allylic, Propargylic,  
     and Allenic Selenides 115  
   Deprotonation of Selenides that have an  
     Additional Anion-stabilizing Group 116  
   Formation by Michael Addition 116  
 Applications of Selenium-stabilized Carbanions 118  
   Based on C–Se Bond Cleavage in Selenoketals  
     and Seleno-orthoesters 118  
   Based on Deprotonation of Selenides that have  
     an Additional Anion-stabilizing Group 121

Based on Deprotonation of Selenoketals and Seleno-orthoesters	124
Based on Deprotonation of Vinyl Selenides	124
Based on Deprotonation of Benzyl Selenides	124
Based on Michael Addition to Phenyl Vinyl Selenide	124
Based on $\alpha$ -Lithio-selenoxides	125
Miscellaneous Studies on Selenium-stabilized Carbanions	126
Part III Compounds with S=N Functional Groups	126
<i>By S. Oae and N. Furukawa</i>	
Introduction	126
<b>1 Di-co-ordinate Sulphur</b>	127
Sulphinyl-amines and -amides	127
Structure	127
Preparation and Reactions	127
Sulphur Di-imides	130
Preparation and properties of (SN) <sub>x</sub>	130
Tetrasulphur Tetranitride	131
Preparation of Other Sulphur Di-imides	131
Reactions	132
Structure	133
Thione S-Imides	133
<b>2 Tri-co-ordinate Sulphur</b>	133
Sulphonylamines and Sulphur Tri-imides	133
Sulphimides and Azasulphonium Salts	134
Preparation and Structure of Sulphimides	134
Reactions of Sulphimides and Azasulphonium Salts	136
Sulphonamidines	140
Preparation of Azasulphonium Salts	141
<b>3 Tetra-co-ordinate Sulphur</b>	143
Sulphoximides	143
Sulphodi-imides	147
<b>4 Selenium and Tellurium Analogues</b>	147
Chapter 3 Thiocarbonyl and Selenocarbonyl Compounds	148
<i>By D. R. Hogg, J. K. Landquist, and A. Ohno</i>	
Part I Thioaldehydes, Thioketones, Thioketens, and their Selenium Analogues	148
<i>By A. Ohno</i>	
Reviews	148

<b>1 Thioaldehydes and Selenoaldehydes</b>	148
Synthesis	148
Transient Species	148
Mass Spectrometry	150
Molecular Orbital Calculations	150
<b>2 Thioketones</b>	150
Synthesis	150
Reactions	152
Spectroscopy	157
<b>3 Thioketens and Selenoketens</b>	158
Synthesis	158
Reactions	159
Spectroscopy	160
Part II Sulphines and Sulphenes	160
<i>By D. R. Hogg</i>	
<b>1 Sulphines</b>	160
<b>2 Sulphenes</b>	163
Part III Thioureas, Thiosemicarbazides, Thioamides, Thiono- and Dithio-carboxylic Acids, and their Selenium Analogues	165
<i>By J. K. Landquist</i>	
Reviews	165
<b>1 Thioureas and Selenoureas</b>	165
Synthesis	165
Physical Properties	168
Reactions	169
Oxidation	169
Alkylation	169
Acyl Derivatives	170
Additions to Multiple Bonds	170
Formation of Thiazoles	172
Miscellaneous Reactions	173
<b>2 Thiosemicarbazides, Dithiocarbazates, and Thiocarbohydrazides</b>	174
Synthesis	174
Physical Properties	174
Reactions	175

<b>3 Thioamides and Selenoamides</b>	177
Synthesis	177
Physical Properties	180
Reactions	182
Hydrolysis	182
Oxidation	182
Alkylation and Arylation	183
Nucleophilic Reactions of the $\alpha$ -Carbon Atom	184
Diels–Alder and Similar Reactions	184
Additions to $\alpha\beta$ -Unsaturated Thioamides	185
Displacement of Sulphur	185
Synthesis of Thiazole Derivatives	186
Synthesis of Other Heterocyclic Compounds	188
Miscellaneous	189
<b>4 Thiono- and Dithio-carboxylic Acids, their Derivatives, and their Selenium Analogues</b>	189
Synthesis of Derivatives of Thionocarboxylic Acids	189
Synthesis of Dithiocarboxylic Acids and their Derivatives	191
Physical Properties	194
Reactions	194
<b>5 Thio- and Dithio-carbamates</b>	197
Synthesis	197
Physical Properties	199
Reactions	199
<b>6 Xanthates and Trithiocarbonates</b>	203
Preparation	203
Physical Properties	204
Reactions	204
Chapter 4 Small-ring Compounds of Sulphur and Selenium	207
<i>By C. G. Venier</i>	
<b>1 Thiirans (Episulphides)</b>	207
Reviews	207
Formation	207
Reactions	210
<b>2 Thiiran Oxides (Episulphoxides and Episulphones)</b>	215
<b>3 Thiiranium Ions (Episulphonium Ions)</b>	215
<b>4 Thiirens and Thiiren Oxides</b>	216
<b>5 Three-membered Rings with More than One Heteroatom</b>	218
<b>6 Thietans</b>	219
Formation	219
Reactions	220

- 7 Thietan Oxides and Imides** 222
  - Formation 222
  - Reactions 222
- 8 Thiet and its Derivatives** 223
  - Formation 223
  - Reactions 224
- 9 Dithietans, Dithiets, and their Derivatives** 224
  - 1,2-Dithietans 224
  - 1,2-Dithiets 224
  - Formation of 1,3-Dithietans 225
  - Reactions of 1,3-Dithietans 226
  - Selenium Derivatives 226
- 10 Four-membered Rings containing Sulphur and Oxygen** 226
- 11 Four-membered Rings containing Sulphur and Nitrogen and/or Phosphorus** 227
  - 1,2-Thiazetidines and their Derivatives 227
  - 1,3-Thiazetidines and their Derivatives 228
  - Other Four-membered Rings containing Sulphur and Nitrogen 228
  - 1,3,2,4-Dithiadiphosphetans 229
  - Four-membered Rings containing Sulphur, Nitrogen, and Phosphorus 230
  - Selenium Derivatives 231
- 12 Four-membered Rings containing Sulphur and Silicon or Germanium** 231
- 13 Thiadiazaboretidines** 231
- 14 Bibliography** 232

Chapter 5 Saturated Cyclic Compounds of Sulphur, Selenium, and Tellurium 233  
*By P. K. Claus*

- 1 Introduction** 233
- 2 Thiolans, Thians, Thiepan, Thiocans, and their Oxides, Dioxides, and Imides** 233
  - Synthesis 233
  - Properties 242
  - Reactions 247
- 3 Compounds containing Two or More Sulphur Atoms in the Ring** 253
  - Di- and Poly-sulphides 253
  - 1,3-Dithiolans, 1,3-Dithians, 1,4-Dithians, and 1,3,5-Trithians 254
  - Medium-sized Dithiacycloalkanes 261



- 4 Sulphur- and Oxygen-containing Rings** 263
  - Sultenes, Sultines, and Sultones 263
  - 1,3-Oxathiolans and 1,3- and 1,4-Oxathians 264
  - Cyclic Sulphites and Sulphates 266
  - Selenium- and Tellurium-containing Rings 268

Chapter 6 Heteroaromatic Compounds of Sulphur,  
Selenium, and Tellurium 271  
*By M. Davis*

- 1 Introduction** 271
- 2 Theoretical and Spectroscopic Studies** 271
  - Molecular Orbital Calculations 271
  - Nuclear Magnetic Resonance 272
- 3 Thiophens, Selenophens, and Tellurophens** 273
  - General 273
  - Ring Synthesis and Destruction 273
  - Reactions and Reactivity 276
  - Rate Data, Substituent Effects, and Hammett Relationships 277
  - Synthetic Uses of Thiophen Derivatives 277
  - Naphthothiophens, especially Thiapseudophenalenones 278
  - Thiophen Rings Fused to other Heteroaromatic Systems that do not contain S, Se, or Te 278
    - Thieno- and Selenolo-pyrroles 278
    - Thienopyridines 278
  - Polythiophens and Related Systems 279
  - Non-classical Thiophens 281
  - Selenophens and Tellurophens 281
- 4 Thiopyrylium and Selenopyrylium Salts** 282
- 5 Thiazoles and Selenazoles** 283
  - General 283
  - Mass Spectrometry 283
  - Synthesis and Reactions 273
  - Fused Systems containing Thiazole 284
  - Selenazoles 285
- 6 Isothiazoles, Isoselenazoles, and Isotellurazoles** 286
  - Synthesis 286
  - Reactions 288
  - Isothiazoles Fused to other Nitrogen-containing Heterocycles 289
  - 1,2-Benzisoselenazole and 1,2-Benzisotellurazole 290

- 7 Oxathiolium and Dithiolium Salts** 290  
General 290  
Synthesis 291  
Physical and Chemical Properties 291
- 8 Thiadiazoles and Related Compounds** 292  
Synthesis of Thiadiazoles 292  
The First S<sup>II</sup>-N Bond in a Natural Product? 293  
Synthesis of Selenadiazoles 293  
Photolysis and Thermolysis of Thiadiazoles and  
Selenadiazoles 294
- 9 Benzodithiazolium Salts and their Selenium Analogues** 295
- 10 Compounds with Two Fused Aromatic Rings, each  
containing Sulphur or Selenium Atoms** 296  
Thienothiophens and their Selenium Analogues 296  
Thienothiazoles and Selenothiazoles 296  
Thienoisothiazoles 297  
Meso-ionic Thiazolo[2,3-*b*]thiazoles 299
- 11 1,6-Dihetera-6a  $\lambda^4$ -thiapentalenes and Related Systems** 299  
Synthesis 299  
Structural and Spectroscopic Studies 300  
'Bond Switch' at  $\pi$ -Hypervalent Sulphur 301

# Abbreviations

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The following abbreviations have been used:

c.d.	circular dichroism
c.i.d.n.p.	chemically induced dynamic nuclear polarization
c.i.m.s.	chemical ionization mass spectrometry
e.s.r.	electron spin resonance
i.r.	infrared
n.q.r.	nuclear quadrupole resonance
p.e.	photoelectron
u.v.	ultraviolet
FVP	flash vacuum pyrolysis
g.l.c.	gas-liquid chromatography
ASIS	aromatic-solvent-induced shift
LIS	lanthanide-induced shift
NOE	nuclear Overhauser effect
CNDO	complete neglect of differential overlap
HOMO	highest occupied molecular orbital
M.O.	molecular orbital
e.e.	enantiomeric excess
AIBN	azobis(isobutyronitrile)
DABCO	1,5-diazabicyclo[2.2.2]octane
DCCI	dicyclohexylcarbodi-imide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulphoxide
HMPA	hexamethylphosphoric acid triamide
LDA	lithium di-isopropylamide
LAH	lithium aluminium hydride
NBS	<i>N</i> -bromosuccinimide
NCS	<i>N</i> -chlorosuccinimide
MCPBA	<i>m</i> -chloroperoxybenzoic acid
PPA	polyphosphoric acid
py	pyridine
TCNE	tetracyanoethylene
TCNQ	tetracyanoquinodimethane
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride

THF tetrahydrofuran

TMEDA tetramethylethylenediamine

Vol. 5, Reference back to a preceding Volume of this series of

Vol. 4 'Specialist Periodical Reports'

# Aliphatic Organosulphur Compounds, Compounds with Exocyclic Sulphur Functional Groups, and their Selenium and Tellurium Analogues

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BY G. C. BARRETT

In spite of the large number of literature citations included in this Chapter, many of the routine papers on preparative chemistry have been excluded. The fact that so much work has been considered worthy of inclusion in this review on the basis of novelty and importance testifies as much to the intricacies and surprises still being found in the chemistry of sulphur- and selenium-containing functional groups as to the continuing growth in importance of these compounds in organic synthesis.

## 1 Textbooks and Reviews

Books published recently include several that are wholly devoted to organosulphur compounds<sup>1a-d</sup> and others<sup>1e-i</sup> in which specific chapters are relevant to the coverage in this chapter. Reviews<sup>2</sup> have appeared that deal with applications of organosulphur compounds in synthesis<sup>2a-d</sup> (including uses of  $\beta$ -keto-sulphides,<sup>2b</sup> vinyl sulphones,<sup>2d</sup> and vinyl sulphides<sup>2e</sup>) and the synthesis of organosulphur compounds,<sup>2f</sup> sulphenyl compounds,<sup>2g</sup> indolethiols,<sup>2h</sup> allenic sulphides<sup>2i</sup> and sulphenamides,<sup>2j</sup> organosilyl sulphides, selenides, and tellurides,<sup>2k</sup> optically active

<sup>1</sup> (a) 'Natural Sulphur Compounds', ed. D. Cavallini, G. E. Gaull, and V. Zappia, Plenum Press, New York and London, 1980; (b) H. Kwart and K. King, 'd-Orbitals in the Chemistry of S, Si, and P', Springer Verlag, Weinheim, 1977; (c) 'Sulfur Reports', ed. A. Senning, Horwood, Chichester, Vol. 1, 1980; (d) 'Topics in Organic Sulphur Chemistry: Proceedings of the 8th International Symposium on Organic Sulphur Chemistry, Portoroz, Yugoslavia', ed. M. Tisler, University Press Ljubljana, 1978; (e) 'Comprehensive Organic Chemistry', ed. Sir Derek H. R. Barton and W. D. Ollis, Pergamon Press, Oxford, 1979; (f) in 'Methodicum Chemicum', 1978, Vol. 7, Part B (ed. F. Korte, Academic Press, New York, 1978), R. M. Wilson and D. N. Buchanan, p. 585 (thiols and thiocarbonyl compounds), K. J. Wynne and I. Haiduc, p. 652 (sulphinyl compounds), and I. Haiduc and K. J. Wynne, p. 670 (sulphonyl compounds); (g) H. J. Reich, in 'Oxidations in Organic Chemistry, Part C', ed. W. S. Trahanovsky, Academic Press, New York, 1978; (h) Sir Derek H. R. Barton and S. V. Ley, *Ciba Found Symp.*, 1978, No. 53, p. 53; (i) 'Chemistry of the Sulphonium Group', ed. S. Patai and C. J. M. Stirling, Wiley, Chichester, 1981.

<sup>2</sup> (a) B. M. Trost, *Acc. Chem. Res.*, 1978, 11, 453; (b) B. M. Trost, *Chem. Rev.*, 1978, 78, 363; (c) L. Field, *Synthesis*, 1978, 713; (d) M. Julia, D. Uguen, A. Righini, M. Launay, and J. N. Verpeaux, *Int. Congr. Ser.-Excerpta Med.*, 1979, 457, 163; (e) S. Blechert, *Nachr. Chem. Tech. Lab.*, 1979, 27, 634; (f) G. Tsuchihashi, *Kagaku Sosetsu*, 1978, 19, 75; (g) E. Kuehle, *Chem. Labor. Betr.*, 1979, 30, 373; (h) T. F. Spande, *Chem. Heterocycl. Compd.*, 1979, 25, 1; (i) W. Reichen, *Chem. Rev.*, 1978, 78, 569; (j) F. A. Davis and U. K. Nadir, *Org. Prep. Proced. Int.*, 1979, 11, 33; (k) D. Brandes, *J.*

(continued overleaf)

sulphur compounds,<sup>2l</sup> sulphur-centred radicals,<sup>2m</sup> episulphonium intermediates,<sup>2n</sup> barriers to S–N bond rotation in sulphenamides,<sup>2o</sup> 1,2-phenylthio-shifts,<sup>2p</sup> thio-Claisen rearrangements,<sup>2q</sup> Pummerer reactions,<sup>2r</sup> and Ramberg–Bäcklund rearrangements.<sup>2s</sup> A review of nucleofugacity of different leaving groups in elimination reactions concerns several sulphur-containing functional groups.<sup>2t</sup>

Organoselenium chemistry has been reviewed from the point of view of applications in synthesis in general,<sup>2u</sup> and for mild oxidative transformations,<sup>18,h</sup> as well as for its relevance in biochemistry.<sup>2v</sup> Coverage of the 1976–7 literature for organotellurium chemistry has been published.<sup>2w</sup>

## 2 Spectroscopic and Other Physical Properties of Organosulphur, Organoselenium, and Organotellurium Compounds

**Molecular Orbital Calculations and Conformational Analysis.**—*syn* Conformations are preferred for vinyl mercaptan,<sup>3,4</sup> for methyl vinyl sulphide,<sup>4</sup> and for methyl allenyl sulphide.<sup>4</sup> Similar M.O. studies of 1,1-bis(methylthio)ethylene,<sup>5</sup> simple dithioacetals,<sup>6</sup> and 1,2-dithiols and 1,2-bis(methylthio)ethane<sup>6</sup> relate to conformational aspects. Continuing themes are represented in alternative explanations for the role of the sulphur atom in determining which proton is most readily released from unsymmetrical sulphides  $R^1CH_2SCH_2R^2$  (both hyperconjugation and C–S polarization are involved<sup>7</sup>). The stabilization of the  $\alpha$ -carbanion is accounted for by the ability of the sulphur atom to allow excess negative charge to encroach into its *sp*-valence shell.<sup>8</sup> Activation of dioxygen by sulphonium salts arises through orbital interactions.<sup>9</sup>

Molecular Orbital (M.O.) studies of reaction intermediates have been reported for the rearrangement of 1-propenethiol,<sup>10</sup> for the addition of sulphenyl halides to ethylene (sulphurane rather than thiiranium salt as intermediate),<sup>11</sup> and for similar additions to alkynes (thiirenium ions or  $\beta$ -alkylthiovinyl cations, depending upon the substituents).<sup>12</sup> Electronic effects of substituents on energy levels of orbitals of

(reference 2 continued)

*Organomet. Chem., Libr.*, 1979, 7, 257; (l) A. Nudelman, *Phosphorus Sulfur*, 1976, 2, 51; (m) K. D. Asmus, *Acc. Chem. Res.*, 1979, 12, 436; (n) V. A. Smit, N. S. Zefirov, I. V. Bodrikov, and M. Z. Krimer, *ibid.*, 1979, 12, 282; (o) G. Yamamoto, *Kagaku No Ryoiki*, 1978, 32, 207; (p) S. Warren, *Acc. Chem. Res.*, 1978, 11, 401; (q) L. Morin, J. Lebaud, D. Paquer, R. Chaussin, and D. Barillier, *Phosphorus Sulfur*, 1979, 7, 69; (r) T. Numata, *Yuki Gosei Kagaku Kyokaiishi*, 1978, 36, 845; (s) L. A. Paquette, *Org. React.*, 1977, 25, 1; (t) C. J. M. Stirling, *Acc. Chem. Res.*, 1979, 12, 198; (u) H. J. Reich, *ibid.*, 1979, 12, 22; J. V. Comasseto, J. T. B. Ferreira, and M. Marcuzzo do Canto, *Quim. Nova*, 1979, 2, 58; K. Kondo and N. Sonoda, *Kagaku (Kyoto)*, 1979, 34, 652 and *Yuki Gosei Kagaku Kyokaiishi*, 1979, 37, 1047; (v) C. P. Downes, C. A. MacAuliffe, and M. R. C. Winter, *Inorg. Perspect. Biol. Med.*, 1979, 2, 241; (w) K. J. Irgolic, *J. Organomet. Chem.*, 1978, 158, 235.

<sup>3</sup> D. G. Lister and P. Palmieri, *J. Mol. Struct.*, 1978, 48, 133.

<sup>4</sup> J. Kao, *J. Am. Chem. Soc.*, 1978, 100, 4685.

<sup>5</sup> G. De Alti, P. Declava, and A. Sgamellotti, *J. Mol. Struct.*, 1979, 53, 129.

<sup>6</sup> M. Ohsaku, N. Bingo, W. Sugikawa, and H. Murata, *Bull. Chem. Soc. Jpn.*, 1979, 52, 355.

<sup>7</sup> W. T. Borden, E. R. Davidson, N. H. Andersen, A. D. Denniston, and N. D. Epiotis, *J. Am. Chem. Soc.*, 1978, 100, 1604.

<sup>8</sup> J. Fabian, P. Schoenfeld, and R. Mayer, *Phosphorus Sulfur*, 1976, 2, 151.

<sup>9</sup> K. Ohkubo, Y. Azuma, and H. Sato, *Oxid. Commun.*, 1979, 1, 49.

<sup>10</sup> V. I. Minkin and R. M. Minyaev, *Zh. Org. Khim.*, 1979, 15, 1569.

<sup>11</sup> V. M. Csizmadia, *Prog. Theor. Org. Chem.*, 1977, 2, 280.

<sup>12</sup> I. G. Csizmadia, V. Lucchini, and G. Modena, *Gazz. Chim. Ital.*, 1978, 108, 543.

sulphur provide the motivation for M.O. studies of substituted phenyl methyl sulphides,<sup>13-15</sup> aryl trifluoromethyl sulphones,<sup>16</sup> and substituted styryl sulphones.<sup>17</sup>

Force-field analysis assigns the *gauche* conformation to  $H_2S_4$  and  $Me_2S_4$ .<sup>18</sup> Continuing studies (see Vol. 5, pp. 2, 7) indicate a preference for the equatorial orientation of the MeS substituent in 5-methylthio-1,3-dithians, although comparison of experiment with theory indicates the limited success of the calculations, since the equatorial preference is substantially larger than predicted.<sup>19</sup> The dangers of generalizations are implied in the results of conformational analysis of  $\alpha$ -substituted cyclohexanones, since the order  $PhSO_2$ , PhS, PhSO emerges for the preferred adoption of the axial conformation,<sup>20</sup> in contrast to the order MeS, MeSO,  $MeSO_2$  established earlier<sup>21</sup> for the corresponding cyclohexanones.

#### Ultraviolet Spectra, Circular Dichroism, and Optical Rotatory Dispersion.—

Routine u.v. studies of the effects of sulphur-containing groups on the spectral absorption characteristics of substituted benzenes (references are collected at the end of this section) continue along familiar lines (see Vol. 5, p. 4). A model for the thioindigo chromophore, *i.e.*  $MeCOC(SMe)=C(SMe)COMe$ , has been shown by X-ray studies<sup>22</sup> to be non-planar, as a result of repulsion between methyl groups.

Studies of the circular dichroism of acyl derivatives of thiolycerols<sup>23</sup> and of 2- or 3-phenylalkyl isothiocyanates<sup>24</sup> constitute extensions of earlier work.

**Additional Bibliography:** B. Yu. Sultanov, B. A. Tagiev, and N. G. Radzhabov, *Azerb. Khim. Zh.*, 1979, 96 [thiophenols]; G. C. Chmutova, A. A. Karel'ov, and N. N. Vtyurina, *Zh. Obshch. Khim.*, 1979, 49, 2275 [solvent effects;  $PhXMe$  ( $X = O, S, Se, \text{ or } Te$ )]; V. Baliah and V. M. Kanagasabapathy, *Indian J. Chem., Sect. A*, 1978, 16, 388 [*p*-dimethylaminophenyl sulphides]; G. V. Ratovskii, T. I. Rozova, M. A. Vasileva, and T. I. Bychkova, *Teor. Eksp. Khim.*, 1978, 14, 245 [vinyl sulphones]; Yu. I. Naumov and V. A. Izmailskii, *Zh. Fiz. Khim.*, 1979, 53, 2030 [*p*-hydroxyphenyl sulphones]; A. F. Moskvin, L. I. Doktorova, E. I. Kazankina, I. A. Reznikova, and V. A. Belyaev, *Zh. Obshch. Khim.*, 1979, 49, 619 [anilinesulphonic acids].

**Infrared, Raman, and Microwave Spectra.**—Brief details of studies which provide information on conformations and electron distributions are summarized at the end of this section. A comparison of the polarized Raman spectra for  $(C^2H_3)_2SO_2$  with far-i.r. data for  $Me_2SO_2$ <sup>25</sup> and polarized i.r. spectra for aryl thiocyanates and selenocyanates<sup>26</sup> represent less routine studies.

<sup>13</sup> G. A. Chmutova, N. N. Vtyurina, T. V. Komina, I. G. Gazizov, and H. Bock, *Zh. Obshch. Khim.*, 1979, 49, 192.

<sup>14</sup> G. A. Chmutova, N. N. Vtyurina, and H. Bock, *Dokl. Akad. Nauk SSSR*, 1979, 244, 1138.

<sup>15</sup> T. Matsuchita, Y. Osamura, N. Misawa, K. Nishimoto, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1979, 52, 2521.

<sup>16</sup> Yu. P. Egorov, Yu. Ya. Borovikov, S. I. Vdovenko, V. E. Didkovskii, V. N. Boiko, and G. M. Shchupak, *Teor. Eksp. Khim.*, 1978, 14, 84 (*Chem. Abstr.*, 1979, 89, 59 523).

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<sup>18</sup> M. Askari, *Tetrahedron Lett.*, 1979, 3173.

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<sup>20</sup> H. Ozbal and W. W. Zajac, *Tetrahedron Lett.*, 1979, 4821.

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<sup>26</sup> E. G. Yarkova, N. R. Safullina, G. A. Chmutova, and I. V. Bautina, *Zh. Obshch. Khim.*, 1979, 49, 2025.

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**Nuclear Magnetic Resonance Spectra.**—Long-range coupling involving the thiol proton and ring protons in 2-methoxybenzenethiol,<sup>27</sup> halogenobenzenethiols,<sup>28</sup> and 2-hydroxybenzenethiol<sup>29</sup> has been suggested to indicate an out-of-plane conformational preference for the SH group in thiophenols (see also Vol. 5, p. 6), and hence reveals an important contrast with the analogous phenols. Other non-routine <sup>1</sup>H n.m.r. studies include those of lanthanide-induced shifts of sulphonium salts<sup>30</sup> and of alkylsulphinylmethyl alkyl sulphides<sup>31</sup> and assignment of the zwitterionic structure (1) to the Schiff bases derived from *o*-formylbenzenethiol.<sup>32</sup> Brief details of other <sup>1</sup>H n.m.r. work (but excluding data compilations) are collected together at the end of this section, where details of <sup>13</sup>C n.m.r. studies are also to be found. More complete coverage of the <sup>13</sup>C n.m.r. literature has been attempted, since missing details are still being located, with the objective of providing a full assessment of the influence of adjacent sulphur-containing functional groups on chemical shifts.

Nitrogen-15 n.m.r. spectra of alkanesulphonamides,<sup>33</sup> benzenesulphonamides,<sup>34</sup> and isothiocyanates<sup>36</sup> have been reported. Nitrogen-14 n.q.r. data on methane-sulphonamide<sup>36</sup> and *NN*-disubstituted analogues<sup>37</sup> have established a valuable application of the technique, *i.e.* to assess the degree of delocalization of the lone

<sup>27</sup> T. Schaefer and T. A. Wildman, *Can. J. Chem.*, 1979, **57**, 450.

<sup>28</sup> T. Schaefer and W. J. E. Parr, *Can. J. Chem.*, 1979, **57**, 1421.

<sup>29</sup> T. Schaefer, T. A. Wildman, and S. R. Salman, *J. Am. Chem. Soc.*, 1980, **102**, 107.

<sup>30</sup> R. L. Caret and A. N. Vennos, *J. Org. Chem.*, 1980, **45**, 361.

<sup>31</sup> P. R. Jones, D. F. Sesin, and J. J. Uebel, *Phosphorus Sulfur*, 1978, **4**, 277.

<sup>32</sup> M. F. Corrigan, I. D. Rae, and B. O. West, *Aust. J. Chem.*, 1978, **31**, 587.

<sup>33</sup> H. R. Kricheldorf, *Angew. Chem.*, 1978, **90**, 489.

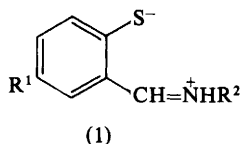
<sup>34</sup> I. I. Schuster, S. H. Doss, and J. D. Roberts, *J. Org. Chem.*, 1978, **43**, 4693.

<sup>35</sup> I. Yavari, J. S. Staral, and J. D. Roberts, *Org. Magn. Reson.*, 1979, **12**, 340.

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<sup>37</sup> D. Ya. Osokin and G. G. Butenko, *Zh. Fiz. Khim.*, 1979, **53**, 130.





pair that is formally located on nitrogen in such compounds.<sup>37</sup> Chlorine-35 n.q.r. studies on  $\alpha$ -chloroalkyl sulphides have been reported.<sup>38</sup>

Selenium-77 n.m.r. data for selenols, selenides, selenonium salts, diselenides, and selenoxy-acids<sup>39</sup> have been obtained under conditions (*i.e.* on the same spectrometer) which allow reliable comparisons of spectral parameters to be made. Benzeneseleninic acids<sup>40</sup> and selenolesters<sup>41</sup> have also been studied by this technique, and <sup>77</sup>Se spin-lattice relaxation times of organoselenium compounds have been collected in a pioneering study.<sup>41a</sup>

Tellurium-125 n.m.r. spectra of telluroesters have been determined.<sup>41</sup>

**Additional Bibliography:** *Proton n.m.r.* G. Llabres, M. Baiwir, L. Christiaens, and J. L. Piette, *Can. J. Chem.*, 1979, **57**, 2967 and G. Llabres, M. Baiwir, L. Christiaens, J. Denoel, L. Laitem, and J. L. Piette, *ibid.*, 1978, **56**, 2003 [PhXMe (X = O, S, Se, or Te) shown to adopt a screw conformation]; W. Walek, A. Priess, and S. Dietzel, *Z. Chem.*, 1978, **18**, 144 [*Z/E* isomerism of RSC(SMe)=NCN]; C. Fournier, B. Lemarie, B. Braillon, D. Paquer, and M. Vazeux, *Org. Magn. Reson.*, 1977, **10**, 20 [cyclobutane-1,1-dithiol]; F. Alcudia, J. L. Garcia Ruano, J. Rodriguez, and F. Sanchez, *Can. J. Chem.*, 1979, **57**, 2420 [ $\beta$ -hydroxyalkyl sulphides, sulphoxides, sulphones, and sulphonium salts, interpreted in terms of conformations]; Y. Takeda, T. Matsuda, and T. Tanaka, *Org. Magn. Reson.*, 1977, **10**, 98 [thiuram mono- and di-sulphides]; A. D. Pershin, I. Kende, V. Cholvad, and K. Mach, *Collect. Czech. Chem. Commun.*, 1978, **43**, 1349 [c.i.d.n.p. in radical recombination in reaction mixtures of azoisobutyronitrile and tetraethylthiuram disulphide]; I. D. Sadekov, A. Ya. Bushkov, and V. P. Metlushenko, *Zh. Obshch. Khim.*, 1978, **48**, 1658 [aryltellurium(IV) halides and isothiocyanates]; I. D. Sadekov, M. L. Cherkinskaya, V. L. Pavlova, V. A. Bren, and V. I. Minkin, *Zh. Obshch. Khim.*, 1978, **48**, 390 [diaryltellurium(IV) halides]; **Carbon-13 n.m.r.** G. Dauphin and A. Cuer, *Org. Magn. Reson.*, 1979, **12**, 557 [MeSH, Me<sub>2</sub>S, Me<sub>2</sub>S<sub>2</sub>, Me<sub>2</sub>S<sub>3</sub>, and EtSSMe]; J. Sandstrom and I. Wennerbeck, *Acta Chem. Scand. Ser. B*, 1978, **32**, 421 [ $\beta$ -dimethylaminovinyl methyl sulphides]; G. A. Kalabin, D. F. Kushnarev, T. G. Mannafov, and A. A. Retinski, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2410; G. A. Kalabin, D. F. Kushnarev, V. M. Bzhezovskii, and G. A. Tschmutova, *Org. Magn. Reson.*, 1979, **12**, 598; G. A. Kalabin and D. F. Kushnarev, *Zh. Strukt. Khim.*, 1979, **20**, 617; and G. A. Kalabin, D. F. Kushnarev, G. A. Chmutova, and L. V. Kashurnikova, *Zh. Org. Khim.*, 1979, **15**, 24 [four studies of cyclopropyl and aryl selenides and aryl selenocyanates]; G. A. Kalabin, D. F. Kushnarev, L. M. Kataeva, L. V. Kashurnikova, and R. I. Vinokurova, *Zh. Org. Khim.*, 1978, **14**, 2478 [diaryl diselenides]; G. A. Kalabin, V. M. Bzhezovskii, B. A. Trofimov, D. F. Kushnarev, A. N. Volkov, A. G. Proidakov, R. N. Kudyakova, and A. N. Khudyakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1833 [conformations of (E)- and (Z)-RSCH=CHC≡CH]; K. H. Park, G. A. Gray, and G. D. Daves, *J. Am. Chem. Soc.*, 1978, **100**, 7475 [indolyldimethylsulphonium salts]; R. G. Petrova, I. I. Kandrov, V. I. Dostovalova, T. D. Churkina, and R. K. Friedlina, *Org. Magn. Reson.*, 1978, **11**, 406 [dithioacetals and 2-(alkylthio)alkyl sulphides]; A. H. Fawcett, K. J. Ivin, and C. D. Stewart, *Org. Magn. Reson.*, 1978, **11**, 360 [aliphatic sulphones and disulphones]; A. W. Douglas, *Can. J. Chem.*, 1978, **56**, 2129 [(Z)-5-fluoro-2-methyl-1-[(p-(methylsulphonyl)phenyl)methylene]-1H-inden-3-ylacetic acid ('Sulindac') and its methylthio-analogues]; S. S. McCrachren and S. A. Evans, *J. Org. Chem.*, 1979, **44**, 3551 and S. W. Bass and S. A. Evans, *ibid.*, 1980, **45**, 710 [sulphoxides, sulphones, thiolsulphonates, thiolsulphonates, and disulphides]; Y. Kosugi and T. Takeuchi, *Org. Magn. Reson.*, 1979, **12**, 435 [sodium sulphinates and sulphonates]; L. H. J. Lajunen and K. Raisanen, *Finn. Chem. Lett.*, 1978, 207 [hydroxynaphthalenesulphonic acids]; R. Radeglia and E. Fanghaenel, *J. Prakt. Chem.*, 1978, **320**,

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**Mass Spectra.**—A continuing investigation into the finer details of the structures of secondary fragmentation products from thiols and sulphides (see Vol. 5, p. 7) involves several research groups. The ion  $\text{CH}_2=\overset{+}{\text{S}}\text{H}$  that is formed from primary thiols by  $\alpha$ -cleavage has been shown by collisional activation mass spectrometry to be more stable than  $\text{CH}_3\text{S}^+$ ,<sup>42</sup> the same technique has been used<sup>43</sup> to show the occurrence of substantial C—S bond cleavage in sulphenyl cations ( $\text{RS}^+$ ) after their formation by field desorption. Broer and Weringa have carried further their painstaking study of the alternative fragmentation course available to sulphide molecular ions, and have used <sup>2</sup>H- and <sup>13</sup>C-labelled sulphides to establish the formation of  $\text{MeS}=\overset{+}{\text{C}}\text{H}_2$  and  $\text{MeCH}=\overset{+}{\text{S}}\text{H}$  by loss of the methyl radical from the molecular ion of ethyl methyl sulphide.<sup>44</sup> They have also ascertained which of the isomeric  $\text{C}_3\text{H}_7\text{S}^+$  ions fragments further into  $\text{H}_2\text{S}$  and ethylene.<sup>45</sup> The formation of methane<sup>46</sup> from  $\text{EtS}^+$  and of hydrogen<sup>47</sup> from  $\text{MeS}^+$  liberates the species  $[\text{CHS}]^+$ .

Ion cyclotron resonance studies of 3-methoxyalkanethiols<sup>48</sup> and homologous sulphides  $\text{MeO}(\text{CH}_2)_n\text{SMe}$  ( $n = 1-3$ )<sup>49</sup> have provided information on the reactivity profile of the methoxymethyl cation towards alcohols, thiols, and amines,<sup>48</sup> and on the preferential abstraction of hydride ion from the carbon atoms that are alpha to sulphur (confirming that, in gas-phase reactions, S is more able than O to stabilize a neighbouring carbonium ion).<sup>49</sup> Gas-phase acidities of dimethyl sulphoxide and representative aliphatic sulphones reveal a lower degree of stabilization of the  $\alpha$ -sulphonyl carbonium ions.<sup>50</sup>

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<sup>42</sup> J. D. Dill and F. W. McLafferty, *J. Am. Chem. Soc.*, 1979, 101, 6526.

<sup>43</sup> R. Weber, F. Borchers, K. Levsen, and P. W. Roellgen, *Z. Naturforsch., Teil A*, 1978, 33, 540.

<sup>44</sup> W. J. Broer, W. D. Weringa, and W. C. Nieuwpoort, *Org. Mass Spectrom.*, 1979, 14, 543.

<sup>45</sup> W. J. Broer and W. D. Weringa, *Org. Mass Spectrom.*, 1979, 14, 36.

<sup>46</sup> W. J. Broer and W. D. Weringa, *Org. Mass Spectrom.*, 1978, 13, 232.

<sup>47</sup> A. G. Harrison, *J. Am. Chem. Soc.*, 1978, 100, 4911.

<sup>48</sup> J. K. Pau, J. K. Kim, and M. C. Caserio, *J. Am. Chem. Soc.*, 1978, 100, 3838.

<sup>49</sup> J. K. Pau, M. B. Ruggera, J. K. Kim, and M. C. Caserio, *J. Am. Chem. Soc.*, 1978, 100, 4242.

<sup>50</sup> J. B. Cumming and P. K. Kebarle, *J. Am. Chem. Soc.*, 1978, 100, 1835.

Zhdanov, O. S. Reshetova, N. G. Kapitanova, Z. L. Gordon, and E. G. Rozantsev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1838 [4,4-bis(ethanesulphonyl)piperidines and ethyl piperidine-3-yl sulphone]; L. K. Liu and C. T. Hong, *Org. Mass Spectrom.*, 1978, 13, 675 [McLafferty rearrangement identified for (*E*)-PhCH=CHSO<sub>2</sub>R]; A. Albasini, M. Melegari, G. Vampa, M. Rinaldi, and A. Rastelli, *Boll. Chim. Farm.*, 1978, 117, 664 [arenesulphonamides]; C. Kascheres and R. van Fossen Bravo, *Org. Mass Spectrom.*, 1979, 14, 293 [benzenesulphonylhydrazides]; A. D. Kossov and J. L. Ocolowitz, *Biomed. Mass Spectrom.*, 1978, 5, 123 [*N*-methyl-*N*-toluene-*p*-sulphonyl-ureas]; V. K. Manzhos, G. E. Zhusupova, R. A. Muzychkina, and T. K. Chumbalov, *Zh. Prikl. Spektrosk.*, 1979, 30, 739 [anthraquinonesulphonic acids]; N. G. Keats and L. A. Summers, *J. Heterocycl. Chem.*, 1979, 16, 1369 [di-(2-pyridyl) selenide]; F. F. Knapp, *Org. Mass Spectrom.*, 1979, 14, 341 [PhTeCH<sub>2</sub>CH(OR)<sub>2</sub> → molecular ion → Ph<sup>+</sup>TeOR].

**Photoelectron Spectra.**—Organosulphur compounds are appropriately represented in the broad evaluation of this technique. The dihedral angle for the C–S–S–C grouping in di-*t*-adamantyl disulphide is 103°,<sup>51</sup> which is on the way to a fully *trans* configuration, favoured<sup>52</sup> for disulphides only when bulky substituents are involved.

Photoelectron spectral data have been collected for MeSCl,<sup>53</sup> MeSBr,<sup>53</sup> MeSCN,<sup>54</sup> and MeSeCN.<sup>54</sup> The trigonal-bipyramidal structure has been established for methylenesulphur tetrafluoride through p.e. spectroscopy, electron diffraction, and X-ray analysis.<sup>55</sup>

**Electron Diffraction.**—Among completed electron-diffraction studies are ethyl methyl sulphide,<sup>56</sup> chloromethyl methyl sulphide,<sup>57</sup> methyl phenyl sulphide,<sup>58</sup> di-(2-pyridyl) sulphide,<sup>59</sup> sulphones,<sup>60</sup> sulfoxides and sulphones,<sup>61</sup> and trifluoromethanesulphonyl chloride.<sup>62</sup> A number of precise analyses of gas-phase conformational equilibria have emerged. Methyl ethyl sulphide shows a preference for the *gauche* conformation rather than for the *trans* form.<sup>56</sup>

**Dipole Moments and Studies of the Kerr Effect.**—A number of references, together with brief details, have been collected from the recent literature:

S. G. Gagarin and R. Z. Zakharyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 31 [MeSH, EtSH, Me<sub>2</sub>S, and Et<sub>2</sub>S]; D. M. Petkovic and J. S. Markovic, *Glas. Hem. Drus., Beograd, 1979*, 44, 535 (*Chem. Abstr.*, 1980, 92, 146 131) [thiols]; V. Baliah and V. M. Kanagasabapathy, *Indian J. Chem., Sect. B*, 1978, 16, 810 [diaryl sulphides]; B. A. Arbutov, A. M. Salikhova, S. M. Shostakovskii, A. N. Vereshchagin, and N. S. Nikolskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2786 [gem-dichlorocyclopropyl sulphides]; O. Exner and J. B. F. N. Engberts, *Collect. Czech. Chem. Commun.*, 1979, 44, 3378 [halogenomethyl sulphones and *N*-nitro-*N*-methyl-arenesulphonamides]; M. S. R. Naidu, S. G. Peeran, and D. B. Reddy, *Indian J. Chem., Sect. B*, 1978, 16, 1090 [unsymmetrically substituted 1,2-di-(arylsulphonyl)-1,2-diphenylethylenes]; P. Ruostesuo, *Finn. Chem. Lett.*, 1978, 159

<sup>51</sup> F. S. Joergensen and J. P. Snyder, *J. Org. Chem.*, 1980, 45, 1015.

<sup>52</sup> F. S. Joergensen and J. P. Snyder, *Tetrahedron*, 1979, 35, 1399.

<sup>53</sup> E. Nagy-Felsobuki and J. B. Peel, *Phosphorus Sulfur*, 1979, 7, 157.

<sup>54</sup> M. V. Andreocci, M. Bossa, C. Furlani, M. N. Piancastelli, C. Cauletti, and T. Tarantelli, *J. Chem. Soc., Faraday Trans. 2*, 1979, 75, 105.

<sup>55</sup> H. Bock, J. E. Boggs, G. Kleemann, D. Lentz, H. Oberhammer, E. M. Peters, K. Seppelt, A. Simon, and B. Solouki, *Angew. Chem.*, 1979, 91, 1008.

<sup>56</sup> K. Ovanagi and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, 1978, 51, 2243.

<sup>57</sup> V. A. Naumov, R. N. Garaeva, G. D. Geize, and F. S. Mailgoff, *Dokl. Akad. Nauk SSSR*, 1979, 245, 650.

<sup>58</sup> N. M. Zaripov, A. V. Golubinskii, G. A. Chmutova, and L. V. Vilkov, *Zh. Strukt. Khim.*, 1978, 19, 894.

<sup>59</sup> B. Rozsondai, I. Hargittai, and G. C. Pappalardo, *Z. Naturforsch., Teil A*, 1979, 34, 752.

<sup>60</sup> I. Hargittai, *Kem. Kozl.*, 1978, 50, 339, 457.

<sup>61</sup> B. Rozsondai, J. H. Moore, D. C. Gregory, and I. Hargittai, *J. Mol. Struct.*, 1979, 51, 69.

<sup>62</sup> J. Brunvoll, I. Hargittai, and M. Kolonits, *Z. Naturforsch., Teil A*, 1978, 33, 1236.

and 166 [benzenesulphenamides]; G. G. Butenko, A. N. Vereshchagin, A. B. Remizov, and R. N. Nurullina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1763 and G. G. Butenko, A. N. Vereshchagin, and D. M. NasYROV, *ibid.*, p. 2034 [methyl arenesulphonates and arenesulphonamides]; R. V. Sendega and T. A. Protsailo, *Ukr. Khim. Zh.*, 1978, **44**, 844 (*Chem. Abstr.*, 1979, **89**, 196 491) [alkyl and alkenyl benzenesulphonates]; A. M. Kamalyutdinova-Salikhova, T. G. Mannafov, R. B. Khismatova, S. G. Vulfson, and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1757 [*gem*-dichlorocyclopropyl aryl selenides].

**X-Ray Crystal Analysis.**—The host-guest partnership arrangements for hexakis-(alkylthiomethyl)benzenes<sup>63</sup> including chiral guests<sup>64</sup> and for the corresponding sulphones<sup>65</sup> with 1,4-dioxan<sup>63</sup> and squalene<sup>64</sup> as guests have been elucidated by X-ray analysis. Diethyl and diphenyl dithioacetals of D-ribose<sup>66</sup> and *N*-sulphinyl benzenesulphonamide<sup>67</sup> have also been studied, the latter compound being revealed as adopting the *cis* configuration and possessing an electron-rich S—N bond. A simple empirical relationship between the S—S bond lengths and the X—C—S—S torsion angles has emerged from a study of the crystal structures of 21 symmetrical disulphides.<sup>68</sup>

The mono- and di-hydrates of Ph<sub>3</sub>SeCl are ionic compounds of five-co-ordinate selenium.<sup>69</sup>

**Electron Spin Resonance Spectra.**—Radicals arising from photolysis of diaryl disulphides (ArS·),<sup>70</sup> and of reaction mixtures of Bu<sup>n</sup>SH and SCl<sub>2</sub> (Bu<sup>n</sup>SS·)<sup>71</sup> have been studied by e.s.r. (a routine monitoring technique used in several of the studies of sulphur radicals mentioned later in this Chapter). Arenesulphonyl cation radicals, formed from 2-alkoxy-5-methylbenzenesulphonyl fluorides and sulphonic acids on treatment with PbO<sub>2</sub> and FSO<sub>3</sub>H,<sup>72</sup> provide a further example of sulphur-centred radicals, while a variation on this aspect is provided by the report of the influence of the alkylthio-group in *p*-(alkylthio)nitrobenzenes on the hyperfine splitting in the spectra of derived radical anions and nitroxides.<sup>73</sup> The alkylthio-group has thus been shown to behave as a  $\pi$ -electron acceptor when a suitable angle exists between the vacant  $\sigma^*$  orbital of the S—R bond and the  $\pi$ -orbital of benzene.<sup>73</sup>

### 3 Thiols, Selenols, and Tellurols

**Preparation.**—An important addition to methods for the reduction of sulphonyl compounds to sulphenyl analogues, *i.e.* the direct reduction of sulphonic acids to thiols using trifluoroacetic anhydride and Bu<sup>n</sup><sub>4</sub>N<sup>+</sup> I<sup>-</sup>,<sup>74</sup> has been reported. A mixture of thiol and the corresponding trifluorothiolacetate is obtained; this, on hydrolysis,

<sup>63</sup> A. D. U. Hardy, D. D. MacNicol, S. Swanson, and D. R. Wilson, *Tetrahedron Lett.*, 1978, 3579; D. D. MacNicol and S. Swanson, *J. Chem. Res. (S)*, 1979, 406.

<sup>64</sup> A. Freer, C. J. Gilmore, D. D. MacNicol, and D. R. Wilson, *Tetrahedron Lett.*, 1980, **21**, 1159.

<sup>65</sup> D. D. MacNicol and S. Swanson, *Tetrahedron Lett.*, 1980, **21**, 205.

<sup>66</sup> A. Ducruix, D. Horton, C. Pascard, J. D. Wander, and T. Prange, *J. Chem. Res. (S)*, 1978, 470.

<sup>67</sup> G. Deleris, C. Courseille, J. Kowalski, and J. Dunogues, *J. Chem. Res. (S)*, 1979, 122.

<sup>68</sup> L. S. Higashi, M. Lundeen, and K. Seff, *J. Am. Chem. Soc.*, 1978, **100**, 8101.

<sup>69</sup> R. V. Mitcham, B. Lee, K. B. Mertes, and R. F. Ziolo, *Inorg. Chem.*, 1979, **18**, 3498.

<sup>70</sup> W. Moerke, A. Jezierski, and H. Singer, *Z. Chem.*, 1979, **19**, 147.

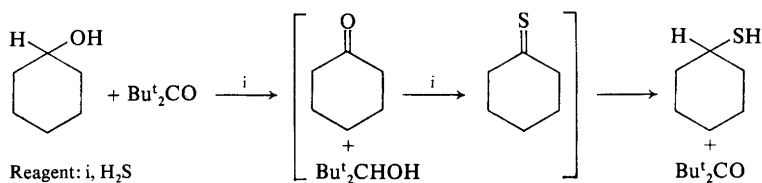
<sup>71</sup> J. E. Bennett and G. Brunton, *J. Chem. Soc., Chem. Commun.*, 1979, 62.

<sup>72</sup> A. P. Rudenko, M. Ya. Zarubin, and A. M. Kutnevich, *Zh. Obshch. Khim.*, 1979, **49**, 954.

<sup>73</sup> A. Alberti, M. Guerra, G. Martelli, F. Bernardi, A. Mangini, and G. F. Pedulli, *J. Am. Chem. Soc.*, 1979, **101**, 4627.

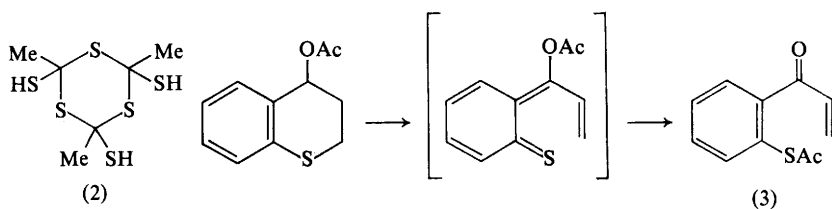
<sup>74</sup> T. Numata, H. Awano, and S. Oae, *Tetrahedron Lett.*, 1980, **21**, 1235.

yields the thiol and easily separable elaboration products.<sup>74</sup> Most of the other recent papers describing preparations of thiols are collected together at the end of this section since, although often describing improved methodology, they are based on well-tried procedures.<sup>75</sup> Among methods using  $\text{H}_2\text{S}$  as reagent is an interesting study that has established a Meerwein-Ponndorf-Verley-type mechanism (Scheme 1) for the conversion of an alcohol into the corresponding thiol, using  $\text{H}_2\text{S}$  and  $\text{Al}_2\text{O}_3$ , with a ketone as co-catalyst.<sup>76</sup>



Scheme 1

Thiocarbonyl compounds offer reliable entries to thiols, and thiourea has been used for the conversion of chloromethylated polystyrene into the corresponding polymeric thiol.<sup>77</sup> *NN*-Dimethylthioformamide<sup>78</sup> and sodium *NN*-dimethyldithiocarbamate<sup>79</sup> have been used similarly, the latter leading to pyridine-2,4- and -2,5-dithiols from diazotized amino-chloropyridines. Another well-established route, *i.e.* conversion of phenols into benzenethiols *via* thionocarbamate intermediates and rearrangement at 200–280 °C, has been used<sup>80</sup> for the synthesis of 4-alkyl- and 4-cyano-derivatives. Reduction of di-*t*-butyl selenone with  $\text{LiAlH}_4$  gives the corresponding selenol,<sup>81</sup> and the reduction by  $\text{NaBH}_4$  of 2-aryl-3-piperidino-indane-1-thione gives the 2-arylidene-1-thiol; an unusual reductive cleavage of an enamine.<sup>82</sup> The thiol (2) is one of several trimers of dithioacetic acid.<sup>83</sup>



<sup>75</sup> G. C. Barrett, in 'Comprehensive Organic Chemistry', ed. Sir Derek H. R. Barton and W. D. Ollis, Pergamon Press, Oxford, 1979, Vol. 3 (ed. D. N. Jones), p.3.

<sup>76</sup> J. Barrault, M. Guisnet, J. Lucien, and R. Maurel, *J. Chem. Res. (S)*, 1978, 474; *Nouv. J. Chem.*, 1979, 3, 15; *Ind. Eng. Chem., Prod. Res. Dev.*, 1978, 17, 354.

<sup>77</sup> P. Kalck, R. Poilblanc, A. Gaset, A. Rovera, and R. P. Martin, *Tetrahedron Lett.*, 1980, 21, 459.

<sup>78</sup> K. Hattori, T. Takido, and K. Habashi, *Nippon Kagaku Kaishi*, 1979, 101 (*Chem. Abstr.*, 1979, 90, 137 380).

<sup>79</sup> K. Krowicki, *Pol. J. Chem.*, 1979, 53, 701, 889.

<sup>80</sup> C. F. Shirley, *Mol. Cryst. Liq. Cryst.*, 1978, 44, 193.

<sup>81</sup> B. J. McKinnon, P. De Mayo, N. C. Payne, and B. Ruge, *Nouv. J. Chim.*, 1978, 2, 91.

<sup>82</sup> V. A. Usov, K. A. Petriashvili, and M. G. Voronkov, *Zh. Org. Khim.*, 1978, 14, 2227.

<sup>83</sup> G. Levesque, A. Mahjoub, and A. Thuillier, *Tetrahedron Lett.*, 1978, 3847.

A conventional route from an alkanol to a thiol, *via* the trifluoromethanesulphonate and treatment with  $\text{MeCOS}^- \text{Na}^+$ , has been used for the synthesis of the surfactant  $\text{C}_{16}\text{H}_{33}\overset{+}{\text{N}}\text{Me}_2\text{CH}_2\text{CH}_2\text{SH Cl}^-$ .<sup>84</sup>

Ring-opening reactions of sulphur-containing heterocyclic compounds which lead to thiols include Birch reduction of thiophen-2-carboxylic acid, to give a mixture of products that includes  $\text{HO}_2\text{CCH}_2\text{CH}=\text{CHCH}_2\text{SH}$  and  $\text{HO}_2\text{CCH}=\text{CHCHMeSH}$ ;<sup>85</sup> photolysis of 4-thiochromanone enol acetate to give (3) by a novel 1,5-acyl migration in the intermediate *o*-thioquinone methylide;<sup>86</sup> and cleavage (by Na in  $\text{NH}_3$ ) of *s*-trithians and related compounds [ $(\text{CH}_2\text{S})_3 \rightarrow \text{MeSCH}_2\text{SCH}_2\text{S}^- \text{Na}^+$ ].<sup>87</sup>

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**Reactions of Thiols, Selenols, and Tellurols.**—Many of the reactions of thiols depend on the high nucleophilicity of the thiolate anion, and lead to sulphides or other sulphur-containing functional groups. Reactions of this type are therefore discussed in later sections of this Chapter.

Alkylthiolate anions are more reactive by a factor of  $10^4$ — $10^5$  than  $\text{OH}^-$  towards tropylium cations and carbonyl compounds.<sup>88</sup> Furthermore,  $\text{PhSe}^-$  is at least five times more nucleophilic than  $\text{PhS}^-$ ,<sup>89</sup> but the latter nucleophile, paradoxically, is capable of dealkylating  $\text{PhSeMe}$ <sup>89</sup> and tertiary amines<sup>90</sup> when in the presence of Pd,  $\text{PdCl}_2$ ,  $\text{Pd}(\text{OAc})_2$ , or  $\text{RuCl}_3$ . Demethylation of methyl ethers<sup>91a</sup> and esters<sup>91b</sup> by treatment with a thiol in the presence of an aluminium trihalide has been reported.

The simplest method yet uncovered for the replacement of the diazonium group by H (or  $^2\text{H}$ ) is the use of  $\text{PhSH}$  (or  $\text{PhS}^2\text{H}$ );<sup>92</sup> so far, the reaction seems to be limited to arenediazonium cations. Further reductive processes that are mediated by thiols are the conversion of 1-nitro-alkenes into alkenes (+  $\text{NaNO}_2 + \text{PhSSPh} + \text{S}_8$ )

<sup>84</sup> R. A. Moss, G. O. Bizzigotti, T. J. Lukas, and W. J. Sanders, *Tetrahedron Lett.*, 1978, 3661.

<sup>85</sup> W. G. Blenderman, M. M. Joullié, and G. Preti, *Tetrahedron Lett.*, 1979, 4985.

<sup>86</sup> I. W. J. Still and T. S. Leong, *Tetrahedron Lett.*, 1979, 3613.

<sup>87</sup> E. Weissflog and M. Schmidt, *Phosphorus Sulfur*, 1979, **6**, 453.

<sup>88</sup> C. D. Ritchie and J. Gandler, *J. Am. Chem. Soc.*, 1979, **101**, 7318.

<sup>89</sup> H. J. Reich and M. L. Cohen, *J. Org. Chem.*, 1979, **44**, 3148.

<sup>90</sup> S.-I. Murahashi and T. Yano, *J. Chem. Soc., Chem. Commun.*, 1979, 270.

<sup>91</sup> (a) M. Node, K. Nishide, M. Sai, K. Ichikawa, K. Fujii, and E. Fujita, *Chem. Lett.*, 1979, 97; (b) M. Node, K. Nishide, M. Sai, and E. Fujita, *Tetrahedron Lett.*, 1978, 5211.

<sup>92</sup> T. Shono, Y. Matsumura, and K. Tsubata, *Chem. Lett.*, 1979, 1051.

by PhSH and Na<sub>2</sub>S,<sup>93</sup> corrole-catalysed photoreduction of benzaldehyde by PhSH,<sup>94</sup> reduction of benzyl halides by RS<sup>-</sup> Et<sub>3</sub>NH<sup>+</sup> or RSe<sup>-</sup> Et<sub>3</sub>NH<sup>+</sup>,<sup>95</sup> and the use of propane-1,3-dithiol in the presence of triethylamine for the reduction of azides to amines.<sup>96</sup>

An 18-crown-6 ether that bears L-cysteinyl residues has been synthesized for use in studies of catalysed hydrolysis,<sup>97</sup> the thiol group being the effective functional group. Several papers have appeared that are based on the principles of addition to multiple bonds. Phenyl trimethylsilyl selenide has been advocated<sup>98</sup> as a convenient source of the phenylselenyl anion, for addition to aldehydes and ketones;<sup>99</sup> the anion is liberated by treatment of PhSeSiMe<sub>3</sub> with KF.<sup>98</sup> Asymmetric induction has been of continuing interest in this field, and addition of achiral thiols to (–)-menthyl crotonate<sup>100</sup> or to achiral cyclohexenols, catalysed by an alkaloid<sup>101a</sup> or by an (*R*)-alaninamide,<sup>100b</sup> leads to moderate enantiomeric excesses. The use of boron trifluoride diethyl etherate as a catalyst for accomplishing Markownikov addition of a thiol to an alkene<sup>102</sup> [PhCH<sub>2</sub>SH → PhCH<sub>2</sub>SCMe<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>C(NHAc)(CO<sub>2</sub>Et)<sub>2</sub>] has not been established as a general method, since the thiolester, rather than the protected hexafluoropenicillamine, results from catalysed addition of PhCH<sub>2</sub>SH to (CF<sub>3</sub>)<sub>2</sub>C=C(NHCOPh)CO<sub>2</sub>H.<sup>103</sup>

Many more references to the recent literature, covering the additions of thiols to multiple bonds, are discussed in the later section 'Synthesis of Sulphides', but the use of Me<sub>2</sub>AlSPh and Me<sub>2</sub>AlSeMe (Me<sub>2</sub>AlLi<sup>+</sup> PhS<sup>-</sup> is more reactive) for the formation of 1,4-adducts with 2-enones<sup>104</sup> and the preferential photoaddition of Bu<sup>n</sup>SH to the C=C bond in the ester moiety of allyl and vinyl acrylates and to *trans*-crotonates<sup>105</sup> are items of unusual interest. Nucleophilic substitution reactions of thiols that lead to sulphides are also mostly covered in the later section. The generation of dianions from prop-2-ene-1-thiol<sup>106</sup> and from α-mercapto-γ-butyrolactone<sup>107</sup> (using RLi with MgBr<sub>2</sub> and LiPr<sup>1</sup><sub>2</sub>N with TMEDA, respectively) and their reactions with aldehydes and ketones provide valuable new uses in synthesis of sulphur nucleophiles, leading to oxirans and αβ-unsaturated esters, respectively, after desulphurization of the adducts.

Dehydrogenation and desulphurization of thiols, and related processes, are involved in reactions of simple alkanethiols with H<sup>108</sup> and O atoms,<sup>109</sup> and in

<sup>93</sup> N. Ono, S. Kawai, K. Tanaka, and A. Kaji, *Tetrahedron Lett.*, 1979, 1733.

<sup>94</sup> Y. Murakami, Y. Aoyama, and K. Tokunaga, *J. Chem. Soc., Chem. Commun.*, 1979, 1018.

<sup>95</sup> L. Hevesi, *Tetrahedron Lett.*, 1979, 3025.

<sup>96</sup> H. Bayley, D. N. Stranding, and J. R. Knowles, *Tetrahedron Lett.*, 1978, 3633.

<sup>97</sup> J. M. Lehn and C. Sirlin, *J. Chem. Soc., Chem. Commun.*, 1978, 949.

<sup>98</sup> M. R. Detty, *Tetrahedron Lett.*, 1978, 5087.

<sup>99</sup> D. Liotta, P. B. Paty, J. Johnston, and G. Zima, *Tetrahedron Lett.*, 1978, 5091.

<sup>100</sup> M. Yoshihara, H. Fujihara, and T. Maeshima, *Chem. Lett.*, 1980, 195.

<sup>101</sup> (a) H. Pluim and H. Wynberg, *Tetrahedron Lett.*, 1979, 1251; (b) S. Inoue and Y. Kawano, *Makromol. Chem.*, 1979, **180**, 1405 (*Chem. Abstr.*, 1979, **91**, 108 216).

<sup>102</sup> G. A. Dilbeck, L. Field, A. A. Gallo, and R. J. Gargiulo, *J. Org. Chem.*, 1978, **43**, 4593.

<sup>103</sup> L. Field and A. A. Gallo, *J. Fluorine Chem.*, 1980, **15**, 29.

<sup>104</sup> A. Itoh, S. Ozawa, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 1980, **21**, 361.

<sup>105</sup> L. I. Komarova, *Zh. Org. Khim.*, 1978, **14**, 737.

<sup>106</sup> M. Pohmakotr, K. H. Geiss, and D. Seebach, *Chem. Ber.*, 1979, **112**, 1420.

<sup>107</sup> K. Tanaka, N. Yamagishi, R. Tanikaga, and A. Kaji, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3619; K. Tanaka, H. Uneme, N. Yamagishi, N. Ono, and A. Kaji, *Chem. Lett.*, 1978, 653.

<sup>108</sup> O. Horie, J. Nishino, and A. Amano, *Int. J. Chem. Kinet.*, 1978, **10**, 1043.

<sup>109</sup> I. R. Seagle, F. Baiocchi, and D. Gutman, *J. Phys. Chem.*, 1978, **82**, 1333.

pyrolysis in the absence of a catalyst<sup>110</sup> or in the presence of poly(metal phthalocyanines).<sup>111</sup> Similarly, photolysis of alkanethiols in the liquid state<sup>112</sup> leads to loss of H<sub>2</sub>S and hydrogen. A useful conversion of thiols into alkanes and thiolacetates employs [Mo(CO)<sub>6</sub>] that is adsorbed on alumina, this being suspended in AcOH.<sup>113</sup>

Straightforward exchange reactions [RSH + HO<sup>2</sup>H = RS<sup>2</sup>H + H<sub>2</sub>O;<sup>114</sup> MeSH + H<sub>2</sub>S *via* a cyclic complex<sup>115</sup>] depend on the acidities of the thiols, which are solvent-dependent.<sup>116</sup>

Excluding the extensive literature on metal complexes carrying bivalent sulphur ligands, some classes of compound formed between thiols and elements near sulphur in the Periodic Table are important in synthetic organic chemistry. White phosphorus gives a tris(alkylthio)phosphine with a mixture of a thiol and its sodium salt in CCl<sub>4</sub> (CHCl<sub>3</sub> is the other organic reaction product).<sup>117</sup> Arenethiolates do not react in the same way, owing to a competing reaction of the intermediate ArS(P<sub>4</sub>)Cl that involves the displacement of ArS<sup>-</sup> (a good leaving group).<sup>117</sup> Desulphurization of thiols and sulphides with MeMgBr or ArMgBr in the presence of [(Ph<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub>] leads to alkenes, toluenes, and biaryls in moderate to high yields.<sup>118</sup> Iron carbonyls give [RSFe(CO)<sub>3</sub>]<sub>2</sub> with thiols, sulphides, and disulphides, and the corresponding disulphanes [S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] and [S<sub>2</sub>Fe<sub>3</sub>(CO)<sub>9</sub>] with S<sub>8</sub>.<sup>119</sup> Although the regeneration of the thiol can be accomplished, potential uses in synthesis do not appear to have been realized.

This Chapter has invariably included brief coverage of biochemically important reactions of thiols, since any insight which can be gained is based on a clear understanding of the fundamental chemistry of the SH group. Accurate determination of the relative numbers of SH groups in enzymes and other complex molecules is commonly achieved through the use of Ellman's reagent and then spectrophotometric assay of the resulting 5-mercapto-2-nitrobenzoic acid. Certain knowledge of the molar absorption coefficient of the dianion of this compound has been a limiting factor in this assay, but the parameters  $\lambda_{\max} = 412 \text{ nm}$ ,  $\epsilon = 14\,150$  have been established for pure samples in dilute aqueous salt solutions.<sup>120</sup> One of the thiol-containing enzymes, glyceraldehyde 3-phosphate dehydrogenase, is efficiently deactivated by 2-nitro-3-(5-nitro-2-furyl)acrylates, and model reactions of this inhibitor with simple thiols have been reported.<sup>121</sup> Carbocyclic analogues of captopril (hetCOCHMeCH<sub>2</sub>SH), a compound with inhibiting activity for angiotensin-converting enzyme, have been synthesized.<sup>122</sup> An intermediate (4) that was isolated during studies of the reduction of 1,3-dimethyl-5-(*p*-nitrophenyl-

<sup>110</sup> N. Barroeta, G. Martin, and J. Capasso, *React. Kinet. Catal. Lett.*, 1978, **9**, 177.

<sup>111</sup> N. Takamiya, T. Iwatsuki, T. Nagai and S. Murai, *Nippon Kagaku Kaishi*, 1979, 825.

<sup>112</sup> W. A. Pryor and E. G. Olsen, *J. Am. Chem. Soc.*, 1978, **100**, 2852.

<sup>113</sup> H. Alper and C. Blais, *J. Chem. Soc., Chem. Commun.*, 1980, 169.

<sup>114</sup> J. J. Khurma and D. V. Fenby, *Aust. J. Chem.*, 1979, **32**, 755.

<sup>115</sup> A. Wawer, *Pol. J. Chem.*, 1979, **53**, 1917.

<sup>116</sup> G. P. Sharnin, V. V. Nurgatui, and B. M. Ginzburg, *Zh. Org. Khim.*, 1979, **15**, 1638.

<sup>117</sup> C. Brown, R. F. Hudson, and G. A. Wartew, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1799.

<sup>118</sup> E. Wenkert, T. W. Ferreira, and E. L. Michelotti, *J. Chem. Soc., Chem. Commun.*, 1979, 637.

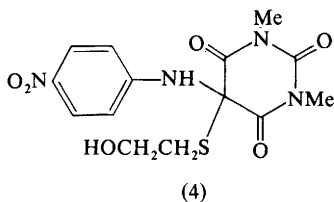
<sup>119</sup> N. S. Nametkin, V. D. Tyurin, and M. A. Kukina, *J. Organomet. Chem.*, 1978, **149**, 355.

<sup>120</sup> P. W. Riddles, R. L. Blakely, and B. Zerner, *Anal. Biochem.*, 1979, **94**, 75.

<sup>121</sup> E. Sturdik, L. Drobnica, S. Balaz, and V. Marko, *Biochem. Pharmacol.*, 1979, **28**, 2525.

<sup>122</sup> A. Sugie and J. Katsube, *Chem. Pharm. Bull.*, 1979, **27**, 1708.





imino)barbituric acid by thiols tends to confirm mechanisms previously advocated for the reduction of flavins by thiols.<sup>123</sup> Enhancement of the rates of hydrolysis of esters by nearby SH and CONH<sub>2</sub> groups has been explained on the basis of a mechanism that involves the formation of an intermediate cyclic imide.<sup>124</sup>

**Thiyl and Related Selenium Radicals.**—Direct generation of thiyl radicals (RS·) from thiols by  $\gamma$ -radiolysis (using a <sup>60</sup>Co source)<sup>125</sup> and indirect formation by the reaction of thiols with triarylmethyl radicals<sup>126</sup> or with selenocyanate anion radicals that are formed by pulse radiolysis of (SeCN)<sub>2</sub><sup>127</sup> are accompanied by cleavage reactions of other bivalent sulphur compounds [photolysis of thionitrites<sup>128</sup> and cleavage of disulphides by Pb(OAc)<sub>4</sub><sup>129</sup>]. The first e.s.r. study of selenuranyl radicals, formed by attack on selenides by the CF<sub>3</sub>S· radical, has been reported.<sup>130</sup>

Oxidative decarboxylation of 4-carboxy-4-methylpentylthiyl radicals, leading to mixtures of 2,2-dimethyltetrahydrothiophens and 5,5-dimethyl-2,3-dihydrothiophens, has been proposed as a model for one of the stages in penicillin biosynthesis.<sup>129</sup> Comparative rate studies have shown that the addition of dioxygen to thiyl radicals is slower than to the corresponding carbon radicals.<sup>131</sup>

#### 4 Thiolesters, Selenolesters, and Tellurolesters

Until recently, the relatively sparse contributions to the literature on thiolesters, R<sup>1</sup>COSR<sup>2</sup>, were easily accommodated as a small paragraph in the 'Thiols' section, but the substantial growth of interesting chemistry involving these compounds necessitates this separate section.

**Preparation.**—Modifications of the standard procedure (R<sup>1</sup>CO<sub>2</sub>H + R<sup>2</sup>SH) employ 4-(dimethylamino)pyridine and dicyclohexylcarbodi-imide,<sup>132</sup> diphenylphosphinyl chloride,<sup>133</sup> or Me<sub>2</sub>NP(O)Cl<sub>2</sub><sup>134</sup> as coupling reagents. Related methods (*e.g.* acyl

<sup>123</sup> J. M. Sayer, P. Coulon, J. Hupp, J. Fauchez, R. Belanger, and E. J. White, *J. Am. Chem. Soc.*, 1979, **101**, 1890.

<sup>124</sup> D. Petz, F. Schnieder, and H. G. Loeffler, *Z. Naturforsch., Teil C*, 1978, **33**, 151.

<sup>125</sup> D. J. Nelson, R. L. Petersen, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1977, 2005.

<sup>126</sup> T. H. Colle and E. S. Lewis, *J. Am. Chem. Soc.*, 1979, **101**, 1810.

<sup>127</sup> R. Badiello and M. Tamba, *Radiochem. Radioanal. Lett.*, 1979, **37**, 165.

<sup>128</sup> H. Chandra, B. G. Gowenlock, and J. Pfab, *J. Chem. Soc., Chem. Commun.*, 1979, 392.

<sup>129</sup> J. E. Baldwin and T. S. Wan, *J. Chem. Soc., Chem. Commun.*, 1979, 249.

<sup>130</sup> J. R. G. Giles, B. P. Roberts, M. J. Perkins, and E. S. Turner, *J. Chem. Soc., Chem. Commun.*, 1980, 504.

<sup>131</sup> K. Schaefer, M. Bonifacic, D. Bahnemann, and K. D. Asmus, *J. Phys. Chem.*, 1978, **82**, 2777.

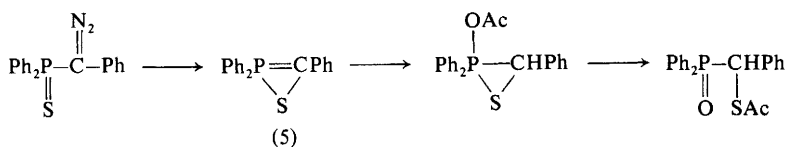
<sup>132</sup> B. Nieses and W. Steglich, *Angew. Chem.*, 1978, **90**, 556.

<sup>133</sup> D. Scholz and D. Eigner, *Monatsh. Chem.*, 1979, **110**, 759.

<sup>134</sup> H.-J. Liu, S. P. Lee, and W. H. Chan, *Synth. Commun.*, 1979, **9**, 91.

chloride +  $\text{Bu}_3\text{SnSR}^{135}$  and carboxylic ester +  $\text{Me}_2\text{AlSeMe}^{136}$  give excellent yields of thioesters and selenoesters, respectively. The latter compounds can also be reached by alkylation of selenocarboxylates.<sup>137</sup> Addition of  $\text{ArSeBr}$  to ethyl vinyl ether gives the aryl selenide  $\text{ArSeCH}_2\text{CHO}$  rather than the selenoester  $\text{ArSeCOMe}$ .<sup>138</sup> Ketones yield  $\beta$ -keto-thioesters by reaction with dithiolcarbonates and  $\text{NaH}$ .<sup>139</sup> Selenoesters have also been prepared from *N*-acylhydrazines and benzeneseleninic acid.<sup>620</sup>

Pummerer rearrangements leading to thioesters are discussed in the later sections on sulphoxides. A superficially related Arbusov-type reaction, with a 1,2-shift of sulphur, through the intermediate (5), has a similar outcome.<sup>140</sup> 2-Thiopyridyl chloroformate has been advocated as a reagent for the conversion of carboxylic acids into their pyridine-2-thioesters under mild conditions.<sup>141</sup>



**Reactions of Thiolacids and Thioesters, Selenoesters, and Telluroesters.**—The well-known reactivity of thiolacids and thioesters as acylating agents is shared with the selenoesters.<sup>136</sup> A novel acylating agent, 2-benzoylthio-1-methylpyridinium chloride, is effective in aqueous solutions.<sup>142</sup>

Uses in synthesis of thiolacids and esters are being explored for possible advantages *vis-à-vis* their oxygen analogues. The Dieckmann cyclization of  $\omega$ -dicarboxylate esters is more easily effected in the thioester series,<sup>143</sup> and the equivalent in the thioester series of the decarboxylation of a  $\beta$ -keto-ester is accomplished by using Raney nickel.<sup>144</sup> Dithiomalonate esters,  $\text{CH}_2(\text{COSEt})_2$ , can be alkylated and reductively dethiocarboxylated by Raney nickel to yield hydroxyethyl compounds, thus reacting as masked ethanol carbanions.<sup>145</sup> Bis-metallated thiolacids,  $\text{RCH}=\text{C}(\text{OLi})\text{SLi}$ , give  $\beta$ -hydroxy-thiolacids with aldehydes and ketones, and thiolactones by reaction with  $\alpha$ -chloro-ketones.<sup>146</sup>

A photochemical Wolff rearrangement of a diazomonthiomalonate<sup>147</sup> [ $\text{MeO}_2\text{C}-\text{C}(\text{N}_2)\text{COSR} \rightarrow \text{MeO}_2\text{CCH}_2\text{SR}$ ] and the use of the same compound in a synthesis of an azetidinone by photolysis with an imine<sup>148</sup> follow established reactions of the

<sup>135</sup> D. N. Harpp, T. Aida, and T. H. Chan, *Tetrahedron Lett.*, 1979, 2853.

<sup>136</sup> A. P. Kozikowski and A. Ames, *J. Org. Chem.*, 1978, **43**, 2735.

<sup>137</sup> H. Ishihara and Y. Hirabayashi, *Chem. Lett.*, 1978, 1007.

<sup>138</sup> R. Baudar and M. Petrzilka, *Helv. Chim. Acta*, 1979, **62**, 1406.

<sup>139</sup> H.-J. Liu, S. K. Attah-Poku, and H. K. Lai, *Synth. Commun.*, 1979, **9**, 883.

<sup>140</sup> M. Yoshifuji, J. Tagawa, and N. Inamoto, *Tetrahedron Lett.*, 1979, 2415.

<sup>141</sup> E. J. Corey and D. A. Clark, *Tetrahedron Lett.*, 1979, 2875.

<sup>142</sup> M. Yamada, Y. Watabe, T. Sakakibara, and R. Sudoh, *J. Chem. Soc., Chem. Commun.*, 1979, 179.

<sup>143</sup> H.-J. Liu and H. K. Lai, *Tetrahedron Lett.*, 1979, 1193.

<sup>144</sup> H.-J. Liu, H. K. Lai, and S. K. Attah-Poku, *Tetrahedron Lett.*, 1979, 4121.

<sup>145</sup> H.-J. Liu and H. K. Lai, *Can. J. Chem.*, 1979, **57**, 2522.

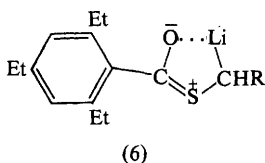
<sup>146</sup> A. M. Sarpeshkar, G. J. Gossick, and J. Wemple, *Tetrahedron Lett.*, 1979, 703.

<sup>147</sup> V. Georgian, S. K. Boyer, and B. Edwards, *J. Org. Chem.*, 1980, **45**, 1686.

<sup>148</sup> V. Georgian, S. K. Boyer, and B. Edwards, *Heterocycles*, 1977, **7**, 1003.

oxygen analogue. Intramolecular Wittig alkene reactions of thioesters, leading to fused azetidinone–pyrroline antibiotics, have been described.<sup>149</sup>

Substitution alpha to the carbonyl group of a thioester is facilitated by prior conversion into silyl<sup>150</sup> or boranyl<sup>151</sup> enolates. Michael addition of cyclopentenone to  $\text{H}_2\text{C}=\text{C}(\text{SBU}^1)\text{OSiMe}_3$ , followed by alkylation with  $\text{BrCH}_2\text{C}\equiv\text{CCH}_2\text{CH}_2\text{OThp}$  (Thp = tetrahydropyranyl) and conventional elaboration, leads to ( $\pm$ )-jasmine keto-lactone.<sup>150</sup> Self-condensation of alkyl arenethioesters, using lithium *N*-hydroxy-2,2,6,6-tetramethylpiperidine, gives products which vary according to the reaction conditions [ $\text{PhCOSEt} \rightarrow (\text{PhCO})_2\text{CHMe}$  at ambient temperatures, but  $\text{PhCOCHMeSCOPh}$  at  $-98^\circ\text{C}$ ].<sup>152</sup> A stable lithium enolate (6) has been discovered during this work. Macrocyclic lactones are accessible from heteroaryl  $\omega$ -hydroxyalkanethiolates by treatment with  $\text{AgClO}_4$ .<sup>153</sup>



Alkylthioketenimines, formed from alkyl  $\alpha$ -aminothiоacetates by treatment with  $\text{RP}(\text{O})\text{Cl}_2$ , give back the original starting material rather than acetamides  $\text{R}^1\text{NHCOC}_2\text{SR}^2$  when they react with water.<sup>154</sup> Further work (see Vol. 5, p. 17) on the ozonolysis of thioesters has implicated *S*-oxide intermediates as the initial reaction products, which undergo an *S,O*-acyl shift and further oxidation to mixed sulphonic–carboxylic anhydrides [ $\text{RCOS}(\text{O})\text{R} \rightarrow \text{RCO}_2\text{SR} \rightarrow \text{RCO}_2\text{SO}_2\text{R}$ ].<sup>155</sup>

A further example of ongoing studies (see Vol. 5, p. 17) is the establishment of competing photolysis and photo-Fries rearrangement processes with aryl areneselenol-<sup>156</sup> and arenetellurol-esters.<sup>157</sup>

Conventional structure–rate studies for the hydrolysis of thioesters have been reported.<sup>158</sup>

## 5 Sulphides, Selenides and Tellurides

**Preparation from Thiols, Selenols, and Tellurols.**—The main methods for the synthesis of sulphides are substantially represented in the recent literature, and those papers whose topics can be clearly indicated by brief details are collected at the end of this section.

<sup>149</sup> R. J. Ponsford, P. M. Roberts, and R. Southgate, *J. Chem. Soc., Chem. Commun.*, 1979, 847; A. J. G. Baxter, R. J. Ponsford, and R. Southgate, *ibid.*, 1980, 429.

<sup>150</sup> H. Gerlach and R. Kuenzler, *Helv. Chim. Acta*, 1978, **61**, 2503.

<sup>151</sup> M. Hiram and S. Masamune, *Tetrahedron Lett.*, 1979, 2225; M. Hiram, D. S. Garvey, L. D. L. Lu, and S. Masamune, *ibid.*, p. 3937.

<sup>152</sup> D. B. Reitz, P. Beak, R. F. Farney, and L. S. Helmick, *J. Am. Chem. Soc.*, 1978, **100**, 5428.

<sup>153</sup> J. S. Nimitz and R. H. Wollenberg, *Tetrahedron Lett.*, 1978, 3523.

<sup>154</sup> L. I. Kruglik and Yu. G. Gololobov, *Zh. Org. Khim.*, 1978, **14**, 747.

<sup>155</sup> M. J. Sousa Lobo and H. J. Chaves das Neves, *Tetrahedron Lett.*, 1978, 2171.

<sup>156</sup> J. Martens, K. Praefcke, and H. Simon, *Chem.-Ztg.*, 1978, **102**, 108.

<sup>157</sup> W. Lohner, J. Martens, K. Praefcke, and H. Simon, *J. Organomet. Chem.*, 1978, **154**, 263.

<sup>158</sup> K. S. Venkatasubban, K. R. Davis, and J. L. Hogg, *J. Am. Chem. Soc.*, 1978, **100**, 6125; T. H. Fife and B. R. De Mark, *ibid.*, 1979, **101**, 7379.

The uses of thiols in the synthesis of sulphides can be discussed under the two main headings (a) additions to unsaturated systems and (b) substitution reactions. Several papers under the former heading have been discussed in an earlier section (p. 11). Addition of thiolate anions to 1-methoxy-<sup>159</sup> and 1-alkylthio-tropenylium fluorosulphonates<sup>160</sup> occurs at C-7. 1,4-Addition of PhSMgI to the enones  $R^1CH=CR^2COR^3$ , followed by addition of the resulting carbanion to a ketone  $R^4COR^5$ , provides a one-pot synthesis of 2-acyl-3-(phenylthio)alkan-1-ols PhSCHR<sup>1</sup>CR<sup>2</sup>(COR<sup>3</sup>)CR<sup>4</sup>R<sup>5</sup>OH.<sup>161</sup> Several papers<sup>162</sup> deal with reactions of thiols with formaldehyde and HCl<sup>162</sup> ( $n-C_8H_{17}SH \rightarrow$  chloromethyl sulphide), with ketones (giving  $\gamma$ -keto-sulphides),<sup>163</sup> with sulphones,<sup>164</sup> with secondary amines,<sup>165</sup> and an interesting reaction with *N*-methylhydroxylamine hydrochloride, giving  $(RSCH_2)_2CMeNOH$ .<sup>166</sup> *NS*-Acetals are formed by the addition of thiols to imines.<sup>167</sup> An unusual conversion of perfluoro-2- and -4-methyl-2-pentenes into 1,3-dienes has been rationalized on the basis of elimination of a sulphenyl fluoride from the initial adduct that is formed with a thiol.<sup>168</sup>

Substitutions employing novel reagents include thallium thiolates and selenolates (PhSTl and PhSeTl from the thiol and selenol, using TIOEt or TIOPh) in reactions with acyl chlorides and  $\alpha$ -halogenocarbonyl compounds,<sup>169</sup> and in the thiolysis of oxirans.<sup>170</sup> Trimethylsilyl phenyl selenide has been used for cleavage of esters (in conjunction with ZnI<sub>2</sub>),<sup>171</sup> ring-opening of oxirans,<sup>172</sup> and Michael additions.<sup>173</sup> Interestingly, Me<sub>2</sub>AlSR (from Me<sub>3</sub>Al and RSH, at 0 °C) was utilized in the thiolysis of methanesulphonates.<sup>174</sup>

Important direct syntheses from alkanols (see Vol. 5, p. 19) have been supplemented by the high-yield synthesis of symmetrical sulphides, using  $(CF_3CH_2O)_2PPh_3$  and a thiol.<sup>175</sup> Other less commonly used leaving groups in syntheses of sulphides from thiols are represented in the processes  $ArCH_2NMe_2 \rightarrow ArCH_2SR$ .<sup>176</sup> dimedonyliodonium ylide  $\rightarrow$  2-phenylthio-5,5-dimethylcyclohexane-

<sup>159</sup> T. Komives, A. F. Marton, S. Holly, and F. Dutka, *React. Kinet. Catal. Lett.*, 1978, **8**, 19; J. P. Guthrie, *J. Am. Chem. Soc.*, 1978, **100**, 5892.

<sup>160</sup> M. Cavazza, G. Morganti, and F. Pietra, *J. Chem. Soc., Chem. Commun.*, 1978, 710.

<sup>161</sup> T. Shono, Y. Matsumura, S. Kashimura, and K. Hatanaka, *J. Am. Chem. Soc.*, 1979, **101**, 4752.

<sup>162</sup> J. Broniarz, J. Pernak, M. Pujanek, and W. Karminski, *Zesz. Nauk Politech. Slask. Chem.*, 1978, **81**, 85 (*Chem. Abstr.*, 1979, **90**, 167 989); J. Broniarz, J. Szymanowski, J. Pernak, and M. Pujanek, *Chem. Stosow.*, 1978, **22**, 201.

<sup>163</sup> V. I. Dronov, R. F. Nigmatullina, L. V. Spirikhin, and Yu. E. Nikitin, *Zh. Org. Khim.*, 1978, **14**, 2357; S. S. Shukurov, K. N. Negmatullaev, M. S. Danyarova, and S. S. Sabirov, *ibid.*, 1979, **15**, 1102.

<sup>164</sup> V. I. Dronov, R. F. Nigmatullina, E. E. Zaev, and Yu. E. Nikitin, *Zh. Org. Khim.*, 1979, **15**, 1706.

<sup>165</sup> A. M. Kuliev, K. Z. Guseinov, N. A. Aliev, A. K. Ibad-Zade, and N. Yu. Ibragimov, *Dokl. Akad. Nauk Az. SSR*, 1977, **33**, 53 (*Chem. Abstr.*, 1979, **89**, 75 228).

<sup>166</sup> K. Ito and M. Sekiya, *Chem. Pharm. Bull.*, 1979, **27**, 1691.

<sup>167</sup> H. Boehme and A. Ingendoh, *Liebigs Ann. Chem.*, 1978, **381**.

<sup>168</sup> M. Maruta and N. Ishikawa, *J. Fluorine Chem.*, 1979, **13**, 111.

<sup>169</sup> M. R. Detty and G. P. Wood, *J. Org. Chem.*, 1980, **45**, 80.

<sup>170</sup> H. A. Klein, *Chem. Ber.*, 1979, **112**, 3037.

<sup>171</sup> N. Miyoshi, H. Ishii, S. Murai, and N. Sonoda, *Chem. Lett.*, 1979, 873.

<sup>172</sup> N. Miyoshi, K. Kondo, S. Murai, and N. Sonoda, *Chem. Lett.*, 1979, 909.

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<sup>174</sup> S. Ozawa, A. Itoh, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 1979, 2909.

<sup>175</sup> T. Kubota, S. Miyashita, T. Kitazume, and N. Ishikawa, *Chem. Lett.*, 1979, 845.

<sup>176</sup> F. I. Gasanov, V. N. Mamedov, M. R. Kulibekov, and A. G. Kuliev, *Azerb. Khim. Zh.*, 1978, **40** (*Chem. Abstr.*, 1980, **91**, 5031).

1,3-dione,<sup>177</sup> and halogenonitrobenzenes → alkyl aryl sulphides with replacement of both halogen and nitro-groups.<sup>178,179</sup> The last-mentioned study is a further example of the role of HMPA in substitution reactions. While an *o*- or *p*-alkylthio-substituent activates an aromatic nitro-group towards nucleophilic substitution (by  $\text{Pr}^1\text{SNa}$  in HMPA),<sup>178,180</sup> the same reagent can bring about the substitution of the halogen atom of unactivated aryl halides.<sup>179</sup> In contrast, the reaction of 2,4-dichloronitrobenzene with  $\text{PhSNa}$  in DMF leads to only Cl-substitution products.<sup>181</sup>  $\beta$ -Aryl-nitroalkanes react with  $\text{MeSNa}$  to yield rearranged  $\text{NO}_2$ -replacement products; the reaction is suggested to involve a phenonium radical intermediate.<sup>182</sup>

A fifty-fold increase in the rate of thiolysis of *p*-nitrophenyl acetate by arylthiolate anions in the presence of  $n\text{-C}_{16}\text{H}_{33}\text{NMe}_3^+ \text{Br}^-$  micelles has been accounted for entirely on the basis of enhanced concentrations of reactants in the micelle phase.<sup>183</sup>

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**Preparation from Sulphenyl and Selenenyl Halides.**—Most of the methods published in the period under review lead to  $\beta$ -halogeno-sulphides through additions

<sup>177</sup> G. F. Koser, S. M. Linden, and Y. J. Shih, *J. Org. Chem.*, 1978, **43**, 2676.

<sup>178</sup> P. Gogolli, L. Testaferri, M. Tingoli, and M. Tiecco, *J. Org. Chem.*, 1979, **44**, 2636.

<sup>179</sup> J. R. Beck and J. A. Yahner, *J. Org. Chem.*, 1978, **43**, 2048, 2052.

<sup>180</sup> P. Cogolli, F. Maiolo, L. Testaferri, M. Tingoli, and M. Tiecco, *J. Org. Chem.*, 1979, **44**, 2642.

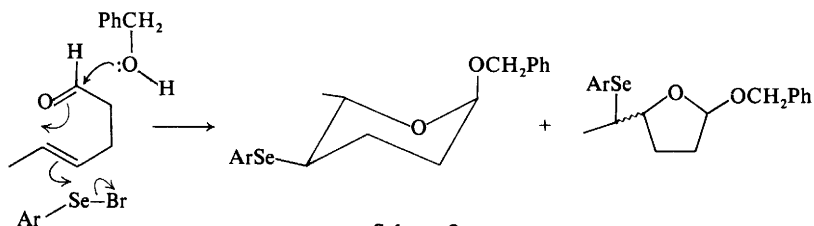
<sup>181</sup> R. F. Miller, J. C. Turley, G. E. Martin, L. Williams, and J. E. Hudson, *Synth. Commun.*, 1978, **8**, 371.

<sup>182</sup> N. Kornblum, J. Widmer, and S. C. Carlson, *J. Am. Chem. Soc.*, 1979, **101**, 658.

<sup>183</sup> I. M. Cuccovia, E. H. Schroeter, P. M. Monteiro, and H. Chaimovich, *J. Org. Chem.*, 1978, **43**, 2248.

to unsaturated systems, or to sulphides through nucleophilic attack at sulphur, but unusual variations on these general themes continue to be reported. Earlier work (see Vol. 5, p. 19), establishing the use of 6-diazopenicillinates for the synthesis of 6-chloro-6-phenylseleno-analogues, has been continued<sup>184</sup> and extended<sup>185</sup> to  $\alpha$ -diazo-ketones, where the presence of the chlorine atom in the initial product was exploited by dehydrochlorination, leading to  $\alpha$ -phenylselenyl- $\beta$ -unsaturated ketones.

While the substantial output from the research groups led by Zefirov and by Schmid and Garratt is aimed at mechanistic details (thiuranium ion intermediates are preferred), other workers continue to seek outlets in general organic synthesis for these reactions. The fact that the initial reaction products carry a halogen atom frequently favours subsequent substitution reactions, and when these involve intramolecular processes, the outcome of reactions of sulphenyl halides can be useful 'cyclofunctionalization' procedures. An interesting example, involving participation by a carbonyl group (Scheme 2), provides a new route to 2,6-dideoxyglycosides.<sup>186</sup> Further studies of the analogous 'phenylsulpheno-(seleneno)lactonization' of unsaturated carboxylic acids,<sup>187</sup> and related cyclizations leading to 2,5-dihydrofurans (rather than vinyloxirans) from  $\alpha$ -allenic alcohols,<sup>188</sup> functionalized tetrahydrofurans (from  $\gamma$ -hydroxy- $\beta$ -keto-alkenes),<sup>189</sup> 1,2-disubstituted 2,3-dihydrocarbazoles (from *o*-alkenyl-anilines),<sup>190</sup> and *cis*-perhydroindanes (from cyclonona-1,5-dienes)<sup>191</sup> illustrate the principle further. The ease with which these reactions occur is notable, but conditions can be found<sup>192</sup> for reactions between PhSeCl and alkenes in which the ensuing Cl-substitution reactions can be avoided. In this context it is relevant that  $\omega$ -hydroxyalkyl-alkynes also add PhSeCl without cyclization.<sup>193</sup> Intermolecular analogues of the cyclization reactions of PhSeCl-alkene adducts are also well established [hydroxyselenation of alkenes,<sup>194</sup>



Scheme 2

<sup>184</sup> P. J. Giddings, D. I. John, and E. J. Thomas, *Tetrahedron Lett.*, 1980, **21**, 395, 399.

<sup>185</sup> D. J. Buckley, S. Kulkowit, and A. McKervey, *J. Chem. Soc., Chem. Commun.*, 1980, 506.

<sup>186</sup> S. Current and K. B. Sharpless, *Tetrahedron Lett.*, 1978, 5075.

<sup>187</sup> K. C. Nicolaou, S. P. Seitz, W. J. Sipio, and J. F. Blount, *J. Am. Chem. Soc.*, 1979, **101**, 3884; D. Goldsmith, D. Liotta, C. Lee, and G. Zima, *Tetrahedron Lett.*, 1979, 4801.

<sup>188</sup> P. L. Beaulieu, V. M. Morisset, and D. G. Garratt, *Tetrahedron Lett.*, 1980, **21**, 129.

<sup>189</sup> Z. Lysenko, F. Ricciardi, J. E. Semple, P. C. Wang, and M. M. Joullié, *Tetrahedron Lett.*, 1978, 2679.

<sup>190</sup> D. L. J. Clive, C. K. Wong, W. A. Kiel, and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 1978, 379.

<sup>191</sup> D. L. J. Clive, G. Chittattu, and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 1978, 441.

<sup>192</sup> D. Liotta and G. Zima, *Tetrahedron Lett.*, 1978, 4977.

<sup>193</sup> C. N. Filer, D. Ahern, R. Fazio, and E. J. Shelton, *J. Org. Chem.*, 1980, **45**, 1313.

<sup>194</sup> A. Toshimitsu, T. Aoai, H. Owada, S. Uemura, and M. Okano, *J. Chem. Soc., Chem. Commun.*, 1980, 412.

or oxoselenation ( $\text{RCH}=\text{CH}_2 \rightarrow \text{RCHBrCH}_2\text{SePh}$ , which with DMSO give  $\text{RCOCH}_2\text{SePh}$ )<sup>195</sup>].

1,2-Adducts result from the addition of arenesulphenyl chlorides to 1,3-butadienes<sup>196</sup> and *O*-silyl dienolates  $\text{Me}_3\text{SiOCH}=\text{CHCH}=\text{CH}_2$ ,<sup>197</sup> the former rearranging to 1,4-adducts spontaneously (excepting the adduct with 1,3-butadiene itself), while the latter lose  $\text{Me}_3\text{SiCl}$ , resulting in overall  $\gamma$ -substitution of  $\alpha\beta$ -unsaturated aldehydes. The corresponding process occurs with  $\text{H}_2\text{C}=\text{CH}-\text{C}(\text{OSiMe}_3)=\text{CHMe}$  and  $\text{PhSeCl}$ .<sup>198</sup>

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Khim.*, 1978, 946 [ $(\text{CF}_3)_2\text{C}=\text{CF}_2 \rightarrow (\text{CF}_3)_2\text{C}(\text{SR})\text{CF}_2\text{Cl}$ ]; N. Pociute, D. Greiciute, and L. Rasteikiene, *Liet. TSR Mokslu Akad. Darb., Ser. B*, 1978, 75 (*Chem. Abstr.*, 1979, **89**, 179 518) [1,2-addition to unsaturated ketones]; K. Toyoshima, T. Okuyama, and T. Fueno, *J. Org. Chem.*, 1978, **43**, 2789 [addition of  $\text{PhSCl}$  to vinyl ethers and sulphides]; A. Chaudhuri, S. K. Bhattacharjee, and P. Sengupta, *Curr. Sci.*, 1978, **47**, 727 [ $\text{ArSBr} + \text{alkene} + \text{EtOH} \rightarrow \beta$ -ethoxyalkyl sulphides]; F. R. Tantasheva, V. S. Savelev, E. A. Berdnikov, and E. G. Kataev, *Zh. Org. Khim.*, 1978, **14**, 478 [ $\text{RSCl} + \text{vinyl sulphones}$ ]; E. V. Komissarova, N. N. Belyaev, and M. D. Stadnichuk, *Zh. Obshch. Khim.*, 1979, **49**, 938; M. D. Stadnichuk, V. A. Ryazantsev, and A. A. Petrov, *ibid.*, p. 956; and V. A. Ryazantsev and M. D. Stadnichuk, *ibid.*, p. 930 [whereas  $\text{Me}_3\text{SiC}\equiv\text{CCH}=\text{CH}_2 + \text{MeSCl} \rightarrow \text{Me}_3\text{SiC}(\text{SMe})=\text{CClCH}=\text{CH}_2$ ,  $\text{Bu}^t\text{C}\equiv\text{CCH}=\text{CH}_2$  gives  $\text{C}=\text{C}$  addition products and  $\text{ArSeCl} + \text{Me}_3\text{SiC}\equiv\text{CCH}=\text{CH}_2$  gives a mixture of  $\text{C}\equiv\text{C}$  and  $\text{C}=\text{C}$  addition products]; G. Capozzi, V. Lucchini, G. Modena, and P. Scrimin, *Nouv. J. Chim.*, 1978, **2**, 95 [ $\text{RSCl} + \text{alkynes}$  in liquid  $\text{SO}_2$ ]; **Substitution reactions of sulphenyl halides** J. F. Harris, *J. Org. Chem.*, 1979, **44**, 563 [free-radical substitution of toluene and saturated alkanes]; A. Chaudhuri and S. K. Bhattacharjee, *Indian J. Chem., Sect. B*, 1979, **18**, 279 [ $\text{ArSBr} + \text{aromatic compounds}$ ]; T. S. Croft, *Phosphorus Sulfur*, 1976, **2**, 133 [phenols +  $\text{CF}_3\text{SCl} \rightarrow$  *ortho*- and *para*-substitution products]; Yu. V. Zeifman, L. T. Lantseva, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1229 and K. Hiroi, Y. Matsuda, and S. Sato, *Chem. Pharm. Bull.*, 1979, **27**, 2338 [sulphenylation of ketone anions and 1,3-dicarbonyl dianions, respectively; see also A. De Groot and B. J. M. Jansen, *Recl. Trav. Chim. Pays-Bas*, 1979, **98**, 487]; D. Caine and W. D. Samuels, *Tetrahedron Lett.*, 1979, 3609 [regioselectivity of  $\alpha$ -phenylsulphenylation of ketone dienolates depends on structure of ketone and nature of reagent ( $\text{PhSCl}$ ,  $\text{PhSSPh}$ , or  $\text{PhSSO}_2\text{Ph}$ )]; K. Anzai, *J. Heterocycl. Chem.*, 1979, **16**, 567 [ $\text{RSCl} + \text{uracil} \rightarrow 5$ -(alkylthio)-derivative; indole  $\rightarrow 3$ -substituted derivative]; M. Raban and L.-J. Cherm, *J. Org. Chem.*, 1980, **45**, 1688 [duplication of indole reaction described in the preceding citation]; Yu. V. Zeifman, L. T. Lantseva, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2640 [bis(trifluoromethyl) carbanions +  $\text{RSCl}$ ]; N. V. Kondratenko, V. I. Popov, L. G. Yurchenko, A. A. Kolomiitsev, and L. M. Yagupolskii, *Zh. Org. Khim.*, 1978, **14**, 1914 [ $\text{ArSCl} + (\text{CF}_3)_3\text{CSH} \rightarrow \text{ArSC}(\text{CF}_3)_3$ ].

<sup>195</sup> S. Raucher, *Tetrahedron Lett.*, 1978, 2261.

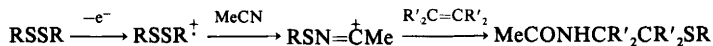
<sup>196</sup> G. H. Schmid, S. Yeroushalmi, and D. G. Garratt, *J. Org. Chem.*, 1980, **45**, 910.

<sup>197</sup> I. Fleming, J. Goldhill, and I. Peterson, *Tetrahedron Lett.*, 1979, 3205.

<sup>198</sup> S. Danishefsky and C. F. Yan, *Synth. Commun.*, 1978, **8**, 211.

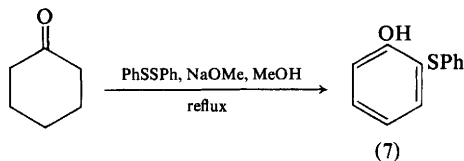
**Preparation from Disulphides, Diselenides, and Ditellurides.**—The use of disulphides as sulphenylating agents towards alkenes and carbanions continue to offer a distinctive alternative to the use of sulphenyl halides for the same purpose. Although reaction conditions are more severe, cleaner results are usually obtained. The special case of the conversion of disulphides into corresponding sulphides is covered in the later section on Reactions of Disulphides.

Irradiation of a mixture of MeSSMe and  $F_2C=CH_2$  with u.v. light gives  $MeSCF_2CH_2SMe$ , a compound which can be prepared less conveniently from  $F_2C=CHBr$  with MeSH and MeSNa.<sup>199</sup> Anodic oxidation of disulphides in the presence of alkenes in MeCN gives  $\beta$ -acetamidoalkyl sulphides:<sup>200</sup>



Related double-functionalization procedures for alkenes have been established for the preparation of 2-acetoxyalkyl phenyl selenides [PhSeSePh with  $Cu(OAc)_2$  and AcOH],<sup>201</sup>  $\beta$ -hydroxyalkyl aryl sulphides [ArSSAr with  $Pb(OAc)_4$  and TFA, for Markownikov 'trans-hydroxysulphenylation'],<sup>202</sup> and  $\beta$ -ketoalkyl selenides [PhSeSePh with  $Br_2$  and  $(Bu^o_3Sn)_2O$ ].<sup>203</sup>

$\alpha$ -Sulphenylation of carbonyl compounds is achieved by the use of a strong base (e.g. aldehyde + KH  $\rightarrow$  potassium enolate  $\rightarrow$  PhSCR'R<sup>2</sup>CHO with PhSSPh<sup>204</sup>), but in the cyclohexanone series these conditions can be too severe.<sup>205</sup> An extraordinary discovery has been made<sup>205</sup> in a search for alternatives to the usual aprotic reaction media used for the sulphenylation of ketones, namely that in MeOH, with NaOMe as the base, dehydrogenative sulphenylation of cyclohexanones occurs, leading to *o*-(phenylthio)phenols (7).



2-Arylsulphenylation of 1,3-dicarbonyl compounds can be effected at room temperature in an  $Et_4N^+ F^-$  emulsion,<sup>206</sup> but dianions  $R^1\overset{-}{C}HCO\overset{-}{C}HR^2$ , formed by successive treatment with NaH and  $Bu^oLi$ , are sulphenylated at the alternative site by PhSSPh.<sup>207</sup>  $\beta$ -Keto-esters, malonates, and  $\alpha$ -cyanoalkanoates can be sulphenylated and decarboxylated in a 'one-pot' process by reaction at 150–160 °C, in HMPA, with PhSSPh and NaI, providing  $\alpha$ -(phenylthio)alkyl ketones,  $\alpha$ -(phenylthio)alkanoates, and  $\alpha$ -cyanoalkyl phenyl sulphides,

<sup>199</sup> D. W. A. Sharp and H. T. Miguel, *Isr. J. Chem.*, 1978, **17**, 144.

<sup>200</sup> A. Bewick, D. E. Coe, J. M. Mellor, and D. J. Walton, *J. Chem. Soc., Chem. Commun.*, 1980, 51.

<sup>201</sup> N. Miyoshi, Y. Ohno, K. Kondo, S. Murai, and N. Sonoda, *Chem. Lett.*, 1979, 1309.

<sup>202</sup> B. M. Trost, M. Ochiai, and P. G. McDougal, *J. Am. Chem. Soc.*, 1978, **100**, 7103.

<sup>203</sup> I. Kuwajima and M. Shimizu, *Tetrahedron Lett.*, 1978, 1277.

<sup>204</sup> P. Groenewegen, H. Kallenberg, and A. van der Gen, *Tetrahedron Lett.*, 1979, 2817.

<sup>205</sup> B. M. Trost and J. H. Rigby, *Tetrahedron Lett.*, 1978, 1667.

<sup>206</sup> J. H. Clark and J. M. Miller, *Can. J. Chem.*, 1978, **56**, 141.

<sup>207</sup> K. Hiroi, Y. Matsuda, and S. Sato, *Synthesis*, 1979, 621.



respectively.<sup>208</sup> The alkyl moiety of the displaced alkoxy carbonyl group appears in the alkyl phenyl sulphide which accompanies the main reaction product.<sup>208</sup> 1,3-Bis(methylthio)-2,2,4,4-tetramethylbicyclo[1.1.0]butane has been established<sup>209</sup> as the product from the parent hydrocarbon with MeSSMe and Bu<sup>n</sup>Li, correcting earlier assignments. Sulphenylation of  $\alpha$ -phenylalkyl cyanides with PhSSPh and KOH in THF gives PhCR(CN)SPh,<sup>210</sup> but acetonitrile gives the dithioacetal (PhS)<sub>2</sub>CHCN. Similarly,<sup>211</sup> the ratio of disulphide to substrate must be carefully controlled to avoid *gem*-bis-phenylsulphenylation in the conversion of *o*-toluate esters into *o*-(phenylthiomethyl) analogues.<sup>211</sup> A more classical approach provides an *erythro*/*threo* mixture of MeSSCHMeSCHMeSMe (a constituent of roast pork) through treatment of 'but-2-ene thio-ozonide' (3,5-dimethyl-1,2,4-trithiolan) with MeLi, then with MeSSMe.<sup>212</sup>

A singlet benzyne intermediate is involved in the conversion of diaryliodonium 2-carboxylates into *o*-diselenides, *o*-ditellurides, and *o*-arylselenoaryl aryl tellurides by reaction with ArSeSeAr, ArTeTeAr, or ArSeTeAr respectively.<sup>213</sup>

**Preparation from Thiocyanates, Selenocyanates, and Tellurocyanates.**—Less commonly used, but nevertheless well-established, routes to sulphides, selenides, and tellurides are offered by the use of these reagents; more space is devoted to the derivatives of the heavier chalcogens.

Appropriate proportions of alkyl thiocyanate and oxalyl chloride condense to give (RSCCl=NCO)<sub>2</sub> or RSCCl=NCOCOCI.<sup>214</sup> A valuable route from alkanols to sulphides,<sup>215</sup> using a thiocyanate together with triphenylphosphine (or, better, tri-*n*-butylphosphine<sup>216</sup>), relies on the rearrangement of an intermediate phosphorane ether R<sup>1</sup>SPPh<sub>3</sub>OR<sup>2</sup>, and consequently it is subject to variable behaviour, depending on the structural features in the alcohol. Whereas ArSCN + HOCH<sub>2</sub>CH<sub>2</sub>OH (Ar = Ph) gives ArSCH<sub>2</sub>CH<sub>2</sub>OH, from which an unsymmetrical 1,2-bis(arylthio)ethane can be obtained by repetition of the process, both hydroxy-groups are substituted in the case of Ar = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, and neither hydroxy-group is substituted when Ar is *p*-MeOC<sub>6</sub>H<sub>4</sub>.<sup>216</sup> The same reaction is suitable for the conversion of alk-2-enols into *p*-nitrophenyl selenides,<sup>217</sup> thus avoiding the 1,3-selenoallylic rearrangements which occur in other routes.

Copper(I or II)-catalysed addition of PhSeCN to an alkene, followed by reaction with an alcohol, gives *trans*- $\beta$ -alkoxyalkyl phenyl selenides.<sup>218</sup> An extension of this reaction has been used<sup>219</sup> to convert cyclo-octa-1,5-diene into a mixture of the isomeric oxygen-bridged 1,4- and 1,5-bis(phenylseleno)cyclo-octanes. The first

<sup>208</sup> M. Asaoka, K. Miyake, and H. Takei, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3008.

<sup>209</sup> P. G. Gassmann and M. J. Mullins, *Tetrahedron Lett.*, 1979, 4457.

<sup>210</sup> E. Marchaud, G. Morel, and A. Foucaud, *Synthesis*, 1978, 360.

<sup>211</sup> F. M. Hauser, R. P. Rhee, S. Prasanna, S. M. Weinreb, and J. H. Dodd, *Synthesis*, 1980, 72.

<sup>212</sup> P. Dubs and M. Joho, *Helv. Chim. Acta*, 1978, **61**, 2809.

<sup>213</sup> J. B. S. Bouilha, N. Petragnani, and V. G. Toscano, *Chem. Ber.*, 1978, **111**, 2510.

<sup>214</sup> W. Boehmer and D. Herrmann, *Liebigs Ann. Chem.*, 1978, 1704.

<sup>215</sup> W. T. Flowers, G. Holt, F. Omogbai, and C. P. Poulos, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1309.

<sup>216</sup> K. A. M. Walker, *Tetrahedron Lett.*, 1977, 4475.

<sup>217</sup> D. L. J. Clive, G. Chittattu, N. J. Curtis, and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 1978, 770.

<sup>218</sup> A. Toshimitsu, T. Aoai, S. Uemura, and M. Okano, *J. Org. Chem.*, 1980, **45**, 1953.

<sup>219</sup> S. Uemura, A. Toshimitsu, T. Aoai, and M. Okano, *J. Chem. Soc., Chem. Commun.*, 1979, 610.

example of the use of  $\text{PhCH}_2\text{TeCN}$  as a *C*-benzyltellurenylation agent<sup>220</sup> gives full details of the synthesis of benzyl *o*-nitrophenyl telluride from *o*- $\text{NO}_2\text{C}_6\text{H}_4\text{Li}$ .

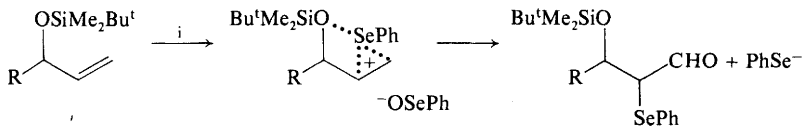
Net *syn*-addition, with Markownikov orientation, has been established for the addition of  $\text{PhSeSCN}$  to (*E*)- and (*Z*)-1-phenylpropene under kinetic control, further interest arising in the fact that the (*Z*)-isomer leads to 2-(phenylselenyl)-1-phenylpropyl thiocyanate, while the (*E*)-isomer gives the corresponding isothiocyanate.<sup>221</sup>

**Preparation of Sulphides, Selenides, and Tellurides using Other Sulphenylation, Selenenylation, and Tellurenylation Reagents.**—Sulphenamides are effective reagents for  $\alpha$ -heteroarylsulphenylation of  $\beta$ -keto-esters.<sup>222</sup> Sulphenamide intermediates are thought to be involved in the asymmetric 2-phenylsulphenylation of 4-alkylcyclohexanones in moderate optical yields, using a benzenesulphenyl halide with a chiral secondary alkylamine.<sup>223</sup>

Thiolsulphonates are effective in sulphenylation reactions, having been used recently for the stereoselective synthesis of allyl vinyl sulphides from  $\text{RCH}=\text{CH}-\text{AlBu}_2\text{Bu}^n$ .<sup>224</sup> Mild reaction conditions are called for in the sulphenylation of active-methylene compounds by  $(\text{ArSO}_2)_2\text{CHSSO}_2\text{Ph}$ .<sup>225</sup>

Alkyl potassium xanthates  $\text{R}^1\text{OCSSK}$  react with organic halides  $\text{R}^2\text{X}$  to give sulphides  $\text{R}^1\text{SR}^2$  ( $\text{R}^1 = \text{Et}$ ,  $\text{R}^2 = 4$ -trifluoromethyl-2,6-dinitrophenyl<sup>226</sup> and  $\text{R}^1, \text{R}^2$  are various alkyl<sup>227</sup>). Under phase-transfer conditions, this is an efficient 'one-pot' synthesis of unsymmetrical sulphides.<sup>227</sup>

Important uses of selenenic and seleninic acids and anhydrides (see also the later sections) have been established, in the synthesis of  $\beta$ -silyloxy- $\alpha$ -(phenylseleno)aldehydes from allyl silyl ethers (Scheme 3)<sup>228</sup> and in the high-yield syntheses of 2-acetoxyalkyl phenyl selenides [using  $\text{PhSe}(\text{O})\text{OH}$  and  $\text{AcOH}$ <sup>229</sup>] and 2-hydroxyalkyl selenides [using  $\text{RSe}(\text{O})\text{OH}$  and  $\text{H}_3\text{PO}_2$ <sup>230</sup>] from alkenes. The effective reagent in the  $\text{RSe}(\text{O})\text{OH}-\text{H}_3\text{PO}_2$  system is assumed<sup>230</sup> to be the selenenic acid  $\text{RSeOH}$ , but this probably needs further consideration.



Reagents: i,  $\text{PhSe}(\text{O})\text{SePh}$

Scheme 3

<sup>220</sup> P. Wiryachitra, S. J. Falcone, and M. P. Cava, *J. Org. Chem.*, 1979, **44**, 3957.

<sup>221</sup> D. G. Garratt, *Can J. Chem.*, 1979, **57**, 2180.

<sup>222</sup> S. Torii, H. Tanaka, and H. Okumoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 267.

<sup>223</sup> K. Hiroi, M. Nishida, A. Nakayama, K. Nakazawa, E. Fujii, and S. Sato, *Chem. Lett.*, 1979, 969.

<sup>224</sup> A. P. Kozikowski, A. Ames, and H. Wetter, *J. Organomet. Chem.*, 1978, **164**, C33.

<sup>225</sup> A. Senning, *Synthesis*, 1980, 412.

<sup>226</sup> J. J. D'Amico, C. C. Tung, W. E. Dahl, and D. J. Dahm, *Phosphorus Sulfur*, 1978, **4**, 267.

<sup>227</sup> I. Degani, R. Fochi, and V. Regondi, *Synthesis*, 1979, 178.

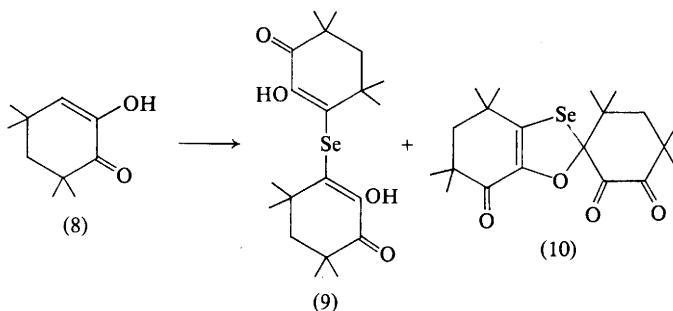
<sup>228</sup> M. Shimizu, R. Takeda, and I. Kuwajima, *Tetrahedron Lett.*, 1979, 3461.

<sup>229</sup> N. Miyoshi, Y. Takai, S. Murai, and N. Sonoda, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1265.

<sup>230</sup> D. Labar, A. Krief, and L. Hevesi, *Tetrahedron Lett.*, 1978, 3967.

**Preparation of Sulphides, Selenides, and Tellurides using the Elements Themselves, or Other Inorganic Sulphur, Selenium, and Tellurium Compounds.**—Symmetrical sulphides can be obtained in 12—66% yields from an alkyl chloride, sulphur, and NaOH in DMSO.<sup>231</sup> The same system with a benzyl cyanide  $R^1PhC(CN)SR^2$  with an alkyl halide  $R^2X$ ;<sup>231,232</sup> some disulphide is also formed in this reaction.<sup>232</sup> Lithium sulphide and persulphide, (which are formed *in situ* from  $S_8$  and  $LiEt_3BH$ , and which remain dissolved in THF) give sulphides and disulphides, respectively, with alkyl halides.<sup>233</sup> Continuing studies are represented in the lithiation of 3,5-disubstituted thien-2-yl sulphides followed by reaction with  $S_8$  and  $MeI$ <sup>234</sup> and in the synthesis of sulphides<sup>235</sup> from alkynes  $[ArSO_2CH_2CH=CMeC\equiv CH + Na_2S \rightarrow (ArSO_2CH_2CH=CMeC\equiv C)_2S]$ . Routine kinetic studies of the reactions of  $Bu^nCl$  with  $Na_2S$  and with  $Bu^nSnA$  have been reported.<sup>236</sup> Sulphides can be prepared from alkenes and  $SCl_2$ .<sup>625</sup>

Selenides and tellurides are formed through the reaction sequences  $PhCH_2MgCl + Se_8 \rightarrow PhCH_2SeMgCl$ , which with  $RN_2^+ Cl^- \rightarrow PhCH_2SeR$ ,<sup>237</sup> and thiophens +  $Te_8 + MeI \rightarrow$  thienyl methyl tellurides.<sup>238</sup> Unexpected selenide by-products have, paradoxically, become common in oxidations by  $SeO_2$ , and the selenides (9) and (10) accompany the expected 1,2-diketone in the oxidation of (8) with  $SeO_2$  in dioxan.<sup>239</sup>



**Miscellaneous Methods of Preparation.**—This Chapter is interwoven with accounts of the reactions of sulphur, selenium, and tellurium compounds which amount to the conversion of one sulphur-containing functional group into another. This small section is included to collect together a variety of methods for the synthesis of sulphides from sulphur compounds other than those mentioned in the preceding sections.

Thiones participate in an ene-reaction with alkyldenecyclohexanes and methyl-

<sup>231</sup> A. Jonczyk, *Angew. Chem.*, 1979, **91**, 228.

<sup>232</sup> E. Marchaud, G. Morel, and A. Foucaud, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1979, **289**, 57.

<sup>233</sup> J. A. Gladysz, V. K. Wong, and B. S. Jick, *J. Chem. Soc., Chem. Commun.*, 1978, 838.

<sup>234</sup> Ya. L. Gol'dfarb and M. A. Kalik, *Zh. Org. Khim.*, 1978, **14**, 2603.

<sup>235</sup> A. D. Bulat, M. A. Antipov, and B. V. Passet, *Zh. Org. Khim.*, 1979, **15**, 2225.

<sup>236</sup> S. R. Rafikov, R. S. Aleev, A. L. Dobrikov, S. N. Salazkin, and V. D. Komissarov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2812.

<sup>237</sup> V. P. Krasnov, V. I. Naddaka, V. P. Garkin, and V. I. Minkin, *Zh. Org. Khim.*, 1978, **14**, 2620.

<sup>238</sup> N. Dereu and J. L. Piette, *Bull. Soc. Chim. Fr., Part 2*, 1979, 623.

<sup>239</sup> T. Laitalainen, T. Simonen, and R. Kivekas, *Tetrahedron Lett.*, 1978, 3079.

cyclohexane to give allyl sulphides.<sup>240</sup> An unusual reaction has been described<sup>241</sup> in which pyridine-4-thione gives di-(4-pyridyl) sulphide in refluxing decalin; pyridine-2-thione reacts similarly. Addition of pyridine-3-thiol to the reaction mixtures gives crossed products. Studies of 1,2- and 1,3-bis(dimethylamino)cyclobutene-dithiones (see Vol. 4, p. 9) have continued, and reactions with MeSH to give various products, including methyl sulphides, have been described.<sup>242</sup> Diphenylphosphino-dithioate esters  $\text{Ph}_2\text{P}(\text{S})\text{SR}$  react with alkyl-lithiums at  $-78^\circ\text{C}$  to establish a general synthesis of unsymmetrical sulphides.<sup>243</sup>

Examples of previously described methods are the ring-opening of thiirans [ethylene sulphide with  $\text{Pr}^n\text{ONa}$  and  $\text{H}_2\text{C}=\text{CHCH}_2\text{Cl} \rightarrow \text{Pr}^n\text{O}(\text{CH}_2\text{CH}_2\text{S})_n\text{CH}_2\text{CH}=\text{CH}_2$  ( $n = 1$  or  $2$ )],<sup>244</sup> the use of a chlorosulphonium salt ( $\text{RCO}_2^-\text{Et}_3\text{NH}^+ + \text{Me}_2\text{S} \rightarrow \text{RCO}_2\text{CH}_2\text{SMe}$ ),<sup>245</sup> C—Se bond cleavage of a diselenoacetal  $[(\text{PhSe})_2\text{CRSiMe}_3 + \text{Bu}^n\text{Li} \rightarrow \text{PhSeCRLi}(\text{SiMe}_3)]$ ,<sup>246</sup> cleavage of sulphimides  $[\text{R}^1\text{R}^2\text{S}=\text{NR}^3 + \text{P}_4\text{S}_{10} \rightarrow \text{R}^1\text{SR}^2]$ ,<sup>247</sup> and methylthiomethylation of phenols (phenols +  $\text{Me}_2\text{S}=\text{NR} \rightarrow o\text{-methylthiomethyl-phenols}$ ).<sup>248</sup>

**Reactions of Sulphides: Simple Reactions and Fundamental Properties.**—This title is used as a collecting point for papers describing the pyrolysis of  $\text{Me}_2\text{S}$  or thiiran (giving  $\text{H}_2\text{C}=\text{CHSH}$  and thiophen),<sup>249</sup> hydrogen abstraction from  $\text{Me}_2\text{S}$  by  $\text{CF}_3\cdot$  radical,<sup>250</sup> oxidation of simple sulphides by singlet oxygen<sup>251</sup> or ozone,<sup>252</sup> C—S bond cleavage of  $\text{Me}_2\text{S}$  by  $\text{H}\cdot$ <sup>253</sup> or using recoil  $^3\text{H}$  atoms,<sup>254</sup> and a study of the exchange equilibrium involving  $\text{PhSMe}$  and  $\text{PhS}^-$ .<sup>255</sup>

Fundamental properties are revealed in kinetic acidity studies (the kinetic acidity of  $m\text{-CF}_3\text{C}_6\text{H}_4\text{SMe}$  is greater than that of the selenium analogue by a factor of 1.38),<sup>256</sup> polarography ( $\text{RSCH}_2\text{CH}_2\text{COCO}_2\text{R}$  is protonated at a carbonyl group rather than at sulphur),<sup>257</sup> voltammetry (three successive anodic peaks for  $\text{Ph}_2\text{Se}$  at Pt in MeCN),<sup>258</sup> and complexation enthalpies of 1, $\omega$ -bis-( $n$ -butylthio)alkanes with

<sup>240</sup> Y. Inoue and D. J. Burton, *J. Fluorine Chem.*, 1979, **14**, 89.

<sup>241</sup> K. Krowicki, *Pol. J. Chem.*, 1978, **52**, 2349.

<sup>242</sup> G. Seitz, R. Schmiedel, and K. Mann, *Arch. Pharm. (Weinheim, Ger.)*, 1977, **310**, 991; G. Seitz, K. Mann, R. Schmiedel, and R. Matusch, *Chem. Ber.*, 1979, **112**, 990; R. Matusch, R. Schmiedel, and G. Seitz, *Liebigs Ann. Chem.*, 1979, 595.

<sup>243</sup> M. Yoshifuji, F. Hanafusa, and N. Inamoto, *Chem. Lett.*, 1979, 723; K. Goda, F. Hanafusa, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 818.

<sup>244</sup> A. A. Rodin, K. A. Vyunov, A. I. Ginak, and E. G. Sochilin, *Zh. Org. Khim.*, 1979, **15**, 2252.

<sup>245</sup> T.-L. Ho, *Synth. Commun.*, 1979, **9**, 267.

<sup>246</sup> D. Van Ende, W. Dumont, and A. Krief, *J. Organomet. Chem.*, 1978, **149**, C10.

<sup>247</sup> I. W. J. Still and K. Turnbull, *Synthesis*, 1978, 540.

<sup>248</sup> T. Yamamoto and M. Okawara, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2443.

<sup>249</sup> E. N. Deryagina, E. N. Sukhomazova, O. B. Bannikova, and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2103.

<sup>250</sup> N. L. Arthur and K. S. Yeo, *Aust. J. Chem.*, 1979, **32**, 2077.

<sup>251</sup> B. M. Monroe, *Photochem. Photobiol.*, 1979, **29**, 761; M. L. Kacher and C. S. Foote, *ibid.*, p. 765.

<sup>252</sup> R. I. Martinez and J. T. Herron, *Int. J. Chem. Kinet.*, 1978, **10**, 433.

<sup>253</sup> T. Yokata and O. P. Strausz, *J. Phys. Chem.*, 1979, **83**, 3196.

<sup>254</sup> M. Casigliani and P. Volpe, *Gazz. Chim. Ital.*, 1979, **109**, 187.

<sup>255</sup> E. S. Lewis and S. Kukes, *J. Am. Chem. Soc.*, 1979, **101**, 417.

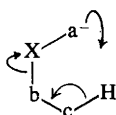
<sup>256</sup> H. J. Reich, F. Chow, and S. K. Shah, *J. Am. Chem. Soc.*, 1979, **101**, 6638.

<sup>257</sup> J. Moiroux, *Electrochim. Acta*, 1978, **23**, 571.

<sup>258</sup> R. Seeber, A. Cinquantini, P. Zanello, and G. A. Mazzocchin, *J. Electroanal. Chem. Interfacial Electrochem.*, 1978, **88**, 137.

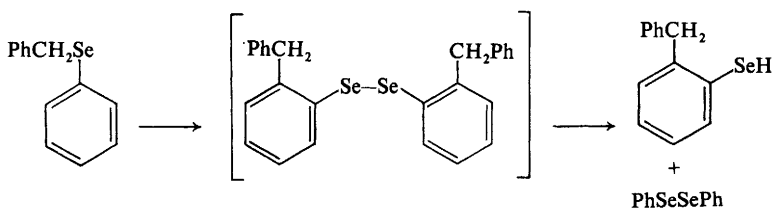
$\text{BBr}_3$ ,  $\text{AlBr}_3$ , and  $\text{GaCl}_3$ <sup>259</sup> (a topic distantly related to an analysis of g.l.c. data for 39 n-alkyl isoalkyl sulphides<sup>260</sup>).

**Reactions of Sulphides, Selenides, and Tellurides: Rearrangements, and C–S, C–Se, and C–Te Bond Cleavage Reactions.**—There is some overlap between this and later sections, since many uses of sulphides, selenides, and tellurides in synthesis involve rearrangements, and most uses in synthesis depend on a clean cleavage of the sulphide, selenide, or telluride functional group.



(11)

An important approach to alkene synthesis, using the so-called  $\alpha\beta$ -elimination (11) of  $\alpha$ -sulphenyl carbanions, has been studied for the synthesis of *cis*-cyclo-octene from allyl, benzyl, and methyl cyclo-octyl sulphides.<sup>261</sup> Photorearrangement of benzyl phenyl sulphides<sup>262</sup> and the corresponding selenides,<sup>263</sup> followed by methylation, gives *o*-arylphenyl methyl sulphides and selenides (Scheme 4). Further studies of the Claisen rearrangements of allyl 2- and 3-thienyl sulphides, leading to 3-(2-)allylthiophen-2-(3-)thiols, respectively, and their cyclization products, have been described.<sup>264</sup> 1,3-Shifts of alkylthio- and arylthio-groups which occur following the creation of a carbonium ion at the  $\alpha$ -carbon atom (or an equivalent process) in alkyl benzyl or phenyl sulphides continue to be studied in several laboratories. Acetolysis of [<sup>13</sup>C]diazomethyl 1-(phenylthio)alkyl ketones gives products resulting from a 1,3-shift of PhS ( $\text{PhSCH}_2\text{CO}^{13}\text{CHN}_2 \rightarrow \text{PhSCH}_2\text{CO}^{13}\text{CH}_2\text{OAc} + \text{PhS}^{13}\text{CH}_2\text{COCH}_2\text{OAc}$ ). The corresponding shift does not occur in the reaction



Scheme 4

<sup>259</sup> L. A. Ganyushin, E. N. Guryanova, and I. P. Romm, *Zh. Obshch. Khim.*, 1978, **48**, 2478.

<sup>260</sup> R. V. Golovnya, V. G. Garbuzov, and T. A. Misharina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 387.

<sup>261</sup> J. F. Biellmann, H. d'Orchymont, and J. L. Schmitt, *J. Am. Chem. Soc.*, 1979, **101**, 3283.

<sup>262</sup> J.-L. Fourrey and P. Jouin, *J. Org. Chem.*, 1979, **44**, 1892.

<sup>263</sup> J.-L. Fourrey, G. Henry, and P. Jouin, *Tetrahedron Lett.*, 1980, **21**, 455.

<sup>264</sup> A. V. Anisimov, V. Fionova, and E. A. Viktorova, *Khim. Geterotsikl. Soedin.*, 1978, 186; A. V. Anisimov, V. F. Ionova, V. K. Govorek, V. S. Babaitsev, and E. A. Viktorova, *Dokl. Akad. Nauk SSSR*, 1979, **244**, 362; A. V. Anisimov, V. F. Ionova, V. S. Babaitsev, and E. A. Viktorova, *Zh. Org. Khim.*, 1979, **15**, 882; A. V. Anisimov, V. F. Ionova, and E. A. Viktorova, *ibid.*, p. 1970.

with the oxygen analogue.<sup>265</sup> Extensive studies<sup>266</sup> of equivalent aminolysis and solvolysis studies of *erythro*/*threo*- $\beta$ -chloroalkyl phenyl sulphides, in which 1,3-shifts are accompanied by E1cb elimination, leading to vinyl sulphides, indicate generally lower rates for the *erythro*-isomers. Detailed assessment of the effect of structure has been reported<sup>267</sup> for the methanolysis of benzyl  $\gamma$ -toluene-*p*-sulphonyloxyalkyl sulphides, PhCH<sub>2</sub>SCR<sup>1</sup>R<sup>2</sup>CH<sub>2</sub>CHR<sup>3</sup>OTs, indicating that at least two of the three groups R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> should be an alkyl group if migration of PhCH<sub>2</sub>S is to occur (a good illustration of the Thorpe–Ingold effect). There is clearly considerable scope for rationalization, with respect to structure and reaction conditions, of the results which have accumulated on the tendency for 1,3-shifts to occur; the corresponding rearrangements of allylic sulphides are discussed in the later section dealing with unsaturated sulphides.

Shifts from S to N in 1-alkyl-2-alkylthio- or -arylthio-imidazoles have been studied.<sup>268</sup>

2-(Alkylthio)cycloalkanones give C–S cleavage products on photolysis in MeOH, in interesting contrast with the behaviour of 2-cyano-analogues, which yield  $\omega$ -cyanoalkanoate esters.<sup>269</sup> Photolysis of 4-alkenyl sulphides, leading to mixtures of thians and thiolans, involves reversible C–S bond homolysis,<sup>270</sup> while insertion into the C–S bond by carbenes through photolysis of ethyl  $\alpha$ -(trimethylstannyl)diazoacetate in Me<sub>2</sub>S leads predominantly (35%) to Me<sub>3</sub>SnCMe(SMe)CO<sub>2</sub>Et, with 12% of MeSCHMeCO<sub>2</sub>Et.<sup>271</sup> Electrochemical cleavage processes are represented in the formation of thiols and alkanes,<sup>272,273</sup> and in the oxidative decarboxylation and cleavage of  $\alpha$ -(phenylthio)alkanoic acids in alcoholic solutions, leading to aldehydes and acetals.<sup>274</sup>

Reductive cleavage of sulphides, selenides, and tellurides on Raney nickel<sup>275</sup> and cleavage by lithium in THF, leading to secondary or tertiary alkyl-lithium compounds,<sup>276</sup> are useful synthetic operations; novel variations are involved in the cleavage of dialkenyl sulphides with Et<sub>3</sub>SiH (giving low yields of silyl sulphides)<sup>277</sup> and of alkenyl, aryl, and allyl sulphides and selenides with PPh<sub>3</sub> and

<sup>265</sup> S. Gladiali, A. Pusino, V. Rosnati, A. Saba, F. Soccolini, and A. Selva, *Gazz. Chim. Ital.*, 1977, **107**, 535; A. Pusino, V. Rosnati, A. Saba, F. Soccolini, and A. Selva, *ibid.*, 1978, **108**, 557.

<sup>266</sup> L. Rasteikiene, V. Zabelaite-Miskiniene, E. Stumbreviciute, M. G. Linkova, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1099; J. Kulis, D. Greiciute, S. Jonusauskas, and L. Rasteikiene, *Zh. Org. Khim.*, 1978, **14**, 1492; L. Rasteikiene, J. Kulis, and V. Vidugiriene, *ibid.*, 1979, **15**, 531; Z. Talaikyte, V. Vidugiriene, and L. Rasteikiene, *Zh. Vses. Khim., O-va.*, 1979, **24**, 102 (*Chem. Abstr.*, 1979, **90**, 185 962); D. Greiciute, J. Kulis, and L. Rasteikiene, *Phosphorus Sulfur*, 1977, **3**, 261.

<sup>267</sup> E. L. Eliel, W. H. Pearson, L. M. Jewell, A. G. Abatjoglou, and W. R. Kenan, *Tetrahedron Lett.*, 1980, **21**, 331.

<sup>268</sup> J. Kister, G. Assef, G. Mille, and J. Metzger, *Can. J. Chem.*, 1979, **57**, 822.

<sup>269</sup> M. Tokuda, Y. Watanabe, and M. Itoh, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 905.

<sup>270</sup> G. Bastien and J. M. Surzur, *Bull. Soc. Chim. Fr., Part 2*, 1979, 601; G. Bastien, M. P. Crozet, E. Flesia, and J. M. Surzur, *ibid.*, p. 606.

<sup>271</sup> W. Ando, M. Takata, and A. Sekiguchi, *J. Chem. Soc., Chem. Commun.*, 1979, 1121.

<sup>272</sup> M. Miyake, Y. Nakayama, M. Nomura, and S. Kikkawa, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 559.

<sup>273</sup> G. Farnia, M. G. Severin, G. Capobianco, and E. Vianello, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1.

<sup>274</sup> J. Nokami, M. Kawada, R. Okawara, S. Torii, and H. Tanaka, *Tetrahedron Lett.*, 1979, 1045.

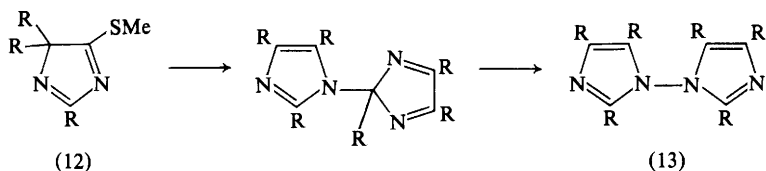
<sup>275</sup> L. Horner and G. Doms, *Phosphorus Sulfur*, 1978, **4**, 259.

<sup>276</sup> C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 1979, **44**, 713.

<sup>277</sup> M. G. Voronkov, S. A. Bolshakova, N. N. Vlasova, S. V. Amosova, and B. A. Trofimov, *Zh. Obshch. Khim.*, 1979, **49**, 1914.

NiCl<sub>2</sub>, leading to alkenes and arenes.<sup>278</sup> In a comparative assessment of the PPh<sub>3</sub>-NiCl<sub>2</sub> system, the order of bond cleavage PhSeMe  $\gg$  PhCl  $>$  PhSMe was established.<sup>278</sup> Several papers describe the conversion of  $\beta$ -hydroxyalkyl sulphides, readily obtained from  $\alpha$ -(alkylthio)alkyl-lithium compounds and carbonyl compounds, into alkenes, using P<sub>2</sub>I<sub>4</sub>, PI<sub>3</sub>, or SOCl<sub>2</sub>,<sup>279</sup> electrochemical reduction,<sup>280</sup> or 1-ethyl-2-fluoropyridinium tetrafluoroborate and LiI.<sup>281</sup> The analogous process with  $\beta$ -hydroxyalkyl selenides, using MeSO<sub>2</sub>Cl and Et<sub>3</sub>N, has also been described.<sup>256</sup> Mild catalytic oxidation, employing physiological conditions {O<sub>2</sub> with [R<sub>2</sub>CO<sup>II</sup>], a cytochrome system, or [Fe(CIO<sub>4</sub>)<sub>2</sub>] with ascorbic acid}, of alkyl phenyl sulphides in which the alkyl group carries an  $\alpha$ -hydrogen atom leads to products from C-S bond cleavage (PhSCHR<sup>1</sup>R<sup>2</sup>  $\rightarrow$  PhSSPh + R<sup>1</sup>COR<sup>2</sup>) and sulphoxides.<sup>282</sup> Whereas  $\beta$ -keto-alkyl sulphides are converted into  $\alpha$ -keto-aldehyde dimethyl acetals by [Ti(NO<sub>3</sub>)<sub>3</sub>] in MeOH, the same treatment of  $\beta$ -keto-alkyl selenides gives  $\alpha\beta$ -unsaturated ketones,<sup>283</sup> as does the oxidation of  $\beta$ -hydroxyalkyl selenides with Jones' reagent.<sup>284</sup> Oxidation without C-Se bond cleavage occurs, however, when  $\beta$ -hydroxyalkyl selenides are treated with *N*-succinimidyldimethylsulphonium chloride and Et<sub>3</sub>N, providing a useful synthesis of  $\beta$ -keto-alkyl selenides.<sup>284</sup>

Free-radical intermediates are involved in the pyrolytic cleavage of C-S bonds of 5-(methylthio)imidazoles, *i.e.* (12)  $\rightarrow$  (13).<sup>285</sup>



**Reactions of Sulphides, Selenides, and Tellurides: Effects of Neighbouring Functional Groups.**—Kinetic studies of dehydrochlorination reactions in the gas phase reveal participation of neighbouring groups in aliphatic 2-chloroethyl sulphides.<sup>286</sup> Physical studies<sup>287</sup> indicate interactions of functional groups in  $\beta$ -keto-sulphides and in the corresponding nitriles. A more unusual example of participation by sulphur is the enhanced rate of reduction by I<sup>-</sup> of  $\gamma$ -(methylthio)alkyl methyl sulphoxides.<sup>288</sup>

Activation of the adjacent proton at  $\alpha$ -sp<sup>3</sup> centres has been exploited in uses of sulphides in synthesis (see later section), and must be the basis for a novel acetoxy-transfer reaction, (14)  $\rightarrow$  (15), that is observed in refluxing benzene

<sup>278</sup> H. Okamura, M. Miura, K. Kosugi, and K. Takei, *Tetrahedron Lett.*, 1980, **21**, 87.

<sup>279</sup> J. N. Denis, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 1979, 4111.

<sup>280</sup> T. Shono, Y. Matsumura, S. Kashimura, and H. Kyutoku, *Tetrahedron Lett.*, 1978, 2807.

<sup>281</sup> T. Mukaiyama and M. Imaoka, *Chem. Lett.*, 1978, 413.

<sup>282</sup> T. Numata, Y. Watanabe, and S. Oae, *Tetrahedron Lett.*, 1979, 1411; 1978, 4933.

<sup>283</sup> Y. Nagao, K. Kaneko, and E. Fujita, *Tetrahedron Lett.*, 1978, 4115.

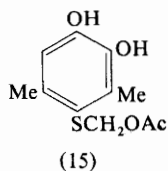
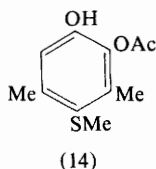
<sup>284</sup> J. Lucchetti and A. Krief, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1979, **288**, 537.

<sup>285</sup> D. Gyorgy, J. Nyitrai, K. Lempert, W. Voelter, and H. Horn, *Chem. Ber.*, 1978, **111**, 1464.

<sup>286</sup> G. Chuchani, I. Martin, and D. B. Bigley, *Int. J. Chem. Kinet.*, 1978, **10**, 649.

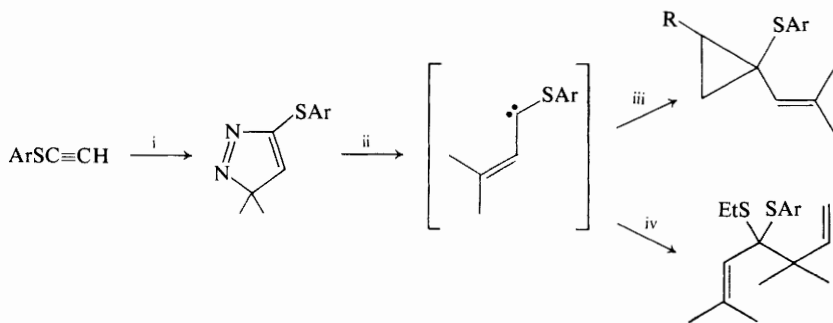
<sup>287</sup> K. C. Kole, C. Sandorfy, M. T. Fabi, P. R. Olivato, R. Rittner, C. Trufem, H. Viertler, and B. Wladislaw, *J. Chem. Soc., Perkin Trans. 2*, 1977, 2025.

<sup>288</sup> J. T. Doi and W. K. Musker, *J. Am. Chem. Soc.*, 1978, **100**, 3533.



solution in the presence of  $\text{Et}_3\text{N}$ .<sup>289</sup> Simple examples of reactions employing sulphenyl-stabilized carbanions are Michael reactions with  $\text{PhSCHLiCN}$ <sup>290</sup> and Knoevenagel condensation of  $\text{MeSCH}_2\text{CN}$ , using 1-(methylthio)-1-alkenyl cyanides.<sup>291</sup> These compounds are also susceptible to reduction by  $\text{NaBH}_4$  [ $\rightarrow \text{RCH}_2\text{CH}(\text{SMe})\text{CN}$ ] and desulphurization with Raney nickel ( $\rightarrow \text{RCH}=\text{CHCN}$ ).

Arylthio-carbenes yield arylthiocyclopropanes with alkenes,<sup>292,293</sup> and add to alkynes<sup>293</sup> and to allyl sulphides.<sup>294</sup> Scheme 5 illustrates a convenient route to vinyl(arylthio)carbenes and their uses in synthesis.



Reagents: i,  $\text{Me}_2\text{CN}_2$ , ether, at  $0^\circ\text{C}$ ; ii,  $h\nu$ ; iii,  $\text{RCH}=\text{CH}_2$ ; iv,  $\text{EtSCH}_2\text{CH}=\text{CMe}_2$

**Scheme 5**

Evidence for the existence in solution of free bis(phenylthio)carbene, formed by the decomposition of  $(\text{PhS})_3\text{CLi}$ , has been reported.<sup>295</sup>

**Uses of Saturated Sulphides, Selenides, and Tellurides in Synthesis.**—These applications are mostly based on the C—C bond-forming reactions of sulphenyl carbanions; the extensive uses of vinyl sulphides and their allyl and propargyl analogues are discussed in a later section. Some methods for C—S or C—Se bond cleavage, which are used to terminate a use in synthesis, have been discussed in an earlier section; other methods, notably the conversion of the sulphide into a sulphoxide followed by pyrolytic elimination of the sulphenic acid, are covered in later sections.

<sup>289</sup> R. R. King, *J. Org. Chem.*, 1979, **44**, 4194.

<sup>290</sup> N. Wang, S. Su, and L. Tsai, *Tetrahedron Lett.*, 1979, 1121.

<sup>291</sup> S. Kano, T. Yokomatsu, T. Ono, S. Hibino, and S. Shibuya, *Chem. Pharm. Bull.*, 1978, **26**, 1874.

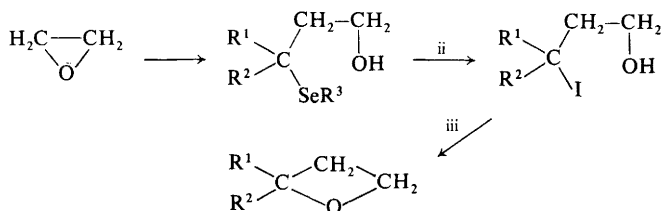
<sup>292</sup> T. Balaji and D. B. Reddy, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3434.

<sup>293</sup> M. Franck-Neumann and J. J. Lohmann, *Tetrahedron Lett.*, 1979, 2075.

<sup>294</sup> M. Franck-Neumann and J. J. Lohmann, *Tetrahedron Lett.*, 1978, 3729.

<sup>295</sup> M. Nitsche, D. Seebach, and A. K. Beck, *Chem. Ber.*, 1978, **111**, 3644.





Reagents: i,  $R^1R^2C(SeR^3)Li$ ; ii, MeI, NaI, DMF,  $CaCO_3$ , at  $80\text{ }^\circ C$ ; iii,  $Bu'O'K$ , DMSO, at  $20\text{ }^\circ C$

**Scheme 6**

'One-carbon' homologations of unusual types are illustrated by the conversion of an oxiran into an oxetan (Scheme 6) through the use of  $\alpha$ -lithioalkyl selenides,<sup>296</sup> a method which can, in principle, involve higher members of the saturated cyclic ether series. Further examples of uses of  $\alpha$ -lithioalkyl selenides<sup>297</sup> have been described: 1,2-addition of  $RSeCHLiCO_2Et$  to cyclohexenone;<sup>297</sup> the use of this reagent for the synthesis of  $\alpha\beta$ -unsaturated esters by condensation with carbonyl compounds;<sup>298</sup> the formation of alkylidenecyclopropanes from  $\alpha$ -lithiocyclopropyl phenyl selenide and primary alkyl halides;<sup>299</sup> the use of  $RSeCH_2Li$  for the conversion of alkyl halides into the next higher homologous 1-alkene;<sup>299</sup> and the use of the dianion of  $PhSeCHMeCO_2H$  for the conversion of an oxiran into an  $\alpha$ -methylene- $\gamma$ -lactone.<sup>300</sup> Corresponding uses of sulphides have also been reported.  $\alpha$ -Lithiocyclopropyl phenyl sulphide reacts with formaldehyde to give  $\alpha$ -(hydroxymethyl)cyclopropyl phenyl sulphide, which gives cyclobutanone with  $TsOH$  and  $HgCl_2$ , in 56% overall yield.<sup>301</sup> The same reagent adds to ketones analogously, and subsequent cleavage of the cyclopropane ring with  $HCl$  and  $ZnCl_2$  gives  $\gamma$ -keto-sulphides ( $R^1COR^2 \rightarrow R^1CHR^2COCH_2CH_2SPh$ ).<sup>302</sup> It may also be added to  $\alpha\beta$ -unsaturated ketones, in which case subsequent cleavage with  $HBr$  and  $ZnBr_2$  gives 1-(phenylthio)buta-1,3-dienes [ $R^1R^2C=CHCOR^3 \rightarrow R^1R^2C=CHCR^3=C(SPh)CH_2CH_2Br$ ].<sup>303</sup>  $\alpha$ -Sulphenyl carbanions ( $R\dot{C}HSPh$ ) and  $BrCH_2CH=CHCO_2Et$  have been utilized in a synthesis of ethyl 2-(phenylthiomethyl)cyclopropanecarboxylate.<sup>304</sup> The use of  $\alpha$ -chloroalkyl sulphides can lead to corresponding products;  $ClCH_2SPh$  brings about  $TiCl_4$ -promoted phenylthiomethylation of silyl enol ethers and enolates, subsequent alkene-forming desulphurization resulting in overall introduction of a methylene group into the  $\alpha$ -position of a ketone.<sup>305,306</sup> A more routine use of an  $\alpha$ -chloromethyl sulphide, *i.e.* the conversion of alcohols into methylthiomethyl ethers,<sup>307</sup> is facilitated by having  $AgNO_3$  and  $Et_3N$  in the reaction mixture.

<sup>296</sup> M. Sevrin and A. Krief, *Tetrahedron Lett.*, 1980, 21, 585.

<sup>297</sup> J. Lucchetti and A. Krief, *Tetrahedron Lett.*, 1978, 2697.

<sup>298</sup> J. Lucchetti and A. Krief, *Tetrahedron Lett.*, 1978, 2693.

<sup>299</sup> S. Halazy and A. Krief, *Tetrahedron Lett.*, 1979, 4233.

<sup>300</sup> N. Petragani and H. M. C. Ferraz, *Synthesis*, 1978, 476.

<sup>301</sup> B. M. Trost and W. C. Venduchick, *Synthesis*, 1978, 821.

<sup>302</sup> R. D. Miller and D. R. McKean, *Tetrahedron Lett.*, 1979, 583.

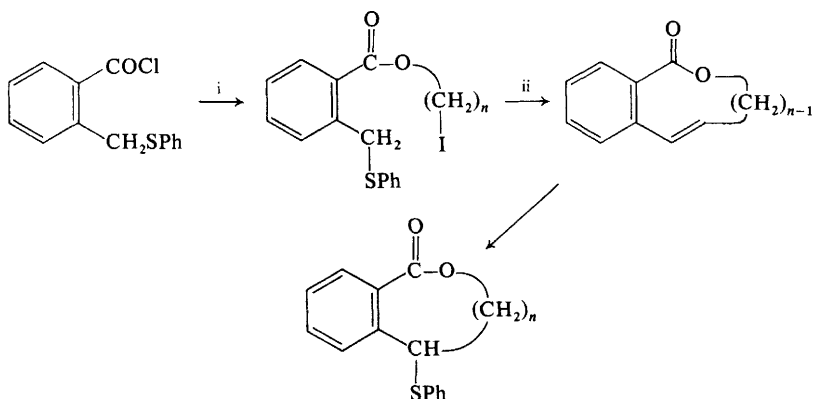
<sup>303</sup> R. D. Miller, D. R. McKean, and D. Kaufmann, *Tetrahedron Lett.*, 1979, 587.

<sup>304</sup> E. Ghera and Y. Ben-David, *Tetrahedron Lett.*, 1979, 4603.

<sup>305</sup> I. Paterson and I. Fleming, *Tetrahedron Lett.*, 1979, 2179.

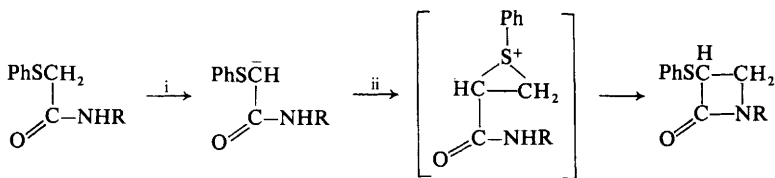
<sup>306</sup> I. Paterson and I. Fleming, *Tetrahedron Lett.*, 1979, 993, 995.

<sup>307</sup> K. Suzuki, J. Inanaga, and M. Yamaguchi, *Chem. Lett.*, 1979, 1277.



Reagents: i,  $\text{HO}(\text{CH}_2)_n\text{I}$ ; ii,  $\text{K}(\text{Me}_3\text{SiN})_2$ , THF

**Scheme 7**



Reagents: i, NaH; ii,  $\text{CH}_2\text{I}_2$

**Scheme 8**

An application of sulphides in the synthesis of natural products, reminiscent of an earlier era of organic chemistry, is the functional group conversion  $\text{RCO}_2\text{Et} \rightarrow \text{RCH}_2\text{OTs} \rightarrow \text{RCH}_2\text{SPh} \rightarrow \text{RCH}_3$  (the last step being brought about with Li and  $\text{EtNH}_2$ ), used in a synthesis of (+)-(3*R*,4*R*)-4-methyl-3-heptanol, a pheromone of the European elm bark beetle (*Scolytus multistriatus*).<sup>308</sup> Cyclization methods based on  $\alpha$ -sulphenyl carbanions include a new macrolide synthesis (Scheme 7),<sup>309</sup> cyclization of (2*E*,6*Z*)-10,11-epoxyfarnesyl phenyl sulphide with  $\text{Bu}^n\text{Li}$  (in DABCO, at  $-78^\circ\text{C}$ ) to form (6*Z*)-hedycaryols,<sup>310</sup> and a convenient [3 + 1]-cyclization (Scheme 8) that leads to  $\beta$ -lactams.<sup>311</sup> Cyclopropanes are formed by the electrolysis of  $\beta$ -arythioalkyl methanesulphonates, themselves formed in straightforward ways from  $\alpha\beta$ -unsaturated ketones *via*  $\beta$ -keto-sulphides.<sup>312</sup> The opposite approach, *i.e.* ring-opening of  $\gamma$ -phenylthiomethyl- or  $\gamma$ -phenylselenomethyl- $\gamma$ -lactones by sodium in liquid  $\text{NH}_3$ , as well as the cleavage of  $\omega$ -phenylselenoalkyl ethers and  $\alpha$ -silyloxyalkyl aryl selenides, leads to alkenes in good

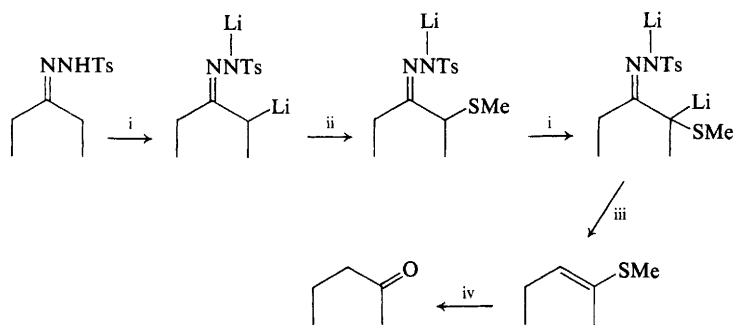
<sup>308</sup> G. Frater, *Helv. Chim. Acta*, 1979, **62**, 2829.

<sup>309</sup> T. Takahashi, K. Kasuga, and J. Tsuji, *Tetrahedron Lett.*, 1978, 4917.

<sup>310</sup> M. Kodama, S. Yokoo, H. Yamada, and S. Ito, *Tetrahedron Lett.*, 1978, 3121.

<sup>311</sup> K. Hirai and Y. Iwano, *Tetrahedron Lett.*, 1979, 2031.

<sup>312</sup> T. Shono, Y. Matsumura, S. Kashimura, and H. Kyutoku, *Tetrahedron Lett.*, 1978, 1205.



Reagents: i,  $\text{Bu}^n\text{Li}$ , hexane, TMEDA, THF at  $-50^\circ\text{C}$ ; ii,  $\text{MeSSMe}$ ; iii,  $\text{NH}_4\text{Cl}, \text{H}_2\text{O}$ ; iv,  $\text{HgCl}_2$ , hot aq. MeCN

Scheme 9

yields;<sup>313</sup> this is effectively a reversal of the 'cyclofunctionalization' process discussed in the earlier section 'Preparations . . . from Sulphenyl Halides'.

A sequence amounting to 1,2-transposition of aliphatic ketones (Scheme 9) illustrates another field of organic synthesis to which sulphides make a contribution.<sup>314</sup>  $\text{PhSeCH}_2\text{CH}_2\text{C}(\text{OMe})_3$  is a useful synthon for 2-substituted acrylates or for  $\alpha$ -methylene- $\gamma$ -butyrolactones after a Claisen orthoester rearrangement with allyl alcohols [ $\text{R}^1\text{R}^2\text{C}=\text{CHCH}_2\text{OH} \rightarrow \text{PhSeCH}_2\text{CH}(\text{CO}_2\text{Me})\text{CR}^1\text{R}^2\text{CH}=\text{CH}_2 \rightarrow \text{H}_2\text{C}=\text{C}(\text{CO}_2\text{Me})\text{CR}^1\text{R}^2\text{CH}=\text{CH}_2$  after elimination of selenoxide].<sup>315</sup>

**Vinyl Sulphides, Selenides, and Tellurides.**—This account is divided into sections covering the synthesis of vinyl sulphides and selenides, their reactions, and their uses in synthesis.

Most main routes to vinyl sulphides and selenides have been represented in recent papers, together with some novel variations. Halogenation–dehydrohalogenation has been applied as a convenient method for introducing a vinylthio-group into organic compounds; a novel procedure was used, involving the reaction of a Grignard reagent or an organolithium compound with  $\text{ClCH}_2\text{CH}_2\text{SCN}$  and treatment of the resulting chloroethyl sulphide with  $\text{Bu}^t\text{OK}$ .<sup>316</sup> This is an alternative to the direct synthesis from alkenes (addition of sulphenyl halide followed by elimination with  $\text{Bu}^t\text{OK}$ ),<sup>317,318</sup> in which *cis*-isomers result from kinetic control (at  $-78^\circ\text{C}$ ) and *trans*-isomers from thermodynamic control (at  $+77^\circ\text{C}$ ).<sup>317</sup> Stereospecific synthesis of (*E*)-1-alkenyl selenides is achieved by the dehydrobromination of 2-bromoalkyl selenides, and (*Z*)-isomers are prepared by the hydroboration of

<sup>313</sup> K. C. Nicolaou, W. J. Sipio, R. L. Magolda, and D. A. Claremon, *J. Chem. Soc., Chem. Commun.*, 1979, 83.

<sup>314</sup> T. Nakai and T. Mimura, *Tetrahedron Lett.*, 1979, 531.

<sup>315</sup> S. Raucher, K.-J. Hwang, and J. E. Macdonald, *Tetrahedron Lett.*, 1979, 3057.

<sup>316</sup> W. Verboom, J. Meijer, and L. Brandsma, *Synthesis*, 1978, 577.

<sup>317</sup> B. Geise and S. Lachheim, *Chem. Ber.*, 1979, 112, 2503.

<sup>318</sup> Y. Masaki, K. Sakuma, and K. Kaji, *Chem. Lett.*, 1979, 1235.

the 1-alkynyl analogues.<sup>319</sup> A general synthesis of  $\alpha$ -phenylseleno- $\alpha\beta$ -unsaturated ketones employs the PhSeCl—pyridine complex as reagent, reacting with  $\alpha\beta$ -unsaturated ketones.<sup>320</sup> 1-Cyanovinyl sulphides may be obtained through the dehydrobromination route, or through condensation of ketones with RSC<sub>2</sub>CN.<sup>321, 291</sup>

A vinylsilane is a useful equivalent of ethylene,<sup>322</sup> adducts with a sulphenyl chloride readily undergoing elimination. Another novel elimination approach,<sup>323</sup> *i.e.* oxidative decarboxylation of 2-substituted 2-(methylthio)propionic acids, is brought about by treatment of the sodium salt of the acid with *N*-chlorosuccinimide.

Synthesis from alkynes has been touched on in the foregoing discussion, and brief details of points of interest are included as part of ref. 319 (see also ref. 365).

Further examples of syntheses of vinyl sulphides from alkene derivatives include unusual examples, such as condensation of indole-3-thiol with ethylene at 180 °C,<sup>324</sup> the reaction of vinylidene chloride with thiourea and benzyl chloride to give PhCH<sub>2</sub>SCH=CHSCH<sub>2</sub>Ph,<sup>325</sup> cathodic reduction of  $\alpha$ -keto-keten dithioacetals [PhCOCH=C(SMe)<sub>2</sub> → PhCOCH=CHSMe],<sup>326</sup> and the use of divinyl sulphoxide as a vinylating agent [R<sub>3</sub>Si(CH<sub>2</sub>)<sub>n</sub>SH + (H<sub>2</sub>C=CH)<sub>2</sub>SO → R<sub>3</sub>Si(CH<sub>2</sub>)<sub>n</sub>SCH=CH<sub>2</sub>; whereas Bu<sup>t</sup>SH → Bu<sup>t</sup>SCH=CH<sub>2</sub> (15%) + Bu<sup>t</sup>SCH<sub>2</sub>CH<sub>2</sub>SOCH=CH<sub>2</sub>].<sup>327</sup>

An unusual reaction in which vinyl sulphides are formed<sup>328</sup> (Scheme 10) is of further interest because a quite different product (MeO<sub>2</sub>CCHR<sup>1</sup>CHR<sup>2</sup>COR<sup>3</sup>) is formed with <sup>-</sup>OMe.

Syntheses of vinyl sulphides from dithioesters include the conversions MeCSSMe → (*E/Z*)-MeSCMe=CHCSSMe<sup>329</sup> and Me<sub>2</sub>CBrCSSMe → (RO)<sub>2</sub>P-(O)SC(SMe)=CMe<sub>2</sub><sup>330</sup> when a trialkyl phosphite was used as the reagent. The conversion RSC(S)CN → (*E/Z*)-RSC(CN)=C(CN)SR occurred during attempted hydrolysis.<sup>331</sup>

<sup>319</sup> S. Raucher, M. R. Hansen, and M. A. Cotter, *J. Org. Chem.*, 1978, **43**, 4885; R. N. Kudyakova, A. N. Volkov, and B. A. Trofimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 213; A. N. Mirskova, N. V. Lutskeya, D. I. Kalikhman, B. A. Shainyan, and M. G. Voronkov, *ibid.*, p. 572; I. A. Aslanov, E. F. Dzhaferov, A. A. Dzhaferov, K. B. Kurbanov, and A. G. Abdullaev, *Azerb. Khim. Zh.*, 1978, 45; G. G. Skvortsova, D. G. Kim, and L. V. Andriyankova, *Khim. Geterotsikl. Soedin.*, 1978, 364; S. V. Amosova, N. N. Skatova, O. A. Tarasova, and B. A. Trofimov, *Zh. Org. Khim.*, 1979, **15**, 2038; A. N. Volkov, R. N. Kudyakova, and B. A. Trofimov, *ibid.*, p. 1554; V. E. Statsyuk, S. P. Korshunov, N. V. Korzhova, and I. V. Bodrikov, *ibid.*, p. 1998; E. Larsson, *J. Prakt. Chem.*, 1978, **320**, 353 and 1979, **321**, 267; D. Schorstein, C. J. Suckling, and R. Wrigglesworth, *J. Chem. Soc., Chem. Commun.*, 1978, 795; B. A. Trofimov, S. V. Amosova, G. K. Musorin, D. F. Kushnarev, and G. A. Kalabin, *Zh. Org. Khim.*, 1979, **15**, 619; M. Hojo, R. Masuda, and S. Takagi, *Synthesis*, 1978, 284.

<sup>320</sup> G. Zima and D. Liotta, *Synth. Commun.*, 1979, **9**, 697.

<sup>321</sup> F. Pochat, *Tetrahedron Lett.*, 1978, 2683.

<sup>322</sup> F. Cooke, R. Moerck, J. Schwindeman, and P. Magnus, *J. Org. Chem.*, 1980, **45**, 1046.

<sup>323</sup> B. M. Trost, M. J. Crimmin, and D. Butler, *J. Org. Chem.*, 1978, **43**, 4549.

<sup>324</sup> G. G. Skvortsova, L. F. Teterina, B. V. Trzhitsinskaya, and V. K. Voronov, *Khim. Geterotsikl. Soedin.*, 1979, 352.

<sup>325</sup> P. Cassoux, R. Lahana, and J. F. Normant, *Bull. Soc. Chim. Fr., Part 2*, 1979, 427.

<sup>326</sup> H. H. Ruettinger, W. D. Rudolf, and H. Matschiner, *J. Prakt. Chem.*, 1979, **321**, 443.

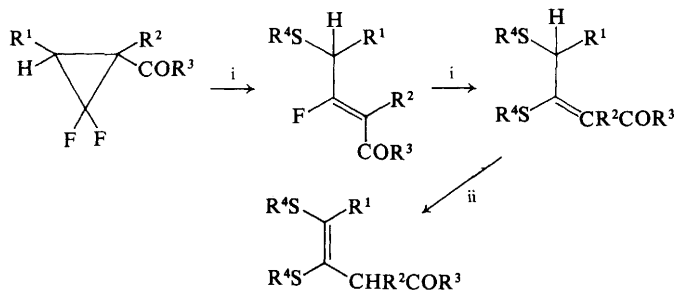
<sup>327</sup> M. G. Voronkov, F. P. Kletsko, N. N. Vlasova, N. K. Gusarova, G. G. Efremova, V. V. Keiko, and B. A. Trofimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1690.

<sup>328</sup> K. Kobayashi, T. Taguchi, T. Morikawa, T. Takase, and H. Takanashi, *Tetrahedron Lett.*, 1980, **21**, 1047.

<sup>329</sup> Z. Yoshida, S. Yoneda, T. Kawase, and M. Inaba, *Tetrahedron Lett.*, 1978, 1285.

<sup>330</sup> Yu. G. Gololobov and M. N. Danchenko, *Zh. Obshch. Khim.*, 1979, **49**, 231.

<sup>331</sup> R. Mayer, W. Thiel, and H. Viola, *Z. Chem.*, 1979, **19**, 56.



Reagents: i,  $\text{R}^4\text{S}^-$ ; ii, KOH, MeOH, THF

**Scheme 10**

Desulphurization and deselenization of vinyl sulphides and selenides has been the feature of several studies recently; in many cases, C–S or C–Se bond cleavage was unexpected, but useful alkene syntheses have been sought successfully, employing  $[\text{Pb}(\text{OAc})_4]$ <sup>332</sup> or a Grignard reagent with  $\text{NiCl}_2$  and  $\text{PPh}_3$ .<sup>333</sup> Keto-vinyl sulphides  $\text{R}^1\text{COCH}=\text{CR}^2\text{SR}^3$  undergo desulphurization and concomitant reduction of  $\text{C}=\text{C}$  with  $\text{NaBH}_4$  and  $\text{CoCl}_2$  or  $\text{NiCl}_2$ ,<sup>334</sup> but with  $\text{LiAlH}_4$  and  $\text{R}^1\text{COCH}=\text{C}(\text{R}^2)\text{SR}^3$  a mixture of reduction product and  $\text{R}^1\text{CH}=\text{CHCOR}^2$  is formed; this arises through allylic rearrangement of the first-formed product, in which the carbonyl group is reduced.<sup>335</sup> Whereas *E* → *Z* photoisomerization of these keto-vinyl sulphides occurs without cleavage,<sup>336</sup> easy displacement of the sulphide group is brought about with a secondary amine in benzene solution, giving the corresponding keto-vinylamine.<sup>337</sup> Vinyl sulphides give alkynes with  $\text{H}_2\text{N}(\text{CH}_2)_3\text{NHK}$ .<sup>338</sup>

A confusing variety of results is accumulating for the competition between deprotonation and C–Se bond cleavage of phenyl vinyl selenide. Butyl-lithium causes cleavage,<sup>338,339</sup> while  $\text{LiNPr}_2$ <sup>339</sup> brings about both metallation and elimination. In other laboratories,  $\text{KNPr}_2$  with  $\text{LiOBu}^t$ ,<sup>340a</sup> or an alkyl-lithium,<sup>340b</sup> is advocated for deprotonation without cleavage (see also refs. 341–345). The conventional procedure for the conversion of a vinyl sulphide or selenide into a ketone, involving acid hydrolysis, has not always been reliable, and further studies (see Vol. 5, p. 26) establish an order of rates vinyl ether > vinyl sulphide > vinyl selenide for this reaction, consistent with the generation of a heteroatom-stabilized carbonium ion in the rate-determining step.<sup>346</sup>

<sup>332</sup> B. M. Trost and Y. Tanigawa, *J. Am. Chem. Soc.*, 1979, **101**, 4413, 4743.

<sup>333</sup> H. Okamura, M. Miura, and H. Takei, *Tetrahedron Lett.*, 1979, 43.

<sup>334</sup> T. Nishio and Y. Omote, *Chem. Lett.*, 1979, 1223.

<sup>335</sup> T. Nishio and Y. Omote, *Chem. Lett.*, 1979, 365.

<sup>336</sup> N. Furukawa, M. Fukumura, T. Nishio, and S. Oae, *Phosphorus Sulfur*, 1978, **5**, 191.

<sup>337</sup> T. Nishio and Y. Omote, *Synthesis*, 1980, 390.

<sup>338</sup> C. A. Brown, *J. Org. Chem.*, 1978, **43**, 3083.

<sup>339</sup> M. Sevrin, J. N. Denis, and A. Krief, *Angew. Chem.*, 1978, **90**, 550.

<sup>340</sup> S. Raucher and G. A. Koolpe, (a) *J. Org. Chem.*, 1978, **43**, 3794; (b) *ibid.*, p. 4252.

<sup>341</sup> R. C. Cookson and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 1978, 821.

<sup>342</sup> R. H. Everhardus, R. Grafing, and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 1978, **97**, 69.

<sup>343</sup> J. J. Fitt and H. W. Gschwend, *J. Org. Chem.*, 1979, **44**, 303.

<sup>344</sup> R. R. Schmidt, H. Speer, and B. Schmid, *Tetrahedron Lett.*, 1979, 4277.

<sup>345</sup> K. Isoe, M. Fuse, H. Kosugi, H. Hagiwara, and H. Uda, *Chem. Lett.*, 1979, 785.

<sup>346</sup> R. A. McLelland and M. Leung, *J. Org. Chem.*, 1980, **45**, 187.

Ozone fails to attack the C=C bond in the expected manner in the case of  $\text{RSCBu}^1=\text{CH}_2$ , and the aldehyde  $\text{RSCHBu}^1\text{CHO}$  is formed.<sup>347</sup> Cleavage of the double bond occurs with the isobutyl isomer<sup>347</sup> and with  $\text{MeSCEt}=\text{CHMe}$ ,<sup>348</sup> giving thioesters, but further products  $\text{EtCOCH(OH)Me}$  or  $\text{EtCH(OH)COMe}$  and  $\text{EtCOCHMeMe}$ , the latter arising through 1,2-migration of MeS, are also formed.<sup>348</sup> Vinyl sulphides derived from camphor are converted into camphorquinone by  $\text{O}_3$  and pyridine.<sup>347</sup> Extensions of these studies might lead to new insights into the roles played by electron distribution and steric effects on the classical ozonolysis reaction.

Mechanistic and routine chemical studies of vinyl sulphides include stereochemical evidence that cycloaddition to TCNE involves a zwitterionic intermediate<sup>349,350</sup> (vinyl sulphides are more reactive than vinyl ethers<sup>350</sup>); the demonstration of [1,7]- $\sigma$ -shifts in 1,7-bis(alkylthio)cycloheptatrienes which account for the rapid tautomeric interconversions;<sup>351</sup> laser-flash photocyclization of aryl vinyl sulphides;<sup>352</sup> and dye-sensitized photo-oxygenation leading to sulphoxides, sulphones, and products from C=C bond cleavage.<sup>353</sup> Hydrolysis of  $\text{RCBr}=\text{C(CN)SEt}$  gives 2-keto-1-cyanoalkyl ethyl sulphides,<sup>354</sup> while reaction with hydrazine gives 3-amino-4-ethylthio-pyrazoles.<sup>355</sup>  $\text{Cl}_2\text{C}=\text{CHSR}^1$  can be converted into (*E/Z*)- $\text{R}^2\text{SCCl}=\text{CHSR}^1$ , ( $\text{R}^2\text{S}$ ) $_2\text{C}=\text{CHSR}^1$ ,  $\text{ClC}\equiv\text{CSR}^1$ , and  $\text{R}^2\text{SC}\equiv\text{CSR}^1$  by treatment with  $\text{R}^2\text{SH}$  and  $\text{KOH}$ ,<sup>356</sup> and the addition of  $\text{R}_3\text{SiH}$  to  $\text{H}_2\text{C}=\text{CHSEt}$  in the presence of  $\text{H}_2\text{PtCl}_6$  or  $[(\text{Ph}_3\text{P})_3\text{RhCl}]$  gives mainly 1-(trialkylsilyl)alkyl sulphides.<sup>357</sup>

Alkylation and other electrophilic reactions of vinyl sulphides and selenides following  $\alpha$ -metallation<sup>339-345</sup> include a number of useful synthetic procedures. Addition of an alkyl-lithium to phenyl vinyl selenide gives the  $\alpha$ -lithio- $\beta$ -alkylated selenide, which, on further alkylation and oxidative deselenation, gives the 1,2-disubstituted ethylene ( $\text{H}_2\text{C}=\text{CHSePh} \rightarrow \text{R}^1\text{CH}_2\text{CHLiSePh} \rightarrow \text{R}^1\text{CH}_2\text{CHR}^2\text{SePh} \rightarrow \text{R}^1\text{CH}=\text{CHR}^2$ ), thus permitting the vinyl selenide to be described as a  $\overset{+}{\text{C}}\text{H}=\overset{-}{\text{C}}\text{H}$  synthon.<sup>346b</sup> A similar overall result ( $\text{RCHO} \rightarrow \text{RCOCH}=\text{CH}_2$ ) is based on acid-catalysed isomerization of 1-(phenylthio)vinyl-lithium-aldehyde adducts, followed by oxidative desulphurization.<sup>341</sup> Metallation of buta-1,3-dienyl ethers and sulphides with  $\text{Bu}^n\text{Li}$  and  $\text{Bu}^t\text{OK}$  occurs at C-1 and can be followed by alkylation with  $\text{MeI}$ ,  $\text{MeSCN}$ , or  $\text{MeCHO}$ ;<sup>342</sup> similar reactions have been described for 3-(dimethylamino)prop-1-enyl phenyl sulphide.<sup>343</sup> Electrophilic attack on (*E*)- $\beta$ -(arylsulphinyl)vinyl sulphides (Scheme 11) occurs at the sulphinyl-substituted carbon atom, mainly with retention of configuration.<sup>344</sup>

<sup>347</sup> R. Chaussin, P. Lriverend, and D. Paquer, *J. Chem. Soc., Chem. Commun.*, 1978, 1032.

<sup>348</sup> M.-P. Strobel, L. Morin, and D. Paquer, *Tetrahedron Lett.*, 1980, 21, 523.

<sup>349</sup> H. Graf and R. Huisgen, *J. Org. Chem.*, 1979, 44, 2594, 2595.

<sup>350</sup> T. Okuyama, M. Nakada, K. Toyoshima, and T. Fueno, *J. Org. Chem.*, 1978, 43, 4546.

<sup>351</sup> M. Cavazza, G. Morganti, and F. Pietra, *Recl. Trav. Chim. Pays-Bas*, 1979, 98, 165.

<sup>352</sup> T. Wolff, *J. Photochem.*, 1979, 11, 215 and *J. Am. Chem. Soc.*, 1978, 100, 6157.

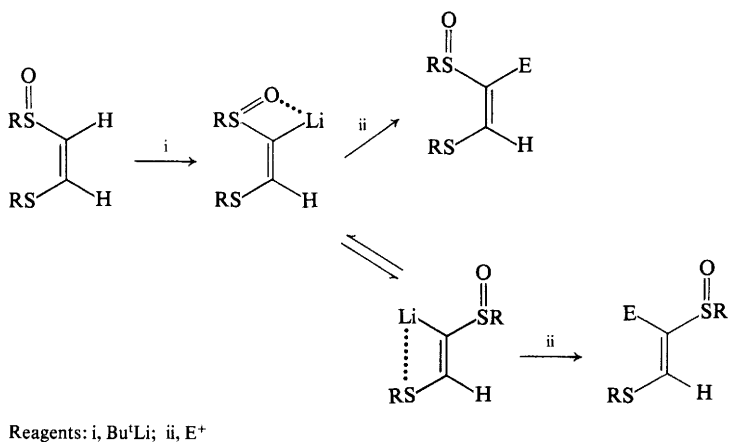
<sup>353</sup> W. Ando, T. Nagashima, K. Saito, and S. Kohmoto, *J. Chem. Soc., Chem. Commun.*, 1979, 154.

<sup>354</sup> F. Pochat, *Tetrahedron Lett.*, 1979, 19.

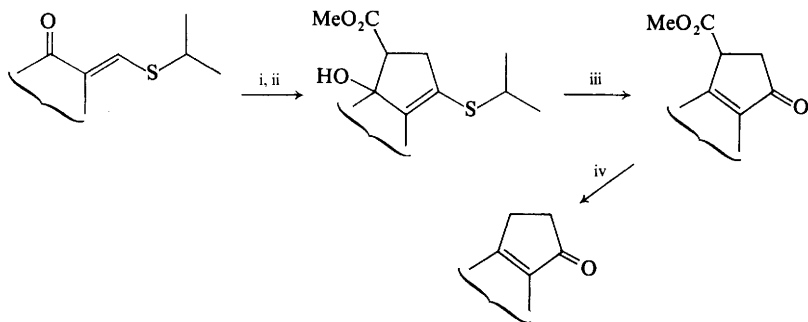
<sup>355</sup> F. Pochat, *Tetrahedron Lett.*, 1979, 2991.

<sup>356</sup> A. N. Mirskova, T. L. Usova, N. V. Lutskaya, I. D. Kalikhman, and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 426.

<sup>357</sup> M. G. Voronkov, N. N. Vlazova, S. V. Kirpichenko, S. A. Bolshakova, V. V. Keiko, E. O. Tsetlina, S. V. Amosova, B. A. Trofimov, and V. Chvalovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 422.



Scheme 11



Reagents: i, lithium 2,2,6,6-tetramethyl-*N*-hydroxypiperidide, at  $-78^{\circ}\text{C}$ ; ii,  $\text{H}_2\text{C}=\text{CHCO}_2\text{Me}$ ; iii, 5% HCl in THF; iv,  $\text{Me}_3\text{SiH}$ , at  $180^{\circ}\text{C}$ , then HCl in refluxing toluene

Scheme 12

Michael addition of 1-lithio-2-methoxycarbonylprop-2-enyl phenyl sulphide to acrylates gives 3-(phenylthio)cyclopentadienones, while addition to aldehydes is followed similarly by cyclization to furan-2-ones.<sup>345</sup> Further uses of vinyl sulphides in syntheses of cyclic compounds include an efficient pentannellation procedure (Scheme 12),<sup>358</sup> cyclization of  $\gamma$ -(3-phenylthio-2-methylprop-2-enyl)- $\beta$ -keto-esters to 3-(phenylthio)cyclohexanones, using TFA,<sup>359</sup> and an aromatic substitution reaction [ $\text{HO}(\text{C}_6\text{H}_4)_2\text{C}(\text{SEt})=\text{CH}_2 \rightarrow 3\text{-phenyl-2-(ethylthio)indene}$ ] that involves attack at the  $\beta$ -carbon atom of the vinyl sulphide moiety, promoted by acid-catalysed dehydration.<sup>360</sup> 1-(Phenylthio)vinylphosphonium salts  $\text{PhSC}(\text{=CH}_2)\text{PPh}_3^+ \text{X}^-$ , have been advocated for use in the synthesis of cyclopentanone by condensation with

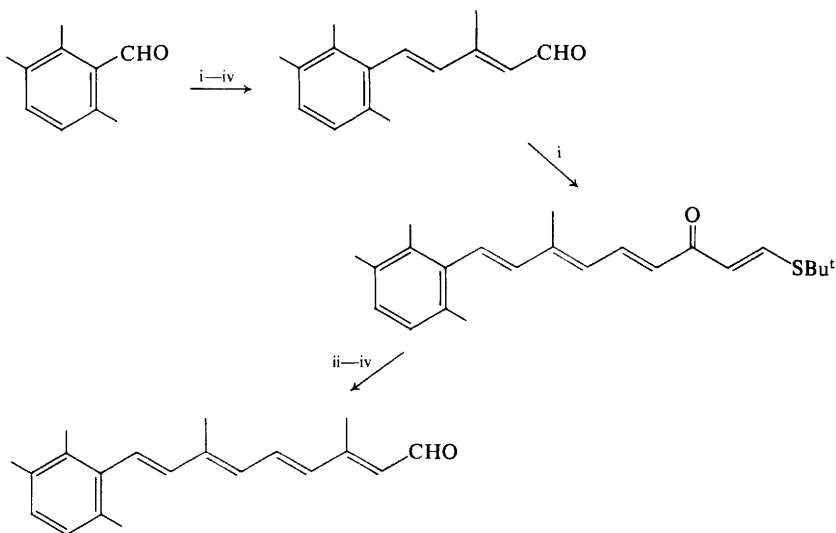
<sup>358</sup> J. P. Marino and L. C. Ketterman, *J. Chem. Soc., Chem. Commun.*, 1979, 946.

<sup>359</sup> A. S. Kende and J. A. Schneider, *Synth. Commun.*, 1979, 9, 419.

<sup>360</sup> M. Braun, *Chem. Ber.*, 1979, 112, 1495.

$\gamma$ -keto-diesters,<sup>361</sup> and cycloaddition of ketens  $\text{PhSCMe}=\text{CO}$  with alkenes and imines leads to substituted cyclobutanones and *trans*- $\alpha$ -(phenylthio)azetidiones, respectively.<sup>362</sup>

The introduction of a (butylthio)methylene group in the  $\text{CH}_2$  group of a ketone  $\text{R}^1\text{R}^2\text{CHCOCH}_2\text{R}^3$  is a useful device for permitting alkylation at the other  $\alpha$ -position by the usual methods, since the vinyl sulphide group can be removed by hydrolysis after serving its blocking function.<sup>363</sup> The acidity of the protons that are beta to sulphur in (*E*)- $\text{MeSCMe}=\text{CMeCO}_2\text{Et}$  is exploited in the stereospecific chain extension  $\text{RCHO} \rightarrow (2Z,4E)\text{-RCH}=\text{CHCH}=\text{CMeCO}_2\text{H}$ , the 5-hydroxy-2-methyl-3-(methylthio)-pent-2-enoic lactone that is formed in the condensation being first desulphurized (by Raney nickel) and then treated with  $\text{Bu}^t\text{OK}$  to bring about dehydrative cleavage.<sup>364</sup> A similar objective, the use of 4-(*t*-butylthio)but-3-en-2-one as a chain-extension agent, has been realized in a synthesis of isorenieratene (Scheme 13).<sup>365,366</sup>



Reagents: i,  $\text{MeCOCH}=\text{CHSBu}^t$ ; ii,  $\text{MeLi}$ ; iii,  $\text{H}^+$ ; iv,  $\text{I}_2$

Scheme 13

**Allenic Sulphides.**—This short section is mainly concerned with alka-1,2-dienyl sulphides and related compounds.<sup>367</sup> The reaction of  $\text{Cl}_2\text{C}=\text{CClC}\equiv\text{CPh}$  or of  $\text{PhCCl}=\text{CClC}\equiv\text{CCl}$  with an alkanethiolate gives  $(\text{RS})_2\text{C}=\text{C}=\text{C}=\text{CPhSR}$ , while

<sup>361</sup> A. T. Hewson, *Tetrahedron Lett.*, 1978, 3267.

<sup>362</sup> M. Ishida, T. Minami, and T. Agawa, *J. Org. Chem.*, 1979, **44**, 2067.

<sup>363</sup> S. Campbell, N. Petragnani, T. Brocksom, and L. Tsuchiya, *Farmaco, Ed. Sci.*, 1978, **33**, 421.

<sup>364</sup> E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, 1979, 2317.

<sup>365</sup> S. Akiyama, S. Nakatsuji, T. Hamamura, M. Kataoka, and M. Nakagawa, *Tetrahedron Lett.*, 1979, 2809.

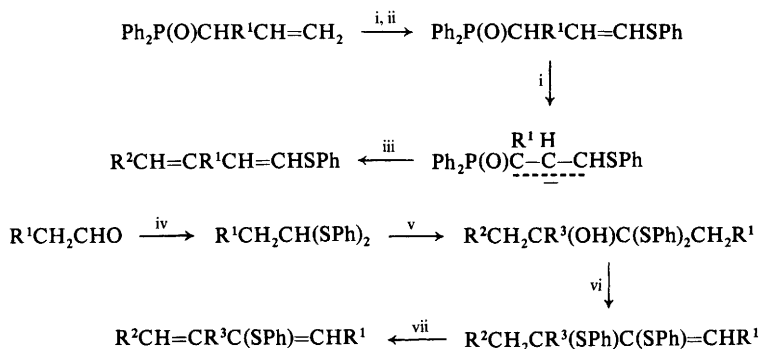
<sup>366</sup> S. Akiyama, S. Nakatsuji, S. Eda, M. Kataoka, and M. Nakagawa, *Tetrahedron Lett.*, 1979, 2813.

<sup>367</sup> A. Roedig and G. Zaby, *Liebigs Ann. Chem.*, 1979, 1606, 1614, 1626.



$\text{Cl}_2\text{C}=\text{C}=\text{C}=\text{CClMe}$  gives  $\text{RSC}\equiv\text{CC}(\text{SR})=\text{CClMe}$ . Similarly,  $\text{Cl}_2\text{C}=\text{CClC}\equiv\text{CCl}$  with five equivalents of  $\text{NaSR}^1$  gives  $(\text{R}^1\text{S})_2\text{C}=\text{C}(\text{SR}^1)\text{C}(\text{SR}^1)=\text{CHSR}^1$ , while  $\text{Cl}_2\text{C}=\text{CClC}\equiv\text{CSR}^2$  gives  $(\text{R}^1\text{S})_2\text{C}=\text{C}=\text{C}(\text{SR}^1)\text{SR}^2$  via  $\text{R}^1\text{SC}\equiv\text{CC}(\text{SR}^1)=\text{C}(\text{SR}^1)\text{SR}^2$ .

**Allyl Sulphides and Selenides.**—Preparative methods described for saturated sulphides may be used for the allyl analogues, and 1,2-phenylthio-shifts can be exploited.<sup>2p</sup> Scheme 14 illustrates some of the methods used, and applications for the separate synthesis of 1- and 2-(phenylthio)buta-1,3-dienes.<sup>368</sup> Dehydrochlorination of adducts formed from trisubstituted alkenes and  $\text{PhSCl}$  yields allyl sulphides.<sup>369</sup>



Reagents: i,  $\text{Bu}^n\text{Li}$ ; ii,  $\text{PhSSPh}$ ; iii,  $\text{R}^2\text{CHO}$ ; iv,  $\text{PhSH}$ ,  $\text{H}^+$ ; v,  $\text{Bu}^n\text{Li}$ ,  $\text{R}^2\text{CH}_2\text{COR}^3$ ; vi,  $\text{SOCl}_2$ ,  $\text{Et}_3\text{N}$ ; vii,  $\text{NaIO}_4$ ; then heat

**Scheme 14**

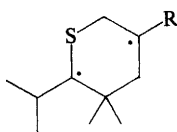
The delocalized anion shown in Scheme 14 is representative of the crucial intermediate in many applications of allyl sulphides in synthesis. The discovery<sup>370</sup> that HMPA induces 1,4-addition of thioallyl anions to  $\alpha\beta$ -unsaturated ketones through the  $\alpha$ -carbon atom of the allyl sulphide makes the use of these compounds more attractive in synthesis, so that they rival organocopper compounds in versatility (see also Chap. 2, Pt. I, p. 97). A special advantage is the fact that conversion of the alkylated allyl sulphide into the corresponding sulphoxide, followed by rearrangement (see later section on 'Sulphoxide-Sulphenate Rearrangements'), places an oxygen function on the  $\gamma$ -carbon atom of the original allyl grouping ( $\text{R}^1\text{SCHR}^2\text{CH}=\text{CHR}^3 \rightarrow \text{R}^2\text{CH}=\text{CHCHR}^3\text{OH}$ ).<sup>369, 370</sup> The same regioselectivity is seen in the preferred  $\gamma$ -alkylation of alkylthioallylboronyl anions  $\text{Li}^+\text{Me}_2\text{CHSCH}=\text{CHCH}_2\text{B}^-\text{Et}_3$ , which are formed from an alkylthioallyl-lithium and a trialkylborane at  $-78^\circ\text{C}$ . An interesting application is the  $\gamma$ -alkylation by allyl halides, leading to head-to-tail 1,5-dienes in good yields.<sup>371</sup> Conversion of geraniol

<sup>368</sup> P. Baldwin, J. I. Grayson, and S. Warren, *J. Chem. Soc., Chem. Commun.*, 1978, 657.

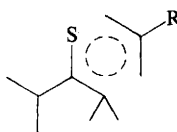
<sup>369</sup> Y. Masaki, K. Hashimoto, and K. Kaji, *Tetrahedron Lett.*, 1978, 4539.

<sup>370</sup> M. R. Binns, R. K. Haynes, T. L. Houston, and W. R. Jackson, *Tetrahedron Lett.*, 1980, 21, 573.

<sup>371</sup> Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, 1979, 157; *Chem. Lett.*, 1979, 385.



(16)



(17)

into fragranol and grandisol skeletons is assisted by a more passive use of a sulphide group, introduced to stabilize an allyl-lithium intermediate.<sup>372</sup>

Thio-Claisen rearrangement of allyl sulphides,  $\text{Me}_2\text{CHC}(=\text{CMe}_2)\text{SCH}_2\text{CH}=\text{CH}_2 \rightleftharpoons \text{Me}_2\text{CHC}(=\text{S})\text{CMe}_2\text{CH}_2\text{CH}=\text{CH}_2$ ,<sup>373</sup> is a reversible [3,3]-sigmatropic process which may involve a biradicaloid (16) or an aromatic (17) transition state, and although experiments favouring the former have been described,<sup>374</sup> more work is needed to make this a firmer hypothesis. The variation of this rearrangement that leads to thioketens ( $\text{R}^1\text{R}^2\text{C}=\text{CHCHR}^3\text{SC}\equiv\text{CR}^4 \rightarrow \text{R}^3\text{CH}=\text{CHCR}^1\text{R}^2\text{CR}^4=\text{C}=\text{S}$ )<sup>375, 376</sup> and their selenium analogues<sup>376</sup> has been described.

Kinetics of the oxidation of diallyl sulphide by singlet oxygen, and its inhibition by rubrene, have been reported.<sup>377</sup> Isomerization studies<sup>378</sup> in which the base-catalysed prop-2-enyl-prop-1-enyl equilibrium for allyl sulphides, sulphoxides, and sulphones were compared have been undertaken, and isolated reports on this topic have been rationalized in terms of electronic distribution in the functional groups.

The cleavage of C-S bonds that accompanies the cross-coupling of allyl sulphides with a Grignard reagent combined with  $\text{NiCl}_2$  and  $\text{PPh}_3$ <sup>379</sup> leads to mixtures of alkenes.

**Acetylenic Sulphides.**—Ethyne phenyl sulphide, formed from bromoacetaldehyde diethyl acetal with  $\text{PhSH}$  by condensation followed by elimination by base, reacts with allyl alcohols to give allyl 2-(phenylthio)vinyl ethers; these, on oxidative desulphurization, lead to 2,4-dienals.<sup>380</sup> A simple new synthesis of 1-alkynyl sulphides ( $\text{CF}_3\text{CH}_2\text{SR}^1 + \text{R}^2\text{Li} \rightarrow \text{R}^2\text{C}\equiv\text{CSR}^1$ )<sup>381</sup> and another route to propargyl sulphides [ $\text{R}^1\text{SH} + (\text{Me}_2\text{N})_2\text{P}(\text{O})\text{OCH}_2\text{C}\equiv\text{CR}^2 + \text{NaOH} \rightarrow \text{R}^1\text{SCH}_2\text{C}\equiv\text{CR}^2$ ]<sup>382</sup> should stimulate new research into applications of these compounds in synthesis. Some possibilities are shown in a reductive cyclization of *N*-substituted succinimides (Scheme 15)<sup>383</sup> and a use of  $\text{PhSeCHLiC}\equiv\text{CLi}$  in a synthesis of 7-hydroxymyoporone (18), revealing the propargyl selenide to be the synthetic equivalent of the synthon  $\overset{+}{\text{C}}\text{H}=\text{CH}\overset{-}{\text{C}}=\text{O}$ .<sup>384</sup>

<sup>372</sup> V. Rautenstrauch, *J. Chem. Soc., Chem. Commun.*, 1978, 519.

<sup>373</sup> P. Metzner, N. P. Thi, and J. Vialle, *Nouv. J. Chim.*, 1978, 2, 179.

<sup>374</sup> P. Metzner, T. N. Pham, and J. Vialle, *J. Chem. Res. (S)*, 1978, 478.

<sup>375</sup> E. Schaumann and F. F. Grabley, *Liebigs Ann. Chem.*, 1979, 1746.

<sup>376</sup> R. S. Sukhai and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 1979, 98, 55.

<sup>377</sup> B. M. Monroe, *Photochem. Photobiol.*, 1979, 29, 761.

<sup>378</sup> V. Svata, M. Prochazka, and V. Bakos, *Collect. Czech. Chem. Commun.*, 1978, 43, 2619.

<sup>379</sup> H. Okamura and H. Takei, *Tetrahedron Lett.*, 1979, 3425.

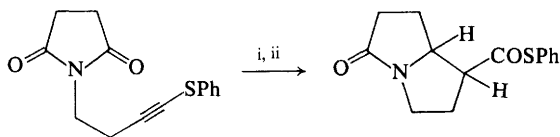
<sup>380</sup> R. C. Cookson and R. Gopalan, *J. Chem. Soc., Chem. Commun.*, 1978, 924.

<sup>381</sup> K. Tanaka, S. Shiraishi, T. Nakai, and N. Ishikawa, *Tetrahedron Lett.*, 1978, 3103.

<sup>382</sup> B. Corbel and J. P. Pangam, *Synthesis*, 1979, 882.

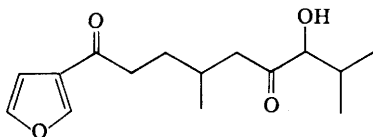
<sup>383</sup> P. M. M. Nossin and W. N. Speckamp, *Tetrahedron Lett.*, 1979, 4411.

<sup>384</sup> H. J. Reich, P. M. Gold, and F. Chow, *Tetrahedron Lett.*, 1979, 4433.



Reagents: i,  $\text{HCO}_2\text{H}$ ; ii,  $\text{H}^+$

Scheme 15



(18)

## 6 Naturally Occurring Organosulphur Compounds

This short section is located immediately before coverage of sulphonium salts, a group of compounds most importantly represented in naturally occurring compounds. Possible roles for *S*-adenosyl-*L*-methionine have stimulated studies with model compounds;<sup>385</sup> similar studies may follow from the fact that Bleomycin  $\text{A}_2$  is a sulphonium salt, carrying the grouping  $-\text{CONH}(\text{CH}_2)_3\overset{\oplus}{\text{S}}\text{Me}_2$ .<sup>386</sup> 5-(Dimethylsulphonio)pentanoic acid has been identified as a constituent of *Diplotaxis tenuifolia*.<sup>387</sup>

Block's book<sup>388</sup> lists a number of simple organosulphur compounds which occur naturally, and further examples include *S*-methylthiomethyl 2-methylbutanethioate,  $\text{MeCH}_2\text{CHMeC}(\text{O})\text{SCH}_2\text{SMe}$  (a new addition to the 24 organosulphur compounds already isolated from the essential oil of hops),<sup>389</sup> and methyl 1-(1-methylthioethyl)-thioethyl disulphide, a constituent of roast pork<sup>212</sup> (see p. 21).

## 7 Sulphonium Salts

The opportunity has been taken to bring together recent papers on trialkyl- and triaryl-sulphonium salts with those covering *S*-heteroatom-sulphonium salts,  $\text{R}^1\text{R}^2\overset{\oplus}{\text{S}}\text{X Y}^-$  ( $\text{X} = \text{halogen}, \text{NR}^3\text{R}^4, \text{OR}^3, \text{ or SR}^3$ ), the latter class having been mostly covered in previous volumes of this series in the sections on sulphides and sulphoxides.

**Trialkyl- and Triaryl-sulphonium, -selenonium, and -telluronium Salts.**—Some modifications of known preparative methods are summarized, with references, at the end of this section. Interesting practical procedures have been described for the

<sup>385</sup> T. Irie and H. Tanida, *J. Org. Chem.*, 1979, **44**, 325.

<sup>386</sup> N. J. Oppenheimer, L. O. Rodriguez, and S. M. Hecht, *Biochemistry*, 1979, **18**, 3439.

<sup>387</sup> F. Larker and J. Hamelin, *Phytochemistry*, 1979, **18**, 1396.

<sup>388</sup> E. Block, 'Reactions of Organosulfur Compounds', Academic Press, New York, 1978.

<sup>389</sup> M. Moir, I. M. Gallacher, J. Hobkirk, J. C. Seaton, and A. Suggett, *Tetrahedron Lett.*, 1980, **21**, 1085.

alkylation of sulphides by alcohols or ethers with a strong acid,<sup>390</sup> by alkyl methanesulphonates,<sup>391</sup> and by trimethylsilylmethyl trifluoromethanesulphonate.<sup>392</sup> The arylation of thiols or selenides has been effected with a diaryliodonium salt, using a copper(II) salt as catalyst,<sup>393</sup> and phenacylation of sulphides with diazoacetophenone has been reported.<sup>394</sup> A similar type of product,  $R^1R^2\overset{\oplus}{S}CHArCOCN$ , has been formed from a sulphide with a *gem*-dicyano-oxiran.<sup>395</sup> Unusual routes to selenonium salts ( $SeOCl_2 + ArMgX \rightarrow Ar_3Se^+ X^-$ ,<sup>396</sup>  $Ph_2SeO + RCH_2NO_2$  with  $Ac_2O$  and  $HX \rightarrow Ph_2\overset{\oplus}{Se}CHRNO_2 X^-$ <sup>397</sup>) and telluronium salts ( $Ar_2TeO +$  active-methylene compounds<sup>398</sup>) have been reported.

Assignment of the (*S*) configuration to (+)-ethylmethylpropylsulphonium 2,4,6-trinitrobenzenesulphonate follows from chemical correlation with (*S*)-lactic acid *via* a (4*S*,6*S*)-4-ethyl-6-methyl-2-oxo-1,4-oxathianium salt intermediate.<sup>399</sup>

An important reaction of sulphonium salts, transfer of an *S*-alkyl group to a nucleophilic species, is also shared with selenonium salts. Both trimethylsulphonium<sup>400</sup> and -selenonium<sup>401</sup> hydroxides are effective methylating agents towards carboxylic acids, thiols, phenols, and other acidic substrates (*e.g.* heteroaromatic NH groups), and the more reactive trimethylselenonium salt has been advocated as a useful alternative to diazomethane which avoids known carcinogenic materials.<sup>401</sup> The (*pro-R*)-methyl group of *S*-methyl-L-methionine is transferred to L-homocystine when catalysed by a jack bean transferase.<sup>402</sup> Further references to papers on this topic, and on other reactions and uses of sulphonium salts in synthesis, which extend well-established chemistry, are summarized at the end of this section. The main topic areas covered in these papers are the synthesis of cyclopropanes and oxirans, and substitution reactions. An interesting combination of reactions is seen in the 'epoxyannulation' of aldehyde and ketone enolates (Scheme 16).<sup>403</sup>

**Additional Bibliography:** N. V. Kondratenko, G. N. Timofeeva, V. I. Popov, and L. M. Yagupolskii, *Zh. Org. Khim.*, 1979, 15, 2432 [sulphides, selenides, or tellurides + MeI and  $AgBF_4$ ]; Y. L. Chow, B. H. Bakker, and K. Iwai, *J. Chem. Soc., Chem. Commun.*, 1980, 521 [styrene,  $Br_2$ , and  $Me_2S +$  base  $\rightarrow PhC(=CH_2)\overset{\oplus}{S}Me_2 Br^-$ ]; M. J. Farrall, T. Durst, and J. M. J. Frechet, *Tetrahedron Lett.*, 1979, 203 [sulphonium-salt-substituted polymeric reagents]; M. Ando and S. Emoto, *Bull. Chem. Soc. Jpn.*, 1978, 51, 2435 [substituted phenyldimethylsulphonium fluorosulphonates]; J. F. King and G. T. Y. Tsang, *J. Chem. Soc., Chem. Commun.*, 1979, 1131 [kinetics of substitution at methylene groups of benzyl in  $(PhCH_2)_2\overset{\oplus}{S}Et BF_4^-$ ]; M. Cavazza, G. Morganti, C. A. Veracini, and F. Pietra, *J. Chem.*

<sup>390</sup> B. Bader and M. Julia, *Tetrahedron Lett.*, 1979, 1101.

<sup>391</sup> S. Kozuka, S. Taniyasu, A. Kikuchi, and K. Ogino, *Chem. Lett.*, 1979, 129.

<sup>392</sup> E. Vedejs and G. R. Martinez, *J. Am. Chem. Soc.*, 1979, 101, 6452.

<sup>393</sup> J. V. Crivello and J. H. W. Lam, *J. Org. Chem.*, 1978, 43, 3055; *Synth. Commun.*, 1979, 9, 151.

<sup>394</sup> W. T. Flowers, G. Holt, and P. McCleery, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1485.

<sup>395</sup> A. Robert, M. T. Thomas, and A. Foucaud, *J. Chem. Soc., Chem. Commun.*, 1979, 1048.

<sup>396</sup> Y. Ishii, Y. Iwama, and M. Ogawa, *Synth. Commun.*, 1978, 8, 93.

<sup>397</sup> S. A. Shevelev, V. V. Semenov, and A. A. Fainzilberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1091.

<sup>398</sup> I. D. Sadekov, A. I. Usachev, A. A. Maksimenko, and V. I. Minkin, *Zh. Obshch. Khim.*, 1978, 48, 934.

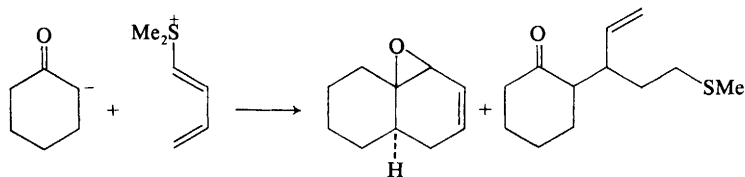
<sup>399</sup> E. Kelstrup, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1037.

<sup>400</sup> K. Yamauchi, T. Tanabe, and M. Kinoshita, *J. Org. Chem.*, 1979, 44, 638.

<sup>401</sup> K. Yamauchi, K. Nakamura, and M. Kinoshita, *Tetrahedron Lett.*, 1979, 1787.

<sup>402</sup> G. Grue-Sorensen, E. Kelstrup, A. Kjaer, and J. O. Madsen, *J. Chem., Soc., Chem. Commun.*, 1980, 19.

<sup>403</sup> M. E. Garst, *J. Org. Chem.*, 1979, 44, 1578.



Scheme 16

*Soc., Chem. Commun.*, 1979, 912 [competition between 3- and 7-substitution in 2-(dimethylsulphonio)cyclohepta-2,4,6-trienone]; D. M. Hedstrand, W. H. Kruizinga, and R. M. Kellogg, *Tetrahedron Lett.*, 1978, 1255 [dye-sensitized photoreduction of phenacylsulphonium salts by transfer of hydride ion from 1,4-dihydropyridines]; T. Minami, I. Niki, and T. Agawa, *Phosphorus Sulfur*, 1977, 3, 55 [demethylation of vinyl dimethylsulphonium salts with  $\text{PhO}^-$ ]; B. A. Arbusov, Yu. V. Belkin, N. A. Polezhaeva, and G. E. Buslaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1625 [demethylation of methylphenylselenonium salts with  $\text{PPh}_3$ ]; P. G. Gassman, T. Miura, and A. Mossman, *J. Chem. Soc., Chem. Commun.*, 1980, 558 [dealkylation of benzylalkylselenonium salts by base;  $\text{NaNH}_2$  leads to a [2,3]-sigmatropic rearrangement, giving 2-alkylbenzyl selenides]; H. J. Reich and M. L. Cohen, *J. Am. Chem. Soc.*, 1979, 101, 1307 [competition between *S*- or *Se*-allylation and  $\alpha$ -alkylation of phenacyl sulphides and selenides; [2,3]-sigmatropic rearrangements of allyl-sulphonium and -selenonium salts]; S. Kano, T. Yokomatsu, and S. Shibuya, *Tetrahedron Lett.*, 1978, 4125 [the [2,3]-sigmatropic rearrangements of  $\beta$ -hydroxy- $\beta$ -phenylalkyl-sulphonium ylides to 3-phenylalk-3-enyl sulphides]; H. Matsuyama, M. Matsumoto, M. Kobayashi, and H. Minato, *Bull. Chem. Soc. Jpn.*, 1979, 52, 1139 [catalysis of sulphide-sulphonium salt equilibrium by  $\text{ArSCN}$ ,  $\text{ArSCF}_3$ , or  $\text{ArSOMe}$ ]; S. Kano, T. Yokomatsu, and S. Shibuya, *J. Chem. Soc., Chem. Commun.*, 1978, 785 [general synthesis of oxirans, using  $\beta$ -hydroxyalkyl-dimethylsulphonium salts]; D. H. Rich and J. P. Tam, *Synthesis*, 1978, 46 [cyclization of derivatives of *S*-methylmethionine to cyclopropanes with  $\text{NaH}$ ]; S. Brandt and P. Helquist, *J. Am. Chem. Soc.*, 1979, 101, 6473 [conversion of alkenes into cyclopropanes with retention of configuration, using  $[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2(\text{CH}_2\text{SMe}_2)]\text{BF}_4^-$ ]; K. Takaki, K. Negoro, and T. Agawa, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1490 [addition of carbanions to vinyl dimethylsulphonium salts, leading to cyclopropanes, alkenes, or 1-pyrrolines]; T. Severin and I. Braentigam, *Chem. Ber.*, 1979, 112, 3007, and E. Vilsmaier and W. Tröger, *Angew. Chem.*, 1979, 91, 860 and *Synthesis*, 1980, 466 [enamino-sulphonium salts].

**Halogeno-sulphonium Salts.**—Uses for *S*-chlorodimethylsulphonium chloride and the corresponding bromine compound have been extended to a conversion of oxirans into  $\alpha$ -halogeno-ketones (Scheme 17),<sup>404</sup> to oxidative dimerization of malonates,<sup>405</sup> and to the conversion of sulphonamides into sulphimides.<sup>405</sup>

The formation of *S*-halogeno-sulphonium salts from the halogen and a sulphide is in competition with an  $\alpha$ -halogenation-oxidation reaction which leads to sulphonyl chlorides when water is present.<sup>406</sup> The initial attack at sulphur may be followed by a Pummerer rearrangement to the adjacent carbon atom, and in the case of unsymmetrical sulphides the regioselectivity is determined by the relative electron density at the  $\alpha$ -carbon atoms.<sup>407</sup>

A mixture of  $\text{ClCH}_2\text{SMe}$  and  $\text{SbCl}_5$  contains the chloro-sulphonium salts  $\text{ClCH}_2\text{SClMe} \text{SbCl}_6^-$  and  $\text{Cl}_2\text{CHSClMe} \text{SbCl}_6^-$ , and not the carbonium salts, as previously claimed.<sup>408</sup> However,  $\text{MeSCCl}_2 \text{SbCl}_6^-$  is formed from  $\text{Cl}_3\text{CSMe}$ .

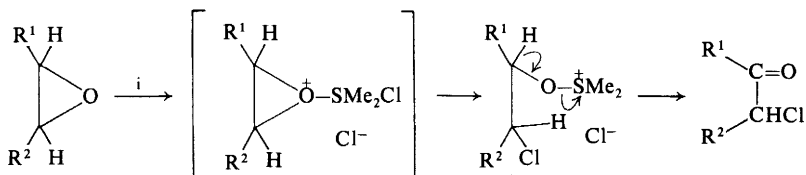
<sup>404</sup> G. A. Olah, Y. D. Vankar, and M. Arvanaghi, *Tetrahedron Lett.*, 1979, 3653.

<sup>405</sup> N. Furukawa, T. Inoue, T. Aida, T. Akasaka, and S. Oae, *Phosphorus Sulfur*, 1978, 4, 15.

<sup>406</sup> R. F. Langler, Z. A. Marini, and E. S. Spalding, *Can. J. Chem.*, 1979, 57, 3193.

<sup>407</sup> T. P. Ahern, D. G. Kay, and R. F. Langler, *Can. J. Chem.*, 1978, 56, 2422.

<sup>408</sup> K. Hartke and E. Akgun, *Chem. Ber.*, 1979, 112, 2436.



Reagents; i,  $\text{Me}_2\text{S}^+\text{Cl}^-$

Scheme 17

**Amino-sulphonium Salts.**—*N*-Chlorosuccinimide reacts with sulphides in the presence of  $\text{SbCl}_5$  to give *S*-succinimidiosulphonium salts, which can undergo Stevens rearrangement to 5-alkylthiomethoxypyrrolin-2-ones.<sup>409</sup> Similar results have been obtained with hydantoin,<sup>410</sup> and analogous reactions are being exploited to effect the *ortho*-substitution of aromatic amines.<sup>411</sup>

*N*-Chlorosuccinimide plus  $\text{Me}_2\text{S}$  is a convenient reagent for introducing a dimethylsulphonio-group, and it forms  $\text{Me}_2\text{NCH}=\text{C}(\text{SMe}_2)\text{CHO Cl}^-$  from the corresponding aldehyde.<sup>412</sup> The reagent can be used with triethylamine to couple carboxylic acids to amines, but its merits relative to other reagents in amide synthesis have not yet been determined, so that its potential for peptide synthesis is as yet unknown.<sup>413</sup>

Dialkylamino-alkoxysulphonium salts  $\text{R}_2\text{N}^+\text{S}(\text{OR})\text{Ph BF}_4^-$  are formed from sulphenamides and an alcohol with  $\text{Bu}^t\text{OCl}$  and  $\text{AgBF}_4$ ;<sup>414</sup> these are conditions which are much milder than those used in the alternative methods of alkylation of sulphinamides.

**Alkoxy-sulphonium Salts.**—Alkylation of sulphoxides by a trialkyloxonium tetrafluoroborate gives these salts, which are relatively stable to air and moisture.<sup>415</sup> The compounds, which are intermediates in one form of the Pummerer rearrangement,<sup>416</sup> are efficient alkylating agents.<sup>415</sup> The role of methyl phenyl sulphide as the catalytic electron-carrier in an electrochemical oxidation of alcohols is proposed to involve alkoxy-sulphonium salt formation, followed by a hydride shift.<sup>417</sup> The fact that some sulphoxide is also formed in this reaction appears to have encouraged the authors in their proposal:  $\text{PhSMe} - 2e^- \rightarrow \text{PhS}^+\text{Me} \rightarrow \text{PhS}^+\text{MeOCHR}^1\text{R}^2 \rightarrow \text{PhS}^+(\text{CH}_2)\text{OCHR}^1\text{R}^2 \rightarrow \text{PhSMe} + \text{R}^1\text{COR}^2$ . However, there are inconsistencies in the adoption of this mechanism, which has been established for dimethyl sulphoxide in the presence of a proton acceptor, particularly since alcohols are readily oxidized in the same electrochemical system in the absence of a

<sup>409</sup> E. Vilsmaier, J. Schuetz, and S. Zimmerer, *Chem. Ber.*, 1979, **112**, 2231.

<sup>410</sup> E. Vilsmaier, R. Bayer, I. Laengenfelder, and U. Wetz, *Chem. Ber.*, 1978, **111**, 1136; E. Vilsmaier, R. Bayer, U. Wetz, and K.-H. Dittrich, *ibid.*, p. 1147.

<sup>411</sup> P. G. Gassmann and H. R. Drewes, *J. Am. Chem. Soc.*, 1978, **100**, 7600.

<sup>412</sup> V. Kral and Z. Arnold, *Collect. Czech. Chem. Commun.*, 1978, **43**, 1248.

<sup>413</sup> K. Takeda, T. Kobayashi, and H. Ogura, *Chem. Pharm. Bull.*, 1979, **27**, 536.

<sup>414</sup> M. Haake and H. Gebbing, *Synthesis*, 1979, 98.

<sup>415</sup> H. U. Wagner and A. Judelbaum, *Angew. Chem.*, 1978, **90**, 487.

<sup>416</sup> S. Wolfe and P. M. Kazmaier, *Can. J. Chem.*, 1979, **57**, 2388, 2397; S. Wolfe, P. M. Kazmaier, and H. Anksi, *ibid.*, p. 2404.

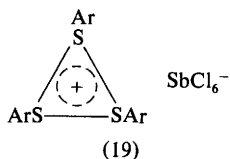
<sup>417</sup> T. Shono, Y. Matsumura, M. Mizoguchi, and J. Hayashi, *Tetrahedron Lett.*, 1979, 3861.

sulphide. The presence of other side-products which would be consistent with the alkoxysulphonium ion intermediate must now be established to give support to the proposed mechanism.

Anomalous results in the conversion of allylic alcohols into halides *via* alkenoxysulphonium salts (formed using dimethyl sulphide and NCS) have been ascribed to participation by remote functional groups in the rearrangement.<sup>418</sup>

**Alkylthio-sulphonium Salts.**—Admirably thorough studies have been made by Caserio and her co-workers on the preparation and reactions of alkylthio-sulphonium salts, which are now being recognized as intermediates in a number of organosulphur reactions.

Alkylation of a disulphide with  $\text{Me}_3\text{O}^+ \text{BF}_4^-$ ,<sup>419</sup> or the reaction of a trifluoroacetoxysulphonium salt with a thiol  $[\text{Me}_2\text{SO} + (\text{CF}_3\text{CO})_2\text{O} \rightarrow \text{Me}_2\overset{\oplus}{\text{S}}\text{OCOCF}_3 \text{CF}_3\text{CO}_2^- \rightarrow \text{Me}_2\overset{\oplus}{\text{S}}\text{SR} \text{CF}_3\text{CO}_2^-]$ <sup>420</sup> are direct methods of synthesis. A bis(arylthio)sulphonium salt, probably better represented as the symmetrical cation (19), is formed either from a disulphide or from an arenesulphenyl chloride with  $\text{SbCl}_5$ .<sup>421</sup>



Alkylthio-sulphonium salts are efficient alkylthiolating agents, and several papers describing comparisons between  $\text{Me}_2\overset{\oplus}{\text{S}}\text{SMe} \text{BF}_4^-$  and  $\text{MeSCl}$  have appeared.<sup>422–424</sup> Labelling studies<sup>422</sup> indicate that the reaction of this salt with diastereoisomeric forms of  $\text{MeSCHMeCHMeSMe}$ , which involves C–S bond cleavage in the latter, is not simply a matter of  $\text{S}_{\text{N}}2$  displacement, or *S*-methylation by the salt. The initial *S*-methylthiolation liberates  $\text{Me}_2\text{S}$ , while a further equilibrium, forming  $\text{MeSSMe}$  and the *S*-methylthiiranium salt, provides all the intermediates needed to account for the formation of  $\text{MeSCHMeCHMe}\overset{\oplus}{\text{S}}\text{Me}_2$  and  $\text{MeSCHMeCHMe}\overset{\oplus}{\text{S}}(\text{Me})\text{SMe}$ .<sup>422</sup> Exchange of  $\text{MeS}$  between  $\text{MeSX}$  ( $\text{X} = \text{Cl}$  or  $-\overset{\oplus}{\text{S}}\text{Me}_2 \text{BF}_4^-$ ) and  $\text{MeSCH}_2\text{CH}=\text{CH}_2$  occurs with the methylthio-sulphonium salt, but not with the sulphenyl chloride.<sup>423</sup> The overall reaction leads to  $\text{MeSCH}_2\text{CH}(\text{SMe})\text{CH}_2\text{X}$  with scrambling of the  $^3\text{H}$ , which indicates a reversible degenerate rearrangement of the intermediate *S*-methylthio-sulphonium ion. Cleavage of both C–S bonds of a dithioacetal by

<sup>418</sup> F. Bellesia, R. Grandi, U. M. Pagnoni, and R. Trave, *J. Chem. Soc., Perkin Trans. 1*, 1979, 851.

<sup>419</sup> J. K. Kim, E. Lingman, and M. C. Caserio, *J. Org. Chem.*, 1978, **43**, 4545.

<sup>420</sup> R. Tanikaga, K. Tanaka, and A. Kaji, *J. Chem. Soc., Chem. Commun.*, 1978, 865.

<sup>421</sup> A. S. Gybin, W. A. Smit, V. S. Bogdanov, M. Z. Krimer, and J. B. Kalyan, *Tetrahedron Lett.*, 1980, **21**, 383.

<sup>422</sup> S. A. Anderson, J. K. Kim, and M. C. Caserio, *J. Org. Chem.*, 1978, **43**, 4822.

<sup>423</sup> J. K. Kim, M. L. Kline, and M. C. Caserio, *J. Am. Chem. Soc.*, 1978, **100**, 6243; J. K. Kim and M. C. Caserio, *J. Org. Chem.*, 1979, **44**, 1897; M. L. Kline, N. Bentov, J. K. Kim, and M. C. Caserio, *ibid.*, p. 1904.

$\text{Me}_2\text{S}^+\text{SMe BF}_4^-$  proceeds *via* methylthio-sulphonium ions, which rearrange by cleavage and re-formation of C–S and S–S bonds by way of an  $\alpha$ -(methylthio)carbonium ion.<sup>424</sup>

Conversions of thiols into disulphides and thiol-sulphonates through their reactions with DMSO and TFAA involve the alkylthio-sulphonium salts as intermediates, the thiol-sulphonate arising when water is present.<sup>420</sup> Bis-(arylthio)sulphonium salts are effective reagents for the conversion of alkenes into thiirans.<sup>421</sup>

## 8 Thioacetals [1-(Alkylthio)alkyl Sulphides] and their Selenium Analogues

**Saturated Thioacetals and Selenoacetals.**—Standard preparations of dithioacetals and diselenoacetals have been developed further. Preparations from carbonyl compounds summarized in ref. 425 indicate current approaches, but some examples show unusual features [ $\text{MeSeH}$  and  $\text{ZnCl}_2 \rightarrow \text{R}^1\text{R}^2\text{C}(\text{SeMe})_2 + \text{R}^1\text{R}^2\text{CHSeMe}$ ,<sup>426</sup> and  $\text{R}^1\text{R}^2\text{C}=\text{CHCHO} + \text{PhSH} \rightarrow \text{R}^1\text{R}^2\text{C}(\text{SPh})\text{CH}_2\text{CH}(\text{SPh})_2$ <sup>427</sup>]. Syntheses from halides [ $\text{CH}_2\text{Br}_2 + \text{ArSNa} + 18\text{-crown-6 ether} \rightarrow \text{CH}_2(\text{SAr})_2$ ,<sup>428</sup>  $\text{H}_2\text{C}=\text{CHCl} + \text{Me}_2\text{S}$  (at 450 °C)  $\rightarrow \text{MeCH}(\text{SMe})_2 + \text{H}_2\text{C}=\text{CHSMe} + 7\%$  of  $\text{H}_2\text{C}=\text{CHSH}$ <sup>429</sup>]; by  $\alpha$ -bis(sulphenylation) of ketones, using a disulphide and NaH,<sup>430,431</sup> by trapping the intermediate in the Pummerer rearrangement of a sulfoxide [ $\text{R}^1\text{SOCH}_2\text{R}^2 + \text{TFAA} \rightarrow \text{R}^1\text{S}^+\text{CHR}^2 \rightarrow \text{R}^1\text{SCHR}^2(\text{SR}^3)$ ];<sup>432</sup> and from thiocarbonyl compounds [ $\text{RCSSEt} + \text{EtMgI} \rightarrow \text{RC}(\text{SEt})_2\text{MgI}$ ;<sup>433</sup> a process used<sup>434</sup> in a synthesis of isoartemesia ketone] have also been recorded. Conversion of an acetal into a dithioacetal [ $2,5\text{-dimethoxytetrahydrofuran} \rightarrow (\text{PhS})_2\text{CH}(\text{CH}_2)_2\text{CH}(\text{SPh})_2$ <sup>435</sup> with PhSH and HCl] and conversion of one dithioacetal [ $\text{PhSCR}^1\text{R}^2\text{CH}_2\text{CH}(\text{SPh})_2$ ]<sup>427,436</sup> into another [1,1-bis(phenylthio)cyclopropanes] by MeLi and TMEDA, illustrate further possibilities, the last-mentioned reaction involving intramolecular nucleophilic displacement of  $\text{PhS}^-$  by a dithioacetal carbanion.

The synthesis of the mono-*S*-oxo-dithioacetal moiety of the antibiotic sparsomycin has been accomplished, starting from *N*-benzyloxycarbonyl-L-cysteine.<sup>437</sup>

*O,S*-Acetals can be prepared by treatment of  $\alpha$ -(phenylthio)alkylboranes with

<sup>424</sup> J. K. Kim, J. K. Pau, and M. C. Caserio, *J. Org. Chem.*, 1979, **44**, 1544.

<sup>425</sup> A. Cravador and A. Krief, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1979, **289**, 267; M. Tazaki and M. Takagi, *Chem. Lett.*, 1979, 767; D. L. J. Clive and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 1978, 356 and *J. Org. Chem.*, 1979, **44**, 1883; H. A. Klein, *Z. Naturforsch., Teil B*, 1979, **34**, 999.

<sup>426</sup> A. Cravador, A. Krief, and L. Hevesi, *J. Chem. Soc., Chem. Commun.*, 1980, 451.

<sup>427</sup> T. Cohen, W. M. Daniewski, and R. B. Weisenfeld, *Tetrahedron Lett.*, 1978, 4665.

<sup>428</sup> S. Tanimoto, T. Imanishi, S. Jo, and M. Okano, *Bull. Inst. Chem. Res., Kyoto Univ.*, 1978, **56**, 297 (*Chem. Abstr.*, 1979, **90**, 168 204).

<sup>429</sup> M. A. Kuznetsova, E. N. Deryagina, and M. G. Voronkov, *Zh. Org. Khim.*, 1979, **15**, 1996.

<sup>430</sup> M. Braun, *Tetrahedron Lett.*, 1978, 3695.

<sup>431</sup> Y. Nagao, K. Kaneko, K. Kawabata, and E. Fujita, *Tetrahedron Lett.*, 1978, 5021.

<sup>432</sup> R. Tanikaga, Y. Hiraki, N. Ono, and A. Kaji, *J. Chem. Soc., Chem. Commun.*, 1980, 41.

<sup>433</sup> A. I. Meyers, T. A. Tait, and D. L. Comins, *Tetrahedron Lett.*, 1978, 4657.

<sup>434</sup> P. Gosselin, S. Masson, and A. Thuillier, *Tetrahedron Lett.*, 1978, 2717.

<sup>435</sup> T. Cohen, D. Ouellette, and W. M. Daniewski, *Tetrahedron Lett.*, 1978, 5063.

<sup>436</sup> T. Cohen and J. R. Matz, *J. Org. Chem.*, 1979, **44**, 4816; T. Cohen and W. M. Daniewski, *Tetrahedron Lett.*, 1978, 2991.

<sup>437</sup> H. C. J. Ottenheim and R. M. J. Liskamp, *Tetrahedron Lett.*, 1978, 2437.



*N*-chlorosuccinimide in MeOH (PhSCHRBR<sub>2</sub> → PhSCHROME),<sup>438</sup> methanolysis of *S*-monomethyl dithioacetal fluorosulphonates,<sup>439</sup> and addition of an alkyl-lithium to thiono-esters.<sup>440</sup> Quantitative studies have been reported for an interesting variation on the simplest preparation, in which hemithioacetals exist in equilibrium with an aldehyde and a mixture of two thiols.<sup>441</sup>

Reactions of thioacetals and selenoacetals are overwhelmingly directed towards applications in synthesis, most of which rely on the formation of stabilized carbanions. The HMPA-induced addition of (PhS)<sub>2</sub>CRLi to  $\alpha\beta$ -unsaturated ketones is almost entirely 1,4-oriented (see also ref. 370), providing a characteristic example of a dithioacetal carbanion as an acyl-ion equivalent<sup>442</sup> (see also Chap. 2, Pt. I, p. 95). Similar uses for the THF-soluble potassium dianion of bis-(ethylthio)acetic acid<sup>443</sup> (a new  $\alpha$ -keto-acid synthon) and alkylselenylcyclopropyl carbanions<sup>444</sup> have been described. Full details have been published<sup>445</sup> of the uses of bis(phenylthio)-carbanions in C—C bond formation with carbonyl compounds which create several synthetic possibilities [(PhS)<sub>2</sub>C(CH<sub>2</sub>R')CHR<sup>2</sup>OH + SOCl<sub>2</sub> + Et<sub>3</sub>N → PhSC(=CHR')CHR<sup>2</sup>SPh → sulphoxide → PhSC-(CHR'OH)=CHR<sup>2</sup> by sulphoxide-sulphenate rearrangement].<sup>446</sup> The C—Se bond cleavage of diselenoacetals,<sup>444</sup> *S*,*Se*-acetals,<sup>442</sup> and seleno-orthoesters<sup>447</sup> is brought about by an alkyl-lithium, but deprotonation without C—Se bond cleavage is carried out with lithium tetramethylpiperidide.<sup>447</sup> This partial deselenation approach allows vinyl selenides and vinylsilanes to be prepared from  $\beta$ -hydroxy- $\alpha$ -trimethylsilyl selenides.<sup>448</sup>

The conclusion to uses of dithioacetals and selenium analogues in synthesis is usually a form of hydrolysis to give an aldehyde or a ketone. New 'dethioacetalization' studies describe uses of NO<sup>+</sup>HSO<sub>4</sub><sup>-</sup>, of either NaNO<sub>2</sub> or NaNO<sub>3</sub> with TFA, or of NO<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>,<sup>449</sup> of isoamyl nitrite,<sup>450</sup> or of Me<sub>2</sub>SBr Br<sup>-</sup>.<sup>451</sup> A comparison of four methods commonly used for dethioacetalization [HgCl<sub>2</sub> with CaCO<sub>3</sub>; HgCl<sub>2</sub> with CuCl<sub>2</sub>; H<sub>2</sub>O<sub>2</sub>; and (PhSe)<sub>2</sub>O] has been made for the corresponding deselenoacetalization.<sup>452</sup> It appears that selenoacetals are more easily cleaved than thioacetals but more prone to elimination to give vinyl selenides.<sup>452</sup> Methyl selenoacetals are more easily cleaved than the phenyl analogues.<sup>452</sup>

<sup>438</sup> A. Mendoza and D. S. Matteson, *J. Organomet. Chem.*, 1978, **156**, 149; *J. Chem. Soc., Chem. Commun.*, 1978, 357.

<sup>439</sup> T. A. Hase and R. Kivikari, *Synth. Commun.*, 1979, **9**, 107.

<sup>440</sup> L. Narasimhan, R. Sanitra, and J. S. Swenton, *J. Chem. Soc., Chem. Commun.*, 1978, 719.

<sup>441</sup> M. S. Kanchuger and L. D. Byers, *J. Am. Chem. Soc.*, 1979, **101**, 3005.

<sup>442</sup> J. Lucchetti, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 1979, 2695; L. Wartski, M. El Bouz, J. Seyden-Penne, W. Dumont, and A. Krief, *ibid.*, p. 1543.

<sup>443</sup> G. S. Bates, *J. Chem. Soc., Chem. Commun.*, 1979, 161.

<sup>444</sup> S. Halazy and A. Krief, *J. Chem. Soc., Chem. Commun.*, 1979, 1136; S. Halazy, J. Lucchetti, and A. Krief, *Tetrahedron Lett.*, 1978, 3971.

<sup>445</sup> P. Blatcher and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1074.

<sup>446</sup> P. Blatcher and S. Warren, *Tetrahedron Lett.*, 1979, 1247.

<sup>447</sup> D. van Ende, A. Cravador, and A. Krief, *J. Organomet. Chem.*, 1979, **177**, 1.

<sup>448</sup> W. Dumont, D. van Ende, and A. Krief, *Tetrahedron Lett.*, 1979, 485.

<sup>449</sup> G. A. Olah, S. C. Narang, G. F. Salem, and B. G. B. Gupta, *Synthesis*, 1979, 273.

<sup>450</sup> K. Fujii, K. Ichikawa, and E. Fujita, *Tetrahedron Lett.*, 1978, 3561.

<sup>451</sup> G. A. Olah, Y. D. Vankar, M. Arvanaghi, and G. K. S. Prakash, *Synthesis*, 1979, 720.

<sup>452</sup> A. Burton, L. Hevesi, W. Dumont, A. Cravador, and A. Krief, *Synthesis*, 1979, 877.

Protection of carboxyl groups using methylthiomethyl esters can be reversed either by oxidation with  $\text{H}_2\text{O}_2$  or methylation, followed by mild hydrolysis.<sup>453</sup>

A small number of papers that cover mechanistic aspects deal with the factors that stabilize the developing carbonium ion in the hydrolysis of *O,S*-thioacetals.<sup>454</sup> An electron-transfer, mild reduction system (iron polyphthalocyanine) has been shown<sup>455</sup> to reduce benzil dithioacetal to the  $\beta$ -keto-sulphide [ $\text{PhCOCHPh}(\text{SPh})_2 \rightarrow \text{PhCOCHPhSPh}$ ]. Homolysis of dithioacetals on heating with  $\text{Bu}^t\text{OOBu}^t$  in  $\text{PhCl}$  followed by a 1,2-shift of an alkylthio-group leads to 1,2-bis-(alkylthio)alkyl compounds.<sup>456</sup>

Synthesis of  $\alpha$ -alkylthioalkyl sulphones by oxidation of dithioacetals with  $\text{KMnO}_4$  has been reported.<sup>457</sup>

**Keten Dithioacetals.**—The structural relationship of these compounds with saturated dithioacetals is shown by their formation from dithioacetal carbanions *via*  $\alpha$ -di(phenylthio)alkylboronate esters and reaction with carbonyl compounds and  $\text{LiNPr}_2$  [ $(\text{PhS})_2\text{CHLi} \rightarrow (\text{PhS})_2\text{CHB}(\text{OR})_2 \rightarrow (\text{PhS})_2\text{C}=\text{CR}^1\text{R}^2$ ].<sup>458</sup> Several alternative routes are available, including one involving the reaction of a carboxylic acid or ester with  $\text{Al}(\text{SPh})_3$ , which has been used with  $\alpha\beta$ -unsaturated esters to give  $\beta$ -(phenylthio)keten dithioacetals [ $\text{R}^1\text{R}^2\text{C}=\text{CR}^3\text{CO}_2\text{R}^4 \rightarrow \text{PhSCR}^1\text{R}^2\text{C}=\text{C}(\text{SPh})_2$ ].<sup>459</sup> Synthesis from thiocarbonyl compounds, including  $\text{CS}_2$ , is a standard route [ $\text{R}^1\text{R}^2\text{CHCS}_2\text{H} \rightarrow \text{dianion with LiNPr}_2 \rightarrow \text{R}^1\text{R}^2\text{C}=\text{C}(\text{SR}^3)_2$  with  $\text{R}^3\text{X}$ ],<sup>460</sup> alk-2-enedithioate esters  $\rightarrow$  conjugated keten dithioacetals;<sup>461</sup>  $\alpha$ -(methylthio)methylenation of ketones with  $\text{CS}_2$ , base, and  $\text{MeI}$ ,<sup>462,463</sup> and similar treatment of phenyl cyanomethyl sulphones also gives the keten dithioacetals:  $\text{PhSO}_2\text{CH}_2\text{CN} \rightarrow \text{PhSO}_2\text{C}(\text{CN})=\text{C}(\text{SMe})_2$ .<sup>464</sup> Difluoroketen dithioacetals  $\text{F}_2\text{C}=\text{C}(\text{SEt})_2$  are available from  $\text{CF}_3\text{CH}(\text{SEt})_2$  by reaction with  $\text{Bu}^n\text{Li}$  or  $\text{LiNPr}^t$ .<sup>465</sup> The further replacement of halogen by organometallic compounds yields the homologues  $\text{RCF}=\text{C}(\text{SEt})_2$ , and the overall process amounts to the conversion of  $\text{CF}_3\text{CO}_2\text{H}$  into  $\text{RCHFCO}_2\text{H}$ , taking into account the other established transformations of functional groups.<sup>465</sup> [2,3]-Sigmatropic rearrangement of  $\text{PhS}-(\text{CHSPh})\text{CH}_2\text{C}\equiv\text{CMe}$  gives  $(\text{PhS})_2\text{C}=\text{CMeCH}=\text{CH}_2$  in high yield,<sup>466</sup> and another

<sup>453</sup> J. M. Gerdes and L. G. Wade, *Tetrahedron Lett.*, 1979, 689.

<sup>454</sup> J. L. Jensen and W. P. Jencks, *J. Am. Chem. Soc.*, 1979, **101**, 1476; J. P. Ferraz and E. H. Cordes, *ibid.*, p. 1488; T. H. Fife and T. J. Przystas, *ibid.*, 1980, **102**, 292.

<sup>455</sup> H. Inoue, T. Nagata, H. Hata, and E. Imoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 469.

<sup>456</sup> R. G. Petrova, T. D. Churkina, and V. I. Dostoralova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1818.

<sup>457</sup> M. Poje and K. Balenovic, *Tetrahedron Lett.*, 1978, 1231.

<sup>458</sup> A. Mendoza and D. S. Matteson, *J. Org. Chem.*, 1979, **44**, 1352.

<sup>459</sup> T. Cohen and R. B. Weisenfeld, *J. Org. Chem.*, 1979, **44**, 3601; T. Cohen, R. E. Gapiński, and R. R. Hutchins, *ibid.*, p. 3599.

<sup>460</sup> F. E. Ziegler and C. M. Chan, *J. Org. Chem.*, 1978, **43**, 3065.

<sup>461</sup> M. Pohmakotr and D. Seebach, *Tetrahedron Lett.*, 1979, 2271.

<sup>462</sup> M. Augustin and C. Groth, *J. Prakt. Chem.*, 1979, **321**, 215.

<sup>463</sup> M. Augustin, C. Groth, H. Kristen, K. Peseke, and C. Wiechmann, *J. Prakt. Chem.*, 1979, **321**, 205.

<sup>464</sup> Y. Tominaga, S. Hidaki, Y. Matsuda, G. Kobayashi, and K. Sakemi, *Yakugaku Zasshi*, 1979, **99**, 540 (*Chem. Abstr.*, 1980, **91**, 157 539); S. Hidaki, Y. Tominaga, Y. Matsuda, G. Kobayashi, and K. Sakemi, *ibid.*, p. 1234.

<sup>465</sup> K. Tanaka, T. Nakai, and N. Ishikawa, *Chem. Lett.*, 1979, 175.

<sup>466</sup> V. Ratovelomanana and S. Julia, *Synth. Commun.*, 1978, **8**, 87; B. Cazes and S. Julia, *Tetrahedron Lett.*, 1978, 4065.

route to conjugated keten dithioacetals is based on carbene insertion into a disulphide  $[\text{ClCMe}_2\text{C}\equiv\text{CH} + \text{MeLi} \rightarrow \text{Me}_2\text{C}=\text{C}=\text{C}: \rightarrow \text{Me}_2\text{C}=\text{C}=\text{C}(\text{SR})_2 \rightarrow \text{H}_2\text{C}=\text{CMeCH}=\text{C}(\text{SR})_2]$ .<sup>467</sup> An alternative rearrangement approach has been used<sup>468</sup> in which the carbene  $(\text{RS})_2\text{C}: (generated from the sodium salt of S-allyl-S'-methylthiocarbonate tosylhydrazone by pyrolysis)$  undergoes a [2,3]-sigmatropic rearrangement and is trapped with MeI to give  $(\text{MeS})_2\text{C}=\text{CR}^1\text{CR}^2=\text{CH}_2$ .<sup>468</sup>

Applications of keten dithioacetals in synthesis that have been reported recently are mainly developments of existing possibilities, *i.e.* cleavage with lithium naphthalenide at  $-78^\circ\text{C}$  to give S-stabilized vinyl-lithium compounds for use in known routes to allyl alcohols or  $\alpha\beta$ -unsaturated carboxylic acids,<sup>459</sup> and nucleophilic substitution of an RS group in a keto-keten dithioacetal or related compounds,<sup>463,464</sup> giving pyridin-2(1*H*)-ones and indolizines,<sup>464</sup> or other heterocyclic compounds.<sup>469</sup> Conjugated keten dithioacetals are valuable synthons,<sup>461,466</sup> and the extension of a carbon skeleton through addition of an alkyl-lithium has been illustrated in a synthesis of (–)-(*E*)-lanceol.<sup>466</sup> 1,1-Bis-(phenylthio)cyclopropanes have been prepared from  $\text{H}_2\text{C}=\text{C}(\text{SPh})_2$  with an allyl sulphide carbanion.<sup>470</sup> Regioselectivity of the alkylation of lithiated  $\text{MeCH}=\text{C}(\text{SR})_2$  is influenced by the structure of the group R, a greater degree of  $\gamma$ -alkylation being associated with greater bulk. Irrespective of this factor, only  $\gamma$ -alkylation is observed in the presence of a copper(I) salt.<sup>471</sup> Addition of dimethyl phosphonate to  $\text{PhCH}=\text{C}(\text{SMe})_2$ , followed by catalytic reduction, yields secondary alkyl phosphonates  $\text{PhCHMeP}(\text{O})(\text{OMe})_2$  in an unusual example of a standard use of keten dithioacetals.<sup>472</sup>

The rotational barrier about the double bond in  $(\text{MeS})_2\text{C}=\text{CRCN}$  ( $\text{R} = \text{NO}_2$ ) is greater than that in the analogue ( $\text{R} = \text{H}$ ).<sup>473</sup>

### 9 Trithio-orthoesters [1,1-Bis(alkylthio)alkyl Sulphides]

Limited but important uses of these compounds as equivalents of the formyl anion include interesting desulphurization techniques. 1,4-Additions to  $\alpha\beta$ -unsaturated carbonyl compounds<sup>474,475</sup> were followed by reduction with  $\text{CrCl}_2$  [ $(\text{PhS})_3\text{CR} \rightarrow (\text{PhS})_2\text{CHR}$ ] and subsequent  $\text{Ag}^+$ -catalysed dethioacetalization with trichloroiso-cyanuric acid, yielding  $\gamma$ -keto-aldehydes.<sup>474</sup>

Three sulphenyl substituents stabilize a carbon radical to a sufficient extent that 1,1,1,2,2,2-hexakis(trifluoromethylthio)ethane undergoes reversible homolysis in benzene solution.<sup>476</sup>

<sup>467</sup> J.-C. Clinet and S. Julia, *J. Chem. Res. (S)*, 1978, 12.

<sup>468</sup> T. Nakai and K. Mikami, *Chem. Lett.*, 1978, 1243.

<sup>469</sup> A. Kumar, H. Ila, and H. Junjappa, *J. Chem. Res. (S)*, 1979, 268; J. P. Marino and J. L. Kostusyk, *Tetrahedron Lett.*, 1979, 2489, 2493.

<sup>470</sup> T. Cohen, R. B. Weisenfeld, and R. E. Gapinski, *J. Org. Chem.*, 1979, **44**, 4744.

<sup>471</sup> F. E. Ziegler and C. C. Tam, *J. Org. Chem.*, 1979, **44**, 3428.

<sup>472</sup> M. Yamashita, T. Miyano, T. Watabe, H. Inokawa, H. Yoshida, T. Ogata, and S. Inokawa, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 466.

<sup>473</sup> C. Dreier, L. Herricksen, S. Karlsson, and J. Sandstrom, *Acta Chem. Scand., Ser. B*, 1978, **32**, 281.

<sup>474</sup> T. Cohen and S. M. Nolan, *Tetrahedron Lett.*, 1978, 3533.

<sup>475</sup> R. A. J. Smith and A. R. Lal, *Aust. J. Chem.*, 1979, **32**, 353.

<sup>476</sup> A. Haas, K. Schlosser, and S. Steenkan, *J. Am. Chem. Soc.*, 1979, **101**, 6282.

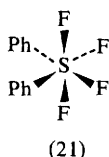
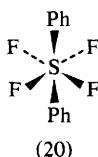
### 10 Sulphuranes and Hypervalent Sulphur, Selenium, and Tellurium Compounds

The particular interest under this heading lies in current studies of sulphuranes, both as synthetic objectives and as reaction intermediates. While the numerous papers dealing with compounds that are multisubstituted at Se and Te atoms are summarized only briefly in this section, the growing interest in Se and Te analogues of reactions of organosulphur compounds will depend more and more on this work.

Extensions of recently established preparations of sulphuranes include the stable thiosulphurane  $\text{CF}_3\text{S}(\text{SCF}_3)\text{OC}(\text{CF}_3)_2$ , formed by oxidative addition of perfluoro-*t*-butyl hypochlorite to bis(trifluoromethyl) disulphide, and its  $\text{C}_6\text{F}_5$  analogues.<sup>477</sup> A member of a further new family,  $(\text{CF}_3)_2\text{S}(\text{OCF}_3)_2$ , was formed by photolysis of  $\text{CF}_3\text{OCl}$  with bis(trifluoromethyl) sulphide, and the corresponding sulphurane oxide was similarly obtained from the bis(trifluoromethyl) sulphoxide.<sup>478</sup> Hydrolysis of these products gives bis(trifluoromethyl) sulphoxide and sulphone, respectively. The sulphurane oxide gives a new type of stable sulphurane oxide,  $(\text{CF}_3)_2\text{S}(\text{O})\text{N}=\text{C}(\text{CF}_3)_2$ , with  $\text{LiN}=\text{C}(\text{CF}_3)_2$ . (+)-Bis-(*o*-hydroxymethylphenyl) sulphoxide gives a chiral spiro-sulphurane with  $\text{MeCOCl}$  at  $-78^\circ\text{C}$ , which gives a racemic sulphurane oxide with ozone;<sup>479</sup> these are applications of methods introduced earlier by Martin's group (see Vol. 4, p. 30), but the stereochemical implications may need to be accepted with caution until studies of the racemization of chiral sulphuranes have been undertaken.

An anomalous reaction  $[\text{Me}_2\ddot{\text{S}}\text{CR}(\text{CN})\text{CO}_2\text{Me} \rightarrow \text{MeO}_2\text{CCR}(\text{CN})\text{CR}(\text{CN})\text{CO}_2\text{Me}]$ , which has been observed during an intended nucleophilic substitution, has been ascribed to homolysis of the sulphurane formed by addition of the nucleophile at sulphur.<sup>480</sup>

Direct fluorination by  $\text{F}_2$ ,<sup>481</sup> or by  $\text{XeF}_2$ ,<sup>482</sup> of sulphides, selenides, and tellurides gives the difluoro-chalcogen(IV) compounds,<sup>481</sup> further fluorination giving 'cis' (21) and 'trans' (20)  $\text{Ph}_2\text{SF}_4$  in the case of the sulphide.<sup>483</sup> The additional bibliography is concerned with preparations and reactions of halogeno-chalcogens.



**Additional Bibliography:** G. Kleeman and K. Seppelt, *Angew. Chem.*, 1978, **90**, 547 and *Chem. Ber.*, 1979, **112**, 1140 [ $\text{MeSF}_3$ ; from  $\text{SClF}_3 + \text{CH}_2\text{C}=\text{O} \rightarrow \text{F}_3\text{SCH}_2\text{COCl}$  and conventional elaboration via  $\text{F}_3\text{SCH}_2\text{Br}$ , from which methylenesulphur tetrafluoride ( $\text{H}_2\text{C}=\text{SF}_4$ ), which shows some of the reactions expected of a carbene, can be prepared, using  $\text{Bu}^n\text{Li}$  at  $-110^\circ\text{C}$ ]; R. A. DeMarco and W. B. Fox, *J. Fluorine Chem.*, 1978, **12**, 137 [addition of HF (from KF and formamide) to  $\text{F}_3\text{SCH}=\text{CH}_2$ ]; A. H. Cowley, D. J. Pagel, and M. L. Walker, *J. Am. Chem. Soc.*, 1978, **100**, 7065

<sup>477</sup> Q. C. Mir, D. P. Babb, and J. M. Shreeve, *J. Am. Chem. Soc.*, 1979, **101**, 3961.

<sup>478</sup> T. Kitazume and J. M. Shreeve, *Inorg. Chem.*, 1978, **17**, 2173.

<sup>479</sup> P. Huszthy, I. Kapovits, A. Kucsman, and L. Radics, *Tetrahedron Lett.*, 1978, 1853.

<sup>480</sup> G. Morel, E. Marchand, and A. Foucaud, *Tetrahedron Lett.*, 1978, 3719.

<sup>481</sup> I. Ruppert, *Chem. Ber.*, 1979, **112**, 3023.

<sup>482</sup> Yu. L. Yagupolskii and T. I. Savina, *Zh. Org. Khim.*, 1979, **15**, 438.

<sup>483</sup> I. Ruppert, *J. Fluorine Chem.*, 1979, **14**, 81.

[(Me<sub>2</sub>N)<sub>x</sub>SF<sub>3-x</sub> from (Me<sub>2</sub>N)<sub>x</sub>SF<sub>4-x</sub> with BF<sub>3</sub>, PF<sub>5</sub>, or AsF<sub>5</sub> in SO<sub>2</sub>]; D. G. Garratt, M. Ujjainwalla, and G. H. Schmid, *J. Org. Chem.*, 1980, **45**, 1206 [stepwise *anti*-addition of alkene to SeCl<sub>4</sub> to give (2*R*,3*R*,5*S*)-(MeCHClCHMe)<sub>2</sub>SeCl<sub>2</sub>]; D. G. Garratt and G. H. Schmid, *Chem. Scr.*, 1977, **11**, 170 [reactions of MeSeCl<sub>3</sub> with alkynes are neither stereospecific nor regioselective]; E. Lehmann, *J. Chem. Res. (S)*, 1978, 42 [CF<sub>3</sub>SeSeCF<sub>3</sub> + BrF<sub>3</sub> → CF<sub>3</sub>SeF<sub>3</sub>]; N. Ya. Derkach, N. P. Tishchenko, and V. G. Voloshchuk, *Zh. Org. Khim.*, 1978, **14**, 958 [R<sup>1</sup>SeR<sup>2</sup> + Ph<sub>2</sub>SeCl<sub>2</sub> + Bu<sup>t</sup>OCl → R<sup>1</sup>R<sup>2</sup>Se(OBu<sup>t</sup>)Cl]; E. S. Mamelov, R. S. Salakhova, and T. M. Gadzhily, *Azerb. Khim. Zh.*, 1979, 107 [R<sup>1</sup>SeCl<sub>2</sub> + R<sup>2</sup>OH → R<sup>1</sup>Se(OR<sup>2</sup>)<sub>2</sub>]; I. D. Sadekov, A. A. Maksimenko, and B. B. Rivkin, *Zh. Org. Khim.*, 1978, **14**, 874 [silyl enol ethers + RTeCl<sub>3</sub> or TeCl<sub>4</sub> → RCOCH<sub>2</sub>TeCl<sub>2</sub>R or (RCOCH<sub>2</sub>)<sub>2</sub>TeCl<sub>2</sub>]; S. Uemura, H. Miyoshi, and M. Okano, *Chem. Lett.*, 1979, 1357 [PhC≡CR + TeCl<sub>4</sub> → (*Z*)-PhCCl=CRTeCl<sub>3</sub>]; J. Bergmann and L. Engman, *J. Organomet. Chem.*, 1979, **181**, 335 [alkene + TeCl<sub>4</sub> → β-chloroalkyltellurium(IV) chloride, while alkene + TeCl<sub>4</sub> + EtOH → β-ethoxyalkyl analogue]; J. Bergmann and L. Engman, *J. Organomet. Chem.*, 1979, **175**, 233 [R<sub>n</sub>TeCl<sub>4-n</sub> + Ni(CO)<sub>4</sub> in DMF → RCO<sub>2</sub>H]; V. Kumar, P. H. Bird, and B. C. Pant, *Synth. React. Inorg. Met.-Org. Chem.*, 1979, **9**, 203 [R<sup>1</sup>Pb or R<sup>1</sup>Pb<sub>2</sub> + R<sup>2</sup>TeCl<sub>3</sub> → R<sup>1</sup>R<sup>2</sup>TeCl<sub>2</sub>]; I. D. Sadekov, A. I. Usachev, and V. I. Minkin, *Zh. Obshch. Khim.*, 1978, **48**, 475 [telluronyl ylide + halogen → Ar<sub>2</sub>TeHal<sub>2</sub>]; T. N. Srivastava, R. C. Srivastava, and M. Singh, *Indian J. Chem., Sect. A*, 1979, **18**, 527 [R<sup>1</sup>TeCl<sub>3</sub> + R<sup>2</sup>M<sup>+</sup>X<sup>-</sup> → (R<sup>2</sup>M<sup>+</sup>)[R<sup>1</sup>TeCl<sub>2</sub>X<sub>2</sub>]<sup>2-</sup> (M = N, P, As, or Sb; X = Cl or Br)]; T. N. Srivastava, R. C. Srivastava, and M. Singh, *J. Organomet. Chem.*, 1978, **160**, 449 [R<sub>2</sub>Te + ICl or (SCN)<sub>2</sub> → R<sub>2</sub>TeICl or R<sub>2</sub>Te(SCN)<sub>2</sub>]; T. N. Srivastava, R. C. Srivastava, and M. Singh, *Inorg. Chim. Acta*, 1979, **33**, 299 [R<sup>1</sup>R<sup>2</sup>Te + R<sup>3</sup>CON(Hal)COR<sup>3</sup> → R<sup>1</sup>R<sup>2</sup>Te(Hal)N(COR<sup>3</sup>)<sub>2</sub>]; V. I. Naddaka, V. P. Garkin, I. D. Sadekov, V. P. Krasnov, and V. I. Minkin, *Zh. Org. Khim.*, 1979, **15**, 896 [R<sup>1</sup>TeCl(OBu<sup>t</sup>) → R<sup>1</sup>Te=NSO<sub>2</sub>R<sup>2</sup>]; F. H. Musa and W. R. McWhinnie, *J. Organomet. Chem.*, 1978, **159**, 37 [R<sub>2</sub>Te(NCS)<sub>2</sub> and Ph<sub>2</sub>MeTe(NCS)<sub>2</sub>, the latter showing telluronyl salt character in DMSO but a covalent structure in C<sup>6</sup>HCl<sub>3</sub>]; I. D. Tseimakh, A. Ya. Bushkov, L. E. Nivorozhkin, and I. D. Sadekov, *Zh. Obshch. Khim.*, 1978, **48**, 1658 [Ar<sub>2</sub>Te + Ar<sup>2</sup>TeCl<sub>2</sub> = Ar<sup>2</sup>TeCl<sub>2</sub> + Ar<sup>2</sup>Te, studied as a function of structure and solvent].

## 11 Sulphoxides, Selenoxides, and Telluroxides

**Preparation.**—Methods involving the oxidation of sulphides and selenides are either well established, and a subsidiary part of recent papers, or are the main feature in papers describing novel modifications of standard methods. Points of interest arising from references on this topic, collected at the end of this section, include the use of standard oxidants [NaIO<sub>4</sub> and Tl(NO<sub>3</sub>)<sub>3</sub>], but adsorbed on silica gel or alumina, and the asymmetric induction, at high levels, that accompanies microbiological or protein-mediated oxidation. 2-Arenesulphonyl-3-aryl-oxaziridines have emerged as suitable reagents for the oxidation of sulphides to sulphoxides,<sup>484</sup> the (–)-camphor-10-sulphonyl analogue showing a low level of enantioselectivity in this process.<sup>485</sup>

A study has been made<sup>486</sup> of the conversion of selenides and tellurides into their mono-oxides, using *N*-chlorosuccinimide or Bu<sup>t</sup>OCl followed by alkaline hydrolysis; some fragmentation of aliphatic selenoxides occurs at this stage.

Other routes to sulphoxides include the first preparation from sulphones (though the direct partial reduction has yet to be discovered). Conversion of a sulphone into the corresponding aryloxy-salt, R<sup>1</sup>S<sup>+</sup>(O)(OR<sup>2</sup>)R<sup>3</sup>X<sup>-</sup>, can be performed surprisingly easily,<sup>487,488</sup> using an arenediazonium tetrafluoroborate. This salt is then open to reduction (with RSH<sup>487</sup> or NaBH<sub>4</sub> with Al<sub>2</sub>O<sub>3</sub><sup>488</sup>), reduction with α-substitution

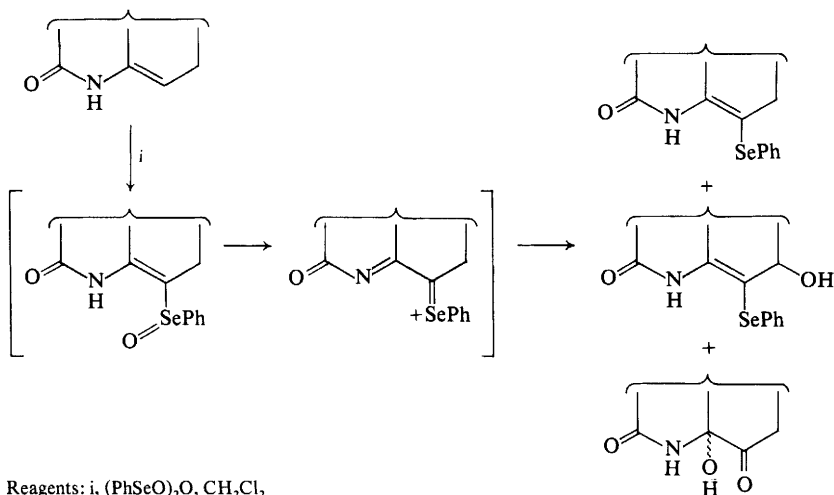
<sup>484</sup> F. A. Davis, R. Jenkins, and S. G. Yocklovich, *Tetrahedron Lett.*, 1978, 5171.

<sup>485</sup> F. A. Davis, R. Jenkins, S. Q. A. Rizvi, and T. W. Panunto, *J. Chem. Soc., Chem. Commun.*, 1979, 600.

<sup>486</sup> M. R. Detty, *J. Org. Chem.*, 1980, **45**, 274.

<sup>487</sup> M. Shimagaki, H. Tsuchiya, Y. Ban, and T. Oishi, *Tetrahedron Lett.*, 1978, 3435.

<sup>488</sup> I. W. J. Still and S. Szilagy, *Synth. Commun.*, 1979, **9**, 923.



Scheme 18

[PhS<sup>+</sup>(O)(OPh)Me + RLi and LiX → PhSOCH<sub>2</sub>X + PhSO<sub>2</sub>Me],<sup>487</sup> or reduction with homologation (with R<sub>2</sub>CuLi and LiX).<sup>487</sup> Standard sulphonylation procedures reported include electrophilic substitution of phenols with ArSOCl and AlCl<sub>3</sub><sup>489</sup> and the preparation of optically active sulfoxides from resolved (–)-menthyl sulphinates with (*E*)-1-alkenylmagnesium bromides<sup>490</sup> or arylthiomethyl-<sup>491</sup> or arylsulphonylmethyl-lithium compounds.<sup>492</sup> A practical route to 1-alkenyl sulphoxides uses non-activated alkynes and sulphenic acids, generated *in situ* from the thermolysis of 2-cyanoethyl phenyl sulphoxides.<sup>493</sup>

The wider use of benzeneseleninic anhydride as a mild oxidant can be expected to generate reports of side-reactions, and the formation of a selenoxide during oxidation of 4-azapregnen-5-ene-3,20-dione (Scheme 18), followed by Pummerer-type reactions, accounts for the observed products.<sup>494</sup>

**Additional Bibliography:** T. Nishio and Y. Omote, *Synthesis*, 1980, 392 [NaIO<sub>4</sub> on silica gel for R<sup>1</sup>COCH<sub>2</sub>CR<sup>2</sup>R<sup>3</sup>SR<sup>4</sup> → R<sup>1</sup>COCH=CR<sup>2</sup>R<sup>3</sup> via the sulphoxide]; K.-T. Liu and Y.-C. Chien, *J. Org. Chem.*, 1978, **43**, 2717 [NaIO<sub>4</sub> on Al<sub>2</sub>O<sub>3</sub>]; K.-T. Liu and Y.-C. Tong, *J. Chem. Res.(S)*, 1979, 276 [NaIO<sub>4</sub> on Al<sub>2</sub>O<sub>3</sub>, with (–)-2-(*S*)-methylbutanol for conversion of sulphide → sulphoxide, but only with 0.6–8.9% enantiomeric excess]; K.-T. Liu, *J. Chin. Chem. Soc. (Taipei)*, 1977, **24**, 217 [Ti(NO<sub>3</sub>)<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> for sulphides → sulphoxides, but with 15% sulphone in the case of Bu<sup>1</sup>S]; E. Abushanab, D. Reed, F. Suzuki, and C. J. Sih, *Tetrahedron Lett.*, 1978, 3415 [*p*-tolyl methyl sulphide gives (+)-(*R*)-sulphoxide with *Mortierella isabellina*, but gives (–)-(*S*)-sulphoxide with *Helminthosporium* sp. NRRL 4671]; T. Sugimoto, T. Kokubo, J. Miyazaki, S. Tanimoto, and M. Okano, *J. Chem. Soc., Chem. Commun.*, 1979, 1052 [diaryl sulphides → sulphoxides and sulphones with H<sub>2</sub>O<sub>2</sub> and bovine serum albumin, the high (>90%) optical purity of the sulphoxides being a cumulative result of stereoselective oxidation of the sulphide and enantioselectivity in the further oxidation to the sulphone]; F. Alcudia, E. Brunet, and J. L. Garcia Ruano, *An. Quim.*, 1979, **75**, 162

<sup>489</sup> D. W. Chasar and T. M. Pratt, *Phosphorus Sulfur*, 1978, **5**, 35.

<sup>490</sup> G. H. Posner and P.-W. Tang, *J. Org. Chem.*, 1978, **43**, 4131.

<sup>491</sup> L. Colombo, C. Gennari, and E. Narisano, *Tetrahedron Lett.*, 1978, 3861.

<sup>492</sup> R. Annunziata, M. Cinquini, and F. Cozzi, *Synthesis*, 1979, 535.

<sup>493</sup> D. N. Jones, P. D. Cottam, and J. Davies, *Tetrahedron Lett.*, 1979, 4977.

<sup>494</sup> T. G. Back and N. Ibrahim, *Tetrahedron Lett.*, 1979, 4931.

[formation of diastereoisomers from (+)-MeSCHPhCH<sub>2</sub>OR → sulphoxide by using NaIO<sub>4</sub>, *m*-chloroperoxybenzoic acid, or H<sub>2</sub>O<sub>2</sub>, but with a higher (80%) enantioselectivity with *m*-chloroperoxybenzoic acid]; C. Srinivasan, P. Kuthalingam, and N. Arumuyan, *Can. J. Chem.*, 1978, **56**, 3043 and *Indian J. Chem., Sect. A*, 1978, **16**, 478 [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]; J. Drabowicz and M. Mikolajczyk, *Synthesis*, 1978, 758 [H<sub>2</sub>O<sub>2</sub> and SeO<sub>2</sub> in MeOH]; J. Drabowicz, W. Midura, and M. Mikolajczyk, *Synthesis*, 1979, 39 [Br<sub>2</sub> and KHC<sub>2</sub>O<sub>3</sub>, suitable for the synthesis of <sup>18</sup>O-enriched sulphoxides in high yields]; N. Kunieda, H. Mochizuki, and M. Kinoshita, *Mem. Fac. Eng., Osaka City Univ.*, 1978, **19**, 207 (*Chem. Abstr.*, 1980, **92**, 5664) [Br<sub>2</sub> and Tröger's base is a system that is potentially suitable for asymmetric synthesis]; L. G. Faehl and J. L. Kice, *J. Org. Chem.*, 1979, **44**, 2357 [*p*-chlorobenzeneselenonic acid (ArSeO<sub>3</sub>H), which, on oxidation of a sulphide to a sulphoxide, is itself reduced to ArSeO<sub>2</sub>H; this is an even more effective oxidant for synthesis of sulphoxides in the presence of acid]; V. A. Likholobov, A. V. Mashkina, M. G. Volkhonskii, and V. N. Yakovleva, *Kinet. Katal.*, 1979, **20**, 1152 [O<sub>2</sub> and inorganic nitrate]; E. Fujita, M. Ochiai, and K. Watanabe, *J. Indian Chem. Soc.*, 1978, **55**, 1226 [Ti(NO<sub>3</sub>)<sub>3</sub>, for selenides → selenoxides]; L. Jirackova, T. Jelinkova, J. Rotschova, and J. Pospisil, *Chem. Ind. (London)*, 1979, 384 [Bu<sup>+</sup>OOH]; H. C. Brown and A. K. Mandal, *J. Org. Chem.*, 1980, **45**, 916 [whereas the use of H<sub>2</sub>O<sub>2</sub> to terminate a hydroboration that is conducted in the presence of Me<sub>2</sub>S and excess NaOH does not oxidize the sulphide, the use of NaOCl is unsatisfactory because it oxidizes the sulphide and not the organoborane]; G. P. Dareshwar and B. D. Hosangadi, *Indian J. Chem., Sect. B*, 1978, **16**, 143 [intramolecular oxidation of *o*-NH<sub>2</sub>COC<sub>6</sub>H<sub>4</sub>SPh → *o*-NH<sub>2</sub>COC<sub>6</sub>H<sub>4</sub>SOPh]; H. S. Laver and J. R. MacCallum, *Photochem. Photobiol.*, 1978, **28**, 91 [photosensitized oxidation]; W. Ando, S. Komoto, and K. Nishizawa, *J. Chem. Soc., Chem. Commun.*, 1978, 894 [methylene-blue-sensitized photo-oxidation of Ph<sub>2</sub>S + Me<sub>2</sub>S<sup>-</sup>C(CO<sub>2</sub>Me)<sub>2</sub> → Ph<sub>2</sub>SO via the oxenoid intermediate rather than a 1,2-dioxetan]; S. Iriuchijima and G. Tsuchihashi, *Yuki Gosei Kagaku Kyokaiishi*, 1978, **36**, 1050 (*Chem. Abstr.*, 1979, **91**, 20 039) [photoaddition with concurrent photo-oxygenation; PhSH + H<sub>2</sub>C=CMeCN → PhSOCH<sub>2</sub>CMe(CN)OH → PhSOCH<sub>2</sub>COMe]; T. Tezuka, H. Miyazaki, and H. Suzuki, *Tetrahedron Lett.*, 1978, 1959 [Sinnreich mechanism for photo-oxygenation of sulphides via persulphoxides, RSCH(OOH)R, (see Vol. 5, pp. 22, 34) was rejected in favour of direct attack of singlet oxygen on sulphur].

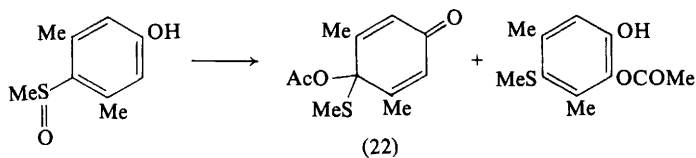
### Deoxygenation of Sulphoxides, Selenoxides, and Telluroxides.—References and brief details from recent papers on this topic include:

G. A. Olah, Y. D. Vankar, and M. Arvanaghi, *Synthesis* 1979, 984 [pyridine or R<sub>3</sub>N with SO<sub>3</sub>, I<sub>2</sub>, and NaI]; G. A. Olah, B. G. B. Gupta, and S. C. Narang, *J. Org. Chem.*, 1978, **43**, 4503 [(Me<sub>2</sub>N)<sub>3</sub>P with I<sub>2</sub>]; G. A. Olah, R. Malhotra, and S. C. Narang, *Synthesis*, 1979, 58 [(COCl)<sub>2</sub> with NaI, or NaI with SOCl<sub>2</sub>, POCl<sub>3</sub>, or PCl<sub>5</sub>]; G. A. Olah, S. C. Narang, B. G. B. Gupta, and R. Malhotra, *Synthesis*, 1979, 61 [Me<sub>2</sub>SiCl<sub>2</sub> with NaX (X = I, CN, SMe, or SCN)]; T. Numata, H. Togo, and S. Oae, *Chem. Lett.*, 1979, 329 [PhSiMe<sub>3</sub>]; M. R. Detty, *J. Org. Chem.*, 1979, **44**, 4528 [PhSeSiMe<sub>3</sub> for the deoxygenation of sulphoxides, selenoxides, and telluroxides]; H. S. D. Soysa and W. P. Weber, *Tetrahedron Lett.*, 1978, 235 [disilathianes, e.g. (Me<sub>2</sub>Si)<sub>2</sub>S]; M. Sekine, H. Yamagata, and T. Hata, *Tetrahedron Lett.*, 1979, 375 [P(O)(SiMe<sub>3</sub>)<sub>3</sub>]; I. W. J. Still, J. N. Reed, and K. Turnbull, *Tetrahedron Lett.*, 1979, 1481 [PSBr<sub>3</sub>]; I. W. J. Still, S. K. Hasan, and K. Turnbull, *Can. J. Chem.*, 1978, **56**, 1423 [P<sub>4</sub>S<sub>10</sub> for deoxygenation of sulphoxides and selenoxides]; J. N. Denis and A. Krief, *Tetrahedron Lett.*, 1979, 3995 [P<sub>2</sub>I<sub>4</sub>]; D. L. J. Clive and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 1979, 168 [B(SePh)<sub>3</sub> or B(SeMe)<sub>3</sub>]; J. Drabowicz and M. Mikolajczyk, *Synthesis*, 1978, 542 [H<sub>2</sub>NC(=NH)SO<sub>2</sub>H with I<sub>2</sub> as catalyst]; V. Ruffato and U. Miotti, *Gazz. Chim. Ital.*, 1978, **108**, 91 [diallyl sulphide and HClO<sub>4</sub>]; I. D. Sadekov and A. A. Maksimenko, *Zh. Org. Khim.*, 1978, **14**, 2621 [tellurides from telluroxides in HCONH<sub>2</sub> at 120–150 °C].

**Reactions of Saturated Sulphoxides and Selenoxides.**—The main reactions of saturated sulphoxides and selenoxides are associated with the nucleophilic properties of the sulphinyl and seleninyl groups, and their activating effect on the adjacent saturated carbon atoms. The Pummerer rearrangement (as well as rearrangements of unsaturated sulphoxides discussed in a later section) and alkene-forming eliminations are instances of the former property; the main consequence of the latter property, the formation of sulphinyl-stabilized carbanions, is covered in Chapter 2.

An extraordinary example of a Pummerer rearrangement<sup>495</sup> is that in which

<sup>495</sup> R. R. King, *J. Org. Chem.*, 1978, **43**, 3784.



4-methylsulphonyl-3,5-xyleneol gives the 4-methylthio-2-acetoxy analogue and (22) on treatment with  $\text{Ac}_2\text{O}$ , and the 4-chloro- and 4-methylthio-2-chloro-analogues on treatment with  $\text{AcCl}$ . This has been accounted for on the basis of acetoxy-sulphonium ion intermediates, as in more typical examples of the reaction. Continuing studies of asymmetric induction accompanying the rearrangement have established an unusually high level (70% e.e.) for optically active  $\beta$ -oxoalkyl sulphoxides when DCCI is used with  $\text{Ac}_2\text{O}$ ,<sup>496</sup> but lower levels with phosphonates ( $\text{R}^1\text{O}$ )<sub>2</sub> $\text{P}(\text{O})\text{CH}_2\text{SOR}^2$ .<sup>497</sup> The sulphoxide of *S*-benzylcysteinylglycine undergoes a Pummerer rearrangement with  $\text{Ac}_2\text{O}$ , to give a 1,3-thiazin-4-one.<sup>498</sup>

Racemization of sulphoxides in non-aqueous solvents containing  $\text{HCl}$  involves an *S*-chlorosulphonium ion, since products from cleavage of the C—S bond and  $\alpha$ -chloro-sulphides are formed.<sup>499–501</sup> Chlorination of sulphoxides leads to  $\alpha$ -chloro-sulphides<sup>501,502</sup> in non-aqueous solvents, while a ‘sulphohaloform’ reaction is brought about by chlorinolysis in aqueous media.<sup>503</sup> This reaction, leading to a sulphonyl chloride, also applies to aliphatic sulphides, which undergo *S*-oxidation.<sup>503</sup> A chiral *N*-halogeno-caprolactam oxidizes the (*S*)-enantiomer of ( $\pm$ )-*p*- $\text{MeC}_6\text{H}_4\text{SOCH}_2\text{Ph}$  to the sulphone at a faster rate than the (*R*)-isomer.<sup>504</sup> An  $\alpha$ -chloro-sulphoxide yields a thiolester by a process that has been wrongly described<sup>505</sup> as a modified Pummerer reaction [ $\text{RCHClS}(\text{O})\text{Ph} + \text{LiNPr}_2 + \text{Me}_3\text{SiCl} \rightarrow \text{RCOSPh}$ ]. The conditions are quite different. Mention has been made in discussing the preceding example of ‘halogeno-Pummerer reactions’ of C—S bond cleavage; this is a process which occurs in aqueous acid media<sup>506</sup> or in TFAA followed by hydrolysis,<sup>507</sup> and which converts benzyl sulphoxides into aromatic aldehydes.

Acid-catalysed exchange between sulphoxides and sulphides occurs *via* sulphonium intermediates,<sup>508</sup> whereas less certainty can be asserted for the mechanistic details of the photo-metathesis  $\text{PhSMe} + \text{PhSe}(\text{=O})\text{Ph} \rightarrow \text{PhS}(\text{=O})\text{Me} + \text{Ph}_2\text{Se}$ .<sup>509</sup>

<sup>496</sup> T. Numata, O. Itoh, and S. Oae, *Tetrahedron Lett.*, 1979, 1869.

<sup>497</sup> M. Mikolajczyk, A. Zatorski, S. Grzejszczak, B. Costisella, and W. Midura, *J. Org. Chem.*, 1978, **43**, 2518.

<sup>498</sup> S. Wolfe, P. M. Kazmaier, and H. Auksi, *Can. J. Chem.*, 1979, **57**, 2412.

<sup>499</sup> E. Ciuffarin and S. Gambarotta, *J. Chem. Res. (S)*, 1978, 274; M. Cioni, E. Ciuffarin, S. Gambarotta, M. Isola, and L. Senatore, *ibid.*, p. 270.

<sup>500</sup> N. Kunieda, T. Numata, and S. Oae, *Phosphorus Sulfur*, 1977, **3**, 1.

<sup>501</sup> J. Klein, *Chem. Lett.*, 1979, 359.

<sup>502</sup> T. Masuda, N. Furukawa, and S. Oae, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2659.

<sup>503</sup> D. G. Kay, R. F. Langler, and J. E. Trenholm, *Can. J. Chem.*, 1979, **57**, 2185.

<sup>504</sup> Y. Sato, N. Kunieda, and M. Kinoshita, *Mem. Fac. Eng., Osaka City Univ.*, 1977, **18**, 435 (*Chem. Abstr.*, 1979, **90**, 22 190).

<sup>505</sup> K. M. More and J. Wemple, *J. Org. Chem.*, 1978, **43**, 2713.

<sup>506</sup> G. A. Russell and J. M. Pecoraro, *J. Org. Chem.*, 1979, **44**, 3990.

<sup>507</sup> H. Sugihara, R. Tanikaga, and A. Kaji, *Synthesis*, 1978, 881.

<sup>508</sup> E. Ciuffarin, S. Gambarotta, M. Isola, and L. Senatore, *J. Chem. Res. (S)*, 1978, 272.

<sup>509</sup> T. Tezuka, H. Suzuki, and H. Miyazaki, *Tetrahedron Lett.*, 1978, 4885.



The c.i.d.n.p. associated with the photolysis of aryl alkyl sulphoxides is consistent with C—S bond homolysis ( $\text{ArSOMe} \rightarrow \text{ArSO}\cdot + \text{Me}\cdot$ ).<sup>510</sup> An optically active *N*-chloro-sulphomimide reacts with a sulphoxide to give the corresponding  $\alpha$ -chloroalkyl sulphoxide with a small degree of enantiomeric excess involving S as the chiral centre.<sup>511</sup> Labelling studies with <sup>18</sup>O would seem to be necessary to establish the oxygen-exchange process which might be involved in this reaction. Exchange of an alkyl group between a sulphoxide and a Grignard reagent has been reported,<sup>512</sup> but this is not the only reaction occurring in this system, since sulphides (including products corresponding to the  $\alpha$ -alkylation of the initial sulphoxide) are the reaction products.<sup>512</sup> Fluorination of sulphoxides gives the hexavalent sulphur compounds  $\text{R}_2\text{S}(\text{O})\text{F}_2$ .<sup>513</sup>

Papers describing reactions of simple sulphoxides and uses of dimethyl sulphoxide as a reagent in organic synthesis are collected together here. The thermal decomposition of dialkyl sulphoxides<sup>514</sup> involves the formation of an alkene, a breakdown reaction not available to dimethyl sulphoxide, although other pathways account for side-products in reactions of this compound. Other reactions of DMSO include those with Se at 110 °C in aqueous KOH, which give  $\text{Me}_2\text{S}$  and  $\text{MeSSMe}$ , but only traces of  $\text{MeSeSeMe}$ ,  $\text{MeSeSMe}$ , and  $\text{MeSCH}_2\text{SeMe}$ ;<sup>515</sup> ion-molecule reactions in the gas phase;<sup>516</sup> oxidation by aqueous Chloramine-T;<sup>517</sup> and  $\gamma$ -radiolysis, which gives methane, ethane, propane, HCHO,  $\text{CO}_2$ , and methyl sulphides, disulphides, thiol sulphonates and  $\text{Me}_3\text{S}^+ \text{MeSO}_3^-$ .<sup>518</sup> DMSO has also been used as a reagent for the photo-oxidation of  $\text{Bu}^n\text{S}$ ;<sup>519</sup> as a reagent with  $\text{Bu}^t\text{Br}$  for the conversion of carboxylic acids into methylthiomethyl esters, the effective species being the Pummerer rearrangement intermediate;<sup>520</sup> and to effect the related reaction  $\text{Cl}_3\text{CCN} \rightarrow \text{Cl}_3\text{CCONHCH}_2\text{SMe}$ .<sup>521</sup> Its use as an oxidizing agent encompasses the oxidation of chloro-thiolformates ( $\text{PhSCOCI} \rightarrow \text{CO}_2 + \text{Me}_2\text{S} + \text{MeSCH}_2\text{Cl}$ );<sup>522</sup> the oxidation of  $\alpha$ -bromo-ketones ( $\text{RCOCH}_2\text{Br} \rightarrow \text{RCOCH}_2\text{SMe}_2$ ,  $\text{Br}^- \rightarrow \text{RCOCHO} + \text{RCOCOSMe} + \text{RCOCO}_2\text{H} + \text{RCO}_2\text{H}$ );<sup>523</sup> the oxidation of alcohols in combination with  $(\text{COCl})_2$ ,<sup>524, 525</sup> or  $\text{SOCl}_2$ ,<sup>524</sup> or TFAA;<sup>526</sup> and a

<sup>510</sup> K. A. Muszkat, K. Praefcke, I. Khait, and R. Lüdersdorf, *J. Chem. Soc., Chem. Commun.*, 1979, 898.

<sup>511</sup> H. Morita, H. Itoh, N. Furukawa, and S. Oae, *Chem. Lett.*, 1978, 817.

<sup>512</sup> N. A. Nesmeyanov, V. A. Kalyavin, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2633.

<sup>513</sup> I. Ruppert, *Angew. Chem.*, 1979, **91**, 941.

<sup>514</sup> Yu. E. Nikitin, E. M. Baranovskaya, and G. G. Bikbaeva, *Zh. Prikl. Khim.*, (Leningrad), 1979, **52**, 430 (*Chem. Abstr.*, 1979, **91**, 38 636).

<sup>515</sup> G. K. Musovin, B. A. Trofimov, S. V. Amosova, V. Yu. Vitkovskii, and G. A. Kalabin, *Zh. Obshch. Khim.*, 1979, **49**, 831.

<sup>516</sup> J. E. Fulford, J. W. Dupuis, and R. E. March, *Can. J. Chem.*, 1978, **56**, 2324.

<sup>517</sup> D. S. Mahadevappa, M. B. Jadhav, and H. M. K. Naidu, *Int. J. Chem. Kinet.*, 1979, **11**, 261.

<sup>518</sup> M. C. Gutierrez, R. Barrera, H. Benz, and R. Parellada, *An. Quim.*, 1977, **73**, 520.

<sup>519</sup> M. A. Fox, P. K. Miller, and M. D. Reiner, *J. Org. Chem.*, 1979, **44**, 1103.

<sup>520</sup> A. Dossena, R. Marchelli, and G. Casnati, *J. Chem. Soc., Chem. Commun.*, 1979, 370.

<sup>521</sup> I. V. Bodrikov, A. A. Michurin, and N. N. Bochkareva, *Zh. Org. Khim.*, 1979, **15**, 436.

<sup>522</sup> A. Queen, A. E. Lemire, A. F. Janzen, and M. N. Paddon-Row, *Can. J. Chem.*, 1978, **56**, 2884.

<sup>523</sup> N. Saldabols and A. Cimanis, *Zh. Org. Khim.*, 1978, **14**, 1910.

<sup>524</sup> K. Omura and D. Swern, *Tetrahedron*, 1978, **34**, 1651.

<sup>525</sup> A. J. Mancuso, S.-L. Huang, and D. Swern, *J. Org. Chem.*, 1978, **43**, 2480; A. J. Mancuso, D. S. Brownfain, and D. Swern, *ibid.*, 1979, **44**, 4148.

<sup>526</sup> S. L. Huang, K. Omura, and D. Swern, *Synthesis*, 1978, 297.

curious observation that, since some labelled  $\text{Me}_2\text{S}$  is formed in the reduction of  $\text{PhCHO}$  by  $\text{NaBH}_4$  in  $[^{14}\text{C}]\text{DMSO}$ , the aldehyde must act as a relay in the reaction through the formation of an alkoxy-sulphonium salt.<sup>527</sup>

Diphenyl selenoxide has been advocated for the oxidation of catechols to *ortho*-quinones in the synthesis of benzylisoquinoline alkaloids.<sup>528</sup>

Elaboration of other functional groups in aliphatic sulphoxides is illustrated in the preparation of  $\alpha$ -chloro- $\beta$ -hydroxyalkyl sulphoxides by the phase-transfer-catalysed reaction of  $\alpha$ -chloroalkyl sulphoxides with carbonyl compounds, and their further conversion into  $\alpha\beta$ -epoxyalkyl sulphoxides.<sup>529</sup> Optically active  $\beta$ -oxoalkyl sulphoxides are reduced by hydride reagents to the  $\beta$ -hydroxyalkyl analogues with 60–70% optical yields.<sup>530</sup> Phenylsulphinylcarbene ( $\text{PhSOCH}_2$ ) is a relatively stable species, thus requiring the sulphinyl group to act as a good electron donor in spite of the conventional view that it is an electron-withdrawing group.<sup>531</sup> This carbene undergoes the expected addition to alkenes, and structure–rate relationships have been reported.<sup>531</sup> Vinylsulphinylcarbenes, formed from 5-alkylsulphinyl-3,3-dimethyl-3*H*-pyrazoles by photolysis, or from sulphinylcyclopropenes, readily undergo sigmatropic [1,2]-rearrangements to vinylsulphines.<sup>532</sup>

The *syn*-elimination of aliphatic sulphoxides and selenoxides has become a widely used method for the introduction of a double bond,<sup>533–542</sup> recent papers referring to elimination reactions of sulphenic acids have involved the preparation of vinyl chlorides<sup>534</sup> and bromomethyl ketones<sup>535</sup> from halogenomethyl phenyl sulphoxides ( $\text{PhSOCHClLi} + \text{RCH}_2\text{X} \rightarrow \text{PhSOCHClCH}_2\text{R} \rightarrow \text{RCH}=\text{CHCl}$ ); the use of  $\gamma$ -keto-sulphoxides as equivalents of vinyl ketones [ $\text{EtSO}(\text{CH}_2)_2\text{COR}^1 \rightarrow \text{EtSOCHR}^2\text{CH}_2\text{COR}^1 \rightarrow \text{R}^2\text{CH}=\text{CHCOR}^1$ ],<sup>536</sup> and the generation of inden-1-one, which was trapped as the Diels–Alder adduct.<sup>537</sup> Similar uses of selenoxides are the conversion of 4,4-disubstituted cyclohex-2-en-1-ones into cyclohexa-2,5-dienones;<sup>538</sup> the sequence  $\text{PhSeBr} + \text{H}_2\text{C}=\text{CHOEt}$ , then an allyl alcohol,  $\rightarrow \text{PhSeCH}_2\text{CH}(\text{OEt})\text{OCR}^1\text{R}^2\text{CR}^3=\text{CR}^4\text{R}^5 \rightarrow \text{R}^1\text{R}^2\text{C}=\text{CR}^3\text{CR}^4\text{R}^5\text{CH}_2\text{CO}_2\text{Et}$  after elimination of selenoxide and Claisen rearrangement;<sup>539</sup> and the preparation of allylic alcohols and oxirans from  $\beta$ -hydroxy-selenoxides.<sup>540,541</sup> In the case of alkyl aryl selenoxides, the areneseleonic acid formed by the *syn*-elimination adds rather readily to the alkene, leading to a  $\beta$ -hydroxy-selenide;<sup>542</sup> this can be avoided by

<sup>527</sup> D. C. Wigfield and R. T. Pon, *J. Chem. Soc., Chem. Commun.*, 1979, 910.

<sup>528</sup> J. P. Marino and A. Schwartz, *Tetrahedron Lett.*, 1979, 3253.

<sup>529</sup> T. Durst, K.-C. Tin, F. De Reinach-Hirtzbach, J. M. Decesare, and D. M. Ryan, *Can. J. Chem.*, 1979, **57**, 258.

<sup>530</sup> R. Annunziata, M. Cinquini, and F. Cozzi, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1687.

<sup>531</sup> C. G. Venier and M. A. Ward, *Tetrahedron Lett.*, 1978, 3215.

<sup>532</sup> M. Franck-Neumann and J. J. Lohmann, *Tetrahedron Lett.*, 1979, 2397.

<sup>533</sup> T. E. Boothe, J. L. Greene, P. B. Shevlin, M. R. Willcott, R. R. Inness, and A. Cornelis, *J. Am. Chem. Soc.*, 1978, **100**, 3874.

<sup>534</sup> V. Reutrakul and P. Thamnuan, *Tetrahedron Lett.*, 1979, 617.

<sup>535</sup> V. Reutrakul, A. Tiensripojammam, K. Kusamran, and S. Nimgirawath, *Chem. Lett.*, 1979, 209.

<sup>536</sup> Y. Nagao, K. Seno, and E. Fujita, *Tetrahedron Lett.*, 1979, 3167.

<sup>537</sup> H. H. Szmant and R. Nanjundiah, *J. Org. Chem.*, 1978, **43**, 1835.

<sup>538</sup> H. Plieninger and W. Gramlich, *Chem. Ber.*, 1978, **111**, 1944; see also T. Kametani, K. Suzuki, H. Kurobe, and H. Nemoto, *J. Chem. Soc., Chem. Commun.*, 1979, 1128.

<sup>539</sup> R. Pitteloud and M. Petrzilka, *Helv. Chim. Acta*, 1979, **62**, 1319.

<sup>540</sup> T. Hori and K. B. Sharpless, *J. Org. Chem.*, 1978, **43**, 1689.

<sup>541</sup> H. J. Reich, S. K. Shah, and F. Chow, *J. Am. Chem. Soc.*, 1979, **101**, 6648.

<sup>542</sup> H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, and D. F. Wendelborn, *J. Org. Chem.*, 1978, **43**, 1697.

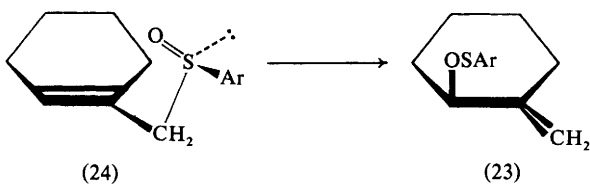
adding an alkylamine to the reaction mixture,<sup>542</sup> or exploited<sup>541</sup> if an overall conversion of the type  $(E)\text{-EtCH}_2\text{CH}=\text{CHPr}^n \rightarrow (E)\text{-EtCH}=\text{CHCH}(\text{OH})\text{Pr}^n$  is needed, simply by oxidizing the  $\beta$ -hydroxy-selenide to the selenoxide and repeating the *syn*-elimination step. Further examples of these alkene-forming methods are discussed in the next section, covering unsaturated sulphoxides.

The planar pericyclic mechanism which is accepted for the sulphoxide-elimination reaction is supported by the temperature-dependence of the relative reaction rates for  $n\text{-C}_7\text{H}_{15}\text{SOPh}$  and its  $\beta\text{-}^2\text{H}$ -analogue.<sup>543</sup>

**Reactions of Unsaturated Sulphoxides and Selenoxides.**—Deferring details of the chemistry of carbanions derived from alkenyl sulphoxides to Chapter 2, the main groupings into which recent work can be separated are preparative studies and rearrangements. The main methods for introducing a sulphinyl group are suitable in one form or another for preparing unsaturated sulphoxides, although special strategies are needed in particular cases, *e.g.* in the preparation of allenyl phenyl sulphides from propargyl alcohols ( $\text{HOCHR}^1\text{R}^2\text{C}\equiv\text{CH} + \text{PhSCl} \rightarrow \text{R}^1\text{R}^2\text{C}=\text{C}=\text{CHSOPh}$ ).<sup>544</sup> This example of a sulphenate-sulphoxide rearrangement is one of several in the recent literature: *e.g.*  $\text{ThpO}(\text{CH}_2)_8\text{CH}(\text{OH})\text{CH}=\text{CHMe} \rightarrow$  sulphenate  $\rightarrow$  sulphoxide, which on elimination yields  $(E)$ -dodeca-9,10-dien-1-ol, which gives the pheromone of the red bollworm moth on acetylation;<sup>545</sup> a similarly organized conversion of a *cis*-allylic alcohol into a *trans*-isomer in a total synthesis of  $(\pm)\text{-PGF}_{2\alpha}$ ;<sup>546</sup> regio- and stereo-specific allylic oxidation in terpene synthesis [ $\text{RCH}_2\text{CH}=\text{CMe}_2 \rightarrow \text{RCH}_2\text{CH}(\text{SPh})\text{CClMe}_2 \rightarrow \text{RCH}_2\text{CH}(\text{SOPh})\text{CMe}=\text{CH}_2 \rightarrow \text{RCH}_2\text{CH}=\text{CMeCH}_2\text{OH}$ ];<sup>547</sup> preparation of  $\beta$ -acetoxy- $\alpha$ -methylene- $\gamma$ -butyrolactones from  $\beta$ -phenylsulphenyl- $\alpha$ -methylene-carboxylic esters;<sup>548</sup> and the synthesis of dienes by regiospecific dehydration of allyl alcohols *via* the selenate-selenoxide-elimination sequence.<sup>549</sup>

Establishment of the absolute configuration of the sulphenate (23) that is formed from one enantiomer of a sulphoxide (24) gives a clear picture of the conformation of the reactant.<sup>550</sup>

The *syn*-elimination of sulphenic and selenenic acids from unsaturated sulphoxides and selenoxides introduces a further site of unsaturation, examples being the addition of allyl alcohols to allenic sulphoxides to give  $\beta$ -(allyloxy)vinyl sulphoxides



<sup>543</sup> H. Kwart, T. J. George, R. Louw, and W. Ultee, *J. Am. Chem. Soc.*, 1978, **100**, 3927.

<sup>544</sup> R. C. Cookson and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 1978, 822.

<sup>545</sup> J. H. Babler and B. J. Invergo, *J. Org. Chem.*, 1979, **44**, 3723.

<sup>546</sup> R. Davis and K. G. Untch, *J. Org. Chem.*, 1979, **44**, 3755.

<sup>547</sup> Y. Masaki, K. Hashimoto, K. Sakuma, and K. Kaji, *J. Chem. Soc., Chem. Commun.*, 1979, 855.

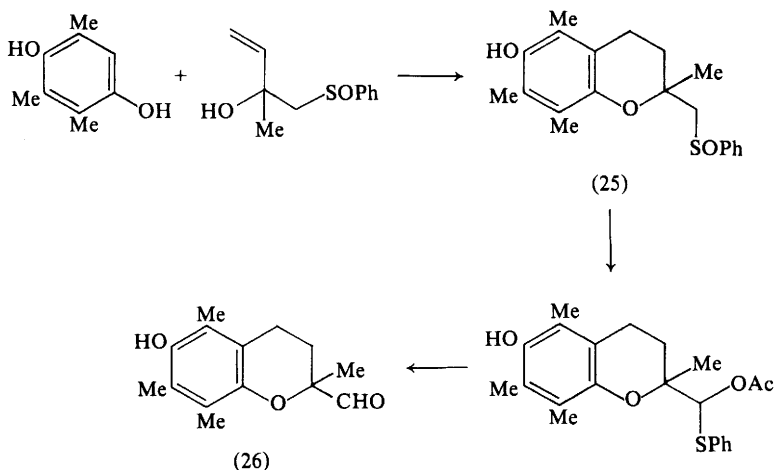
<sup>548</sup> J.-P. Corbet and C. Benzra, *Tetrahedron Lett.*, 1979, 4003.

<sup>549</sup> H. J. Reich, I. L. Reich, and S. Wollowitz, *J. Am. Chem. Soc.*, 1978, **100**, 5981.

<sup>550</sup> R. W. Hoffmann, R. Gerlach, and S. Goldmann, *Tetrahedron Lett.*, 1978, 2599.

(which, after Claisen rearrangement and elimination, give  $\bar{2},4$ -dienones)<sup>551</sup> and the conversion of  $\alpha$ -alkylidene- $\gamma$ -lactones into dienes  $RCH=C(CO_2Me)CH=CH_2$  via  $\alpha$ -(2-phenylseleninylethyl)acrylates.<sup>552</sup>

$\alpha$ -Phenylsulphonylacrylates  $(RCH_2)_2C=C(CO_2Me)SOPh$  have two rearrangement pathways open to them; the vinylogous Pummerer rearrangement, leading to  $\gamma$ -hydroxy- or -acetoxy-alkyl sulphides, or a prototropic shift in aqueous pyridine, followed by rearrangement of the resulting allyl sulphoxides to the sulphenates, which give the  $\gamma$ -hydroxy-acrylates on hydrolysis.<sup>553</sup> In an 'additive Pummerer rearrangement' of these compounds, using  $AcCl$ ,  $TFAA$ , or  $SOCl_2$  as reagents,  $\gamma$ -substituted sulphides are formed.<sup>553</sup> C-S Bond cleavage of 1,3-dienyl,<sup>554</sup> allenyl,<sup>554</sup> and alkenyl<sup>555</sup> sulphoxides follows reactions with alkyl-lithium compounds, leading to terminal allenes in the last named series. Organocopper reagents  $R_2CuLi$  react with allenyl sulphoxides to give the 2-alkylated 1-lithio-allyl compounds<sup>556</sup> and with allyl sulphoxides to cause  $\gamma$ -substitution.<sup>557</sup> After desulphurization of the  $\gamma$ -substituted products, this constitutes a synthesis of trisubstituted alkenes. The *cis*-addition of organocopper(i) compounds to alkynyl sulphoxides<sup>558</sup> and a simpler equivalent alkylation of ethynyl sulphoxides, using a malonate,<sup>559</sup> have been described. The reaction of trimethylhydroquinone with the allyl alcohol  $H_2C=CHCMe(OH)CH_2SOPh$ , catalysed by  $BF_3 \cdot Et_2O$  or  $SnCl_4$ , gives (25), which by Pummerer rearrangement and hydrolysis yields the chroman-2-aldehyde (26); this is an intermediate in a new synthesis of  $\alpha$ -tocopherol.<sup>560</sup>



<sup>551</sup> R. C. Cookson and R. Gopalan, *J. Chem. Soc., Chem. Commun.*, 1978, 608.

<sup>552</sup> T. R. Hoye and A. J. Caruso, *Tetrahedron Lett.*, 1978, 4611.

<sup>553</sup> S. Yamigawa, H. Sato, N. Hoshi, H. Kosugi, and H. Uda, *J. Chem. Soc., Perkin Trans. 1*, 1979, 570.

<sup>554</sup> G. Neef, U. Eder, and A. Seeger, *Tetrahedron Lett.*, 1980, 21, 903.

<sup>555</sup> G. H. Posner, P.-W. Tang, and J. P. Mallamo, *Tetrahedron Lett.*, 1978, 3995.

<sup>556</sup> J. Berlan and K. Koosha, *J. Organomet. Chem.*, 1978, **153**, 107.

<sup>557</sup> Y. Masaki, K. Sakuma, and K. Kaji, *J. Chem. Soc., Chem. Commun.*, 1980, 434.

<sup>558</sup> W. E. Truce and M. J. Lusch, *J. Org. Chem.*, 1978, **43**, 2252.

<sup>559</sup> I. Hori and T. Oishi, *Tetrahedron Lett.*, 1979, 4087.

<sup>560</sup> J. M. Akkermann, H. de Koning, and H. O. Huisman, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2124.

Further Diels–Alder syntheses using  $\beta$ -phenylsulphinyl- $\alpha\beta$ -unsaturated carbonyl compounds (see Vol. 5, p. 39) have established these compounds as useful  $\alpha\beta$ -ethynylcarbonyl synthons,<sup>561</sup> taking into account the scope for *syn*-elimination that is offered by the products.

**Physical Properties and Stereochemistry of Sulphoxides.**—Resolution of sulphoxides, sulphinates, and thiol sulphinates *via*  $\beta$ -cyclodextrin inclusion complexes is not efficient (<15%) with alkyl, aryl, or benzyl sulphoxides, but reaches 68% in the case of MeS(O)OPr.<sup>562</sup> Photoracemization of 1-naphthyl methyl sulphoxide in a cholesteric phase leads to less than 2% e.e. at equilibrium.<sup>563</sup>

Benzyl and 1-phenylethyl *t*-butyl sulphoxides have been shown, by measurement of dipole moments, to adopt the same conformation in solution (involving close approach of bulky groups) as has been established for the solid state through *X*-ray crystal analysis.<sup>564</sup>

## 12 Sulphones

**Preparation of Saturated Sulphones.**—Oxidation of sulphides and sulphoxides, using H<sub>2</sub>O<sub>2</sub>,<sup>565,566</sup> illustrates a standard method, though in the case of keten dithioacetals some C=C bond cleavage occurs,<sup>566</sup> and trifluoroperoxyacetic acid is more satisfactory.<sup>566</sup> Oxidation of sulphides to sulphones with hypochlorous acid can be stopped at the sulphoxide stage.<sup>567</sup> The same reagent is involved in the oxidative chlorinolysis of *n*-butyl glycidyl sulphoxide to Bu<sup>n</sup>SO<sub>2</sub>CH<sub>2</sub>CHCl-CH<sub>2</sub>Cl.<sup>568</sup> A combination of PhSeSePh with H<sub>2</sub>O<sub>2</sub>, presumably PhSe(O)OOH, has been used as a mild, selective method of oxidation.<sup>569</sup>

Preparations from sulphinic acids, SO<sub>2</sub>, other simple sulphur compounds, and sulphonyl halides are reported in the papers that are listed (with brief details) at the end of this section. The AlCl<sub>3</sub>-catalysed rearrangement of an aryl arenesulphonate gives the corresponding diaryl sulphone.<sup>570</sup>

**Additional Bibliography:** R. A. Hancock and S. T. Orszulik, *Tetrahedron Lett.*, 1979, 3789 [PhSO<sub>2</sub>Cu + ArTl(OCOCF<sub>3</sub>)<sub>2</sub>]; P. Messinger and H. Greve, *Arch. Pharm. (Weinheim, Ger.)*, 1978, **311**, 827, 280 [RSO<sub>2</sub>H → RSO<sub>2</sub>CH<sub>2</sub>OH; Michael additions and Mannich reactions involving RSO<sub>2</sub>H]; F. Manescalchi, M. Orena, and D. Savoia, *Synthesis*, 1979, 445 [benzenesulphinates salts of polymer-bound cations, with alkyl halides]; U. M. Dzhemilev, R. V. Kunakova, R. L. Gaisin, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2702; U. M. Dzhemilev, R. V. Kunakova, R. L. Gaisin, E. V. Vasileva, and G. A. Tolstikov, *Zh. Org. Khim.*, 1978, **14**, 2223; and R. V. Kunakova, G. A. Tolstikov, U. M. Dzhemilev, F. V. Sharipova, and D. L. Sazikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 931 [telomerization of butadiene with RSO<sub>2</sub>H, catalysed by Pd, Ph<sub>3</sub>P, and

<sup>561</sup> S. Danishefsky, T. Harayama, and R. K. Singh, *J. Am. Chem. Soc.*, 1979, **101**, 7008.

<sup>562</sup> M. Mikolajczyk and J. Drabowicz, *J. Am. Chem. Soc.*, 1978, **100**, 2510.

<sup>563</sup> C. Eskenazi, J. F. Nicoud, and H. B. Kagan, *J. Org. Chem.*, 1979, **44**, 995.

<sup>564</sup> M. Hirota, Y. Takahashi, M. Nishio, and K. Nishihata, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2358.

<sup>565</sup> A. Bergman and C. A. Wachtmeister, *Chemosphere*, 1978, **7**, 949.

<sup>566</sup> N. P. Petukhova, N. E. Dontsova, O. M. Sazonova, and E. N. Prilezhaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2654.

<sup>567</sup> A. R. Derzhinskii, L. D. Konyushkin, and E. N. Prilezhaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2070.

<sup>568</sup> A. R. Derzhinskii, L. D. Konyushkin, and E. N. Prilezhaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2650.

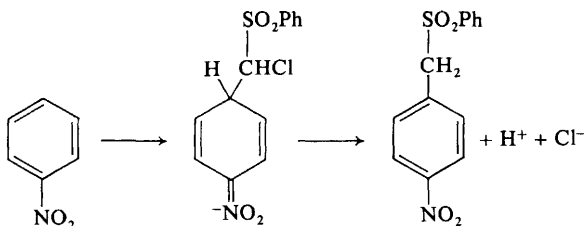
<sup>569</sup> K. C. Nicolau, R. L. Magolda, and W. E. Barnette, *J. Chem. Soc., Chem. Commun.*, 1978, 375.

<sup>570</sup> N. K. Undavia, M. L. Dhanani, and K. A. Thaker, *J. Inst. Chem. (India)*, 1978, **50**, 38 (*Chem. Abstr.*, 1979, **89**, 108 476).

Et<sub>3</sub>Al]; K. B. Rall, A. I. Vildavskaya, and A. A. Pterov, *Zh. Org. Khim.*, 1978, **14**, 1107 [ArSO<sub>2</sub>Na + vinylacetylenes]; J. Wildeman and A. M. Van Leusen, *Synthesis*, 1979, 733; A. D. Bulat, M. A. Antipov, and B. V. Passet, *Zh. Org. Khim.*, 1979, **15**, 651; R. Moreau, Y. Adam, and P. Loiseau, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1978, **287**, 39; and V. N. Mikhailova, A. D. Bulat, and V. P. Yurevich, *Zh. Obshch. Khim.*, 1978, **48**, 217 [RSO<sub>2</sub>Na + alkyl and alkenyl halides]; V. M. Naidan, G. D. Naidan, and G. V. Litvin, *Zh. Org. Khim.*, 1978, **14**, 2622 [styrene, PhN<sub>2</sub><sup>+</sup>Cl<sup>-</sup>, and SO<sub>2</sub>]; Yu. A. Moskvichev, M. I. Farberov, I. M. Rubleva, and G. V. Samchenko, *Khim. Prom-st. (Moscow)*, 1978, 262 (*Chem. Abstr.*, 1979, **89**, 23 886) [PhCl + SOCl<sub>2</sub> + SO<sub>3</sub> → (4-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SO<sub>2</sub>]; L. K. Liu, Y. Chi, and K. Y. Jan, *J. Org. Chem.*, 1980, **45**, 406 [ $\beta$ -iodo-sulphones from RSO<sub>2</sub>I with CuCl<sub>2</sub> + alkene]; M. M. Tanaskov and M. D. Stadnichuk, *Zh. Obshch. Khim.*, 1978, **48**, 1140 [CuCl-catalysed addition of RSO<sub>2</sub>Cl to alkenes and alkynes *via* RSO<sub>2</sub>-]; A. V. Kalabina, M. A. Vasileva, and T. I. Bychkova, *Zh. Org. Khim.*, 1979, **15**, 268 [u.v.-AIBN-initiated addition of RSO<sub>2</sub>Cl to vinyl ethers]; A. I. Khodair, A. A. Abdel-Wahab, and A. M. El-Khawaga, *Z. Naturforsch., Teil B*, 1978, **33**, 403 [R<sup>1</sup>SO<sub>2</sub>F + R<sup>2</sup>MgBr → sulphones, but no reaction occurs with organocadmium reagents]; Yu. A. Moskvichev, I. M. Rubleva, B. N. Bychkov, G. S. Mironov, and M. I. Farberov, *Kinet. Katal.*, 1978, **19**, 895 [aromatic sulphonylation with ArSO<sub>2</sub>Cl and FeCl<sub>3</sub>].

**Reactions of Saturated Sulphones.**—Applications of sulphones in synthesis are discussed in a later section, and sulphonyl-stabilized carbanions are dealt with elsewhere in this Volume. This section is therefore concerned with reactions of saturated alkyl and aryl sulphones, particularly C—S bond cleavage reactions, on which many applications of sulphones in synthesis depend.

Phase-transfer catalysis is a useful adjunct to the alkylation of benzyl<sup>571</sup> and iodomethyl<sup>572</sup> aryl sulphones. In the latter case, an  $\alpha$ -proton is substituted, rather than the halogen, and this same initial deprotonation has been proposed<sup>573</sup> for the novel, quaintly-named, ‘vicarious’ nucleophilic substitution of nitrobenzene by ClCH<sub>2</sub>SO<sub>2</sub>Ph in the presence of NaOH (Scheme 19). The novel  $\alpha$ -keto-sulphones ArCOSO<sub>2</sub>Ar are obtained by ozonolysis of the  $\alpha$ -diazo- or  $\alpha$ -alkoxymethylene analogues.<sup>574</sup>



Scheme 19

An intramolecular electron-transfer/radical anion mechanism has been advocated<sup>575</sup> for the Truce–Smiles-type rearrangement of *t*-butyl aryl sulphones by Bu<sup>n</sup>Li at  $-78^{\circ}\text{C}$ , *ortho*-lithiation of the aryl moiety being followed by migration of the *t*-butyl group to the metallated site. Other methods of C—S bond cleavage that are covered in recent papers include photolysis<sup>576</sup> and electrochemical reduction,<sup>577</sup>

<sup>571</sup> J. Golinski, A. Jonczyk, and M. Makosza, *Synthesis*, 1979, 461.

<sup>572</sup> A. Jonczyk and T. Pytlewski, *Synthesis*, 1978, 883.

<sup>573</sup> J. Golinski and M. Makosza, *Tetrahedron Lett.*, 1978, 3495.

<sup>574</sup> K. Schank and F. Werner, *Liebigs Ann. Chem.*, 1979, 1977.

<sup>575</sup> D. M. Snyder and W. E. Truce, *J. Am. Chem. Soc.*, 1979, **101**, 5432.

<sup>576</sup> R. F. Langler, Z. A. Marini, and J. A. Pincock, *Can. J. Chem.*, 1978, **56**, 903.

<sup>577</sup> B. Lamm and K. Ankner, *Acta Chem. Scand., Ser. B*, 1978, **32**, 264; E. A. Berdnikov, S. B. Fedorov, and Yu. M. Kargin, *Zh. Obshch. Khim.*, 1978, **48**, 875; S. Gambino, P. Martigny, G. Mousset, and J. Simonet, *J. Electroanal. Chem. Interfacial Electrochem.*, 1978, **90**, 105.

the former method leading to sulphinic acids and sulphonyl chlorides in hydrochloric acid,<sup>576</sup> and the latter yielding sulphinic acids and alkenes with alkyl sulphones that carry an electronegative  $\beta$ -substituent.<sup>577</sup> Analogously,  $\beta$ -trimethylsilylalkyl phenyl sulphones undergo fluoride-ion-induced elimination ( $\text{PhSO}_2\text{-CHRCH}_2\text{SiMe}_3 \rightarrow \text{RCH}=\text{CH}_2$ ).<sup>578</sup> Diastereoisomers of 1-methyl-2-bromopropyl phenyl sulphone yield *cis*- and *trans*-but-2-enes with tri-*n*-butylstannyl radicals, the non-stereospecific nature of the process indicating rapid rotation within the intermediate 2-phenylsulphonyl-1-methylpropyl radicals.<sup>579</sup> Fluorinolysis of dimethyl sulphone yields  $\text{CF}_3\text{SOF}$ ,  $\text{CF}_3\text{OSOF}$ , and  $\text{CHF}_2\text{OSO}_2\text{F}$ .<sup>580</sup>

**Unsaturated Sulphones.**—In addition to modified versions of methods used for the synthesis of saturated sulphones [e.g.  $\text{ArSO}_2\text{H} + \text{H}_2\text{C}=\text{CHCR}^1=\text{CHR}^2 \rightarrow \text{H}_2\text{C}=\text{CHCR}^1(\text{CH}_2\text{R}^2)\text{SO}_2\text{Ar}$ ;<sup>581</sup> peroxide-initiated addition of  $\text{RSO}_2\text{Br}$  to alkynes;<sup>582</sup> formation of rearranged allyl sulphones from  $\text{RSO}_2\text{Cl} +$  allyl-cobaloxime;<sup>583</sup>  $\text{RSO}_2\text{Na} +$  alk-1-enylmercury halides;<sup>584</sup>  $\text{RSO}_2\text{Na} +$  1,3-diene with  $\text{PdCl}_2$ ;<sup>585</sup> Michael addition of oxazolin-5-ones<sup>586</sup> and organocuprates<sup>587</sup> to ethynyl phenyl sulphones], standard methods of introducing double bonds have been applied to saturated sulphones and are summarized at the end of this section.

Rearrangements of allyl sulphones during electrolysis compete with reduction,<sup>588</sup> while a synthesis of allenyl sulphones by rearrangement of propargylic sulphinates<sup>589</sup> illustrates a different aspect of organosulphur rearrangements. Deprotonation of  $\delta$ -oxo-alkenyl sulphones  $\text{MeCOCHR}^1=\text{CHCHR}^2\text{SO}_2\text{Ph}$  provides an interesting example in which comparisons between carbonyl and sulphonyl groups can be made; alkylation of the derived carbanion occurs preferentially  $\gamma$  to  $\text{C}=\text{O}$  because sulphonyl groups tend to deconjugate to greater extents than carbonyl groups.<sup>590</sup>

Grignard reagents, in the presence of copper(II) acetylacetonate, effect nucleophilic substitution of the sulphonyl group and provide homologated alkenes.<sup>591</sup> 1-Alkynyl sulphones behave similarly with Grignard reagents and with alkyl-lithium compounds,<sup>592</sup> although some isomerization also takes place. The organolithium compounds effect  $\alpha$ -lithiation of vinyl sulphides at  $-95^\circ\text{C}$ ,<sup>593</sup> providing a useful synthesis of *trans*-2-substituted cyclopropyl sulphones from *trans*- $\text{BrCH}_2\text{CH}=\text{CHSO}_2\text{Ph}$ .<sup>594</sup> The  $\alpha$ -position in allyl sulphides is also lithiated,

<sup>578</sup> P. J. Kocienski, *Tetrahedron Lett.*, 1979, 2649.

<sup>579</sup> T. E. Boothe, J. L. Greene, and P. B. Shevlin, *J. Org. Chem.*, 1980, **45**, 794.

<sup>580</sup> L. A. Harmon and R. J. Lagow, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2675.

<sup>581</sup> M. Julia, M. Nel, and L. Saussine, *J. Organomet. Chem.*, 1979, **181**, C17.

<sup>582</sup> W. Boell, *Liebigs Ann. Chem.*, 1979, 1665.

<sup>583</sup> A. E. Crease, B. D. Gupta, M. D. Johnson, E. Bialkowska, K. N. V. Duong, and A. Gaudemer, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2611.

<sup>584</sup> J. Hershberger and G. A. Russell, *Synthesis*, 1980, 475.

<sup>585</sup> Y. Tamaru, M. Kagotani, and Z. Yoshida, *J. Chem. Soc., Chem. Commun.*, 1978, 367.

<sup>586</sup> W. Steglich and H. Wegmann, *Synthesis*, 1980, 481.

<sup>587</sup> V. Fiandanese, G. Marchese, and F. Naso, *Tetrahedron Lett.*, 1978, 5131.

<sup>588</sup> J. Y. Pape and J. Simonet, *Electrochim. Acta*, 1978, **23**, 445.

<sup>589</sup> M. Cinquini, F. Cozzi, and M. Pelosi, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1430.

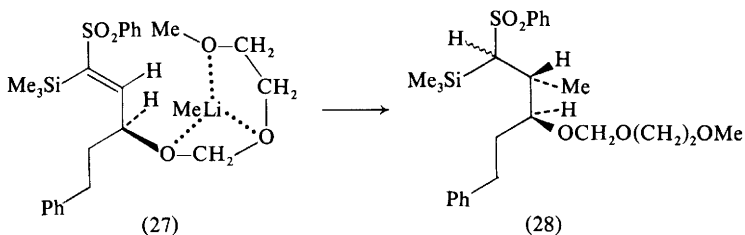
<sup>590</sup> P. T. Lansbury and R. W. Erwin, *Tetrahedron Lett.*, 1978, 2675.

<sup>591</sup> M. Julia, A. Righini, and J.-N. Verpeaux, *Tetrahedron Lett.*, 1979, 2393.

<sup>592</sup> R. L. Smorada and W. E. Truce, *J. Org. Chem.*, 1979, **44**, 3444.

<sup>593</sup> J. J. Eisch and J. E. Galle, *J. Org. Chem.*, 1979, **44**, 3279.

<sup>594</sup> J. J. Eisch and J. E. Galle, *J. Org. Chem.*, 1979, **44**, 3277.



and the resulting carbanion can participate in Michael reactions.<sup>595</sup> Electrochemical reduction of methyl styryl sulphone in the presence of  $\text{Bu}^t\text{Cl}$  gives sulphone-replacement products  $\text{PhCH}=\text{CHBu}^t$  and  $4\text{-Bu}^t\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$ , as well as the reduction products styryl methyl sulphide and  $\text{PhCHBu}^t\text{CH}_2\text{SO}_2\text{Me}$  and the corresponding sulphoxide.<sup>596</sup> The addition process in this example is also seen in the addition of  $\text{MeLi}$  to the enantiomer (27); the extraordinarily high level (>99%) of asymmetric induction (especially remarkable in an acyclic case), leading to the *threo*-isomer (28), has been taken<sup>597</sup> to indicate efficient co-ordination of the lithium cation.

Addition reactions of vinyl sulphones (Diels–Alder addition,<sup>598</sup> [2 + 2]-photocycloaddition,<sup>599</sup> and conventional functionalization processes, e.g.  $\text{IN}_3 \rightarrow 2\text{-azido-1-iodoalkyl sulphones}$ <sup>600</sup>) and substitution reactions of  $\beta$ -halogeno-vinyl sulphones<sup>601</sup> have been reported. A point of interest in the cycloaddition study is the effect of (*E*)–(*Z*) equilibration in hindering the participation of simple vinyl sulphones in photocycloaddition reactions.<sup>599</sup> Elimination of  $\text{SO}_2$  has been observed in the photolysis of 3-oxo-alk-1-enyl sulphones in benzene, giving radicals which attack the solvent.<sup>602</sup>

**Additional Bibliography:** P. Messinger and H. Greve, *Arch. Pharm. (Weinheim, Ger.)*, 1979, **312**, 792 [bromination–dehydrobromination of alkyl aryl sulphones]; M. Yamamoto, *Nippon Kagaku Kaishi*, 1978, 771 (*Chem. Abstr.*, 1979, **89**, 108 474) [methyl phenyl sulphone +  $\text{RCHO}$  and micelles]; K. Laping and M. Hanack, *Tetrahedron Lett.*, 1979, 1309 [ $\text{C}_6\text{F}_5\text{SO}_2\text{MgX} + \text{R}^1\text{COR}^2$ , followed by elimination of  $\text{H}_2\text{O}$ ]; P. O. Ellingsen and K. Undheim, *Acta Chem. Scand., Sect. B*, 1979, **33**, 528 [Horner–Wittig reaction with  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{SO}_2\text{Ph}$ ]; Y. Ueno, H. Setoi, and M. Okawara, *Chem. Lett.*, 1979, 47 and H. Kotake, K. Inomata, and M. Sumita, *ibid.*, 1978, 717 [de-acylative methylenation of arylsulphonylmethyl ketones with  $\text{HCHO}$ ].

**Sulphones Used in Synthesis.**—The range of examples of reactions of sulphones discussed in the preceding section makes clear the scope for applications in synthesis. Most applications are based on sulphonyl carbanions, and are covered in the next Chapter, but ring syntheses are illustrated by a novel synthesis of naphthalene that involves the condensation of *o*-formylbenzyl *p*-tolyl sulphones

<sup>595</sup> G. A. Kraus and K. Frazier, *Synth. Commun.*, 1978, **8**, 483.

<sup>596</sup> H. Lund and C. Degrand, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1978, **287**, 535.

<sup>597</sup> M. Isobe, M. Kitamura, and T. Goto, *Tetrahedron Lett.*, 1979, 3465.

<sup>598</sup> R. V. C. Carr and L. A. Paquette, *J. Am. Chem. Soc.*, 1980, **102**, 853.

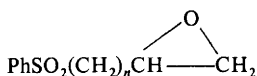
<sup>599</sup> M. A. A. M. El Tabei, N. V. Kirby, and S. T. Reid, *Tetrahedron Lett.*, 1980, **21**, 565.

<sup>600</sup> Y. Tamura, J. Haruta, S. M. Bayomi, M. W. Chun, S. Kwon, and M. Ikeda, *Chem. Pharm. Bull.*, 1978, **26**, 784.

<sup>601</sup> M. S. R. Naidu and S. G. Peeran, *Indian J. Chem., Sect. B*, 1978, **16**, 1086; A. V. Martynov, A. N. Mirskova, I. D. Kalikhman, P. V. Makerov, and M. G. Voronkov, *Zh. Org. Khim.*, 1979, **15**, 427.

<sup>602</sup> Y. Tamura, H. Kiyokawa, and Y. Kita, *Chem. Pharm. Bull.*, 1979, **27**, 676.





(29)

with  $\alpha\beta$ -unsaturated ketones,<sup>603</sup> the cyclization of epoxyalkyl phenyl sulphones (29) with MeMgI to give cyclobutanols ( $n = 2$ ) and cyclopentanols ( $n = 3$ ),<sup>604</sup> and the thermal extrusion of SO<sub>2</sub> from Me(CH<sub>2</sub>)<sub>5</sub>C(=CH<sub>2</sub>)CH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Me to give a disubstituted  $\gamma$ -lactone.<sup>605</sup> Pyrolysis of sulphones has been reviewed.<sup>606</sup> The synthesis of alkynes, R<sup>1</sup>C $\equiv$ CR<sup>2</sup>, from carboxylic acids, R<sup>1</sup>CO<sub>2</sub>H, *via*  $\beta$ -keto-alkyl sulphones and their enol phosphates<sup>607,608</sup> has been used in a synthesis of cyclododecyne.<sup>607</sup> Effective procedures for the cleavage of C—S bonds (reduction with sodium amalgam continues to be frequently used,<sup>598</sup> and Bu<sub>3</sub>SnH gives good yields of terminal alkenes from ArSO<sub>2</sub>CHRCH=CH<sub>2</sub><sup>609</sup>) support syntheses of homologated allyl alcohols<sup>610</sup> and  $\alpha\beta$ -unsaturated ketones<sup>611</sup> *via*  $\beta\gamma$ -epoxy-alkyl sulphones [a disadvantage being the formation of (*E*)/(*Z*) mixtures of allyl alcohols<sup>610</sup>]. Similarly, phenyl *trans*-2-chlorovinyl sulphone<sup>612</sup> and ethynyl phenyl sulphone<sup>586</sup> serve as equivalents of a vinyl cation in the synthesis of  $\alpha$ -vinyl- $\alpha$ -amino-acids.

### 13 Sulphenic and Selenenic Acids, and their Derivatives

**Sulphenic and Selenenic Acids.**—Flash vacuum pyrolysis of alkyl methyl sulphoxides or methyl methanethiolsulphinate, MeS(O)SMe, gives methane-sulphenic acid, characterized by microwave spectrometry as a dico-ordinate sulphur species, MeSOH, in the gas phase, with geometry similar to that of H<sub>2</sub>S<sub>2</sub>. This important study establishes the viability of separate molecules of the simplest sulphenic acid in the gas phase and also provides further examples of the self-condensation reactions used earlier to infer the transient generation of sulphenic acids in organosulphur reactions. Thus,<sup>613</sup> MeS(O)SMe is formed on cooling the reaction mixture, but thioformaldehyde is formed at 750 °C. Extension of this work<sup>614</sup> to the formation of ethenesulphenic and (*E*)-1-propenesulphenic acids has been stimulated by the establishment of the structure of the lachrymatory factor in onion (*Allium cepa*) as (*Z*)-propanethial *S*-oxide, formed from the propene-sulphenic acid that is liberated by the action of alliinase on *trans*-(+)-*S*-(1-propenyl)-L-cysteine sulphoxide *in vivo*. Pyrolysis of *N*-substituted azetidin-

<sup>603</sup> J. Wildeman, P. C. Borgen, H. Phim, P. H. F. M. Rouwette, and A. M. van Leusen, *Tetrahedron Lett.*, 1978, 2213.

<sup>604</sup> B. C. Corbel, J. M. Decesare, and T. Durst, *Can. J. Chem.*, 1978, **56**, 505.

<sup>605</sup> R. D. Little, S. Wolf, T. Smestad, S. C. Seike, L. W. Lindner, and L. Patron, *Synth. Commun.*, 1979, **9**, 545.

<sup>606</sup> F. Vögtle and L. Rossa, *Angew. Chem.*, 1979, **91**, 534.

<sup>607</sup> P. A. Bartlett, F. R. Green, and E. H. Rose, *J. Am. Chem. Soc.*, 1978, **100**, 4852.

<sup>608</sup> B. Lythgoe and I. Waterhouse, *Tetrahedron Lett.*, 1978, 2625.

<sup>609</sup> Y. Ueno, S. Aoki, and M. Okawara, *J. Am. Chem. Soc.*, 1979, **101**, 5414.

<sup>610</sup> P. J. Kocienski, *Tetrahedron Lett.*, 1979, 441.

<sup>611</sup> J. C. Saddler, P. C. Conrad, and P.L. Fuchs, *Tetrahedron Lett.*, 1978, 5079.

<sup>612</sup> B. W. Metcalf and E. Bonilavri, *J. Chem. Soc., Chem. Commun.*, 1978, 914.

<sup>613</sup> R. E. Penn, E. Block, and L. K. Revell, *J. Am. Chem. Soc.*, 1978, **100**, 3622.

<sup>614</sup> E. Block, R. E. Penn, and L. K. Revell, *J. Am. Chem. Soc.*, 1979, **101**, 2200.

2-on-yl sulphoxides generates azetidinonesulphenic acids, which may be trapped intramolecularly if the *N*-substituent is an alk-2-enyl group, leading to penam sulphoxides,<sup>615a</sup> but which yield 4-thionoazetidin-2-ones *via* thiolsulphinates when the *N*-substituent is an alk-2-enyl group.<sup>615b</sup> Details of other recent papers dealing with pyrolysis of sulphoxides can be found in the 'Sulphoxides' section. Pyrolysis of sulphinimides  $\text{ArS(O)N=CHR}$  gives areneseulphenic acids.<sup>616</sup>

Generation of sulphenic acid anions from disulphides by chlorinolysis and hydrolysis in aqueous media competes with oxidation to sulphonic acids.<sup>617</sup> Full details have been published<sup>618</sup> of the propensity for attack by electrophiles at both S and O in the sulphenate anions that are generated by the hydrolysis of disulphides and sulphenic acid derivatives.

Simple selenenic acids are also generated by pyrolysis of selenoxides,<sup>315</sup> and show some distinctive properties compared with sulphenic acids; thus,<sup>541,542,619</sup> addition to alkenes gives  $\beta$ -hydroxy-selenides. In the case of cyclo-octa-1,5-dienes, the cyclic ether corresponding to the introduction of phenylseleno-groups at C-1 and C-6 is the reaction product.<sup>619</sup> The oxidative reactivity of 'PhSeOH' has been illustrated in a previous section,<sup>228-230</sup> and further examples are the synthesis of selenolesters from *N*-acyl-hydrazines<sup>620</sup> ( $\text{RCONHNH}_2 \rightarrow [\text{RCON=NH}] \rightarrow \text{RCON=NSePh} \rightarrow \text{RCOSePh}$ ) and the PhSeSePh-catalysed oxidation of benzylic and primary allyl alcohols with  $\text{Bu}^t\text{OOH}$ ,<sup>621</sup> a reaction which is considered to involve the areneseelenenic acid or its anhydride. The reaction is also applicable to saturated alcohols if bis-(2,4,6-trimethylphenyl) diselenide is used.<sup>621</sup> The general picture presented in these reactions suggests that the structure 'RSeOH' can only be an approximation of the true structure of the organoselenium reagents involved.

**Sulphenate Esters.**—The essence of sulphenate ester chemistry is contained in an account of continuing mechanistic studies,<sup>622</sup> showing that S—O bond cleavage of  $\text{CF}_3\text{SOCH}_2\text{Ar}$  occurs on ethanolysis, while its  $\text{CCl}_3$  analogue undergoes cleavage of the C—O bond.<sup>622</sup> References to allyl sulphenates are discussed with unsaturated sulphoxides in an earlier section.

**Sulphenyl and Selenenyl Halides.**—The preparation of these compounds by halogenolysis of disulphides and diselenides, a particular example being the preparation of the stable 3-nitropyridine-2-sulphenyl chloride and bromide,<sup>623</sup> has not proved suitable for sulphenyl fluorides. Evidence for the existence of PhSF as an intermediate in the conversion of diphenyl disulphide into thianthrene has been provided by <sup>19</sup>F n.m.r. studies.<sup>624</sup> Addition of  $\text{SCl}_2$  to alkenes<sup>625</sup> is rarely used, since

<sup>615</sup> (a) A. C. Kaura, C. D. Maycock, and R. J. Stoodley, *J. Chem. Soc., Chem. Commun.*, 1980, 34; (b) M. D. Bachi, O. Goldberg, A. Gross, and J. Vaya, *J. Org. Chem.*, 1980, **45**, 1477, 1481.

<sup>616</sup> F. A. Davis, A. J. Friedman, and U. K. Nadir, *J. Am. Chem. Soc.*, 1978, **100**, 2844.

<sup>617</sup> V. N. R. Pillai and P. V. Padmanabhan, *J. Indian Chem. Soc.*, 1978, **55**, 279 (*Chem. Abstr.*, 1979, **89**, 163 195).

<sup>618</sup> D. R. Hogg and A. Robertson, *J. Chem. Soc. Perkin Trans. 1*, 1979, 1125.

<sup>619</sup> R. M. Scarbrough, A. B. Smith, W. E. Barnette, and K. C. Nicolaou, *J. Org. Chem.*, 1979, **44**, 1742.

<sup>620</sup> T. G. Back and S. Collins, *Tetrahedron Lett.*, 1979, 2661.

<sup>621</sup> M. Shimizu and I. Kuwajima, *Tetrahedron Lett.*, 1979, 2801.

<sup>622</sup> S. Braverman and H. Manor, *Phosphorus Sulfur*, 1976, **2**, 215.

<sup>623</sup> R. Matsueda and K. Aiba, *Chem. Lett.*, 1978, 951.

<sup>624</sup> F. Seel, R. Budenz, R. D. Flaccus, and R. Stark, *J. Fluorine Chem.*, 1978, **12**, 437.

<sup>625</sup> M. Mühlstädt, N. Stransky, E. Kleinpeter, and H. Meinhold, *J. Prakt. Chem.*, 1978, **320**, 107.

the  $\beta$ -chloro-alkanesulphenyl chloride that is formed adds to the alkene to give the symmetrical sulphide.

References to addition reactions of sulphenyl halides with alkenes and alkynes are given in the 'Sulphides' section. An incidental bonus from a study of the addition of PhSCl to adamantylideneadamantane<sup>626</sup> is the formation of the 4e-chloro-derivative and PhSSPh, *via* an intermediate thiiranium salt. Sulphenyl and selenenyl chlorides have been used for the dehydration of aldoximes to nitriles.<sup>627</sup> Whereas sulphinyl chlorides yield sulphinate esters with alkoxytrimethylsilanes, no reaction occurs with sulphenyl chlorides.<sup>628</sup>

**Sulphenamides and Selenenamides.**—Most of the methods of preparation reported in the recent literature are based on the straightforward route from a sulphenyl or selenenyl halide by reaction with an amine, and these papers are listed at the end of this section. Oxidative condensation of a thiol with an amine, using  $K_2S_2O_8$ ,<sup>629</sup> cleavage (in liquid  $NH_3$ ) of 4,4'-bis(nitrophenyl) disulphide<sup>630</sup> or of methyl benzenesulphenate,<sup>631</sup> and the reaction of an *N*-chloro-amide with selenium, to give  $(RCONH)_2SeCl_2$ , or with a selenenyl chloride, to give  $RCONHSeRCl_2$ ,<sup>632</sup> are more unusual routes.

Reactions involving cleavage of an S—N bond include anodic oxidation<sup>633,634</sup> or oxidation with  $PbO_2$ ,<sup>635</sup> giving sulphonic acids<sup>633</sup> or phenazines<sup>634,635</sup> *via* nitrenes; reaction with a thiol, giving a disulphide;<sup>636</sup> ammonolysis, giving thiols, amines, disulphides, and thiosulphenamides  $ArSSNH_2$  *via* sulphonium salt intermediates;<sup>637</sup> and a reaction with an isocyanide, giving an *S*-substituted isothiourea by insertion into the S—N bond.<sup>638</sup> Rearrangements [ $RSNMePh \rightarrow o$ - and  $p$ - $RSC_6H_4NHMe$ <sup>639</sup> and  $Ar^1N(SR^1)CR^2=NAr^2 \rightarrow Ar^1N=CR^2N(SR^1)Ar^2$ <sup>640</sup>] also involve S—N bond cleavage. Radicals  $Ar^1\dot{N}SAr^2$ , formed by abstraction of H from sulphenanilides, have been studied by e.s.r. spectroscopy,<sup>641</sup> and the sulphenylnitrenes that are formed by oxidation of 2,4-dinitrobenzenesulphenamide with  $Pb(OAc)_4$ <sup>642</sup> yield aziridines with alkenes and  $ArSN^+-\dot{N}H_2SAr$  with the sulphenamide, from which  $ArNHSAr$  is formed by two successive Smiles rearrangements.

Rotational barriers in arenesulphenamides, established by dynamic <sup>1</sup>H n.m.r. spectroscopy, are considered to arise from a balance of steric and electronic

<sup>626</sup> J. Bolster, R. M. Kellogg, E. W. Meijer, and H. Wynberg, *Tetrahedron Lett.*, 1979, 285.

<sup>627</sup> G. Sosnovsky and J. A. Krogh, *Z. Naturforsch., Teil B*, 1979, **34**, 511.

<sup>628</sup> D. N. Harpp, B. T. Friedlander, C. Larsen, K. Steliou, and A. Stockton, *J. Org. Chem.*, 1978, **43**, 3481.

<sup>629</sup> V. A. Ignatov, P. G. Valkov, S. V. Sukhanov, and A. N. Lazovenko, *Zh. Obshch. Khim.*, 1979, **49**, 841.

<sup>630</sup> R. Sato, S. Takizawa, and S. Oae, *Phosphorus Sulfur*, 1979, **7**, 185.

<sup>631</sup> D. A. Armitage and M. J. Clark, *Phosphorus Sulfur*, 1978, **5**, 41.

<sup>632</sup> N. Ya. Derkach, T. V. Lyapina, and E. S. Levchenko, *Zh. Org. Khim.*, 1978, **14**, 280.

<sup>633</sup> H. Sayo, K. Mori, and T. Michida, *Chem. Pharm. Bull.*, 1979, **27**, 2093.

<sup>634</sup> H. Sayo, K. Mori, A. Ueda, and T. Michida, *Chem. Pharm. Bull.*, 1978, **26**, 1682.

<sup>635</sup> H. Sayo, K. Mori, and T. Michida, *Chem. Pharm. Bull.*, 1979, **27**, 2316.

<sup>636</sup> V. A. Ignatov, *Zh. Obshch. Khim.*, 1979, **49**, 1122.

<sup>637</sup> R. Sato, K. Araya, Y. Takikawa, S. Takizawa, and S. Oae, *Phosphorus Sulfur*, 1978, **5**, 245.

<sup>638</sup> J. P. Chupp, J. J. D'Amico, and K. L. Leschinsky, *J. Org. Chem.*, 1978, **43**, 3553.

<sup>639</sup> P. Aimpour and N. E. Heimer, *J. Org. Chem.*, 1978, **43**, 2061.

<sup>640</sup> L. P. Olekhnovich, I. E. Mikhailov, N. M. Ivanchenko, Yu. A. Zhdanov, and V. I. Minkin, *Zh. Org. Khim.*, 1979, **15**, 1355.

<sup>641</sup> Y. Miura, Y. Katsura, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1121.

<sup>642</sup> R. S. Atkinson and B. D. Judkins, *J. Chem. Soc., Chem. Commun.*, 1979, 832, 833.

effects,<sup>643</sup> but probing into the details to try to secure a less vague interpretation has led to this being a controversial subject over recent years.<sup>644</sup> Rotational barriers for hydroxylamines cannot be accounted for by any of the proposed mechanisms for sulphenamides.<sup>644</sup> The high barriers to rotation that lead to there being separable diastereoisomers of *N*-heteroaryl amino-sulphenamides are due to restricted rotation about the N—N bond, not the S—N bond.<sup>645</sup>

Sulphenimines  $\text{ArSN}=\text{CR}^1\text{CO}_2\text{R}^2$  are formed from an arenesulphenyl chloride with an  $\alpha$ -amino-acid ester in the presence of an acid scavenger, and they yield  $\alpha$ -keto-esters by reaction with  $\text{PPh}_3$  and silica gel.<sup>646</sup> Sulphenimines  $\text{PhSN}=\text{CR}^1\text{CH}_2\text{R}^2$  are formed by the alkylation of carbanions formed from a thiolate and a nitrile.<sup>647</sup>

**Additional Bibliography:** K. B. Kurbanov, Z. A. Mamedov, and S. T. Akhmedov, *Azerb. Khim. Zh.*, 1978, 50 (*Chem. Abstr.*, 1980, **91**, 5006) [ $\text{ArSNR}_2$  from  $\text{ArSCl}$ ]; I. V. Koval, T. G. Oleinik, and M. M. Kremlev, *Zh. Org. Khim.*, 1979, **15**, 2319 [ $\text{Ar}^1\text{SCl} + \text{Ar}^2\text{SO}_2\text{NH}_2$ ]; ref. 720 [ $\text{RSCl} + \text{AcNHSiMe}_3$ ]; A. Darmadi and M. Kaschani-Motlagh, *Z. Anorg. Allg. Chem.*, 1979, **448**, 35 [ $\text{CF}_3\text{SeBr} + \text{NH}_3 \rightarrow (\text{CF}_3\text{Se})_n\text{NH}_{3-n}$ ].

**Thionitrites and Thionitrates.**—Treatment of a thiol with  $\text{N}_2\text{O}_4$  gives the corresponding thionitrite  $\text{RSNO}$ ,<sup>648</sup> further reaction with  $\text{N}_2\text{O}_4$  leading to the sulphonic acid or the thiolsulphonate. *t*-Butyl thionitrite or the corresponding thionitrate  $\text{Bu}^t\text{SNO}_2$  (formed from a thiol and  $\text{N}_2\text{O}_4$ ), can be used with a copper(II) halide to convert anilines into halogenobenzenes.<sup>649</sup> Thionitrates also convert *p*-amino-phenols into *p*-benzoquinone-*t*-butylthioimines.<sup>650</sup>

#### 14 Thiocyanates and Isothiocyanates, and their Selenium and Tellurium Analogues

**Thiocyanates.**—Relatively little new work has appeared in the period under review that concerns reactions of these compounds, but modifications of known preparative methods continue to be studied. These papers are mostly to be found at the end of this section. Several sections of a recent book<sup>651</sup> deal with these compounds in some depth.

A novel method for the synthesis of thiocyanates amounts to the overall conversion  $\text{RNH}_2 \rightarrow \text{RSCN}$ .<sup>652</sup> The amine is allowed to react with 2,4,6-triphenylpyrylium thiocyanate and the resulting pyridinium thiocyanate is pyrolysed at 180—200 °C. The point is made<sup>652</sup> that this method is safer than the classical diazotization—substitution sequence for bringing about this conversion (illustrated recently for 3-aminothiophens, to give 3-thienyl thiocyanates and selenocyanates<sup>653</sup>).

<sup>643</sup> M. Raban and G. Yamamoto, *J. Am. Chem. Soc.*, 1979, **101**, 5890.

<sup>644</sup> D. Kost and E. Berman, *Tetrahedron Lett.*, 1980, **21**, 1065.

<sup>645</sup> R. S. Atkinson, B. D. Judkins, and B. H. Patwardhan, *Tetrahedron Lett.*, 1978, 3137.

<sup>646</sup> E. M. Gordon and J. Pluscec, *J. Org. Chem.*, 1979, **44**, 1218.

<sup>647</sup> F. A. Davis and P. A. Mancinelli, *J. Org. Chem.*, 1978, **43**, 1797.

<sup>648</sup> Y. H. Kim, K. Shinhama, D. Fukushima, and S. Oae, *Tetrahedron Lett.*, 1978, 1211.

<sup>649</sup> Y. H. Kim, K. Shinhama, and S. Oae, *Tetrahedron Lett.*, 1978, 4519.

<sup>650</sup> S. Oae, K. Shinhama, and Y. H. Kim, *Chem. Lett.*, 1979, 1077.

<sup>651</sup> 'Chemistry of Cyanates and their Thio Derivatives', ed. S. Patai, Wiley, Chichester, 1977.

<sup>652</sup> A. R. Katritzky and S. S. Thind, *J. Chem. Soc., Chem. Commun.*, 1979, 138; A. R. Katritzky, U. Gruntz, N. Mongelli, and M. C. Rezende, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1953.

<sup>653</sup> C. Paulmier, *Bull. Soc. Chim. Fr., Part 2*, 1979, 237.

Many examples of isomerization into isothiocyanates are found in papers describing the uses of thiocyanates in synthesis, one of which is based on their sulphenylation reactivity  $[\text{H}_2\text{C}=\text{C}(\text{CH}_2\text{SCN})_2 \rightarrow \text{H}_2\text{C}=\text{C}(\text{CH}_2\text{NCS})_2 + 1,2,6,7\text{-tetrathia-4,9-dimethylenecyclodecane}]$ .<sup>654</sup> This rearrangement is brought about for poly(alkylbenzyl) thiocyanates and benzyl selenocyanates by u.v. irradiation.<sup>655</sup> Allyl thiocyanates undergo [3,3]-sigmatropic rearrangement during distillation  $[\text{R}^1\text{O}_2\text{CCH}=\text{CR}^2\text{CH}_2\text{SCN} \rightarrow \text{R}^1\text{O}_2\text{CC}(\text{NCS})=\text{CR}^2\text{Me}]$ .<sup>656</sup> Thiocyanates are also useful in thiazolinone synthesis,<sup>657</sup> and an interesting variation of the Japp-Klingemann reaction  $[\text{MeCOCH}(\text{COMe})\text{SCN} + \text{ArN}_2^+ \text{Cl}^-]$ , giving 2-acetyl-4-aryl-5-imino- $\Delta^2$ -1,3,4-thiadiazoline] has been reported.<sup>658</sup>

Conversion of a thiocyanate into a nitrile  $[(\text{EtO}_2\text{C})_2\text{CHSCN} \rightarrow (\text{EtO}_2\text{C})_2\text{CHCN}]$  with aqueous  $\text{MeNH}_2$  or  $\text{NH}_3$  is suggested to proceed *via* formation of a thiiran, followed by extrusion of sulphur,<sup>659</sup> but other mechanisms must also be considered. 2-Nitrophenyl thiocyanate with  $\text{Bu}^n_3\text{P}$  is an effective reagent for coupling carboxylic acids with amines,<sup>660</sup> and it may have considerable value in peptide synthesis.

Methods of preparation of selenocyanates are entirely analogous to those of thiocyanates, and the papers listed at the end of this section include examples of methods. The previously unknown compound  $\text{PhTeCN}$  is formed in only low yield from  $\text{PhTeTePh}$  and  $\text{KCN}$ , but in high yield through reductive cyanation of  $\text{ArTeCl}$ , and by the general route from  $\text{ArTeBr}$  with  $\text{KCN}$ .<sup>661</sup>

**Additional Bibliography:** K. Fujiki, T. Nishio, and Y. Omote, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 614 [photosubstitution of halogenobenzenes with  $\text{SCN}^-$ ]; G. Cainelli, F. Manescalchi, and M. Panunzio, *Synthesis*, 1979, 141 and C. R. Harrison and P. Hodge, *ibid.*, 1980, 299 [alkyl halide +  $\text{SCN}^-$  that is bound to an ion-exchange resin]; M. S. Korobov, L. E. Nivorozhkin, V. I. Minkin, M. M. Levkovich, and S. I. Testoevaya, *Zh. Org. Khim.*, 1978, **14**, 788 [ $\text{MeCCl}=\text{CMeCHO} + \text{SCN}^-$ ]; D. G. Garratt, M. D. Ryan, and M. Ujjainwalla, *Can. J. Chem.*, 1979, **57**, 2145 [alkenes +  $\text{PhSeSCN}$ ]; K. Falkenstein, C. Wolff, and W. Tochtermann, *Liebigs Ann. Chem.*, 1979, 1483 [ring opening of oxanorbornadiene by  $\text{SCN}^-$ ]; V. R. Kartashov, N. F. Akimkina, E. V. Skorobogatova, and N. L. Sanina, *Zh. Org. Khim.*, 1979, **15**, 545 and *Kinet. Katal.*, 1978, **19**, 785 [alkenes +  $(\text{SCN})_2$ ]; R. J. Maxwell and L. S. Silbert, *Tetrahedron Lett.*, 1978, 4991 and *J. Am. Oil Chem. Soc.*, 1978, **55**, 583 [alkenes +  $(\text{SCN})_2$  or  $\text{ISCN}$  which is in equilibrium with  $\text{I}_2 + (\text{SCN})_2$ ]; P. D. Woodgate, H. H. Lee, P. S. Rutledge, and R. C. Cambie, *Synthesis*, 1978, 152 [alkenes +  $\text{I}_2 + \text{KSeCN}$ ]; R. C. Cambie, H. H. Lee, P. S. Rutledge, and P. D. Woodgate, *J. Chem. Soc., Perkin Trans. 1*, 1979, 757, 765 [alkenes +  $\text{ISCN}$ ]; I. V. Bodrikov, L. I. Kovaleva, L. V. Chumakov, and N. S. Zefirov, *Zh. Org. Khim.*, 1978, **14**, 2457 [alkene +  $\text{RSSCN}$ ]; K. Tamao, T. Kakui, and M. Kumada, *Tetrahedron Lett.*, 1980, 111 [(*E*)-alkenyl pentafluorosilicates + copper(II) thiocyanate]; Y. Tamura, T. Kawasaki, N. Goida, and Y. Kita, *Tetrahedron Lett.*, 1979, 1129 [epoxy-ketones +  $\text{Ph}_3\text{P}(\text{SCN})_2$ ]; Y. Tamura, M. Adachi, T. Kawasaki, and Y. Kita, *Tetrahedron Lett.*, 1979, 2251 [primary alcohols +  $\text{Ph}_3\text{P}(\text{SeCN})_2$  at  $-60^\circ\text{C}$ ]; J. Burski, J. Kieszkowski, J. Michalski, M. Pakulski, and A. Skowronska, *J. Chem. Soc., Chem. Commun.*, 1978, 940 [alcohols + chlorophosphoranes + lead thiocyanate]; C. Paulmier, *Bull. Soc. Chim. Fr., Part 2*, 1979, 592 [thiophens +  $\text{Br}_2$  and  $\text{SCN}^-$ ]; D. N. Harpp, B. T. Friedlander, and R. A. Smith, *Synthesis*, 1979, 181 [ $\text{Me}_3\text{SiCN} + \text{RSCl}$ ]; K. Fujiki, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 3065 [1-alkoxy-naphthalenes +  $\text{Cu}(\text{SCN})_2 \rightarrow 4$ -thiocyanates]; V. M. Naidan, G. D. Naidan, and A. V. Dombrovskii, *Zh. Obshch. Khim.*, 1979, **49**, 1829 [ $\text{H}_2\text{C}=\text{CR}^1\text{R}^2$  with  $\text{ArN}_2^+ \text{HSO}_4^-$  and  $\text{NH}_4\text{SCN} \rightarrow \text{ArCH}_2\text{CR}^1\text{R}^2\text{SCN}$ , while with  $\text{SO}_2 + \text{ArN}_2^+ \text{HSO}_4^- + \text{NH}_4\text{SCN} \rightarrow \text{ArSO}_2\text{CH}_2\text{CR}^1\text{R}^2$ ].

<sup>654</sup> M. Mülhstädt, G. Winkler, A. Koennecke, and B. Schulze, *Z. Chem.*, 1978, **18**, 89; B. Schulze, M. Mülhstädt, and I. Schubert, *ibid.*, 1979, **19**, 41.

<sup>655</sup> H. Suzuki, M. Usuki, and T. Hanafusa, *Synthesis*, 1979, 705 and *Bull. Chem. Soc. Jpn.*, 1979, **52**, 836.

<sup>656</sup> R. A. Volkmann, *Synth. Commun.*, 1978, **8**, 541.

<sup>657</sup> G. C. Barrett, *Tetrahedron*, 1980, **36**, 2123.

<sup>658</sup> N. F. Eweiss and A. Osman, *Tetrahedron Lett.*, 1979, 1169.

<sup>659</sup> S. Kambe and T. Hayashi, *Chem. Ind. (London)*, 1979, 479.

<sup>660</sup> P. A. Grieco, D. S. Clark, and G. P. Withers, *J. Org. Chem.*, 1979, **44**, 2945.

<sup>661</sup> S. J. Falcone and M. P. Cava, *J. Org. Chem.*, 1980, **45**, 1044.

SCN]; A. Toshimitsu, Y. Kozawa, S. Uemura, and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1273 [alkene + KSeCN and CuCl<sub>2</sub> in EtOH →  $\beta$ -alkoxy-selenocyanates]; A. Toshimitsu, S. Uemura, and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1206 [diene + KSeCN and CuCl<sub>2</sub> → saturated cyclic selenides rather than selenocyanates]; S. Rajappa, T. G. Rajagopalan, R. Sreenivasan, and S. Kanal, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2001 [pyrolysis of *N*-aryl-*N'*-benzoyl-thioureas → ArSCN].

**Isothiocyanates.**—Reference has been made in the preceding section to the formation of mixtures of thiocyanates and isothiocyanates in syntheses employing metal thiocyanates. Specific methods of synthesis for isothiocyanates are illustrated in  $\text{RNH}_2 + \text{CS}_2 + \text{As}_2\text{O}_3 \rightarrow \text{RNCS}$ ;<sup>662</sup>  $\text{Ph}_2\text{CHC(S)NHR} + \text{BuLi} \rightarrow \text{Ph}_2\text{C=C(S}^-\text{)NHR} \rightarrow \text{Ph}_2\text{C=C=NR}$ , which, with  $\text{CS}_2$ , →  $\text{RNCS}$ ;<sup>663</sup> and  $\text{RNC} + (\text{ArCOS})_2 \rightarrow \text{RNCS}$ .<sup>664</sup> Various ring-opening reactions lead to unsaturated isothiocyanates [5,5-disubstituted thiazoline-2-thiones →  $\text{R}^1\text{R}^2\text{C=CR}^3\text{NCS}$  with  $(\text{MeO})_3\text{P}$ ;<sup>665</sup> 2-methyl-oxazoles with  $\text{CS}_2$  and base → 2-isothiocyanatovinyl acetates<sup>666</sup>]. Dehydrobromination of  $\alpha$ -bromoalkyl isothiocyanates, formed from the alkyl analogues and NBS,<sup>667</sup> yields vinyl isothiocyanates.<sup>668</sup> Competition between substitution of bromine and addition to the carbon atom of the isothiocyanate group is reported in the formation of  $\alpha$ -bromoalkyl isothiocyanates.<sup>668</sup> The latter route is adopted preferentially by softer nucleophiles, and subsequent hydrolysis gives aldehydes and ketones, and therefore provides an overall transformation  $\text{R}^1\text{R}^2\text{CHNH}_2 \rightarrow \text{R}^1\text{COR}^2$ . Addition to the carbon atom of isothiocyanate is the characteristic reaction of this class, illustrated in the ring-opening of 3-dimethylamino-2-phenyl-2*H*-azirines<sup>669</sup> with  $\text{MeNCS} \rightarrow \text{RCH=CPhC(NMe}_2\text{)=NC(S)NHMe}$ , while other isothiocyanates give products from cleavage of the 1,3-bond. Other examples include the synthesis of thio-oximes ( $\text{PhNCS} + \text{R}^1\text{R}^2\text{C=NONa} \rightarrow \text{R}^1\text{R}^2\text{C=NOC(S)NHPh} \rightarrow \text{R}^1\text{R}^2\text{C=NSR}^3$ ),<sup>670</sup> the formation of bis(imino)thietans with isocyanides,<sup>671</sup> and the production of imino-1,3-oxathietans from cyclobutene-3,4-diones and  $\text{EtO}_2\text{CNCS}$ <sup>672</sup> through [2 + 2] cycloadditions to the C=S moiety.

Photolysis of isothiocyanates yields isocyanides.<sup>673</sup> Iodine forms charge-transfer complexes, comparative studies indicating that isothiocyanates are more powerful donors than the corresponding thiocyanates.<sup>674</sup>

Enzymic hydrolysates of glucosinolates from seeds of nine species of *Tropaeolum* contain volatile isothiocyanates.<sup>675</sup>

<sup>662</sup> I. Okuda and H. Sugiyama, *Yuki Gosei Kagaku Kyokaiishi*, 1978, **36**, 1090 (*Chem. Abstr.*, 1979, **90**, 137 196).

<sup>663</sup> T. Fujinami, N. Otani, and S. Sakai, *Nippon Kagaku Kaishi*, 1978, 265 (*Chem. Abstr.*, 1978, **88**, 169 697).

<sup>664</sup> S. Tanaka, K. Masue, and M. Okano, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 659.

<sup>665</sup> A. Q. Hussein, A. Abu-Taha, and J. C. Jochims, *Chem. Ber.*, 1978, **111**, 3750.

<sup>666</sup> A. W. Faull and R. Hull, *J. Chem. Res. (S)*, 1979, **240**, 148.

<sup>667</sup> A. Q. Hussein and J. C. Jochims, *Chem. Ber.*, 1979, **112**, 1948.

<sup>668</sup> A. Q. Hussein and J. C. Jochims, *Chem. Ber.*, 1979, **112**, 1956.

<sup>669</sup> E. Schaumann and S. Grabley, *Liebigs Ann. Chem.*, 1978, 1568.

<sup>670</sup> R. F. Hudson and H. Dj-Forudian, *J. Chem. Soc., Perkin Trans. 1*, 1978, 12; *Phosphorus Sulfur*, 1978, **4**, 9.

<sup>671</sup> G. L'abbé, L. Huybrechts, J.-P. Declercq, G. Germain, and M. Van Meerseche, *J. Chem. Soc., Chem. Commun.*, 1979, 160.

<sup>672</sup> G. Seitz and R. Sutrisno, *Synthesis*, 1978, 831.

<sup>673</sup> R. Jahn and U. Schmidt, *Monatsh. Chem.*, 1978, **109**, 161.

<sup>674</sup> C. Raby and J. Buxeraud, *Bull. Soc. Chim. Fr., Part 2*, 1978, 439.

<sup>675</sup> A. Kjaer, J. Ogaard Madsen, and Y. Maeda, *Phytochemistry*, 1978, **17**, 1285.

### 15 Sulphinic and Seleninic Acids, and their Derivatives

**Sulphinic and Seleninic Acids.**—An improved method of preparation of simple sulphinic acids, using sulphur dioxide<sup>676</sup> with a Grignard reagent or an organolithium compound (also applied for the preparation of  $F_2C=CFSO_2H$  from  $F_2C=CFLi$ <sup>677</sup>), and a promising use of organoaluminium compounds for the same purpose<sup>678</sup> offer convenient access to these compounds. Camphene has been converted into the *endo*-sulphinic acid *via* the tris(camphanyl)aluminium reagent.<sup>678</sup> Other organometallic compounds for which  $SO_2$ -insertion studies have been reported<sup>679</sup> generally tend to form *O*-sulphinates (*i.e.* C—O bond formation).

Certain reactions of alkenes in liquid  $SO_2$  can be accounted for on the basis of addition of  $SO_2$  followed by elimination of sulphoxylic acid,  $H_2SO_2$ , through an ene reaction (*e.g.* aromatization of cyclohexa-1,4-diene<sup>680</sup> and the easy exchange of allylic protons in solutions of alkenes in  $SO_2$ <sup>681</sup>). The rationalization of allylic oxidation by  $SeO_2$  on the basis of allylseleninic acid intermediates in a 1973 paper<sup>682</sup> has been largely supported,<sup>683</sup> though with more complexities arising from ionic intermediates than originally proposed.

Routes to sulphinic acids from the cleavage of sulphones, discussed in an earlier section, involve more drastic reaction conditions than are needed for the cleavage of *N*-(alkylsulphonylmethyl)imides, themselves formed from thiols through standard procedures [ $RCON(COR)CH_2Br + RSH \rightarrow RCON(COR)CH_2SR \rightarrow RCON(COR)CH_2SO_2R \rightarrow RSO_2Na$  with  $NaOEt$ ].<sup>684</sup> Sulphides, disulphides, or their oxides undergo oxidative cleavage to sulphinic and sulphonic acids with superoxide anion.<sup>685</sup> Oxidative chlorinolysis of disulphides gives sulphinyl chlorides,<sup>686</sup> and a route to perfluoroalkanesulphinic acids depends on the addition of  $R_2NSF_3$  to a perfluoroalkene [ $R^1R^2CFSF_2NR_2 \rightarrow R^1R^2CFSONR_2 \rightarrow R^1R^2CFSO_2H$ , the last step being effected with conc.  $H_2SO_4$ ].<sup>687</sup>

In a modified standard route, arenesulphonyl chlorides are easily reduced to sulphinic acids, using a saturated hydrocarbon and  $AlCl_3$ .<sup>688</sup>

Allyl sulphinates, formed by ring-opening of certain cyclic sulphinamides in aqueous alkali, readily undergo loss of  $SO_2$  through a pericyclic route [ $(Z)\text{-ArSO}_2\text{NHCHMeCH=CHCHMeSO}_2^- \rightarrow (E)\text{-ArSO}_2\text{NHCHMeCH}_2\text{CH=}$

<sup>676</sup> H. W. Pinnick and M. A. Reynolds, *J. Org. Chem.*, 1979, **44**, 160.

<sup>677</sup> R. Sarwetre, D. Masure, C. Chuit, and J. F. Normant, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1979, **288**, 335.

<sup>678</sup> A. V. Kuchin, L. I. Akhmetov, V. P. Yurev, and G. A. Tolstikov, *Zhur. Obshch. Khim.*, 1978, **48**, 469; *ibid.*, 1979, **49**, 401.

<sup>679</sup> A. Dormond, C. Moise, A. Dahchour, and J. Tiroufflet, *J. Organomet. Chem.*, 1979, **177**, 181; R. G. Severson and A. Wojcicki, *J. Am. Chem. Soc.*, 1979, **101**, 877; A. E. Crease and M. D. Johnson, *ibid.*, 1978, **100**, 8013.

<sup>680</sup> D. Masilamani and M. M. Rogic, *Tetrahedron Lett.*, 1978, 3785.

<sup>681</sup> D. Masilamani and M. M. Rogic, *J. Am. Chem. Soc.*, 1978, **100**, 4634.

<sup>682</sup> D. Arigoni, A. Vasella, K. B. Sharpless, and H. P. Jensen, *J. Am. Chem. Soc.*, 1973, **95**, 7917.

<sup>683</sup> L. M. Stephenson and D. R. Speth, *J. Org. Chem.*, 1979, **44**, 4683; see also W.-D. Woggon, F. Ruther, and H. Egli, *J. Chem. Soc., Chem. Commun.*, 1980, 706.

<sup>684</sup> M. Uchino, K. Suzuki, and M. Sekiya, *Chem. Pharm. Bull.*, 1978, **26**, 1837.

<sup>685</sup> T. Takata, Y. H. Kim, and S. Oae, *Tetrahedron Lett.*, 1979, 821.

<sup>686</sup> A. Etienne, G. Baills, G. Lonchambon, and B. Desmazieres, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1979, **288**, 493.

<sup>687</sup> O. A. Radchenko, A. Ya. Ichenko, L. N. Markovskii, and L. M. Yagupolskii, *Zh. Org. Khim.*, 1978, **14**, 275.

<sup>688</sup> R. Fields, G. Holt, M. O. A. Orabi, and B. Naseeri-Noori, *J. Chem. Soc., Perkin Trans. 1*, 1979, 233.

CHMe],<sup>689</sup> thus supporting the interpretation of rearrangements of alkenes in liquid SO<sub>2</sub> that is based on the instability of allyl sulphinic acids. Sodium salts of sulphinic acids take the role of co-catalyst in PdCl<sub>2</sub>-catalysed dimerization of butadiene in an alcohol solvent, leading to octa-2,7-dienyl alkyl ethers,<sup>690</sup> and act as arylating agents towards cyclo-octa-1,5-diene in the presence of PdCl<sub>2</sub>.<sup>691</sup>

Oxidation of sulphinic acids by air (under u.v. irradiation) gives sulphonic acids,<sup>692</sup> but N<sub>2</sub>O<sub>4</sub> leads to unstable sulphonyl nitrites RSO<sub>2</sub>NO rather than to oxidized products.<sup>693</sup>

Seleninic acids are effective catalysts for the conversion of alkenes into oxirans and of sulphides into sulphones by H<sub>2</sub>O<sub>2</sub>.<sup>694</sup> They can be used for the partial oxidation of thiols, three equivalents of the thiol with PhSe(O)OH giving equimolar amounts of PhSeSR and RSSR.<sup>695</sup> Benzeneseleninic anhydride (ref. 1*h*), formed by oxidation of PhSeSePh with HNO<sub>3</sub><sup>696-698</sup> or with *t*-butyl hydroperoxide,<sup>699</sup> continues to show promise as an oxidizing agent. It oxidizes alcohols under essentially neutral conditions,<sup>696</sup> converts benzylic hydrocarbons into aldehydes or ketones,<sup>697</sup> introduces conjugated double bonds into lactones,<sup>697</sup> converts thiocarbonyl compounds into their carbonyl analogues,<sup>698</sup> and produces  $\alpha$ -phenylseleno-alkyl ketones from alkenes<sup>699</sup> (see also Vol. 5, p. 54 and ref. 494 for further uses of benzeneseleninic anhydride).

**Sulphinyl and Seleninyl Halides.**—Chlorinolysis of *N*-(alkylsulphinylmethyl)-phthalimides [PhtCH<sub>2</sub>S(O)R → RS(O)Cl]<sup>700</sup> and the formation of  $\alpha$ -chloro-alkane-sulphinyl chlorides from reactive methylene compounds with SOCl<sub>2</sub> and pyridine<sup>701</sup> illustrate new examples of known methods of preparation. The latter compounds have been shown to yield  $\alpha$ -chloro-sulphines on reaction with a tertiary amine (MeCHClSOCl → MeCCl=S=O → MeCCl<sub>2</sub>SOCl).<sup>702</sup>

**Sulphinate Esters.**—Methods of preparation from sulphinyl chlorides<sup>628, 703-705</sup> by reaction with alcohols,<sup>703, 704</sup> with silyl ethers,<sup>628, 703</sup> or with hydroxylamines,<sup>705</sup> from sulphinic acids,<sup>706, 707</sup> from sulphonylates [(RO)<sub>2</sub>S + H<sub>2</sub>C=CHCH<sub>2</sub>Br (at 105-

<sup>689</sup> W. L. Mock and R. M. Nugent, *J. Org. Chem.*, 1978, **43**, 3433.

<sup>690</sup> Y. Tamaru, M. Kagotani, R. Suzuki, and Z. Yoshida, *Chem. Lett.*, 1978, 1329.

<sup>691</sup> Y. Tamaru and Z. Yoshida, *Tetrahedron Lett.*, 1978, 4527.

<sup>692</sup> G. Ricci, S. Dupre, G. Federici, G. Spoto, R. M. Matarese, and D. Cavallini, *Physiol. Chem., Phys.*, 1978, **10**, 435.

<sup>693</sup> S. Oae, K. Shinhama, and Y. H. Kim, *Tetrahedron Lett.*, 1979, 3307.

<sup>694</sup> H. J. Reich, F. Chow, and S. L. Peake, *Synthesis*, 1978, 299.

<sup>695</sup> J. L. Kice and T. W. S. Lee, *J. Am. Chem. Soc.*, 1978, **100**, 5094.

<sup>696</sup> D. H. R. Barton, A. G. Brewster, R. A. H. F. Hui, D. J. Lester, S. V. Ley, and T. G. Back, *J. Chem. Soc., Chem. Commun.*, 1978, 952.

<sup>697</sup> D. H. R. Barton, R. A. H. F. Hui, D. J. Lester, and S. V. Ley, *Tetrahedron Lett.*, 1979, 3331.

<sup>698</sup> D. H. R. Barton, N. J. Cussans, and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 1978, 393.

<sup>699</sup> M. Shimizu, R. Takeda, and I. Kuwajima, *Tetrahedron Lett.*, 1979, 419.

<sup>700</sup> M. Uchino, K. Suzuki, and M. Sekiya, *Chem. Pharm. Bull.*, 1979, **27**, 1199.

<sup>701</sup> K. Oka and S. Hara, *J. Org. Chem.*, 1978, **43**, 4533.

<sup>702</sup> L. A. Carpino and J. R. Williams, *J. Org. Chem.*, 1979, **44**, 1177.

<sup>703</sup> E. Wenschuh, C. Steyer, and G. Baer, *Z. Chem.*, 1979, **19**, 211.

<sup>704</sup> A. Hessing, M. Jaspers, and I. Schwermann, *Chem. Ber.*, 1979, **112**, 2903.

<sup>705</sup> J. P. Bleeker and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, 1979, **98**, 120.

<sup>706</sup> M. Furukawa, T. Okawara, Y. Noguchi, and M. Nishikawa, *Synthesis*, 1978, 441.

<sup>707</sup> G. Lonchambon, A. Delacroix, R. Garreau, J. N. Veltz, and J. Petit, *Bull. Soc. Chim. Fr., Part 2*, 1979, 541.



115 °C)  $\rightarrow$   $\text{H}_2\text{C}=\text{CHCH}_2\text{S}(\text{O})\text{OR}$ ],<sup>708</sup> and by electrolysis of arenethiols or disulphides in AcOH with an alcohol<sup>709</sup> include specific points of interest. Thus the methanolysis of  $\text{R}^1\text{R}^2\text{CHS}(\text{O})\text{Cl}$  proceeds by nucleophilic substitution at S, not *via* the sulphine (see ref. 702 for contrast),<sup>704</sup> and  $\text{Bu}^t\text{S}(\text{O})\text{ONHCONR}_2$ , prepared from the sulphinyl chloride and  $\text{R}_2\text{NCONHOH}$ , rearranges to  $\text{Bu}^t\text{SO}_2\text{NHCONR}_2$  *via* a radical cage mechanism,<sup>705</sup> as demonstrated by  $^1\text{H}$  c.i.d.n.p. Three different methods of effecting the overall condensation of a sulphinic acid with an alcohol have been compared.<sup>706</sup>

Alkyl ethenesulphinates,  $\text{H}_2\text{C}=\text{CHS}(\text{O})\text{OR}$ , are obtained by elimination reactions of the  $\beta$ -halogenoethyl or  $\beta$ -tosyloxyethyl analogues.<sup>707</sup> A redox-disproportionation mechanism<sup>710</sup> accounts for the formation of benzils and diaryl disulphides, together with arenesulphonates and thiolsulphonates, through base-catalysed or thermal decomposition of desyl arenesulphinates. Other mechanistic studies deal with solvolysis<sup>711</sup> and stereochemical aspects of displacements at sulphinyl sulphur (see also the 'Sulphoxides' section), which occurs with inversion with higher alkyl esters, but with racemization in the case of methyl esters.<sup>712</sup> Evidence for the general inversion mechanism is provided by the slower  $^{18}\text{O}$ - $^{16}\text{O}$  exchange compared with the rate of racemization of alkyl arenesulphinates by  $(\text{Cl}_3\text{CCO})_2\text{O}$ ,<sup>713</sup> and this mechanism is relied on in the synthesis of chiral sulphoxides from sulphinates.<sup>490</sup>

Further examples of the use of propargyl sulphinates (see Vol. 5, p. 55) in syntheses of allenes by reaction with organocopper reagents  $(\text{RCuBr})\text{MgX} \cdot \text{LiBr}^{714-717}$  include a synthesis of (*R*)-allenes<sup>714</sup> and one of vinyl-allenes.<sup>716</sup>

The role played by benzeneseleninic acid or by phenylseleninyl chloride in promoting the rearrangement of *N*-aryl-benzohydroxamic acids  $\text{PhCONArOH}$  to *p*-hydroxy-benzanilides relies on the formation of seleninate or selenenate esters, respectively, followed by Claisen-type shifts to *ortho*- and then *para*-positions.<sup>718</sup>

**Sulphinamides.**—A simple synthesis, based on the oxidation of sulphenamides<sup>719</sup> using *N*-chlorosuccinimide and aqueous  $\text{KHCO}_3$ , involves *S*-chlorosulphonium ion intermediates. Oxidation of *N*-acetyl-sulphenamides with *m*-chloroperoxybenzoic acid gives the corresponding alkyl- or aryl-sulphinyl-acetamides.<sup>720</sup>

## 16 Sulphonic and Selenonic Acids, and their Derivatives

**Preparation of Sulphonic Acids.**—The main topics under this heading in the recent literature are very much the same as for the past ten years or more, involving

<sup>708</sup> E. Wenschuh, R. Fahsl, and P. Weingate, *Z. Chem.*, 1978, **18**, 379.

<sup>709</sup> J. Nokami, Y. Fujita, and R. Okawara, *Tetrahedron Lett.*, 1979, 3659.

<sup>710</sup> W. Mueller and K. Schank, *Chem. Ber.*, 1978, **111**, 2870.

<sup>711</sup> S. Braverman and H. Manor, *Phosphorus Sulfur*, 1976, **2**, 213.

<sup>712</sup> M. Mikolajczyk, J. Drabowicz, and H. Slebocka-Tilk, *J. Am. Chem. Soc.*, 1979, **101**, 1302.

<sup>713</sup> J. Drabowicz and S. Oae, *Tetrahedron*, 1978, **34**, 63.

<sup>714</sup> H. Westmijze and P. Vermeer, *Tetrahedron Lett.*, 1979, 4101.

<sup>715</sup> H. Kleijn, C. J. Elsevier, H. Westmijze, J. Meijer, and P. Vermeer, *Tetrahedron Lett.*, 1979, 3101.

<sup>716</sup> H. Kleijn, H. Westmijze, K. Kruihof, and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 1979, **98**, 27.

<sup>717</sup> P. Vermeer, H. Westmijze, H. Kleijn, and L. A. Van Dijk, *Recl. Trav. Chim. Pays-Bas*, 1978, **97**, 56.

<sup>718</sup> T. Frejd and K. B. Sharpless, *Tetrahedron Lett.*, 1978, 2239.

<sup>719</sup> M. Haake, H. Gebbing, and H. Benack, *Synthesis*, 1979, 97.

<sup>720</sup> D. N. Harpp, D. F. Mullins, K. Stelieth, and I. Triassi, *J. Org. Chem.*, 1979, **44**, 4196.

aromatic substitution through various strategies, including irradiation of mixtures of hydrocarbon,  $\text{SO}_2$ , and  $\text{O}_2$ .<sup>721</sup> Sulphonic acids have also been obtained by the oxidation of 2-thiouracils with  $\text{MnO}_4^-$ ;<sup>722</sup> the electrofluorination of sulpholene to give  $\text{C}_4\text{F}_9\text{SO}_2\text{F}$  and perfluorosulpholene, which gives  $\text{H}(\text{CF}_2)_4\text{SO}_3\text{H}$  on alkaline hydrolysis;<sup>723</sup> and by bisulphite-addition routes [formation of an anionic  $\sigma$ -complex between 2,4,6-( $\text{NO}_2$ )<sub>3</sub> $\text{C}_6\text{H}_2\text{NMeCH}_2\text{CH}_2\text{OH}$  and  $\text{HSO}_3^-$ ;<sup>724</sup> and the formation of mixtures of  $\text{ArCH}(\text{NH}_2\text{R})\text{SO}_3^-$  and  $\text{ArCH}(\text{OH})\text{SO}_3^- \text{NH}_3\text{R}^+$  from Schiff bases with  $\text{H}_2\text{SO}_3$ <sup>+</sup>]. Long-chain alkanesulphonic acids  $\text{Me}(\text{CH}_2)_{11}\text{CH}_2\text{SO}_3\text{H}$  were obtained from the bromide and  $\text{H}_2\text{NC}(^{35}\text{S})\text{NH}_2$ , followed by oxidation.<sup>726</sup>

In contradiction to other reports claiming a cycloaddition mechanism, a sulphinylamine gives an  $\alpha$ -amino-sulphonic acid  $\text{R}^1\text{NHCHR}^2\text{SO}_3\text{H}$  with aldehydes through successive hydrolysis and then condensation and bisulphite-addition reactions.<sup>727</sup>

**Additional Bibliography:** Y. Muramoto, H. Asakura, and H. Suzuki, *Nippon Kagaku Kaishi*, 1979, 297 [o- and p- $\text{IC}_6\text{H}_4\text{OEt}$  disproportionate during sulphonation with >80%  $\text{H}_2\text{SO}_4$ , yielding 2,4-di-iodophenetole together with phenolesulphonic acids and their iodo-homologues]; F. P. DeHaan, W. D. Covey, G. L. Delker, N. J. Baker, J. F. Feigon, K. D. Miller, and E. D. Stelter, *J. Am. Chem. Soc.*, 1979, **101**, 336 [studies of Olah's  $\pi$ -complex mechanism]; E. N. Krylov, *Zh. Org. Khim.*, 1978, **48**, 2475 [steric interactions determining *ortho/para* ratios in sulphonation]; A. Braendstroem, G. Strandlund, and P. O. Lagerstroem, *Acta Chem. Scand., Sect. B*, 1979, **33**, 567 [kinetics of sulphonation of o-alkyl-phenols by  $\text{ClSO}_3\text{H}$ ]; P. Sartori and G. Bauer, *J. Fluorine Chem.*, 1978, **12**, 203 and 1979, **14**, 201 [sulphonation, in liquid  $\text{SO}_3$ , of various polyfluorobenzenes to mono-, di-, and tri-sulphonic acids]; T. Shimura and E. Manda, *Nippon Kagaku Kaishi*, 1978, 1588 (*Chem. Abstr.*, 1979, **90**, 121 275) [contrary to an early report that anthracene with  $\text{SO}_3$  and pyridine gives only anthracene-1-sulphonic acid, the products are 2- (4%), 1- (14%), 1,5-di- (10%), 1,8-di (60%), and 2,6- and 2,7-di-sulphonic acids (12%)]; P. K. Maarsen, R. Bregman, and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1863 [*m*- $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$  gives 2,5-di-, 2,4,5-tri-, and 2,3,4,6-tetra-sulphonic acids]; ref. 728 [ $\text{CF}_3\text{C}(\text{OEt})=\text{CF}_2 + \text{SO}_3 \rightarrow \text{CF}_3\text{COCF}_2\text{SO}_3\text{H}$ ].

**Reactions of Sulphonic and Selenonic Acids.**— $\text{CF}_3\text{COCF}_2\text{SO}_3\text{H}$  is a very strong acid, adding readily to  $\text{F}_2\text{C}=\text{CF}_2$  below 0 °C and yielding esters with trifluorovinyl ethers.<sup>728</sup> Desulphonation of aminobenzenesulphonic acids can be brought about in  $\text{CF}_3\text{SO}_3\text{H}$  if electron-donating groups are located *ortho* or *para* to the sulphonic acid group.<sup>729</sup> Photolysis of sodium anthracene-9-sulphonate produces both desulphonylation (9-anthranol anion +  $\text{SO}_2$ ) and desulphonation (anthracene +  $\text{SO}_3$ ).<sup>730</sup>

A useful practical study<sup>731</sup> has shown that arenesulphonic acids can be extracted from aqueous solutions into immiscible organic solvents as ion-pairs with amines.

The propensity for selenonic acids to react as oxidizing agents has been known for a long time, but this has been regarded more as an interesting contrast between

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<sup>722</sup> F. Freeman, D. L. Bond, S. M. Chernow, P. A. Davidson, and E. M. Karchefski, *Int. J. Chem. Kinet.*, 1978, **10**, 911.

<sup>723</sup> H. Buerger, F. Heyder, G. Pawelke, and H. Niederprum, *J. Fluorine Chem.*, 1979, **13**, 251.

<sup>724</sup> G. F. Bernasconi and H.-C. Wang, *Int. J. Chem. Kinet.*, 1979, **11**, 375.

<sup>725</sup> D. R. Clark and P. Miles, *J. Chem. Res. (S)*, 1978, 124.

<sup>726</sup> A. J. Taylor, A. H. Olavesen, and C. James, *J. Labelled Compd. Radiopharm.*, 1978, **14**, 249.

<sup>727</sup> J. Mirek and S. Rachwal, *Phosphorus Sulfur*, 1977, **3**, 333.

<sup>728</sup> C. G. Krespan, *J. Org. Chem.*, 1979, **44**, 4924.

<sup>729</sup> E. E. Gilbert, *Phosphorus Sulfur*, 1977, **3**, 7.

<sup>730</sup> Y. Izawa, N. Suzuki, A. Inoue, K. Ito, and T. Ito, *J. Org. Chem.*, 1979, **44**, 4581.

<sup>731</sup> A. Brandstrom and G. Strandlund, *Acta Chem. Scand., Ser. B*, 1978, **32**, 489.

the sulphonic and selenonic acids rather than a property to be exploited in synthesis. The selective reactivity of *p*-ClC<sub>6</sub>H<sub>4</sub>SeO<sub>3</sub>H is shown in its reactions with alkyl sulphides, yielding sulphoxides and the corresponding seleninic acid, which oxidizes further sulphide to sulphoxide even more readily if acid is present.<sup>732</sup>

**Sulphonyl Halides.**—A novel synthesis exploiting C—O bond cleavage of a sulphonate [ROH → ROSO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup> X<sup>-</sup> → RSC(NH<sub>2</sub>)=NH<sub>2</sub><sup>+</sup> X<sup>-</sup> → RSO<sub>2</sub>Cl]<sup>733</sup> contrasts with an example illustrating standard methods (RCHFCI → RCHFSC<sub>6</sub>H<sub>5</sub> → RCHF<sub>2</sub>SO<sub>2</sub>Cl),<sup>734</sup> Cl<sub>2</sub> plus H<sub>2</sub>O being used in the last step in both cases. ‘Sulphochlorination’ of alkanes, using SO<sub>2</sub> and Cl<sub>2</sub> at -20 °C, gives mixtures of alkanesulphonyl chlorides in ratios that are characteristic of free-radical attack.<sup>735</sup> ClSO<sub>3</sub>H is also used in the synthesis of sulphonyl chlorides, a typical example being the substitution of dichlorophenols.<sup>736</sup> Sulphonyl fluorides have been prepared from sulphonyl chlorides, using ZnF<sub>2</sub> or AgF at 100 °C,<sup>737</sup> and the reverse process has been accomplished, using HCl and AlCl<sub>3</sub>.<sup>738</sup> Electrofluorinolysis of sulphones has also been established (e.g.<sup>723</sup> sulpholene → C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>F).

Some unusual reactions of aliphatic sulphonyl chlorides can be traced to sulphene formation, e.g. MeSO<sub>2</sub>Cl + Et<sub>3</sub>N in MeCN → H<sub>2</sub>C=SO<sub>2</sub> → tetramer → (2-py)O<sub>3</sub>SCH(SO<sub>2</sub>Me)SO<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>Me (2-py = 2-pyridyl),<sup>739a</sup> and R<sup>1</sup>R<sup>2</sup>CHSO<sub>2</sub>Cl + CH<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub> → Me<sub>2</sub>NCH<sub>2</sub>CR<sup>1</sup>R<sup>2</sup>SO<sub>2</sub>NMe<sub>2</sub> and other products.<sup>739b</sup> Unexpected transformations of functional groups have been observed in reactions with sulphonyl chlorides, such as a synthesis of di-*t*-butyl ether (a compound which cannot be synthesized by the classical Williamson synthesis) from Bu<sup>-</sup>O<sup>-</sup> Na<sup>+</sup> and RSO<sub>2</sub>Cl, together with 2-methylpropene, which proceeds *via* the sulphonate ester.<sup>740</sup> CF<sub>3</sub>SO<sub>2</sub>Cl acts as a mild chlorinating agent for carbon acids [RCH(CO<sub>2</sub>Et)<sub>2</sub> → RCCl(CO<sub>2</sub>Et)<sub>2</sub>], as well as a powerful sulphonylation agent.<sup>741</sup> A novel displacement of the chlorosulphonyl group during an attempted reduction with lithium aluminium hydride has been described (RSO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>Cl → RSO<sub>2</sub>Et rather than the expected RSO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH).<sup>742</sup>

Sulphonyl fluorides are stable compounds and are reluctant to undergo displacement of a halogen atom; H<sub>2</sub>C=CHSO<sub>2</sub>F accordingly gives derivatives of ethanesulphonyl fluoride with active-methylene compounds, amines, and thiols.<sup>743</sup> Photolysis of XCOCF<sub>2</sub>SO<sub>2</sub>F (X = Cl, Br, or I) gives XCF<sub>2</sub>SO<sub>2</sub>F.<sup>744</sup>

<sup>732</sup> L. G. Faehl and J. L. Kice, *J. Org. Chem.*, 1979, **44**, 2357.

<sup>733</sup> J. F. King and M. Aslam, *Synthesis*, 1980, 285.

<sup>734</sup> G. G. I. Moore, *J. Org. Chem.*, 1979, **44**, 1708.

<sup>735</sup> H. Berthold, H. H. Huenecke, D. Burghardt, M. Hampel, D. Helwig, F. D. Kopinke, S. Krebes, H. Niegel, and W. Pritzkow, *J. Prakt. Chem.*, 1979, **321**, 279; F. D. Kopinke, W. Kroeckel, W. Pritzkow, K. Mathew, and R. Radeaglia, *ibid.*, p. 107.

<sup>736</sup> R. J. Cremlyn and T. Cronje, *Phosphorus Sulfur*, 1979, **6**, 413.

<sup>737</sup> I. I. Maletina, A. A. Mironova, T. I. Savina, and Yu. L. Yagupolskii, *Zh. Org. Khim.*, 1979, **15**, 2416.

<sup>738</sup> A. F. Eleev, G. A. Sokolskii, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2084.

<sup>739</sup> (a) J. S. Grossert, M. M. Bharadwaj, R. F. Langler, T. S. Cameron, and R. E. Cordes, *Can. J. Chem.*, 1978, **56**, 1183; (b) H. Boehme and G. Pindur, *Chem. Ber.*, 1978, **111**, 3294.

<sup>740</sup> H. Masada, T. Yonemitsu, and K. Hirota, *Tetrahedron Lett.*, 1979, 1315.

<sup>741</sup> G. H. Hakimelahi and G. Just, *Tetrahedron Lett.*, 1979, 3643, 3645.

<sup>742</sup> H. O. Fong, W. R. Hardstaff, D. G. Kay, R. F. Langler, R. H. Morse, and D. N. Sandoval, *Can. J. Chem.*, 1979, **57**, 1206.

<sup>743</sup> J. J. Krutak, R. D. Burpitt, W. H. Moore, and J. A. Hyatt, *J. Org. Chem.*, 1979, **44**, 3847.

<sup>744</sup> N. D. Volkov, V. P. Nazaretyan, and L. M. Yagupolskii, *Synthesis*, 1979, 972.

Routine mechanistic studies (solvolysis of  $\text{PhCH}_2\text{SO}_2\text{Cl}$ <sup>745</sup> and of  $\text{ArSO}_2\text{Cl}$  or  $\text{ArSO}_2\text{Br}$ ;<sup>746</sup> aminolysis of arenesulphonyl chlorides<sup>747</sup> and of toluene-*p*-sulphonyl bromide, catalysed by imidazole;<sup>748</sup> and the reaction of  $\text{ArSO}_2\text{Cl}$  with phenols<sup>749</sup>) have been reported.

**Sulphonate Esters.**—Most methods of preparation are straightforward, employing sulphonyl halides (phase-transfer conditions are advantageous<sup>750</sup> for  $\text{ArSO}_2\text{Cl} + \text{RCH}_2\text{OH}$ ), and less familiar sulphonyl peroxides continue to be promoted ( $\text{ArCH}_2\text{NH}_2 \rightarrow O\text{-sulphonyl-hydroxylamines} \rightarrow \text{imines}$ ).<sup>751</sup> More attention is paid here to the recent literature on trifluoromethanesulphonates, whose preparations, though using conventional types of reagent, *e.g.*  $(\text{CF}_3\text{SO}_2)_2\text{O}$ ,<sup>752–754</sup>  $\text{RSO}_2\text{OCOCF}_3$ ,<sup>755</sup> or  $\text{CF}_3\text{SO}_2\text{OCOCF}_3$ ,<sup>756</sup> are frequently accompanied by unusual features. Vinyl triflates can be prepared in one step from ketones,  $(\text{CF}_3\text{SO}_2)_2\text{O}$ , and 2,6-di-*t*-butyl-4-methylpyridine,<sup>752</sup> and 1-(ethynyl)vinyl triflates from protected ethynyl ketones  $\text{R}_2\text{CHCOC}\equiv\text{CSiMe}_3$ .<sup>753</sup> Non-enolizable cycloalkanones give 1,1-bis-triflated cycloalkanes under these conditions,<sup>754</sup> but 2-norcaranone yields 2-(2-triflyloxyethyl)cyclohex-1-enyl triflate through sulphonylation of an enol accompanied by opening of a cyclopropane ring.<sup>754</sup> Forcing conditions (200 °C, for 24 h, in benzene) are required for the preparation of  $\text{CF}_3\text{SO}_3\text{CF}_3$  from  $\text{CF}_3\text{SO}_3\text{Ag}$  and  $\text{CF}_3\text{I}$ .<sup>758</sup>

While reductive cleavage of a protected 3-*O*-triflyl-hexofuranose by irradiation in the presence of a trace of Na in liquid  $\text{NH}_3$  involves C—O bond homolysis,<sup>757</sup> the first example of  $\text{SO}_2\text{—O}$  bond fission of an alkyl triflate has been provided in a use of  $\text{CF}_3\text{SO}_3\text{CF}_3$  for the synthesis of trifluoromethyl sulphones, using an enamine as the alkylation agent.<sup>758</sup> Conversion of a methyl alkanesulphonate into the corresponding silyl ester, thence into the mixed anhydride  $\text{RSO}_2\text{OCOCF}_3$ , has been reported,<sup>755</sup> as an alternative to the direct preparation from  $\text{CF}_3\text{SO}_3\text{H}$  and TFA with a three-fold excess of  $\text{P}_4\text{O}_{10}$ .<sup>756</sup> Cleavage of a C—O bond is illustrated in the first use of a sulphonyloxy moiety as the leaving group in the nucleophilic substitution of pyrimidines,<sup>759</sup> in reductive displacement by  $\text{NaBH}_4$  in aprotic solvents (*e.g.* DMSO, HMPA, and sulpholane),<sup>760</sup> and in the conversion of toluene-*p*-sulphonates into peroxides by  $\text{KO}_2$  ( $\text{ROTs} + \text{O}_2^- \rightarrow \text{ROO}^- \rightarrow \text{ROO}^-$

<sup>745</sup> I. Lee and W. K. Kim, *Taehan Hwahak Hoechi*, 1978, **22**, 111.

<sup>746</sup> B. G. Gnedin and S. N. Ivanov, *Zh. Org. Khim.*, 1978, **14**, 1497.

<sup>747</sup> B. Giese and K. Heuck, *Chem. Ber.*, 1978, **111**, 1384.

<sup>748</sup> V. G. Zaslavskii, L. M. Litvinenko, T. N. Solomoichenko and V. A. Savelova, *Ukr. Khim. Zh.*, 1980, **46**, 169.

<sup>749</sup> R. V. Vizgert and N. N. Maksimenko, *Zh. Obshch. Khim.*, 1978, **48**, 2776.

<sup>750</sup> W. Szeja, *Synthesis*, 1979, 822.

<sup>751</sup> R. V. Hofmann and E. L. Belfoure, *J. Am. Chem. Soc.*, 1979, **101**, 5687.

<sup>752</sup> P. J. Stang and W. Treptow, *Synthesis*, 1980, 283.

<sup>753</sup> P. J. Stang and T. E. Fisk, *Synthesis*, 1979, 438.

<sup>754</sup> A. Garcia Fraile, A. Garcia Martinez, A. Herrera Fernandez, and J. M. Sanchez Garcia, *An. Quim.*, 1979, **75**, 723; A. Garcia Martinez, I. Espada Rios, and E. Teso Vilar, *Synthesis*, 1979, 382.

<sup>755</sup> A. G. Shipov and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1979, **49**, 1915.

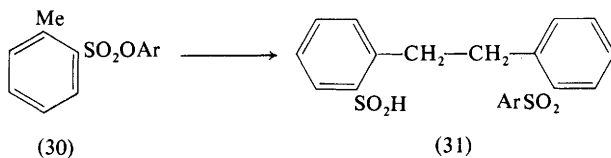
<sup>756</sup> T. R. Forbus and J. C. Martin, *J. Org. Chem.*, 1979, **44**, 313.

<sup>757</sup> T. Tsuchiya, F. Nakamura, and S. Umezawa, *Tetrahedron Lett.*, 1979, 2805.

<sup>758</sup> Y. Kobayashi, T. Yoshida, and I. Kumadaki, *Tetrahedron Lett.*, 1979, 3865.

<sup>759</sup> S. R. James, *J. Chem. Res. (S)*, 1979, 125.

<sup>760</sup> R. O. Hutchins, D. Kandasamy, F. Dux, C. A. Maryanoff, D. Rotstein, B. Goldsmith, W. Burgoyne, F. Cistone, J. Dalessandro, and J. Puglis, *J. Org. Chem.*, 1978, **43**, 2259.



→ ROOR).<sup>761</sup> Cleavage of a C–S bond {Ar<sup>1</sup>SO<sub>2</sub>OAr<sup>2</sup> → Ar<sup>1</sup>–Ar<sup>1</sup> through the use of PhMgBr + [(Ph<sub>3</sub>P)NiCl<sub>2</sub>]<sup>762</sup> has been described, and an alternative form of cleavage [(30) → (31)] is brought about with Bu<sup>n</sup>Li at –72 °C.<sup>763</sup> The displacement reaction of PhN(O)=NOTs with PhCH<sub>2</sub>MgCl did not occur quite as expected, giving PhN(O)=NCHPhCHPhN=N(O)Ph, and is presumed to involve radical intermediates.<sup>764</sup>

Routine mechanistic studies (solvolysis of 1-cyclobutenyl nonafluorobutanoate *via* vinyl cations;<sup>765</sup> hydrolysis of phenyl methanesulphonates and phenylsulphonylacetates,<sup>766</sup> alkyl alkanesulphonates,<sup>767</sup> and toluene-*p*-sulphonylmethyl benzenesulphonate;<sup>768</sup> and arenethiolysis of methyl sulphonates<sup>769</sup>) have been reported.

**Sulphonyl Hypochlorites.**—Further work (see Vol. 5, p. 61) has revealed that CF<sub>3</sub>SO<sub>2</sub>OCl adds readily to alkenes and displaces Cl or Br from alkyl halides to give triflates, but the potential of this class of compound is severely limited by the danger of explosions when in contact with readily oxidized compounds.<sup>770</sup>

**Sulphonamides.**—Oxidative amidation of sulphinic acids gives primary sulphonamides, though the severe reaction conditions (18% oleum with NaN<sub>3</sub>)<sup>771</sup> restrict the potential of this route. Selective aminosulphonation of anilines, using ClSO<sub>2</sub>NCO and AlCl<sub>3</sub>, depends on the formation of cyclic *N*-carbamoylsulphonamides.<sup>772</sup> More conventional preparative methods are covered in the conversion of naphthalene-1-thiol into 4-(2-hydroxyethylsulphonyl)naphthalene-1-sulphonamide (an assessment of standard routes has been made),<sup>773</sup> and in the preparation of alkanesulphonyl-<sup>774</sup> and trifluoromethanesulphonyl-hydroxylamines<sup>775</sup> from hydroxylamines and the sulphonyl chlorides. In the latter study,<sup>774,775</sup> conditions favouring *N*- rather than *O*-sulphonylation were established.

<sup>761</sup> R. A. Johnson, E. G. Nidy, and M. V. Merritt, *J. Am. Chem. Soc.*, 1978, **100**, 7960.

<sup>762</sup> E. Wenkert, E. L. Michelotti, and C. S. Swindell, *J. Am. Chem. Soc.*, 1979, **101**, 2246.

<sup>763</sup> W. E. Truce and B. Van Gemert, *J. Am. Chem. Soc.*, 1978, **100**, 5525.

<sup>764</sup> V. N. Yandovskii, U. Traore, I. V. Tselinskii, and E. Yu. Dobrodumova, *Zh. Org. Khim.*, 1978, **14**, 2014.

<sup>765</sup> M. Hanack, E. J. Carnahan, A. Krowczynski, W. Schoberth, L. R. S. Subramanian, and K. Subramanian, *J. Am. Chem. Soc.*, 1979, **101**, 100.

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<sup>767</sup> Yu. G. Skrypnik, *Kinet. Katal.*, 1978, **19**, 1613.

<sup>768</sup> H. A. J. Holterman and J. B. F. N. Engberts, *J. Phys. Chem.*, 1979, **83**, 443.

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<sup>770</sup> Y. Katsuhara and D. D. DesMarteau, *J. Am. Chem. Soc.*, 1979, **101**, 1039.

<sup>771</sup> O. A. Radchenko, *Zh. Org. Khim.*, 1979, **15**, 2420.

<sup>772</sup> Y. Girard, J. G. Atkinson, and J. Rokach, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1043.

<sup>773</sup> G. H. Daub and T. W. Whaley, *J. Org. Chem.*, 1978, **43**, 4659.

<sup>774</sup> U. Hermann, M. Yaktapour, and C. Bleifert, *Z. Naturforsch., Teil B*, 1978, **33**, 574.

<sup>775</sup> V. Kellner and C. Bleifert, *J. Fluorine Chem.*, 1978, **12**, 249.

Bis(trifluoromethanesulphonyl)amides, though effective in C—C bond-forming reactions [ $\text{PhCH}_2\text{N}(\text{SO}_2\text{CF}_3)_2 + \text{Me}_2\text{CuLi} \rightarrow \text{PhCH}_2\text{Me}$ ; and the alkylation of malonates]<sup>776</sup> and other nucleophilic substitution reactions ( $\text{I}^-$  in HMPA  $\rightarrow$  iodides),<sup>777</sup> are susceptible to S—N bond cleavage by bases.<sup>777,778</sup> A novel anionic rearrangement, brought about by NaCN in HMPA at 140 °C, originates in this tendency to cleavage [ $\text{PhCH}_2\text{N}(\text{SO}_2\text{Ar})_2 \rightarrow \text{PhCH}_2\text{N}^-\text{SO}_2\text{Ar Na}^+ \rightarrow \text{PhCH}_2\text{NHAr} + \text{SO}_2$ ].<sup>778</sup> The stabilization of an amide anion by the sulphonyl group is responsible for the range of reactions of *N*-sodio-*N*-chloro-sulphonamides, Chloramine-T giving *N*-alkylation products (including *N*-sulphonyl-aziridines) with vinyl and allyl chlorides;<sup>779</sup> a remarkable double *ortho*-substitution reaction of *p*-( $\text{PhSO}_2\text{NH}$ )- $\text{C}_6\text{H}_4\text{NHSO}_2\text{Ph}$  by Chloramine-B gives 2,5-bis-(phenylsulphonylamino)-*NN'*-bis(phenylsulphonyl)-*p*-benzoquinoneimine.<sup>780</sup>

Cleavage of a sulphonamide to give amines is an essential element in the use of sulphonylation for protection of amines in synthesis. Cathodic reduction<sup>781</sup> and photolysis<sup>782,783</sup> continue to be explored, and though generally serviceable, side-products are often encountered. Photolysis of *N*-alkyl arenesulphonamides at 254 nm in ether gives products of both S—C and S—N bond cleavage ( $\text{ArH}$  and  $\text{ArSO}_3^- \text{R}_2\text{NH}_2^+$ ,  $\text{ArSO}_2\text{SAr}$ , and  $\text{ArSSAr}$ ).<sup>783</sup> *N*-Phenyl trifluoromethanesulphonamide undergoes cleavage into the imine and  $\text{CF}_3\text{SO}_2\text{H}$  by *N*-alkylation with an  $\alpha$ -bromo-ketone.<sup>784</sup> The rearrangement of sulphonanilides to *o*-methylamino-phenyl sulphones that is induced by sulphuric acid has been studied.<sup>785</sup>

**Sulphonyl Azides, Azosulphones, and Sulphonyl Isocyanates.**—The particular interest in sulphonyl azides lies in their thermolysis into singlet sulphonylnitrenes, and the products of their reactions with the solvent; thus alkylbenzenes and arenesulphonyl azides give azepines and aryl sulphonamides,<sup>786</sup> anthracene gives sulphonamides *via* aziridines,<sup>787</sup> and 3,5- $\text{Me}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{SO}_2\text{N}_3$  gives a variety of intramolecular cyclization and intermolecular substitution products.<sup>788</sup>

Thermolysis of phenylazo *p*-tolyl sulphone in the presence of toluene-*p*-sulphonyl iodide is a convenient method for generating sulphonyl radicals<sup>789</sup> ( $\text{PhN}=\text{N}-\text{SO}_2\text{C}_6\text{H}_4\text{Me}-p + p-\text{MeC}_6\text{H}_4\text{SO}_2\text{I} \rightarrow \text{PhI} + \text{N}_2 + p-\text{MeC}_6\text{H}_4\text{SO}_2\cdot$ ).

The stable 1,4-dipoles  $\text{R}^1\text{SO}_2\text{N}^-\text{CONMe}^+\text{(SMe)NMe}_2$  are formed by addition of *S*-methyl-isothioureas to sulphonyl isocyanides.<sup>790</sup>

<sup>776</sup> P. Müller and N. T. M. Phuong, *Tetrahedron Lett.*, 1978, 4727.

<sup>777</sup> R. S. Glass and R. J. Swedo, *J. Org. Chem.*, 1978, **43**, 2291.

<sup>778</sup> P. Müller and N. T. M. Phuong, *Helv. Chim. Acta*, 1979, **62**, 494.

<sup>779</sup> N. A. Rybakova, L. N. Kiseleva, and V. I. Dostovalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2571.

<sup>780</sup> N. P. Bezverkhii and M. M. Kremlev, *Zh. Org. Khim.*, 1978, **14**, 2596.

<sup>781</sup> R. Kossai, G. Jeminet, and J. Simonet, *Electrochim. Acta*, 1977, **22**, 1395.

<sup>782</sup> J. A. Pincock and A. Jurgens, *Tetrahedron Lett.*, 1979, 1029.

<sup>783</sup> J.-P. Pete and C. Portella, *J. Chem. Res. (S)*, 1979, 20.

<sup>784</sup> R. J. Bergeron and P. G. Hoffman, *J. Org. Chem.*, 1979, **44**, 1835.

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<sup>786</sup> N. R. Ayyangar, M. V. Phatak, A. K. Purchitt, and B. D. Tilak, *Chem. Ind. (London)*, 1979, 853.

<sup>787</sup> J. G. Krause, *Chem. Ind. (London)*, 1978, 271.

<sup>788</sup> R. A. Abramovitch and S. Wake, *Heterocycles*, 1978, **11**, 377.

<sup>789</sup> C. M. M. da Silva Correa, *J. Chem. Soc., Perkin Trans. I*, 1979, 1519.

<sup>790</sup> E. Schaumann, E. Kausch, J. P. Imbert, and G. Adiwidjaja, *Chem. Ber.*, 1978, **111**, 1475.

## 17 Disulphides, Diselenides, and Ditetellurides

**Preparation.**—Many examples of the incidental formation of disulphides have been discussed in preceding sections, but few of these have undergone development as potential preparative methods, since there is no shortage of routes to these compounds. However, routes to unsymmetrical disulphides in particular, and from a wider range of starting materials, continue to be developed. Recent papers are collected at the end of this section, with brief details of their contents, where continuing development of known methods is concerned.

Aralkyl trimethylsilyl sulphides  $\text{RSSiMe}_3$  give disulphides with sulphenyl chlorides,<sup>628</sup> and symmetrical diselenides are formed from the selenium analogues with  $\text{I}_2$  ( $\text{PhSeSiMe}_3 \rightarrow \text{PhSeSePh} + \text{Me}_3\text{SiI}$ ).<sup>791</sup> The formation of unsymmetrical disulphides from steroidal  $\Delta^{1,4}$ -diene-3-thiones and 2-nitrobenzenesulphenyl chloride is in accordance with the concept of hard and soft acids and bases, the 'soft' thione nucleophile reacting with the 'soft' sulphenyl halide, but not with the 'hard' sulphonyl chloride.<sup>792</sup> The resulting  $\Delta^{1,3,5}$ -trienyl 2-nitrophenyl disulphides participate in thiol-disulphide exchange (see next section).

An interesting observation, that  $(\text{Bu}^n_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SR})_4]$  catalyses the oxidation of thiols to disulphides,<sup>793</sup> emerges from a study of this cluster as an analogue of the active site of non-haem iron-sulphur proteins. The adduct formed between thioacetamide and *p*-benzoquinone is capable of 'non-oxidative' formation of disulphides<sup>794</sup> from thiols; this is a curious reaction, possibly with some relevance to processes *in vivo* that involve flavins, but further work is required to determine the correct structure of the effective oxidant. Another unusual conversion of a thiol into the corresponding disulphide involves an arenesulphonyl chloride as reagent, with a three-fold excess of a thiol, in EtOH.<sup>795</sup> Benzenesulphinat anions are converted into disulphides with  $\text{EtOP}(\text{O})\text{H}_2$ .<sup>796</sup>

Full details of the preparation of symmetrical diselenides from aldehydes, with  $\text{NaBH}_4$  and  $\text{H}_2\text{Se}$  in the presence of an amine (see Vol. 5, p. 65), have now been published.<sup>797</sup> Symmetrical *o*-aminophenyl ditellurides are formed from *ortho*-mercuriated azobenzenes with tellurium(-II) or (-IV) salts.<sup>798</sup>

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<sup>791</sup> M. R. Detty, *Tetrahedron Lett.*, 1979, 4189.

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<sup>793</sup> T. Nagano, K. Yoshikawa, and M. Hirobe, *Tetrahedron Lett.*, 1980, **21**, 297.

<sup>794</sup> V. Horak and W. B. Manning, *J. Org. Chem.*, 1979, **44**, 120.

<sup>795</sup> D. Cipris and D. Pouli, *Synth. Commun.*, 1979, **9**, 207.

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<sup>797</sup> J. W. Lewicki, W. H. H. Gunther, and J. Y. C. Chu, *J. Org. Chem.*, 1978, **43**, 2672.

<sup>798</sup> R. E. Cobbleddick, F. W. B. Einstein, W. R. McWhinnie, and F. H. Musa, *J. Chem. Res. (S)*, 1979, 145.

E. S. Huyser and H.-N. Tang, *ACS Symp. Ser.*, No. 69, *Organic Free Radicals*, 1978, 25 [photo-oxidation of thiols sensitized by methylene blue]; F. Bottino, S. Foti, and S. Pappalardo, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1712 [*m*-dimethoxybenzene +  $\text{SCl}_2$  or  $\text{S}_2\text{Cl}_2$  in the presence of Fe gives linear polysulphides  $\text{ArS}_n\text{Ar}$  and  $\text{Ar}^1\text{SAr}^2\text{SAr}^1$ ]; W. Buder, *Z. Naturforsch., Teil B*, 1979, **34**, 790 [ $\{(\text{MeO})_3\text{Si}(\text{CH}_2)_3\}_n\text{S}_n$  ( $n = 1-4$ )]; L. Field and R. Ravichandran, *J. Org. Chem.*, 1979, **44**, 2624 [unsymmetrical *t*-alkyl disulphides through standard routes from thiols with  $\text{RSSO}_2\text{R}$  or  $\text{RSNO}$ ]; J. Lazar and E. Vinkler, *Acta Chim. Acad. Sci. Hung.*, 1979, **101**, 175 [disproportionation of sodium salts of thiolsulphonates in DMF]; Y. Yano, A. Kurushima, and W. Tagaki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2739 [ $\text{PhCH}_2\text{SCN} \rightarrow \text{PhSSPh}$  by  $\text{OH}^-$  in phase-transfer conditions]; ref. 805 [disulphides from trisulphides and  $(\text{RO})_3\text{P}$ ].

**Reactions of Disulphides, Diselenides, and Ditellurides.**—Cleavage of S—S bonds is the predominant reaction of disulphides, and earlier sections have covered the use of these compounds as sulphenylation agents. Thiol–disulphide interchange is a familiar example of this process, and the relative rates of the disulphide-forming step involving Ellman's reagent and 3-hydroxypropanethiol to give the mixed disulphide, and the slower ensuing equilibrium  $\text{R}^1\text{SSR}^2 + \text{R}^2\text{S}^- = \text{R}^2\text{SSR}^2 + \text{R}^1\text{S}^-$ , have been related to the electron-donating properties of the group  $\text{R}^2$ .<sup>799</sup> Thiolysis of bis-(*N*-phthalimido) disulphide is catalysed by amines.<sup>800</sup>

Pulse radiolysis of cystamine in aqueous solutions gives the anion radical  $\text{RSSR}^-$  as the first product, which undergoes cleavage into  $\text{RS}^\bullet$  and  $\text{RS}^-$ , from which a variety of products is formed, in proportions that are determined by the various additives.<sup>801</sup>

Extrusion of sulphur from disulphides<sup>802–804</sup> and trisulphides<sup>805</sup> gives sulphides and disulphides, respectively, by treatment with phosphines<sup>802, 803</sup> (a polymeric aminophosphine has been advocated<sup>802</sup>), phosphites,<sup>804, 805</sup> and  $\text{MeHgOAc}$ .<sup>804</sup> Ionic pathways continue to be preferred for these reactions,<sup>805</sup> and concurrent electrophilic and nucleophilic mechanisms are in operation, according to interpretations of kinetic data for the reaction with dimethyl disulphide.<sup>804</sup> A new view on nucleophilic attack is advanced in this work,<sup>804</sup> where the encounter involves the  $\sigma^*$  orbital of the S—S bond. Further support is given<sup>806</sup> by c.i.d.n.p. to a radical mechanism that involves  $\text{PhCH}_2\text{Se}^\bullet$  for the reaction of dibenzyl selenide with  $\text{Ph}_3\text{P}$ .<sup>806</sup> The process  $\text{PhTeTePh} + \text{RN}_2^+ \text{Cl}^- \rightarrow \text{RTeCl}_2\text{Ph}$ <sup>807</sup> in the presence of  $[\text{Cu}(\text{OAc})_2]$  may be more easily understood on this basis.

M.O. predictions, that dibenzyl disulphide is deprotonated faster than the corresponding sulphide, are supported by experiment. A rate factor of *ca.* 7.5 has been determined.<sup>808</sup>

## 18 Thiolsulphinates

Mild oxidation procedures that are used for the conversion of sulphides into sulphoxides (*m*-chloroperoxybenzoic acid<sup>809</sup> and 2-arylsulphonyl-3-aryl-

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<sup>805</sup> D. N. Harpp and R. A. Smith, *J. Org. Chem.*, 1979, **44**, 4140.

<sup>806</sup> G. Vermeersch, N. Febvay-Garot, S. Caplain, A. Couture, and A. Lablache-Combiere, *Tetrahedron Lett.*, 1979, 609.

<sup>807</sup> I. D. Sadekov and A. A. Maksimenko, *Zh. Org. Khim.*, 1978, **14**, 2620.

<sup>808</sup> S. Wolfe and D. Schirlin, *Tetrahedron Lett.*, 1980, **21**, 827.

<sup>809</sup> D. N. Harpp and A. Granata, *Synthesis*, 1978, 782.



oxaziridines<sup>484</sup>) have also been applied to the oxidation of disulphides to thiolsulphinates. Further oxidation to the thiolsulphonate has been noticed.<sup>809,818</sup>

Reactions of thiolsulphinates show a different profile from those for sulphoxides because of the tendency for nucleophilic S—S bond cleavage and protonation at sulphenyl sulphur to occur.<sup>810,811</sup> Acid-catalysed and dialkyl-sulphide-catalysed decomposition of PhS(O)SBU<sup>t</sup> in AcOH has as the rate-determining step the attack of the sulphide on the protonated sulphenyl sulphur atom,<sup>811</sup> giving PhSOH and R<sub>2</sub>SSBU<sup>t</sup>. Other reactions (PhSOH → PhSSR<sub>2</sub> → further intermediates) account for the eventual products, *i.e.* PhSSBU<sup>t</sup> and PhSO<sub>2</sub>SPh. The thiolsulphonate is invariably formed through a similar pathway in other reactions [R<sup>1</sup>S(O)SR<sup>2</sup> + Cl<sub>3</sub>CSCl → R<sup>1</sup>SO<sub>2</sub>SR<sup>1</sup> + R<sup>2</sup>SSCCl<sub>3</sub> + R<sup>2</sup>SCl<sup>812</sup>].

Oxidation of disulphides and thiolsulphinates with excess N<sub>2</sub>O<sub>4</sub> gives mixtures of thiolsulphonates, indicating S—S bond cleavage into sulphenyl and sulphinyl nitrites and nitrates, followed by recombination.<sup>813</sup>

Pummerer reactions with β-keto-sulphoxides have been shown to involve thiolsulphinates (see Vol. 5, p. 37). Further studies of the Pummerer reaction<sup>814</sup> of <sup>13</sup>C- and <sup>18</sup>O-labelled benzyl phenylmethanethiolsulphonate [PhCH<sub>2</sub>S(O)SCH<sub>2</sub>Ph + Ac<sub>2</sub>O → PhCH<sub>2</sub>S(O)CH(SAc)Ph as a 1:1 *erythro:threo* mixture] have led to a revised mechanism in which cleavage into the sulphenic acid and thiobenzaldehyde occurs. This initial cleavage is reversible, but the alternative recombination, PhCH<sub>2</sub>SOH + PhCHS → PhCH<sub>2</sub>S(O)CH(SH)Ph, accounts well for the scrambling of the label and the stereochemistry. In contrast, thiolsulphinates give transient mixed sulphinic anhydrides RS(O)OCOCF<sub>3</sub> with TFAA, as suggested by trapping by alkenes to give β-trifluoroacetoxy-alkyl sulphides.<sup>815</sup>

## 19 α-Disulphoxides

A new item of indirect evidence for the existence of these compounds as reaction intermediates<sup>816</sup> has been reported in radical-scavenging and spin-trapping experiments for the reaction of an aryl arenethiolsulphinates with AcOOH. The generation in this system of arenethylsulphinyl radicals from cleavage of an α-disulphoxide provides the best interpretation of the mode of formation of products derived from the arenethylsulphonyl radicals, and is in support of earlier conclusions by Kice and Oae. A review<sup>817</sup> of this earlier work, together with other reactions (hydrolysis of thiolsulphinates, and oxidation of sulphenylnitrites to thiolsulphonates with N<sub>2</sub>O<sub>4</sub>) has appeared.

## 20 Thiolsulphonates

These are stable oxidation products of disulphides, and can be reached by oxidation of disulphides with *m*-chloroperoxybenzoic acid<sup>809,818</sup> (RCH<sub>2</sub>SSPh gives

<sup>810</sup> J. L. Kice and C.-C. A. Liu, *J. Org. Chem.*, 1979, **44**, 1918.

<sup>811</sup> T.-L. Ju, J. L. Kice, and C. G. Venier, *J. Org. Chem.*, 1979, **44**, 610.

<sup>812</sup> J. Pintye, G. Stajer, and E. Vinkler, *Acta Chim. Acad. Sci. Hung.*, 1977, **95**, 307.

<sup>813</sup> S. Oae, D. Fukushima, and Y. H. Kim, *Chem. Lett.*, 1978, 279.

<sup>814</sup> N. Furukawa, T. Morishita, T. Akasaka, S. Oae, and K. Uneyama, *Tetrahedron Lett.*, 1978, 1567.

<sup>815</sup> N. Furukawa, T. Morishita, T. Akasaka, and S. Oae, *Tetrahedron Lett.*, 1979, 3973.

<sup>816</sup> B. C. Gilbert, B. Gill, and M. J. Ramsden, *Chem. Ind. (London)*, 1979, 283.

<sup>817</sup> S. Oae, *Kagaku (Kyoto)*, 1978, **33**, 240 (*Chem. Abstr.*, 1978, **89**, 23 853).

<sup>818</sup> A. K. Bhattacharya and A. G. Hortmann, *J. Org. Chem.*, 1978, **43**, 2728.

$\text{RCH}_2\text{SO}_2\text{SPh}^{818}$ ) or from thiolsulphinates with  $\text{NaIO}_4^{819}$  (see also preceding sections of this Chapter). Hydrolysis and other reactions that generate sulphenic acids [ $\text{RS(O)CO}_2\text{R} + \text{HCl} \rightarrow \text{ClCO}_2\text{R} + \text{RSSR} + \text{RSO}_2\text{SR}$ ,<sup>820</sup> and  $\text{ArSBr} + \text{OH}^- \rightarrow \text{ArSSAr}$ ,  $\text{ArSR}$ , and  $\text{RSSO}_3^-$ , *via* a thiolsulphonate;<sup>821</sup> see also the 'Sulphenic Acids' section] commonly lead to thiolsulphonates. Parent salts  $\text{ArSO}_2\text{S}^- \text{M}^+$  are readily prepared.<sup>822</sup>

Thiolsulphonates react as typical sulphenylation reagents towards nucleophiles,<sup>810</sup> and their use in the synthesis of sulphides has been reviewed earlier in this Chapter. Sulphenylation of dithiocarboxylate anions [ $\text{RC(S)}^- \rightarrow \text{RC(S)(S)SSMe}$ ] has been demonstrated.<sup>823</sup> A novel related group of compounds  $\text{R}^1\text{SSSO}_2\text{R}^2$  has been prepared by similar S—S bond-forming methods, and undergoes spontaneous conversion into thiolsulphonates in polar solvents, presumably through  $\text{R}^1\text{S}^+ \text{R}^2\text{SO}_2\text{S}^-$ .<sup>824</sup>

<sup>819</sup> Y. H. Kim, T. Takata, and S. Oae, *Tetrahedron Lett.*, 1978, 2305.

<sup>820</sup> T. Wakui, Y. Nakamura, and S. Motoki, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3081.

<sup>821</sup> A. Chaudhuri and S. K. Bhattacharjee, *Curr. Sci.*, 1978, **47**, 731.

<sup>822</sup> H. G. Hansen and A. Senning, *J. Chem. Soc., Chem. Commun.*, 1979, 1135.

<sup>823</sup> R. S. Sukhai and L. Brandsma, *Synthesis*, 1979, 971.

<sup>824</sup> D. N. Harpp, D. K. Ash, and R. A. Smith, *J. Org. Chem.*, 1979, **44**, 4135.

# 2

## Ylides of Sulphur, Selenium, and Tellurium, and Related Structures

BY E. BLOCK, D. L. J. CLIVE, N. FURUKAWA & S. OAE

### PART I: Ylides and Carbanionic Compounds of Sulphur by E. Block

#### 1 Introduction

A substantial majority of the 375 papers referred to in this section deal with the application of anionic and ylidic sulphur reagents in organic synthesis, particularly *vis-à-vis* C—C bond formation in ring-closure, -contraction, or -expansion reactions, and C=O, C=C, and C≡C bond formation under gentle conditions. Sulphur has been teamed up with silicon, tin, halogen, boron, and aluminium functionalities, and the conditions of carbanion and ylide formation have been refined, to permit precise control over product stereochemistry and regiochemistry (e.g. 1,2- versus 1,4-addition to enones,  $\alpha$  versus  $\gamma$ -substitution in allylic systems,  $\alpha$ -proton abstraction versus  $\gamma$ -proton abstraction, and Michael addition in vinyl-sulphur systems). A number of general reviews have been published on 'sulphur in synthesis' and related subjects,<sup>1</sup> while sections of other reviews deal with lithio-sulphur compounds.<sup>2</sup> Coverage of sulphur anions and ylides is included in a recent book<sup>3</sup> and in chapters in *Methodicum Chemicum*<sup>4</sup> and in *Comprehensive Organic Chemistry*.<sup>5</sup> In Volume 5 of these Reports it was observed that 'the use of sulphur-containing carbanions and ylides in synthesis is now so commonplace that complete coverage of the literature within the restraints of space is impractical'. While this statement rings even truer now, it is hoped that most of the notable and representative applications of anionic and ylidic sulphur compounds in organic synthesis published in the past 24 months will be found in these pages.

Two general studies of sulphur-stabilized carbanions, employing n.m.r. and other

<sup>1</sup> E. Block, *Aldrichimica Acta*, 1978, **11**, 51; L. Field, *Synthesis*, 1978, 713; S. F. Martin, *ibid.*, 1979, 633; B. M. Trost, *Acc. Chem. Res.*, 1978, **11**, 453; B. M. Trost, *Chem. Rev.*, 1978, **78**, 363; S. Warren, *Acc. Chem. Res.*, 1978, **11**, 401.

<sup>2</sup> H. W. Gschwend and H. R. Rodriguez, *Org. React.*, 1979, **26**, 1; E. M. Kaiser, *J. Organomet. Chem.*, 1979, **183**, 1.

<sup>3</sup> J. C. Stowell, 'Carbanions in Organic Synthesis,' Wiley-Interscience, New York, 1979.

<sup>4</sup> 'Methodicum Chemicum', Vol. 7B, ed. H. Zimmer and K. Niedenzu, Academic Press, New York, 1978 (Chapters by R. M. Wilson and D. N. Buchanan, and by D. C. Lankin and H. Zimmer).

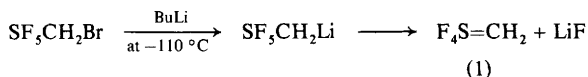
<sup>5</sup> G. C. Barrett, T. Durst, and C. R. Johnson, in 'Comprehensive Organic Chemistry', Vol. 3, ed. D. N. Jones, Pergamon Press, Oxford, 1979 (three separate chapters).

spectroscopic methods, have been published.<sup>6,7</sup> The agreement between experimental conclusions and *ab initio* calculations, while adequate for the  $\alpha$ -sulphenyl carbanion, is not particularly good for the  $\alpha$ -sulphinyl and  $\alpha$ -sulphonyl carbanions due to interactions with the cation and solvent. One interesting observation is that the order of oxidation potentials for the process  $R^- \rightarrow R\cdot + e^-$  is  $\alpha$ -sulphenyl carbanion  $>$   $\alpha$ -sulphinyl carbanion  $\gg$   $\alpha$ -sulphonyl carbanion,<sup>7</sup> in accord with data on free-radical stability.<sup>8</sup> In connection with the metallation of organosulphur compounds it might be noted that *N*-benzylidenebenzylamine is reported to be a useful coloured (red-purple) indicator in metallations involving organolithium compounds.<sup>9</sup>

In contrast with the spate of activity in the area of theoretical calculations on sulphur carbanions and ylides reported in Volume 5, only a single, brief paper has been published in this area in the past two years. This interesting study predicts (and experimentally substantiates) the greater stability of  $\alpha$ -disulphide carbanions compared to  $\alpha$ -sulphenyl carbanions.<sup>10</sup>

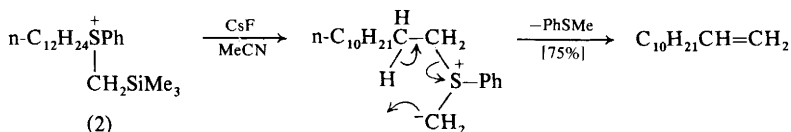
## 2 Sulphonium Ylides

**Synthesis and Properties.**—Perhaps the most interesting new compound that might be included in this section is the ‘non-ylidic’  $F_4S=CH_2$  (1),<sup>11</sup> a colourless, stable gas that boils at  $-19^\circ C$  and has been synthesized as shown. The carbon chemical shift of 43.9 p.p.m. is very different from that for phosphonium ylides, suggesting that there is little negative charge on the carbon atom in (1). Carbon is  $sp^2$ -hybridized and the barrier to rotation about the C=S bond (estimated bond order is 1.9) is greater than  $25 \text{ kcal mol}^{-1}$ ; this precludes free rotation at room temperature.



Irradiation of (1) yields ethylene and sulphur tetrafluoride. Further information on this fascinating new molecule is eagerly awaited. Fluoride-induced cleavage of the carbon–silicon bond in (2) exemplifies a new method of preparing sulphur ylides which might prove valuable in cases where the use of strong bases is precluded.<sup>12</sup>

Additional examples of polymer-supported sulphonium ylides have appeared,<sup>13</sup> including a nice example where the ylide is generated under phase-transfer



<sup>6</sup> G. Chassaing and A. Marquet, *Tetrahedron*, 1978, **34**, 1399.

<sup>7</sup> S.-I. Nishi and M. Matsuda, *J. Am. Chem. Soc.*, 1979, **101**, 4632.

<sup>8</sup> E. Block, ‘Reactions of Organosulfur Compounds’, Academic Press, New York, 1978, Ch. 5.

<sup>9</sup> L. Duhamel and J. C. Plaquevent, *J. Org. Chem.*, 1979, **44**, 3404.

<sup>10</sup> S. Wolfe and D. Schirlin, *Tetrahedron Lett.*, 1980, **21**, 827.

<sup>11</sup> G. Kleemann and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 516; 1979, **18**, 944.

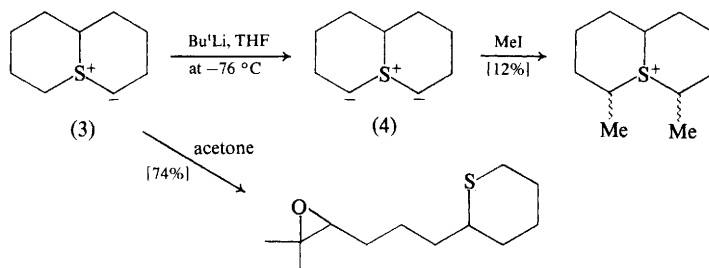
<sup>12</sup> E. Vedejs and G. R. Martinez, *J. Am. Chem. Soc.*, 1979, **101**, 6452.

<sup>13</sup> S. Tanimoto, Y. Imazu, T. Sugimoto, and M. Okano, *Bull. Inst. Chem. Res. Kyoto Univ.*, 1978, **56**, 345 (*Chem. Abstr.*, 1979, **91**, 21 365).

conditions and the recycling of the polymeric system is possible without loss of reactivity<sup>14</sup>. New syntheses have been reported for trimethylsilyl<sup>15</sup> and trimethylstannyl-sulphonium<sup>16</sup> ylides, mono<sup>17</sup> and tris-(sulphonio)-cyclopentadienylides,<sup>18</sup> ylide salts,<sup>19</sup> and  $\alpha$ -nitrosulphonium ylides.<sup>20</sup> Sulphonium ylides are formed on reaction of sulphides with 1,1-dicyano-epoxides<sup>21</sup> and with 2-diazo-1,3-diketones on irradiation.<sup>22</sup> Other methods include the condensation of DMSO with active-methylene compounds in the presence of 3-sulphopropanoic anhydride<sup>23</sup> and the reaction of stabilized anions with enamino-sulphonium salts.<sup>24</sup>

The first X-ray structure of a thiabenzene derivative, *i.e.* 1-benzoyl-2-methyl-2-thianaphthalene, has been reported.<sup>25</sup> The geometry is similar to that of open-chain benzoyl-stabilized ylides with pyramidal sulphur. Other studies point to the ylidic character of '9,10-diphenyl-10-thia-anthracene'.<sup>26</sup> N.m.r. data, including <sup>13</sup>C n.m.r. chemical shifts, have been presented for indole-3-sulphonium ylides<sup>27</sup> and carbonyl-stabilized sulphonium ylides and their Pd<sup>II</sup> complexes.<sup>28</sup> Infrared spectra of  $\alpha$ -nitrosulphonium ylides have been analysed.<sup>29</sup> Further details have been provided of a study of the pyramidal inversion of unstabilized sulphonium ylides<sup>30</sup> (see Chap. 5, pp. 243 and 251).

**Reactions.**—In Volume 5 (p. 74), an example of the formation and alkylation of a sulphonium ylide anion was given. Another example (4) has now been described,<sup>30</sup>



<sup>14</sup> M. J. Farrall, T. Durst, and J. M. J. Frechet, *Tetrahedron Lett.*, 1979, 203.

<sup>15</sup> F. Cooke, P. Magnus, and G. L. Bundy, *J. Chem. Soc., Chem. Commun.*, 1978, 714.

<sup>16</sup> W. Ando, M. Takata, and A. Sekiguchi, *J. Chem. Soc., Chem. Commun.*, 1979, 1121.

<sup>17</sup> K. Friedrich, W. Amann, and H. Fritz, *Chem. Ber.*, 1979, **112**, 1269.

<sup>18</sup> K. H. Schlingensiefel and K. Hartke, *Liebigs Ann. Chem.*, 1978, 1754.

<sup>19</sup> N. N. Magdesieva and V. A. Danilenko, *Zh. Org. Khim.*, 1979, **15**, 379.

<sup>20</sup> V. V. Semenov and S. A. Shevelev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2355.

<sup>21</sup> A. Robert, M. T. Thomas, and A. Foucaud, *J. Chem. Soc., Chem. Commun.*, 1979, 1048.

<sup>22</sup> V. A. Nikolaev, Y. Frenkh, and I. K. Korobitsyna, *Zh. Org. Khim.*, 1978, **14**, 1433

<sup>23</sup> K. Schank and C. Schunknecht, *Synthesis*, 1978, 678.

<sup>24</sup> T. Severin and I. Brautigam, *Chem. Ber.*, 1979, **112**, 3007.

<sup>25</sup> M. Hori, T. Kataoka, H. Shimizu, S. Ohno, K. Narita, H. Takayanagi, H. Ogura, and Y. Itaka, *Tetrahedron Lett.*, 1979, 4315.

<sup>26</sup> M. Hori, T. Kataoka, H. Shimizu, Y. Itagaki, and T. Higuchi, *Tetrahedron Lett.*, 1979, 1603.

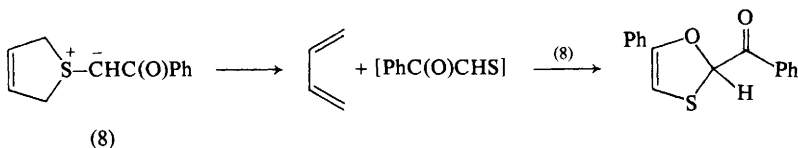
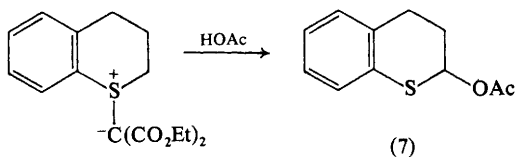
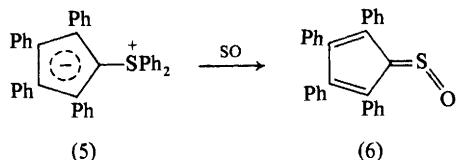
<sup>27</sup> K. H. Park, G. A. Gray, and G. D. Daves, Jr., *J. Am. Chem. Soc.*, 1978, **100**, 7475; K.-W. Park and G. D. Daves, Jr., *J. Org. Chem.*, 1980, **45**, 780.

<sup>28</sup> G. Fronza, P. Bravo, and C. Ticozzi, *J. Organomet. Chem.*, 1978, **157**, 299.

<sup>29</sup> K. I. Rezhikova, O. P. Shitov, A. P. Seleznev, V. A. Tartakovskii, and V. A. Shlyapochnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1129.

<sup>30</sup> D. M. Roush, E. M. Price, L. K. Templeton, D. H. Templeton, and C. H. Heathcock, *J. Am. Chem. Soc.*, 1979, **101**, 2971.

along with other reactions of the precursor sulphonium ylide (3).<sup>30,31</sup> Among the diverse reactions of sulphonium ylides examined in the past two years are photosensitized oxidation;<sup>32</sup> reaction with sulphur monoxide, giving a sulphine [e.g. (5)→(6)];<sup>33</sup> Stevens rearrangement in cyclophane syntheses;<sup>34</sup> reaction with Group VA and VIA elements, leading to demethylation and trans-ylidation among other processes;<sup>35</sup> solvolysis, leading to  $\alpha$ -substituted sulphides [e.g. (7)];<sup>36</sup> fragmentation [e.g. (8)<sup>37</sup>]; alkylation of cyclic ylides (see Chap. 5, p. 247);<sup>38</sup> *O*-methylation of oximes;<sup>39</sup> and epoxide formation with diphenylsulphonium cyclopropylide,<sup>40</sup> allylic ylides [e.g. (9)],<sup>41</sup> or dimethylsulphonium methylide.<sup>42</sup> While most sulphur ylides react with simple ketones to give epoxides, a few instances are known where olefin



<sup>31</sup> K. Tokuno, F. Miyoshi, Y. Arata, Y. Itatani, Y. Arakawa, and T. Ohashi, *Yakugaku Zasshi*, 1978, **98**, 1005 (*Chem. Abstr.*, 1979, **90**, 6195).

<sup>32</sup> W. Ando, S. Kohmoto, and K. Nishizawa, *J. Chem. Soc., Chem. Commun.*, 1978, 894; W. Ando, S. Kohmoto, H. Miyazaki, K. Nishizawa, and H. Tsumaki, *Photochem. Photobiol.*, 1979, **30**, 81.

<sup>33</sup> B. F. Bonini, G. Maccagnani, G. Mazzanti, P. Pedrini, and P. Piccinelli, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1720.

<sup>34</sup> (a) J. R. Davy, M. N. Iskander, and J. A. Reiss, *Aust. J. Chem.*, 1979, **32**, 1067; (b) M. W. Haenel and A. Flatow, *Chem. Ber.*, 1979, **112**, 249; (c) D. Kamp and V. Boekelheide, *J. Org. Chem.*, 1978, **43**, 3475; (d) D. N. Leach and J. A. Reiss, *ibid.*, p. 2484; (e) D. N. Leach and J. A. Reiss, *Tetrahedron Lett.*, 1979, 4501; (f) D. N. Leach and J. A. Reiss, *Aust. J. Chem.*, 1979, **32**, 361; (g) T. Otsubo, D. Stusche, and V. Boekelheide, *J. Org. Chem.*, 1978, **43**, 3466; (h) I. D. Reingold, W. Schmidt, and V. Boekelheide, *J. Am. Chem. Soc.*, 1979, **101**, 2121.

<sup>35</sup> B. A. Arbusov, Yu. V. Belkin, N. A. Polezhaeva, and G. E. Buslaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1643; B. A. Arbusov, Yu. V. Belkin, and N. A. Polezhaeva, *ibid.*, 1979, 1893; N. N. Magdesieva and V. A. Danilenko, *J. Gen. Chem. USSR (Engl. Transl.)*, 1979, **49**, 1740; H. Matsuyama, M. Matsumoto, M. Kobayashi, and H. Minato, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1139.

<sup>36</sup> R. Pellicciari, M. Curini, P. Ceccherelli, and B. Natalini, *Gazz. Chim. Ital.*, 1978, **108**, 671

<sup>37</sup> U. J. Kempe, T. Kempe, and T. Norin, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1547.

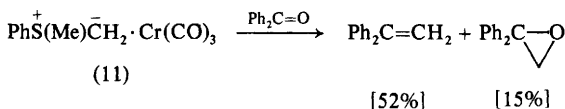
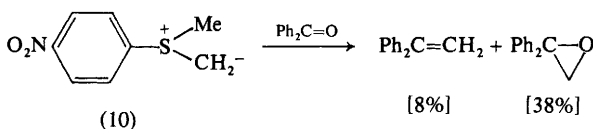
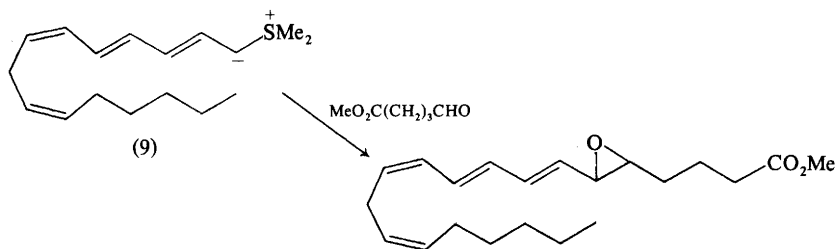
<sup>38</sup> A. Garbesi, *Tetrahedron Lett.*, 1980, **21**, 547.

<sup>39</sup> S. Tanimoto, T. Yamadera, T. Sugimoto, and M. Okano, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 627.

<sup>40</sup> M. Hanack, E. J. Carnahan, A. Krowczynski, W. Schobert, L. R. Subramanian, and K. Subramanian, *J. Am. Chem. Soc.*, 1979, **101**, 100; B. M. Trost, Y. Nishimura, K. Yamamoto, and S. S. McElvain, *ibid.*, p. 1328.

<sup>41</sup> E. J. Corey, Y. Arai, and C. Mioskowski, *J. Am. Chem. Soc.*, 1979, **101**, 6748.

<sup>42</sup> (a) Y.-I. Lin, S. A. Lang, Jr., C. M. Seifert, R. G. Child, G. O. Morton, and P. F. Fabio, *J. Org. Chem.*, 1979, **44**, 4701; (b) T. J. McCarthy, W. F. Conner, and S. M. Rosenfeld, *Synth. Commun.*, 1978, **8**, 379; (c) D. R. Morton, Jr. and F. C. Brokaw, *J. Org. Chem.*, 1979, **44**, 2880.



formation also occurs, apparently by 'Wittig-type' transition states. Thus *p*-nitrophenyl ylide (10) and the chromium–ylide complex (11) both give some 1,1-diphenylethylene on reaction with benzophenone.<sup>43</sup> It is argued that strong electron-withdrawing effects by the *p*-nitrophenyl and tricarbonylchromium groups make attack at the sulphur atom by the negative oxygen competitive with attack by oxygen at carbon. The formation of a highly stabilized olefin is also important since only very low yields of olefins are found upon reaction of (11) with cyclohexanone.<sup>43</sup>

Other reactions of sulphonium ylides include  $\alpha,\beta'$ -elimination,<sup>12,16,44</sup> metal-mediated carbene-transfer to olefins,<sup>45,46</sup> insertion into aromatic C–H bonds<sup>47</sup> or other carbenoid-type processes,<sup>48</sup> formation of Pd<sup>II</sup> complexes,<sup>49</sup> addition to enones (forming cyclopropyl ketones<sup>50</sup> or heterocycles<sup>51</sup>), reaction with isoquinoline 2-oxide,<sup>52</sup> and [2,3]-sigmatropic rearrangements<sup>53–57</sup> [as in the case of (12)<sup>58</sup>] or

<sup>43</sup> A. Ceccon, F. Miconi, and A. Venzo, *J. Organomet. Chem.*, 1979, **181**, C4.

<sup>44</sup> V. Cere, C. Paolucci, S. Pollicino, E. Sandri, and A. Fava, *J. Org. Chem.* 1979, **44**, 4128.

<sup>45</sup> J. Cuffe, R. J. Gillespie, and A. E. A. Porter, *J. Chem. Soc., Chem. Commun.*, 1978, 641.

<sup>46</sup> R. J. Gillespie and A. E. A. Porter, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2624.

<sup>47</sup> R. J. Gillespie and A. E. A. Porter, *J. Chem. Soc., Chem. Commun.*, 1979, 50.

<sup>48</sup> G. Ege and K. Gilbert, *Tetrahedron Lett.*, 1979, 1567.

<sup>49</sup> H. Nishiyama, *J. Organomet. Chem.*, 1979, **165**, 407.

<sup>50</sup> M. Chiericato, P. Dalla Croce, and E. Licandro, *J. Chem. Soc., Perkin Trans. 1*, 1979, 211.

<sup>51</sup> T. Nishio, M. Sugawara, and Y. Omote, *J. Heterocycl. Chem.*, 1979, **16**, 815.

<sup>52</sup> M. Watanabe, M. Aono, T. Kinoshita, and S. Furukawa, *Yakugaku Zasshi*, 1978, **98**, 198 (*Chem. Abstr.*, 1978, **89**, 6199).

<sup>53</sup> G. Morel, S. Khamsithideth, and A. Foucaud, *J. Chem. Soc., Chem. Commun.*, 1978, 274.

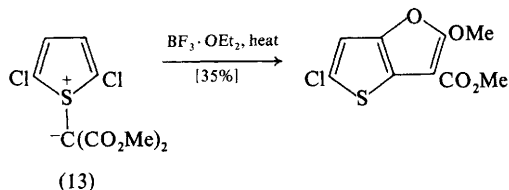
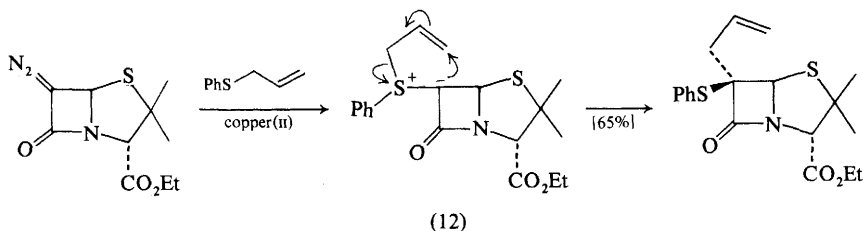
<sup>54</sup> G. Morel, E. Marchand, and A. Foucaud, *Tetrahedron Lett.*, 1978, 3719.

<sup>55</sup> M. Franck-Neumann and J. J. Lohmann, *Tetrahedron Lett.*, 1978, 3729.

<sup>56</sup> K. Ogura, S. Furukawa, and G.-I. Tsuchihashi, *J. Am. Chem. Soc.*, 1980, **102**, 2125.

<sup>57</sup> H. J. Reich and M. L. Cohen, *J. Am. Chem. Soc.*, 1979, **101**, 1307.

<sup>58</sup> P. J. Giddings, D. I. John, and E. J. Thomas, *Tetrahedron Lett.*, 1980, **21**, 395.

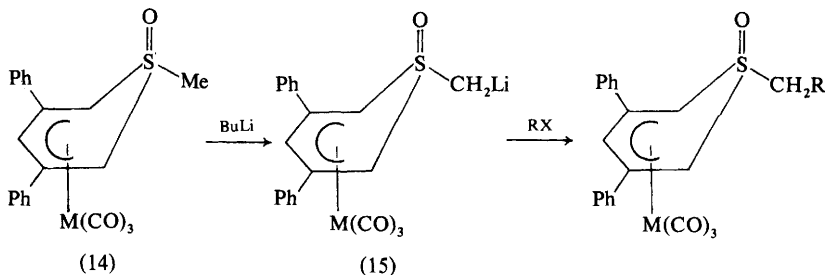


mechanistically more complex rearrangements [as in the case of (13)<sup>59</sup>]. A number of papers have appeared on Vedejs' ring-growing sequence (see Vol. 4, p. 84),<sup>60</sup> including reactions involving unstabilized sulphonium ylides<sup>61</sup> and stereochemical and conformational studies of the reaction.<sup>44,62,63</sup> (see also Chap. 5, p. 240).

### 3 Oxosulphonium and Amino-oxosulphonium Ylides

**Synthesis and Properties.**—Additional details have been published on the preparation of oxosulphonium ylides from sulfoximides<sup>64</sup> (see Chap. 2, Pt III, p. 144) and of phosphorylated oxosulphonium ylides.<sup>65</sup>

**Reactions.**—1-Methyl-3,5-diphenylthiabenzene 1-oxide is a novel sulphur ylide ligand in tricarbonyl-chromium, -molybdenum, and -tungsten complexes (14),



<sup>59</sup> R. J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A. E. A. Porter, *J. Chem. Soc., Chem. Commun.*, 1979, 366.

<sup>60</sup> E. Vedejs, M. J. Arco, D. W. Powell, J. M. Renga, and S. P. Singer, *J. Org. Chem.*, 1978, **43**, 4831.

<sup>61</sup> V. Cere, C. Paolucci, S. Pollicino, E. Sandri, and A. Fava, *J. Org. Chem.*, 1978, **43**, 4826.

<sup>62</sup> E. Vedejs and M. J. Mullins, *J. Org. Chem.*, 1979, **44**, 2947.

<sup>63</sup> E. Vedejs, M. J. Arnost, and J. P. Hagen, *J. Org. Chem.*, 1979, **44**, 3230.

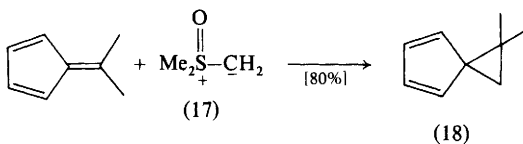
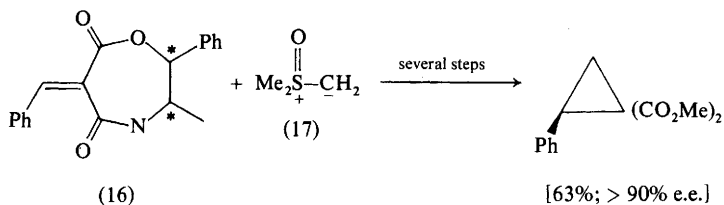
<sup>64</sup> N. Furukawa, F. Takahashi, T. Yoshimura, and S. Oae, *Tetrahedron* 1979, **35**, 317.

<sup>65</sup> V. P. Lysenko, I. E. Boldeskul, R. A. Loktionova, and Yu. G. Gololobov, *Zh. Obshch. Khim.*, 1979, **49**, 1230; 1978, **48**, 978; also see L. F. Kasukhin, M. N. Ponomarchuk, V. P. Kysenko, and Yu. G. Gololobov, *Ukr. Khim. Zh.*, 1978, **44**, 519.



which have been found to have a non-planar ring and to undergo lithiation at the S-methyl group to produce (15).<sup>66</sup> An asymmetric synthesis of cyclopropanes is based on the addition of dimethylsulfonium methylide (17) to the heterocycle (16).<sup>67</sup> Ylide (17) has also been employed in the synthesis of the spirocyclopentadiene (18),<sup>68</sup> benzoxepin and benzopyran-5-one derivatives,<sup>69</sup> tropolones,<sup>70</sup> cyclopropanes and vinylcyclopropanes,<sup>71</sup> thiabenzene S-oxides,<sup>72</sup> ( $\pm$ )-laurencin,<sup>73</sup> isoxazoline N-oxides,<sup>74</sup> nitro-<sup>75</sup> and cyano-cyclopropanes,<sup>76</sup> and hydro-azulenones,<sup>77</sup> amongst other compounds.<sup>78</sup>

Michael addition to (dimethylamino)phenylvinylsulfonium salts (19) is thought to involve amino-oxosulfonium ylide intermediates such as (20).<sup>79</sup>



#### 4 Oxy- and Aza-sulfonium Ylides

**Oxysulfonium Ylides.**—Reagents that are related to DMSO are now in routine use for the selective oxidation of alcohols to aldehydes and ketones. The particularly effective combination of DMSO and oxalyl chloride followed by triethylamine<sup>80</sup> has been shown to involve the intermediacy of a chlorodimethylsulfonium salt (21).<sup>81</sup>

<sup>66</sup> L. Weber, C. Kruger, and Y.-H. Tsay, *Chem. Ber.*, 1978, **111**, 1709; L. Weber, *ibid.*, 1979, **112**, 99; L. Weber, *ibid.*, p. 3828.

<sup>67</sup> T. Mukaiyama, K. Fujimoto, and T. Takeda, *Chem. Lett.*, 1979, 1207.

<sup>68</sup> W.-D. Schroer and W. Friedrichsen, *Liebigs Ann. Chem.*, 1978, 1648.

<sup>69</sup> P. Bravo, C. Ticozzi, G. Fronza, R. Bernardi, and D. Maggi, *Gazz. Chim. Ital.*, 1979, **109**, 137; P. Bravo and C. Ticozzi, *ibid.*, p. 169.

<sup>70</sup> D. A. Evans, D. J. Hart, and P. M. Koelsch, *J. Am. Chem. Soc.*, 1978, **100**, 4593.

<sup>71</sup> D. Brule, J. C. Chalchat, and R. Vessiere, *Bull. Soc. Chim. Fr., Part 2*, 1978, 385.

<sup>72</sup> P. Bennett, J. A. Donnelly, and M. J. Fox, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2990; J. A. Donnelly, M. J. Fox, and J. G. Hoey, *ibid.*, p. 2629.

<sup>73</sup> T. Masamune, H. Murase, H. Matsue, and A. Murai, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 135.

<sup>74</sup> T. Sakakibara and R. Sudoh, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1193.

<sup>75</sup> T. Sakakibara, R. Sudoh, and T. Nakagawa, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1189.

<sup>76</sup> J. J. McCullough and C. Manning, *J. Org. Chem.*, 1978, **43**, 2839.

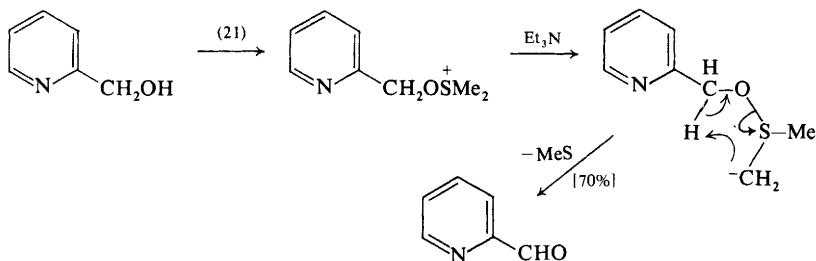
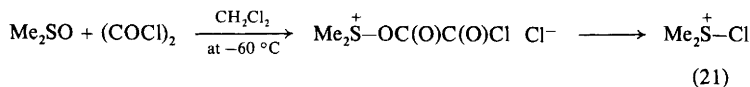
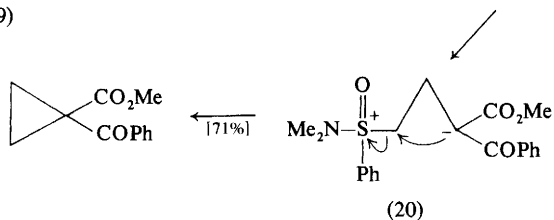
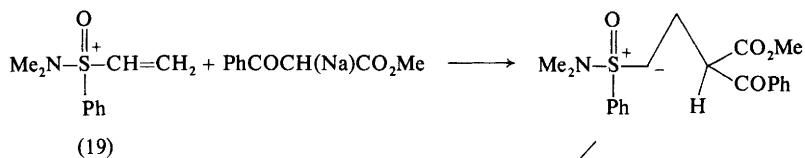
<sup>77</sup> P. Geetha, K. Narasimhan, and S. Swaminathan, *Tetrahedron Lett.*, 1979, 565.

<sup>78</sup> R. Faragher, T. L. Gilchrist, and I. W. Southon, *Tetrahedron Lett.*, 1979, 4113; S. Hagen, T. Anthonen, and L. Kilaas, *Tetrahedron*, 1979, **35**, 2583; L. Kohout and J. Fajkos, *Collect. Czech. Chem. Commun.*, 1978, **43**, 1134.

<sup>79</sup> C. R. Johnson, J. P. Lockard, and E. R. Kennedy, *J. Org. Chem.*, 1980, **45**, 264.

<sup>80</sup> K. Omura and S. Swern, *Tetrahedron*, 1978, **34**, 1651.

<sup>81</sup> A. J. Mancuso, D. S. Brownfain, and D. Swern, *J. Org. Chem.*, 1979, **44**, 4148.



The DMSO–oxalyl chloride pair gives excellent results in the oxidation of long-chain alcohols to aldehydes,<sup>82</sup> amongst other recent examples<sup>83–86</sup> (see also Chap. 2, Pt III, p. 134). The DMSO–trifluoroacetic anhydride combination has been found to give best results with di-isopropylethylamine as base,<sup>87</sup> and it has been applied to the syntheses of carbohydrate derivatives,<sup>88</sup> ascorbic acid,<sup>89</sup> 7,12-dimethylbenz[*a*]anthracene metabolites and related systems,<sup>90</sup> and the tricyclic ketone (22).<sup>91</sup> In the latter case, other related oxidation procedures [DMSO–(COCl)<sub>2</sub>, Me<sub>2</sub>S–*N*-chlorosuccinimide (NCS), and DMSO–DCCI–py–TFA] were less satisfactory. The pair DMSO–(CCl<sub>3</sub>CO)<sub>2</sub>O has been used in a synthesis

<sup>82</sup> A. J. Mancuso, S.-L. Huang, and D. Swern, *J. Org. Chem.*, 1978, **43**, 2480.

<sup>83</sup> (a) E. Dimitriadis and R. A. Massy-Westropp, *Aust. J. Chem.*, 1979, **32**, 2003; (b) R. M. Jacobson and R. A. Raths, *J. Org. Chem.*, 1979, **44**, 4013; (c) W. R. Roush, *J. Am. Chem. Soc.*, 1980, **102**, 1390.

<sup>84</sup> E. L. Eliel and W. J. Frazee, *J. Org. Chem.*, 1979, **44**, 3598.

<sup>85</sup> N. Sueda, H. Ohrui, and H. Kuzuhara, *Tetrahedron Lett.*, 1979, 2039.

<sup>86</sup> F. M. Hauser and S. Prasanna, *J. Org. Chem.*, 1979, **44**, 2596.

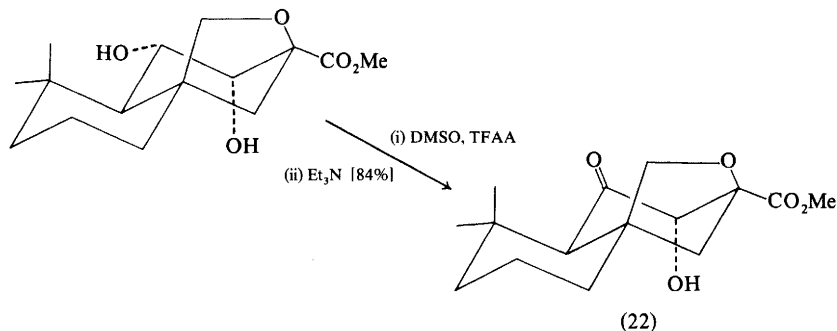
<sup>87</sup> S. L. Huang, K. Omura, and D. Swern, *Synthesis*, 1978, 297.

<sup>88</sup> K. Sato and J. Yoshimura, *Carbohydr. Res.*, 1979, **73**, 75; J. Yoshimura, K. Sato, and H. Hashimoto, *Chem. Lett.*, 1977, 1327.

<sup>89</sup> T. C. Crawford and R. Breitenbach, *J. Chem. Soc., Chem. Commun.*, 1979, 388.

<sup>90</sup> K. B. Sukumaran and R. G. Harvey, *J. Am. Chem. Soc.*, 1979, **101**, 1353; P. P. Fu, C. Cortez, K. B. Sukumaran, and R. G. Harvey, *J. Org. Chem.*, 1979, **44**, 4265.

<sup>91</sup> O. D. Dailey, Jr. and P. L. Fuchs, *J. Org. Chem.*, 1980, **45**, 216.



of gibberellic acid,<sup>92</sup> the Moffatt reagent (DMSO-carbodi-imide-py-TFA) is favoured over other procedures in syntheses of *N*-methylmaysenine<sup>93</sup> and ( $\pm$ )-warburganal,<sup>94</sup> DMSO-SO<sub>3</sub>-py has been employed in the synthesis of juncosol,<sup>95</sup> and the pair DMSO-chlorosulphonyl isocyanate has been touted as a particularly mild alternative to existing reagents.<sup>96</sup> A report has been published on the use of Me<sub>2</sub>S plus NCS (a combination which gives Me<sub>2</sub>S<sup>+</sup>Cl<sup>-</sup>),<sup>97</sup> which is effective in converting  $\beta$ -hydroxy-selenides into  $\beta$ -keto-selenides; this is a situation in which DMSO-TFAA and the Moffatt procedure fail.<sup>98</sup> Oxysulphonium ylides are probable intermediates in the conversion of oxirans into  $\alpha$ -chloro-ketones using chlorosulphonium salts,<sup>99</sup> in the *ortho*-substitution of phenols *via* aryloxysulphonium salts,<sup>100</sup> and in the novel electrochemical oxidation of alcohols in the presence of catalytic quantities of thioanisole (Scheme 1); a procedure which is thought to involve the cation radical (23) or the dication (24).<sup>101</sup>

**Azasulphonium Ylides.**—Azasulphonium ylides, which are intermediates in the rearrangements of *N*-aryl-azasulphonium salts in the *ortho*-functionalization of aromatic amines,<sup>102</sup> can be isolated as stable compounds if suitable substituents are incorporated.<sup>103</sup>

## 5 Thiocarbonyl Ylides

The  $\Delta^3$ -1,3,4-thiadiazoline-thiocarbonyl ylide-thiiran-olefin transformation (see Vol. 4, p. 89) has been employed in the synthesis of some unsaturated  $\beta$ -lactams,<sup>104</sup>

<sup>92</sup> E. J. Corey, R. L. Danheiser, S. Chandrasekaran, P. Siret, G. E. Keck, and J. L. Gras, *J. Am. Chem. Soc.*, 1978, **100**, 8031.

<sup>93</sup> E. J. Corey, L. O. Weigel, D. Floyd, and M. G. Bock, *J. Am. Chem. Soc.*, 1978, **100**, 2916.

<sup>94</sup> T. Nakata, H. Akita, T. Naito and T. Oishi, *J. Am. Chem. Soc.*, 1979, **101**, 4400.

<sup>95</sup> A. S. Kende and D. P. Curran, *J. Am. Chem. Soc.*, 1979, **101**, 1857.

<sup>96</sup> G. A. Olah, Y. D. Vankar, and M. Arvanaghi, *Synthesis*, 1980, 141.

<sup>97</sup> E. J. Corey, C. U. Kim, and P. F. Misco, *Org. Synth.*, 1978, **58**, 122.

<sup>98</sup> R. Baudat and M. Petrzilka, *Helv. Chim. Acta*, 1979, **62**, 1406; also see S. Raucher, *Tetrahedron Lett.*, 1978, 2261.

<sup>99</sup> G. A. Olah, Y. D. Vankar, and M. Arvanaghi, *Tetrahedron Lett.*, 1979, 3653.

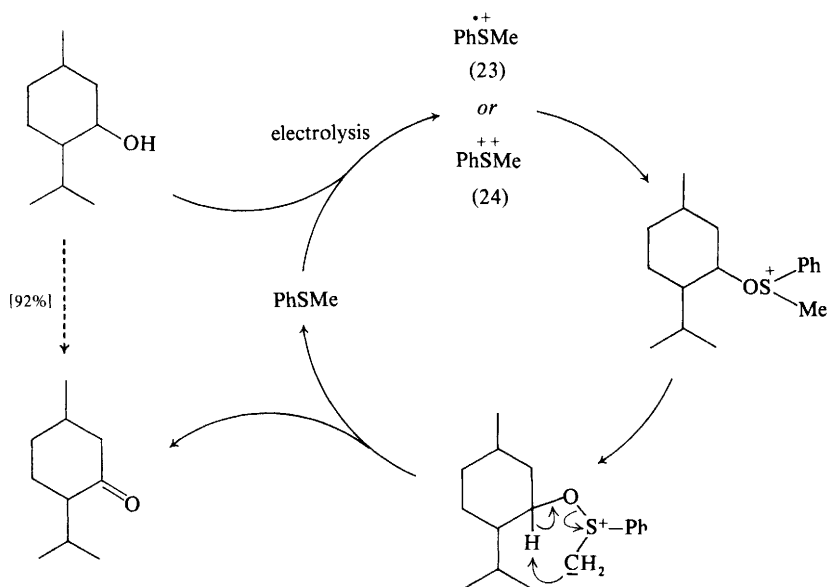
<sup>100</sup> P. G. Gassman and D. R. Amick, *J. Am. Chem. Soc.*, 1978, **100**, 7611.

<sup>101</sup> T. Shono, Y. Matsumura, M. Mizoguchi, and J. Hayashi, *Tetrahedron Lett.*, 1979, 3861.

<sup>102</sup> P. G. Gassman and H. R. Drewes, *J. Am. Chem. Soc.*, 1978, **100**, 7600.

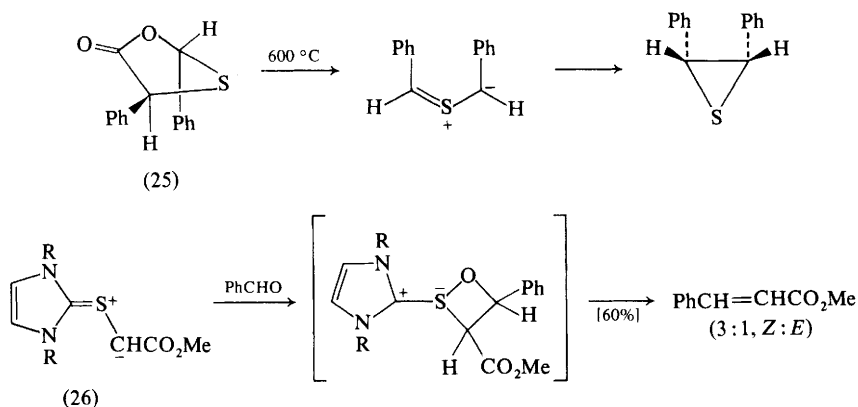
<sup>103</sup> L. N. Markovskii, Yu. G. Shermolovich, V. V. Vasil'ev, I. E. Boldeskul, S. S. Trach, and N. S. Zefirov, *Zh. Org. Khim.*, 1978, **14**, 1659.

<sup>104</sup> M. D. Bachi, O. Goldberg, and A. Gross, *Tetrahedron Lett.*, 1978, 4167.



Scheme 1

some hindered olefins such as bis-(2,2,5,5-tetramethylcyclopentylidene),<sup>105</sup> octamethyl-4,4'-bis-( $\Delta^{1,2}$ -pyrazolinylidene),<sup>106</sup> an adamantylidene,<sup>107</sup> and thiiran-containing cyclophanes (where the reaction stopped at the thiiran stage).<sup>108</sup> Flash vacuum pyrolysis of 1,3-oxathiolan-5-ones (25) has been found to give thiirans *via* thiocarbonyl ylides<sup>109</sup> (see Chap. 5, p. 268). Burgess has reported the interesting discovery that thiocarbonyl ylides such as (26) can undergo a Wittig-type reaction



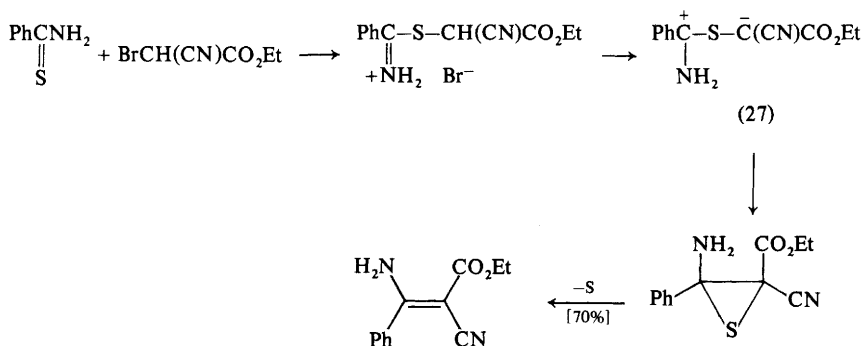
<sup>105</sup> A. Krebs and W. Ruger, *Tetrahedron Lett.*, 1979, 1305.

<sup>106</sup> R. J. Bushby and M. D. Pollard, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2401.

<sup>107</sup> F. Cordt, R. M. Frank, and D. Lenoir, *Tetrahedron Lett.*, 1979, 505.

<sup>108</sup> M. Atzmüller and F. Vögtle, *Chem. Ber.*, 1979, **112**, 138.

<sup>109</sup> T. B. Cameron and H. W. Pinnick, *J. Am. Chem. Soc.*, 1979, **101**, 4755; 1980, **102**, 744.

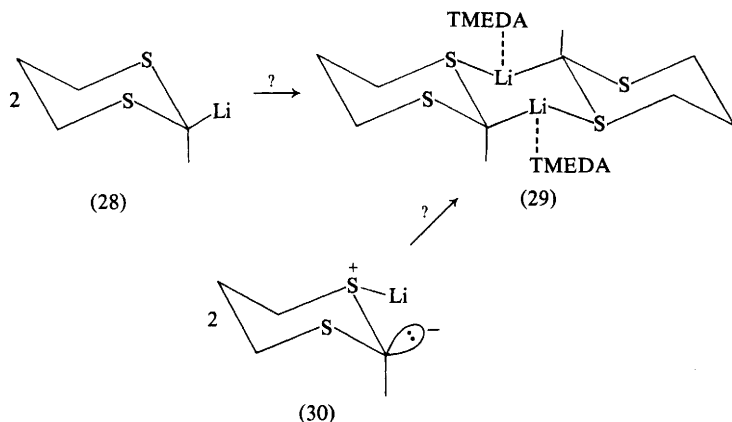


with benzaldehyde.<sup>110</sup> Another olefin-forming reaction that is thought to involve the thiocarbonyl ylide (27) has been described.<sup>111</sup>

## 6 Sulphenyl Carbanions

**Synthesis and Properties.**—The surprising result of a crystal-structure determination for the TMEDA complex of 2-lithio-2-methyl-1,3-dithian is that the complex (29) is dimeric.<sup>112</sup> The lithium atoms, which are equatorial, interact about equally strongly with the carbanionoid-carbon of one ring ( $\text{C-Li} = 2.186 \text{ \AA}$ ) as with the sulphur of the other ( $\text{S-Li} = 2.516 \text{ \AA}$ ), so that it is impossible to decide between the alternative descriptions of the complex as a dimer of the C-Li monomer (28) or of the S-Li monomer (30). Steric factors are thought to be at least as important as the anomeric effect in favouring the equatorial position of lithium. Dimeric structures analogous to (29) may well be preserved in solutions of 2-lithio-1,3-dithians in THF, where the oxygen of the solvent molecules can take over the role of the nitrogen atoms of TMEDA.<sup>112</sup>

In other work, the barriers to rotation and to inversion in 2-lithio-2-phenyl-



<sup>110</sup> E. M. Burgess and M. C. Pulcrano, *J. Am. Chem. Soc.*, 1978, **100**, 6538.

<sup>111</sup> H. Singh and C. S. Gandhi, *Synth. Commun.*, 1978, **8**, 469.

<sup>112</sup> R. Amstutz, D. Seebach, P. Seiler, B. Schweizer, and J. D. Dunitz, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 53.

1,3-dithians have been determined, using  $^{13}\text{C}$  and  $^7\text{Li}$  n.m.r. spectroscopy<sup>113</sup> (see Chap. 5, p. 260). A  $^{13}\text{C}$  n.m.r. study of 2-lithio-1,3-dithian and (phenylthio)methyl anions has shown the carbanion-carbons to be nearly pyramidal,<sup>6</sup> and a kinetic study has revealed that dibenzyl disulphide undergoes deprotonation 7.5 times faster than dibenzyl sulphide, in accord with theoretical calculations which show  $\alpha$ -dithiocarbanions, (e.g.  $\text{RSSCH}_2^-$ ) to be more stable than  $\alpha$ -thiocarbanions (e.g.  $\text{RSC}_2^-$ ).<sup>10</sup> The anion from dibenzyl disulphide undergoes a rapid Wittig rearrangement, giving, on methylation,  $\alpha$ -(methylthio)benzyl sulphide.<sup>10</sup>

A full report has appeared on the preparation and reactions of thiolate dianions derived from propene-3-thiol and 2-methylpropene-3-thiol.<sup>114</sup> Lithiation of *o*-alkyl- and *o,o'*-dialkyl-(alkylthio)benzenes with *n*-butyl-lithium has been shown to occur at the  $\alpha$ -thioalkyl position, at the *ortho*-position of the ring, and at the benzylic position(s), the relative amounts being dependent on the nature of the alkyl groups.<sup>115</sup>

**Reactions.**—*1,3-Dithianyl Anions.* 1,3-Dithianyl anions continue to find wide-ranging utility in the synthesis of diverse structures, including 2-deoxy-L-lyxose derivatives,<sup>116</sup> eburnamine precursors,<sup>117</sup> 1,2-diformyl-6,6-dimethylcyclohex-2-en-1-ol,<sup>118</sup> cannabinoids,<sup>119</sup> tertiary acyloins,<sup>120</sup> cyclitols,<sup>121</sup> unsaturated carboxylic acids,<sup>122</sup> the terpenes egomaketone<sup>123</sup> and  $\alpha$ - and  $\beta$ -curcumene,<sup>124</sup> (20*S*)-20-hydroxycholesterol,<sup>125</sup> norpyrenophorin, pyrenophorin, and vermiculine,<sup>126</sup> compounds with chiral methyl groups,<sup>127</sup> (+)-*trans*-burseran,<sup>128</sup> enones,<sup>129</sup> the macrocyclic lactam *N*-methylmaysenine,<sup>93,130</sup> olivin,<sup>131</sup> macrocyclic acetylacetone crown ethers,<sup>132</sup> [5.1]metacyclophane,<sup>133</sup> ( $\pm$ )-laurencin,<sup>73</sup> monosaccharides,<sup>134</sup>  $\gamma$ -keto-esters and their precursors,<sup>135</sup> muscarine analogues,<sup>136</sup> quinols,<sup>137</sup> *epi*-

<sup>113</sup> L. F. Kuyper and E. L. Eliel, *J. Organomet. Chem.*, 1978, **156**, 245.

<sup>114</sup> M. Pohmakotr, K.-H. Geiss, and D. Seebach, *Chem. Ber.*, 1979, **112**, 1420.

<sup>115</sup> S. Cabiddu, S. Melis, P. P. Piras, and F. Sotgiu, *J. Organomet. Chem.*, 1979, **178**, 291.

<sup>116</sup> E. Hungerbuhler, D. Seebach, and D. Wasmuth, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 958.

<sup>117</sup> S. Takano, S. Hatakeyama, and K. Ogasawara, *J. Chem. Soc., Perkin Trans. 1*, 1980, 457.

<sup>118</sup> A. J. G. M. Peterse, J. H. Roskam, and A. de Groot, *Recl. Trav. Chim. Pays-Bas*, 1978, **97**, 249.

<sup>119</sup> C. G. Pitt, H. H. Seltzman, Y. Sayed, C. E. Twine, Jr., and D. L. Williams, *J. Org. Chem.*, 1979, **44**, 677; D. B. Uliss, G. R. Handrick, H. C. Dalzell, and R. K. Razdan, *J. Am. Chem. Soc.*, 1978, **100**, 2929.

<sup>120</sup> L. Colombo, C. Gennari, C. Scolastico, and M. G. Beretta, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1036.

<sup>121</sup> M. Funabashi, K. Kobayashi, and J. Yoshimura, *J. Org. Chem.*, 1979, **44**, 1618.

<sup>122</sup> K. C. Nicolaou, S. P. Seitz, W. J. Sipio, and J. F. Blount, *J. Am. Chem. Soc.*, 1979, **101**, 3884.

<sup>123</sup> A. Hoppmann and P. Weyerstahl, *Tetrahedron*, 1978, **34**, 1723.

<sup>124</sup> H. H. Bokel, A. Hoppmann, and P. Weyerstahl, *Tetrahedron*, 1980, **36**, 651.

<sup>125</sup> M. Koreeda and N. Kozumi, *Tetrahedron Lett.*, 1978, 1641.

<sup>126</sup> B. Seuring and D. Seebach, *Liebigs Ann. Chem.*, 1978, 2044.

<sup>127</sup> B. T. Golding, P. V. Ioannou, and I. F. Eckhard, *J. Chem. Soc., Perkin Trans. 1*, 1978, 774.

<sup>128</sup> K. Tomioka, T. Ishiguro, and K. Koga, *J. Chem. Soc., Chem. Commun.*, 1979, 652.

<sup>129</sup> Y. Nagao, K. Seno, and E. Fujita, *Tetrahedron Lett.*, 1979, 3167.

<sup>130</sup> E. J. Corey, L. O. Weigel, A. R. Chamberlin, and B. Lipshutz, *J. Am. Chem. Soc.*, 1980, **102**, 1439.

<sup>131</sup> J. H. Dodd and S. M. Weinreb, *Tetrahedron Lett.*, 1979, 3593.

<sup>132</sup> A. H. Alberts and D. J. Cram, *J. Am. Chem. Soc.*, 1979, **101**, 3545.

<sup>133</sup> N. Finch and C. W. Gemenden, *J. Org. Chem.*, 1979, **44**, 2804.

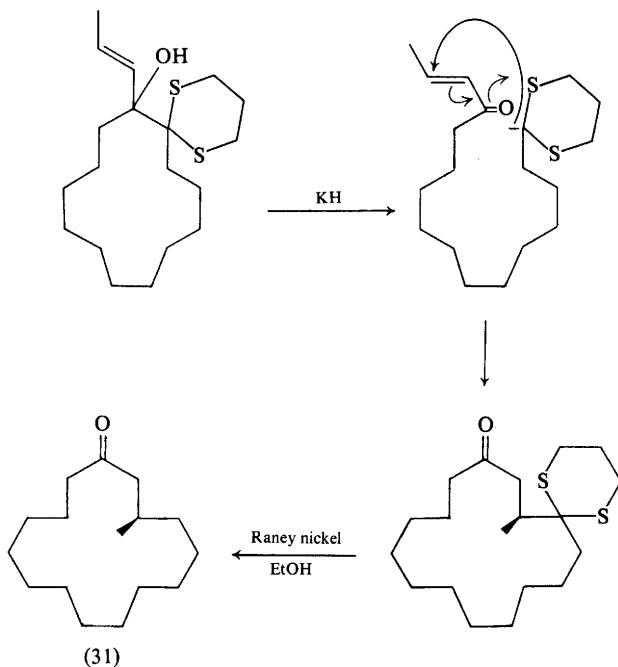
<sup>134</sup> H. Ogura, K. Furuhashi, H. Takahashi, and Y. Iitaka, *Chem. Pharm. Bull.*, 1978, **26**, 2782.

<sup>135</sup> Y. Tamaru, T. Harada, H. Iwamoto, and Z.-I. Yoshida, *J. Am. Chem. Soc.*, 1978, **100**, 5221; W. D. Woessner and P. S. Solera, *Synth. Commun.*, 1978, **8**, 279.

<sup>136</sup> Z. Lysenko, F. Ricciardi, J. E. Semple, P. C. Wang, and M. M. Joullie, *Tetrahedron Lett.*, 1978, 2679.

<sup>137</sup> K. A. Parker and J. R. Andrade, *J. Org. Chem.*, 1979, **44**, 3964.

7-hydroxymyoporone,<sup>138</sup> butyrolactones,<sup>139</sup> and  $\beta$ -diketone enol ethers.<sup>140</sup> A novel synthesis of (*d,l*)-muscone (31) involves a two-carbon ring-expansion process.<sup>141</sup> 2-Lithio-2-trimethylsilyl-1,3-dithian reacts with sulphur dioxide in a Wittig-like reaction to give the appropriate sulphine (see also Chap. 3, Pt II, p. 160, and Vol. 5, p. 133).<sup>142</sup>



The 1,2-adducts (32) of 2-lithio-1,3-dithians and cyclohex-2-enone can be isomerized to the more stable 1,4-adducts (33) by conversion into the potassium alkoxides (but not the less dissociated sodium or lithium salts).<sup>141</sup> Direct formation of enone 1,4-adducts occurs when HMPA-THF is used as the solvent,<sup>143,144</sup> and enolate trapping can be effected when the initial enone 1,4-adduct is treated with methyl iodide.<sup>143</sup> The allylic anion derived from (34) undergoes  $\alpha$ ,1,4-addition to cyclohexenone in the presence of CuI (Scheme 2).<sup>145</sup> In the absence of the copper salt, both  $\gamma$ -1,4- and  $\alpha$ -1,4-addition occur, with the former predominating. In contrast, allylation of (34) in the presence of CuI occurs primarily at the  $\gamma$ -position, while  $\alpha$ -allylation is observed otherwise.<sup>146</sup> The lithio-anion of 2-( $\beta$ -styryl)-

<sup>138</sup> H. J. Reich, P. M. Gold, and F. Chow, *Tetrahedron Lett.*, 1979, 4433.

<sup>139</sup> G. A. Kraus and B. Roth, *J. Org. Chem.*, 1978, **43**, 2072.

<sup>140</sup> P. S. Tobin, S. K. Basu, R. S. Grosserode, and D. M. S. Wheeler, *J. Org. Chem.*, 1980, **45**, 1250.

<sup>141</sup> S. R. Wilson and R. N. Risra, *J. Org. Chem.*, 1978, **43**, 4903.

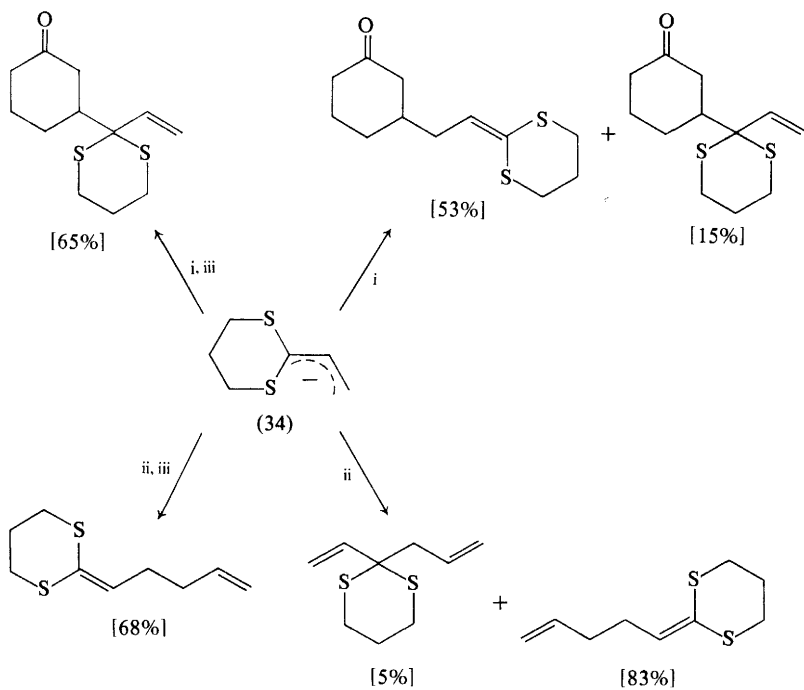
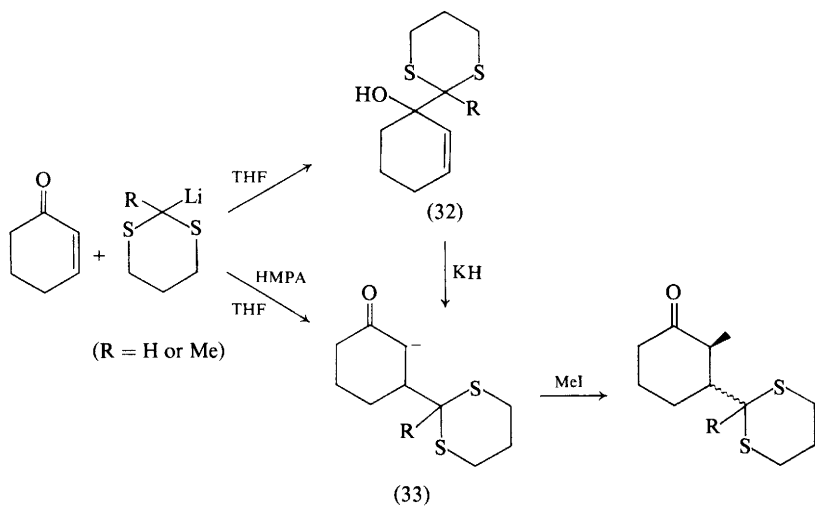
<sup>142</sup> M. van der Leij, P. A. T. W. Porskamp, B. H. M. Lammerink, and B. Zwanenburg, *Tetrahedron Lett.*, 1978, 811.

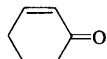

<sup>143</sup> J. Lucchetti, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 1979, 2695.

<sup>144</sup> C. A. Brown and A. Yamaichi, *J. Chem. Soc., Chem. Commun.*, 1979, 100.

<sup>145</sup> F. E. Ziegler and C. C. Tam, *Tetrahedron Lett.*, 1979, 4717.

<sup>146</sup> F. E. Ziegler and C. C. Tam, *J. Org. Chem.*, 1979, **44**, 3428.

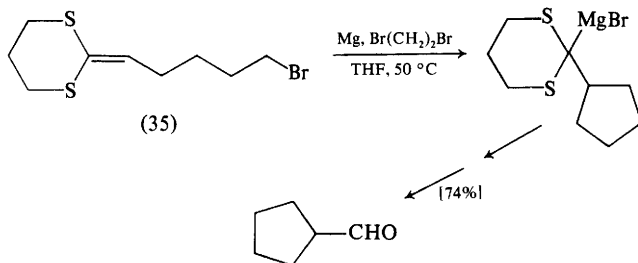


Reagents: i, ; ii, ; iii, CuI

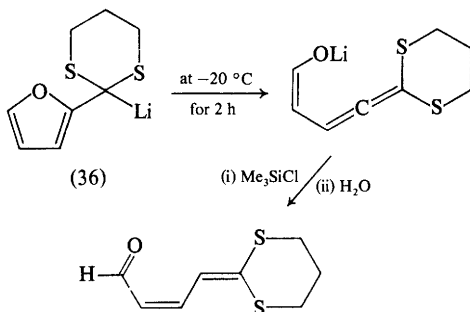
Scheme 2



1,3-dithian, which is the  $\gamma$ -phenyl analogue of (34), has been found to undergo substitution at the  $\alpha$ -position with hard electrophiles [e.g.  $D^+$ ,  $Me_3SiCl$ , and  $(MeO)_2SO_2$ ] and at the  $\gamma$ -position with softer electrophiles (e.g.  $RI$  and  $RBr$ ).<sup>147</sup> 2-Alkylidene-1,3-dithians can be prepared through the reaction of 2-lithio-1,3-dithians with 2,2'-dipyridyl disulphide.<sup>148</sup> An example of an intramolecular Michael addition to a 2-alkylidene-1,3-dithian (35) has been described.<sup>149</sup>



Additional reactions involving 1,3-dithianyl anions include nucleophilic substitution on *N*-methylindoletricarboxylchromium(o)<sup>150a</sup> and on toluenetri-carboxylchromium(o);<sup>150b</sup> one-electron transfer, proton abstraction, and alkylation by 2-chlorothiols and 2-chloro-oxolan<sup>151</sup> and by 2-halogeno-2-nitropropane (one-electron transfer only);<sup>152</sup> cleavage of  $\alpha$ -keto-1,3-dithians;<sup>153</sup> intramolecular alkylation of an epoxy-2-lithio-1,3-dithian that is generated by low-temperature transmetalation of a 2-(tributylstannyl)-1,3-dithian;<sup>154</sup> and opening of the furan ring in 2-(2'-furyl)-2-lithio-1,3-dithian (36).<sup>155</sup>



<sup>147</sup> W. S. Murphy and S. Wattanasin, *Tetrahedron Lett.*, 1979, 1827.

<sup>148</sup> Y. Nagao, K. Seno, and E. Fujita, *Tetrahedron Lett.*, 1979, 4403.

<sup>149</sup> N. H. Andersen, P. F. Duffy, A. D. Denniston, and D. B. Grotjahn, *Tetrahedron Lett.*, 1978, 4315.

<sup>150</sup> (a) A. P. Kozikowski and K. Isobe, *J. Chem. Soc., Chem. Commun.*, 1978, 1076; (b) M. F. Semmelhack, H. T. Hall, Jr., R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 3535.

<sup>151</sup> C. G. Kruse, E. K. Poels, and A. van der Gen, *J. Org. Chem.*, 1979, **44**, 2911.

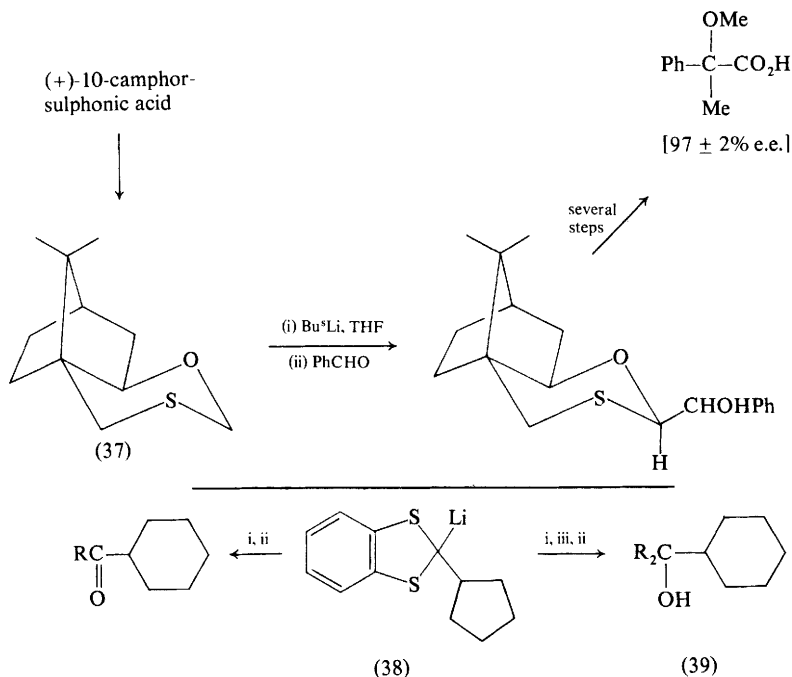
<sup>152</sup> G. A. Russell, M. Jawdasiuk, and M. Makosza, *J. Am. Chem. Soc.*, 1979, **101**, 2355.

<sup>153</sup> S. Takano, M. Takahashi, S. Hatakeyama, and K. Ogasawara, *J. Chem. Soc., Chem. Commun.*, 1979, 556.

<sup>154</sup> D. Seebach, I. Willert, A. K. Beck, and B. T. Grobel, *Helv. Chim. Acta*, 1978, **61**, 2510.

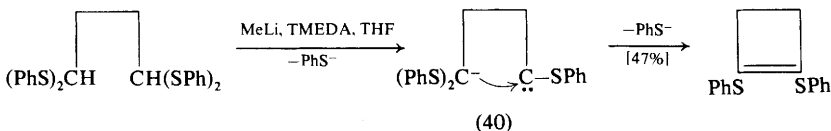
<sup>155</sup> M. J. Taschner and G. A. Kraus, *J. Org. Chem.*, 1978, **43**, 4235.

A number of anionic systems that are related to 1,3-dithian have been studied, including the anion from the unusual 1,3-oxathian (37) [which has been employed with excellent results in an asymmetric synthesis],<sup>84</sup> the 1,3-dithiolan anion (38)<sup>156</sup> [which reacts with trialkylboranes (as well as with other electrophiles)<sup>157</sup> to give, after oxidative work-up, ketones or tertiary alcohols (39), as shown in Scheme 3], and 2-substituted 1,3-dithiolan anions [which fragment to give aromatic dithioesters]<sup>158</sup> (see Chap. 3, Pt III, p. 191).



**Scheme 3**

*Acyclic Thioacetal and Orthothioformate Anions.* A number of unusual and synthetically useful ring-forming reactions that are thought to involve thioacetal anions such as (40) and (41) have been reported by Cohen.<sup>159</sup> A procedure

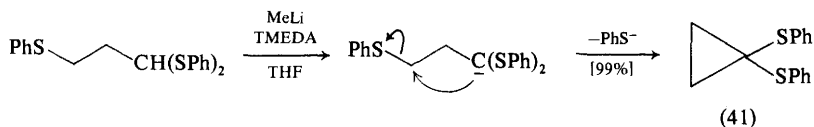


<sup>156</sup> S. Ncube, A. Pelter, and K. Smith, *Tetrahedron Lett.*, 1979, 1893, 1895.

<sup>157</sup> S. Ncube, A. Pelter, K. Smith, P. Blatcher, and S. Warren, *Tetrahedron Lett.*, 1978, 2345.

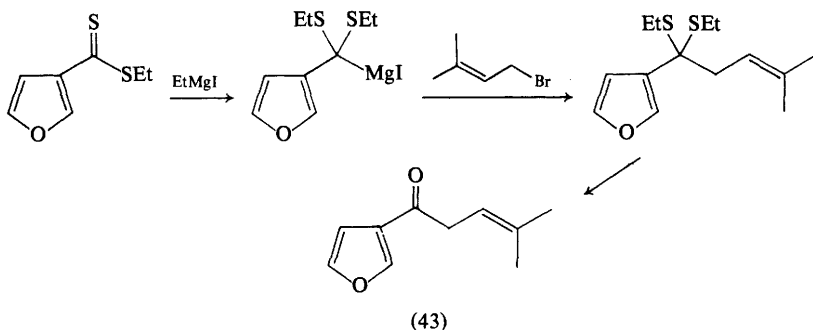
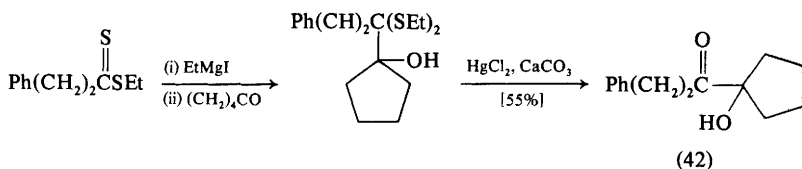
<sup>158</sup> N. C. Gonnella, M. V. Lakshmikantham, and M. P. Cava, *Synth. Commun.*, 1979, 9, 17.

<sup>159</sup> (a) T. Cohen and W. M. Daniewski, *Tetrahedron Lett.*, 1978, 2991; (b) T. Cohen, D. Ouellete, and W. M. Daniewski, *ibid.*, p. 5063; (c) T. Cohen, R. B. Weisenfeld, and R. E. Gapinski, *J. Org. Chem.*, 1979, 44, 4744; T. Cohen and J. R. Matz, *ibid.*, p. 4816.



described in *Organic Syntheses* and another report have appeared on the preparation of 1-phenylthio-1,3-butadienes *via* thioacetal anions,<sup>160</sup> while a related paper provides a synthesis of acyclic dienones.<sup>161</sup> In THF-HMPA, bis-(phenylthio)methyl-lithium adds predominantly (92%) 1,4 to cyclohexenone, in contrast to addition in the absence of HMPA (ratio 55 : 45 of 1,4- : 1,2-addition).<sup>143</sup>

Thiophilic addition to dithioesters followed by capture of the thioacetal anion with an electrophile provides a useful approach to the formation of carbonyl compounds such as (42)<sup>162</sup> and (43),<sup>163</sup> and has been elegantly employed in the total synthesis of the macrocycles ( $\pm$ )-maysine and ( $\pm$ )-4,5-deoxymaysine.<sup>164</sup> Trimethyl borate has been used to convert bis(phenylthio)methyl-lithium into the keten thioacetal (45)<sup>165</sup> *via* the boron-containing carbanion (44), as shown in Scheme 4.<sup>166</sup> Bis(phenylthio)methyl-lithium and related compounds are also the key reagents in the preparation of 2-(phenylthio)-enones, 2-(phenylthio)-butadienes,<sup>167</sup>  $\alpha$ -(phenyl-



<sup>160</sup> T. Cohen and R. J. Ruffner, *Org. Synth.*, 1979, **59**, 202; T. Cohen, R. E. Gapinski, and R. B. Hutchins, *J. Org. Chem.*, 1979, **44**, 3599.

<sup>161</sup> M. Pohmakotr and D. Seebach, *Tetrahedron Lett.*, 1979, 2271.

<sup>162</sup> A. I. Meyers, T. A. Tait, and D. L. Comins, *Tetrahedron Lett.*, 1978, 4657.

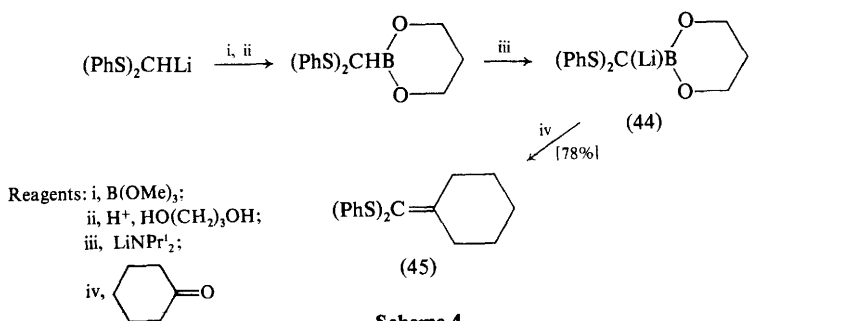
<sup>163</sup> P. Gosselin, S. Masson, and A. Thuillier, *J. Org. Chem.*, 1979, **44**, 2807.

<sup>164</sup> A. I. Meyers, D. M. Roland, D. L. Comins, R. Henning, M. P. Fleming, and K. Shimizu, *J. Am. Chem. Soc.*, 1979, **101**, 4732; A. I. Meyers, D. L. Comins, D. M. Roland, R. Henning, and K. Shimizu, *ibid.*, p. 7104.

<sup>165</sup> A. Mendoza and D. S. Matteson, *J. Org. Chem.*, 1979, **44**, 1352.

<sup>166</sup> D. S. Matteson and K. Arne, *J. Am. Chem. Soc.*, 1978, **100**, 1325.

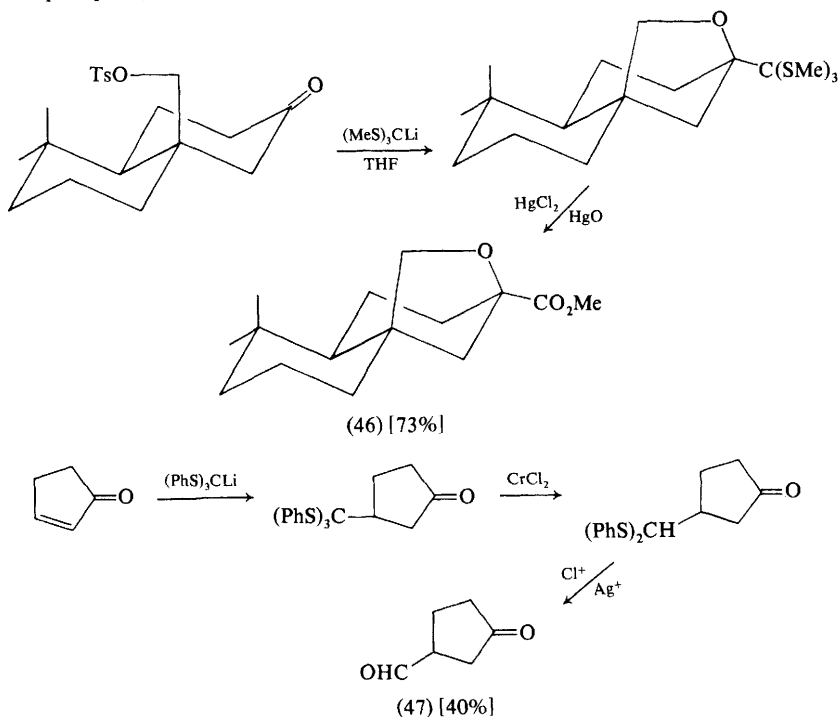
<sup>167</sup> P. Blatcher, J. I. Gryson, and S. Warren, *J. Chem. Soc., Chem. Commun.*, 1978, 657; P. Blatcher and S. Warren, *Tetrahedron Lett.*, 1979, 1247.



Scheme 4

thio)-ketones,<sup>168</sup> and ( $\pm$ )-hinokinin.<sup>169</sup> The dianion from bis(ethylthio)acetic acid has also been used in organic synthesis.<sup>170</sup>

Orthothioformate anions have been utilized in the generation of the ester (46)<sup>91</sup> and 1,4-dicarbonyl compounds such as (47).<sup>171,172</sup> A full report has appeared on the decomposition of orthothioformate anions to bis(arythio)-carbenes<sup>173</sup> (see also Chap. 1, p. 47).



<sup>168</sup> P. Blatcher and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1074.

<sup>169</sup> A. Ichihara, N. Nio, Y. Terayama, R. Kimura, and S. Sakamura, *Tetrahedron Lett.*, 1979, 3731.

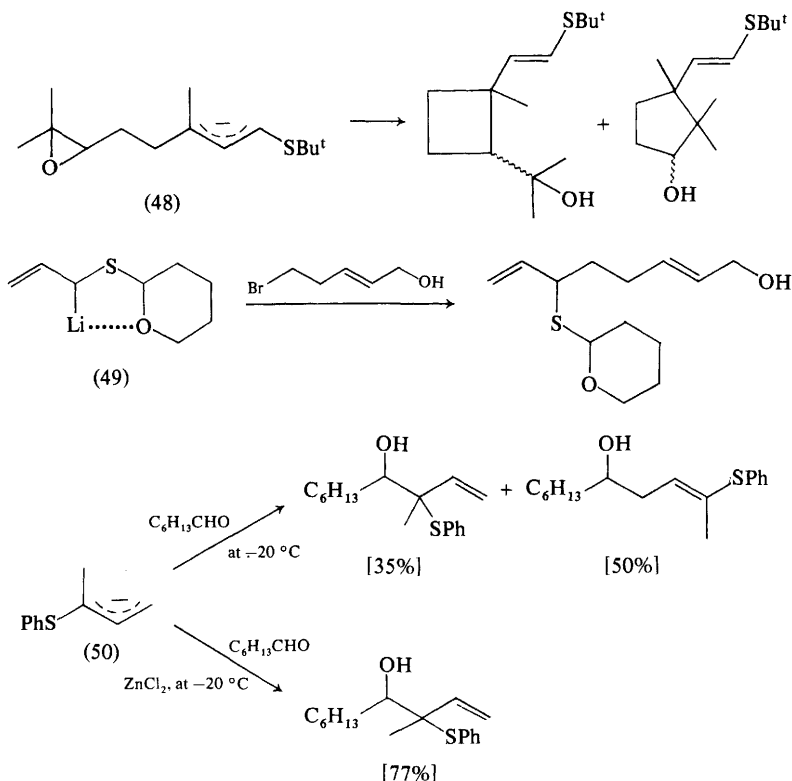
<sup>170</sup> G. S. Bates, *J. Chem. Soc., Chem. Commun.*, 1979, 161.

<sup>171</sup> T. Cohen and S. M. Nolan, *Tetrahedron Lett.*, 1978, 3533.

<sup>172</sup> R. A. J. Smith and A. R. Lal, *Aust. J. Chem.*, 1979, **32**, 353.

<sup>173</sup> M. Nitsche, D. Seebach, and A. K. Beck, *Chem. Ber.*, 1978, **111**, 3644.

**Thioallyl and Related Anions.** Regio-control in reactions of thioallylic carbanions has been a subject of considerable interest during the past several years (see also Chap. 1, p. 37). Intramolecular  $\gamma$ -alkylation of the anion (48), prepared from the  $\beta\gamma$ -unsaturated compound with butyl-lithium in TMEDA, is a key step in an approach to grandisol and its isomers,<sup>174</sup> while exclusive  $\alpha$ -alkylation is seen with the anion (49).<sup>63</sup> Both  $\alpha$ - and  $\gamma$ -hydroxyalkylation are observed with the propene-3-thiol and 2-methylpropene-3-thiol dianions<sup>114</sup> and with the anion from 3-methyl-3-(phenylthio)propene (50).<sup>175</sup> In the last case, regio-control can be achieved through the addition of  $\text{ZnCl}_2$ . Similar regio-control in the alkylation and hydroxyalkylation of thioallylic carbanions may be realized through the formation of boron<sup>176,177</sup> and aluminium<sup>178</sup> 'ate' complexes (51). In the absence of the 'ate' complex, a mixture of the products of  $\alpha$ - and  $\gamma$ -hydroxyalkylation (in the ratio 43 : 57) is formed.<sup>178</sup>  $\alpha\gamma'$ -Coupling occurs when the boron 'ate' complex (51) reacts with allylic halides.<sup>176</sup>



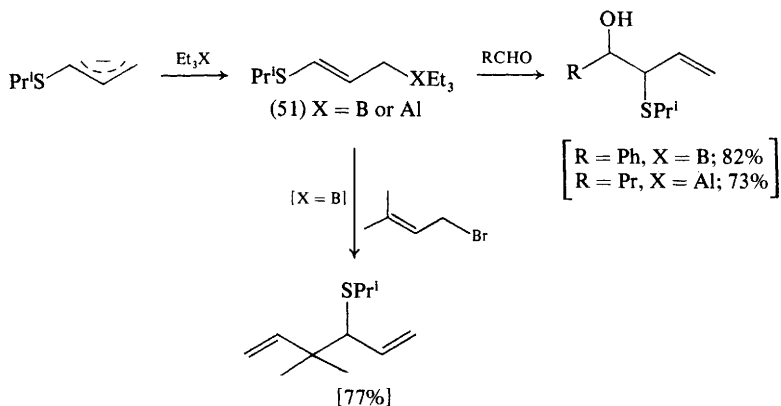
<sup>174</sup> V. Rautenstrauch, *J. Chem. Soc., Chem. Commun.*, 1978, 519.

<sup>175</sup> J.-F. Biellmann and D. Schirlin, *Synth. Commun.*, 1978, **8**, 409.

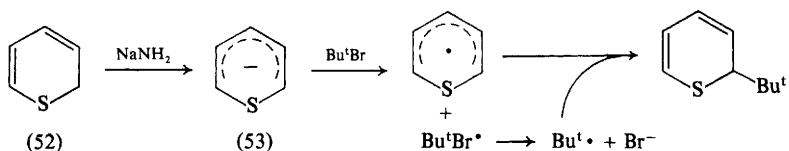
<sup>176</sup> Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, 1979, 157; Y. Yamamoto, H. Yatagai, and K. Maruyama, *Chem. Lett.*, 1979, 385.

<sup>177</sup> Y. Yamamoto and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, 1980, 239.

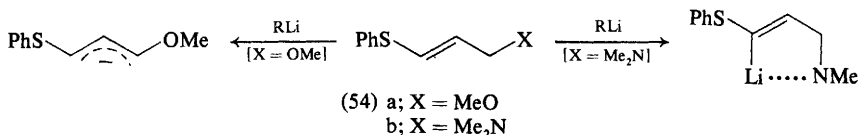
<sup>178</sup> Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Org. Chem.*, 1980, **45**, 195.



Methylthioallyl anion undergoes  $\alpha$ -1,4-addition to enones in the presence of HMPA, while 1,2-addition occurs in its absence.<sup>179</sup> The anion (53) derived from 2*H*-thiopyran (52) by abstraction of the 6-proton (this is the anion that is favoured under conditions of thermodynamic control) has been found to undergo alkylation with Bu<sup>t</sup>Br.<sup>180</sup> Rather than involving an unprecedented S<sub>N</sub>2 attack at Bu<sup>t</sup>Br, the reaction may involve a one-electron-transfer process.<sup>159d</sup> Other studies on the reactions of anions related to (53) have been published.<sup>181</sup> Thioallylic anions have been employed in syntheses of 2-vinylthian,<sup>61</sup> 1,1-disilylalk-2-enes,<sup>182</sup> and the natural products mokupalide,<sup>183</sup> manicone,<sup>184</sup> (±)-laurencin,<sup>73</sup> and (6*Z*)-hedycarylol isomers,<sup>185</sup> amongst other compounds.<sup>186</sup>



*α*-Thiovinyl Anions. An interesting example of substituent effects on the position of metallation is provided by vinyl sulphides (54a) and (54b).<sup>187</sup> The results have been interpreted in terms of the superior ability of nitrogen, compared to oxygen, to



<sup>179</sup> M. R. Binns, R. K. Haynes, T. L. Houston, and W. R. Jackson, *Tetrahedron Lett.*, 1980, **21**, 573.

<sup>180</sup> R. Graffing, H. D. Verkruijsse, and L. Brandsma, *J. Chem. Soc., Chem. Commun.*, 1978, 596.

<sup>181</sup> R. Graffing and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 23.

<sup>182</sup> H. Wetter, *Helv. Chim. Acta*, 1978, **61**, 3072.

<sup>183</sup> F. W. Sum and L. Weiler, *J. Am. Chem. Soc.*, 1979, **101**, 4401.

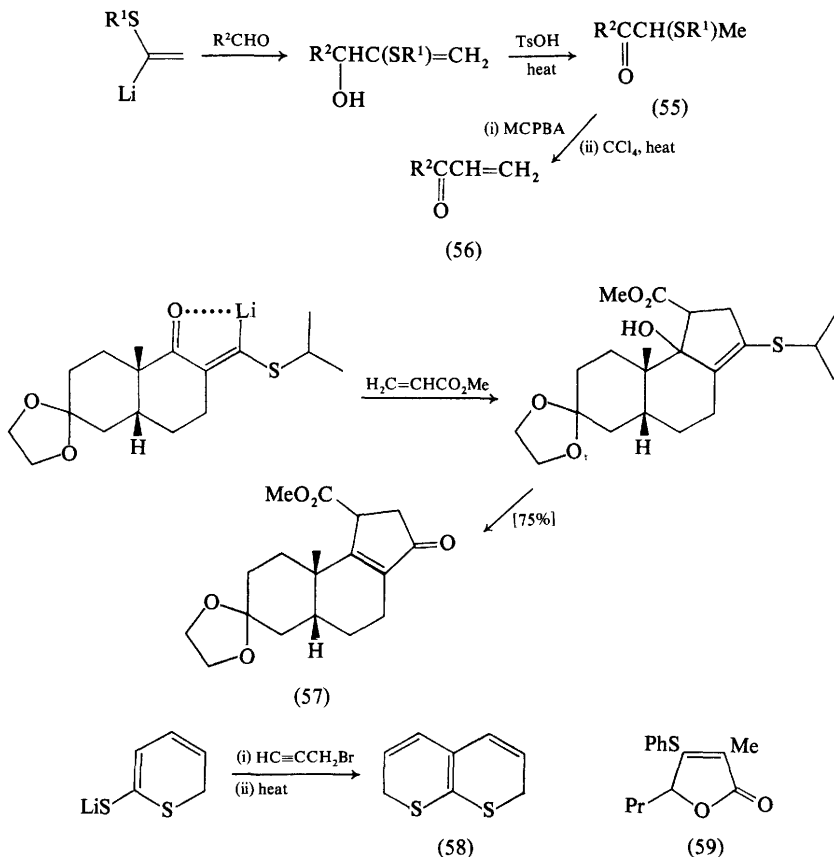
<sup>184</sup> T. Mimura, Y. Kimura, and T. Nakai, *Chem. Lett.*, 1979, 1361.

<sup>185</sup> M. Kodama, S.-I. Yokoo, H. Yamada, and S. Ito, *Tetrahedron Lett.*, 1978, 3121.

<sup>186</sup> T. Hayashi, N. Fujitaka, T. Oishi, and T. Takeshima, *Tetrahedron Lett.*, 1980, **21**, 303.

<sup>187</sup> J. J. Fitt and H. W. Gschwend, *J. Org. Chem.*, 1979, **44**, 303.

function as a ligand for the internal chelation of lithium.  $\alpha$ -Thiovinyl anions, prepared by the reductive desulphurization of keten thioacetals with lithium naphthalide<sup>188</sup> or by deprotonation of vinyl sulphides, have been used in the synthesis of  $\alpha$ -(alkylthio)- or  $\alpha$ -(arylthio)-ketones (55) and the enones (56),<sup>189,190</sup> of the annelated cyclopentenone (57),<sup>191</sup> of the heterocycle (58),<sup>192</sup> and of the butenolide (59) prepared from  $\text{PhSC}(\text{Li})=\text{C}(\text{Me})\text{CO}_2\text{Me}$  and butanal.<sup>193</sup> More work has appeared on reactions of tetrathiafulvalenyl-lithium<sup>194</sup> and an account of the preparation and reactions of  $\alpha$ -thioallenyl-lithium compounds has been published.<sup>195</sup>



<sup>188</sup> T. Cohen and R. B. Weisenfeld, *J. Org. Chem.*, 1979, **44**, 3601.

<sup>189</sup> M. Braun, *Tetrahedron Lett.*, 1978, 3695.

<sup>190</sup> R. C. Cookson and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 1978, 821.

<sup>191</sup> J. P. Marino and L. C. Katterman, *J. Chem. Soc., Chem. Commun.*, 1979, 946.

<sup>192</sup> R. Graffing and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 1978, **97**, 208; *Synthesis*, 1978, 578.

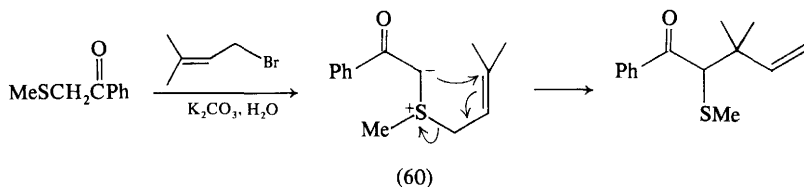
<sup>193</sup> K. Isobe, M. Fuse, H. Kosugi, H. Hagiwara, and H. Iida, *Chem. Lett.*, 1979, 785.

<sup>194</sup> D. C. Green and R. W. Allen, *J. Chem. Soc., Chem. Commun.*, 1978, 832; *J. Org. Chem.*, 1979, **44**, 1476.

<sup>195</sup> R. C. Cookson and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 1978, 822.

*Miscellaneous  $\alpha$ -Thiocarbanions.* 1-Lithio-1-(phenylthio)cyclopropane, which can be prepared by lithium-sulphur exchange or by reductive lithiation of cyclopropanone thioacetals,<sup>196</sup> or by lithiation followed by cyclization of 1,3-bis-(phenylthio)propane,<sup>197</sup> has been used in the generation of cyclobutanone,<sup>198</sup> a tetrahydrochromanone,<sup>199</sup> alkylidenecyclopropanes,<sup>200</sup> and various ketones<sup>201</sup> and alcohols.<sup>197</sup>

$\alpha$ -(Methylthio)acetophenone, in the presence of a base such as  $K_2CO_3$  (which should be too weak to effect deprotonation) still undergoes allylation by what appears to be an  $S_N2'$  process. In fact what is probably involved is  $S$ -allylation followed by ylide formation and [2,3]-sigmatropic rearrangement, as in (60).<sup>56,57</sup> The anions of  $\alpha$ -(ethylthio)-ketones have been utilized in preparations of  $\alpha$ -diketones and their derivatives,<sup>202</sup> while the anion of an  $\alpha$ -(phenylthio)-ketone serves as a precursor for the terpene perilla ketone.<sup>203</sup>



$\alpha$ -(Phenylthio)- or  $\alpha$ -(methylthio)-ester anions have found application in the synthesis of recifeolide (61),<sup>204</sup> avenaciolide,<sup>205</sup> (*dl*)-aplysinatin,<sup>206</sup> furans,<sup>207</sup> and olefins,<sup>208</sup> amongst other uses,<sup>209</sup> while the  $\alpha$ -mercapto- $\gamma$ -butyrolactone dianion provides an entry to  $\alpha$ -alkylidene- $\gamma$ -butyrolactones (62)<sup>210</sup> and the reaction of  $\alpha$ -(phenylthio)acetamide dianions (63) with di-iodomethane provides an interesting route to  $\beta$ -lactams.<sup>211</sup> Phenylthioalkyl-lithiums containing  $\alpha$ -silyl or  $\alpha$ -boranyl substituents have been converted into olefins<sup>212</sup> and ketones,<sup>166</sup> respectively.  $\alpha$ -Lithio- $\alpha$ -(phenylthio)acetonitrile undergoes 1,4-addition to cyclohex-2-enone at room temperature but predominantly 1,2-addition at  $-78^\circ C$ .<sup>213</sup>

<sup>196</sup> T. Cohen and J. R. Matz, *Synth. Commun.*, 1980, **10**, 311; T. Cohen, W. M. Daniewski, and R. B. Weisenfeld, *Tetrahedron Lett.*, 1978, 4665.

<sup>197</sup> K. Tanaka, H. Uneme, S. Matsui, R. Tanikaga, and A. Kaji, *Chem. Lett.* 1980, 287.

<sup>198</sup> B. M. Trost and W. C. Vladuchick, *Synthesis*, 1978, 821.

<sup>199</sup> B. M. Trost and J. H. Rigby, *J. Org. Chem.*, 1978, **43**, 2938.

<sup>200</sup> S. Halazy and A. Krief, *Tetrahedron Lett.*, 1979, 4233.

<sup>201</sup> R. D. Miller and D. R. McKean, *Tetrahedron Lett.*, 1979, 583; R. D. Miller, D. R. McKean, and D. Kaufmann, *ibid.*, p. 587.

<sup>202</sup> Y. Nagao, K. Kaneko, and E. Fujita, *Tetrahedron Lett.*, 1978, 4115.

<sup>203</sup> K. Inomata, M. Sumita, and H. Kotake, *Chem. Lett.*, 1979, 709.

<sup>204</sup> T. Takahashi, S. Hashiguchi, K. Kasuga, and J. Tsuji, *J. Am. Chem. Soc.*, 1978, **100**, 7424.

<sup>205</sup> J. L. Herrmann, M. H. Berger, and R. H. Schlessinger, *J. Am. Chem. Soc.*, 1979, **101**, 1544.

<sup>206</sup> T. R. Hoye and M. J. Kurth, *J. Am. Chem. Soc.*, 1979, **101**, 5065.

<sup>207</sup> K. Inomata, S. Aoyama, and H. Kotake, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 930.

<sup>208</sup> M. Baboulene and G. Sturtz, *J. Organomet. Chem.*, 1979, **177**, 27.

<sup>209</sup> S. Torii, H. Okumoto, and H. Tanaka, *J. Org. Chem.*, 1980, **45**, 1330.

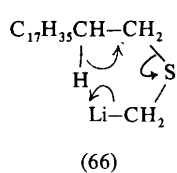
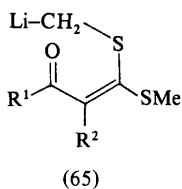
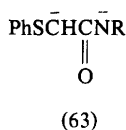
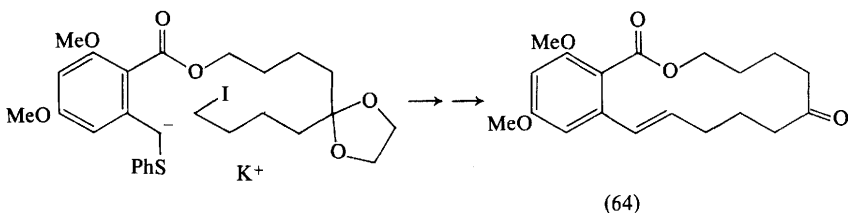
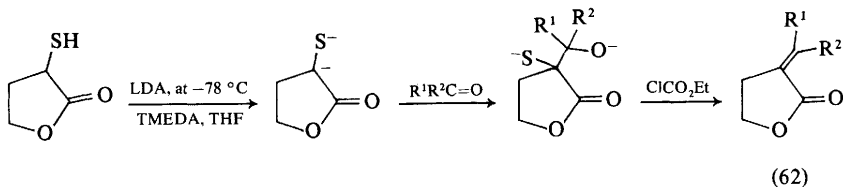
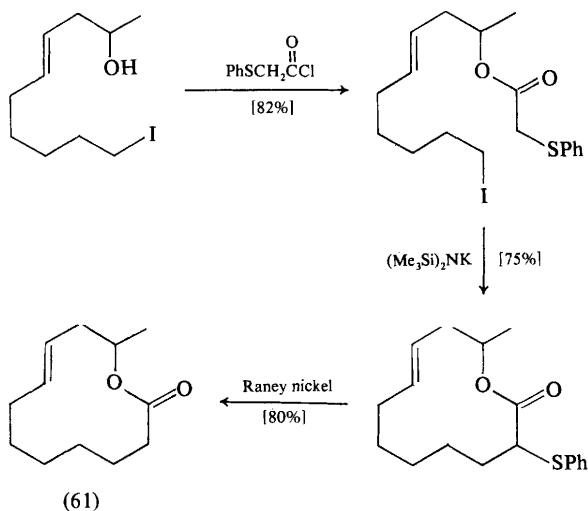
<sup>210</sup> K. Tanaka, H. Uneme, N. Yamagishi, N. Ono, and A. Kaji, *Chem. Lett.*, 1978, 653.

<sup>211</sup> K. Hirai and Y. Iwano, *Tetrahedron Lett.*, 1979, 2031.

<sup>212</sup> T. Agawa, M. Ishikawa, M. Komatsu, and Y. Ohshiro, *Chem. Lett.*, 1980, 335.

<sup>213</sup> N.-Y. Wang, S.-S. Su, and L.-Y. Tsai, *Tetrahedron Lett.*, 1979, 1121.





$\alpha$ -(Arylthio)- or  $\alpha$ -(alkylthio)-benzylic anions undergo facile intermolecular<sup>214,215</sup> or intramolecular alkylation in the syntheses of *O*-methyl-( $\pm$ )-lasiodiplodin<sup>216</sup> and ( $\pm$ )-zearalenone dimethyl ether (64),<sup>216</sup> undergo Wittig rearrangements with

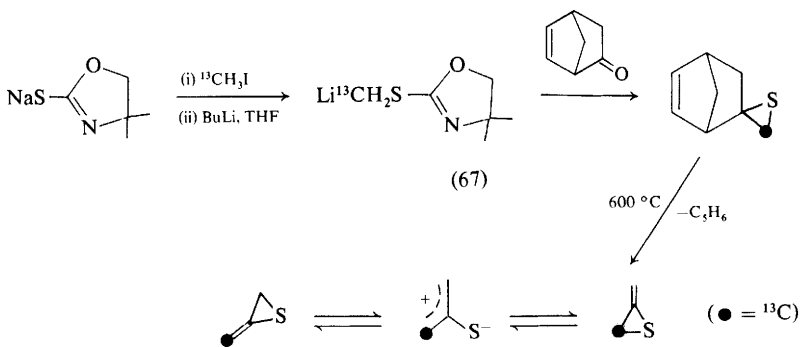
<sup>214</sup> J. Ackrell, *J. Org. Chem.*, 1978, **43**, 4892.

<sup>215</sup> B. L. Soltz and J. Y. Corey, *J. Organomet. Chem.*, 1979, **171**, 291.

<sup>216</sup> T. Takahashi, K. Kasuga, M. Takahashi, and J. Tsuji, *J. Am. Chem. Soc.*, 1979, **101**, 5072; T. Takahashi, K. Kasuga, and J. Tsuji, *Tetrahedron Lett.*, 1978, 4917.

resultant ring contraction<sup>124</sup> in the formation of cyclophanes,<sup>34a,217,218</sup> react with carboxylate salts to give  $\alpha$ -(thioalkyl)-ketones,<sup>219</sup> and can be transformed into sulphur-free alkyl-lithium compounds.<sup>220</sup>

A new thiophen synthesis is based on deprotonation and cyclization of the resultant carbanion (65) of a keten dimethylthioacetal.<sup>221</sup> Other applications of  $\alpha$ -(phenylthio)- or  $\alpha$ -(alkylthio)-alkyl-lithiums include preparations of disparlure (the sex pheromone of the gypsy moth)<sup>222</sup> and other chiral epoxides,<sup>223</sup> of an anti-peptic-ulcer diterpene from *Croton sublyratus*,<sup>224</sup> of carbene-thiometal chelates through reaction with  $[\text{Cr}(\text{CO})_6]$  or  $[\text{W}(\text{CO})_6]$ ,<sup>225</sup> of olefins *via*  $\beta$ -hydroxy-sulphides,<sup>226</sup> and of Michael adducts of enones.<sup>227</sup> In other work, the chiral solvent 1,4-dimethylamino-2,3-dimethoxybutane is employed in enantioselective addition reactions of  $\alpha$ -thio-carbanions with ketones and Michael acceptors.<sup>228</sup>  $\alpha, \beta'$ -Elimination of  $\alpha$ -thio-carbanions such as (66) provides a useful synthesis of olefins,<sup>229</sup> and a 2-(lithiomethylthio)- $\Delta^2$ -oxazoline (67) has been used to prepare a <sup>13</sup>C-labelled thiiran for a microwave study of the valence tautomerism of allene episulphide.<sup>230</sup>



## 7 Sulphinyl and Sulphiliminyll Carbanions

**Synthesis and Properties.**—The carbanion carbons in  $\alpha$ -lithiothian 1-oxide<sup>231</sup> and  $\text{PhS}(\text{O})\text{CH}_2\text{Li}^6$  have been found by <sup>13</sup>C n.m.r. spectroscopy to be nearly planar ( $sp^2$ -hybridized), presumably due to a chelated structure such as (68).<sup>6,7</sup> Interest

<sup>217</sup> M. W. Haenel, *Tetrahedron Lett.*, 1978, 4007.

<sup>218</sup> D. Kamp and V. Boekelheide, *J. Org. Chem.*, 1978, **43**, 3470.

<sup>219</sup> S. Kano, T. Yokomatsu, and S. Shibuya, *J. Org. Chem.*, 1978, **43**, 4366.

<sup>220</sup> C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 1979, **44**, 713.

<sup>221</sup> J. P. Marino and J. L. Kostusyk, *Tetrahedron Lett.*, 1979, 2489, 2493.

<sup>222</sup> W. H. Pirkle and P. L. Rinaldi, *J. Org. Chem.*, 1979, **44**, 1025.

<sup>223</sup> W. H. Pirkle and P. L. Rinaldi, *J. Org. Chem.*, 1978, **43**, 3803.

<sup>224</sup> A. Ogiso, E. Kitazawa, M. Kurabayashi, A. Sato, S. Takahashi, H. Noguchi, H. Kuwano, S. Kobayashi, and H. Mishima, *Chem. Pharm. Bull.*, 1978, **26**, 3117.

<sup>225</sup> H. G. Raubenheimer, S. Lotz, H. W. Viljoen, and A. A. Chalmers, *J. Organomet. Chem.*, 1978, **152**, 73.

<sup>226</sup> J. N. Denis, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 1979, 4111.

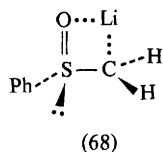
<sup>227</sup> L. Wartski, M. El Bouz, J. Seyden-Penne, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 1979, 1543.

<sup>228</sup> D. Seebach and W. Langer, *Helv. Chim. Acta*, 1979, **62**, 1701; W. Langer and D. Seebach, *ibid.*, p. 1710.

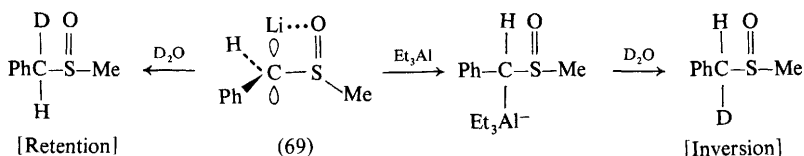
<sup>229</sup> J-F. Biellmann, H. d'Orchymont, and J.-L. Schmitt, *J. Am. Chem. Soc.*, 1979, **101**, 3283.

<sup>230</sup> E. Block, R. E. Penn, M. D. Ennis, T. A. Owens, and S. L. Yu, *J. Am. Chem. Soc.*, 1978, **100**, 7436.

<sup>231</sup> R. Lett and G. Chassaing, *Tetrahedron*, 1978, **34**, 2705.



continues in the stereochemistry of reactions of  $\alpha$ -sulphinyl carbanions with 'chelating' and 'non-chelating' reagents (e.g.  $D_2O$  and MeI, respectively; see Vol. 5, p. 91). Thus it has been found that *solid* lithiobenzyl methyl sulphoxide reacts completely stereospecifically with inversion with MeI vapour at 25 °C whereas the analogous reaction in solution is only stereoselective.<sup>232</sup> The solid lithio-compound does not react stereospecifically with chelating reagents such as  $D_2O$  or EtOD. In solution, the normal stereochemistry of the deuteration of lithiobenzyl methyl sulphoxide (retention) can be reversed by the prior addition of  $Et_3Al$ , which is thought to afford an 'ate complex' (69).<sup>178</sup> In contrast to  $\alpha$ -lithiothian 1-oxide and acyclic  $\alpha$ -sulphinyl carbanions,  $\alpha$ -lithiothiepan 1-oxide and  $\alpha$ -lithiothiocan 1-oxide both react with MeI with predominant retention of stereochemistry (*cis*-methylation).<sup>61, 233</sup>



**Reactions.**—Asymmetric syntheses involving  $\alpha$ -sulphinyl carbanions have been described, including the preparation of  $\beta$ -methoxy- $\beta$ -phenylacetaldehyde *via* a chiral dithioacetal mono-*S*-oxide anion<sup>234</sup> and of lactones,<sup>235</sup>  $\beta$ -hydroxy-lactones, and esters such as (*R*)-mevalonolactone.<sup>236</sup>  $\alpha$ -Sulphinyl carbanions are intermediates in the reaction of sulphines with carbanions (thiophilic addition) which can lead ultimately to ketones<sup>237</sup> or olefins<sup>238, 239</sup> (see also Chap. 3, Pt II, p. 162).

An  $\alpha\beta$ -unsaturated sulphoxide (72) is the final product isolated when *cis*-1,2-diphenylthiiran *S*-oxide (70) is treated with butyl-lithium, followed by alkylation.<sup>240</sup> The lithio-thiiran *S*-oxide (71) is a presumed intermediate. A number of papers have dealt with the reactions of alkyl-lithiums or other strong bases with  $\alpha\beta$ -unsaturated sulphoxides. The reactions observed include (a)  $\alpha$ -deprotonation, affording  $\alpha$ -sulphinylvinyl anions, which turn out to be surprisingly configuration-

<sup>232</sup> J. F. Biellmann, J. F. Blanzat, and J. J. Vicens, *J. Am. Chem. Soc.*, 1980, **102**, 2460.

<sup>233</sup> V. Cere, S. Pollicino, E. Sandri, and A. Fava, *Tetrahedron Lett.*, 1978, 5239.

<sup>234</sup> L. Colombo, C. Gennari, C. Scolastico, G. Guanti, and E. Narisano, *J. Chem. Soc., Chem. Commun.*, 1979, 591.

<sup>235</sup> F. Matloubi and G. Solladié, *Tetrahedron Lett.*, 1979, 2141.

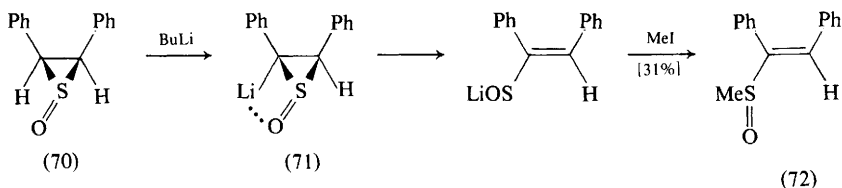
<sup>236</sup> E. Abushanab, D. Reed, F. Suzuki, and C. J. Sih, *Tetrahedron Lett.*, 1978, 3415; C. Mioskowski and G. Solladié, *Tetrahedron*, 1980, **36**, 227.

<sup>237</sup> G. E. Veenstra and B. Zwanenburg, *Tetrahedron*, 1978, **34**, 1585.

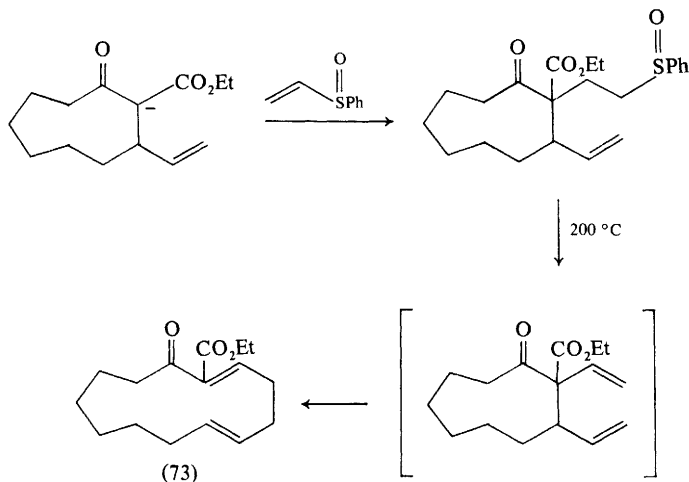
<sup>238</sup> M. van der Leij, H. J. M. Strijtveen, and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 45.

<sup>239</sup> J. A. Loontjes, M. van der Leij, and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 39.

<sup>240</sup> B. F. Bonini, G. Maccagnani, G. Mazzanti, and P. Piccinelli, *Tetrahedron Lett.*, 1979, 3987.



ally unstable,<sup>241–243</sup> (b) Michael addition, providing an approach to prostaglandins<sup>244</sup> and medium-sized rings such as (73),<sup>245</sup> and, occasionally, (c) loss of sulphur.<sup>246</sup>  $\alpha$ -Sulphinylallenyl anions have also been generated.<sup>195</sup>



The easily formed  $\alpha$ -chloro- $\alpha$ -phenylsulphinyl  $\alpha$ -lithio-compounds (74) provide the starting point for syntheses of epoxy-sulphones (76;  $\text{R}^1 = \text{R}^2 = \text{H}$ ),<sup>247</sup> enones (75;  $\text{R}^1 = \text{R}^2 = \text{Me}$ ),<sup>248</sup> vinyl chlorides (77),<sup>249</sup> and thioesters (78), as shown in Scheme 5.<sup>250</sup> Methyl methylthiomethyl sulphoxide anion has been used to make 2-arylpropanoate esters<sup>251</sup> and 1,4-diketone precursors,<sup>252</sup> while other types of substituted  $\alpha$ -sulphinyl carbanions have been utilized in the preparation of

<sup>241</sup> G. H. Posner, P.-W. Tang, and J. P. Mallamo, *Tetrahedron Lett.*, 1978, 3995.

<sup>242</sup> R. R. Schmidt, H. Speer, and B. Schmid, *Tetrahedron Lett.*, 1979, 4277.

<sup>243</sup> H. Okamura, Y. Mitsuhiro, M. Miura, and H. Takei, *Chem. Lett.*, 1978, 517.

<sup>244</sup> R. David and K. G. Untch, *J. Org. Chem.*, 1979, **44**, 3755.

<sup>245</sup> J. Bruhn, H. Heimgartner, and H. Schmid, *Helv. Chim. Acta*, 1979, **62**, 2630.

<sup>246</sup> G. Neef, U. Eder, and A. Seeger, *Tetrahedron Lett.*, 1980, **21**, 903.

<sup>247</sup> T. Durst, K.-C. Tin, F. de Reinach-Hirtzbach, J. M. Decesare, and M. D. Ryan, *Can. J. Chem.*, 1979, **57**, 258.

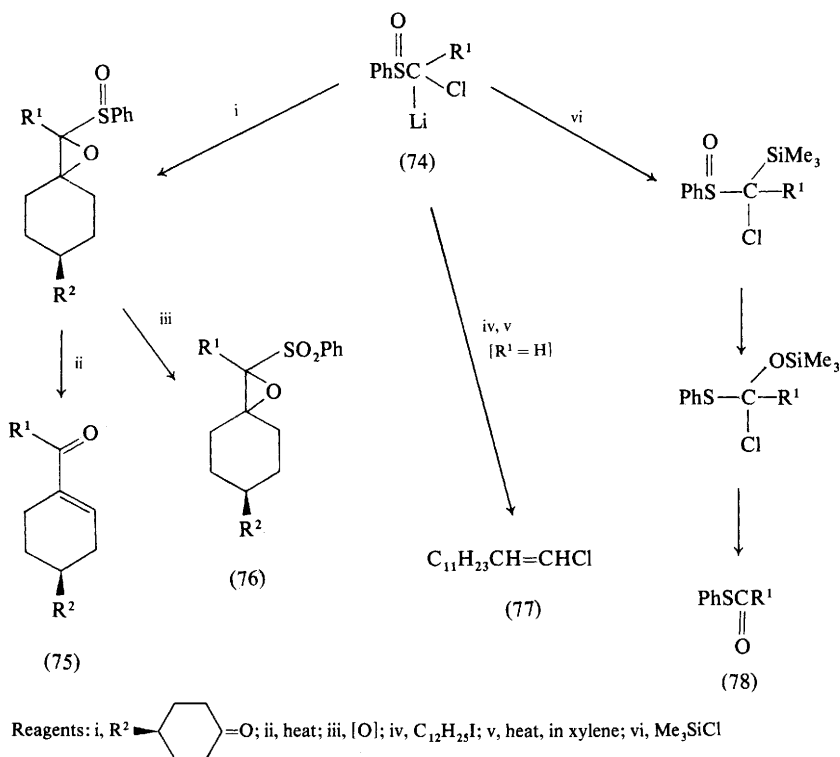
<sup>248</sup> D. G. Taber and B. P. Gunn, *J. Org. Chem.*, 1979, **44**, 450.

<sup>249</sup> V. Reutrakul and P. Thamnuan, *Tetrahedron Lett.*, 1979, 617.

<sup>250</sup> K. M. More and J. Wemple, *J. Org. Chem.*, 1978, **43**, 2713.

<sup>251</sup> K. Ogura, S. Mitamura, K. Kishi, and G.-I. Tsuchihashi, *Synthesis*, 1979, 880; K. Ogura, Y. Ito, and G.-I. Tsuchihashi, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2013.

<sup>252</sup> K. Ogura, M. Yamashita, and G.-I. Tsuchihashi, *Tetrahedron Lett.*, 1978, 1303.



Scheme 5

(*E*)-hotrienol,<sup>253</sup> brefeldin A,<sup>254</sup> cyclobutenes,<sup>255</sup> dienes,<sup>256</sup>  $\alpha,\beta$ -unsaturated sulphides,<sup>257</sup> and allylic alcohols.<sup>258</sup> *N*-Tosylsulphilimine (79) can be readily converted into its anion, which converts ketones into oxirans.<sup>259</sup>

<sup>253</sup> E. Guittet and S. Julia, *Synth. Commun.*, 1979, **9**, 317.

<sup>254</sup> P. A. Bartlett and F. R. Green, III, *J. Am. Chem. Soc.*, 1978, **100**, 4858.

<sup>255</sup> S. R. Wilson, L. R. Phillips, Y. Pelister, and J. C. Huffman, *J. Am. Chem. Soc.*, 1979, **101**, 7373.

<sup>256</sup> B. M. Trost, L. Weber, P. Strege, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, 1978, **100**, 3426.

<sup>257</sup> T. Kojima and T. Fujisawa, *Chem. Lett.*, 1978, 1425.

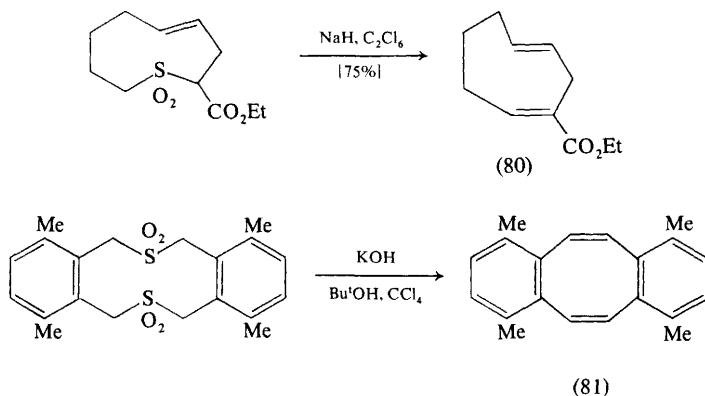
<sup>258</sup> R. W. Hoffmann, S. Goldmann, N. Maak, R. Gerlach, F. Frickel, and G. Steinbach, *Chem. Ber.*, 1980, **113**, 819.

<sup>259</sup> C. R. Johnson, K. Mori, and A. Nakanishi, *J. Org. Chem.*, 1979, **44**, 2065.

## 8 Sulphonyl and Sulphonimidoyl Carbanions

**Synthesis and Properties.**—Evidence has been presented for the formation of 1,1,1-trilithio-derivatives of alkyl aryl sulphones.<sup>260</sup>  $\alpha$ -Iodo- $\alpha$ -sulphonyl carbanions have been generated for the first time.<sup>261</sup> A phase-transfer system involving a quaternary ammonium salt and aqueous sodium hydroxide was sufficient to effect deprotonation in the presence of various alkylating agents. Additional details have appeared of a <sup>13</sup>C n.m.r. study of  $\alpha$ -sulphonyl carbanions.<sup>6</sup> The effect of  $\alpha$ -phenyl groups on the acidity<sup>262</sup> and the direction of alkene-forming eliminations in sulphones<sup>263</sup> has been studied. One interesting conclusion is that, owing to unfavourable steric interactions between the phenyl and sulphonyl groups, the  $\alpha$ -phenyl substituent can actually *impede* carbanion formation.

**Reactions.**—The Ramberg–Bäcklund reaction provides a useful route to medium-sized ring polyenes, as illustrated by the syntheses of (80)<sup>63,264</sup> and (81),<sup>265</sup> although poor yields are obtained in the synthesis of cyclophanedienes.<sup>34b</sup>



Intramolecular alkylation, acylation, and carbonyl addition by  $\alpha$ -sulphonyl carbanions, followed by reductive removal of the sulphur function, has also received considerable attention as a means of generating medium-sized rings, such as ( $\pm$ )-recifeolide (61) (note the use of a  $\pi$ -allylpalladium complex as the electrophile; see Scheme 6),<sup>266</sup> cycloundecanone (82) (Scheme 7),<sup>267</sup> and neocembrene.<sup>268</sup> Other polycyclic systems, such as ( $\pm$ )-zizaene,<sup>269</sup> potential dodecahedrane precursors,<sup>270</sup>

<sup>260</sup> A. Roggero, T. Salvatori, A. Proni, and A. Mazzei, *J. Organomet. Chem.*, 1979, **177**, 313.

<sup>261</sup> A. Jonczyk and T. Pytlewski, *Synthesis*, 1978, 883.

<sup>262</sup> F. Hibbert, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1171.

<sup>263</sup> P. J. Thomas and C. J. M. Stirling, *J. Chem. Soc., Chem. Commun.*, 1978, 975.

<sup>264</sup> E. Vedejs and S. P. Singer, *J. Org. Chem.*, 1978, **43**, 4884.

<sup>265</sup> M.-K. Au, T.-W. Siu, T. C. W. Mak, and T.-L. Chan, *Tetrahedron Lett.*, 1978, 4269.

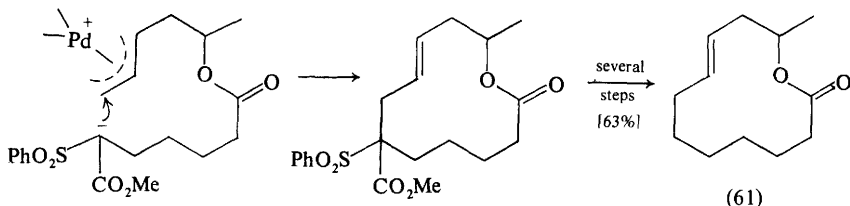
<sup>266</sup> B. M. Trost and T. R. Verhoeven, *Tetrahedron Lett.*, 1978, 2275; *J. Am. Chem. Soc.*, 1979, **101**, 1595.

<sup>267</sup> Y. Ohtsuka and T. Oishi, *Tetrahedron Lett.*, 1979, 4487.

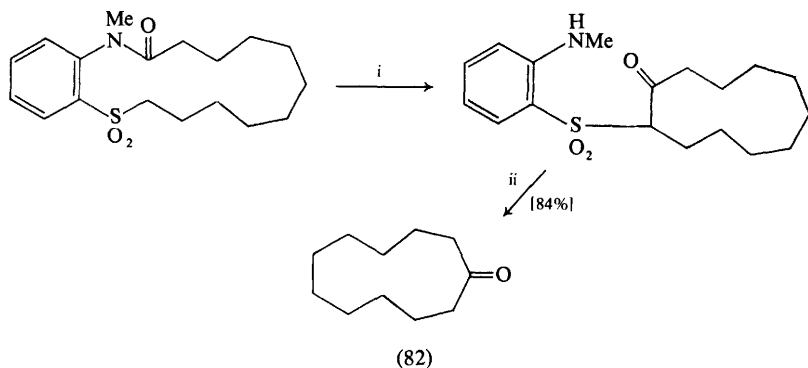
<sup>268</sup> H. Takayanagi, T. Ueyehara, and T. Kato, *J. Chem. Soc., Chem. Commun.*, 1978, 359.

<sup>269</sup> E. Piers and J. Bannville, *J. Chem. Soc., Chem. Commun.*, 1979, 1138.

<sup>270</sup> N. J. Hales and L. A. Paquette, *J. Org. Chem.*, 1979, **44**, 4603.



Scheme 6



Reagents: i,  $\text{KO}^t\text{Bu}$ , THF, DMSO; ii, Al amalgam

Scheme 7

and hinesol (83),<sup>271</sup> have been synthesized, together with  $\gamma$ -butyrolactones<sup>272</sup> and other cyclic carbonyl compounds.<sup>273, 274</sup>

Incorporation of the trimethylsilyl function into sulphur-containing molecules permits elimination reactions under neutral conditions, as in the case of (84),<sup>275</sup> amongst other examples,<sup>276</sup> and facilitates Michael addition to vinyl sulphones such as (85),<sup>277</sup> where steric control is achieved through co-ordination of the lithium to the polyether function. A related example, involving steric repulsion by a trialkylsilyloxy-group, has appeared.<sup>278</sup> If the trimethylsilyl group in systems such as (85) is replaced by hydrogen, abstraction of the  $\alpha$ -vinyl proton may occur, affording  $\alpha$ -sulphonylvinyl carbanions, which can be trapped with electrophiles.<sup>277b, 279</sup> Grignard reagents undergo Michael addition to vinyl sulphones such as (86), which then cyclizes.<sup>280, 281</sup> A spectacular example, apparently involving abstraction of an

<sup>271</sup> D. A. Chass, D. Buddhasukh, and P. D. Magnus, *J. Org. Chem.*, 1978, **43**, 1750.

<sup>272</sup> V. Reutrakul, P. Tuchinda, and K. Kusamran, *Chem. Lett.*, 1979, 1055.

<sup>273</sup> E. A. Harrison, Jr., and K. C. Rice, *J. Org. Chem.*, 1979, **44**, 2977.

<sup>274</sup> K. Schank and H.-G. Schmitt, *Chem. Ber.*, 1978, **111**, 3497.

<sup>275</sup> P. J. Kocienski, *Tetrahedron Lett.*, 1979, 2649.

<sup>276</sup> H. J. Reich, J. J. Rusek, and R. E. Olson, *J. Am. Chem. Soc.*, 1979, **101**, 2225.

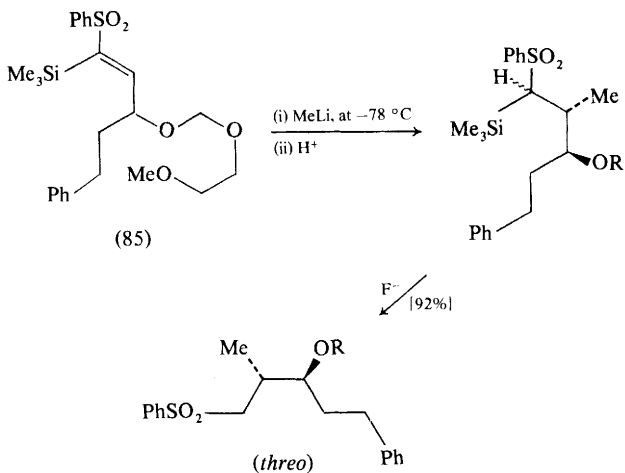
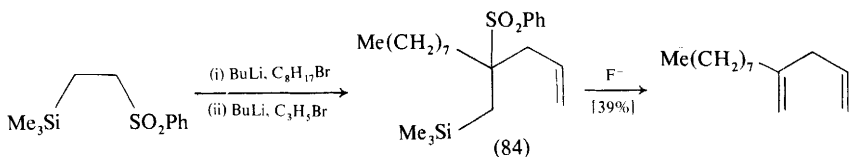
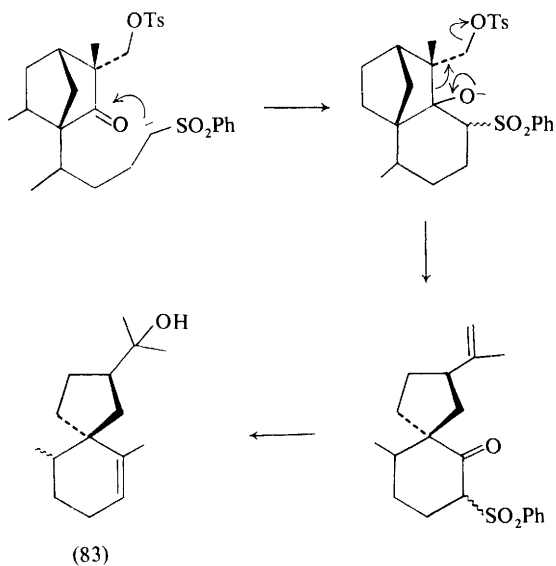
<sup>277</sup> M. Isobe, M. Kitamura, and T. Goto, (a) *Tetrahedron Lett.*, 1979, 3465; (b) *Chem. Lett.*, 1980, 331.

<sup>278</sup> J. C. Saddler, P. C. Conrad, and P. L. Fuchs, *Tetrahedron Lett.*, 1978, 5079.

<sup>279</sup> J. J. Eisch and J. E. Galle, *J. Org. Chem.*, 1979, **44**, 3279.

<sup>280</sup> J. J. Eisch and J. E. Galle, *J. Org. Chem.*, 1979, **44**, 3277.

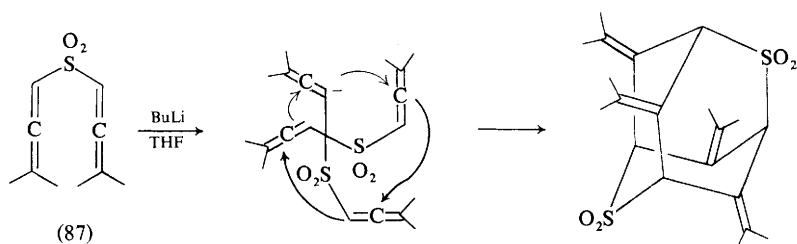
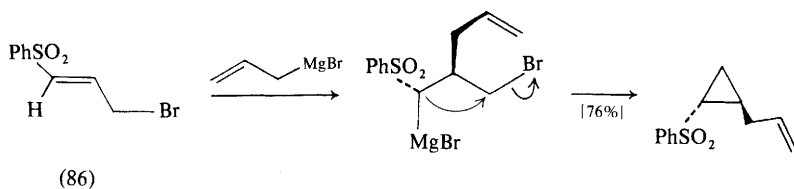
<sup>281</sup> E. Ghera and Y. Ben-David, *Tetrahedron Lett.*, 1979, 4603.



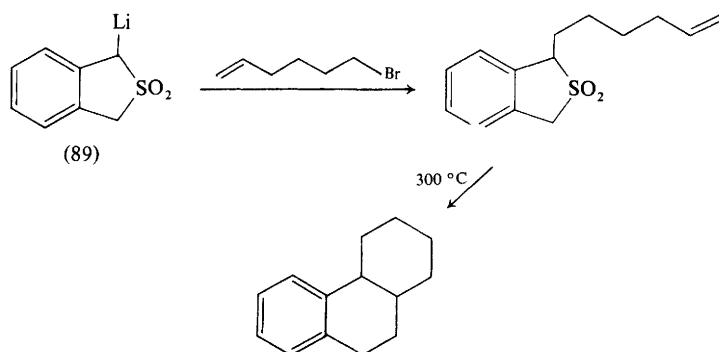
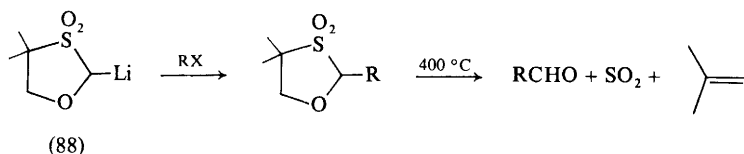
$\alpha$ -sulphonylvinyl proton to give an anion, which then undergoes self Michael addition, is the reaction of bis(allenyl) sulfone (87) with butyl-lithium, giving a 2,6-dithia-adamantane derivative.<sup>282</sup>

<sup>282</sup> S. Braverman, D. Reisman, and M. Sprecher, *Tetrahedron Lett.*, 1979, 901.





Alkylation of anions (88)<sup>283</sup> and (89),<sup>284,285</sup> followed by pyrolysis, provides novel methods of synthesis of carbonyl compounds and polycyclic hydrocarbons (including steroids), respectively. A synthesis of polycyclic hydrocarbons related to that based on the anion (89) involves alkylation of a benzocyclobutenyl-sulfonyl carbanion.<sup>286</sup> Alkylation of a thietan 1,1-dioxide carbanion (90), followed by photolysis of the product, affords cyclopropanes.<sup>287</sup>



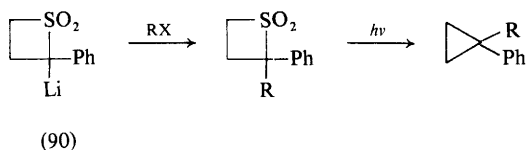
<sup>283</sup> G. W. Gokel, H. M. Gerdes, D. E. Miles, J. M. Hufnal, and G. A. Zerby, *Tetrahedron Lett.*, 1979, 3375; G. W. Gokel and H. M. Gerdes, *ibid.*, p. 3379.

<sup>284</sup> K. C. Nicolaou and W. E. Barnette, *J. Chem. Soc., Chem. Commun.*, 1979, 1119.

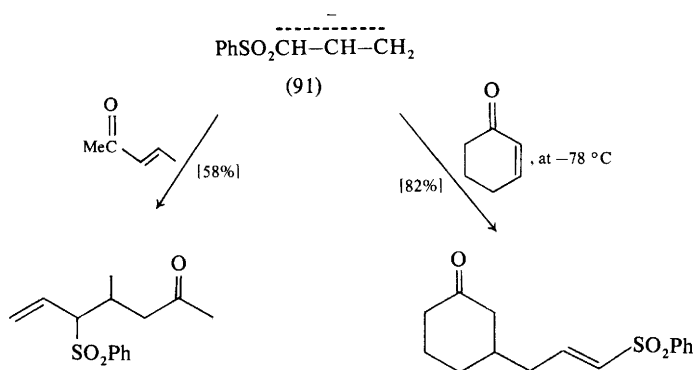
<sup>285</sup> W. Oppolzer, D. A. Roberts, and T. G. C. Bird, *Helv. Chim. Acta*, 1979, **62**, 2017.

<sup>286</sup> B. D. Gowland and T. Durst, *Can. J. Chem.*, 1979, **57**, 1462.

<sup>287</sup> J. D. Finlay, D. J. H. Smith, and T. Durst, *Synthesis*, 1978, 579.



All-*trans*-geranylgeraniol and other olefins have been synthesized through the reaction of allylic sulphonyl carbanions (or other functionalized  $\alpha$ -sulphonyl carbanions) with  $\pi$ -allylpalladium complexes.<sup>256,288</sup> Other applications of allylic sulphonyl anions include syntheses of the marine hexaprene mokupalide,<sup>183</sup> nerol and isogeraniol,<sup>289</sup> solanesol,<sup>290</sup> labda-7,14-dien-13-ol,<sup>291</sup> 1 $\alpha$ -hydroxy-tachysterol,<sup>292</sup> and certain alkynes,<sup>293</sup> and allylic alcohols.<sup>294</sup> At low temperatures, allylsulphonyl carbanions (91) will undergo  $\gamma$ - and well as  $\alpha$ -addition to Michael acceptors.<sup>295</sup> The presence of a  $\gamma$ -keto-group also promotes  $\gamma$ -substitution of allylsulphonyl carbanions.<sup>296</sup>



Miscellaneous reactions of  $\alpha$ -sulphonyl carbanions with electrophiles include processes involving arylsulphonylmethyl methyl ether anions,<sup>274,297,298</sup>  $\alpha$ -sulphonyl sulphone anions,<sup>299</sup> perfluorobutylsulphonylmethylmagnesium halides,<sup>300</sup> nucleophilic substitution in aromatic nitro-compounds by  $\alpha$ -halogenosulphonyl

<sup>288</sup> B. M. Trost, L. Weiber, P. E. Strege, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, 1978, **100**, 3416; B. M. Trost and F. W. Gowland, *J. Org. Chem.*, 1979, **44**, 3448; B. M. Trost and D. M. T. Chan, *J. Am. Chem. Soc.*, 1979, **101**, 6432; B. M. Trost, T. R. Verhoeven, and J. M. Fortunak, *Tetrahedron Lett.*, 1979, 2301.

<sup>289</sup> A. M. Moiseenkov, E. V. Polunin, and A. V. Semenovskiy, *Tetrahedron Lett.*, 1979, 4759.

<sup>290</sup> Y. Masaki, K. Hashimoto, and K. Kaji, *Tetrahedron Lett.*, 1978, 5123.

<sup>291</sup> S. Torii, K. Uneyama, I. Kawahara, and M. Kuyama, *Chem. Lett.*, 1978, 455.

<sup>292</sup> P. J. Kocienski, B. Lythgoe, and I. Waterhouse, *Tetrahedron Lett.*, 1979, 4419.

<sup>293</sup> B. Lythgoe and I. Waterhouse, *Tetrahedron Lett.*, 1978, 2625.

<sup>294</sup> P. J. Kocienski, *Tetrahedron Lett.*, 1979, 441.

<sup>295</sup> G. A. Kraus and K. Frazier, *Synth. Commun.*, 1978, **8**, 483.

<sup>296</sup> P. T. Lansbury and R. W. Erwin, *Tetrahedron Lett.*, 1978, 2675.

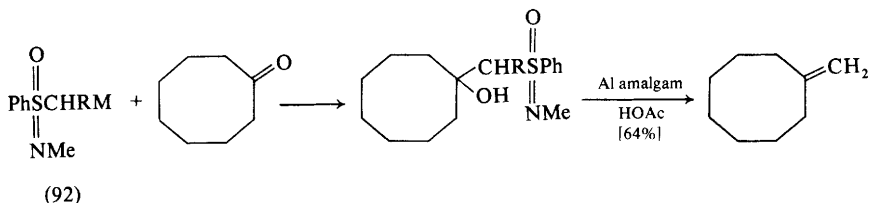
<sup>297</sup> K. Schank and F. Werner, *Liebigs Ann. Chem.*, 1979, 1977.

<sup>298</sup> K. Schank, F. Schroeder, and A. Weber, *Liebigs Ann. Chem.*, 1979, 547.

<sup>299</sup> H. Bohme and B. Clement, *Tetrahedron Lett.*, 1979, 1737.

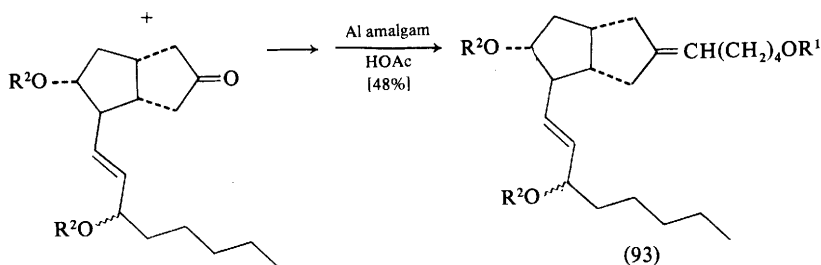
<sup>300</sup> K. Laping and M. Hanack, *Tetrahedron Lett.*, 1979, 1309.

carbanions,<sup>301</sup> Michael additions<sup>86,281,302</sup> and new syntheses of nitriles,<sup>303</sup>  $\alpha$ -oxo-sulphones.<sup>297</sup> but-2-enolides,<sup>304</sup>  $\alpha\beta$ -unsaturated sulphones,<sup>305-307</sup> vitamin D<sub>3</sub> metabolites,<sup>308</sup> cyclopropyl compounds,<sup>309</sup> dienes by 1,2-addition to  $\alpha\beta$ -unsaturated aldehydes,<sup>310</sup> and alkenes.<sup>311</sup>



*N*-Methylphenylsulphonimidoylmethyl-lithium (92; R = H, M = Li) and its derivatives provide a useful alternative to the Wittig reaction, occasionally succeeding where the Wittig reaction proves troublesome,<sup>312</sup> as in the synthesis of gascardic acid<sup>313</sup> or the prostacycline model compound (93).<sup>42c</sup>  $\alpha$ -Halogeno-sulphoximides undergo processes analogous to the Ramberg-Bäcklund rearrangement and the Darzens-type condensation on treatment with base, presumably *via* the appropriate sulphonimidoyl carbanions<sup>314,315</sup> (see also Chap. 2, Pt III, p. 145).

[92; R = (CH<sub>2</sub>)<sub>4</sub>OR<sup>1</sup>, M = MgBr]



**Acknowledgement.** During the period in which this review was prepared, the author received support from NSF and the donors of the Petroleum Research Fund, administered by the American Chemical Society, and this is gratefully acknowledged.

<sup>301</sup> J. Golinski and M. Makosza, *Tetrahedron Lett.*, 1978, 3495.

<sup>302</sup> J. Wildeman, P. C. Borgen, and H. Plum, *Tetrahedron Lett.*, 1978, 2213.

<sup>303</sup> P. A. Wade, S. D. Morrow, S. A. Hardinger, M. S. Saft, and H. R. Hinney, *J. Chem. Soc., Chem. Commun.*, 1980, 287.

<sup>304</sup> G. K. Cooper and L. J. Dolby, *J. Org. Chem.*, 1979, **44**, 3414.

<sup>305</sup> H. Kotake, K. Inomata, and M. Sumita, *Chem. Lett.*, 1978, 717.

<sup>306</sup> M. Julia, A. Righini, and D. Uguen, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1646.

<sup>307</sup> Y. Ueno, H. Setoi, and M. Okawara, *Chem. Lett.*, 1979, 47.

<sup>308</sup> B. M. Trost, P. R. Bernstein, and P. C. Funfschilling, *J. Am. Chem. Soc.*, 1979, **101**, 4378.

<sup>309</sup> Y.-H. Chang and H. W. Pinnick, *J. Org. Chem.*, 1978, **43**, 373; also see C. L. Bumgardner, J. R. Lever, and S. T. Purrington, *ibid.*, 1980, **45**, 749.

<sup>310</sup> P. J. Kocienski, B. Lythgoe, and S. Ruston, *J. Chem. Soc., Perkin Trans. 1*, 1978, 829.

<sup>311</sup> P. A. Bartlett, F. R. Green, III, and E. H. Rose, *J. Am. Chem. Soc.*, 1978, **100**, 4852.

<sup>312</sup> C. R. Johnson and R. A. Kirchoff, *J. Am. Chem. Soc.*, 1979, **101**, 3602.

<sup>313</sup> R. K. Boeckman, Jr., D. M. Blum, and S. D. Arthur, *J. Am. Chem. Soc.*, 1979, **101**, 5060.

<sup>314</sup> C. R. Johnson and H. G. Corkins, *J. Org. Chem.*, 1978, **43**, 4140.

<sup>315</sup> H. G. Corkins, L. Veenstra, and C. R. Johnson, *J. Org. Chem.*, 1978, **43**, 4233.

**PART II: Ylides and Carbanionic Compounds of Selenium and Tellurium**

by D. L. J. Clive

**Reviews.**—Several reviews have appeared<sup>1-5</sup> that deal, at least in part, with the topics of this Part.

**1 Ylides**

A number of ylides<sup>6-14</sup> and, in the case of selenium, related zwitterionic species<sup>15-19</sup> have been reported. Compounds (1),<sup>6</sup> (2),<sup>10</sup> and (3)<sup>15,16</sup> are representative of this literature, which deals with preparative details and simple chemical properties.

Ylide formation can sometimes limit the synthetic utility of selenium-substituted enolates.<sup>20</sup> For example, alkylation of (4) with prenyl iodide gave a mixture of (5) and (6) in which the latter, formed from the ylide (7), predominates.<sup>20</sup>

**2 Selenium-stabilized Carbanions**

Sufficient information on selenium-stabilized carbanions is now available both to require and to allow classification of the field. The carbanions may be of several types, depending on the oxidation level (selenide or selenoxide) of the heteroatom and on the status of the appendages.

**Methods of Preparation.**—Deprotonation of selenoxides  $\text{PhSe}(\text{O})\text{CHR}^1\text{R}^2$  ( $\text{R}^1, \text{R}^2 = \text{alkyl or H}$ ) usually proceeds well with amide bases (typically  $\text{LDA}^{1,3,5}$ ), but deprotonation of selenides  $\text{ArSeCHR}^1\text{R}^2$  in a synthetically useful fashion is

<sup>1</sup> D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049.

<sup>2</sup> K. J. Irgolic, *J. Organomet. Chem.*, 1978, **158**, 235, 267.

<sup>3</sup> H. J. Reich, *Acc. Chem. Res.*, 1979, **12**, 22.

<sup>4</sup> I. D. Sadekov, Ya. A. Bushkov, and V. I. Minkin, *Russ. Chem. Rev. (Engl. Transl.)*, 1979, **48**, 343.

<sup>5</sup> H. J. Reich, in 'Oxidation in Organic Chemistry', Part C, ed. W. S. Trahanovsky, Academic Press, New York, 1978, p. 1.

<sup>6</sup> B. A. Arbuzov, Yu. V. Belkin, N. A. Polezhaeva, and G. E. Buslaeva, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, 1072.

<sup>7</sup> N. Ya. Derkach, N. P. Tishchenko, and V. G. Voloshchuk, *J. Org. Chem. USSR (Engl. Transl.)*, 1978, **14**, 896.

<sup>8</sup> N. N. Magdesieva, R. A. Kyandzhetsian, and O. A. Rakitin, *Ref. Dokl. Soobshch.—Mendeleevsk. S'ezd Obshch. Prikl. Khim.*, 11th, 1975, **2**, 89-90 (*Chem. Abstr.*, 1978, **88**, 169 715).

<sup>9</sup> N. N. Magdesieva and R. A. Kyandzhetsian, *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki*, 1979, 235 (*Chem. Abstr.*, 1979, **90**, 186 792).

<sup>10</sup> I. D. Sadekov, A. I. Usachev, and V. I. Minkin, *J. Gen. Chem. USSR (Engl. Transl.)*, 1978, **48**, 427.

<sup>11</sup> I. D. Sadekov, A. I. Usachev, A. A. Maksimenko, and V. I. Minkin, *J. Gen. Chem. USSR (Engl. Transl.)*, 1978, **48**, 853.

<sup>12</sup> S. Tamagaki, I. Hatanaka, and S. Kozuka, *Mem. Fac. Eng. Osaka City Univ.*, 1977, **18**, 81 (*Chem. Abstr.*, 1979, **90**, 22 481).

<sup>13</sup> K. Friedrich, W. Amann, and H. Fritz, *Chem. Ber.*, 1979, **112**, 1267.

<sup>14</sup> V. V. Semenov, L. G. Mel'nikova, S. A. Shevelev, and A. A. Fainzil'berg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 138.

<sup>15</sup> N. N. Magdesieva and V. A. Danilenko, *J. Org. Chem. USSR (Engl. Transl.)*, 1979, **15**, 332.

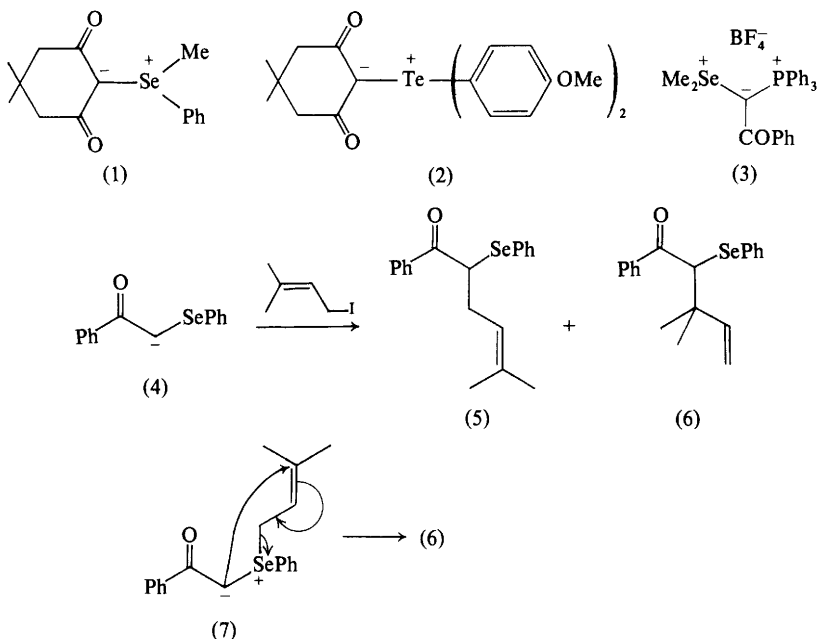
<sup>16</sup> N. N. Magdesieva and V. A. Danilenko, *J. Gen. Chem. USSR (Engl. Transl.)*, 1979, **49**, 1740.

<sup>17</sup> N. N. Magdesieva and V. A. Danilenko, *J. Org. Chem. USSR (Engl. Transl.)*, 1979, **15**, 1857.

<sup>18</sup> N. N. Magdesieva and R. A. Kyandzhetsian, *J. Org. Chem., USSR (Engl. Transl.)*, 1979, **15**, 2169.

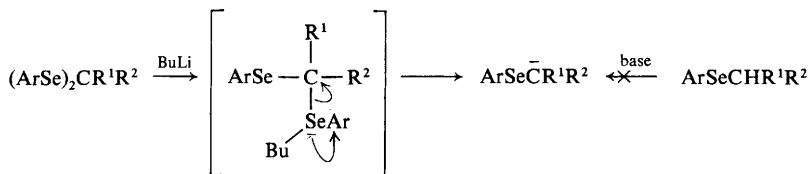
<sup>19</sup> N. N. Magdesieva and V. A. Danilenko, *J. Org. Chem. USSR (Engl. Transl.)*, 1979, **15**, 2428.

<sup>20</sup> H. J. Reich and M. L. Cohen, *J. Am. Chem. Soc.*, 1979, **101**, 1307.



possible only for certain constituents  $R^1$  and  $R^2$ . Even then, a careful choice of conditions must be made.<sup>1,3,5</sup>

In the case of  $ArSeCHR^1R^2$ , two competing reactions are possible when the selenide is treated with a base: deprotonation or nucleophilic attack at selenium. The latter mechanism leads to C–Se bond cleavage and, when deliberately applied to selenoketals, it provides a good route to those carbanions whose substitution pattern renders them unavailable by deprotonation (Scheme 1). The accessibility of carbanions by deprotonation can be summarized in the following way. (The analysis does not include selenophens,<sup>21</sup> and the yields that are quoted below represent minimum values because they refer in each case to a further transformation product of the carbanion.)



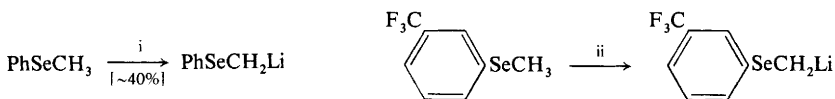
**Scheme 1**

(i) *Deprotonation of Aryl Alkyl Selenides  $ArSeR$* . Scheme 2 shows the transformations in this category that have been reported.<sup>3,22,23</sup> Lithium 2,2,6,6-tetra-

<sup>21</sup> J. Morel, C. Paulmier, D. Semard, and P. Pastour, *C.R. Hebd. Seances Acad. Sci., Ser. C.*, 1970, **270**, 825; L. Christiaens, R. Dufour, and M. Renson, *Bull. Soc. Chim. Belg.*, 1970, **79**, 143.

<sup>22</sup> D. Seebach and N. Peleties, *Chem. Ber.*, 1972, **105**, 511.

<sup>23</sup> H. J. Reich, F. Chow, and S. K. Shah, *J. Am. Chem. Soc.*, 1979, **101**, 6638.



Reagents: i, BuLi, THF, TMEDA, at  $>0^\circ\text{C}$  (ref. 22); ii, LiTMP, at  $-40$  or  $-55^\circ\text{C}$  (refs. 3, 23)

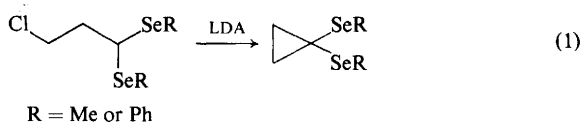
Scheme 2

methylpiperidide (LiTMP) is kinetically much more powerful than LDA. This property, together with the acidifying effect of the  $\text{CF}_3$  group, makes it possible to deprotonate the aryl-substituted compound as shown. Potassium di-isopropylamide (KDA), which, unlike LDA, can deprotonate vinyl selenides (see later), does not<sup>24</sup> deprotonate butyl phenyl selenide. Ethyl phenyl selenide is not satisfactorily deprotonated by LDA,<sup>23</sup> but KDA is reported to work.<sup>25</sup> Cyclopropyl phenyl selenide is not deprotonated (at least in THF) by LDA, LiTMP, or lithium diethylamide.<sup>23</sup>

(ii) *Deprotonation of Selenoketals ( $\text{ArSe}$ )<sub>2</sub>CHR and Seleno-orthoesters ( $\text{RSe}$ )<sub>3</sub>CH.* Deprotonation of  $(\text{PhSe})_2\text{CH}_2$  is readily accomplished with lithium amide bases: lithium di-isobutylamide in THF at  $-78^\circ\text{C}$  affords  $(\text{PhSe})_2\text{CHLi}$  (91%).<sup>22</sup> LDA is also very efficient (98% yield) in THF at  $-30^\circ\text{C}$ <sup>26,27</sup> or at  $-78^\circ\text{C}$ ,<sup>23</sup> and ether is another satisfactory solvent.<sup>23</sup>

Selenoketals of the type  $(\text{PhSe})_2\text{CHR}$  ( $\text{R} = \text{alkyl}$ ) are more difficult to metallate than the unsubstituted compound.<sup>27</sup> Butyl-lithium is unsuitable,<sup>27</sup> but appropriate conditions have been found: KDA<sup>24</sup> in THF at  $-78^\circ\text{C}$  is an effective reagent, at least for the few examples studied<sup>24</sup> [ $\text{R} = \text{Me}$  (98%),  $\text{R} = \text{Pr}^1$  (71%),  $\text{R} = \text{C}_{10}\text{H}_{21}$  (98%)]. Lithium 2,2,6,6-tetramethylpiperidide (LiTMP), at  $-30^\circ\text{C}$ , in THF containing HMPA, was evaluated in two cases<sup>27</sup> ( $\text{R} = \text{Me}$  and  $\text{C}_6\text{H}_{13}$ ), the carbanions being formed in better than 80% yield. Use of LDA with HMPA as an essential<sup>28</sup> additive was effective<sup>27</sup> (74% yield) for the simplest example ( $\text{R} = \text{Me}$ ), but for  $\text{R} = \text{C}_6\text{H}_{13}$  the extent of deprotonation was only about 44% under conditions in which LiTMP produced the carbanion in 86% yield.<sup>27</sup>

Bis(methylseleno)ketals,  $(\text{MeSe})_2\text{CHR}$  ( $\text{R} = \text{H}$  or alkyl), are not metallated by LiTMP or LDA under conditions that were studied<sup>27</sup> with the bis(phenylseleno)-analogues. However, the ring-closure shown in reaction (1) occurs efficiently in the presence of LDA.<sup>29</sup>



<sup>24</sup> S. Raucher and G. A. Koolpe, *J. Org. Chem.*, 1978, **43**, 3794.

<sup>25</sup> Ref. 23, footnote 19.

<sup>26</sup> Ref. 24, footnote 16.

<sup>27</sup> D. Van Ende, A. Cravador, and A. Krief, *J. Organomet. Chem.*, 1979, **177**, 1.

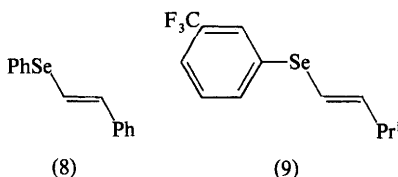
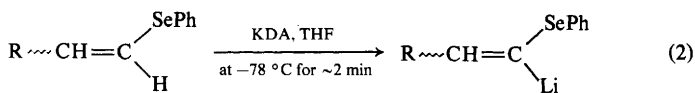
<sup>28</sup> Cf. Ref. 23.

<sup>29</sup> S. Halazy, J. Lucchetti, and A. Krief, *Tetrahedron Lett.*, 1978, 3971.

Tris(methylseleno)methane is deprotonated by LDA<sup>27,29,30</sup> and tris(phenylseleno)methane by lithium di-isobutylamide.<sup>22</sup>

(iii) *Deprotonation of Benzyl Selenides PhSeCHRPh (R = alkyl).* Deprotonation of benzyl phenyl selenide is readily effected (81%) with LDA at  $-78\text{ }^{\circ}\text{C}$ ,<sup>23,31,32</sup> but the anion is not formed with potassium t-butoxide,<sup>31</sup> and C–Se bond cleavage results with BuLi.<sup>31</sup> The higher homologue PhSeCH(Me)Ph is not appreciably deprotonated by LDA.<sup>23,32</sup> [For benzyl selenides with additional anion-stabilizing groups, see Section (vi).]

(iv) *Deprotonation of Vinyl Selenides RCH=CHSePh.* Potassium di-isopropylamide is suitable<sup>24</sup> for making selenium-stabilized vinyl carbanions [reaction (2)], but not LDA, potassium hexamethyldisilazane, or BuLi. These carbanions should be used promptly, to minimize the ejection of phenylselenolate anion.<sup>24</sup> In the case where R = Me, allylic deprotonation occurs instead.<sup>24</sup> In other studies,<sup>3,33,34</sup> lithium amide bases (including LDA) were used for the deprotonation of vinyl selenides: LDA at  $-50\text{ }^{\circ}\text{C}$ ,<sup>3</sup> or at  $-78\text{ }^{\circ}\text{C}$ ,<sup>33</sup> (in the presence<sup>33</sup> or absence<sup>33</sup> of HMPA<sup>28</sup>) for phenyl vinyl selenide; LDA at  $-78\text{ }^{\circ}\text{C}$  for *m*-(trifluoromethyl)phenyl vinyl selenide<sup>3</sup> and for compound (8)<sup>3</sup>; and LiTMP at  $-78\text{ }^{\circ}\text{C}$  for compound (9).<sup>3</sup> [For deprotonation of an allenic selenide, see Section (v)].



(v) *Deprotonation of Allylic, Propargylic, and Allenic Selenides.* Several examples in this category have been studied,<sup>1,3,35</sup> and LDA appears to be generally suitable except when the  $\alpha$ -position carries an alkyl group<sup>1,36</sup> (Scheme 3<sup>35,36</sup>). Propargylic selenides (10) and (11) are deprotonated by LDA at  $-78\text{ }^{\circ}\text{C}$  to yield the lithium salts (12) and (13), respectively.<sup>3,37</sup> Glyme may also be used as the solvent, at least for generating (12).<sup>37</sup>  $\alpha$ -Methyl compounds (14) are not deprotonated by LDA.<sup>23</sup> The allenic carbanion (15) is produced<sup>3</sup> by the action of LDA, at  $-78\text{ }^{\circ}\text{C}$ , on (16), (17), or (18), two equivalents of the base being needed in the latter case. [For related examples, see Section (vi)].

<sup>30</sup> D. Van Ende, W. Dumont, and A. Krief, *J. Organomet. Chem.*, 1978, **149**, C10.

<sup>31</sup> R. H. Mitchell, *J. Chem. Soc., Chem. Commun.*, 1974, 990.

<sup>32</sup> H. J. Reich and S. K. Shah, *J. Am. Chem. Soc.*, 1975, **97**, 3250.

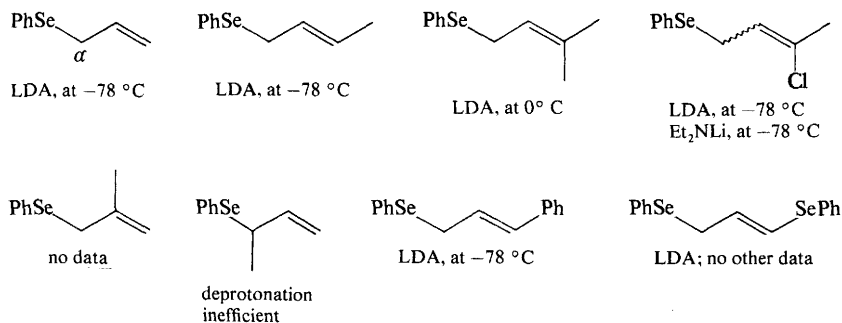
<sup>33</sup> M. Sevrin, J. N. Denis, and A. Krief, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 526.

<sup>34</sup> Ref. 23, footnote 21.

<sup>35</sup> H. J. Reich, R. E. Olson, and M. C. Clark, *J. Am. Chem. Soc.*, 1980, **102**, 1423.

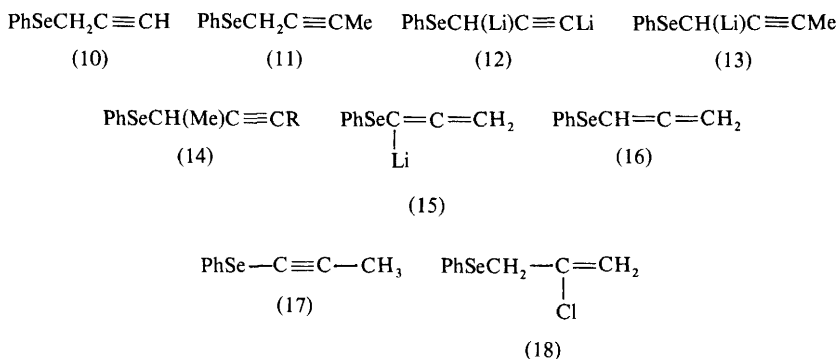
<sup>36</sup> H. J. Reich, *J. Org. Chem.*, 1975, **40**, 2570.

<sup>37</sup> H. J. Reich and S. K. Shah, *J. Am. Chem. Soc.*, 1977, **99**, 263.



*Selenides and the conditions under which they were deprotonated*

**Scheme 3**



(vi) *Deprotonation of Selenides that have an Additional Anion-stabilizing Group; ArSeCH(R)X.* Generally, LDA in THF at -78 °C has been used; Table 1 lists the main examples.<sup>3, 20, 23, 32, 35, 36, 38–47</sup>

(vii) *Formation of Selenium-stabilized Carbanions by Michael Addition.* Another approach to selenium-stabilized carbanions is *via* β-addition of a carbanion to a vinyl selenide.<sup>33, 48, 49</sup> Under the correct conditions (dimethoxymethane or ether as solvent, and a reaction temperature of 0 °C), BuLi, Pr<sup>t</sup>Li, and Bu<sup>t</sup>Li react in a Michael fashion as shown in reaction (3).

<sup>38</sup> J. Lucchetti and A. Krief, *Tetrahedron Lett.*, 1978, 2693.

<sup>39</sup> K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Am. Chem. Soc.*, 1973, **95**, 6137.

<sup>40</sup> F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. E. Drucker, J. Gerhold, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, 1977, **42**, 326.

<sup>41</sup> N. Petragani and H. M. C. Ferraz, *Synthesis*, 1978, 476.

<sup>42</sup> H. J. Reich and S. K. Shah, *J. Org. Chem.*, 1977, **42**, 1773.

<sup>43</sup> K. Sachdev and H. S. Sachdev, *Tetrahedron Lett.*, 1977, 814; *ibid.*, 1976, 4223.

<sup>44</sup> B.-T. Gröbel and D. Seebach, *Chem. Ber.*, 1977, **110**, 852.

<sup>45</sup> P. A. Grieco and Y. Yokoyama, *J. Am. Chem. Soc.*, 1977, **99**, 5210.

<sup>46</sup> Y. Masuyama, Y. Ueno, and M. Okawara, *Chem. Lett.*, 1977, 835.

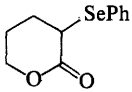
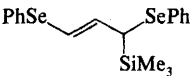
<sup>47</sup> J. V. Comasseto and N. Petragani, *J. Organomet. Chem.*, 1978, **152**, 295.

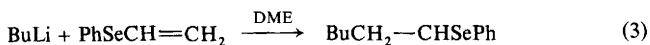
<sup>48</sup> S. Raucher and G. A. Koolpe, *J. Org. Chem.*, 1978, **43**, 4252.

<sup>49</sup> T. Kauffmann, H. Ahlers, H.-J. Tilhard, and A. Woltermann, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 710.



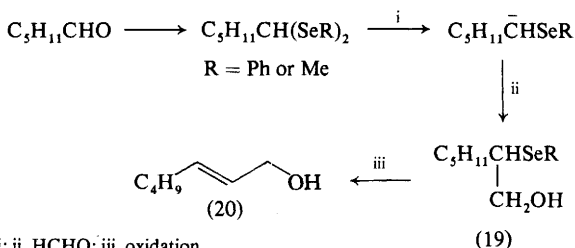
**Table 1** Conditions under which the compounds ArSeCH(R)X have been deprotonated to produce carbanions

Selenide	Conditions	Ref.
PhSeCH <sub>2</sub> CO <sub>2</sub> R (R = alkyl)	LDA	38
	<i>c</i> -C <sub>6</sub> H <sub>11</sub> N(Li)Pr <sup>l</sup>	39
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> SeCH <sub>2</sub> CO <sub>2</sub> Me	LDA	38
MeSeCH <sub>2</sub> CO <sub>2</sub> Me	LDA	38
PhSeCH <sub>2</sub> COPh	LDA	20
	KH, DMSO	40
	LDA	38
PhSeCHRCO <sub>2</sub> <sup>-</sup>	LDA, at -78 °C (R = H) or 0—40 °C (R = Me)	23, 41
PhSeCH <sub>2</sub> SiMe <sub>3</sub>	Bu <sup>s</sup> Li, TMEDA, hexane, at 25 °C	32, 42
	LDA, TMEDA, THF	43
<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SeCH <sub>2</sub> SiMe <sub>3</sub>	LiTMP, THF, at -40 °C (or Et <sub>2</sub> O)	23, 42
	LDA	28, 42
<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SeCH <sub>2</sub> OMe	LiTMP, at -78 °C	3, 23
PhSeCH <sub>2</sub> OMe	LiTMP (Deprotonation incomplete)	23
PhSeCHPh	Et <sub>2</sub> NLi, at 0 °C	32, 42
	LDA	44
SiMe <sub>3</sub>		
<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SeCHPh	Et <sub>2</sub> NLi, at -78 °C	42
SiMe <sub>3</sub>		
PhSeCHSePh	LDA, at 0 °C	44
SiMe <sub>3</sub>		
PhSeCHCH=CH <sub>2</sub>	Et <sub>2</sub> NLi, at -78 °C	36
SiMe <sub>3</sub>		
PhSe 	Et <sub>2</sub> NLi	35
SiMe <sub>3</sub>		
PhSeCHC <sub>6</sub> H <sub>13</sub>	LDA	45
CN		
PhSeCHR (R = H or alkyl)	aq. NaOH, Bu <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	46
CN		
PhSeCHR (R = H or alkyl)	BuLi, THF, at -78 °C	47
	NaH, THF-HMPA, at +80 °C	47
(O)P(OEt) <sub>2</sub>		



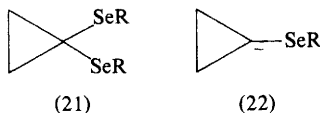
**Applications of Selenium-stabilized Carbanions.** The previous sections show that many selenides are not effectively deprotonated, and so the corresponding  $\alpha$ -lithio-selenides must be prepared by other routes, such as cleavage of selenoketals (see Scheme 1) or of seleno-orthoesters. An alternative (but indirect) procedure is the low-temperature (usually at  $-78^\circ\text{C}$ ) deprotonation (by LDA) of selenoxides that are generated *in situ* at temperatures below  $0^\circ\text{C}$ .<sup>1,3,5</sup> A further approach involves Michael addition to vinyl selenides.

*Applications Based on C–Se Bond Cleavage in Selenoketals and Seleno-orthoesters.* Primary allylic alcohols are available by homologation of aldehydes (Scheme 4).<sup>50</sup> In this method the selenoxide fragmentation (19)  $\rightarrow$  (20) is best done with *t*-butyl hydroperoxide in the presence of alumina.



Scheme 4

Cyclopropanone selenoketals such as (21; R = Ph or Me), which are prepared<sup>29,51</sup> by ring-closure processes, behave normally when treated with BuLi in THF<sup>29,51</sup> to give the corresponding  $\alpha$ -lithio-selenides (22). These species are highly nucleophilic, but they are more basic than other selenium-stabilized carbanions.<sup>29</sup> Enhanced nucleophilicity towards carbonyl compounds, at least for (22; R = Me), is observed<sup>52</sup> by generating the carbanion in ether; in this solvent, Bu<sup>t</sup>Li (rather than Bu<sup>n</sup>Li) is required.<sup>52</sup> The  $\alpha$ -lithio-selenides (22) have been treated with a variety of simple electrophiles, such as CO<sub>2</sub>,<sup>52</sup> aldehydes,<sup>29,52</sup> ketones,<sup>29,52</sup> and primary alkyl halides.<sup>53</sup> In the latter case, the presence of HMPA is necessary in the alkylation step if acceptable yields are to be produced. Scheme 5 illustrates two typical reactions. The formation of (23) merits comment because the ketone employed is



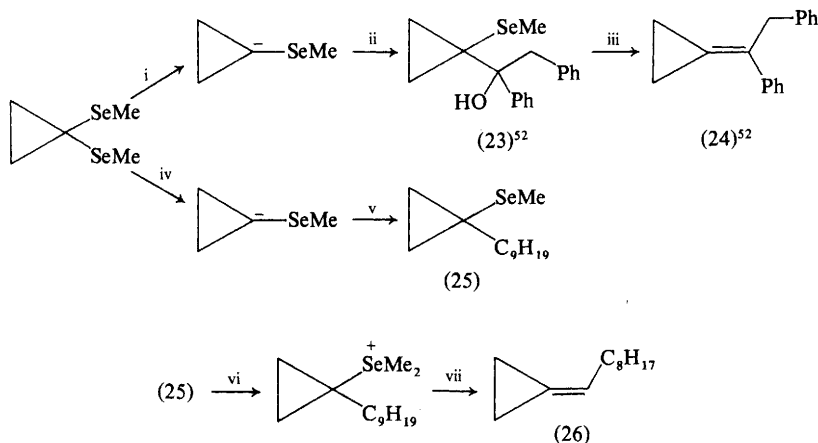
<sup>50</sup> D. Labar, W. Dumont, L. Hevesi, and A. Krief, *Tetrahedron Lett.*, 1978, 1145.

<sup>51</sup> H. J. Reich, S. K. Shah, and F. Chow, *J. Am. Chem. Soc.*, 1979, **101**, 6648.

<sup>52</sup> S. Halazy and A. Krief, *J. Chem. Soc., Chem. Commun.*, 1979, 1136.

<sup>53</sup> S. Halazy and A. Krief, *Tetrahedron Lett.*, 1979, 4233.

readily enolized. Hydroxy-selenides such as (23) yield olefins under a variety of conditions and, for example, (23) is converted into (24) in the presence of phosphorus tri-iodide and triethylamine.<sup>52</sup> Selenides such as (25) also afford regiochemically pure olefins by the sequence shown.<sup>53</sup> The transformation (25) → (26) can be carried through the phenyl series, starting with (21; R = Ph),<sup>53</sup> and the methodology represented by Scheme 5 provides a simple route to  $\alpha$ -olefins, starting from alkyl halides (e.g.  $C_8H_{17}CH_2Br$ ) and  $MeSeCH_2Li$ .<sup>53</sup>



Reagents: i,  $Bu^iLi$ ,  $Et_2O$ ; ii,  $PhCOCH_2Ph$ ; iii,  $PI_3$ ,  $Et_3N$ ; iv,  $BuLi$ ,  $THF$ ; v,  $C_9H_{19}Br$ ,  $HMPA$ ; vi,  $MeSO_3F$ ; vii, excess  $Bu^iOK$

**Scheme 5**

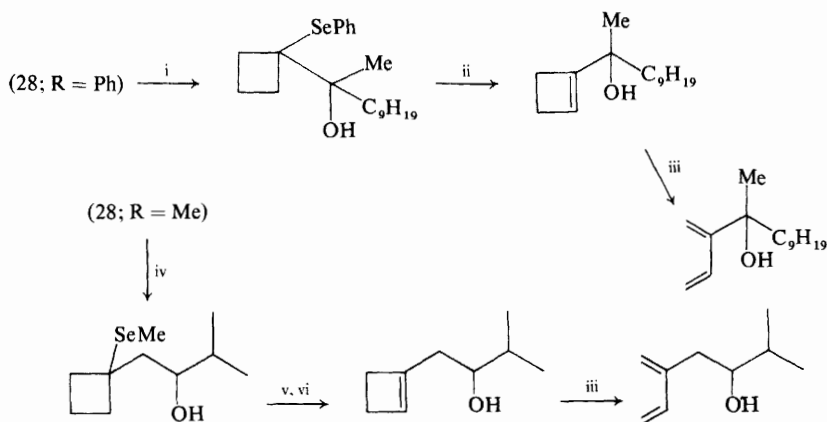
Cyclobutanone selenoketals (27; R = Ph or Me) behave in a similar way.<sup>54</sup> Treatment with  $BuLi$  in  $THF$  generates the lithium salts (28), and these have been quenched with simple electrophiles (e.g. undecanal, undecan-2-one, 1-halogenonane, and 1,2-epoxyoctane).<sup>54</sup> The reactions constitute a useful route to dienes (Scheme 6).




Bis(seleno)ketals are converted into olefins by copper(I)-mediated coupling of the derived  $\alpha$ -lithio-selenides,<sup>55</sup> as shown in Scheme 7. Bis(phenylseleno)ketals may also be used, and two *different*  $\alpha$ -lithio-selenides can be coupled.

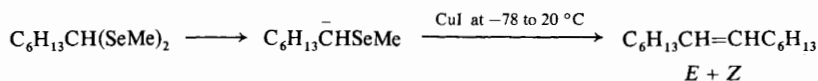
<sup>54</sup> S. Halazy and A. Krief, *Tetrahedron Lett.*, 1980, **21**, 1997.

<sup>55</sup> J. Lucchetti, J. Remion, and A. Krief, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1979, **288**, 553.

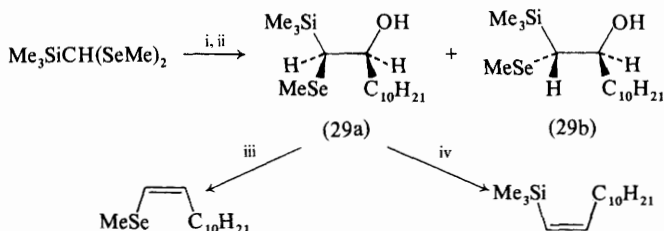


Reagents: i,  $C_9H_{19}COMe$ ; ii,  $Bu^tO_2H$ ; iii, heat; iv, ; v,  $MeI, Ag^+$ ; vi,  $Bu^tOK$

Scheme 6



Scheme 7



Reagents: i,  $BuLi$ ; ii,  $C_{10}H_{21}CHO$ ; iii,  $Bu^tOK$ ; iv,  $POCl_3, Et_3N$

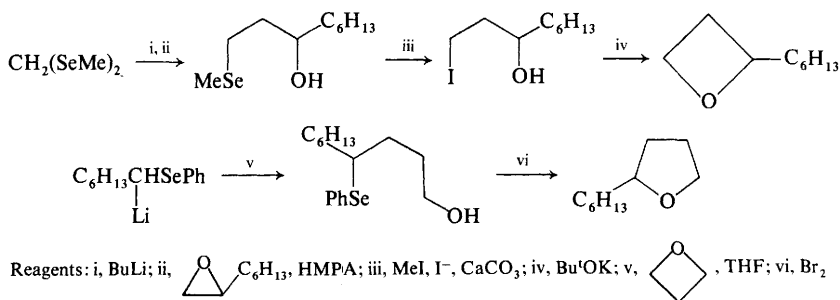
Scheme 8

Isomeric  $\alpha$ -silyl- $\beta$ -hydroxy-selenides, such as (29), prepared by the selenoketal-BuLi methodology, are often easily separated,<sup>56</sup> and treatment with  $Bu^tOK$  yields olefins (*i.e.* vinyl selenides) while exposure to  $POCl_3$  and  $Et_3N$  or to  $SOCl_2$  and  $Et_3N$  affords vinylsilanes (Scheme 8).  $\alpha$ -Silyl- $\beta$ -hydroxy-selenides can also be converted into vinyl bromides and into ketones.<sup>56</sup>

Selenoketals also constitute starting materials for the preparation of oxetans and tetrahydrofurans<sup>57</sup> (Scheme 9).

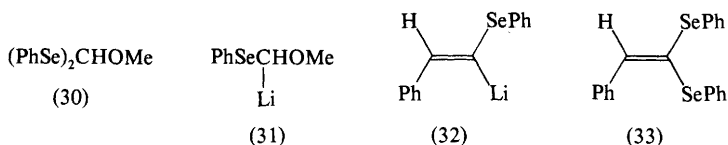
<sup>56</sup> W. Dumont, D. Van Ende, and A. Krief, *Tetrahedron Lett.*, 1979, 485.

<sup>57</sup> M. Sevrin and A. Krief, *Tetrahedron Lett.*, 1980, 21, 585.

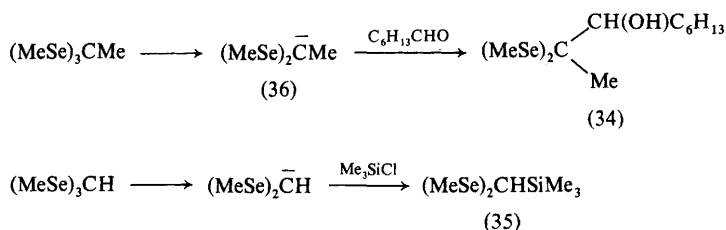


Scheme 9

Full experimental details are available<sup>23</sup> for the sequence PhSeCH<sub>2</sub>Li + ketone or aldehyde → β-hydroxy-selenide → olefin. The action of BuLi on (30) generates (31),<sup>23</sup> and the vinyl carbanion (32) is available in the same way from (33).<sup>58</sup>



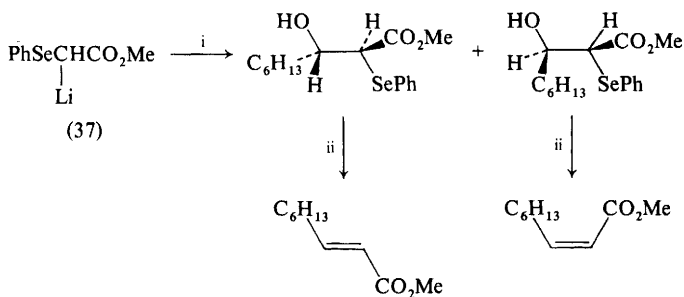
Carbanions produced by the reaction of seleno-orthoesters with BuLi have been treated with common electrophiles (e.g. Me<sub>3</sub>SiCl, propylene oxide, primary alkyl halides, aldehydes, and ketones).<sup>27</sup> The syntheses of (34) and (35) are representative.<sup>27</sup> The anion (36) undergoes 1,2-addition with enones, but, in the presence of HMPA, the thermodynamically more stable 1,4-adduct is obtained.<sup>59</sup>



*Applications Based on Deprotonation of Selenides that have an Additional Anion-stabilizing Group.* The salt (37) was treated with a variety of aldehydes and, where the resulting β-hydroxy-selenides<sup>38</sup> were separable, they easily afforded αβ-unsaturated esters by an elimination process.<sup>1,23,38</sup> The various methods for the elimination are usually stereospecific (Scheme 10).<sup>23,38</sup> The salts (38),<sup>38</sup> (39),<sup>38</sup> (40),<sup>38</sup> and (41)<sup>23</sup> (all generated by deprotonation) behave similarly, and the methyl analogue of the last compound has been used<sup>41</sup> for the construction of α-methylene lactones (Scheme 11). Salts (37), (39), and (40) give mainly 1,2-adducts with

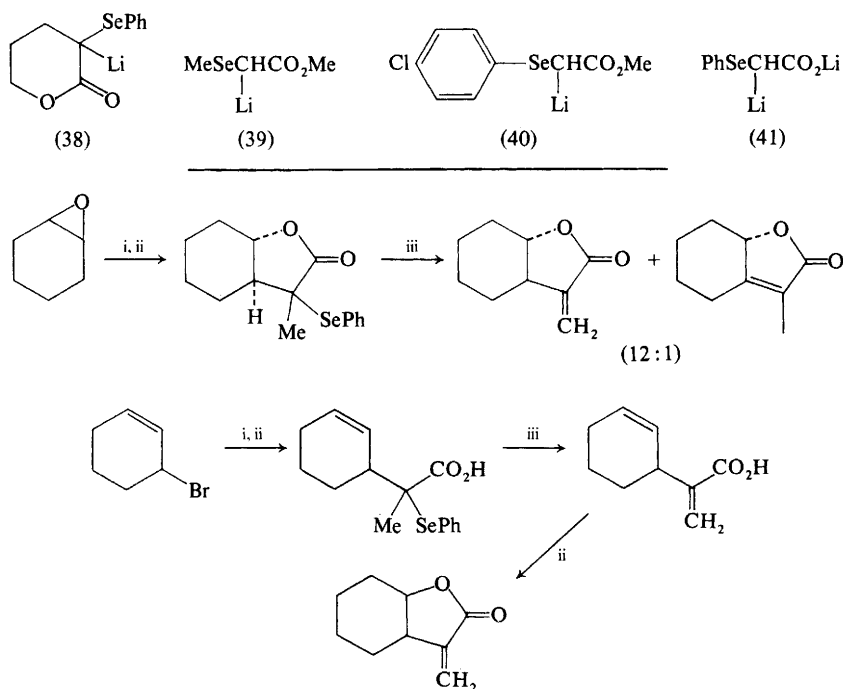
<sup>58</sup> B.-T. Gröbel and D. Seebach, *Chem. Ber.*, 1977, **110**, 867.

<sup>59</sup> J. Lucchetti, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 1979, 2695.



Reagents: i,  $\text{C}_6\text{H}_{13}\text{CHO}$ ; ii,  $\text{SOCl}_2$ ,  $\text{Et}_3\text{N}$

**Scheme 10**



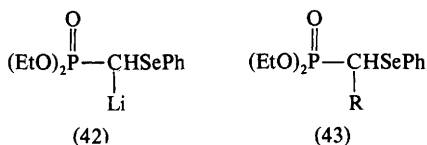
Reagents: i,  $\text{PhSeC(Me)LiCO}_2\text{Li}$ ; ii,  $\text{H}^+$ ; iii, oxidation

**Scheme 11**

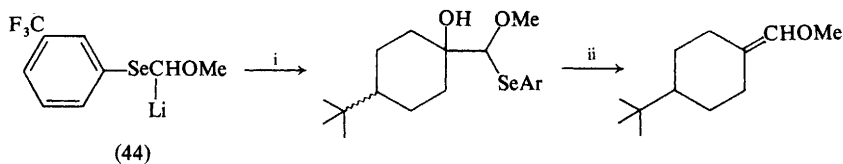
enones in THF at  $-78^\circ\text{C}$ .<sup>60</sup> In the presence of HMPA the major product is the 1,4-adduct.<sup>60</sup>

The phosphorus reagent (42) can be alkylated<sup>47</sup> with alkyl halides. The products (43) can be deprotonated (by NaH or BuLi) and then used in Wittig reactions to afford vinyl selenides as *E/Z* mixtures.<sup>47</sup>

<sup>60</sup> J. Lucchetti and A. Krief, *Tetrahedron Lett.*, 1978, 2697.

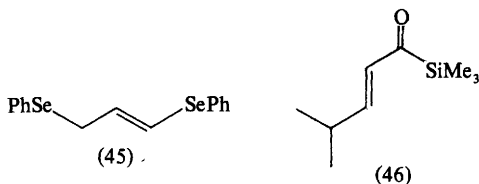


Prenylation of (4) (see p. 112), generated by the action of LDA,<sup>20</sup> has been mentioned in the section on ylides. The  $\alpha$ -lithio-selenide (44),<sup>23</sup> made with LiTMP, has been used to prepare enol ethers (Scheme 12).<sup>23</sup> Deprotonation (by LDA) of the allylic selenide (45)<sup>35</sup> is the first step in the synthesis of the silyl ketone (46).<sup>35</sup> The  $\alpha,\gamma$ -dithiopropargyl selenide (12) [see p. 116] has also been converted into an

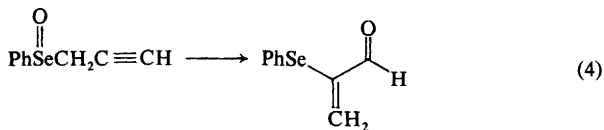


Reagents: i, Bu<sup>t</sup>-=O; ii, MsCl, Et<sub>3</sub>N

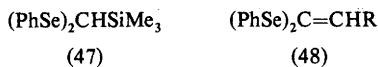
**Scheme 12**



$\alpha\beta$ -unsaturated silyl ketone<sup>61</sup> and has been elaborated into a metabolite of mould-damaged sweet potatoes.<sup>62</sup> The synthesis is based on the finding<sup>37</sup> that propargyl selenoxides rearrange to  $\alpha$ -phenylseleno-enones at a low temperature (*ca.*  $-30^\circ\text{C}$ ), as shown in reaction (4).



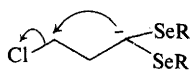
Deprotonation (by LDA) of (47) followed by reaction with benzaldehyde, formaldehyde, or propanal gives (48; R = Ph, H, or Et).<sup>44</sup>



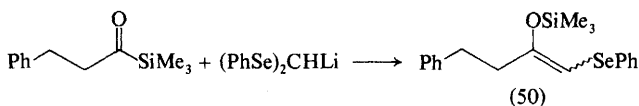
<sup>61</sup> H. J. Reich, J. J. Rusek, and R. E. Olson, *J. Am. Chem. Soc.*, 1979, **101**, 2225.

<sup>62</sup> H. J. Reich, P. M. Gold, and F. Chow, *Tetrahedron Lett.*, 1979, 4433.

*Applications Based on Deprotonation of Selenoketals*  $(R^1Se)_2CHR^2$  ( $R^2 = \text{alkyl}$ ) and *Seleno-orthoesters*. Deprotonation, usually with KDA, of selenoketals  $(PhSe)_2CHR^2$  ( $R^2 = \text{alkyl}$ ) gives<sup>24</sup> carbanions that react efficiently with common electrophiles [primary alkyl<sup>24,27</sup> and benzyl halides,<sup>24</sup> aldehydes,<sup>24,27</sup> ketones,<sup>24,27</sup> and (for  $R^2 = \text{alkyl}$  or H) epoxides<sup>24,27,51</sup>]. A few of the resulting selenoketals have been hydrolysed under very mild conditions.<sup>24</sup> Carbanions derived from selenoketals undergo intramolecular reactions [e.g. (49)]<sup>29</sup> when appropriately substituted, and can be used in the synthesis of silyl enol ethers, e.g. (50).<sup>61</sup>



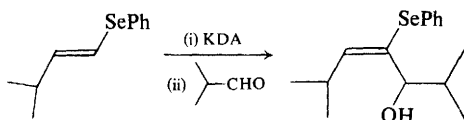
(49)



(50)

The orthoester  $(MeSe)_3CH$  gives, with LDA, the salt  $(MeSe)_3CLi$ , whose reactions with alkyl halides,<sup>27</sup> epoxides,<sup>29,27</sup> and heptanal<sup>27</sup> have been demonstrated.

*Applications Based on Deprotonation of Vinyl Selenides*. Deprotonation (by KDA) of phenyl vinyl selenide<sup>24</sup> and prompt treatment with electrophiles such as representatives of the compound classes alkyl halides, aldehydes, enones, and epoxides gives the expected products.<sup>63</sup> Scheme 13 shows a typical example and illustrates the preservation of stereochemistry about the double bond.<sup>24</sup> Vinyl selenides can be hydrolysed to ketones.<sup>24</sup>



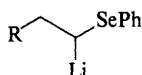
Scheme 13

*Applications Based on Deprotonation of Benzyl Selenides*  $PhSeCHRPh$  ( $R = H$  or *alkyl*). Only a low degree of stereoselection is observed<sup>23</sup> in the reaction of  $PhSeCH(Li)Ph$  with benzaldehyde and propanal. The derived alcohols of (*RS,SR*) and (*RR,SS*) configuration were converted into olefins (using  $MsCl$  and  $Et_3N$ ), the former giving the (*Z*)-olefin and the latter the (*E*)-isomer.<sup>23</sup> In further experiments the salt  $PhSeCH(Li)Ph$  was alkylated with several alkyl halides and with propylene oxide.<sup>23</sup>

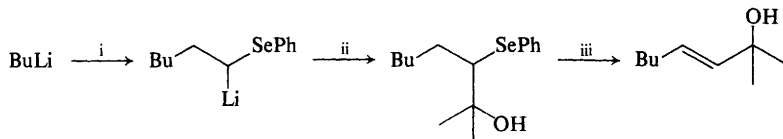
*Applications Based on Michael Addition to Phenyl Vinyl Selenide*. The  $\alpha$ -lithio-selenides (51), (52), and (53), which were generated<sup>48</sup> by treating phenyl vinyl selenide with the appropriate organolithium in dimethoxymethane<sup>48</sup> or in ether,<sup>33,48</sup>

<sup>63</sup> See also ref. 8.



(51) R = Bu<sup>n</sup>(52) R = Pr<sup>i</sup>(53) R = Bu<sup>t</sup>

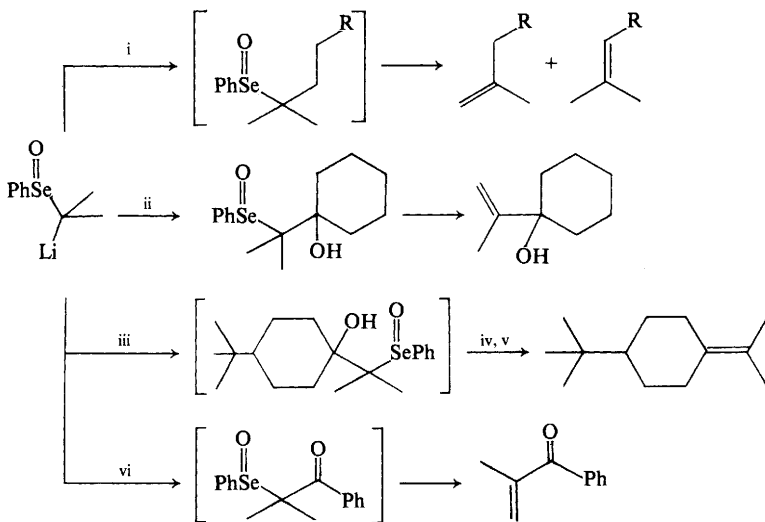
were quenched with common electrophiles chosen from the following types: alkyl halides (in the presence of HMPA), PhSeBr, Me<sub>3</sub>SiCl, aldehydes, ketones, PhCN, and D<sub>2</sub>O. The C–C connective route<sup>48</sup> shown in Scheme 14 inserts a two-carbon unit between the organolithium compound and the electrophile.



Reagents: i, H<sub>2</sub>C=CHSePh; ii, Me<sub>2</sub>CO; iii, oxidation

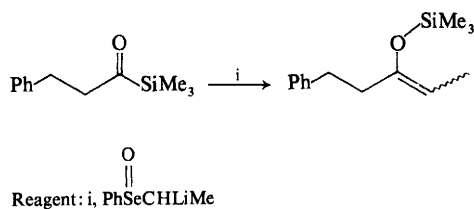
Scheme 14

*Applications Based on  $\alpha$ -Lithio-selenoxides.* Full details have appeared<sup>51</sup> on the uses of  $\alpha$ -lithio-selenoxides, generated by low-temperature deprotonation of selenoxides with LDA. They are probably less nucleophilic than the corresponding  $\alpha$ -lithio-selenides. Their reactions leading to olefins, allylic alcohols, and (less well explored) enones are summarized in Scheme 15, and they have also been applied in the synthesis<sup>61</sup> of silyl enol ethers (Scheme 16).



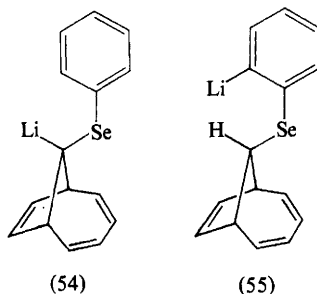
Reagents: i, R-CH<sub>2</sub>-CH<sub>2</sub>-Br; ii, cyclohexanone; iii, Bu<sup>t</sup>-cyclohexanone; iv, reduce; v, MsCl, Et<sub>3</sub>N; vi, PhCO<sub>2</sub>Me

Scheme 15



Scheme 16

**Miscellaneous Studies on Selenium-stabilized Carbanions.**—Generation of the carbanion (54) led to products derived from (55), which is formed by an intramolecular electron-transfer *via* proton exchange.<sup>64</sup> Selenium appears to



stabilize an adjacent carbanion less effectively than sulphur.<sup>3,23</sup> Some  $\text{p}K_{\text{a}}$  values that are relevant to the deprotonation of selenides have been discussed.<sup>23,51</sup> Base-induced elimination of  $\text{HBr}$  from  $\beta$ -bromo-selenides has been reported,<sup>65</sup> and  $\text{MeSeCH}_2\text{Li}$  was found<sup>66</sup> not to react satisfactorily with an aldehyde group in a study that led to the synthesis of aphidicolin.

### PART III: Compounds with $\text{S}=\text{N}$ Functional Groups

*by S. Oae and N. Furukawa*

**Introduction.**—In this Part, compounds containing the  $\text{S}=\text{N}$  group (which does not always imply that they have typical double-bond character) have been described. The growing interest in the chemistry of these compounds has been shown by several review articles; for example, sulphur nitrides ( $\text{SN}_x$ ) have been extensively

<sup>64</sup> H. M. J. Gillissen, P. Schipper, P. J. J. M. Van Ool, and M. H. Buck, *J. Org. Chem.*, 1980, **45**, 319.

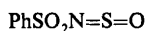
<sup>65</sup> S. Raucher, R. Hansen, and M. A. Colter, *J. Org. Chem.*, 1978, **43**, 4885.

<sup>66</sup> E. J. Corey, M. A. Tius, and J. Das, *J. Am. Chem. Soc.*, 1980, **102**, 1742, footnote 24d.

investigated because of their interesting structures<sup>1-4</sup> and their physical properties, such as superconductivity.<sup>5,6</sup> Cyclic sulphur-nitrogen compounds have also been summarized.<sup>7-9</sup> The chemistry of sulphimides,<sup>10</sup> sulphoximides,<sup>11</sup> and sulphodiimides<sup>12</sup> has also been reviewed. The biologically important role of methionine sulphoximides has been described.<sup>13</sup>

### 1 Di-co-ordinate Sulphur

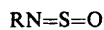
**Sulphinyl-amines and -amides.**—*Structure.* X-Ray crystallographic analyses<sup>14,15</sup> and infrared,<sup>16</sup> nitrogen-15 n.m.r.,<sup>17</sup> and dipole-moment measurements<sup>18</sup> of several *N*-sulphinylanilines and *N*-sulphinyl-sulphonamides have been performed. These spectral analyses have revealed that the compounds (1) and (2; Ar = Ph) have *syn*-coplanar configurations around the N=S linkage; this is in accordance with the previous observations except in the case of the mesityl analogue (2; Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), in which the mesityl ring is perpendicular to the N=S=O plane.



(1)



(2)



(3) R = Me, Et, MeS, or Me<sub>2</sub>N

*Preparation and Reactions.* The first preparation and characterization of potassium thiazate (KNSO) has been reported.<sup>19</sup> Perfluoroaromatic *N*-sulphinyl compounds (3; R = C<sub>6</sub>F<sub>5</sub>S or C<sub>6</sub>F<sub>5</sub>SO) have been prepared by treating the corresponding perfluoroaromatic sulphur acid amides C<sub>6</sub>F<sub>5</sub>S(O)<sub>*n*</sub>NH<sub>2</sub> (*n* = 0 or 1) with SOCl<sub>2</sub> or the sulphenyl chloride with Me<sub>3</sub>SiNSO.<sup>20</sup> Treatment of the sulphinyl compounds (3; R = MeS or Me<sub>2</sub>N) with Me<sub>3</sub>O<sup>+</sup> BF<sub>4</sub><sup>-</sup> yields the corresponding *N*- or *S*-methylated salts, which undergo [4 + 2]-cycloaddition reactions with dienes to afford the

<sup>1</sup> G. B. Street and W. D. Gill, *NATO Conf. Ser.*, [Ser] 6, 1978, 1, 301 (*Chem. Abstr.* 1979, 91, 67 639).

<sup>2</sup> T. Nakajima, *Yoyuen*, 1979, 22, 7 (*Chem. Abstr.* 1979, 91, 116 460).

<sup>3</sup> C. Bernard and G. Robert, *Bull. Soc. Chim. Fr., Part 2*, 1978, 395.

<sup>4</sup> D. G. Stojakovic, *Glas. Hem. Drus. Beograd*, 1978, 43, 775 (*Chem. Abstr.* 1979, 91, 166 870).

<sup>5</sup> M. M. Labes, P. Love, and L. F. Nichols, *Chem. Rev.*, 1979, 79, 1.

<sup>6</sup> A. J. Banister, *Phosphorus Sulfur*, 1979, 6, 421.

<sup>7</sup> A. J. Banister, *Phosphorus Sulfur*, 1978, 5, 147.

<sup>8</sup> I. Haiduc, *Method. Chim.*, 1978, 7, 789.

<sup>9</sup> H. W. Roesky, *Adv. Inorg. Chem. Radiochem.*, 1979, 22, 239.

<sup>10</sup> (a) S. Oae, 'Organic Chemistry of Sulfur,' Plenum Press, New York, 1977, p. 383; (b) A. Kuczman and I. Kapovits, *Phosphorus Sulfur*, 1977, 3, 9; (c) N. Furukawa, *Kagaku No Ryoiki*, 1978, 32, 31; (d) R. Appel and J. Kohnke, *Method. Chim.*, 1978, 7, 743; (e) C. R. Johnson, in 'Comprehensive Organic Chemistry' Vol. 3, ed. D. N. Jones, Pergamon Press, Oxford, 1979, p. 215.

<sup>11</sup> Ref. 10e, p. 233.

<sup>12</sup> Ref. 10e, p. 237.

<sup>13</sup> A. Meister, *Enzyme-Act. Irreversible Inhibitors, Proc. Int. Symp.*, 1978, 187 (*Chem. Abstr.* 1980, 92, 71 523).

<sup>14</sup> B. Degerer and A. Gieren, *Naturwissenschaften*, 1979, 66, 470.

<sup>15</sup> G. Deleris, C. Courseille, J. Kowalski, and J. Dunogues, *J. Chem. Res. (S)*, 1979, 122.

<sup>16</sup> R. Meiji, A. Oskman, and D. J. Stufkens, *J. Mol. Struct.*, 1979, 51, 37.

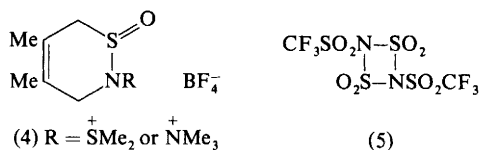
<sup>17</sup> I. Yavari, J. S. Staral, and J. D. Roberts, *Org. Magn. Reson.*, 1979, 12, 340.

<sup>18</sup> W. Waclawek and C. Puchala, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1978, 26, 337.

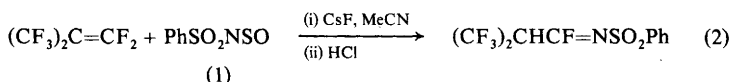
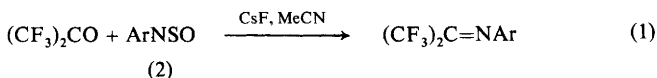
<sup>19</sup> D. A. Armitage and J. C. Brand, *J. Chem. Soc., Chem. Commun.*, 1979, 1078.

<sup>20</sup> I. Glander and A. Golloch, *J. Fluorine Chem.*, 1979, 14, 403.

corresponding adducts (4)<sup>21</sup> (see Vol. 5, p. 102). Trifluoromethanesulphonyl sulphinylamide, CF<sub>3</sub>SO<sub>2</sub>NSO, affords the dimer (5) upon treatment with SO<sub>3</sub>.<sup>22</sup>



Several other *N*-sulphinyl-amines or -amides can be prepared or generated, without isolation, and added to olefins,<sup>23</sup> ketones,<sup>24</sup> or enamines and ynamines.<sup>25</sup> Similarly, *N*-sulphinyl-sulphonamides (1) and sulphinyl-amines (2; Ar = Ph or *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) react with hexafluoroacetone or polyfluoro-olefins in aprotic solvents in the presence of CsF [see reactions (1) and (2)], affording, directly, the imino-compounds; these are undoubtedly formed *via* initial formation of the [2 + 2]-cyclo-adducts.<sup>26</sup>



Isocyanides are prepared in high yields by treating various aliphatic, aromatic, and heterocyclic sulphinylamines with dichlorocarbene (generated under phase-transfer conditions), using KOH as a base together with 18-crown-6 or dibenzo-18-crown-6 in benzene solution.<sup>27</sup> Aliphatic *N*-sulphinyl-amines can be converted into the corresponding primary amines *via* a [3,3]sigmatropic rearrangement of their  $\alpha$ -allylated derivatives. Allylic sulphinyl-amides are formed initially, as shown in Scheme 1.<sup>28</sup>

New metal-R insertion complexes between  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}\}$  (R = alkyl or aryl) and (1) or sulphur di-imides have been reported.<sup>29,30</sup> The photolysis of *N*-phenyl-*N'*-sulphinylhydrazine in aromatic solvents generates phenyl radicals; these undergo addition to the solvents, affording biphenyls.<sup>31</sup>

*N*-Thiosulphinyl-amines (6)<sup>32</sup> or -anilines (7; R<sup>2</sup> = N=S=S)<sup>33</sup> have been prepared

<sup>21</sup> M. Rössert, W. Kraus, and G. Kresze, *Tetrahedron Lett.*, 1978, 4669.

<sup>22</sup> H. W. Roesky, R. Aramaki, and L. Schoenfelder, *Z. Naturforsch., Teil B*, 1978, **33**, 1072.

<sup>23</sup> J. A. Kloek and K. L. Leschinsky, *J. Org. Chem.*, 1980, **45**, 721.

<sup>24</sup> J. E. Semple and M. M. Joullé, *J. Org. Chem.*, 1978, **43**, 3066.

<sup>25</sup> T. Nagai, T. Shingaki, M. Inagaki, and T. Oshima, *Bull. Soc. Chem. Jpn.*, 1979, **52**, 1102.

<sup>26</sup> Yu. V. Zeifman, E. G. Ter-Gabriélyan, D. P. Del'tsova, and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 396.

<sup>27</sup> R. Mayer, R. Beckert, and G. Domschke, *Ger. P.* 128 531 (1978).

<sup>28</sup> F. M. Schell, J. P. Carter, and C. Wiaux-Zamar, *J. Am. Chem. Soc.*, 1978, **100**, 2894.

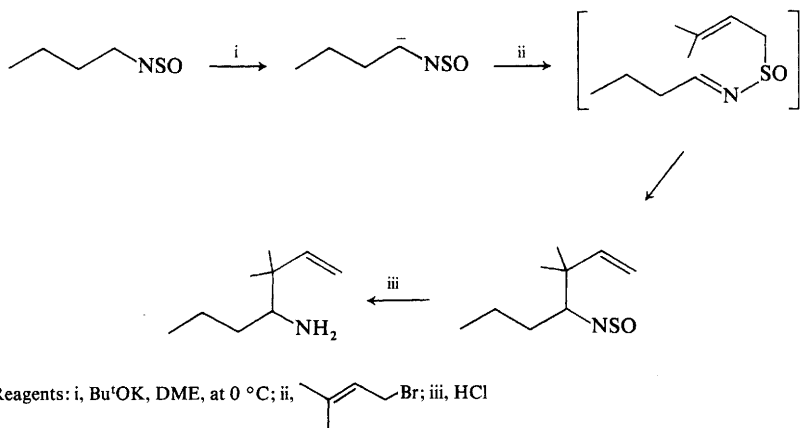
<sup>29</sup> R. G. Severson and A. Wojcicki, *J. Organomet. Chem.*, 1978, **149**, C66.

<sup>30</sup> R. G. Severson, T. W. Leung, and A. Wojcicki, *Inorg. Chem.*, 1980, **19**, 915.

<sup>31</sup> G. Deluca, G. Renzi, and A. Pizzabiocca, *Chem. Ind. (London)*, 1979, 899.

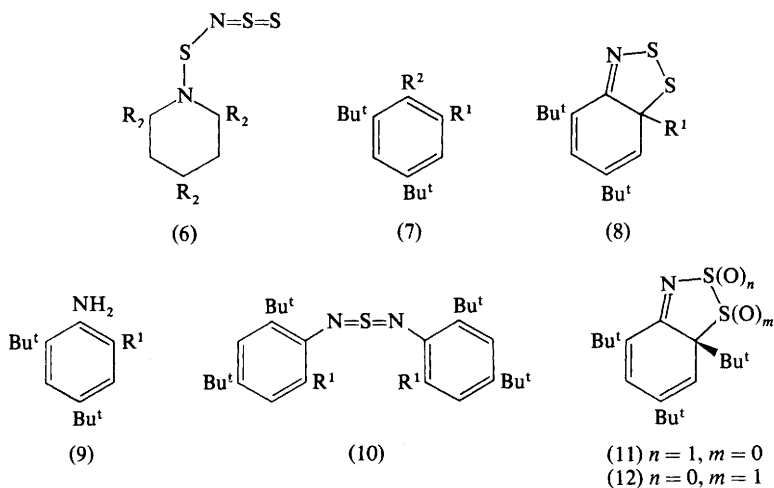
<sup>32</sup> N. Soma, S. Moriyama, T. Yoshioka, and T. Nishimura, *Japan. Kokai* 78 124 273.

<sup>33</sup> Y. Inagaki, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1998.



Scheme 1

and both their physical and their chemical properties extensively studied. Among the compounds (7; R<sup>1</sup> = Me, R<sup>2</sup> = N=S=S), (7; R<sup>1</sup> = Me, R<sup>2</sup> = N=S=O), and (7; R<sup>1</sup> = Me, R<sup>2</sup> = Br), the dipole moment of the N=S=O group is the largest, while the charge separation of the N=S=S group is about half that of the N=S=O group.<sup>34,35</sup>



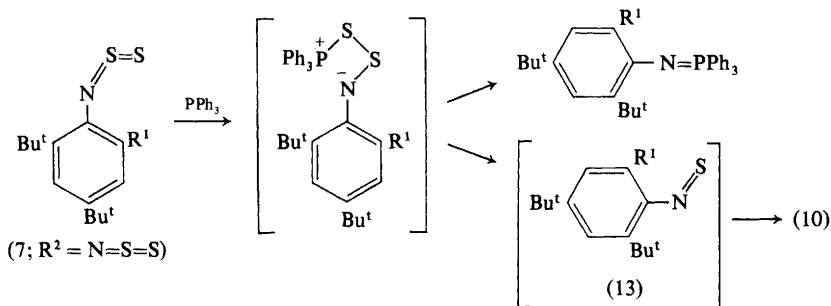
Thermolysis of (7; R<sup>2</sup> = N=S=S) affords a new type of heterocycle (8) together with the parent aniline (9), while photolysis of (7; R<sup>2</sup> = N=S=S) gives (9) and the sulphur di-imide (10).<sup>36</sup> The compound (7; R<sup>1</sup> = Bu<sup>t</sup>, R<sup>2</sup> = N=S=S) has been found to be in equilibrium with (8; R<sup>1</sup> = Bu<sup>t</sup>), and the thermodynamic parameters of the equilibrium (which were determined by n.m.r. spectroscopy) indicate that (7) is the

<sup>34</sup> Y. Inagaki, R. Okazaki, and N. Inamoto, *Heterocycles.*, 1978, **9**, 1613.

<sup>35</sup> Y. Inagaki, R. Okazaki, N. Inamoto, and T. Shimoizawa, *Chem. Lett.*, 1978, 1217.

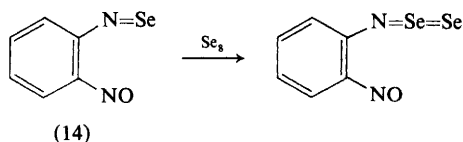
<sup>36</sup> Y. Inagaki, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2002.

more favoured.<sup>37</sup> Both (7) and (8) react with a number of electrophiles and nucleophiles, such as MCPBA, bromine, amines, phosphines, or Grignard reagents.<sup>38,39</sup> Oxidation of (7;  $R^1 = \text{Me}$ ,  $R^2 = \text{N}=\text{S}=\text{S}$ ) gives mainly the corresponding *N*-sulfinyl derivatives (7;  $R^1 = \text{Me}$ ,  $R^2 = \text{N}=\text{S}=\text{O}$ ) and (9), while that of (8;  $R = \text{Bu}^t$ ) affords two new heterocyclic compounds (11) and (12). The steric structures of (11) and (12) have been determined by spectroscopic and *X*-ray analyses. Meanwhile, the mechanisms for the reactions of (7;  $R^2 = \text{N}=\text{S}=\text{S}$ ) and (8) with nucleophiles have also been discussed, and (13) is considered to be an intermediate which would be formed by treatment of (7;  $R^2 = \text{N}=\text{S}=\text{S}$ ) with such nucleophiles as triphenylphosphine (Scheme 2).



**Scheme 2**

The selenium analogue of (13) has been generated by the photolysis of 2,1,3-benzoselenadiazole 1-oxide and identified as a transient species, having the structure (14), by u.v. spectroscopy. Compound (14) gives the selenium analogue of (7;  $R^2 = \text{N}=\text{S}=\text{S}$ ) as another transient species upon treatment with  $\text{Se}_8$ , generated by flash photolysis<sup>40</sup> (see also Chap. 6, p. 295).



**Sulphur Di-imides.**—*Preparation and Properties of (SN)<sub>x</sub>.* This and related sulphur–nitrogen compounds have created interest both in their preparation and their physical properties (see Vol. 5, p. 103). Pyrolysis of  $\text{S}_2\text{N}_4$  gives either  $(\text{SN})_x$  or  $\text{S}_2\text{N}_2$ , depending on the reaction conditions.<sup>41,42</sup> The physical and spectroscopic

<sup>37</sup> Y. Inagaki, R. Okazaki, N. Inamoto, K. Yamada, and H. Kawazura, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2008.

<sup>38</sup> Y. Inagaki, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3615.

<sup>39</sup> Y. Inagaki, T. Hosogai, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 205.

<sup>40</sup> C. L. Pedersen, *Tetrahedron Lett.*, 1979, 745.

<sup>41</sup> P. Love, G. Myer, H. I. Kao, M. M. Labeo, W. R. Junker, and C. Elbaum, *Ann. N.Y. Acad. Sci.*, 1978, **313**, 745.

<sup>42</sup> R. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1979, 478.

properties of  $(\text{SN})_x$ , such as thermopower,<sup>43</sup> mass spectroscopy,<sup>44</sup> optical spectroscopy,<sup>45</sup> molecular-beam electric deflection analysis,<sup>46</sup> e.p.r. spectroscopy,<sup>47</sup> electrical conductivity,<sup>48</sup> and superconductivity,<sup>49</sup> have been reported. The structure and properties of halogenated  $(\text{SN})_x$  have also been investigated.<sup>50-52</sup>

**Tetrasulphur Tetranitride.** This compound has been used as a sulphur-transfer agent, reacting, for example, with ketones or acetylenes to afford thiadiazoles<sup>53,54</sup> (see also Chap. 6, p. 292). Furthermore, it reacts with triphenylphosphine, yielding  $(\text{Ph}_3\text{P}=\text{N})_2 \cdot \text{S}_4\text{N}_4$ , which has been characterized by *X*-ray spectroscopic analysis.<sup>55</sup> The reaction with  $[\text{Pt}(\text{PPh}_3)_4]$  gives some novel platinum complexes, such as  $[\text{Pt}(\text{N}_4\text{S}_4)(\text{PPh}_3)_2]$ .<sup>56</sup> Brominations of  $\text{S}_4\text{N}_4$  afford either  $(\text{SNBr}_{0.4})_x$  (in the gas-phase reaction),  $\text{S}_4\text{N}_3\text{Br}_3$  (in the liquid-phase reaction), or  $\text{S}_5\text{N}_3\text{Br}$  and  $\text{CS}_3\text{N}_2\text{Br}_2$  (in solution in  $\text{CS}_2$ ).<sup>57</sup> A new sulphur nitride,  $\text{S}_5\text{N}_6$ , has been prepared and its *X*-ray, Raman, and u.v.—visible spectra have been presented.<sup>58,59</sup> Some other sulphur nitride derivatives, such as  $\text{S}_4\text{N}_3\text{X}$  ( $\text{X} = \text{Cl}, \text{F}, \text{or } \text{SbCl}_6$ ),<sup>60</sup>  $\text{S}_4\text{N}_3\text{X}$  ( $\text{X} = \text{TeBr}_3, \text{TeBr}_6, \text{or } \text{SbCl}_4$ ),<sup>61</sup> and  $\text{Pb}(\text{S}_2\text{N}_2)$ ,<sup>62</sup> have been prepared. The structures of  $[\text{Bu}_4\text{N}]^+[\text{S}_3\text{N}_3]^-$  and  $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{S}_4\text{N}]^-$  have been determined by *X*-ray spectroscopic analysis; both of the anions  $[\text{S}_3\text{N}_3]^-$  and  $[\text{S}_4\text{N}]^-$  were shown to have essentially planar structures.<sup>63,64</sup>

**Preparation of Other Sulphur Di-imides.** Pyrolysis of *N*-sulphinylaniline has been found to give sulphur di-imides in the presence of a nickel(0) catalyst.<sup>65</sup> Sulphur di-imides that have the general structure  $\text{RN}=\text{S}=\text{NR}$  ( $\text{R} = \text{Me}_3\text{Si}, \text{Me}_3\text{Sn}, \text{or } \text{C}_6\text{F}_5$ )

<sup>43</sup> L. J. Azvedo, P. M. Chikin, W. G. Clark, W. W. Fuller, and J. Hammann, *Phys. Rev. B: Condens. Matter*, 1979, **22**, 4450.

<sup>44</sup> N. Ueno, K. Kugita, O. Koga, S. Suzuki, K. Yoshino, and K. Kaneto, *Jpn. J. Appl. Phys.*, 1979, **18**, 1597.

<sup>45</sup> Z. Iqbal and D. S. Downs, *Chem. Phys.*, 1979, **44**, 137.

<sup>46</sup> R. R. Cavanagh, R. S. Altman, D. R. Herschbach, and W. Klemperer, *J. Am. Chem. Soc.*, 1979, **101**, 4734.

<sup>47</sup> P. Love and M. M. Labes, *J. Chem. Phys.*, 1979, **70**, 5147.

<sup>48</sup> R. Nowak, W. Kutner, H. R. Mark, Jr., and A. G. MacDiarmid, *Ann. N.Y. Acad. Sci.*, 1978, **313**, 767.

<sup>49</sup> P. Barrett, R. G. Chambers, P. Feenan, W. G. Herrenclen-Harker, M. G. Priestley, R. W. Trimder, and S. F. J. Read, *J. Phys. F*, 1980, **10**, L89.

<sup>50</sup> Z. Iqbal, R. H. Baughman, J. Keppinger, and A. G. MacDiarmid, *Ann. N.Y. Acad. Sci.*, 1978, **313**, 775.

<sup>51</sup> C. Bernard, P. Tougain, and G. Robert, *Ann. Chim. (Paris)*, 1979, **4**, 591.

<sup>52</sup> J. W. Macklin, G. B. Street, and W. D. Gill, *J. Phys. Chem.*, 1979, **70**, 2425.

<sup>53</sup> S. Mataka, A. Hosoki, K. Takahashi, and M. Tashiro, *Synthesis*, 1979, 524.

<sup>54</sup> S. Mataka, K. Takahashi, Y. Yamada, and M. Tashiro, *J. Heterocycl. Chem.*, 1979, **16**, 1009.

<sup>55</sup> J. Bojes, T. Chivers, G. Maclean, and R. T. Oakley, *Can. J. Chem.*, 1979, **57**, 3171.

<sup>56</sup> A. A. Bhattacharyya, J. A. Maclean, Jr., and A. G. Turner, *Inorg. Chem.*, 1979, **34**, L199.

<sup>57</sup> G. Wolmerchauser, G. B. Street, and R. D. Smith, *Inorg. Chem.*, 1979, **18**, 383.

<sup>58</sup> T. Chivers and J. Proctor, *J. Chem. Soc., Chem. Commun.*, 1978, 642.

<sup>59</sup> T. Chivers and J. Proctor, *Can. J. Chem.*, 1979, **57**, 1286.

<sup>60</sup> T. Chivers, L. Fielding, W. G. Laidlaw, and M. Trsic, *Inorg. Chem.*, 1979, **18**, 3379.

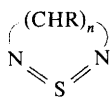
<sup>61</sup> R. C. Paul, R. P. Sharma, R. D. Verma, and J. K. Puri, *Indian J. Chem., Sect. A*, 1979, **18**, 516.

<sup>62</sup> D. T. Haworth and G. Y. Liu, *J. Inorg. Nucl. Chem.*, 1980, **42**, 137.

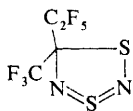
<sup>63</sup> J. Bojes, T. Chivers, W. G. Laidlaw, and M. Trsic, *J. Am. Chem. Soc.*, 1979, **101**, 4517.

<sup>64</sup> T. Chivers and R. T. Oakley, *J. Chem. Soc., Chem. Commun.*, 1979, 752.

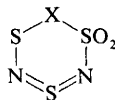
<sup>65</sup> D. Walther, E. D. Dinjus, and H. Wolf, *Z. Chem.*, 1979, **19**, 381.



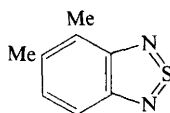
- (15) R = H,  $n = 2$   
 (16) R = H,  $n = 3$   
 (17) R = CF<sub>3</sub>,  $n = 2$



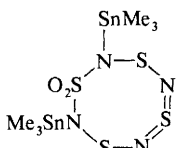
(18)



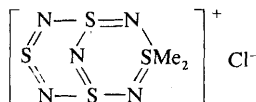
- (19) X = NBu<sup>n</sup>  
 (20) X = N=S=N



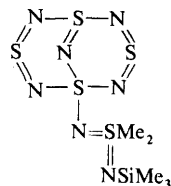
(21)



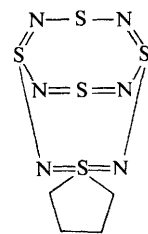
(22)



(23)



(24)



(25)

have been shown to be good starting materials for the preparation of both acyclic and cyclic sulphur di-imides, of various types, *e.g.* (15)—(25).<sup>66-72</sup>

**Reactions.** A reformed systematic nomenclature of sulphur–nitrogen heterocycles has been proposed.<sup>73</sup> Besides the preparation of these cyclic sulphur–nitrogen compounds, Roesky *et al.* have investigated extensively the preparation and reactions of new types of cyclic and bicyclic sulphur–nitrogen heterocycles and elucidated their structural and bonding characteristics, mainly by X-ray crystallographic analysis; *e.g.*, the structures of [S<sub>3</sub>N<sub>2</sub>Me<sub>2</sub>CO]<sup>+</sup> [AsF<sub>6</sub>]<sup>-</sup>, S<sub>4</sub>N<sub>4</sub>O<sub>2</sub>(SnMe<sub>3</sub>)<sub>2</sub>, S<sub>4</sub>N<sub>4</sub>SO<sub>3</sub>, and the S<sub>3</sub>N<sub>2</sub><sup>+</sup> ion.<sup>74-79</sup> Correlations between structures and bonding parameters such as bond angles and bond lengths have been presented.<sup>80,81</sup>

<sup>66</sup> I. Legly, G. Kreze, M. Berger, W. Kobahn, and H. Schaefer, *Acta Chim. Acad. Sci. Hung.*, 1978, **96**, 275.

<sup>67</sup> U. Kingebiel and D. Bentmann, *Z. Naturforsch., Teil B*, 1979, **34**, 123.

<sup>68</sup> H. W. Roesky, W. Schmieder, and K. Ambrosius, *Z. Naturforsch., Teil B*, 1979, **34**, 197.

<sup>69</sup> W. Bludssus and R. Mews, *J. Chem. Soc., Chem. Commun.*, 1979, 35.

<sup>70</sup> H. W. Roesky, M. Witt, M. Diehl, J. W. Batt, and H. Fuess, *Chem. Ber.*, 1979, **112**, 1372.

<sup>71</sup> H. W. Roesky, M. N. Rao, T. Nakajima, and W. S. Sheldrick, *Chem. Ber.*, 1979, **112**, 3531.

<sup>72</sup> H. W. Roesky, C. Graf, M. N. S. Rao, B. Krebs, and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 780.

<sup>73</sup> H. G. Heal and A. J. Banister, *Phosphorus Sulfur*, 1978, **5**, 95.

<sup>74</sup> H. W. Roesky, T. Muller, and E. Rodek, *J. Chem. Soc., Chem. Commun.*, 1979, 439.

<sup>75</sup> H. W. Roesky, M. Witt, B. Krebs, and M. Hein, *Z. Naturforsch., Teil B*, 1979, **34**, 814.

<sup>76</sup> H. W. Roesky, M. Witt, B. Krebs, and H. J. Korte, *Angew. Chem.*, 1979, **91**, 444.

<sup>77</sup> H. W. Roesky, M. Witt, J. W. Batt, H. Fuess, F. J. Balta Calleja, and F. Ania, *Z. Anorg. Allg. Chem.*, 1979, **458**, 225.

<sup>78</sup> E. Rodek, N. Amin, and H. W. Roesky, *Z. Anorg. Allg. Chem.*, 1979, **457**, 123.

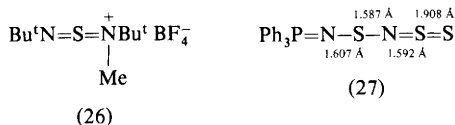
<sup>79</sup> B. Krebs, G. Henkel, S. Pohl, and H. W. Roesky, *Chem. Ber.*, 1980, **113**, 226.

<sup>80</sup> H. W. Roesky, *Angew. Chem.*, 1979, **91**, 112.

<sup>81</sup> A. J. Banister and J. A. Durrant, *J. Chem. Res. (S)*, 1978, 152.



**Structure.** Ultraviolet<sup>82</sup> and mass-spectral analyses<sup>83</sup> have been reported. X-Ray analyses of some N=S=N compounds have also been performed.<sup>3</sup> In the compounds (26)<sup>83</sup> and (27),<sup>84</sup> both N=S=S and N=S=N groups form nearly coplanar configurations. The S=N bond lengths have been determined, and are shown. The S—N bond length of (27), *i.e.* 1.592 Å, is half-way between that of a double bond and that of a single bond, which that of S=S displays somewhat more double-bond character.



The crystal structure of naphtho[1,8-*cd*;4,5-*c'd'*]bis(thiadiazine) has been determined. The results suggest a relatively small contribution of the valence-bond structure involving the naphthalene nucleus.<sup>85</sup> A calculation of the reflectivity of (SN)<sub>x</sub> has been performed.<sup>86</sup> A valence structure analysis of S<sub>2</sub>N<sub>2</sub> by means of INDO calculations has been carried out.<sup>87</sup> The structures of S<sub>4</sub>N<sub>5</sub><sup>-</sup>, S<sub>4</sub>N<sub>5</sub><sup>+</sup>, and S<sub>5</sub>N<sub>6</sub> have also been discussed, starting from M.O. theory.<sup>88</sup> The orientations of the cycloadditions of S<sub>4</sub>N<sub>4</sub>, As<sub>4</sub>N<sub>4</sub>, and As<sub>4</sub>Se<sub>4</sub> with olefins have been discussed. The prediction for S<sub>4</sub>N<sub>4</sub> and olefins rationalizes the experimental observations, while no experimental results have been obtained for As<sub>4</sub>S<sub>4</sub> and As<sub>4</sub>Se<sub>4</sub>; rather different results are expected, in view of the dissimilarity of the orbital patterns of the LUMO's of As<sub>4</sub>X<sub>4</sub> (X = S or Se) and those of S<sub>4</sub>N<sub>4</sub>.<sup>89</sup>

**Thione S-Imides.**—Compounds of this type, which have a —C=S=N— group within the molecule, have been prepared recently (see Vol. 5, p. 107). Thione S-imides (28) have been shown to react readily as 1,2- or 1,3-dipolar compounds with olefins, imines, oximes, aldehydes, or thiones, yielding 1,3-dipolar cycloadducts or Diels–Alder-type adducts<sup>90–92</sup> (see also Chap. 3, Pt II, p. 163).

## 2 Tri-co-ordinate Sulphur

**Sulphonylamines and Sulphur Tri-imides.**—A gas-phase electron-diffraction study of the molecular structure of imido-disulphonyl chloride, NH(SO<sub>2</sub>Cl)<sub>2</sub>, indicates that this exists as a single conformer, having C<sub>2</sub> symmetry.<sup>93</sup> Further details on the sulphur tri-imides (Bu<sup>t</sup>N=)<sub>2</sub>S=NSiMe<sub>3</sub> and S(=NBu<sup>t</sup>)<sub>3</sub> have been reported<sup>94</sup> (see

<sup>82</sup> J. Fabian, R. Mayer, and S. Bleisch, *Phosphorus Sulfur*, 1979, 7, 61.

<sup>83</sup> A. Gieren and B. Dederer, *J. Chem. Res. (S)*, 1979, 41.

<sup>84</sup> T. Chivers, R. T. Oakley, A. W. Cordes, and P. Swepston, *J. Chem. Soc., Chem. Commun.*, 1980, 35.

<sup>85</sup> A. Gieren, V. Lamm, R. C. Haddon, and M. L. Kaplan, *J. Am. Chem. Soc.*, 1979, 101, 7279.

<sup>86</sup> H. Numata, *Phys. Lett. A*, 1979, 72, 453.

<sup>87</sup> H. Fujimoto and T. Yokoyama, *Bull. Chem. Soc. Jpn.*, 1980, 53, 800.

<sup>88</sup> R. Bartzko and R. Gleiter, *Chem. Ber.*, 1980, 113, 1138.

<sup>89</sup> T. Yamabe, K. Tanaka, A. Tachikawa, K. Fukui, and H. Kato, *J. Phys. Chem.*, 1979, 83, 767.

<sup>90</sup> T. Saito and S. Motoki, *Chem. Lett.*, 1978, 591.

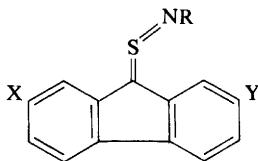
<sup>91</sup> T. Saito and S. Motoki, *J. Org. Chem.*, 1979, 44, 2493.

<sup>92</sup> T. Saito, I. Oikawa, and S. Motoki, *Bull. Chem. Soc. Jpn.*, 1980, 53, 1023.

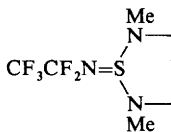
<sup>93</sup> B. Beagley, R. Moutran, S. P. Narula, and V. Ulbrecht, *J. Mol. Struct.*, 1979, 56, 207.

<sup>94</sup> F. M. Tesky, R. Mews, and O. Glemser, *Z. Anorg. Allg. Chem.*, 1979, 452, 103.

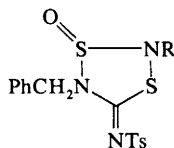
Vol. 5, p. 107) and the tri-imides (29) have also been synthesized, from  $\text{CF}_3\text{CF}_2\text{N}=\text{SF}_2$  and the diamine.<sup>95</sup> Several dithiadiazolines (30; R = *p*- $\text{NO}_2\text{C}_6\text{H}_4$ , *p*- $\text{ClC}_6\text{H}_4$ , Pr, SiMe<sub>3</sub>, or Ts) have been prepared, in 30–75% yields, by treating 4-benzyl-5-tosylimino-1,2,3,4-thiaziazoline with RNSO, while hydrolysis of these dithiadiazolines has been found to give  $\text{PhCH}_2\text{NHC}(=\text{NTs})\text{SNHR}$ .<sup>96</sup>



(28)

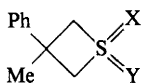


(29)

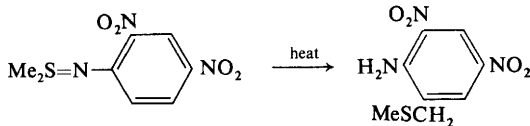


(30)

**Sulphimides and Azasulphonium Salts.**—*Preparation and Structure of Sulphimides.* Several new procedures for the preparation of sulphimides have been published. Sulphonamides, on treatment with DMSO and oxalyl chloride, can be converted into the corresponding *N*-substituted sulphimides  $\text{ArSO}_2\text{N}=\text{SMe}_2$ . This reaction can be applied to compounds containing substituents having strong electron-withdrawing effects, e.g. sulphonyl or *p*-nitrophenyl.<sup>97</sup> Various thietan derivatives (31), such as sulphoxides, sulphimides, sulphonium salts, and sulphoximides, have been prepared with dry Chloramine-T, and their isomers separated.<sup>98</sup>



(31) X = O, Y = lone pair  
X = NTs, Y = lone pair  
X = NTs, Y = O



(32)

Another improved synthesis of various symmetric and unsymmetric *N*-(toluene-*p*-sulphonyl)-sulphimides is by the treatment of the sulphides with solid Chloramine-T under phase-transfer catalytic conditions, using tetrabutylammonium salts as the catalyst, in  $\text{CH}_2\text{Cl}_2$ .<sup>99</sup> *S*-Vinyl-sulphimides can be prepared by the following three methods; (a) treatment of vinyl sulphides with Chloramine-T, (b) base-catalysed elimination of HCl from 2-(halogenoethyl)aryl-sulphimides, and (c) elimination of acetic acid from  $\beta$ -acetoxy-sulphimides with bases.<sup>100</sup> *N*-2,4-Dinitrophenyl-*SS*-dimethylsulphimide (32) can be prepared by the sequential treatment of DMSO with  $\text{P}_2\text{O}_5$  in DMF, then with 2,4-dinitroaniline, and finally

<sup>95</sup> O. Glemser and J. M. Shreeve, *Inorg. Chem.*, 1979, **18**, 213.

<sup>96</sup> G. L'abbé, A. van Asch, J. P. Declercq, G. Germain, and M. Van Meerssche, *Bull. Soc. Chim. Belg.*, 1978, **87**, 285.

<sup>97</sup> S. L. Huang and D. Swern, *J. Org. Chem.*, 1978, **43**, 4537.

<sup>98</sup> M. Buza, K. K. Andersen, and M. D. Pazdon, *J. Org. Chem.*, 1978, **43**, 3827.

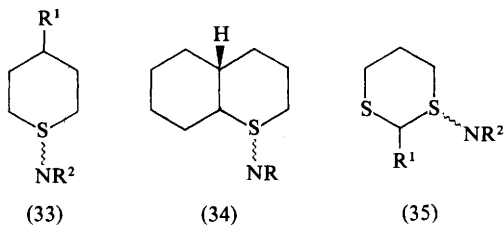
<sup>99</sup> C. R. Johnson, K. Mori, and A. Nakanishi, *J. Org. Chem.*, 1979, **44**, 2065.

<sup>100</sup> T. Yamamoto, M. Kakimoto, and M. Okawara, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 841.

with  $\text{NEt}_3$ . Heating (32) with  $\text{Et}_3\text{N}$  in DMF at  $100^\circ\text{C}$  slowly afforded the rearranged product, i.e. 4,6-dinitro-2-(methylthiomethyl)aniline,<sup>101</sup> while heating the sulphimide (32) with phenols gave the *o*-methylthiomethylated phenols.<sup>102</sup>

The copper-catalysed thermolysis of toluene-*p*-sulphonyl azide in the presence of various sulphides also affords the corresponding sulphimides.<sup>103</sup> A kinetic study on the reactions of Chloramine-T with *ortho*-substituted sulphides indicates a marked steric hindrance by *ortho*-substituents, while the anchimeric effect of *ortho*-groups that have a carbonyl function decreases in the order  $\text{CH}_2\text{CO}_2\text{H} \approx \text{CH}_2\text{CO}_2\text{Me} < \text{CH}_2\text{CO}_2^- < \text{CO}_2\text{Me} \approx \text{CO}_2\text{H} < \text{CO}_2^-$ .<sup>104</sup>

Ethoxycarbonylnitrene (generated photochemically from the azide) also reacts with 4-*t*-butylthian, affording a nearly 1:1 mixture of both *cis*- and *trans*-sulphimides. This non-stereoselectivity in the reaction of the nitrene is in marked contrast with that of the reaction of carbenes with the thian; the thian reacts with both bis(alkoxycarbonyl)- and bis(diacetyl)-carbenes, giving the *trans*-ylides as the sole products<sup>105</sup> (see Vol. 4, p. 112). Various sulphimides of cyclic sulphides, e.g. thians, *cis*- and *trans*-thiadecalins, oxathians, and dithians, can be prepared by treating the sulphides either with anilines and *N*-chlorosuccinimide or with  $\text{Bu}^t\text{OCl}$ . In this reaction, the formation of (33;  $\text{R}^1 = \text{Bu}^t$ ,  $\text{R}^2 = p\text{-ClC}_6\text{H}_4$ ) with an equatorial S—N bond is more favoured than that of (33) with an axially orientated S—N linkage. Meanwhile, the sulphimides (33) having axial S—N bonds can be prepared from conformationally rigid sulphoxides with equatorial S—O bonds. Formation of sulphimides of rigid ring systems such as (34) proceeds by an  $\text{S}_{\text{N}}2$  reaction of the cyclic sulphide on the *N*-chloro-aniline, while reactions of conformationally mobile cyclic sulphides with *N*-chlorosuccinimide may occur *via* succinimidoyl azasulphonium ions as intermediates. Conformational equilibria of these sulphimides have been determined by low-temperature  $^{13}\text{C}$  n.m.r. spectroscopy. The sulphimides (35) have been prepared and their configurations and conformations also determined by  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectroscopy. The compounds (35;  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = p\text{-ClC}_6\text{H}_4$ ) rearrange stereospecifically to the corresponding 2-(2'-amino-5'-chlorophenyl)-1,3-dithians.<sup>106–109</sup> X-Ray photoelectron spectroscopic measurements of various sulphimides have revealed that these thermally stable sulphimides



<sup>101</sup> T. Yamamoto, Y. Harigaya, and M. Okawara, *Tetrahedron*, 1978, **34**, 3097.

<sup>102</sup> T. Yamamoto and M. Okawara, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2443.

<sup>103</sup> P. Svoronos and V. Horak, *Synthesis*, 1979, 596.

<sup>104</sup> F. Ruff, I. Kapovits, J. Rábai, and Á. Kucsman, *Tetrahedron*, 1978, **34**, 2767.

<sup>105</sup> D. C. Appleton, D. C. Bull, J. McKenna, J. M. McKenna, and A. R. Walley, *J. Chem. Soc., Perkin Trans. 2*, 1980, 385.

<sup>106</sup> P. K. Claus, W. Rieder, and F. W. Vierhapper, *Monatsh. Chem.*, 1978, **109**, 609.

<sup>107</sup> J. Bailer, P. K. Claus, and F. W. Vierhapper, *Tetrahedron*, 1979, **35**, 1373.

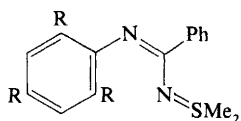
<sup>108</sup> P. K. Claus, F. W. Vierhapper, and K. L. Willer, *J. Org. Chem.*, 1979, **44**, 2863.

<sup>109</sup> J. Bailer, P. K. Claus, and F. W. Vierhapper, *Tetrahedron*, 1980, **36**, 901.

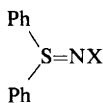
are best represented by a semi-polar canonical structure, since the contribution of  $3d-2p$   $\pi$ -interaction is of little importance in the structure of sulphimides.<sup>110</sup>

*Reactions of Sulphimides and Azasulphonium Salts.* Pyrolysis of sulphimides that have  $\beta$ -protons has been reviewed in detail.<sup>111</sup>

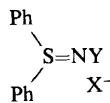
In contrast to the high stability of *N*-tosyl-*SS*-diaryl-sulphimides, the corresponding *N*-acyl-*SS*-diaryl-sulphimides undergo both thermal and photochemical decompositions to afford the corresponding isocyanates and diaryl sulphides quantitatively. Photochemical decomposition has been confirmed to generate partially the singlet nitrene, while kinetic investigations suggest that the thermolysis proceeds exclusively *via* a concerted migration of the alkyl group from carbonyl-carbon to imino-nitrogen that is similar to that in the Curtius rearrangement of acid azides.<sup>112-114</sup> Photolysis of *SS*-dimethyl-*N*-aryl-benzimidoyl-sulphimide that has two *ortho*-alkyl substituents (36) generates imidoynitrenes [ $\text{ArN}=\text{C}(\text{Ph})\text{N}:$ ]; these give carbodi-imides and cyclopenta[*d*]pyrimidines by initial cyclization followed by a [1,5]-imidoyl shift.<sup>115,116</sup> *N*-Chloro- and *N*-bromo-sulphimides (37; X = Cl or Br), prepared from the sulphimide with *N*-chloro- or *N*-bromo-succinimide, have been shown to react with sulphides, phosphines, and tertiary amines, yielding a new type of sulphimide derivative (38; Y =  $\ddot{\text{S}}\text{R}_2$ ,  $\ddot{\text{P}}\text{R}_3$ , or  $\ddot{\text{N}}\text{R}_3$ ). *X*-Ray analysis of the salt [38; Y =  $\ddot{\text{S}}\text{Ph}(\text{Me})$ , X =  $\text{ClO}_4$ ] indicates that the (Ph)<sub>2</sub>S-N bond is shorter than the N-S(Ph)Me bond, demonstrating that the charge is localized mainly on the sulphur atom of the group Y.<sup>117</sup> The mechanism of formation of (38) has been investigated kinetically and stereochemically.<sup>118</sup>



(36)



(37)



(38)

*N*-Tosyl-*S*-alkyl-*S*-aryl-sulphimides or the cycloalkyl-sulphimides (39;  $n = 2, 3$ , or 4) have been shown to react with hydroxide ion in methanol solution, affording either the corresponding sulfoxide, or the hemithioacetal (40), or a mixture of both products. Kinetic studies, including studies using the  $\alpha$ -deuteriated compounds, have revealed that the formation of (40) proceeds *via* an *E1cB* path that involves rate-determining cleavage of the S-N bond.<sup>119</sup>

Sulphimides can be reduced readily by  $\text{P}_2\text{S}_5$ ,<sup>120</sup> or by the thiol- $\text{Me}_2\text{SiCl}$

<sup>110</sup> S. Tsuchiya and M. Seno, *J. Org. Chem.*, 1979, **44**, 2850.

<sup>111</sup> S. Oae and N. Furukawa, *Tetrahedron*, 1977, **33**, 2359 (Tetrahedron Report No. 37).

<sup>112</sup> N. Furukawa, T. Nishio, M. Fukumura, and S. Oae, *Chem. Lett.*, 1978, 209.

<sup>113</sup> N. Furukawa, M. Fukumura, T. Nishio, and S. Oae, *Phosphorus Sulfur*, 1978, **5**, 231.

<sup>114</sup> N. Furukawa, M. Fukumura, T. Nishio, and S. Oae, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3599.

<sup>115</sup> T. L. Gilchrist, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1871.

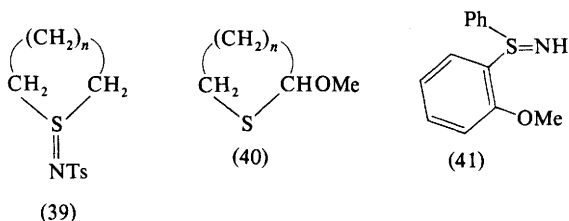
<sup>116</sup> C. W. Rees, *Pure Appl. Chem.*, 1979, **51**, 1243.

<sup>117</sup> Y. Nishikawa, Y. Matsuura, M. Kakudo, T. Akasaka, N. Furukawa, and S. Oae, *Chem. Lett.*, 1978, 447.

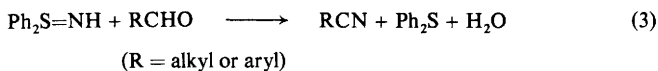
<sup>118</sup> T. Akasaka, T. Yoshimura, N. Furukawa, and S. Oae, *Phosphorus Sulfur*, 1978, **4**, 211.

<sup>119</sup> T. Masuda, N. Furukawa, T. Aida, and S. Oae, *Phosphorus Sulfur*, 1979, **6**, 429.

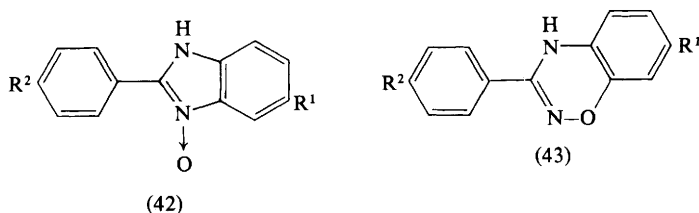
<sup>120</sup> I. W. J. Still and K. Turnbull, *Synthesis*, 1978, 540.



system,<sup>121</sup> at room temperature, to the corresponding sulphides. The Michael-type addition of 'free' diphenylsulphimide to various electrophilic olefins gives mainly the corresponding *trans*-aziridines and enamino-ketones. When optically active 'free' (+)-(*R*)-*S*-*o*-methoxyphenyl-*S*-phenylsulphimide (41), prepared either by asymmetric induction or by resolution of the racemate by seeding with the optically pure compound (41), is treated with an electrophilic olefin such as benzalacetophenone, optically active 2-benzoyl-3-phenylaziridine of *ca.* 30% optical purity is obtained.<sup>122</sup> Recently, aryl 'free' sulphimides have been found to react with various aryl or alkyl aldehydes, affording aryl or alkyl nitriles in excellent yields [reaction (3)].<sup>123</sup> Transformation of *N*-benzyl-*SS*-difluorosulphimide ( $F_2S=N-CH_2Ph$ ) into the nitrile sulphide ( $PhC\equiv N\rightarrow S$ ) has been shown to be catalysed by fluoride ion.<sup>124</sup>



Sulphimides have been shown to undergo cycloaddition (see Vol. 5, p. 109). *N*-Aryl-*SS*-dimethylsulphimides react with nitrile oxides  $p-R^2C_6H_4C\equiv N\rightarrow O$ , affording either (42) or (43).<sup>125</sup> Meanwhile, *N*-heterocyclyl-sulphimides (44) can be prepared, and they afford new heterocycles upon treatment with ketens, through a 1,3-dipolar cycloaddition which eventually gives compound (45).<sup>126, 127</sup> *N*-Phthalimido-*SS*-dimethylsulphimide has been prepared by oxidation of a mixture of *N*-aminophthalimide and dimethyl sulphide with  $Pb(OAc)_4$ . Further reaction, in refluxing benzene, generates the *N*-phthalimido-nitrene, which dimerizes to the



<sup>121</sup> T. Numata, H. Togo, and S. Oae, *Chem. Lett.*, 1979, 329.

<sup>122</sup> N. Furukawa, T. Yoshimura, M. Ohtsu, T. Akasaka, and S. Oae, *Tetrahedron*, 1980, **36**, 73.

<sup>123</sup> N. Furukawa, M. Fukumura, T. Akasaka, T. Yoshimura, and S. Oae, *Tetrahedron Lett.*, 1980, **21**, 761.

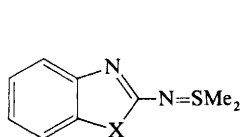
<sup>124</sup> M. J. Sanders, S. L. Dye, A. G. Miller, and J. R. Grunwell, *J. Org. Chem.*, 1979, **44**, 510.

<sup>125</sup> S. Shiraishi, T. Shigemoto, and S. Ogawa, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 563.

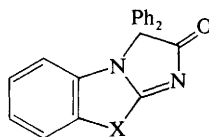
<sup>126</sup> M. Sakamoto, K. Miyazawa, K. Kuwabara, and Y. Tomimatsu, *Heterocycles*, 1979, **12**, 231.

<sup>127</sup> M. Sakamoto, K. Miyazawa, K. Kuwabara and Y. Tomimatsu, *Chem. Pharm. Bull.*, 1979, **27**, 2116.

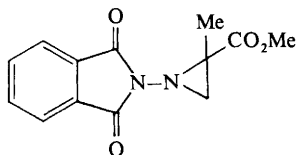
azo-compound or else reacts with methyl methacrylate to afford the aziridine (46).<sup>128</sup> The reaction of 1,2,3-tri(alkylthio)cyclopropenium ions with *N*-acetyl-*S,S*-dimethylsulphimide yields a new type of compound (47).<sup>129</sup>



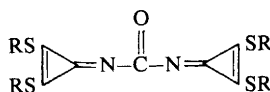
(44) X = O or S



(45) X = O or S

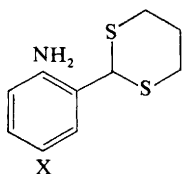


(46)

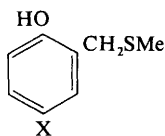


(47)

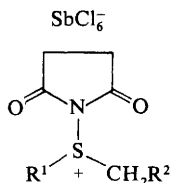
Azasulphonium ylides have been extensively studied (see Vol. 5, pp. 81–2 and 111) because of their well-known synthetic utility for exclusive *ortho*-functionalization of aromatic amines or phenols. By this process, various functionalized anilines (48) and phenols (49) have been synthesized.<sup>102,109,130,131</sup> The other main direction of investigation involves the treatment of succinimido- or hydantoinyl-sulphonium salts [e.g. (50) and (51)] with tertiary amines, which affords interesting [2,3]- or [1,3]-sigmatropically rearranged products [e.g. (52)].<sup>132,133</sup> The amino-sulphonium salt (51), upon treatment with a carboxylic acid, forms the corresponding carboxy-sulphonium salt as an intermediate, which then reacts with amines to form the acid amides.<sup>134</sup> The synthesis of 9-alkyl-<sup>135</sup> or of 9-phenyl-thioxanthene-*N*-(toluene-*p*-sulphonyl)sulphimides (53) has been reported.<sup>136</sup> The configuration of (53) has been determined by <sup>1</sup>H n.m.r.



(48)



(49)



(50)

<sup>128</sup> M. Edward, T. G. Gilchrist, C. J. Harris, and C. W. Rees, *J. Chem. Res. (S)*, 1979, 114.

<sup>129</sup> S. Inoue, G. Yasuda, and T. Hori, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3653.

<sup>130</sup> P. G. Gassman and H. R. Drewes, *J. Am. Chem. Soc.*, 1978, **100**, 7600.

<sup>131</sup> P. G. Gassman and D. R. Amick, *J. Am. Chem. Soc.*, 1978, **100**, 7611.

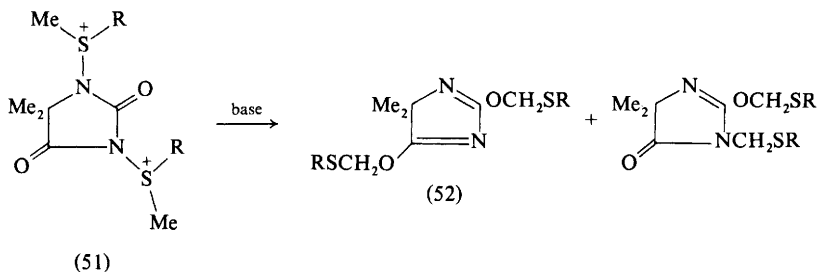
<sup>132</sup> E. Vilsmaier, J. Schults, and S. Zimmerer, *Chem. Ber.*, 1979, **112**, 2231.

<sup>133</sup> E. Vilsmaier, W. Treger, W. Sprugel, and K. Gagel, *Chem. Ber.*, 1979, **112**, 2997.

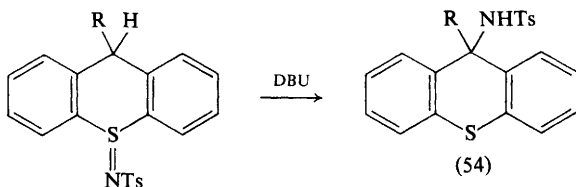
<sup>134</sup> K. Takeda, T. Kobayashi, and H. Ogura, *Chem. Pharm. Bull.*, 1979, **27**, 536.

<sup>135</sup> Y. Tamura, Y. Nishikawa, C. Mukai, K. Sakamoto, M. Ikeda, and M. Kise, *J. Org. Chem.*, 1979, **44**, 1684.

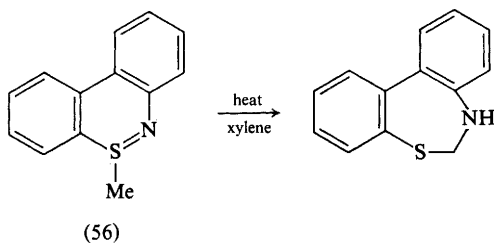
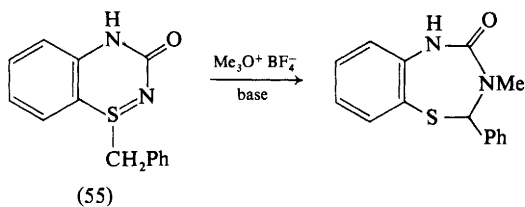
<sup>136</sup> Y. Tamura, C. Mukai, Y. Nishikawa, and M. Ikeda, *J. Org. Chem.*, 1979, **44**, 3296.



spectroscopy and compared with that of the corresponding sulphoxide. Compound (53) has been shown to rearrange to the 9-*N*-toluene-*p*-sulphonamido-9-substituted-thioxanthene (54) upon treatment with bases. The rates of this base-catalysed rearrangement fall in the order *trans*-Me > *cis*-Me > *cis*-Et > *trans*-Pr<sup>1</sup>.



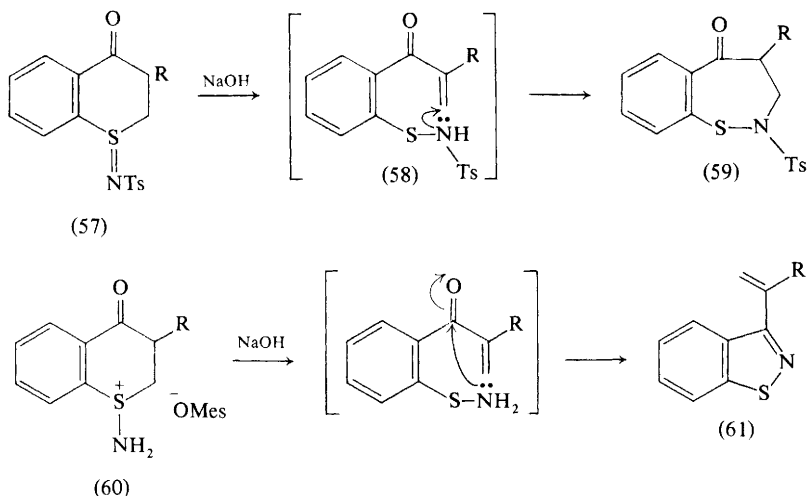
The cyclic sulphimides (55)<sup>137</sup> and (56)<sup>138</sup> have been synthesized, and both thermal and base-catalysed rearrangements of these sulphimides have been shown to result in ring-enlargement to afford heterocyclic compounds.



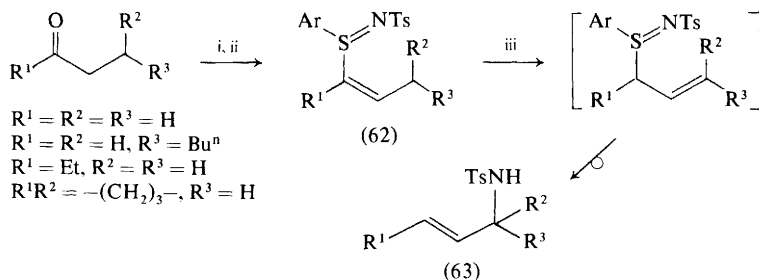
<sup>137</sup> T. L. Gilchrist, C. W. Rees, and I. W. Southon, *J. Chem. Res. (S)*, 1979, 214.

<sup>138</sup> M. Hori, T. Kataoka, H. Shimizu, and K. Matsuo, *Tetrahedron Lett.*, 1979, 3969.

Base-promoted ring-enlargement of the sulphimide (57) to tetrahydro-1,2-benzothiazepine-5-one (59) has been confirmed to proceed *via* incipient formation of the sulphenamide (58) as an intermediate. However, similar treatment of the aminosulphonium salt (60) affords the ring-contracted isothiazole (61).<sup>139</sup>



A new application, the transformation of carbonyl compounds into the allylamines (63), has been carried out by treatment of vinylic sulphimides (62) with a strong base, as shown in Scheme 3.<sup>140</sup>



Reagents: i, ArSH, P<sub>2</sub>O<sub>5</sub>, CH<sub>2</sub>Cl<sub>2</sub>; ii, Chloramine-T; iii, NaOEt, EtOH, at 50 °C

**Scheme 3**

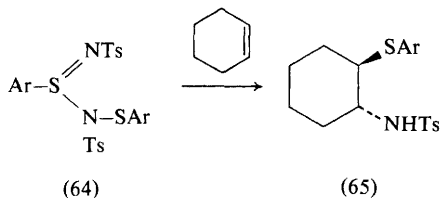
**Sulphonamidines.** Diaryl disulphides have been found to react with Chloramine-T to afford (64), which is a binary sulphenylating/aminating agent and which gives stereospecific *trans*-adducts (65) upon treatment with olefins.<sup>141</sup>

<sup>139</sup> Y. Tamura, S. M. Bayomi, C. Mukai, M. Ikeda, M. Murase, and M. Kise, *Tetrahedron Lett.*, 1980, 21, 533.

<sup>140</sup> M. Kakimoto, T. Yamamoto, and M. Okawara, *Tetrahedron Lett.*, 1979, 623.

<sup>141</sup> D. H. R. Barton, M. R. Britten-Kley, and D. Ferreira, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1682.





A number of symmetrical and unsymmetrical disulphides afford sulphinimidoyl chlorides (66) in good yields when disulphides are treated with *NN*-dichloro-amides or *NN*-dichloro-amines,<sup>142</sup> while treatment of monochloro- or monobromo-acid amides with sulphur and  $\text{SCl}_2$  or  $\text{S}_2\text{Cl}_2$  gives the dichloro-sulphimides  $\text{RCON}=\text{SCl}_2$  ( $\text{R} = \text{Bu}^t$ ,  $\text{ClCH}_2$ ,  $\text{Ph}$ , or aryl)<sup>140</sup> or sulphur di-imides in high yields.<sup>143</sup> Cycloadditions of *N*-acyl-*S*-chloro-sulphimines in the reactions with active-methylene compounds which give *N*-acyl-sulphenamides and  $\text{ClCHXY}$  have also been reported.<sup>144</sup> By this process, *S*-aryl-*S*-alkylamino-sulphonium methylides  $p\text{-R}^1\text{C}_6\text{H}_4\text{S}(\text{NHCMe}_2\text{R}^2)=\text{CR}^3\text{R}^4$  ( $\text{R}^1 = \text{Bu}^t$ ,  $\text{Ph}$ ,  $\text{PhSO}_2$ , or  $\text{ToI}$ ;  $\text{R}^2 = \text{Me}$  or  $\text{CN}$ ;  $\text{R}^3 = \text{R}^4 = \text{MeCO}$  or  $\text{CN}$ , or  $\text{R}^3 = \text{CN}$ ,  $\text{R}^4 = \text{CO}_2\text{Et}$ ) can be obtained.<sup>139,145,146</sup> The n.m.r. chemical shifts of the compounds (66) and the substituent effects of  $\text{R}^1$  have been shown to follow a linear free-energy relationship.<sup>147</sup> Treatment of various mercaptides with *NN*-dichloroarenesulphonamides has been shown to give the corresponding sulphonyl sulphinamidines (67),<sup>148-154</sup> and their acidities and details of their complex formation have also been reported.<sup>155</sup>



(66)  $\text{R}^1 = \text{Bu}^t$ ,  $\text{Me}_2(\text{CN})\text{C}$ ,  $\text{PhSO}_2$ , or aryl  
 $\text{R}^2 = \text{Bu}$ ,  $\text{PhCH}_2$ ,  $\text{Ph}$ , or aryl

*Preparation of Azasulphonium Salts.* Oxidation of methionine with  $\text{I}_2$  to give the cyclic sulphimide is catalysed by general bases, and the rate of the reaction does not give a linear Brönsted plot. The mechanism is proposed to involve the formation

<sup>142</sup> E. S. Levchenko, L. V. Budnik, and T. N. Dubinina, *Zh. Org. Khim.*, 1978, **14**, 1846.

<sup>143</sup> G. S. Borovikova, E. S. Levchenko, and E. M. Dorokhova, *Zh. Org. Khim.*, 1979, **15**, 479.

<sup>144</sup> T. N. Dubinina and E. S. Levchenko, *Zh. Org. Khim.*, 1979, **15**, 743.

<sup>145</sup> E. S. Levchenko and L. V. Budnik, *Zh. Org. Khim.*, 1979, **15**, 748.

<sup>146</sup> L. N. Markovskii, Yu. G. Shermolovich, V. V. Vasil'ev, I. E. Boldeskul, S. S. Trach, and N. S. Zefirov, *Zh. Org. Khim.*, 1978, **14**, 1659.

<sup>147</sup> Yu. P. Egorov and T. G. Zabolotnaya, *Teor. Eksp. Khim.*, 1979, **15**, 265.

<sup>148</sup> R. P. Naumenko, V. I. Sheremet, and M. M. Kremlev, *Vopr. Khim. Khim. Tekhnol.*, 1978, **51**, 57.

<sup>149</sup> R. P. Naumenko, V. I. Sheremet, and M. M. Kremlev, *Vopr. Khim. Khim. Tekhnol.*, 1978, **51**, 3.

<sup>150</sup> A. V. Kharchenko, I. V. Koval, and M. M. Kremlev, *Zh. Org. Khim.*, 1979, **15**, 443.

<sup>151</sup> I. V. Koval, T. G. Oleinik, and M. M. Kremlev, *Zh. Org. Khim.*, 1979, **15**, 2319.

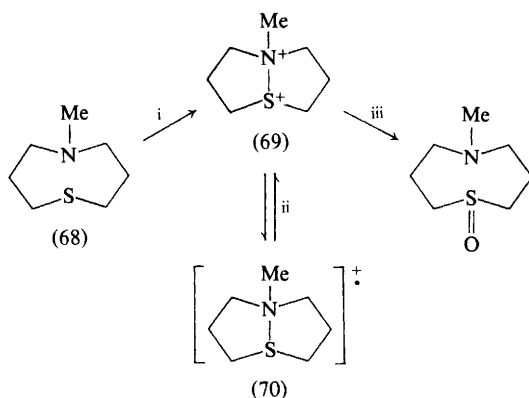
<sup>152</sup> I. V. Koval, A. I. Tarasenko, T. G. Oleinik, and M. M. Kremlev, *Zh. Org. Khim.*, 1979, **15**, 1004.

<sup>153</sup> I. V. Koval, T. G. Oleinik, and M. M. Kremlev, *Vopr. Khim. Khim. Tekhnol.*, 1979, **54**, 24.

<sup>154</sup> S. I. Zlotchenko, M. M. Kremlev, L. P. Yaroshenko, and N. G. Monastyrnaya, *Vopr. Khim. Khim. Tekhnol.*, 1979, **55**, 100.

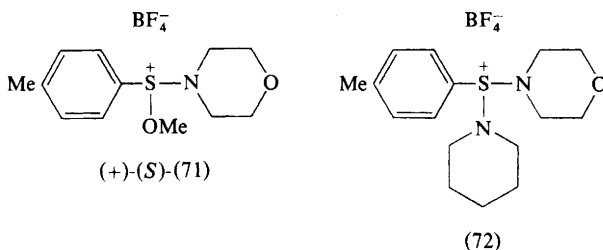
<sup>155</sup> R. P. Naumenko, V. I. Sheremet, and M. M. Kremlev, *Vopr. Khim. Khim. Tekhnol.*, 1978, **50**, 60.

of a tetra-co-ordinate sulphurane intermediate.<sup>156</sup> L-Methionine gives two diastereoisomeric isothiazolinium salts.<sup>157</sup> 5-Methyl-1-thia-5-azacyclo-octane (68) generates the dication (69), and hence the radical cation (70) of  $R_3N-SR_2$ , upon electrophilic oxidation<sup>158</sup> (Scheme 4). In addition to these azasulphonium salts, several other new 'onium salts have been prepared and characterized by  $^1H$  and  $^{19}F$  n.m.r. spectroscopies or by X-ray crystallography,<sup>159,160</sup> viz  $[(Me_2N)_xSF_{3-x}]^+ X^-$ ,  $[(Me_2N)_3S]^+ X^-$ , and  $(Me_3ZN)_3S$  ( $X = BF_4^-$  or  $PF_6^-$ ;  $Z = Si$  or  $C$ ). Optically active alkoxy-aminosulphonium (71) and the related azasulphonium salts (72) have been prepared, the former by methylation of the corresponding sulphinamide. Optically active (71) can transmethylate unsymmetrical tertiary amines or sulphides to give the optically active quaternary ammonium salts and sulphonium salts respectively.<sup>161</sup>



Reagents: i,  $NOBF_4$ ; ii, (70), MeCN; iii, hydrolysis

Scheme 4



<sup>156</sup> P. R. Young and L.-S. Hsieh, *J. Am. Chem. Soc.*, 1978, **100**, 7121.

<sup>157</sup> D. Lambeth and D. W. Swank, *J. Org. Chem.*, 1979, **44**, 2632.

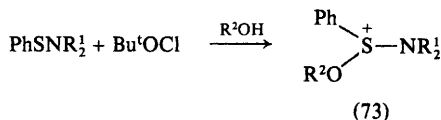
<sup>158</sup> W. K. Musker, A. S. Hirschon, and J. T. Doi, *J. Am. Chem. Soc.*, 1978, **100**, 7754.

<sup>159</sup> A. H. Cowley, D. J. Pagel, and M. L. Walker, *J. Am. Chem. Soc.*, 1978, **100**, 7065.

<sup>160</sup> S. Pohl, B. Krebs, U. Seyer, and G. Henkel, *Chem. Ber.*, 1979, **112**, 1751.

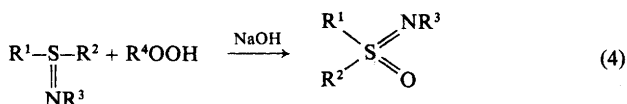
<sup>161</sup> K. Okuma, H. Minato, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 435.

*NN*-Dialkyl-sulphenamides have been shown to react with *t*-butyl hypochlorite in the presence of an alcohol to afford a new type of *S*-alkoxy-*NN*-dialkyl-aminosulphonium salt [73; R<sup>1</sup> = Me, R<sup>2</sup> = (CH<sub>2</sub>)<sub>5</sub> or (CH<sub>2</sub>)<sub>2</sub>O(CH<sub>2</sub>)<sub>2</sub>].<sup>162, 163</sup>



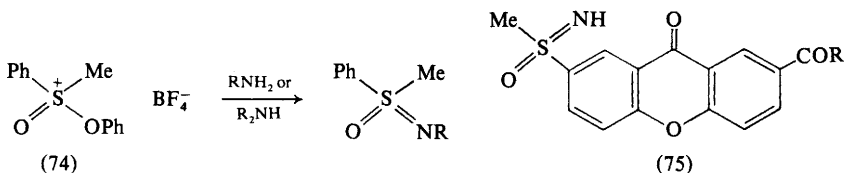
### 3 Tetra-co-ordinate Sulphur

**Sulphoximides.**—One of the general procedures is the oxidation of the corresponding sulphimides with KMnO<sub>4</sub>.<sup>164</sup> In this case, the addition of MgSO<sub>4</sub> generally improves the yields of sulphoximides.<sup>165</sup> *N*-Acyl or -sulphonyl substituted sulphimides undergo facile oxidation with H<sub>2</sub>O<sub>2</sub><sup>166</sup> or MCPBA<sup>167</sup> under alkaline conditions. By this method, rather reactive *S*-benzyl-sulphoximides, unobtainable with other procedures, can be obtained in good yields, as shown in reaction (4).



(R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl, or aralkyl; R<sup>3</sup> = R<sup>5</sup>CO, R<sup>6</sup>SO<sub>2</sub>, or Ar)

Aryloxysulphoxonium salts (74), prepared by treating the sulphones with arenediazonium salts, react with primary or secondary amines to give the corresponding sulphoximides. The reaction is considered to proceed through an S<sub>N</sub>2 process on the sulphur atom.<sup>168–170</sup> These methods can be used to prepare *N*-alkylated sulphoximides. When the sulphoximide (75; R = OH) is heated at 230 °C for 2 minutes, an intermolecular methyl-transfer reaction can be observed, from the sulphoximide to the carboxylic acid group, to give (75; R = OMe). This



<sup>162</sup> M. Haake and H. Gebbing, *Synthesis*, 1979, 98.

<sup>163</sup> M. Haake, H. Gebbing, and H. Benack, *Synthesis*, 1979, 97.

<sup>164</sup> D. H. Evans and R. G. Greenwald, U.S. P. 4 113 738 (*Chem. Abstr.*, 1979, **90**, 72 210).

<sup>165</sup> S. Oae, N. Furukawa, T. Akasaka, and M. Moriyama, Japan. Kokai 78 09 717.

<sup>166</sup> C. R. Johnson and R. A. Kirchhoff, *J. Org. Chem.*, 1979, **44**, 2280.

<sup>167</sup> S. H. Huang and D. Swern, *J. Org. Chem.*, 1979, **44**, 2510.

<sup>168</sup> M. Shimagaki, H. Tsuchiya, Y. Ban, and T. Oishi, *Tetrahedron Lett.*, 1978, 3435.

<sup>169</sup> I. W. J. Still and S. Szilagyi, *Synth. Commun.*, 1979, **9**, 923.

<sup>170</sup> G. R. Chalkley, D. J. Snodin, G. Stevens, and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1580.

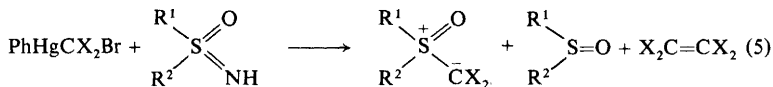
novel type of methyl-transfer can also be observed in the treatment of methyl phenyl sulphoximide with benzoic acid at 240 °C, which forms methyl benzoate in 15% yield.<sup>171</sup>

Sulphoximides having longer alkyl chains or quaternary ammonium functional groups that contain heterocyclic groups such as thiophenyl, furanyl, or pyridyl have been prepared.<sup>172</sup> *S*-Hexadecyl-*S*-phenyl-(or *p*-tolyl)-sulphoximides have been prepared and tested as surfactants for the hydrolysis of esters.<sup>173</sup>

Optically active *N*-halogeno-sulphimides, upon hydrolysis under alkaline conditions, give the corresponding sulphoximides. This unusual substitution reaction proceeds with nearly quantitative (96%) retention of configuration.<sup>174</sup> Similar treatment of the *N*-chloro-*SS*-diaryl-sulphimides with Chloramine-T in anhydrous acetonitrile, followed by treatment with H<sub>2</sub>SO<sub>4</sub>, gives the diaryl sulphone di-imines Ar<sub>2</sub>S(=NH)<sub>2</sub>.<sup>175</sup> The reaction of optically active *N*-chloromethyl-*S*-phenylsulphoximide with sulphoxides gives optically active  $\alpha$ -chloro-sulphoxides directly, but in low optical yields.<sup>176</sup> Upon photolysis or thermolysis in the presence of a radical initiator such as AIBN or benzoyl peroxide, *N*-chloro- or *N*-bromo-*SS*-diaryl-sulphoximides generate the corresponding sulphoximidoyl radicals, which add to olefins or abstract hydrogen from toluene. These homolytic chain reactions have been described in detail.<sup>177,178</sup> A novel preparation of an optically active oxysulphonium ylide in the reaction of an optically active sulphoximide with dimethyl diazomalonate has also been described.<sup>179</sup> The stereochemical cycle is shown in Scheme 5.<sup>180</sup>

A similar deimination of sulphoximides by phenyl(trihalogenomethyl)mercury compounds and subsequent substitution by the carbene species also affords the corresponding oxysulphonium ylides [reaction (5)].<sup>181</sup>

Treatment of various vinylic sulphoximides R<sup>1</sup>SO(=NR<sup>2</sup>)CH=CHR<sup>3</sup> (R<sup>1</sup> = Tol, PhCH<sub>2</sub>, or naphthyl; R<sup>2</sup> = phthalimido; R<sup>3</sup> = H, and R<sup>1</sup> = Tol, R<sup>2</sup> = phthalimido, R<sup>3</sup> = Me) with 0.5 molar equivalents of (–)-ephedrine results in a Michael addition with asymmetric induction, affording optically active sulphoximides in up to 46% enantiomeric excess.<sup>182</sup>



<sup>171</sup> A. C. Barnes, P. W. Hairsine, D. P. Kay, P. J. Ramm, and J. B. Taylor, *J. Heterocycl. Chem.*, 1979, **16**, 1089.

<sup>172</sup> P. Stoss, G. Satzinger, M. H. Herrmann, and W. Heldt, Ger. Offen. 2 758 613 (*Chem. Abstr.*, 1979, **91**, 107 878).

<sup>173</sup> S. Jugé and G. Meyer, *Tetrahedron*, 1980, **36**, 959.

<sup>174</sup> T. Akasaka, T. Yoshimura, N. Furukawa, and S. Oae, *Chem. Lett.*, 1978, 417.

<sup>175</sup> N. Furukawa, K. Akutagawa, T. Yoshimura, T. Akasaka, and S. Oae, *Synthesis*, 1979, 289.

<sup>176</sup> H. Morita, H. Itoh, N. Furukawa, and S. Oae, *Chem. Lett.*, 1978, 817.

<sup>177</sup> T. Akasaka, N. Furukawa, and S. Oae, *Chem. Lett.*, 1979, 529.

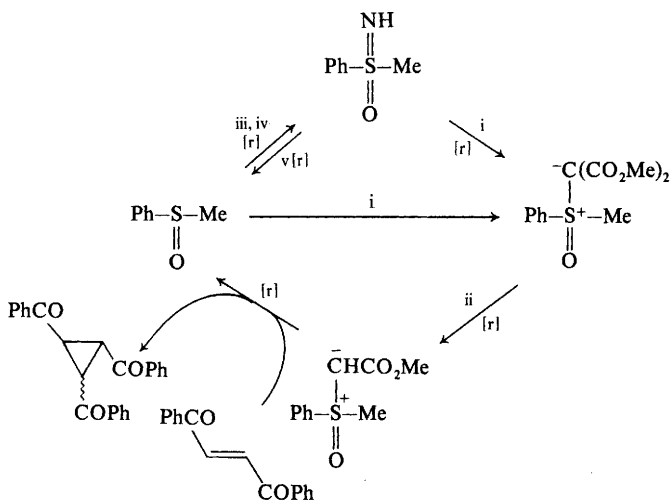
<sup>178</sup> T. Akasaka, N. Furukawa, and S. Oae, *Tetrahedron Lett.*, 1979, 2035.

<sup>179</sup> N. Furukawa, F. Takahashi, T. Yoshimura, and S. Oae, *Tetrahedron Lett.*, 1977, 3633.

<sup>180</sup> N. Furukawa, F. Takahashi, T. Yoshimura, and S. Oae, *Tetrahedron*, 1979, **35**, 317.

<sup>181</sup> J. Iqbal and W. Rahman, *J. Organomet. Chem.*, 1979, **169**, 141.

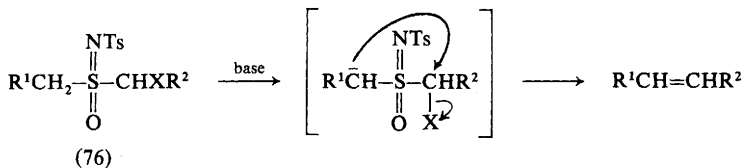
<sup>182</sup> R. Annunziata and M. Cinquini, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1684.



Reagents: i,  $N_2C(CO_2Me)_2$ ,  $CuSO_4$ , benzene; ii,  $KOH$ , aq.  $MeOH$ ; iii,  $TsN_3$ ; iv, conc.  $H_2SO_4$ ; v,  $NaNO_2$

Scheme 5

$\alpha$ -Halogeno-sulphoximides are interesting sulphoximide derivatives and have various uses. They are, for example, alkylating reagents like sulphonium salts or S-ylides. Preparation is achieved either by the direct  $\alpha$ -halogenation of the *N*-methyl derivatives, by treatment of *N*-methylsulphoximides with *t*-butyl hypochlorite, or by imination of  $\alpha$ -chloro-sulphoxides with *O*-mesitylenesulphonylhydroxylamine.<sup>183</sup> Regioselectivity and stereoselectivity for halogenation have been described.<sup>184</sup> Dialkyl  $\alpha$ -halogeno-sulphoximides (76;  $R^1, R^2 = Et, Pr$ , or  $Ph$ ;  $R^1 = H$  or  $Me$ ) have been shown to undergo base-promoted Ramberg-Bäcklund-type rearrangement to afford eventually the olefins. The stereochemistry of the formation of olefins depends upon the substituents; when  $R = Ph$ , the *Z*-isomers are predominantly formed, but the *E*-isomers predominate if  $R$  is an alkyl group.<sup>185</sup>



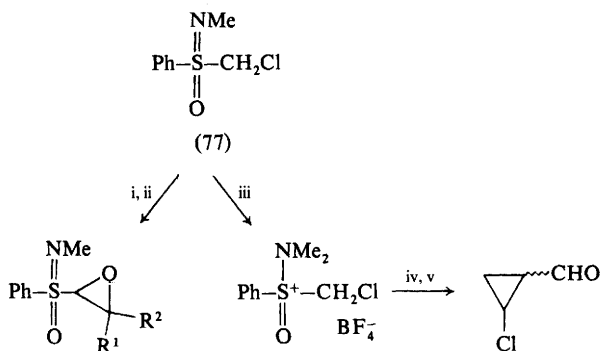
Similar sulphoximides (77) have also been found to condense with various ketones and aldehydes to give epoxides or simple adducts. The mode of the reaction varies with the type of ketone or aldehyde used (Scheme 6).<sup>186</sup>

<sup>183</sup> C. R. Johnson and C. J. Stark, Jr., *Tetrahedron Lett.*, 1979, 4713.

<sup>184</sup> C. R. Johnson and H. G. Corkins, *J. Org. Chem.*, 1978, **43**, 4136.

<sup>185</sup> C. R. Johnson and H. G. Corkins, *J. Org. Chem.*, 1978, **43**, 4140.

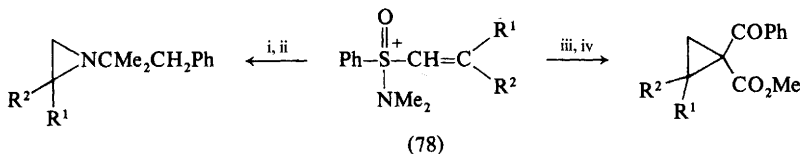
<sup>186</sup> H. G. Corkins, L. Veenstra, and C. R. Johnson, *J. Org. Chem.*, 1978, **43**, 4283.



Reagents: i, Bu<sup>t</sup>OK; ii, R<sup>1</sup>COR<sup>2</sup>; iii, Me<sub>3</sub>O<sup>+</sup> BF<sub>4</sub><sup>-</sup>; iv, NaH, DMSO; v, H<sub>2</sub>C=CHCHO

**Scheme 6**

$\beta$ -Hydroxy-sulphoximides, prepared by condensation of the lithium salts of the sulphoximides with aldehydes or ketones, undergo reductive elimination of the sulphoximide groups upon treatment with aluminium amalgam, forming the corresponding alkenes.<sup>187</sup>  $\beta$ -Hydroxy-sulphoximides, after dehydration and treatment of the resulting vinylic sulphoxides with Me<sub>3</sub>O<sup>+</sup> BF<sub>4</sub><sup>-</sup>, give the sulphoximide salts (78). Michael addition of active methylenic compounds or imines to the compounds (78) and subsequent elimination of *NN*-dimethylbenzenesulphinamide can give cyclopropanes or aziridines (Scheme 7). An optically active (78), when it reacted with, e.g., methyl cyanoacetate, gave 1-cyano-2-phenylcyclopropane of 25.5% optical purity.<sup>188</sup>



Reagents: i, NEt<sub>3</sub>; ii, PhCH<sub>2</sub>CMe<sub>2</sub>NH<sub>2</sub>; iii, NaOMe; iv, PhCOCH<sub>2</sub>CO<sub>2</sub>Me

**Scheme 7**

*N*-Tosyl-*SS*-dimethylsulphoximide reacts with ketones under basic conditions in DMSO and unexpectedly affords oxetans.<sup>189</sup> Synthetic methods and applications of sulphoximidoyl chlorides (79) have been developed. An optically active (79) has also been prepared. Since the sulphoximidoyl chloride has a highly electrophilic central sulphur atom, a number of nitrogen- and oxygen-containing nucleophiles have been shown to react with (79) to give the substituted products.<sup>190-192</sup>

<sup>187</sup> C. R. Johnson and R. A. Kirchhoff, *J. Am. Chem. Soc.*, 1979, **101**, 3602.

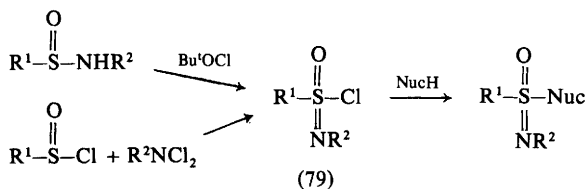
<sup>188</sup> C. R. Johnson, J. P. Lockard, and E. R. Kennedy, *J. Org. Chem.*, 1980, **45**, 264.

<sup>189</sup> S. C. Welch and A. S. C. P. Rao, *J. Am. Chem. Soc.*, 1979, **101**, 6135.

<sup>190</sup> C. R. Johnson, E. U. Jonsson, and A. Wambsgans, *J. Org. Chem.*, 1979, **44**, 2055.

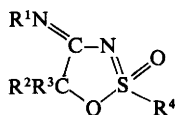
<sup>191</sup> C. R. Johnson and A. Wambsgans, *J. Org. Chem.*, 1979, **44**, 2278.

<sup>192</sup> C. R. Johnson, E. U. Jonsson, and A. Wambsgans, *J. Org. Chem.*, 1979, **44**, 2061.



The Michael addition of sulphoximides to, e.g., dimethyl acetylenedicarboxylate has been carried out, affording the corresponding adducts. The stereochemical course of the addition has been investigated.<sup>193</sup>

Cyclic oxygen analogues (80) of sulphoximides can also be prepared.<sup>194,195</sup> The biological role of L-methionine sulphoximide and its effect upon glutamine synthetase has been investigated.<sup>196</sup>



(80) R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> are alkyl

**Sulphodi-imides.**—Methods of preparation of a few sulphodi-imides have been reported.<sup>71,72,197</sup> An aza-analogue of sulphurane has also been prepared.<sup>198</sup>

#### 4 Selenium and Tellurium Analogues

Selenium di-imides can be prepared in nearly quantitative yields by treating RN(SiMe<sub>3</sub>)<sub>2</sub> with SeF<sub>4</sub> or SeCl<sub>4</sub>. The di-imides react with RSO<sub>2</sub>N=SeCl<sub>2</sub> to give the unsymmetrical selenium imides RN=Se=NSO<sub>2</sub>R.<sup>199</sup>

Sulphurane analogues of telluryl compounds are also known to give telluryl-imides similarly. Simple treatment of telluryl or selenyl oxides with primary amines in CHCl<sub>3</sub> also yields the corresponding telluryl- or selenyl-imides.<sup>200</sup>

<sup>193</sup> Y. Tamura, S. M. Bayomi, M. Tsunekawa, and M. Ikeda, *Chem. Pharm. Bull.*, 1979, **27**, 2137.

<sup>194</sup> G. L'abbé and A. Verbruggen, *Tetrahedron Lett.*, 1979, 49.

<sup>195</sup> G. L'abbé, C. C. Yu, and S. Toppet, *J. Org. Chem.*, 1979, **44**, 3991.

<sup>196</sup> A. Shrake, E. J. Whiting, Jr., and A. Ginsburg, *J. Biol. Chem.*, 1980, **255**, 581.

<sup>197</sup> W. Heider and O. Glemser, *Chem. Ber.*, 1979, **113**, 237.

<sup>198</sup> L. J. Adzima, C. C. Chiang, I. C. Paul, and J. C. Martin, *J. Am. Chem. Soc.*, 1978, **100**, 953.

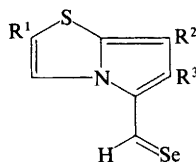
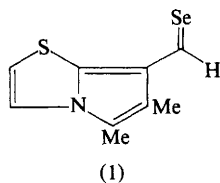
<sup>199</sup> N. Ya. Derkach, G. G. Barashenko, and E. S. Levchenko, *Zh. Org. Khim.*, 1979, **15**, 1547.

<sup>200</sup> V. I. Naddaka, V. P. Carkin, I. D. Sadekov, V. P. Krasnov, and V. I. Minkin, *Zh. Org. Khim.*, 1979, **15**, 896.

## 3

## Thiocarbonyl and Selenocarbonyl Compounds

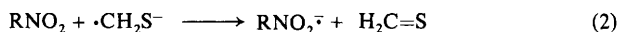
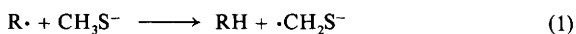
BY D. R. HOGG, J. K. LANDQUIST &amp; A. OHNO

**PART I: Thioaldehydes, Thioketones, Thioketens, and their Selenium Analogues**  
by A. Ohno**Reviews.**—No important review has been published in the past two years.**1 Thioaldehydes and Selenoaldehydes****Synthesis.**—No report concerned with the preparation and identification of stable thioaldehydes has appeared; however, pyrrolo[2,1-*b*]thiazole-7- (1) and -5-carbo-selenoaldehydes (2)—(4) have been synthesized by the selenoformylation of pyrrolo[2,1-*b*]thiazoles and characterized by their  $^1\text{H}$  n.m.r. and u.v. spectra.<sup>1</sup> With the exception of (4), these selenoaldehydes are stable, green, crystalline compounds.

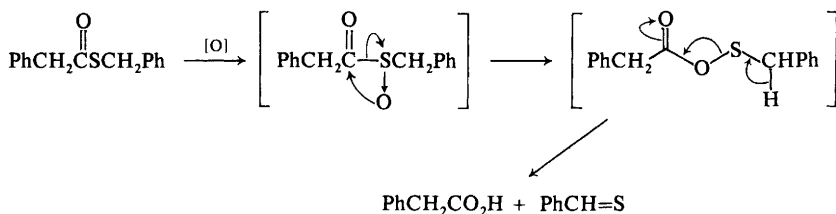
- (2)  $\text{R}^1 = \text{H}, \text{R}^2 = \text{R}^3 = \text{Me}$   
 (3)  $\text{R}^1 = \text{R}^3 = \text{H}, \text{R}^2 = \text{Me}$   
 (4)  $\text{R}^1 = \text{R}^3 = \text{Me}, \text{R}^2 = \text{H}$

**Transient Species.**—Because of their instability, no attempt at identifying the intermediacy of thio- or seleno-aldehydes has yet been successful. However, product analyses and mechanistic considerations suggest that thio- or seleno-aldehydes are formed as intermediates in certain reactions. For example, thioformaldehyde has been proposed as a transient species in the reaction of nitroalkanes with sodium methanethiolate, as shown in reactions (1) and (2).<sup>2</sup> The<sup>1</sup> D. H. Reid, R. G. Webster, and S. McKenzie, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2334.<sup>2</sup> N. Kornblum, S. C. Carlson, and R. G. Smith, *J. Am. Chem. Soc.*, 1979, **101**, 647.

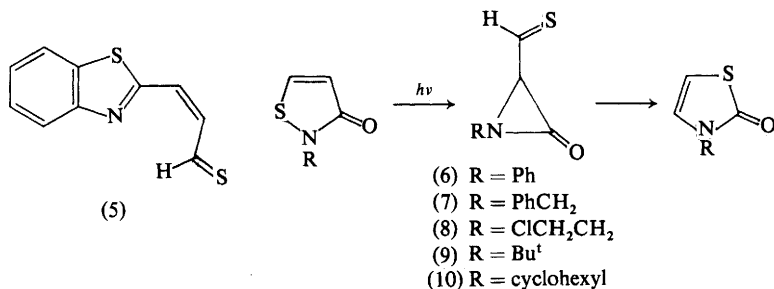




thioformaldehyde that is formed reacts with excess methanethiolate anion to form dimethyl trithiocarbonate. Ozonolysis of benzyl phenylthioacetate in 1,2-dichloroethane affords phenylacetic acid and thiobenzaldehyde (Scheme 1).<sup>3</sup> The latter compound is further oxidized to benzoic acid and, in part, benzaldehyde under the reaction conditions. When 2-azidophenyl 2'-thienyl sulphide is subjected to thermolysis or photolysis, pyrrolo[2,1-*b*]benzothiazole is obtained. The thioaldehyde (5) has been proposed as an intermediate.<sup>4</sup> Photoisomerization of isothiazol-3(2*H*)-ones yields thiazol-2(3*H*)-ones, probably through a ring-contraction–ring-expansion mechanism, and an  $\alpha$ -lactam that is substituted by a thioformyl group, *e.g.* (6)–(10), may be an intermediate.<sup>5</sup>



Scheme 1



2,5-Dihydrothiophenium phenacylide, in refluxing benzene, is decomposed directly or through 2-benzoyl-3,6-dihydro-2*H*-thiopyran into 2-phenylthioglyoxal (11), as shown in Scheme 2.<sup>6</sup> The thioglyoxal is trapped by the thiophenium phenacylide to give 2-benzoyl-5-phenyl-1,3-oxathiole.

The reaction of an aldehyde with sodium hydrogen selenide and an amine hydrochloride generates a selenoaldehyde, which is reduced *in situ* to a symmetric diselenide by sodium borohydride.<sup>7</sup>

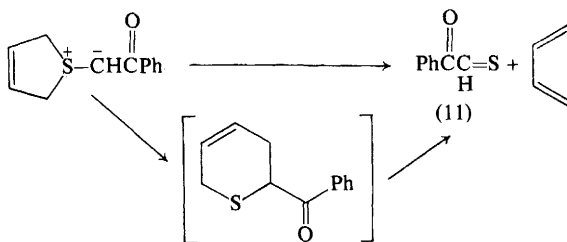
<sup>3</sup> H. J. Chaves das Neves and L. S. Godinho, *Tetrahedron*, 1979, **35**, 2053.

<sup>4</sup> J. M. Lindley, O. Meth-Cohn, and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1198.

<sup>5</sup> J. Rokach and P. Hamel, *J. Chem. Soc., Chem. Commun.*, 1979, 786.

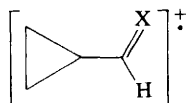
<sup>6</sup> U. J. Kempe, T. Kempe, and T. Norin, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1547.

<sup>7</sup> J. W. Lewicki, W. H. H. Günther, and J. Y. C. Chu, *J. Org. Chem.*, 1978, **43**, 2672.



Scheme 2

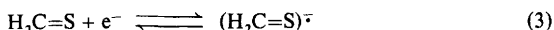
**Mass Spectrometry.**—It has been revealed by collisional activation mass spectral studies that protonated thioformaldehyde is about 5—10 kcal mol<sup>-1</sup> more stable in the structure H<sub>2</sub>C=SH<sup>+</sup> than in the structure H<sub>3</sub>C-S<sup>+</sup>, which is in reversed order from that of the oxygen analogue.<sup>8</sup> Mass-spectrometric fragmentation studies of selenophen and tellurophen suggest that the cation radical of cyclopropenyl selenoaldehyde (12) is clearly discernible while the corresponding tellurium analogue (13) is poorly represented in the spectrum of tellurophen.<sup>9</sup>



(12) X = Se

(13) X = Te

**Molecular Orbital Calculations.**—The ground state of the anion radical of thioformaldehyde (<sup>2</sup>B<sub>1</sub>) is calculated, on the basis of the PNO-CEPA *ab initio* method, to be bound, near to its quasi-planar equilibrium geometry [reaction (3)].



The acquisition of an electron should cause only small changes in the H<sub>2</sub>C group but a lengthening of the C=S bond.<sup>10</sup>

## 2 Thioketones

**Synthesis.**—The highly hindered thioketones (14)—(17) have been prepared [in the yields shown] by the reaction of triphenylphosphorylidene hydrazone with elemental sulphur, by heating the mixture at 130—140 °C under vacuum (1—5 mmHg).<sup>11</sup> The yields are considerably improved when the corresponding hydrazones are allowed to react with disulphur dichloride in the presence of triethylamine in benzene, at 0 °C to room temperature.<sup>12</sup> With the latter method, the yields of (15)—(17) are quantitative. Thioketones (18)—(20) have also been

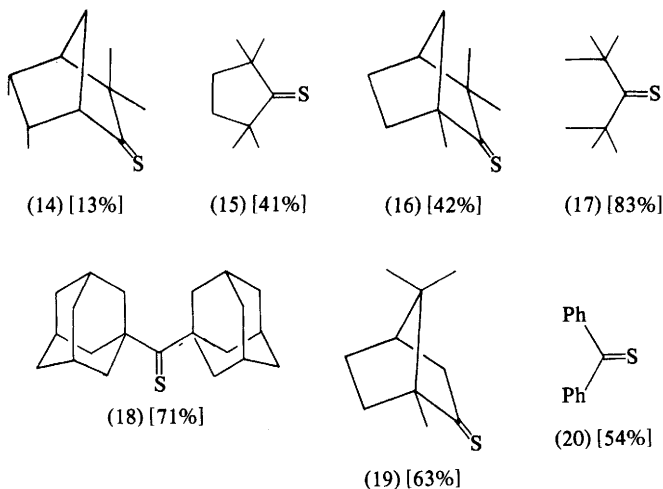
<sup>8</sup> J. D. Dill and F. W. McLafferty, *J. Am. Chem. Soc.*, 1978, **100**, 2907.

<sup>9</sup> F. Fringuelli and A. Taticchi, *J. Heterocycl. Chem.*, 1978, **15**, 137.

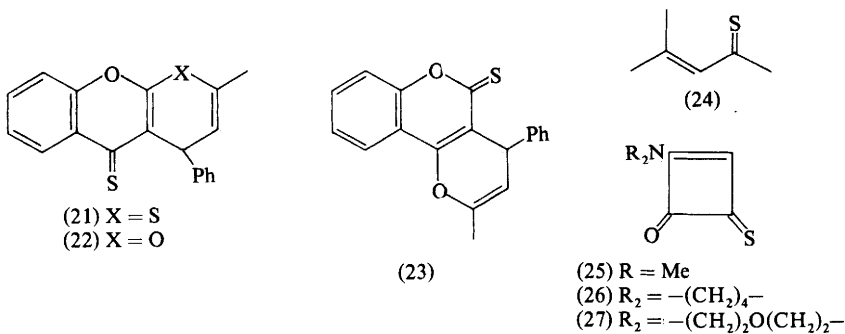
<sup>10</sup> P. Rosmus and H. Bock, *J. Chem. Soc., Chem. Commun.*, 1979, 334.

<sup>11</sup> P. de Mayo, G. L. R. Petrašiūnas, and A. C. Weedon, *Tetrahedron Lett.*, 1978, 4621.

<sup>12</sup> R. Okazaki, K. Inoue, and N. Inamoto, *Tetrahedron Lett.*, 1979, 3673.



prepared by the latter method.  $\Delta^{1,4}$ -Diene-3-thiones have been prepared from corticosterone-1,4-dien-3-ones and phosphorus pentasulphide.<sup>13</sup> However, the corresponding  $\Delta^4$ -ene-3-thiones were not isolated when testosterone acetate or androst-4-ene-3,11,17-trione was subjected to the reaction.<sup>13</sup> The enethiones can be trapped *in situ*, giving the expected diene sulphides. Cyclocumarol and phosphorus pentasulphide react to give the three heterocyclic thiones (21)—(23).<sup>13</sup> The more simple enethione (24) has been prepared and found to be stable at  $-60^\circ\text{C}$ .<sup>14</sup> The reaction of an aminocyclobutenedione with phosphorus pentasulphide in dichloromethane affords a 1-amino-4-oxo-3-thioxocyclobutene, e.g. (25)—(27), instead of its corresponding 3-oxo-4-thioxo-isomer.<sup>15</sup> A number of dianions (28)—(31) of thiosquaric acid have also been prepared by Seitz and his co-workers.<sup>16</sup>

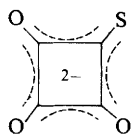


<sup>13</sup> D. H. R. Barton, L. S. L. Choi, R. H. Hesse, M. M. Pechet, and C. Wilshire, *J. Chem. Soc., Perkin Trans. I*, 1979, 1166.

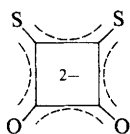
<sup>14</sup> P. Beslin, D. Lagain, and J. Vialle, *Tetrahedron Lett.*, 1979, 2677.

<sup>15</sup> G. Seitz, H. Morck, R. Schmiedel, and R. Sutrisno, *Synthesis*, 1969, 361.

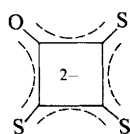
<sup>16</sup> G. Seitz, K. Mann, R. Schmiedel, and R. Matusch, *Chem. Ber.*, 1979, **112**, 990.



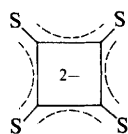
(28)



(29)

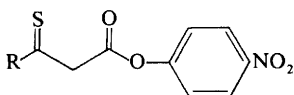


(30)



(31)

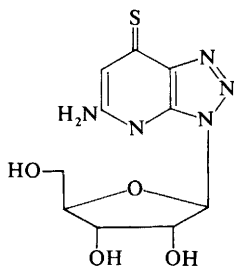
A modification of the Pinner reaction provides a facile device to prepare  $\beta$ -thio-esters: from the corresponding  $\beta$ -amino-esters in DMF, the thiones (32)—(34) have been synthesized by their reaction with hydrogen sulphide in the presence of trifluoroacetic acid.<sup>17</sup> Thiation in DMF has also been applied to the synthesis of the heterocyclic thione (35) from a 7-chlorotriazolopyridine derivative.<sup>18</sup> The sulphur–nitrogen bond in an isothiazolium ion has been cleaved by sodium hydrogen sulphide in acetonitrile to give the enamino-thione (36).<sup>19</sup>



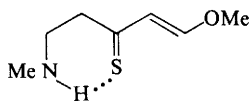
(32) R = Ph [76%]

(33) R = *p*-MeOC<sub>6</sub>H<sub>4</sub> [98%]

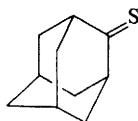
(34) R = Me [85%]



(35)



(36)



(37)

**Reactions.**—Photochemical reduction of adamantanethione (37) has been studied in detail.<sup>20</sup> The  $\pi, \pi^*$ -state ( $S_2$ ) of the thione abstracts a hydrogen atom from the solvent alkane. Depending on the viscosity of the solvent, most of the reaction occurs by radical combination within the solvent cage, but a small percentage escapes, to be trapped by ground-state thione. Evidence is provided that any chain sequence deriving from the escaping radicals must be short ( $k = 6.7 \times 10^7$  l mol<sup>-1</sup> s<sup>-1</sup> in cyclohexane and  $6.3 \times 10^7$  l mol<sup>-1</sup> s<sup>-1</sup> in cyclopentane). Di-*t*-butyl thioketone (17) has also been subjected to photoreduction.<sup>21</sup> Only compounds that have an aromatic moiety or an amino-group can reduce the  $n, \pi^*$ -state of thione to

<sup>17</sup> F. DiNinno and E. V. Linek, *J. Org. Chem.*, 1979, **44**, 3271.

<sup>18</sup> B. L. Cline, R. P. Panzica, and L. B. Townsend, *J. Org. Chem.*, 1978, **43**, 4910.

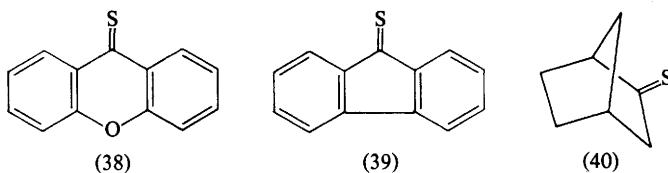
<sup>19</sup> A. G. Briggs, J. Czyzewski, and D. H. Reid, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2340.

<sup>20</sup> K. Y. Law and P. de Mayo, *J. Am. Chem. Soc.*, 1979, **101**, 3251.

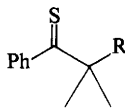
<sup>21</sup> A. Ohno, M. Uohama, K. Nakamura, and S. Oka, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1521.

its corresponding thiol. A charge-transfer-type exciplex has been proposed, but without unambiguous proof.

Rajee and Ramamurthy have proposed that singlet oxygen is involved in the photo-oxidation of the thiones (16), (19), (37), and (38)—(40) to the corresponding ketones.<sup>22</sup> On the other hand, Tamagaki and his co-workers have reported that the thioketone (17) is photo-oxidized to di-*t*-butyl ketone by ground-state oxygen, whereas the photo-oxidation by singlet oxygen affords di-*t*-butylsulphine.<sup>23</sup>



When the thione (17) is photo-excited to its  $\pi, \pi^*$ -state, hydrogen-abstraction from alkanes and cycloaddition to olefins takes place, which is in remarkable contrast with the reactivity of (17) in the  $n, \pi^*$ -state.<sup>24</sup>



(41) R is a variety of alkyl groups

The mechanism of hydrogen-abstraction of aryl alkyl thioketones (41) to give cyclopentyl thiols has been investigated.<sup>25</sup> By comparison of the rate of hydrogen-abstraction to give a 1,5-biradical with that of product formation, it has been shown that only about one-tenth of the biradicals cyclize. The rest disproportionate to give the original thioketone. The existence of an intermediate and the singlet state as the reactive state have been confirmed. It is also mentioned that hydrogen-abstraction takes place in a similar manner to the alkanone type II singlet process  $^1(n, \pi^*)$ , although the active species in the photochemistry of thioketones is in the  $\pi, \pi^*$ -state.

When xanthenthione (38) is excited to its  $n, \pi^*$ -state, [2 + 2]cycloaddition proceeds with bis(alkylthio)ethyne. The cyclo-adduct [(42) or (43)] is in thermal equilibrium with its 'open' isomer [(44) or (45)].<sup>26</sup> A similar reaction of (37) with acenaphthylene, indene, or *N*-phenylmaleimide affords a spirothietan derivative in good yield.<sup>27</sup> Thioxanthenthione in the  $n, \pi^*$ -state cyclo-adds to alkyl- or alkoxy-substituted butatrienes, giving the thietans (46)—(49).<sup>28</sup>

<sup>22</sup> R. Rajee and V. Ramamurthy, *Tetrahedron Lett.*, 1978, 5127.

<sup>23</sup> S. Tamagaki, R. Akatsuka, M. Nakamura, and S. Kozuka, *Tetrahedron Lett.*, 1979, 3665.

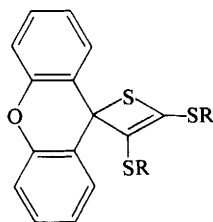
<sup>24</sup> R. Rajee and V. Ramamurthy, *Tetrahedron Lett.*, 1978, 3463.

<sup>25</sup> K. W. Ho and P. de Mayo, *J. Am. Chem. Soc.*, 1979, **101**, 5725.

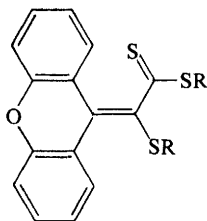
<sup>26</sup> A. C. Brouwer, A. V. E. George, D. Seykens, and H. J. T. Bos, *Tetrahedron Lett.*, 1978, 4839.

<sup>27</sup> H. Gotthardt and S. Nieberl, *Chem. Ber.*, 1978, **111**, 1471.

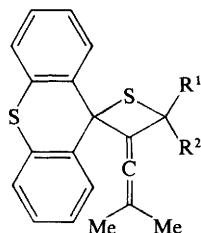
<sup>28</sup> R. G. Visser and H. J. T. Bos, *Tetrahedron Lett.*, 1979, 4857.



(42) R = Me

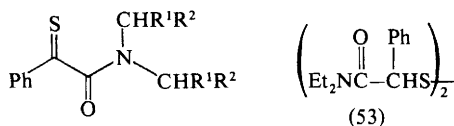
(43) R = Bu<sup>t</sup>

(44) R = Me

(45) R = Bu<sup>t</sup>(46) R<sup>1</sup> = H, R<sup>2</sup> = OMe(47) R<sup>1</sup> = H, R<sup>2</sup> = OBu<sup>t</sup>(48) R<sup>1</sup> = H, R<sup>2</sup> = OPh(49) R<sup>1</sup> = R<sup>2</sup> = Me

The photochemical formation of thietan from (–)-3-menthyl methacrylate and xanthenethione (38) or 4,4'-dimethoxythiobenzophenone proceeds with three to four-and-a-half times higher optical purity through the triplet  $n,\pi^*$ -state (17–18% e.e.) of the thione than through the singlet  $\pi,\pi^*$ -state (4–6% e.e.).<sup>29</sup> It has been proposed that the carbon-carbon single bond in the biradical triplet intermediate allows the closure to the four-membered ring to occur preferentially, by the pathway of lowest energy, and thus increases the selectivity of the reaction. The synchronous reaction pathway from the singlet  $\pi,\pi^*$ -state does not involve such a rotation.

*NN*-Di-isopropyl- and *NN*-di-*s*-butyl- $\alpha$ -phenylthioacetamides, (50) and (51), undergo  $\gamma$ -hydrogen-abstraction, instead of  $\delta$ -hydrogen-abstraction, on irradiation, to give the corresponding  $\beta$ -lactams. The same reaction with (52) affords a disulphide (53).<sup>30</sup> The selective abstraction of  $\gamma$ -hydrogen has been interpreted in terms of an electron-transfer mechanism.

(50) R<sup>1</sup> = R<sup>2</sup> = Me(51) R<sup>1</sup> = Me, R<sup>2</sup> = Et(52) R<sup>1</sup> = H, R<sup>2</sup> = Me

Thioacetylacetone in the enol form can be tautomerized to the enethiol form on irradiation with light of wavelength 353 nm, at –178 °C.<sup>31</sup> The interconversion between enol and enethiol forms is reversible.

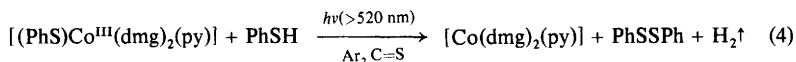
Photo-irradiation (with light of wavelength longer than 520 nm) of a mixture of thiobenzophenone, benzenethiol, and a cobalt(III) complex in acetonitrile results in the generation of hydrogen gas, as shown in reaction (4).<sup>32</sup> The yield is better than 300%, based on the amount of thioketone that is consumed or cobalt(III) that is reduced. Thiobenzophenone (20) plays a catalytic role.

<sup>29</sup> H. Gotthardt and W. Lenz, *Tetrahedron Lett.*, 1979, 2879.

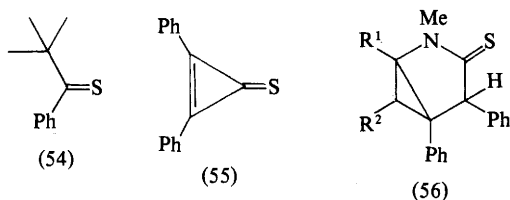
<sup>30</sup> H. Aoyama, S. Suzuki, T. Hasegawa, and Y. Omote, *J. Chem. Soc., Chem. Commun.*, 1979, 899.

<sup>31</sup> L. Carlsen and F. Dues, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1533.

<sup>32</sup> S. Oishi and K. Nozaki, *Chem. Lett.*, 1979, 549.



Reactions of thioketones with nucleophilic reagents have been studied to some extent. Thiobenzophenone (20) and its 4,4'-substituted derivatives react with cyclopentadienyliron dicarbonyl anion and cyclopentadienyl-molybdenum or -tungsten tricarbonyl anion at room temperature to give fulvenes.<sup>33</sup> Phase-transfer catalysis conditions improve the yields. An electron-transfer mechanism has been proposed for this desulphurization and coupling reaction. An electron-transfer mechanism has also been proposed for the reduction of thiopivalophenone (54) by 1-benzyl-1,4-dihydropyridinamide in acetonitrile.<sup>34</sup> 2,3-Diphenylcyclopropene-thione (55) reacts with *N*-methylarylamines to give the bicyclic thioamides (56).<sup>35</sup> The formation of a thioketen as an intermediate has been suggested. A similar reaction scheme has also been proposed for the reaction of (55) with 3,4-dihydroisoquinoline.<sup>36</sup>



Reactions of dialkyl thioketones and cycloalkanethiones with trialkyl phosphites give dialkyl 1-alkylthio- or 1-mercapto-dialkyl- and -cycloalkyl-phosphonates, respectively.<sup>37,38</sup> Initial attack by the phosphorus atom takes place on the thiocarbonyl-carbon atom to form a betaine, which is converted into product by an alkyl migration or by a proton migration. The reaction of 4*H*-pyran-4-thiones with ammonia gives 1*H*-pyridine-4-thiones or bis-(4-pyridyl) disulphides, whereas that of 3-methoxy-2-methyl-4*H*-pyran-4-thione with guanidine affords 1,3-thiazine derivatives. 4*H*-Pyran-4-thiones react with hydrazine to give pyridazines, pyrazoles, and 1-amino-1*H*-pyridine-4-thiones. 4*H*-Pyran-4-thiones having a hydroxy-group in the  $\beta$ -position give the corresponding pyridazine derivatives.<sup>39</sup>

Active-methylene compounds are converted into the corresponding thioketones by successive reaction with thionyl chloride and triphenylphosphine.<sup>40</sup> The thioketones thus prepared are too unstable to be isolated, and they undergo dimerization to give the 1,3-dithietans (57)–(59). However, the intermediacy of thioketones has been confirmed by u.v. spectrometry. The transient formation of thioketone and then its dimerization or a Diels–Alder reaction with an olefin has

<sup>33</sup> H. Alper and H.-N. Paik, *J. Am. Chem. Soc.*, 1978, **100**, 508.

<sup>34</sup> A. Ohno, S. Yasui, K. Nakamura, and S. Oka, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 290.

<sup>35</sup> T. Eicher, J. L. Weber, and J. Kopf, *Liebigs Ann. Chem.*, 1978, 1222.

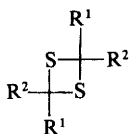
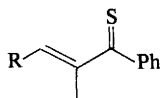
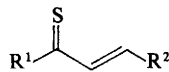
<sup>36</sup> T. Eicher and D. Krause, *Tetrahedron Lett.*, 1979, 1213.

<sup>37</sup> S. Yoneda, T. Kawase, and Z. Yoshida, *J. Org. Chem.*, 1978, **43**, 1980.

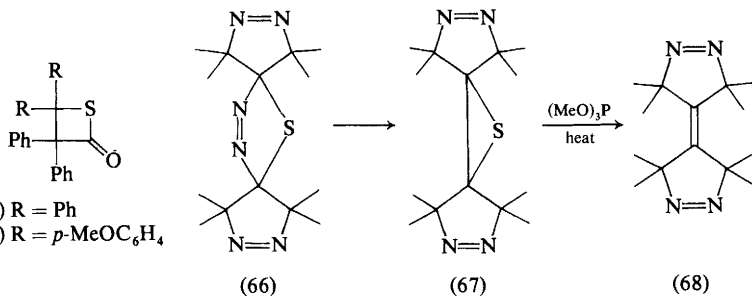
<sup>38</sup> T. Kawase, S. Yoneda, and Z. Yoshida, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3342.

<sup>39</sup> H. Besso, K. Imafuku, and H. Matsumura, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 179.

<sup>40</sup> K. Oka, *J. Org. Chem.*, 1979, **44**, 1736.

(57)  $R^1 = R^2 = \text{CO}_2\text{Et}$ (58)  $R^1 = \text{PhCO}$ ,  $R^2 = \text{Ph}$ (59)  $R^1 = \text{Ph}$ ,  $R^2 = \text{CO}_2\text{Et}$ (60)  $R = p\text{-MeOC}_6\text{H}_4$ (61)  $R = p\text{-ClC}_6\text{H}_4$ (62)  $R^1 = R^2 = \text{Ph}$ (63)  $R^1 = \text{Ph}$ ,  $R^2 = \text{Me}$ 

also been reported for the  $\alpha\beta$ -unsaturated compounds (60)—(63).<sup>41,42</sup> Thiophen derivatives are prepared from diethyl acetylsuccinate through diethyl thioacetylsuccinate, followed by its enethiolization and cyclization.<sup>43</sup> The addition of thioketones to unsaturated compounds is a versatile method for the preparation of heterocycles: treatment of thiobenzophenone (20) and its 4,4'-dimethoxy-derivative with diphenylketen gives the corresponding  $\beta$ -thiolactones (64) and (65), respectively.<sup>44</sup> Highly crowded olefins have been synthesized by the reaction of thioketones with diazo-compounds.<sup>45,46</sup> The adduct (66) is heated, as the solid, to give the episulphide (67); this, on heating with trimethyl phosphite, gives the olefin (68). Similar methods have been employed for the preparation of various adamantylidenealkanes and their derivatives.<sup>47</sup> Thiobenzophenone (20) is allowed to react with azibenzil to give a 1,3-oxathiole and/or a  $\beta$ -thiolactone, whereas the same reaction with thiofluorenone (39) yields a keto-episulphide.<sup>48</sup> 1,3-Oxathioles have also been synthesized from monothiobenzils and diazomethanes.<sup>49</sup>

(64)  $R = \text{Ph}$ (65)  $R = p\text{-MeOC}_6\text{H}_4$ 

(66)

(67)

(68)

At this point it is appropriate to summarize the chemistry of thioquinones. Thermolysis of *p*-quino-bis(benzo-1,3-dithiole) *S*-oxide affords cyclic tri- and tetra-sulphides in about 30% combined yield. The intermediacy of *o*-dithioquinone (69) and species derived from it by desulphurization [e.g. (70) and (71)] has been

<sup>41</sup> J.-P. Guémas, A. Reliquet, F. Reliquet, and H. Quiniou, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1979, **288**, 89.

<sup>42</sup> T. Karakasa and S. Motoki, *J. Org. Chem.*, 1978, **43**, 4147.

<sup>43</sup> F. Duus, *J. Chem. Soc., Perkin Trans. 1*, 1978, 293.

<sup>44</sup> H. Kohn, P. Charumilind, and Y. Gopichand, *J. Org. Chem.*, 1978, **43**, 4961.

<sup>45</sup> R. J. Bushby, M. D. Pollard, and W. S. McDonald, *Tetrahedron Lett.*, 1978, 3851.

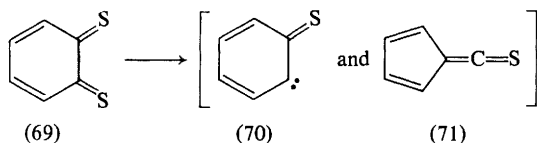
<sup>46</sup> R. J. Bushby and M. D. Pollard, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2401.

<sup>47</sup> F. Cordt, R. M. Frank, and D. Lenoir, *Tetrahedron Lett.*, 1979, 505.

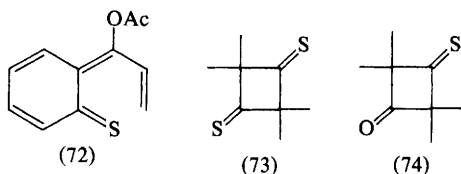
<sup>48</sup> S. Matoka, S. Ishi-i, and M. Tashiro, *J. Org. Chem.*, 1978, **43**, 3730.

<sup>49</sup> C. Bak and K. Praefcke, *Chem. Ber.*, 1979, **112**, 2744.





suggested.<sup>50</sup> *o*-Thiobenzoquinone methide is generated, by photochemical desulphonylation, from 3*H*-1,2-benzodithiole 2,2-dioxide.<sup>51</sup> The methide undergoes [4 + 2]cycloaddition with *N*-phenylmaleimide. The cycloadditions of *o*-thioquinone methide with olefins are also reported in several papers.<sup>52-54</sup> The enol acetate of 4-thiochromanone undergoes ring-opening on photolysis. A novel 1,5-acyl migration from oxygen to sulphur in the intermediate *o*-thioquinone methide (72) has been suggested.<sup>55</sup> Nitrogen analogues of *o*-thioquinone methide are also generated by photolysis of *N*-phenyl-2-benzothiazolinone<sup>56</sup> and by the reaction of phenothiazine derivatives with trialkyl phosphites.<sup>57</sup>



**Spectroscopy.**—Photoelectron spectroscopy and electronic absorption and emission spectra indicate that there exists a strong interaction between the two thiocarbonyl groups in (73), whereas the carbonyl and thiocarbonyl groups in (74) interact only weakly.<sup>58</sup> U.v., i.r., and <sup>13</sup>C n.m.r. spectra have been reported for compounds (28)—(31).<sup>16</sup> The relative stabilities of tautomers of  $\beta$ -thioxoketones have been studied on the basis of u.v. and n.m.r. spectroscopies and of molecular orbital calculations.<sup>59</sup> It is concluded that when the thioxoketone is substituted by at least one vinyl group, the enol form is more stable than the enethiol form, whereas methyl and/or phenyl substituents stabilize the enethiol form more than the enol form. E.s.r. spectroscopy has revealed that thiobenzoylphenylmethylene has the triplet biradical structure (75) and that the carbon-carbon bond in (75) has greater double-bond character than the carbon-sulphur bond.<sup>60</sup>

It has been suggested, from *X*-ray crystallography, that there is little interaction between the two sulphur atoms of (3-methyl-4-phenyl- $\Delta^4$ -thiazolin-2-ylidene)thioacetophenone (76).<sup>61</sup>

<sup>50</sup> M. Sato, M. V. Lakshmiathanam, M. C. Cava, and A. F. Garito, *J. Org. Chem.*, 1978, **43**, 2084.

<sup>51</sup> A. G. Hortmann, A. J. Aron, and A. K. Bhattacharya, *J. Org. Chem.*, 1978, **43**, 3374.

<sup>52</sup> R. Okazaki, F. Ishii, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 309.

<sup>53</sup> R. Okazaki, K.-T. Kang, K. Sunagawa, and N. Inamoto, *Chem. Lett.*, 1978, 55.

<sup>54</sup> R. Okazaki, F. Ishii, K. Sunagawa, and N. Inamoto, *Chem. Lett.*, 1978, 51.

<sup>55</sup> I. W. J. Still and T. S. Leong, *Tetrahedron Lett.*, 1979, 3613.

<sup>56</sup> L. R. Sousa and J. G. Bucher, III, *Tetrahedron Lett.*, 1978, 2267.

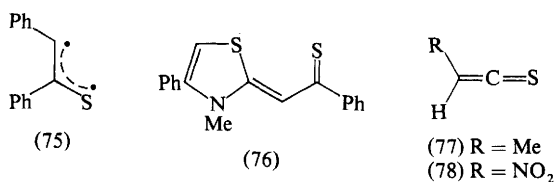
<sup>57</sup> J. I. G. Cadogan and N. J. Tweddle, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1278.

<sup>58</sup> K. N. Tantry, P. K. Basu, V. Ramamurthy, C. N. R. Rao, E. A. Seddon, and J. C. Green, *Tetrahedron Lett.*, 1979, 4787.

<sup>59</sup> L. Carlsen and F. Duus, *J. Am. Chem. Soc.*, 1979, **100**, 281.

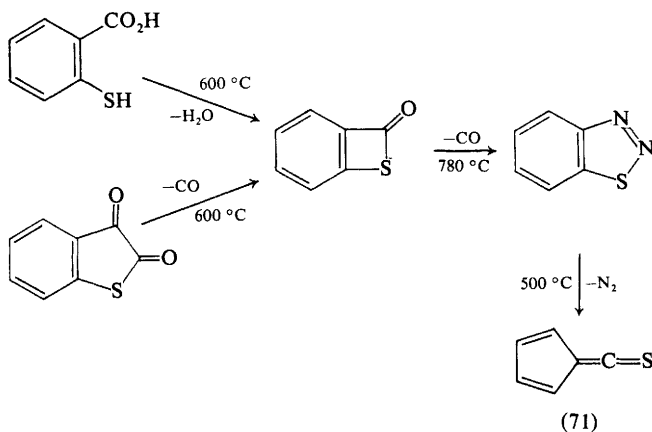
<sup>60</sup> H. Murai, T. Torres, and O. P. Strausz, *J. Am. Chem. Soc.*, 1979, **101**, 3976.

<sup>61</sup> R. J. S. Beer, D. McMonagle, M. S. S. Siddiqui, A. Hordvik, and K. Jynge, *Tetrahedron*, 1979, **35**, 1199.



### 3 Thioketens and Selenoketens

**Synthesis.**—4- or 5-Substituted isothiazoles give thioketens on gas-phase thermolysis at about 600 °C.<sup>62</sup> Chemical trapping of an intermediate and measurement of activation parameters have revealed the reaction mechanism. Dimethylamine was used to trap the thioketens (77) and (78). Thermolysis has also been applied to the synthesis of the thioketen (71), as shown in Scheme 3,<sup>63</sup> the formation of which was established by photoelectron spectroscopy.



Scheme 3

Photochemical elimination of nitrogen from a bicyclic 1,2,3-thiadiazole results in the formation of a thioketen, *e.g.* (79), instead of a thiiren (see Scheme 4),<sup>64</sup> which is in contrast to the reaction of monocyclic thiadiazoles. When 1,2,3-selenadiazoles are subjected to thermolysis at 500—600 °C, they give the selenoketens (80)—(82).<sup>65</sup> The selenoketens have been trapped and characterized at -196 °C.

The reaction of a ketone with a thioalkynolate gives a β-thionolactone. The intermediacy of a thioketen has been suggested.<sup>66</sup>

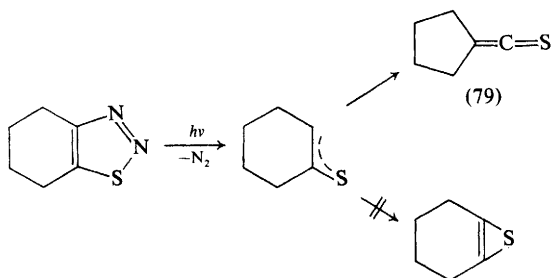
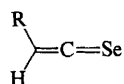
<sup>62</sup> G. E. Castillo and H. E. Bertorello, *J. Chem. Soc., Perkin Trans. 1*, 1978, 325.

<sup>63</sup> R. Schulz and A. Schweig, *Tetrahedron Lett.*, 1979, 59.

<sup>64</sup> U. Timm, H. Bühl, and H. Meier, *J. Heterocycl. Chem.*, 1978, **15**, 697.

<sup>65</sup> A. Holm, C. Berg, C. Bjerre, B. Bak, and H. Svanholt, *J. Chem. Soc., Chem. Commun.*, 1979, 99.

<sup>66</sup> N. Miyaura, T. Yanagi, and A. Suzuki, *Chem. Lett.*, 1979, 535.

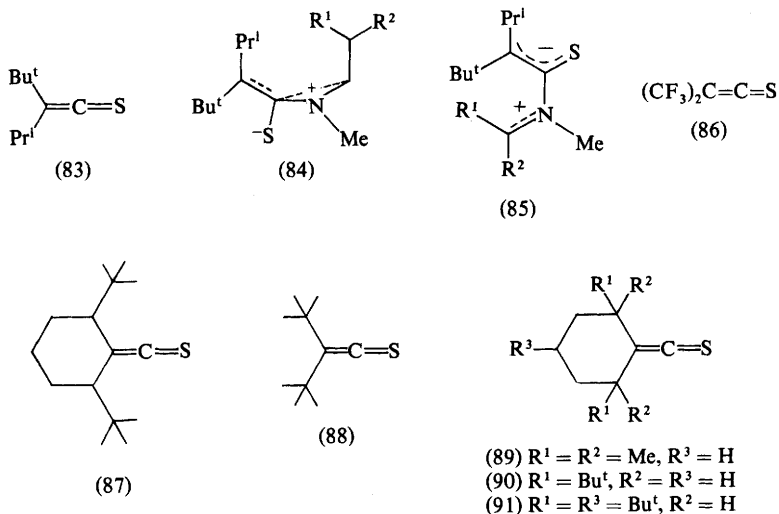

**Scheme 4**


(80) R = H

(81) R = Me

 (82) R = Bu<sup>t</sup>

**Reactions.**—Thioketen (83) reacts with azomethines to give  $\beta$ -thiolactams. It has been suggested that the dipolar species (84) is formed, instead of the classical dipolar species (85), in the rate-determining step of the cycloaddition.<sup>67</sup> Bis-(trifluoromethyl)thioketen (86) adds to azomethines, isothiocyanates, and azides to form 1,3,5-dithiazines and thiazetidines, 1,3-dithietans, and  $\Delta^3$ -1,2,3,4-thiazolines, respectively.<sup>68</sup> The thioketen (86) also undergoes [4 + 2]cycloadditions with dienes.<sup>68</sup>


<sup>67</sup> E. Schaumann and J. Ehlers, *Chem. Ber.*, 1979, **112**, 1000.

<sup>68</sup> M. S. Raasch, *J. Org. Chem.*, 1978, **43**, 2500.

**Spectroscopy.**—The ionization potentials of thioketen (79) have been measured by means of photoelectron spectroscopy and found to be 8.52, 8.67, and 11.14 eV.<sup>63</sup> The structure of thioketen (87) has been studied by *X*-ray crystallography, and it was found that the length of the carbon–carbon double bond is similar to that in the corresponding oxygen analogue.<sup>69</sup>

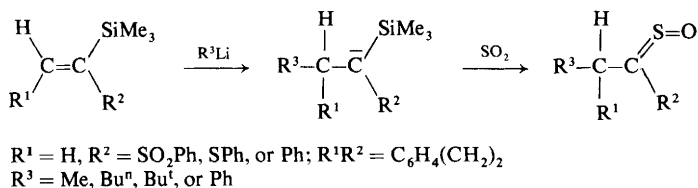
The radical anions of the dialkyl thioketens (83) and (88)—(91) have been investigated by electrochemical methods and e.s.r. spectroscopy. The results indicate that the molecules have non-planar  $C_s$  geometry, and this supports the suggestion that these radical anions are  $\sigma$ -radicals.<sup>70</sup>

## PART II: Sulphines and Sulphenes by D. R. Hogg

### 1 Sulphines

Sulphine,  $H_2C=S=O$ , generated by vacuum pyrolysis of 1,3-dithietan 1-oxide (see Vol. 4, p. 136) or allyl methyl sulphoxide, has been trapped in an argon matrix at 18 K and its i.r. spectrum studied.<sup>1</sup> A complete vibrational assignment is proposed. The region of low ionization energy of the p.e. spectra of  $(p-XC_6H_4)_2C=S=O$  ( $X = H, OMe, Me, I, Br, Cl, \text{ or } NO_2$ ) has been assigned on the basis of perturbation M.O. theory arguments coupled with CNDO/2 calculations and substituent effects.<sup>2</sup> The HOMO has  $\pi$ -symmetry, unlike that for the corresponding thioketones, which is mainly sulphur lone-pair.

Preparation of sulphines by the alkylation of sulphur dioxide, using  $\alpha$ -silyl carbanions (see Vol. 5, p. 133), has been extended by the development of an alternative synthesis of the carbanions by addition of organolithium compounds to vinylsilanes,<sup>3</sup> as shown in Scheme 1.



Scheme 1

<sup>69</sup> E. Schaumann, S. Harto, and G. Adiwidjaja, *Chem. Ber.*, 1979, **112**, 2698.

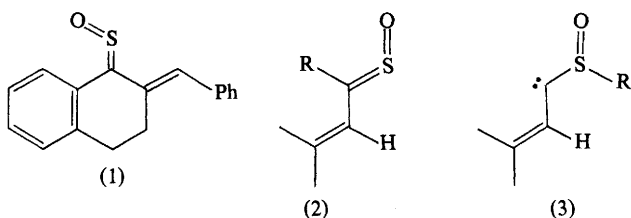
<sup>70</sup> C.-P. Klags, S. Köhler, E. Schaumann, W. Schmäser, and J. Voss, *J. Phys. Chem.*, 1979, **83**, 738.

<sup>1</sup> D. E. Powers, C. A. Arrington, W. C. Harris, E. Block, and V. F. Kalasinsky, *J. Phys. Chem.*, 1979, **83**, 1890.

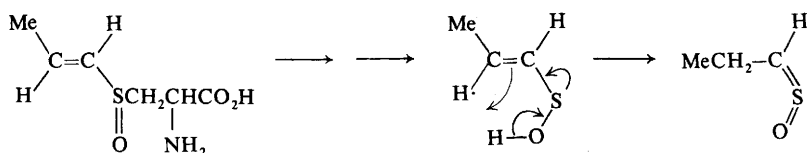
<sup>2</sup> F. Bernardi, F. P. Colonna, C. Distefano, G. Maccagnani, and G. Spunta, *Z. Naturforsch., Teil A*, 1978, **33**, 468.

<sup>3</sup> M. van der Leij and B. Zwanenburg, *Tetrahedron Lett.*, 1978, 3383.

The  $\alpha\beta$ -unsaturated sulphine (1) was obtained as a transient intermediate by oxidation of the dimer of 2-benzylidene-1-thiotetralone with MCPBA, followed by pyrolysis of the resulting product in boiling xylene.<sup>4</sup> The vinylsulphines (2) were obtained by rearrangement of the vinylsulphinylcarbenes (3) that were generated by photolysis of 5-alkylsulphinyl-3,3-dimethyl-3H-pyrazoles or by spontaneous ring-opening of the corresponding sulphinylcyclopropenes.<sup>5</sup> Allyl groups migrated without rearrangement. The sulphines (2) were trapped by addition to dimethyl-diazomethane (see also Chap. 2, Pt I, p. 82).



The principal component of the lachrymatory factor of the onion (*Allium cepa*) has been identified by flash vacuum pyrolysis (FVP)/microwave techniques as (*Z*)-propanethial *S*-oxide,  $\text{CH}_3\text{CH}_2\text{CH}=\text{S}=\text{O}$ .<sup>6</sup> It functions as a 1,3-dipole and as a dipolarophile, and it dimerizes in cold benzene to give<sup>7</sup> principally *trans*-3,4-diethyl-1,2-dithietan 1,1-dioxide rather than 2,4-diethyl-1,3-dithietan 1,3-dioxide, as previously proposed. Formation of this sulphine from its cellular precursor, *trans*-(+)-*S*-(prop-1-enyl)-L-cysteine sulphoxide, is suggested<sup>6</sup> to involve the formation of a Schiff base and the elimination of (*E*)-prop-1-enesulphenic acid, which then rearranges to the sulphine (Scheme 2).



Scheme 2

*t*-Butyl vinyl sulphoxide and *t*-butyl prop-1-enyl sulphoxide were shown to give similarly the corresponding sulphines on FVP at 250 °C, and the n.m.r spectra of the products were compared.<sup>6</sup> In the latter case, the intermediate sulphenic acid was trapped with methyl propiolate.<sup>7</sup>

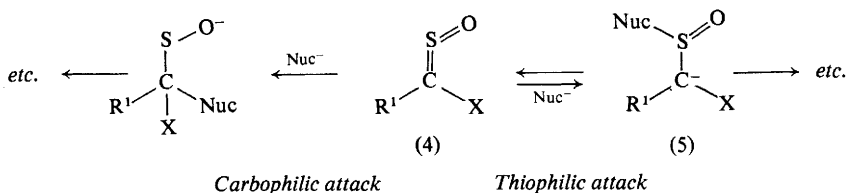
The various reactions of nucleophiles with sulphines continue to be explored; Scheme 3 provides a summary. Functionalized carbanions, e.g.  $\text{XCH}_2^-$  ( $\text{X} = \text{CN}$ ,  $\text{SOMe}$ , or  $\text{SO}_2\text{C}_6\text{H}_4\text{Me-}p$ ) or  $\text{CHRCONEt}_2$ , proceed by the more usual thiophilic

<sup>4</sup> T. Karakasa and S. Motoki, *Tetrahedron Lett.*, 1979, 3961.

<sup>5</sup> M. Franck-Neumann and J. J. Lohmann, *Tetrahedron Lett.*, 1979, 2397.

<sup>6</sup> E. Block, R. E. Penn, and L. K. Reville, *J. Am. Chem. Soc.*, 1979, **101**, 2200; E. Block, L. K. Reville, and A. A. Bazzi, *Tetrahedron Lett.*, 1980, **21**, 1277.

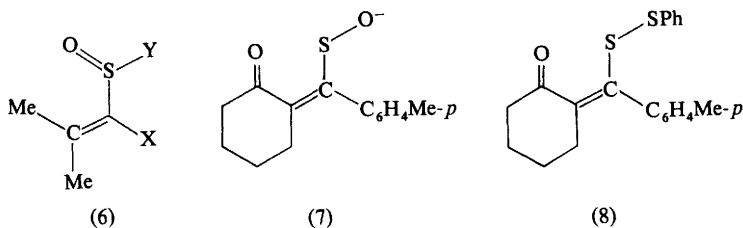
<sup>7</sup> E. Block, A. A. Bazzi, and L. K. Reville, *J. Am. Chem. Soc.*, 1980, **102**, 2490.



Scheme 3

mechanism; after quenching, they give the appropriate sulphoxide.<sup>8</sup> When the  $pK_a$  of the nucleophile is similar to that of the anion (5), the equilibrium may be displaced, and hence formation of product may be favoured, by using an excess of nucleophile, so that the dianion is formed. Desulphonylation occurs under certain conditions. Methyl-lithium reacts thiophilically with (alkyl- or aryl-thio)sulphines (4;  $X = SR^2$  or SPh) to give the anions of dithioacetal monoxides; these are equivalents of acyl anions, and they may be allowed to react with suitable electrophiles.<sup>9</sup> The dithioacetal monoxides give the corresponding aldehydes<sup>9</sup> and the unsymmetrical disulphides<sup>10</sup>  $R^2SSMe$  or  $PhSSMe$ , in excellent yields, on acidolytic cleavage. With a suitable leaving-group on the  $\alpha$ -carbon atom and an absence of  $\alpha$ -hydrogen atoms (loss of which would give a vinylsulphenate), the anion (5) could be stabilized by elimination. Thus (4;  $X = SMe$ ;  $R^1 = CMe_2SO_2C_6H_4Me-p$ ) reacts thiophilically with Grignard reagents, carbanions, and alcohols in the presence of base, to give  $\alpha\beta$ -unsaturated sulphoxides or sulphinate esters [6;  $X = SMe$ ;  $Y = Ph, CH_2Ph, CH_2SO_2Ph, CH(CN)Ph, OMe, \text{ or } OEt$ ].<sup>11</sup>

$\alpha$ -Oxo-carbanions, e.g. 2-lithiocyclohexanone and lithiated  $\alpha$ -tetralone, have a low tendency to thiophilic reaction, and they do not react with di-*p*-tolylsulphine. They react with *p*-tolyl(phenylthio)sulphine (4;  $R^1 = C_6H_4Me-p$ ,  $X = SPh$ ) by a carbophilic pathway and loss of the elements of benzenethiol to give the intermediate vinylsulphenate anion (7), which reacts further with benzenethiol to give the disulphide (8).<sup>12</sup> Anion (7) can be trapped as the methyl sulphoxide with methyl iodide, or as the appropriate thiophen *S*-oxide with phenacyl bromide or ethyl bromoacetate.



Di-*t*-butylsulphine has been suggested to undergo a one-electron transfer from *t*-butylmagnesium chloride to give eventually *t*-butyl alcohol and di-*t*-butyl

<sup>8</sup> J. A. Loontjes, M. van der Leij, and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 39.

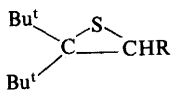
<sup>9</sup> G. E. Veenstra and B. Zwanenburg, *Tetrahedron*, 1978, **34**, 1585.

<sup>10</sup> B. Zwanenburg and P. Kielbasinski, *Tetrahedron*, 1979, **35**, 169.

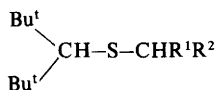
<sup>11</sup> M. van der Leij, H. J. M. Strijveen, and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 45.

<sup>12</sup> M. van der Leij and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 49.

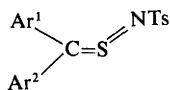
thioketone.<sup>13</sup> With primary and secondary alkylmagnesium halides, an initial thiophilic reaction has been proposed to occur. The anion (5;  $R^1 = X = Bu^t$ ; Nuc = Me, Et,  $PhCH_2$ , or allyl) from the primary Grignard reagent was suggested to undergo removal of a proton followed by simultaneous ring-closure and extrusion of oxygen, to give the thiiran (9). In contrast, the anion (5;  $R^1 = X = Bu^t$ , Nuc =  $Pr^i$  or cyclohexyl) from the secondary Grignard has been proposed to react by a one-electron transfer followed by loss of oxygen, to give the sulphide (10).<sup>13</sup>



(9)



(10)



(11)

Sulphines react with diphenylnitrilimine,  $Ph\overset{+}{C} = N\overset{-}{N}Ph$ , to give the corresponding 1,3,4-thiadiazoline 1-oxides in good yields.<sup>14</sup> As with other 1,3-dipoles, the regiochemistry resembles that of the corresponding diaryl thioketones (see Vol. 5, p. 136), but product equilibration *via* ring-opening leads to loss of the steric integrity of the sulphine during addition.

Co-ordination compounds of platinum that involve sulphines as ligands have been prepared.<sup>15</sup> Geometrical isomers of thione *S*-imides (11), which are the nitrogen analogues of sulphines, have been reported,<sup>16</sup> and thiosulphines,  $R^1R^2C=S=S$ , have been postulated as new reactive intermediates.<sup>17</sup>

## 2 Sulphenes

Further work on the base-catalysed hydrolysis of 2,4-dinitrophenyl arylmethane-sulphonates by the *ElcBi* mechanism (see Vol. 4, p. 139) has revealed a change in the rate-limiting step in concentrated pyridine buffers from the proton-transfer stage to the breakdown of an encounter complex of the sulphene with 2,4-dinitrophenoxide ion. Studies of substituent effects in these reactions have been extended.<sup>18</sup>

Sulphenes have been postulated as intermediates in the substitution reactions of  $\alpha$ -disulphones, which follow an elimination/addition mechanism with all except the most weakly basic strong nucleophiles.<sup>19</sup> Alkyl sulphinyl sulphones follow the direct substitution mechanism.<sup>19</sup> Although perfluorodisulphene has not yet been prepared from the sulphonyl chloride or by fluorination of disulphene, it is obtainable by oxidation (with  $CrO_3$  and  $HNO_3$ ) of tetrafluoro-1,3-dithietan. The perchloro-compound is obtained similarly (by  $KMnO_4$  plus HOAc).<sup>20</sup>

<sup>13</sup> A. Ohno, M. Uohama, K. Nakamura, and S. Oka, *J. Org. Chem.*, 1979, **44**, 2244.

<sup>14</sup> B. F. Bonini, G. Maccagnani, G. Mazzanti, L. Thijs, G. E. Veenstra, and B. Zwanenburg, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1218.

<sup>15</sup> J. W. Gosselink, G. van Koten, K. Vrieze, B. Zwanenburg, and B. H. M. Lammerink, *J. Organomet. Chem.*, 1979, **179**, 411; J. W. Gosselink, A. M. F. Brouwers, G. van Koten, and K. Vrieze, *J. Chem. Soc., Chem. Commun.*, 1979, 1045.

<sup>16</sup> A. Tangerman and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1979, **98**, 127.

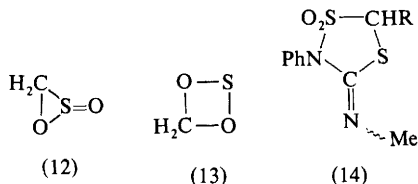
<sup>17</sup> A. Senning, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 941.

<sup>18</sup> S. Thea and A. Williams, *J. Chem. Soc., Chem. Commun.*, 1979, 715; S. Thea, M. G. Harum, and A. Williams, *ibid.*, 1979, 717.

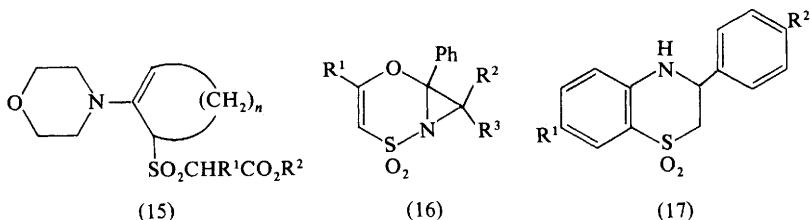
<sup>19</sup> J. L. Kice, O. Farning, and S.-M. Woo, *Phosphorus Sulfur*, 1979, **7**, 47.

<sup>20</sup> R. Seelinger and W. Sundermeyer, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 223.

Sulphenes having at least one aryl substituent are known to react with sulphur dioxide to give the appropriate carbonyl compounds. Sulphur dioxide is not an efficient sulphene trap, and the yields of carbonyl compounds are not high.  $^{18}\text{O}$ -Labelling shows<sup>21</sup> that the oxygen of the carbonyl group does not arise exclusively from the sulphur dioxide, and hence that the mechanism is complex. Exchange of sulphur dioxide with the sulphene could not be detected.<sup>21</sup> CNDO/B calculations of the potential-energy surface for the combination of carbene and sulphur dioxide to give sulphene, and its cyclization to the  $\alpha$ -sultine (12), have been reported.<sup>22</sup> A cyclic sulphoxylic ester (13) has been suggested as an intermediate.



Further cycloadditions have been reported. 4-Methyl-5-(phenylimino)-1,2,3,4-thiazotriazoline acts as a masked 1,3-dipole and reacts with sulphenes, with loss of nitrogen, to give<sup>23</sup> the sultams (14).  $\alpha$ -Alkoxy carbonyl-sulphenes undergo cycloaddition with isobutenylmorpholine, but give uncyclized enamine derivatives (15) with cyclopent- and cyclohex-enylmorpholines.<sup>24</sup> Trimethylsilylsulphene reacts similarly with isobutenylmorpholine and also forms a cyclo-adduct with 1,1-diethoxyethane.<sup>25</sup>  $\alpha$ -Keto-sulphenes react with 3-substituted 2-phenylazirines by a concerted process to give<sup>26</sup> the oxathiazolines (16). 1,4-Cycloaddition reactions of sulphene to propenones (giving 1,2-oxathiin, 2,2-dioxides),<sup>27</sup> to 3-aminomethylene-4-piperidones (giving 4-amino-3,4,5,6,7,8-hexahydro-1,2-oxathiino[5,6-c]pyridine 2,2-dioxides),<sup>28</sup> and to the corresponding quinolones<sup>28</sup> have been reported. Similar additions to 5-aminomethylene-1,5,6,7-tetrahydroindol-4-ones gave the new tricyclic heterocyclic system 3,4,5,6-tetrahydro-7*H*-1,2-oxathiino[6,5-*e*]indole.<sup>29</sup> Ad-



<sup>21</sup> J. F. King and M. Aslam, *Can. J. Chem.*, 1979, **57**, 3278.

<sup>22</sup> L. Carlsen and J. P. Snyder, *J. Org. Chem.*, 1978, **43**, 2216.

<sup>23</sup> G. L'abbè, A. Timmerman, C. Martens, and S. Toppet, *J. Org. Chem.*, 1978, **43**, 4951.

<sup>24</sup> A. Etienne and B. Desmazieres, *J. Chem. Res. (S)*, 1978, 484.

<sup>25</sup> A. G. Shipov, A. V. Kisin, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1979, **49**, 1170.

<sup>26</sup> O. Tsuge and M. Noguchi, *Heterocycles*, 1978, **9**, 423.

<sup>27</sup> F. Evangelisti, P. Schenone, and A. Bargagna, *J. Heterocycl. Chem.*, 1979, **16**, 217; A. Bargagna, P. Schenone, F. Bondavalli, and M. Longbardi, *ibid.*, 1980, **17**, 33.

<sup>28</sup> L. Mosti, P. Schenone, and G. Menozzi, *J. Heterocycl. Chem.*, 1979, **16**, 177.

<sup>29</sup> L. Mosti, P. Schenone, and G. Menozzi, *J. Heterocycl. Chem.*, 1979, **16**, 913.



dition of sulphene to the Schiff base  $p\text{-R}^1\text{C}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{R}^2\text{-}p$  is suggested<sup>30</sup> to form a 1,2-thiazetidine, which then undergoes migration of  $\text{SO}_2$  and proton transfer to give the benzothiazine (17).

Syntheses of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{CO})_3\text{SO}_2\text{CH}_2\text{D}]^{31}$  and  $[(\text{Ph}_3\text{P})\text{Mn}(\text{CO})_4\text{SO}_2\text{CH}_3]^{32}$  that involve the insertion of sulphene into the metal–deuterium and the metal–hydrogen bond have been reported.

### PART III: Thioureas, Thiosemicarbazides, Thioamides, Thiono- and Dithio-carboxylic Acids, and their Selenium Analogues by J. K. Landquist

**Reviews.**—Two reference books<sup>1,2</sup> that deal with topics covered in this chapter have been published, and there have been reviews of the chemistry of aromatic thioureas<sup>3</sup> and of the applications in organic synthesis of thioamides and thioureas,<sup>4</sup> and of thiophosgene.<sup>5</sup>

#### 1 Thioureas and Selenoureas

**Synthesis.**—Diarylthioureas have been made from arylamines and either bis-(alkoxythiocarbonyl) disulphides<sup>6</sup> or  $\text{CS}_2$  and an alumina catalyst.<sup>7</sup> The standard reaction of amines with isothiocyanates was used in the preparation of adamantyl-<sup>8,9</sup> and glycosyl-<sup>10,11</sup> thioureas. Benzoyl isothiocyanate, when treated with sterically hindered amines, e.g.  $\text{Pr}_2\text{NH}$  or dicyclohexylamine, gives

<sup>30</sup> M. Rai, S. Kumar, K. Krishan, and A. Singh, *Chem. Ind. (London)*, 1979, 26.

<sup>31</sup> I.-P. Lorenz, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 285.

<sup>32</sup> I.-P. Lorenz, A. Baur, and K. Hintzer, *J. Organomet. Chem.*, 1979, **182**, 375.

<sup>1</sup> F. Duus, in 'Comprehensive Organic Chemistry,' Vol. 3, ed. D. N. Jones, Pergamon Press, Oxford, 1979.

<sup>2</sup> S. Scheithauer and R. Mayer, 'Topics in Sulfur Chemistry, Vol. 4, Thio- and dithio-carboxylic acids and their derivatives,' Georg Thieme Verlag, Stuttgart, 1979.

<sup>3</sup> L. Grehn, *Acta Univ. Ups., Abstr. Uppsala Diss. Fac. Sci.*, 1979, 509.

<sup>4</sup> H. Singh, *J. Indian Chem. Soc.*, 1979, **56**, 545.

<sup>5</sup> S. Sharma, *Synthesis*, 1978, 803.

<sup>6</sup> P. P. Gnatyuk, V. A. Malii, G. A. Pestova, and S. V. Tsarenko, USSR P. 694 502/1979 (*Chem. Abstr.*, 1980, **92**, 76 149).

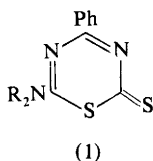
<sup>7</sup> M. K. Gadzhiev and Sh. Sh. Barabadze, *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.*, 1979, **5**, 128 (*Chem. Abstr.*, 1980, **92**, 76 073).

<sup>8</sup> A. Kreuzberger and A. Tantawy, *Arch. Pharm. (Weinheim, Ger.)*, 1978, **311**, 770.

<sup>9</sup> J. W. Tilley, P. Levitan, and M. J. Kramer, *J. Med. Chem.*, 1979, **22**, 1009.

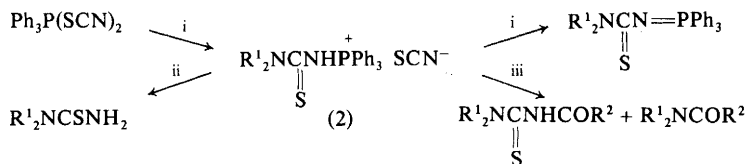
<sup>10</sup> H. Takahashi, N. Nimura, and H. Ogura, *Chem. Pharm. Bull.*, 1979, **27**, 1130.

<sup>11</sup> H. Takahashi, K. Takeda, N. Nimura, and H. Ogura, *Chem. Pharm. Bull.*, 1979, **27**, 1137.



1,3,5-thiadiazine-2-thiones (1) instead of acylthioureas, possibly because the acylthiourea is attacked by benzoyl isothiocyanate with loss of benzoic acid.<sup>12</sup>

A general method for preparing 1,1-disubstituted thioureas in 50—80% yield employs the combined reagent triphenylphosphine–thiocyanogen (Scheme 1).<sup>13,14</sup>



Reagents: i,  $R_2NH$ ; ii,  $H_2O$ ; iii,  $R^2CO_2H$

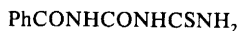
**Scheme 1**

The intermediate phosphonium thiocyanate (2) gives phosphinimines with an excess of amine, and acylthioureas and amides when treated with carboxylic acids. A Beckmann rearrangement of amidoximes  $RC(NO_2)NH_2$  with  $PhSO_2Cl$  in pyridine, followed by treatment with  $H_2S$ , gives thioureas  $RNHCSNH_2$  in 55—76% yields.<sup>15</sup>

The radical phenylation of thiourea or of  $NN'$ -diphenylthiourea to give the  $S$ -phenyl derivatives proceeds better with nitrosoacetanilides than with phenylazotriphenylmethane as the source of radicals.<sup>16,17</sup>



(3)



(4)

Addition of  $H_2S$  to alkyldicyanamides affords 1-alkyl-1-cyanothiureas, and then (with  $NEt_3$  catalysis) 3-alkyl-dithiobiurets (3).<sup>18</sup> 3-Alkyl-2-thiobiurets are made similarly from 1-alkyl-1-cyanoureas. 1-Benzoyl-2-thiobiuret is obtained from benzoyl isothiocyanate and urea,<sup>19,20</sup> and it rearranges to 1-benzoyl-4-thiobiuret (4)

<sup>12</sup> H. Hartmann, L. Beyer, and E. Hoyer, *J. Prakt. Chem.*, 1978, **320**, 647.

<sup>13</sup> Y. Tamura, M. Adachi, T. Kawasaki, and Y. Kita, *Tetrahedron Lett.*, 1978, 1753.

<sup>14</sup> Y. Tamura, T. Kawasaki, M. Adachi, and Y. Kita, *Chem. Pharm. Bull.*, 1979, **27**, 1636.

<sup>15</sup> M. V. Arnaudov, *Dokl. Bolg. Akad. Nauk*, 1978, **31**, 309 (*Chem. Abstr.*, 1978, **89**, 197 131).

<sup>16</sup> B. V. Kopylova, I. I. Kandror, and R. Kh. Freidlina, *Dokl. Akad. Nauk SSSR*, 1978, **243**, 1197 (*Chem. Abstr.*, 1979, **90**, 103 583).

<sup>17</sup> B. V. Kopylova, I. I. Kandror, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1138 (*Chem. Abstr.*, 1979, **91**, 91 320).

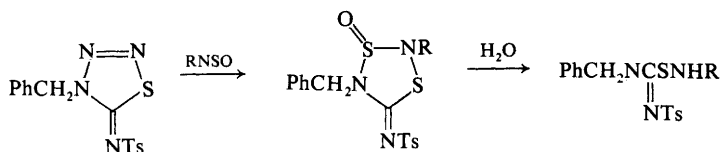
<sup>18</sup> P. H. Benders and P. A. E. van Erkelens, *Synthesis*, 1978, 775.

<sup>19</sup> M. N. Basyouni and A. M. A. El-Khamry, *Chem. Ind. (London)*, 1978, 670.

<sup>20</sup> M. N. Basyouni and A. M. A. El-Khamry, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3728.

when heated in water.<sup>21</sup> Acid hydrolysis affords a convenient preparation of monothioiuret. Thiocarbamoylcarbodi-imides are made by treatment of 1,1,5-trisubstituted dithiobiurets with cyanuric chloride and  $\text{NEt}_3$ .<sup>22</sup> They readily dimerize to 1,3,5-thiadiazines unless they are stabilized by bulky substituents, and with water, alcohols, and amines they provide monothioiurets, *O*-alkyl-thioisobiurets, and thiocarbamoylguanidines, respectively. The thiocarbamidic sulphur atom of thioureas has been protected by *t*-butylation before reaction with, e.g., isothiocyanates. The protecting group is readily removed with warm dilute  $\text{HCl}$ .<sup>23</sup>

Among the more unusual thiourea derivatives are crown ethers containing thiourea links<sup>24</sup> and *N*-(phenylthiocarbamoyl)ethyleneimine oligomers, which are selective adsorbents for  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  ions.<sup>25</sup> *S*-Amino-isothioureas are obtained by hydrolysis of 5-arylsulphonylimino-1,3,2,4-dithiadiazolidine 3-oxides, which are made from 4-alkyl-5-arylsulphonylimino-1,2,3,4-thiaziazolines and *N*-sulphinylamines as shown in Scheme 2.<sup>26</sup> Phosphorylated isothioureas  $\text{R}^1\text{NHC}(\text{SR}^2)=\text{NP}(\text{X})\text{R}^3\text{R}^4$  have been prepared from  $\text{R}^1\text{NHC}(\text{SR}^2)=\text{NH}$  and  $\text{ClP}(\text{X})\text{R}^3\text{R}^4$  ( $\text{X} = \text{O}$  or  $\text{S}$ ),<sup>27</sup> and *N*-(trimethylsilyl)thioureas were obtained from  $\text{Me}_3\text{SiCl}$  and mono-, di-, or tri-substituted thioureas with  $\text{NEt}_3$  or  $\text{BuLi}$ .<sup>28</sup> The reaction of halogenodiorganylboranes with *N*-(trimethylsilyl)thioureas affords thioureido- or isothioureido-boranes, with displacement of the trimethylsilyl group.<sup>29</sup>



Scheme 2

Persubstituted guanidines, e.g. pentamethylguanidine, react with activated isothiocyanates to give stable dipolar compounds (5), which may be protonated to give thiocarbamoylguanidinium salts (6). The analogous dipole (7), from  $\text{CS}_2$  and pentamethylguanidine, undergoes a [2 + 2] cycloreversion to  $\text{MeNCs}$  and tetramethylthiourea on heating.<sup>30</sup> Similar compounds made from tetramethylisothiourea and isothiocyanates give methyl *NN*-dimethyldithiocarbamate by [2 + 2] cycloreversion.<sup>31</sup>

<sup>21</sup> D. L. Klayman and J. P. Scovill, *J. Org. Chem.*, 1979, **44**, 630.

<sup>22</sup> J. Goerdeler and R. Losch, *Chem. Ber.*, 1980, **113**, 79.

<sup>23</sup> M. H. Damle, *Indian J. Chem., Sect. B*, 1978, **16**, 396 (*Chem. Abstr.*, 1978, **89**, 146 401).

<sup>24</sup> A. V. Bogatsky, N. G. Lukyanenko, and T. I. Kirichenko, *Tetrahedron Lett.*, 1980, **21**, 313.

<sup>25</sup> H. Tsukube, T. Araki, H. Inoue, and A. Nakamura, *J. Polym. Sci., Polym. Lett. Ed.*, 1979, **17**, 437 (*Chem. Abstr.*, 1979, **91**, 75 052).

<sup>26</sup> G. L'abbé, A. Van Asch, J. P. Declercq, G. Germain, and M. Van Meerssche, *Bull. Soc. Chim. Belg.*, 1978, **87**, 285.

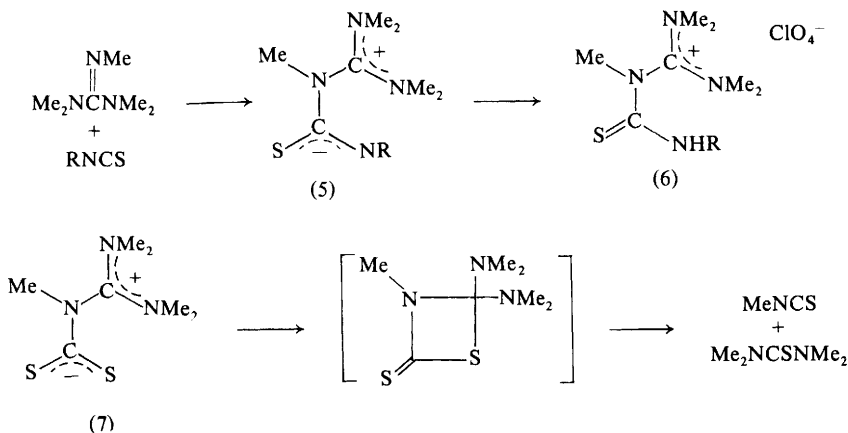
<sup>27</sup> L. Ya. Bogel'fer, V. N. Zontova, V. V. Negrebetskii, A. F. Grapov, S. F. Dymova, and N. N. Mel'nikov, *Zh. Obshch. Khim.*, 1978, **48**, 1729 (*Chem. Abstr.*, 1978, **89**, 163 666).

<sup>28</sup> W. Walter, H. Kubel, and H-W. Luke, *Liebigs Ann. Chem.*, 1979, 263.

<sup>29</sup> W. Maringgele, *Z. Naturforsch., Teil B*, 1980, **35**, 164.

<sup>30</sup> E. Schaumann, E. Kausch, and E. Rossmann, *Liebigs Ann. Chem.*, 1978, 1543.

<sup>31</sup> E. Schaumann and E. Kausch, *Liebigs Ann. Chem.*, 1978, 1560.



An improved method for the preparation of selenoureas from *S*-methylisothioureas and  $\text{H}_2\text{Se}$  has been described.<sup>32</sup>

**Physical Properties.**—Physicochemical investigation of thioureas has continued on many lines already reported in earlier volumes. The i.r. spectra of *NN*-dimethylthiourea and *NN*-dimethylselenourea and their *N*-deuteriated and *S*-methyl derivatives have been measured and fundamental frequencies assigned.<sup>33</sup> I.r. spectra of ethylenethiourea and ethyleneselenourea were also reported.<sup>34</sup> The conformation of the  $\text{NHCSNH}$  grouping in *NN'*-diarylthioureas has been investigated by i.r. spectroscopy.<sup>35</sup> A neutron-diffraction study of thiourea at 293 K showed the molecule to be planar, with one hydrogen atom  $\sim 0.07 \text{ \AA}$  out of plane, this being associated with strong hydrogen-bonding that links molecules in chains.<sup>36</sup> The bond-electron distribution has been investigated, using a refined model.<sup>37</sup> The binding energies of sulphur 2*p*, nitrogen 1*s*, and carbon 1*s* electrons in some alkylated thioureas and related thiocarbonyl compounds have been determined by *X*-ray p.e. spectroscopy.<sup>38</sup> The positive charge in isothiouronium salts is concentrated on carbon and nitrogen.

The electronic and  $^1\text{H}$  n.m.r. spectra of monothiobiuret and dithiobiuret have been determined, and the results of quantum-mechanical calculations were used in a discussion of the electronic structures, p.e. and electronic spectra, and conformational stability.<sup>39</sup> The structures of some (trimethylsilyl)thioureas were determined

<sup>32</sup> V. I. Cohen, *Synthesis*, 1980, 60.

<sup>33</sup> K. Dwarakanath and D. N. Sathyanarayana, *Indian J. Pure Appl. Phys.*, 1979, **17**, 171 (*Chem. Abstr.*, 1979, **91**, 107 351).

<sup>34</sup> K. Dwarakanath and D. N. Sathyanarayana, *Indian J. Chem., Sect. A*, 1979, **18**, 302 (*Chem. Abstr.*, 1980, **92**, 31 344).

<sup>35</sup> B. Galabov, G. Vassilev, N. Neykova, and A. Galabov, *J. Mol. Struct.*, 1978, **44**, 15.

<sup>36</sup> D. Mullen, G. Heger, and W. Treutmann, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1979, **148**, 95 (*Chem. Abstr.*, 1979, **90**, 178 467).

<sup>37</sup> D. Mullen and E. Hellner, *Acta Crystallogr., Sect. B*, 1978, **34**, 2789.

<sup>38</sup> R. Szargan, R. Scheibe, L. Beyer, Ya. V. Salyn, and V. I. Nefedov, *Tetrahedron*, 1979, **35**, 59.

<sup>39</sup> V. C. Kyothi Bhasu, D. N. Sathyanarayana, and C. C. Patel, *Proc. Indian Acad. Sci., Sect. A*, 1979, **88**, 91 (*Chem. Abstr.*, 1979, **91**, 65 395).

by i.r. and  $^1\text{H}$  n.m.r. spectrometry and the barriers to rotation about C—N bonds were measured.<sup>28</sup> Further work on dynamic  $^1\text{H}$  and  $^{13}\text{C}$  effects in tetramethylthiourea, arising from restricted rotation about C—N bonds, has been reported.<sup>40</sup>

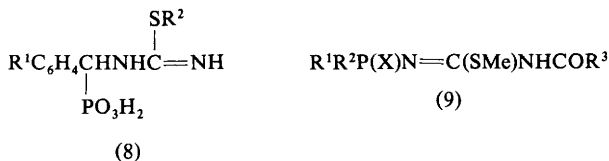
X-Ray diffraction analysis of the 1:1 complex of thiourea with bis-[2-(*o*-methoxyphenoxy)ethoxyethyl] ether showed that the hydrogen atoms of the amino-groups are hydrogen-bonded to all the oxygen atoms, showing bifurcated hydrogen bonds.<sup>41</sup>

**Reactions.—Oxidation.** Thioureas and alkyl derivatives are oxidized very rapidly by  $\text{ICl}_3$  in the presence of  $\text{NaHCO}_3$  [reaction (1)]. Titration of the liberated iodine



(by  $\text{ICl}_3$ , to regenerate  $\text{ICl}_3$ ) gives an analytical method for thioureas or their precursors (*i.e.* amines or isothiocyanates).<sup>42</sup> Thiourea, ethylenethiourea, and *N*-phenylthiourea are oxidized to the corresponding formamidinesulphenic acids by microsomal amine oxidase from pigs' liver. Formamidinesulphenic acids were identified as intermediates.<sup>43</sup> Oxidation of mixtures of *NN'*-diarylthiourea and thiosemicarbazide with  $\text{H}_2\text{O}_2$  affords 3-amino-4-aryl-5-aryl-amino-1,2,4-triazoles.<sup>44</sup>

**Alkylation.** The heat of reaction of tetramethylthiourea with methyl iodide in MeCN has been measured, and the kinetics of the reaction were studied in various solvents.<sup>45</sup> The reaction is second-order when it occurs in polar solvents, but in non-polar solvents the kinetics are complicated by the formation of aggregates of ions. The kinetics of the reaction of thiourea with chloroacetic acid and bromoacetic acid have also been measured.<sup>46</sup> The reaction of tetra(hydroxymethyl)phosphonium chloride with thiourea or phenylthiourea occurs through a methylol group, with subsequent loss of formaldehyde, to give, *e.g.*,  $\text{PhNHC}(\text{S})\text{NHCH}_2\text{P}(\text{O})(\text{CH}_2\text{OH})_2$ .<sup>47</sup> Condensation of thiourea with aromatic aldehydes and triphenyl phosphite, followed by hydrolysis and *S*-alkylation, affords 1-(*S*-alkylisothioureido)benzylphosphonic acids (8), which are intermediates for the preparation of 1-guanidinobenzylphosphonic acids.<sup>48</sup>



<sup>40</sup> F. A. L. Anet and M. Ghiaci, *J. Am. Chem. Soc.*, 1979, **101**, 6857.

<sup>41</sup> I.-H. Suh and W. Saenger, *Angew. Chem.*, 1978, **90**, 565.

<sup>42</sup> K. V. Verma, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2155.

<sup>43</sup> D. M. Ziegler, *Biochem. Soc. Trans.*, 1978, **6**, 94.

<sup>44</sup> K. N. Rajasekharan, *Indian J. Chem., Sect. B*, 1979, **17**, 69 (*Chem. Abstr.*, 1980, **92**, 22 475).

<sup>45</sup> Y. Kondo, S. Hirano, and N. Tokura, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1738.

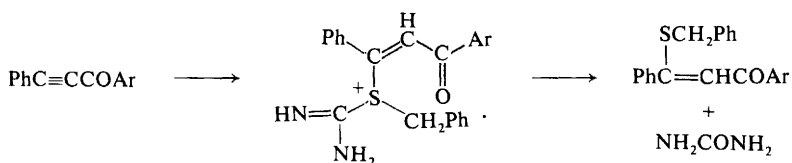
<sup>46</sup> J. Kaválek, S. El-Bahaie, and V. Štěrba, *Collect. Czech. Chem. Commun.*, 1980, **45**, 263.

<sup>47</sup> S. Bhatnagar, J. C. Gupta, K. Lal, and H. L. Bhatnagar, *Indian J. Chem., Sect. A*, 1978, **16**, 356 (*Chem. Abstr.*, 1978, **89**, 146 994).

<sup>48</sup> J. Oleksyszyn and R. Tyka, *Pol. J. Chem.*, 1978, **52**, 1949 (*Chem. Abstr.*, 1979, **90**, 104 066).

*Acyl Derivatives.* Acylation of  $N^1$ -phosphorylated or -thiophosphorylated  $S$ -methylisothiourea occurs at N-2, giving (9).<sup>49</sup> Arylamines are converted into aryl isothiocyanates by condensation with benzoyl isothiocyanate and thermal decomposition of the benzoylthiourea in boiling *o*-dichlorobenzene. The yield improves on dilution.<sup>50</sup>

*Additions to Multiple Bonds.* In most of the reactions reported recently, the addition of a thiourea to a multiple bond has been followed by cyclization at another reactive centre. An exception is the reaction of  $S$ -benzylisothiourea with arylalkynes, which gives  $\alpha$ -aryl- $\beta$ -(benzylmercapto)styrenes (Scheme 3), and not the expected 4,6-diaryl-2-(benzylthio)pyrimidines.<sup>51</sup> Cycloaddition of thiourea to divinyl sulphide in the presence of acids gives salts of 6-amino-2,4-dimethyl-1,3,5-dithiazine.<sup>52</sup> Thiourea condenses with chalcone to give 3,6-dihydro-2-oxo-4,6-diphenyl-1,3-thiazine (10),<sup>53</sup> but with other  $\alpha\beta$ -unsaturated ketones, e.g. 2-methylene-3-oxoquinuclidine<sup>54</sup> and cyclohex-2-enones,<sup>55</sup> only the nitrogen atoms are involved, giving the hexahydropyrimidines (11) and (12) respectively. Addition of thiourea to the benzoquinones (13) occurs through the sulphur atom, subsequent cyclization giving benzoxathioles (14).<sup>56</sup> Condensation of dimethyl acetylenedicarboxylate with 1-methyl- and 1-ethyl-thiourea gives the isomeric 1,3-thiazines (15) and (16) in the ratio 43:38 ( $R = \text{Me}$ ) and 54:22 ( $R = \text{Et}$ ).<sup>57</sup> Mono- and di-substituted selenoureas condense with dimethyl acetylenedicarboxylate, giving the 1,3-selenazines (17;  $R^1 = \text{H}$ ,  $R^2 = \text{benzyl or Ar}$ ) and (17;  $R^1 = R^2 = \text{Me or Ar}$ ).<sup>58</sup>



Scheme 3

Carbonyl sulphide reacts with  $S$ -benzylisothiourea, giving 2-imino-4-oxo-6-thioxohexahydro-1,3,5-triazine (18;  $R = \text{H}$ ), and with  $S$ -benzyl- $N$ -methylisothiourea to give the dimethyl derivative (18;  $R = \text{Me}$ ).<sup>59</sup> Chlorosulphonyl iso-

<sup>49</sup> A. F. Grapov, A. F. Vasil'ev, V. N. Zontova, V. V. Galushina, and N. N. Mel'nikov, *Zh. Obshch. Khim.*, 1979, **49**, 2474 (*Chem. Abstr.*, 1980, **92**, 110 135).

<sup>50</sup> S. Rajappa, T. G. Rajagopalan, R. Sreenivasan, and S. Kanal, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2001.

<sup>51</sup> F. G. Baddar, F. H. Hajjar, and N. R. El-Rayyes, *J. Heterocycl. Chem.*, 1978, **15**, 105.

<sup>52</sup> B. A. Trofimov, G. M. Gavrilova, G. A. Kalabin, V. V. Bairov, and S. V. Amosova, *Khim. Geterotsikl. Soedin.*, 1979, 1466.

<sup>53</sup> D. N. Dhar, A. K. Singh, and H. C. Misra, *Indian J. Chem., Sect. B*, 1979, **17**, 25 (*Chem. Abstr.*, 1980, **92**, 6483).

<sup>54</sup> V. A. Bondarenko, E. E. Mikhlina, T. Ya. Filipenko, K. F. Turchin, Yu. N. Sheinker, and L. N. Yakhontov, *Khim. Geterotsikl. Soedin.*, 1979, 1393.

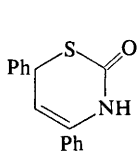
<sup>55</sup> W. Wendelin and W. Kern, *Monatsh. Chem.*, 1979, **110**, 1345.

<sup>56</sup> K. Srihari and V. Sundaramurthy, *Indian J. Chem., Sect. B*, 1979, **18**, 80 (*Chem. Abstr.*, 1980, **92**, 41 484).

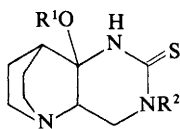
<sup>57</sup> L. I. Giannola, S. Palazzo, P. Agozzino, L. Lamartina, and L. Ceraulo, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1428.

<sup>58</sup> A. Shafiee, F. Assadi, and V. I. Cohen, *J. Heterocycl. Chem.*, 1978, **15**, 39.

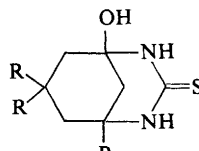
<sup>59</sup> J. M. Parnandiwar, *Indian J. Chem., Sect. B*, 1978, **16**, 927 (*Chem. Abstr.*, 1979, **91**, 20 456).



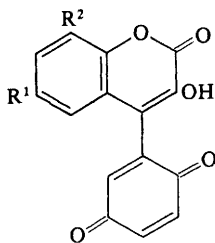
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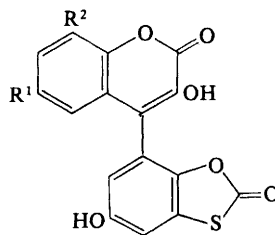
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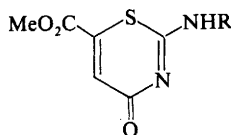
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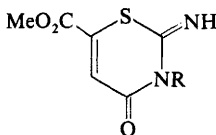
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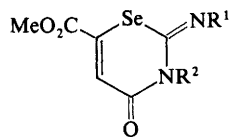
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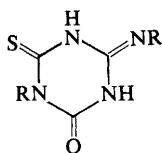
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(16)



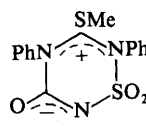
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(18)



(19)



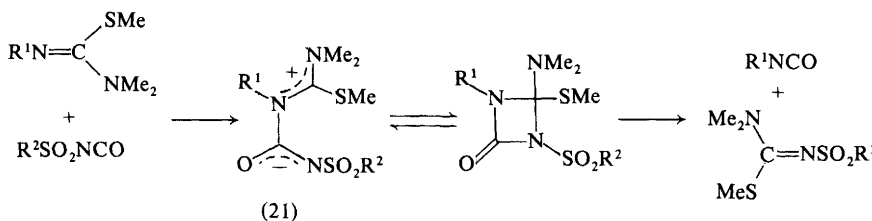
(20)

cyanate condenses with *S*-methyl-*N*-phenylthiourea and with *S*-methyl-*NN'*-diphenylthiourea to give the thiazines (19) and (20) respectively.<sup>60</sup> Per-substituted *S*-methylisothiureas add to sulphonyl isocyanates to give dipolar compounds (21), which are stable if  $R^1 = \text{Me}$  but which undergo [2 + 2] cycloreversion to isocyanates and *N*-sulphonyl-*S*-methyl-isothiureas if  $R^1$  is more bulky. Benzoyl and thiobenzoyl isocyanates behave similarly.<sup>61</sup>

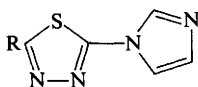
The reactive thiourea *NN'*-thiocarbonyldi-imidazole reacts with aliphatic

<sup>60</sup> S. Karady, J. S. Amato, D. Dortmund, A. A. Patchett, R. A. Reamer, R. J. Tull, and L. M. Weinstock, *Heterocycles*, 1979, **12**, 1199.

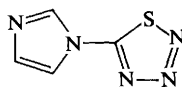
<sup>61</sup> E. Schaumann, E. Kausch, J-P. Imbert, and G. Adiwidjaja, *Chem. Ber.*, 1978, **111**, 1475.



diazo-compounds to give 5-substituted-2-(1-imidazolyl)-1,3,4-thiadiazoles (22), and with  $\text{HN}_3$  or with  $\text{Me}_3\text{SiN}_3 + \text{CSCl}_2$ , giving 5-(1-imidazolyl)-1,2,3,4-thiadiazole (23).<sup>62</sup>



(22)



(23)

**Formation of Thiazoles.** The widely exploited synthetic applications of thioureas to give thiazole derivatives include the preparation of 2-imino-4-thiazolidinones from chloroacetamide<sup>63</sup> or  $\alpha$ -(alkoxycarbonyl)alkyl phosphates  $(\text{R}^1\text{O})_2\text{P}(\text{O})\text{OCHR}^2\text{CO}_2\text{R}^3$ ;<sup>64</sup> and also of 2-aminothiazoles from 2-chloro- and 1,3-dichloro-2,3-epoxybutanes,<sup>65</sup> 1,1,4-trichlorobut-1-en-3-one,<sup>66</sup>  $\beta$ -chloronitroso-compounds  $\text{R}^1\text{CH}(\text{NO})\text{CCIR}^2\text{R}^3$ ,<sup>67</sup> and phenyl(trichloromethyl)carbinol.<sup>68</sup> *N*-Acyl-*N'*-mono-substituted thioureas react with phenacyl bromide to give thiazolines (24), and not 5-acylthiazoles, as previously reported. The latter compounds, e.g. (25), are obtained by the reaction of phenacyl bromide with the *O*-methyl-*N'*-phenyl derivatives of the acylthiourea (from methyl benzimidate and phenyl isothiocyanate) or with the addition products of *N*-arylbenzamidines with phenyl isothiocyanate.<sup>69</sup> Bromonitromethane reacts with *N*-benzimidoyl-*N'*-phenylthiourea, giving a poor yield of the thiazole (26), the main product being 5-anilino-3-phenyl-1,2,4-thiadiazole.<sup>70</sup>

Application of the Hugershoff cyclization (of arylthioureas with bromine) to pyrrolylthioureas<sup>71</sup> and to *N*-acyl-*N'*-(3-thienyl)thioureas<sup>72</sup> gave pyrrolothiazoles

<sup>62</sup> A. Martvoň, L. Floch, and S. Sekretár, *Tetrahedron*, 1978, **34**, 453.

<sup>63</sup> L. I. Mizrakh, L. Yu. Polonskaya, B. I. Bryantsev, and T. M. Ivanova, *Zh. Org. Khim.*, 1978, **14**, 1553 (*Chem. Abstr.*, 1978, **89**, 163 482).

<sup>64</sup> L. I. Mizrakh, L. Yu. Polonskaya, B. I. Bryantsev, and T. N. Doronchenkova, *Zh. Obshch. Khim.*, 1978, **48**, 568 (*Chem. Abstr.*, 1978, **89**, 43 255).

<sup>65</sup> A. A. Durgaryan, G. E. Esayan, and R. H. Arakelyan, *Arm. Khim. Zh.*, 1979, **32**, 29 (*Chem. Abstr.*, 1979, **91**, 123 664).

<sup>66</sup> A. N. Mirskova, G. G. Levkovskaya, I. D. Kalikhman, and M. G. Voronkov, *Zh. Org. Khim.*, 1979, **15**, 2301 (*Chem. Abstr.*, 1980, **92**, 128 792).

<sup>67</sup> J. Beger, C. Thielemann, and P. D. Thong, *J. Prakt. Chem.*, 1979, **321**, 249.

<sup>68</sup> W. Reeve and W. R. Coley, *Can. J. Chem.*, 1979, **57**, 444.

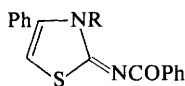
<sup>69</sup> S. Rajappa, M. D. Nair, B. G. Advani, R. Sreenivasan, and J. A. Desai, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1762.

<sup>70</sup> S. Rajappa and B. G. Advani, *Indian J. Chem., Sect. B*, 1978, **16**, 749 (*Chem. Abstr.*, 1979, **90**, 152 059).

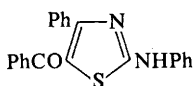
<sup>71</sup> L. Grehn, *Chem. Scr.*, 1979, **13**, 78 (*Chem. Abstr.*, 1980, **92**, 6454).

<sup>72</sup> L. Grehn, *J. Heterocycl. Chem.*, 1978, **15**, 81.

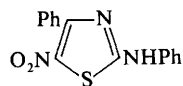




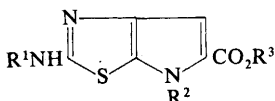
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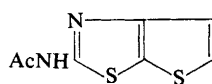
(25)



(26)



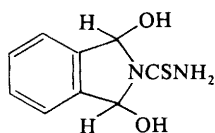
(27)



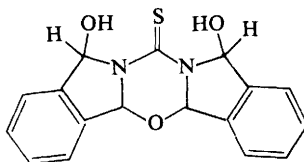
(28)

(27) and thienothiazoles (28), but the analogous 2-thienylthioureas were brominated at positions 3 or 5 in the thiophen ring, and they did not cyclize.

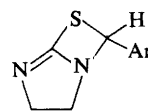
**Miscellaneous Reactions.** Tetramethylthiourea forms 1:1 adducts with arsenic trihalides and arylarsenic dihalides.<sup>73</sup> The nitrosation of dimethylamine by sodium nitrite at pH 4 is catalysed by thiourea, less efficiently by *NN'*-dimethylthiourea, and more efficiently by tetramethylthiourea.<sup>74</sup> Base-catalysed condensation of thiourea with phthalaldehyde gives *N*-thiocarbamoyl-1,3-dihydroxyisoindoline (29)



(29)

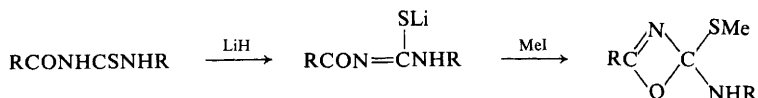


(30)



(31)

and the 1:2-adduct (30).<sup>75</sup> Ethylenethiourea reacts with aromatic aldehydes and  $\text{BF}_3$  etherate to give 2-aryl-1,3-thiazetidines (31).<sup>76</sup> 2*H*-1,3-Oxazetes are obtained by lithiation of acylthioureas and treatment with methyl iodide (Scheme 4).<sup>77</sup>



Scheme 4

The cyclodesulphurization of *N*-(*o*-aminoaryl)- or *N*-(6-aminopyrimidin-5-yl)-*N'*-glycosylthioureas to give (glycosylamino)benzimidazoles and (glycosyl-

<sup>73</sup> D. J. Williams and K. J. Wynne, *Inorg. Chem.*, 1978, **17**, 1108.

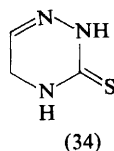
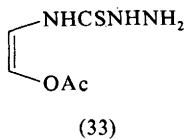
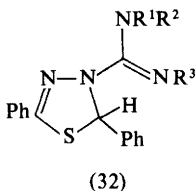
<sup>74</sup> M. Masui, C. Ueda, T. Yasuoka, and H. Ohmori, *Chem. Pharm. Bull.*, 1979, **27**, 1274.

<sup>75</sup> R. D. Reynolds, D. F. Guanci, C. B. Neynaber, and R. J. Conboy, *J. Org. Chem.*, 1978, **43**, 3838.

<sup>76</sup> M. Yokoyama and H. Monma, *Tetrahedron Lett.*, 1980, **21**, 293.

<sup>77</sup> P. Kristian, P. Kutschky, and M. Dzurilla, *Collect. Czech. Chem. Commun.*, 1979, **44**, 1324.

amino)purines is achieved smoothly with methyl iodide and  $\text{NEt}_3$  in THF.<sup>78</sup> The reaction of 2,4,6-triphenylpyrylium perchlorate and thiourea in boiling THF gives 2,4,6-triphenylpyridine; with *S*-alkylisothioureas, 2-alkylthio-4,6-diarylpyrimidines are formed with elimination of acetophenone, and *NN'*-diphenylthiourea gives 1,2,4,6-tetraphenylpyridinium perchlorate.<sup>79</sup> Some reactions of thio-bis(formamides) to give isothioureido-pyrimidines and -1,3,5-triazines have been described.<sup>80,81</sup> Thioureas react with 1-chloro-1,4-diphenyl-2,3-diazabutadiene to give, unexpectedly, thiadiazoline-2-carboxamides (32), the sulphur atom becoming separated from the rest of the thiourea by two atoms.<sup>82</sup>



## 2 Thiosemicarbazides, Dithiocarbazates, and Thiocarbohydrazides

**Synthesis.**—Many syntheses have been directed to the preparation of thiosemicarbazones for testing as possible therapeutic agents.<sup>83–85</sup> Following the discovery of antimalarial activity in 2-acetylpyridine 4-phenylthiosemicarbazone, many related substances have been made;<sup>83</sup> aryl isothiocyanates were treated with 2-acetylpyridine hydrazone to give the substituted thiosemicarbazone, or with hydrazine to give 4-(aryl)thiosemicarbazides. Alternatively, methyl dithiocarbazate,  $\text{MeSC}(=\text{S})\text{NHNH}_2$ , was condensed with 2-acetylpyridine to give methyl 3-[1-(2-pyridyl)ethylidene]hydrazine carbodithioate, which reacted with arylamines with elimination of methanethiol. Alkyl dithiocarbazates from *n*-propyl to *n*-nonyl have been prepared for the first time, by alkylation of hydrazinium dithiocarbazate,  $\text{NH}_2\text{NHC}(=\text{S})\text{SH}\cdot\text{NH}_2\text{NH}_2$ , and corresponding alkyl dithiocarbamoyl derivatives of picolino-, nicotino-, and isonicotino-hydrazides were made.<sup>86</sup> 2-Acetoxyvinyl isothiocyanate and hydrazine react at room temperature to give 4-( $\beta$ -acetoxyvinyl)thiosemicarbazide (33), but dihydro-1,2,4-triazine-3-thione (34) is obtained at higher temperatures.<sup>87</sup>

**Physical Properties.**—The Raman and i.r. spectra of thiocarbohydrazide and of  $[\text{H}_6]$ thiocarbohydrazide, and of their complexes with  $\text{CdCl}_2$ , have been measured,

<sup>78</sup> H. Takahashi, N. Nimura, N. Obata, H. Sakai, and H. Ogura, *Chem. Pharm. Bull.*, 1979, **27**, 1153.

<sup>79</sup> E. A. Zvezdina, M. P. Zhdanova, and G. N. Dorofeenko, *Khim. Geterotsikl. Soedin.*, 1979, 324.

<sup>80</sup> R. Evers, *Z. Chem.*, 1979, **19**, 250.

<sup>81</sup> R. Evers and E. Fischer, *Z. Chem.*, 1979, **19**, 290.

<sup>82</sup> W. T. Flowers, S. F. Moss, J. F. Robinson, D. R. Taylor, A. E. Tipping, and M. J. Haley, *J. Chem. Soc., Chem. Commun.*, 1979, 149.

<sup>83</sup> D. L. Klayman, J. F. Bartosevich, T. S. Griffin, C. J. Mason, and J. P. Scovill, *J. Med. Chem.*, 1979, **22**, 855.

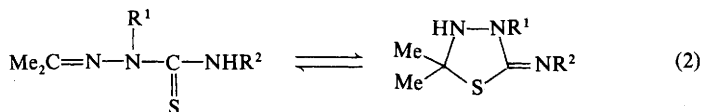
<sup>84</sup> A. Wahab, *Arzneim.-Forsch.*, 1979, **29**, 466.

<sup>85</sup> A. Andreani, D. Bonazzi, V. Cavrini, R. Gatti, G. Giovanninetti, M. Rambaldi, L. Franchi, A. Nanetti, and M. A. Guarda, *Farmaco., Ed. Sci.*, 1978, **33**, 754.

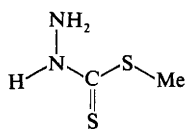
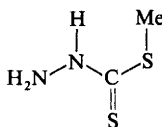
<sup>86</sup> S. Kubota, M. Uda, Y. Mori, F. Kametani, and H. Terada, *J. Med. Chem.*, 1978, **21**, 591.

<sup>87</sup> A. W. Faull and R. Hull, *J. Chem. Res. (S)*, 1979, 240.

calculations of force constants were carried out, and vibrational assignments were made.<sup>88</sup> The ring-chain tautomerism of acetone thiosemicarbazone and of its *N*<sup>2</sup>- and *N*<sup>4</sup>-methyl derivatives [reaction (2)] was investigated by n.m.r. spectroscopy. The cyclic form is favoured in deuterio-TFA and the acyclic form in (<sup>2</sup>H<sub>6</sub>)DMSO, but the 2,4-dimethyl derivative is cyclic in both solvents.<sup>89</sup>



Several conformational studies have been reported.<sup>90-92</sup> The *trans,cis* conformer (35) of *S*-methyl dithiocarbazate was isolated by low-temperature crystallization and was subjected to *X*-ray crystal analysis.<sup>92</sup> The known solid conformer (36) is the *cis,trans* one.

(35) *trans,cis*(36) *cis,trans*

**Reactions.**—Successive alkylations of the two sulphur atoms in potassium *β*-toluene-*p*-sulphonyldithiocarbazate,  $\text{TsNHNHCS}_2^- \text{K}^+$ , with different alkyl groups, to give unsymmetrical dithiocarbonate toluene-*p*-sulphonylhydrazones, are stereoselective, the last alkyl group introduced going *cis* to the toluene-*p*-sulphonylimino-group.<sup>93</sup> The dianions derived from these compounds, e.g. with BuLi, are also alkylated stereoselectively. Thermolysis of the sodium salts of *S*-alkyl *S'*-methyl dithiocarbonate toluene-*p*-sulphonylhydrazones, followed by methylation, affords a convenient synthesis of 1,1-bis(methylthio)buta-1,3-dienes *via* a [2,3]sigmatropic rearrangement of a dithiocarbene,<sup>94</sup> as shown in Scheme 5.

Condensation of thiosemicarbazide with 2-methylene-3-oxoquinuclidine affords the thiocarbamoylpyrazoline (37).<sup>54</sup> 2,4,6-Triphenylpyrylium perchlorate reacts with thiosemicarbazide, giving 1-thiocarbamido-2,4,6-triphenylpyridinium perchlorate.<sup>79</sup> Desyl bromide,  $\text{PhCOCHBrPh}$ , reacts with 4-alkyl-thiosemicarbazides  $\text{NH}_2\text{NHCSNHR}$  to give 2-alkylamino-1,3,4-thiadiazines (38), 3-aminothiazolone-2-alkylimides (39), or 3-alkylthiazolone-2-hydrazones (40), depending on the substituents present.<sup>95</sup> Similar isomeric products may be prepared selectively

<sup>88</sup> K. Dwarakanath, D. N. Sathyanarayana, and K. Volka, *Bull. Soc. Chim. Belg.*, 1978, **87**, 667, 677.

<sup>89</sup> M. Uda and S. Kubota, *J. Heterocycl. Chem.*, 1979, **16**, 1273.

<sup>90</sup> C. Gors, F. Baert, J. P. Henichart, and R. Houssin, *J. Mol. Struct.*, 1979, **55**, 223.

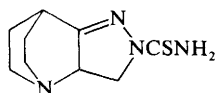
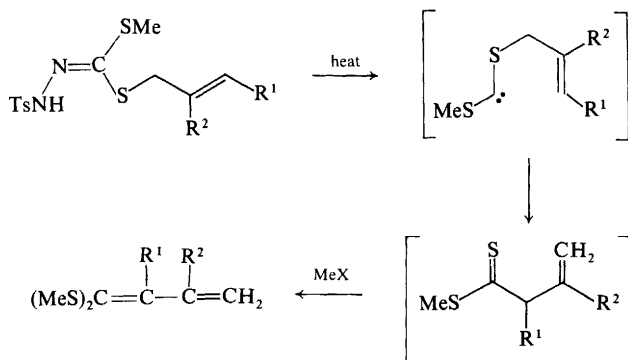
<sup>91</sup> V. V. Dunina, E. I. Kazakova, V. M. Potapov, and E. G. Rukhadze, *Zh. Org. Khim.*, 1978, **14**, 2075 (*Chem. Abstr.*, 1979, **90**, 71 645).

<sup>92</sup> R. Mattes and H. Weber, *J. Chem. Soc., Dalton Trans.*, 1980, 423.

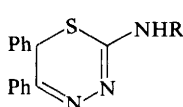
<sup>93</sup> T. Nakai and K. Mikami, *Chem. Lett.*, 1979, 465.

<sup>94</sup> T. Nakai and K. Mikami, *Chem. Lett.*, 1978, 1243.

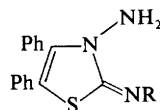
<sup>95</sup> E. Bulka, W. D. Pfeiffer, C. Trölsch, E. Dilk, H. Gärtner, and D. Daniel, *Collect. Czech. Chem. Commun.*, 1978, **43**, 1227.



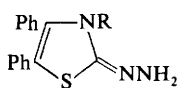
(37)



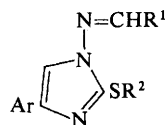
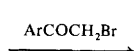
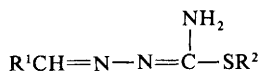
(38)



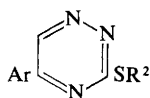
(39)



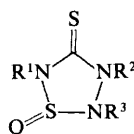
(40)



(41)



(42)



(43)

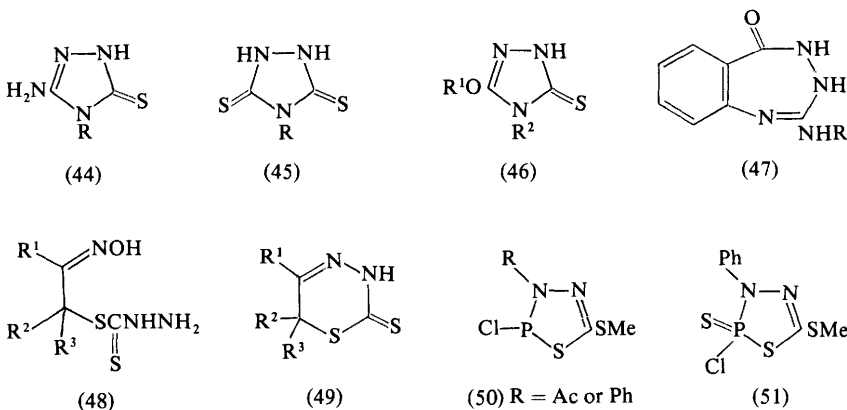
from thiosemicarbazide and ethyl 4-chloroacetoacetate by varying the acidity, solvent polarity, and temperature.<sup>96</sup> Isothiosemicarbazones of aromatic aldehydes and ketones react with phenacyl bromides to give 2-mercaptoimidazole derivatives (41), but isothiosemicarbazones of aliphatic aldehydes give poor yields of (41), and 3,5-disubstituted 1,2,4-triazines (42) are produced.<sup>97</sup> 1,2,4-Trisubstituted thiosemicarbazides react with thionyl chloride and pyridine, giving 1,2,3,5-thiazolidine-4-thione 1-oxides (43).<sup>98</sup>

<sup>96</sup> E. Campaigne and T. P. Selby, *J. Heterocycl. Chem.*, 1978, **15**, 401.

<sup>97</sup> C. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1846.

<sup>98</sup> S. D. Ziman, *J. Heterocycl. Chem.*, 1979, **16**, 895.

Cyclization of 1-alkylthiocarbamoyl-3-thiosemicarbazides,  $\text{RNHCSNHNH-CSNH}_2$ , in alkaline media gives both 4-alkyl-5-amino-1,2,4-triazoline-3-thiones (44), by loss of  $\text{H}_2\text{S}$ , and 4-alkyl-1,2,4-triazolidine-3,5-dithiones (45), by loss of  $\text{NH}_3$ . 1-Alkoxythiocarbonyl-3-thiosemicarbazides lose  $\text{H}_2\text{S}$  under weakly alkaline conditions, giving 5-alkoxy-1,2,4-triazoline-3-thiones (46), but in strong alkali they eliminate alcohol, giving (45). 1-Alkoxythiocarbonyl-3-thiosemicarbazides cyclize to 5-thiono-1,2,4-triazolidin-3-ones in both weak and strong alkali.<sup>99</sup> Other cyclizations of (acyl)thiosemicarbazides<sup>100</sup> and of *S*-alkyl *N*-acyldithiocarbazates<sup>101</sup> have been reported. Cyclodesulphurization of 1-(*o*-aminobenzoyl)thiosemicarbazides with DCCI gives benzotriazepin-5-ones (47).<sup>102</sup> Rate constants for the ring-closure of 1-methylisatin 3-thiosemicarbazones to indolotriazines have been determined.<sup>103</sup>



Salts of dithiocarbazic acid,  $\text{NH}_2\text{NHCS}_2^- \text{M}^+$ , react with  $\beta$ -chloro-nitroso-compounds  $\text{R}^1\text{CH}(\text{NO})\text{CR}^2\text{R}^3\text{Cl}$ , giving  $\beta$ -oximinoalkyl esters (48), which readily cyclize to 6H-1,3,4-thiadiazine-2-thiones (49).<sup>104</sup> Methyl *N*-phenyldithiocarbazate reacts with  $\text{PCl}_3$  and  $\text{PSCl}_3$  to give the phosphorus heterocycles (50) and (51), in which the chlorine atoms are labile and may be replaced by nucleophiles. Methyl *N*-acetyldithiocarbazate reacts similarly with  $\text{PCl}_3$ , but with  $\text{POCl}_3$  or  $\text{PSCl}_3$  it is dehydrated to give 2-methyl-5-methylthio-1,2,4-thiadiazolium chloride.<sup>105</sup>

### 3 Thioamides and Selenoamides

**Synthesis.**—The addition of  $\text{H}_2\text{S}$  to nitriles to give primary thioamides is conveniently performed in the presence of a phase-transfer catalyst in dilute aqueous  $\text{Na}_2\text{S}$  and a liquid organic phase.<sup>106</sup> Other examples of this reaction employ

<sup>99</sup> H. W. Altland and P. A. Graham, *J. Heterocycl. Chem.*, 1978, **15**, 377.

<sup>100</sup> M. Balogh, I. Hermecz, Z. Mészáros, and L. Pusztay, *J. Heterocycl. Chem.*, 1980, **17**, 175.

<sup>101</sup> G. Mazzone and F. Bonina, *Farmaco, Ed. Sci.*, 1978, **33**, 438.

<sup>102</sup> A. Mohsen, M. E. Omar, and F. A. Ashour, *J. Heterocycl. Chem.*, 1979, **16**, 1435.

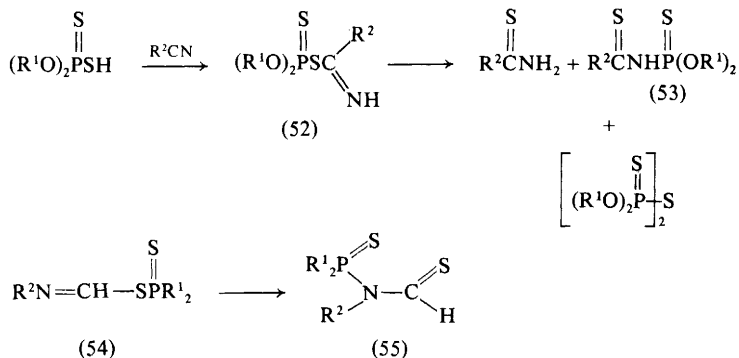
<sup>103</sup> A. B. Tomchin and U. Lepp, *Zh. Org. Khim.*, 1978, **14**, 1544 (*Chem. Abstr.*, 1979, **90**, 6362).

<sup>104</sup> J. Beger, C. Thielemann, and P. D. Thong, *J. Prakt. Chem.*, 1979, **321**, 959.

<sup>105</sup> N. I. Shvetsov-Shilovskii, D. P. Nesterenko, and A. A. Stepanova, *Zh. Obshch. Khim.*, 1979, **49**, 1896 (*Chem. Abstr.*, 1980, **92**, 41 846).

<sup>106</sup> L. Cassar, S. Panossian, and C. Giordano, *Synthesis*, 1978, 917.

$\text{NH}_3$ ,  $\text{NEt}_3$ , or pyridine as the basic catalyst.<sup>107-110</sup> Nitriles are also converted into thioamide derivatives in the presence of the Lewis acids  $\text{SnCl}_4$  and  $\text{AsF}_5$ , using  $\text{AcSH}^{111}$  and  $\text{Et}_4\text{N}^+ \text{SH}^-$ <sup>112</sup> as sources of  $\text{SH}^-$ . Nitriles react with *OO*-dialkyl *S*-hydrogen phosphorodithioates, giving unstable adducts (52), which react further with the dialkyl phosphorodithioate to give thioamides, phosphorylated thioamides (53), and sulphides.<sup>113</sup> Benzoxonitrile and *OO*-dialkyl *O*-hydrogen phosphorothionates give similar products in low yield.<sup>114</sup> Isocyanides react with  $\text{R}_2\text{P}(\text{S})\text{SH}$  ( $\text{R}^1 = \text{alkoxy or Ph}$ ), giving *S*-thiophosphorylated thioformamides (54), which rearrange to the *N*-isomers (55).<sup>115</sup>



Treatment of *N*-methyl-benzoylacetanilide with  $\text{P}_4\text{S}_{10}$  gave *N*-methyl-*N*-phenyl- $\beta$ -mercaptothiocinnamamide (56), which was isolated as its palladium complex.<sup>116</sup> Further examples of the thionation of carboxamides by  $\text{P}_4\text{S}_{10}$ <sup>117,118</sup> and by *p*-methoxyphenylthionophosphine sulphide dimer<sup>119,120</sup> have been reported. The latter reagent caused the thioamides (57) to cyclize to 6-ethylthieno[2,3-*d*]-[1,3]thiazine-4-thiones (58) when the reaction time was prolonged.<sup>119</sup> Carbox-

<sup>107</sup> L. N. Kulaeva, A. D. Grabenko, and P. S. Pel'kis, *Khim. Geterotsikl. Soedin.*, 1978, 909.

<sup>108</sup> S. N. Banerjee and C. Ressler, *Int. J. Pept. Protein Res.*, 1979, **14**, 234.

<sup>109</sup> T. Jaworski and J. Terpinski, *Pol. J. Chem.*, 1978, **52**, 2067 (*Chem. Abstr.*, 1979, **90**, 54 437).

<sup>110</sup> V. A. Pechenyuk, L. B. Dashkevich, S. A. Chistyakova, and E. N. Kuvayeva, *Zh. Org. Khim.*, 1978, **14**, 745 (*Chem. Abstr.*, 1978, **89**, 42 389).

<sup>111</sup> T. A. Tember-Kovaleva, R. A. Slavinskaya, and T. N. Sumarokova, *Zh. Obshch. Khim.*, 1978, **48**, 1556 (*Chem. Abstr.*, 1978, **89**, 172 822).

<sup>112</sup> L. Kolditz and I. Beierlein, *Z. Chem.*, 1978, **18**, 452.

<sup>113</sup> A. N. Pudovik, R. A. Cherkasov, M. G. Zimin, and N. G. Zabiroy, *Zh. Obshch. Khim.*, 1978, **48**, 926 (*Chem. Abstr.*, 1978, **89**, 107 958); *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 861 (*Chem. Abstr.*, 1979, **91**, 56 575).

<sup>114</sup> M. G. Zimin, N. G. Zabiroy, and A. N. Pudovik, *Zh. Obshch. Khim.*, 1979, **49**, 1164 (*Chem. Abstr.*, 1979, **91**, 74 316).

<sup>115</sup> M. G. Zimin, N. G. Zabiroy, V. I. Nikitina, and A. N. Pudovik, *Zh. Obshch. Khim.*, 1979, **49**, 2651 (*Chem. Abstr.*, 1980, **92**, 129 027).

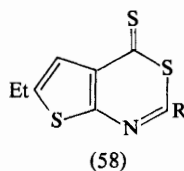
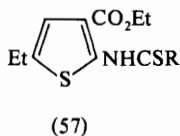
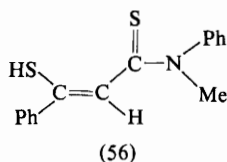
<sup>116</sup> S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.*, 1978, **26**, 3028.

<sup>117</sup> J. S. Davidson, *Synthesis*, 1979, 359.

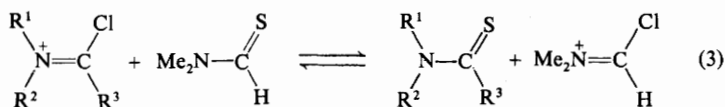
<sup>118</sup> J. K. Schneider, P. Hofstetter, E. Pretsch, D. Ammann, and W. Simon, *Helv. Chim. Acta*, 1980, **63**, 217.

<sup>119</sup> K. Clausen and S. O. Lawesson, *Nouv. J. Chim.*, 1980, **4**, 43.

<sup>120</sup> H. Fritz, P. Hug, S. O. Lawesson, E. Logemann, B. S. Pedersen, H. Sauter, S. Scheibye, and T. Winkler, *Bull. Soc. Chim. Belg.*, 1978, **87**, 525.



amides are also converted into thioamides by the organophosphorus compounds  $(\text{Me}_2\text{N})_x\text{P}(\text{S})\text{Cl}_{3-x}$ , but not by  $(\text{Me}_2\text{N})_3\text{PS}$ .<sup>121</sup> Diethylthiocarbamoyl chloride converts primary carboxamides and thioamides into nitriles, and tertiary amides into thioamides. The reaction mechanism that has been proposed involves the formation of an iminium salt (59), which rearranges to (60). Elimination of COS and  $\text{Et}_2\text{NH}\cdot\text{HCl}$  from either (59) or (60) (if  $\text{R}^1 = \text{R}^2 = \text{H}$ ) will give a nitrile, and elimination of  $\text{Et}_2\text{NCOCl}$  from (60) gives a thioamide.<sup>122</sup> Chloroiminium salts (Vilsmeier reagents) react reversibly with thioamides with interchange of sulphur and chlorine [reaction (3)]; if the equilibrium is favourable, the new thioamide may be isolated after hydrolysis of the reaction mixture.<sup>123</sup>



The reaction of Grignard reagents with triphenylphosphine thiocyanate,  $\text{Ph}_3\text{P}(\text{SCN})_2$ , is a convenient method for preparing *N*-unsubstituted thioamides in fair yield.<sup>124</sup> The application of the Willgerodt–Kindler reaction to aromatic aldehydes and primary aliphatic amines to yield  $\text{ArCSNHR}$  has been reported.<sup>125, 126</sup> Thioamides are not obtained with aromatic amines. Nitrobenzyl halides react with sulphur and secondary amines in a dipolar aprotic solvent at 20 °C to give nitrothiobenzamides, but reduction of the nitro-group also occurs at higher temperatures.<sup>127</sup>

A thiocarbamoyl group may be introduced directly into anisole and *o*- or *m*-dimethoxybenzenes by treatment with  $\text{KSCN}$  in PPA at 60 °C or with concentrated  $\text{H}_2\text{SO}_4$  at room temperature to give the thioanisamides (61) in ca. 50% yield.<sup>128</sup> Substituted thiocarbamoyl groups are introduced by the reaction of

<sup>121</sup> B. S. Pedersen and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1977, **86**, 693.

<sup>122</sup> M. Ogata and H. Matsumoto, *Heterocycles*, 1978, **11**, 139.

<sup>123</sup> M. Helbert, J. P. Renou, and M. L. Martin, *Tetrahedron*, 1979, **35**, 1087.

<sup>124</sup> Y. Tamura, T. Kawasaki, M. Adachi, and Y. Kita, *Synthesis*, 1979, 887.

<sup>125</sup> R. C. Moreau, P. Loiseau, J. Bernard, F. Sébastien, and R. Leroy, *Eur. J. Med. Chem.*, 1979, **14**, 317.

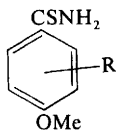
<sup>126</sup> R. C. Moreau and P. Loiseau, *Ann. Pharm. Fr.*, 1978, **36**, 269.

<sup>127</sup> R. Mayer, H. Viola, J. Reichert, and W. Krause, *J. Prakt. Chem.*, 1978, **320**, 313.

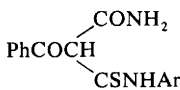
<sup>128</sup> S. Sastry and N. A. Kudav, *Indian J. Chem., Sect. B*, 1979, **18**, 455 (*Chem. Abstr.*, 1980, **92**, 128 540).

isothiocyanates with benzoylacetamide [giving (62)],<sup>129</sup> with Schiff bases (reacting as enamines) [giving (63)],<sup>130,131</sup> and with 2-(lithiomethyl)phenyl isocyanide [giving (64)], which may be cyclized by LDA to an indole-3-thiocarboxamide].<sup>132</sup>

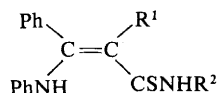
Addition of H<sub>2</sub>S to 1-(dialkylamino)pent-3-en-1-yne gives high yields of the thioamides (65).<sup>133</sup> Polymeric thioamides are obtained from bis-(dithioesters) and diamines by uncatalysed polycondensation in benzene-DMF at room temperature.<sup>134</sup> Monothio-diaroylamines, RC(O)NHC(S)R, are made by hydrolysis of the dithiazolium salts (66), e.g. by NEt<sub>3</sub> in aqueous ethanol.<sup>135</sup>



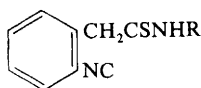
(61)



(62)



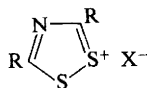
(63)



(64)



(65)



(66)

The preparation of thioacetylhydrazide, MeCSNHNH<sub>2</sub>, has now been accomplished, both from the known nickel complex and from carboxymethyl dithioacetate [MeC(=S)SCH<sub>2</sub>CO<sub>2</sub>H] and hydrazine.<sup>136</sup> It is stable at -30 °C, but at room temperature it changes into 1,4-dihydro-3,6-dimethyl-1,2,4,5-tetrazine and at its melting point (95—96 °C) into 4-amino-3,5-dimethyl-1,2,4-triazole.

Aromatic and heteroaromatic selenocarboxamides are obtained in high yield from nitriles and Al<sub>2</sub>Se<sub>3</sub> in a pyridine-NEt<sub>3</sub>-H<sub>2</sub>O system.<sup>137</sup>

**Physical Properties.**—In studies of the secondary thioamide function, the i.r. and, where possible, the Raman spectra of a series of *N*-methyl-thioamides XCSNHMe (X = CSNHMe, CSNH<sub>2</sub>, CONH<sub>2</sub>, or CO<sub>2</sub>K) and of *N*- and *C*-deuteriated products were determined, vibrational analyses were proposed, and the results were compared with data for other *N*-methyl-thioamides.<sup>138,139</sup> The <sup>13</sup>C n.m.r. spectra of a series of tertiary thioamides of formic, acetic, trifluoroacetic, propionic, and

<sup>129</sup> R. G. Dubenko, E. F. Gorbenko, and P. S. Pel'kis, *Zh. Org. Khim.*, 1979, **15**, 1483 (*Chem. Abstr.*, 1979, **91**, 174 975).

<sup>130</sup> W. Zankowska-Jasinska and H. Borowiec, *Pol. J. Chem.*, 1978, **52**, 1155 (*Chem. Abstr.*, 1978, **89**, 163 536).

<sup>131</sup> W. Zankowska-Jasinska and H. Borowiec, *Pol. J. Chem.*, 1978, **52**, 1683 (*Chem. Abstr.*, 1979, **90**, 54 632).

<sup>132</sup> Y. Ito, K. Kobayashi, and T. Saegusa, *Tetrahedron Lett.*, 1979, 1039.

<sup>133</sup> S. E. Tolchinskii, I. A. Maretina, and A. A. Petrov, *Zh. Org. Chem.*, 1979, **15**, 650 (*Chem. Abstr.*, 1979, **91**, 19 860).

<sup>134</sup> G. Levesque and J. C. Gressier, *J. Polym. Sci., Polym. Lett. Ed.*, 1979, **17**, 281 (*Chem. Abstr.*, 1979, **91**, 21 171).

<sup>135</sup> J. Liebscher and H. Hartmann, Ger. (East) P. 135 901 (*Chem. Abstr.*, 1979, **91**, 193 019).

<sup>136</sup> K. A. Jensen and E. Larsen, *Acta Chem. Scand., Ser. A*, 1979, **33**, 137.

<sup>137</sup> V. I. Cohen, *Synthesis*, 1978, 668.

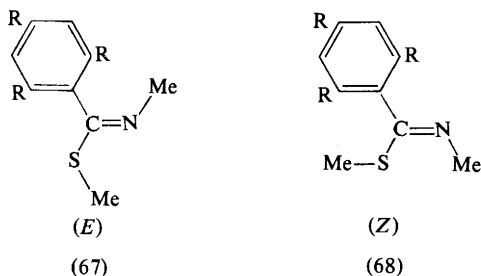
<sup>138</sup> H. O. Desseyn, A. J. Aarts, E. Esmans, and M. A. Herman, *Spectrochim. Acta, Part A*, 1979, **35**, 1203.

<sup>139</sup> H. O. Desseyn, A. J. Aarts, and M. A. Herman, *Spectrochim. Acta, Part A*, 1980, **36**, 59.

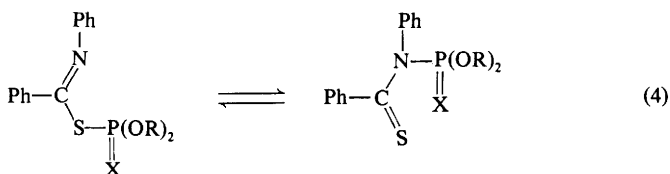


butyric acids were completely assigned, and a linear relationship was found between the  $^{13}\text{C}$  shifts of  $\text{C}=\text{S}$  in ethyl-thioamides and  $\text{C}=\text{O}$  in ethyl-amides.<sup>120</sup>

The stereochemistry of methyl *N*-methylthiobenzimidates, e.g. (67) and (68), that have substituents at one or more of the 2-, 4-, and 6-positions has been investigated.



The  $^{13}\text{C}$  n.m.r. spectra of *E/Z* mixtures of twelve compounds were assigned and the angles of twist about the aryl-imino-carbon bond were determined.<sup>140</sup> Subsequently, the pure (*E*)- and (*Z*)-isomers were obtained by preparative t.l.c. at 258 K or by stereospecific syntheses from (*E*)- and (*Z*)-thioamides. The chemical shifts of the protons in the methyl groups were measured and the (*E*):(*Z*) ratios and the barriers to isomerization were determined by  $^1\text{H}$  n.m.r. spectroscopy.<sup>141</sup> The conformational states of some *NN*-di(primary alkyl)-amides and -thioamides were studied by dynamic  $^1\text{H}$  n.m.r. spectroscopy, and the barriers to the interconversion of enantiomers that were thus found were in good agreement with molecular mechanics calculations.<sup>142</sup> I.r. and n.m.r. data for optically active thioamides  $\text{R}^1\text{CSNR}^2\text{CHMeR}^3$  indicate that there are mixtures of (*E*) and (*Z*) conformers,<sup>143</sup> and i.r. and  $^{31}\text{P}$  n.m.r. studies of phosphorylated thiobenzamides provide evidence of a tautomeric equilibrium [reaction (4)], the amide form being favoured in more



polar solvents.<sup>144</sup> The heats of vaporization of *NN*-dimethylthiobenzamide and of methyl *N*-methylthiobenzimidate, and the heats of methylation of these compounds with  $\text{MeOSO}_2\text{F}$ , show an enthalpy difference that favours the thioamide structure.<sup>145</sup>

<sup>140</sup> W. Walter, W. Ruback, and C. O. Meese, *Org. Magn. Reson.*, 1978, **11**, 612.

<sup>141</sup> W. Walter, W. Ruback, and C. O. Meese, *Chem. Ber.*, 1980, **113**, 171.

<sup>142</sup> U. Berg, M. Grimaud, and J. Sandström, *Nouv. J. Chim.*, 1979, **3**, 175.

<sup>143</sup> V. V. Dunina, V. M. Potapov, E. G. Rukhadze, and E. I. Kazakova, *Zh. Org. Khim.*, 1978, **14**, 2064 (*Chem. Abstr.*, 1979, **90**, 86 614).

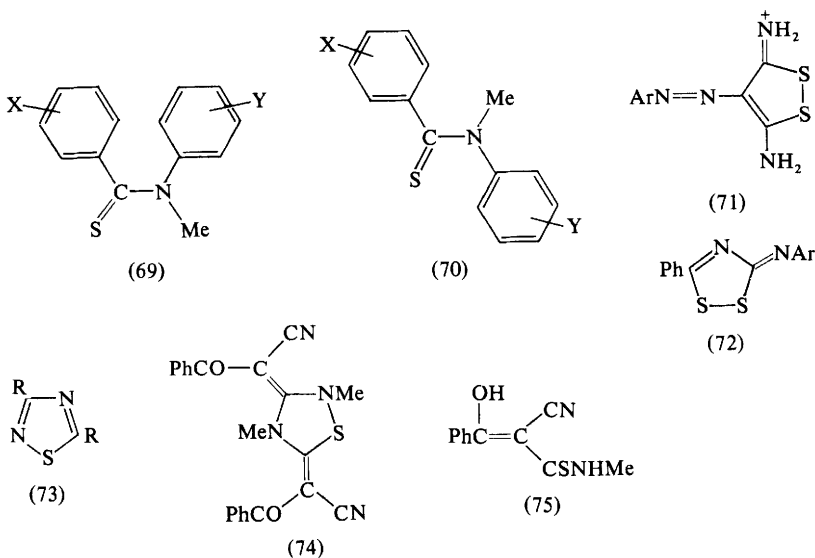
<sup>144</sup> M. G. Zimin, M. M. Afanas'ev, and A. N. Pudovik, *Zh. Obshch. Khim.*, 1979, **49**, 2621 (*Chem. Abstr.*, 1980, **92**, 110 306).

<sup>145</sup> P. Beak, J-K. Lee, and J. M. Ziegler, *J. Org. Chem.*, 1978, **43**, 1536.

The i.r. spectra of selenoacetamide and the *N*-deuteriated species have been determined and fundamental frequencies assigned.<sup>146</sup>

**Reactions.**—*Hydrolysis.* In several kinetic studies of the hydrolysis of thioamides, the formation of a tetrahedral intermediate by addition of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  to the thiocarbonyl group has been postulated.<sup>147–149</sup> In dilute sulphuric acid the intermediate from thioacetanilide undergoes C–S bond cleavage, giving  $\text{H}_2\text{S}$  and acetanilide, which is then hydrolysed, but in 48% acid there is C–N bond cleavage, with the formation of aniline and thiolacetic acid.<sup>147</sup> Alkaline hydrolysis of thiobenzamides proceeds by a slow nucleophilic addition of  $\text{OH}^-$  to  $\text{C}=\text{S}$  and a fast decomposition to give predominantly the amide.<sup>148</sup> Basic methanolysis of *N*-aryl-*N*-(methyl)thiobenzamides, however, goes by C–N bond cleavage of the intermediate, with liberation of the *N*-methylarylamine.<sup>150</sup> Thioanilides, when treated with  $\text{Na}_2\text{PdCl}_4$ , give complexes which are desulphurized by wet DMSO, giving anilides.<sup>151</sup>

*Oxidation.* The rates of formation of *S*-oxides of substituted *N*-(methyl)-thiobenzanilides by oxidation with  $\text{H}_2\text{O}_2$  in aqueous dioxan have been measured and the effects of substituents were analysed. The results suggest that the thioanilides have the (*E*) configuration (69), and not the (*Z*)-form (70).<sup>152</sup> Oxidation



<sup>146</sup> K. R. Gayathri-Devi, D. N. Sathyanarayana, and K. Volka, *Spectrochim. Acta, Part A*, 1978, **34**, 1137.

<sup>147</sup> J. T. Edward and S. C. Wong, *J. Am. Chem. Soc.*, 1979, **101**, 1807.

<sup>148</sup> J. Mollin and P. Bouchalová, *Collect. Czech. Chem. Commun.*, 1978, **43**, 2283.

<sup>149</sup> R. Ahmad and A. A. Khan, *Indian J. Chem., Sect. A*, 1979, **18**, 264 (*Chem. Abstr.*, 1980, **92**, 21 725).

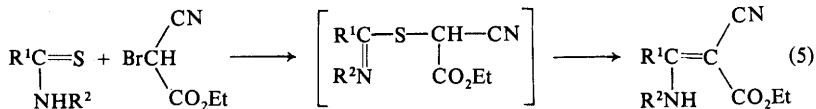
<sup>150</sup> T. J. Broxton, L. W. Deady, and J. E. Rowe, *Aust. J. Chem.*, 1978, **31**, 1731.

<sup>151</sup> H. Alper and J. K. Currie, *J. Organomet. Chem.*, 1979, **168**, 369.

<sup>152</sup> W. Walter and O. H. Bauer, *Liebigs Ann. Chem.*, 1979, 248.

by bromine of the arylhydrazones of dithiomesoxalic acid diamide (from arenediazonium salts and dithiomalonamide) gives 3,5-diamino-4-aryazo-1,2-dithiolium salts (71),<sup>107</sup> and similar oxidation of  $\text{PhCH}_2\text{SC(Ph)=NCSNHAr}$  gives the dithiazoles (72), with elimination of the benzyl group.<sup>153</sup> Oxidation of thiobenzamides with nitrous acid in concentrated hydrochloric acid gives the corresponding benzonitriles and 1,2,4-thiadiazoles (73). 2,6-Dichlorothiobenzamide, however, gives 2,6-dichlorophenyl isothiocyanate as the main product (33%).<sup>154</sup> The 1,2,4-thiadiazolidine (74) is obtained by oxidation of (75) with  $\text{I}_2$  and  $\text{NEt}_3$ .<sup>155</sup>

**Alkylation and Arylation.** The *S*-methylation of thioamides by diazomethane is catalysed by silica gel.<sup>156</sup> *S*-Phenyl derivatives of thiobenzanilides are obtained in high yield by radical arylation with nitrosoacetanilide or phenylazotriphenylmethane.<sup>157,158</sup> Thiols are made from alkyl (or cycloalkyl, or aralkyl) halides by their reaction with dimethylthioformamide and treatment of the imidium ester with methanol; other methods of hydrolysis lead to side-reactions, giving impure products.<sup>159</sup> Mono- and bi-protic thiocarboxamides condense with ethyl bromo-cyanoacetate and one equivalent of  $\text{NaOEt}$  with spontaneous separation of sulphur and the formation of  $\beta$ -amino- $\alpha$ -cyano-acrylates, as shown in reaction (5).<sup>160</sup> The



similar sulphide contractions *via* alkylative coupling described previously<sup>161</sup> (see Vol. 2, p. 235) employed trialkyl phosphite or triphenylphosphine to remove sulphur from the postulated episulphide intermediate. Biprotic thiocarboxamides behave as sources of  $\text{H}_2\text{S}$  when treated with  $\alpha$ -halogenated ketones, esters, or nitriles and ethoxide ion under non-hydrolytic conditions, and give nitriles and symmetrical sulphides derived from the halogenated compound.<sup>162</sup> Thioacetamide has similarly been used to provide sulphur in the synthesis of many-membered cyclic sulphides (thiophanes).<sup>163</sup>

1,4-Benzoquinone and thioacetamide react by Michael addition at the sulphur atom; with an excess of quinone, oxidation and cyclization occur, to give (76). At lower quinone ratios, acetonitrile is eliminated from the Michael adduct to give

<sup>153</sup> R. Rai and V. K. Verma, *Indian J. Chem., Sect. B*, 1979, **18**, 284 (*Chem. Abstr.*, 1980, **92**, 94 310).

<sup>154</sup> M. Badahir, S. Nitz, H. Parlar, and F. Korte, *Z. Naturforsch., Teil. B*, 1979, **34**, 768.

<sup>155</sup> H. Kunzek, E. Nesener, and J. Voigt, *Z. Chem.*, 1978, **18**, 172.

<sup>156</sup> H. Nishiyama, H. Nagase, and K. Ohno, *Tetrahedron Lett.*, 1979, 4671.

<sup>157</sup> R. Kh. Freidlina, I. I. Kandror, and I. O. Bragina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1165 (*Chem. Abstr.*, 1979, **91**, 56 580).

<sup>158</sup> I. I. Kandror, I. O. Bragina, and R. Kh. Freidlina, *Dokl. Akad. Nauk SSSR*, 1979, **249**, 867 (*Chem. Abstr.*, 1980, **92**, 163 665).

<sup>159</sup> K. Hattori, T. Takido, and K. Itabashi, *Nippon Kagaku Kaishi*, 1979, 105 (*Chem. Abstr.*, 1979, **90**, 137 380).

<sup>160</sup> H. Singh and C. S. Gandhi, *J. Chem. Res. (S)*, 1978, 407; *Synth. Commun.*, 1978, **8**, 469.

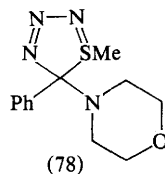
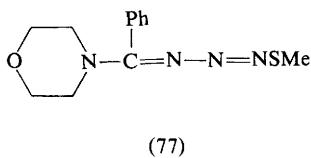
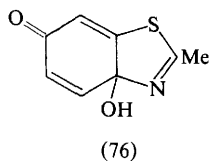
<sup>161</sup> M. Roth, P. Dubs, E. Götschi, and A. Eschenmoser, *Helv. Chim. Acta*, 1971, **54**, 710.

<sup>162</sup> H. Singh and C. S. Gandhi, *Synth. Commun.*, 1979, **9**, 569.

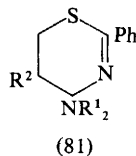
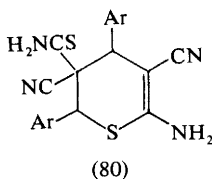
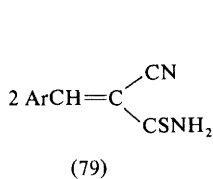
<sup>163</sup> E. Hammerschmidt, W. Bieber, and F. Vögtle, *Chem. Ber.*, 1978, **111**, 2445.

2,5-dihydroxythiophenol, which may then be oxidized to the disulphide. Sterically hindered quinones act only as oxidizing agents.<sup>164</sup>

Keten *SS*-acetals are obtained from thioamides that have at least one hydrogen atom  $\alpha$ - to the thiocarbonyl group by *S*-methylation and treatment of the imidium ester with propane-1,3-dithiol.<sup>165</sup> Treatment of the imidium esters from *NN*-disubstituted thioamides with 4-amino-4-methylpentan-2-ol gives 2-substituted 4,6,6-trimethyl-5,6-dihydro-1,3-oxazines,<sup>166</sup> and with sodium azide they give alkylidene-triazenes (1,2,3-triazabutadienes) (77),<sup>167</sup> not dihydrothia(*S*<sup>IV</sup>)triazoles (78), as previously claimed<sup>168</sup> (see Vol. 3, p. 399). Structure (77) was demonstrated by *X*-ray studies.



**Nucleophilic Reactions of the  $\alpha$ -Carbon Atom.** Thioacetamide condenses with dimethylformamide dimethyl acetal, giving *trans*-3-(dimethylamino)thioacrylamide.<sup>169</sup> The Japp-Klingemann reaction with 3-(phenylthiocarbamoyl)pentane-2,4-dione effects acetyl cleavage, giving 2-methyl-1-(phenylthiocarbamoyl)glyoxal arylhydrazones,<sup>170</sup> and with (arylothiocarbamoyl)benzoylacetamides (62) it displaces the carboxamido-group.<sup>129</sup> Aldehydes condense with cyanothioacetamide to give 3-aryl-2-cyano-thioacrylamides (79), which dimerize reversibly to thiopyran derivatives (80).<sup>171</sup>



**Diels-Alder and Similar Reactions.** Thiobenzoylformamidines,  $\text{PhC(S)N=CH-NR}_2$ , behave as dienes, reacting with dienophiles to give dihydro-1,3-thiazines (81).<sup>172</sup> On the other hand, cyanothioformamides, and especially their *N*-acyl

<sup>164</sup> V. Horak and W. B. Manning, *J. Org. Chem.*, 1979, **44**, 120.

<sup>165</sup> T. Harada, Y. Tamaru, and Z. Yoshida, *Tetrahedron Lett.*, 1979, 3525.

<sup>166</sup> T. Harada, Y. Tamaru, and Z. Yoshida, *Chem. Lett.*, 1979, 1353.

<sup>167</sup> G. L'abbé, A. Wilcox, J. P. Declercq, G. Germain, and M. Van Meerssche, *Bull. Soc. Chim. Belg.*, 1979, **88**, 107.

<sup>168</sup> S. I. Mathew and F. Stansfield, *J. Chem. Soc., Perkin Trans. 1*, 1974, 540.

<sup>169</sup> S. Rajappa and B. G. Advani, *Indian J. Chem., Sect. B*, 1978, **16**, 819 (*Chem. Abstr.*, 1979, **90**, 86 694).

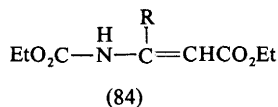
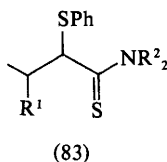
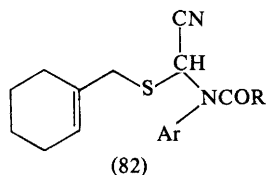
<sup>170</sup> F. A. Amer, A. H. Harhash, and M. A. Awad, *Z. Naturforsch., Teil. B*, 1978, **33**, 660.

<sup>171</sup> J. S. A. Brunskill, A. De, and D. F. Ewing, *J. Chem. Soc., Perkin Trans. 1*, 1978, 629.

<sup>172</sup> J. C. Meslin and H. Quiniou, *Bull. Soc. Chim. Fr., Part 2*, 1979, 347.

derivatives, are dienophiles which add dienes across the C=S bond<sup>173</sup> and which also undergo cycloaddition with 1,3-dipolar compounds such as diazoalkanes, diphenylnitrilimine, benzonitrile oxide, and phenyl azide to give heterocyclic adducts or their decomposition products.<sup>174</sup> Acylated cyanothioformanilides add to methylenecyclohexane or to  $\beta$ -pinene by the ene-reaction, giving unsaturated sulphides, e.g. (82).<sup>175</sup>

*Additions to  $\alpha\beta$ -Unsaturated Thioamides.* Thiourea and toluene-*p*-sulphonic acid add to phenylthiopropionilide, PhC $\equiv$ CCSNHPh, to give an isothiuronium toluene-*p*-sulphonate, from which *N*-phenyl- $\beta$ -mercaptothiocinnamamide is obtained by hydrolysis.<sup>176</sup> Organolithium compounds R<sup>1</sup>Li and Grignard reagents react with  $\alpha\beta$ -unsaturated thioamides by 1,4-addition. The lithium enolate anion can be captured by its reaction with electrophiles; e.g., with PhSSPh to give (83).<sup>177, 178</sup> Soft nucleophiles, e.g. sodiomalonic ester, are unreactive or give intractable mixtures when treated with  $\alpha\beta$ -unsaturated thioamides, but in the presence of a Pd<sup>II</sup> salt they give  $\alpha$ -palladiated  $\beta$ -substituted thioamides, which are more stable than oxa-( $\pi$ -allyl)palladium complexes.<sup>179</sup> The palladium may be removed by hydrogenation. Thiobenzamides are recovered unchanged after treatment with two equivalents of an arylmagnesium bromide, but with four equivalents of Grignard reagent the intermediate Ar<sup>1</sup>C(=NMgBr)SMgBr is attacked; it gives a thiobenzophenone Ar<sup>1</sup>C(=S)Ar<sup>2</sup> and a benzophenone imide Ar<sup>1</sup>C(=NH)Ar<sup>2</sup>. The ratio of the products depends on the nature of Ar<sup>1</sup> and Ar<sup>2</sup>. *N*-Substituted thiobenzamides are unreactive.<sup>180</sup>



*Displacement of Sulphur.* The Wittig reaction of resonance-stabilized phosphorus ylides with thioacyl-urethanes gives acylated enamines, e.g. (84), from which  $\beta$ -keto-esters are obtained by hydrolysis.<sup>181</sup> Hydrazine displaces sulphur in thioanilides, giving amidrazones,<sup>117</sup> but with two equivalents of arylselenoamides it gives 2,5-diaryl-1,3,4-selenadiazoles.<sup>182</sup> Selenoamides react with an excess of hydrazine to give 1,2,4,5-tetrazines (see also Chap. 6, p. 294). 1,2-Bis(thiobenzamido)ethane, when treated with NEt<sub>3</sub> and HgO, cyclizes to 2-phenyl-

<sup>173</sup> K. Friedrich and M. Zamkanej, *Chem. Ber.*, 1979, **112**, 1867.

<sup>174</sup> K. Friedrich and M. Zamkanej, *Chem. Ber.*, 1979, **112**, 1873.

<sup>175</sup> K. Friedrich and M. Zamkanej, *Chem. Ber.*, 1979, **112**, 1916.

<sup>176</sup> S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.*, 1978, **26**, 1021.

<sup>177</sup> Y. Tamaru, T. Harada, H. Iwamoto, and Z. Yoshida, *J. Am. Chem. Soc.*, 1978, **100**, 5221.

<sup>178</sup> Y. Tamaru, T. Harada, and Z. Yoshida, *J. Am. Chem. Soc.*, 1979, **101**, 1316.

<sup>179</sup> Y. Tamaru, M. Kagotani, and Z. Yoshida, *J. Org. Chem.*, 1979, **44**, 2816.

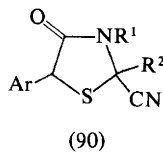
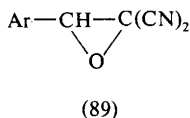
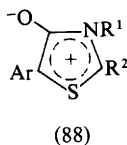
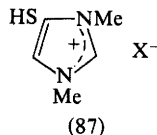
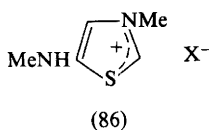
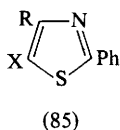
<sup>180</sup> T. Karakasa, T. Hanzawa, and S. Motoki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3469.

<sup>181</sup> A. Gossauer, F. Roessler, H. Züch, and L. Ernst, *Liebigs Ann. Chem.*, 1979, 1309.

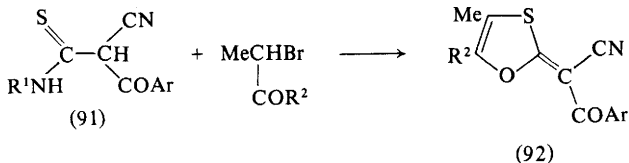
<sup>182</sup> V. I. Cohen, *J. Heterocycl. Chem.*, 1979, **16**, 365.

1-thiobenzoyl-2-imidazoline, and with ethylenediamine and HgO it gives two molecules of 2-phenylimidazoline.<sup>183</sup>

*Synthesis of Thiazole Derivatives.* *N*-Thiobenzoyl- $\alpha$ -amino-acids, when treated with TFAA, give 5-(2'-benzamidoacyloxy)-2-phenylthiazoles (85; X = OCOCHR<sub>2</sub>NHCOPh), half of the starting material serving to acylate the hydroxythiazole. The corresponding amides give 2-phenyl-5-(trifluoroacetamido)thiazoles (85; X = NHCOCF<sub>3</sub>), and thiobenzoyl-leucine methyl ester is converted into benzoyl-leucine methyl ester.<sup>184</sup> *N*-Formyl- and *N*-thioformyl-sarcosine *N*-methylthioamide cyclize to 5-methylamino-1,3-thiazolium salts (86) and the isomeric 4-mercapto-1,3-imidazolium salts (87) when TFA is present. The latter give the meso-ionic compound anhydro-1,3-dimethyl-4-mercaptoimidazolium hydroxide when treated with a base.<sup>185</sup> Meso-ionic anhydro-4-hydroxythiazolium hydroxides (88) are obtained from *gem*-dicyano-epoxides (89) and *N*-mono-substituted thioamides,<sup>186</sup> a side-reaction giving some thiazolidinone (90).



The Hantzsch thiazole synthesis from thioamides and  $\alpha$ -halogeno-ketones has been applied to *NN*-(dimethyl)dithio-oxamide to give 2-(dimethylthiocarbamoyl)thiazoles,<sup>187</sup> but in some cases it took another course. Thus, 1-alkylthiocarbamoyl-1-cyanoacetophenones (91) react with bromo-ketones with elimination of alkylamine, giving 2-methylidene-1,3-oxathioles (92).<sup>188</sup> The thioanilide of acetoacetic acid reacts with 2-bromo-1-tetralone to give the spiro-



<sup>183</sup> G. Ewin and J. O. Hill, *Aust. J. Chem.*, 1979, **32**, 441.

<sup>184</sup> G. C. Barrett, *Tetrahedron*, 1978, **34**, 611.

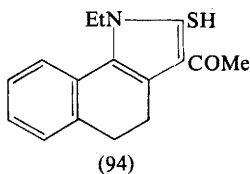
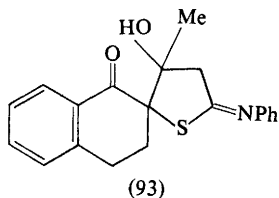
<sup>185</sup> M. Begtrup, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1132.

<sup>186</sup> M. Baudy, A. Robert, and A. Foucaud, *J. Org. Chem.*, 1978, **43**, 3732.

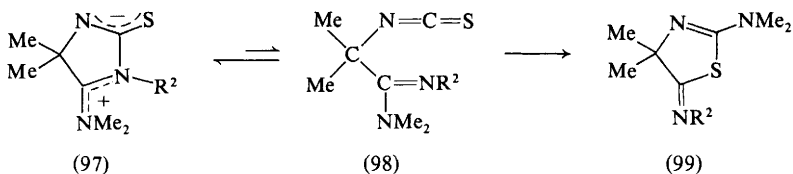
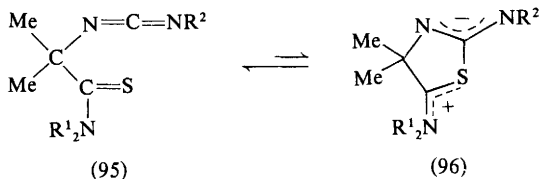
<sup>187</sup> H. U. Kibbel, E. Peters, and M. Michalik, *Z. Chem.*, 1979, **19**, 19.

<sup>188</sup> H. Dehne and P. Krey, *Z. Chem.*, 1979, **19**, 251.

compound (93), and the corresponding *N*-ethylthioamide gives the analogous ethylimino-compound, but the major product in this case is the benzindole derivative (94).<sup>189</sup> (See also Chap. 6, p. 285.)



The  $\alpha$ -thiocarbamoylcarbodi-imides (95), which are obtained by the reaction of sterically hindered isothiocyanates  $R^2NCS$  with 3-dialkylamino-2,2-dimethyl-2*H*-azirines<sup>190</sup> (see Vol. 5, pp. 141, 158), are in equilibrium with the dipolar species (96). This last compound is not detectable by spectroscopy, but its presence may be demonstrated by its protonation or by its reduction with  $NaBH_4$  to give stable thiazolidine derivatives. The carbodi-imides (95;  $R^1 = Me$ ) rearrange on heating, to give the dipolar imidazoles (97), in which some participation of the acyclic structure (98) is suggested by the low barrier to rotation of the dimethylamino-group (from n.m.r. studies) and by a further isomerization to give (99).<sup>191</sup> This behaviour is closely paralleled by the properties of the adducts of 3-dialkylamino-2,2-dimethyl-2*H*-azirines with carbon disulphide, which exist in the solid state as heterocyclic dipolar compounds and as  $\alpha$ -(dialkylthiocarbamoyl)isopropyl isothiocyanates when melted.<sup>192, 193</sup>



When pentafluorophenylthioureas or pentafluorophenyl thio- or dithio-carbamates are heated in DMF, they cyclize to give 4,5,6,7-tetrafluorobenzo-

<sup>189</sup> E. H. Marten and C. A. Maggiali, *J. Heterocycl. Chem.*, 1978, **15**, 1277.

<sup>190</sup> E. Schaumann, E. Kausch, and W. Walter, *Chem. Ber.*, 1977, **110**, 820.

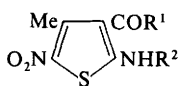
<sup>191</sup> E. Schaumann, H. Behr, and G. Adiwidjaja, *Liebigs Ann. Chem.*, 1979, 1322.

<sup>192</sup> S. Chaloupka, H. Heimgartner, H. Schmid, H. Link, P. Schönholzer, and K. Bernauer, *Helv. Chim. Acta*, 1976, **59**, 2566.

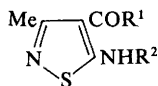
<sup>193</sup> E. Schaumann, E. Kausch, S. Grabley, and H. Behr, *Chem. Ber.*, 1978, **111**, 1486.

thiazoles. Thionation of acyl derivatives of pentafluoroaniline with  $P_4S_{10}$  in dioxan at 90 °C causes cyclization to tetrafluorobenzothiazoles, but  $N^1$ -acyl- $N^2$ -(pentafluorophenyl)hydrazines can be thionated to thiohydrazides, which cyclize to 5,6,7,8-tetrafluorobenzo-1,3,4-thiadiazines when heated in DMF.<sup>194</sup>

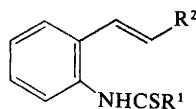
**Synthesis of Other Heterocyclic Compounds.** Nitrothiophens (100) are produced by the reaction of bromonitromethane with  $\alpha$ -acyl- $\beta$ -aminocrotonic thioamides, but if the amino-group is primary the reaction also gives 1,2-thiazoles (101).<sup>195</sup> The photochemical synthesis of quinolines by irradiation of  $N$ -(*o*-styryl)thioamides (102) involves elimination of  $H_2S$ .<sup>196</sup> Benzoylthioacetanilides  $PhCOCH_2CSNHAr$  and phosgene give 4-arylimino-2-oxo-6-phenyl-1,3-oxathiins (103), which rearrange in acid solution to 3-aryl-2,3-dihydro-2-oxo-6-phenyl-1,3-oxazine-4-thiones (104).<sup>197</sup> A general route to 6*H*-1,3,5-oxathiazines (105) by  $\alpha$ -thioamidoalkylation of aldehydes  $R^4CHO$  with  $R^1C(S)NHCH(OR^3)R^2$  has been described.<sup>198</sup> The reaction of  $N$ -methyl- $N$ -(trimethylsilyl)thiobenzamide with diphenylketen or tosyl isocyanate gives the heterocyclic compounds (106) and (107) respectively.<sup>199</sup> Thiobenzoyl isocyanates give 2:1 adducts with trimethylsilyl cyanide which have been formulated as 1,3,5-thiadiazepine derivatives (108).<sup>200</sup>



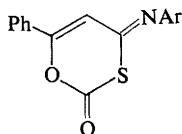
(100)



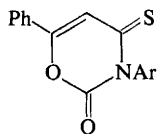
(101)



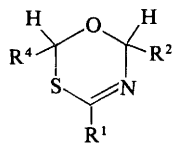
(102)



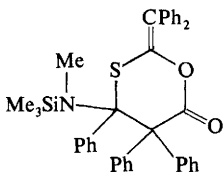
(103)



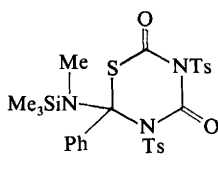
(104)



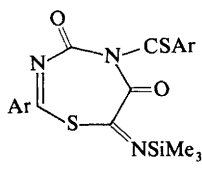
(105)



(106)



(107)



(108)

<sup>194</sup> F. E. Herkes, *J. Fluorine Chem.*, 1979, **13**, 1.

<sup>195</sup> S. Rajappa and R. Sreenivasan, *Indian J. Chem., Sect. B*, 1978, **16**, 752 (*Chem. Abstr.*, 1979, **90**, 151 899).

<sup>196</sup> P. de Mayo, L. K. Sydnos, and G. Wenska, *J. Chem. Soc., Chem. Commun.*, 1979, 499.

<sup>197</sup> W. Zankowska-Jasinska, Z. Kamela, and U. Zieba, *Pol. J. Chem.*, 1979, **53**, 1251 (*Chem. Abstr.*, 1980, **92**, 6480).

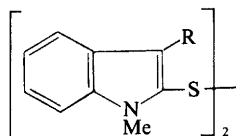
<sup>198</sup> C. Giordano, A. Belli, R. Erbea, and S. Panossian, *Synthesis*, 1979, 801.

<sup>199</sup> W. Walter, H. W. Lueke, and T. Proll, *J. Organomet. Chem.*, 1979, **173**, 33.

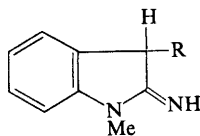
<sup>200</sup> O. Tsuge and S. Urano, *Heterocycles*, 1979, **12**, 1319.



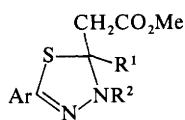
*N*-Aryl-*N*-methyl-*N'*-thioacylhydrazines,  $\text{RCH}_2\text{C}(\text{S})\text{NHNMePh}$ , cyclize to bis-(1-methyl-2-indolyl) disulphides (109) and salts of 2-aminoindoline (110) when  $\text{POCl}_3$  or  $\text{PCl}_3$  is present.<sup>201</sup> Some cycloadditions of thioacylhydrazines give 1,3,4-thiadiazole derivatives: addition of thioaroylhydrazines to methyl propiolate or dimethyl acetylenedicarboxylate gives (111;  $\text{R}^1 = \text{H}$  or  $\text{CO}_2\text{Me}$ ),<sup>202</sup> and *N*-alkyl-*N*-thioaroylhydrazines react with aryldibromodiazabutadienes  $\text{ArCH}=\text{N}-\text{N}=\text{CBr}_2$  to give the 1,3,4-thiadiazolium bromides (112), which are converted into meso-ionic 1,3,4-thiadiazolidine-2-benzylidenehydrazinides (113) by treatment with anhydrous  $\text{NH}_3$  or  $\text{NEt}_3$ .<sup>203</sup>



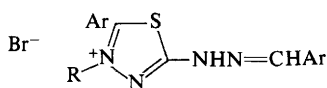
(109)



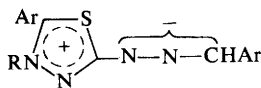
(110)



(111)



(112)



(113)

**Miscellaneous.** Unstable 2,4,6-triphenyl-1-thioacylaminopyridinium salts are obtained from thioacylhydrazines and 2,4,6-triphenylpyridium tetrafluoroborate. They decompose on heating to give nitriles, triphenylpyridine, and sulphur.<sup>204</sup> Radical anions of *NN*-dialkyl-benzamides, -thiobenzamides, and -selenobenzamides, generated by electrochemical reduction in anhydrous DMF, were studied by e.p.r. spectroscopy. The  $\text{CSNR}_2$  and  $\text{CSeNR}_2$  groups withdraw much spin density from the aromatic ring, and are comparable with the nitro-group in this respect. The new thioamides and selenoamides have been made from the amides and  $\text{P}_4\text{S}_{10}$  or  $\text{P}_4\text{Se}_{10}$  in dry pyridine.<sup>205</sup>

#### 4 Thiono- and Dithio-carboxylic Acids, their Derivatives, and their Selenium Analogues

**Synthesis of Derivatives of Thionocarboxylic Acids.**—Thiono-esters are obtained by the reaction of dialkoxycarbonium ions with  $\text{Na}_2\text{S}$  or anhydrous  $\text{NaHS}$  in acetonitrile (Scheme 6).<sup>206</sup> Cyclic carbonium salts from 1,2- or 1,3-diols give monothiono-esters of these diols. The tetrahedral intermediates in this process may be alkylated to give

<sup>201</sup> A. N. Kost, G. A. Golubeva, and A. G. Popova, *Khim. Geterotsykl. Soedin.*, 1979, 344.

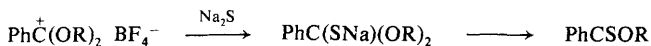
<sup>202</sup> N. D. Heindel, G. Friedrich, and M. C. Tsai, *J. Heterocycl. Chem.*, 1980, 17, 191.

<sup>203</sup> E. Cawkill, W. D. Ollis, C. A. Ramsden, and G. P. Rowson, *J. Chem. Soc., Perkin Trans. 1*, 1979, 724.

<sup>204</sup> A. R. Katritzky, J. Lewis, and P-L. Nie, *J. Chem. Soc., Perkin Trans. 1*, 1979, 446.

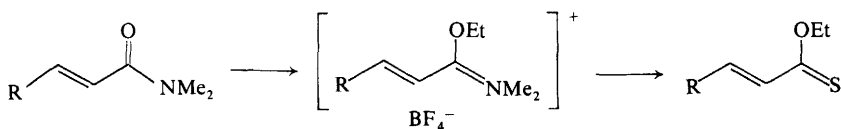
<sup>205</sup> J. Voss and F. R. Bruhn, *Liebigs Ann. Chem.*, 1979, 1931.

<sup>206</sup> F. Khouri and M. K. Kaloustian, *Tetrahedron Lett.*, 1978, 5067.



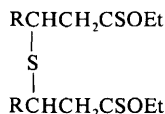
Scheme 6

monothio-orthoesters.<sup>207</sup>  $\alpha\beta$ -Unsaturated thiono-esters have been made by thiolysis of imidates from cinnamic, crotonic, and fumaric acids at low temperatures (Scheme 7). At higher temperatures there is also addition of  $\text{H}_2\text{S}$  at the  $\beta$ -position, giving (114), which may be converted into the unsaturated thiono-ester by heating.<sup>208</sup> The reaction of alkyl halides with the potassium or mercury(II) salt of thioacetic acid gives only thioesters.<sup>209</sup> Equimolecular amounts of organosilyl-thianes  $(\text{R}_3\text{Si})_2\text{S}$  and carboxylic acid halides react to give thiono-esters  $\text{R}_3\text{SiOC}(\text{S})\text{R}^2$ , but with an excess of the acid halide the product is a diacyl sulphide  $(\text{R}^2\text{CO})_2\text{S}$ .<sup>210</sup> The product described as 'dithiobenzoyl oxide',  $(\text{PhCS})_2\text{O}$ ,<sup>211</sup> is, in fact, a mixture of benzoic acid and benzylidene thiobenzoate,  $\text{PhCH}(\text{SCOPh})_2$ .<sup>212</sup> The kinetics of the thermal decomposition of 5-phenyl-1,2,3,4-thiaziazole in the temperature range 52.2—61.5 °C to give benzonitrile, sulphur, and nitrogen suggest that thiobenzoyl azide is an intermediate in the process. At ~100 °C the decomposition gives phenyl isothiocyanate and nitrogen.<sup>213</sup> Oxythioacetyl chloride (115) was obtained by dehydrochlorination of 1-chloroethanesulphonyl chloride with  $\text{NEt}_3$  in ether at -30 °C. It was too unstable to be isolated.<sup>214</sup>

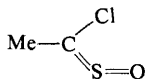


Scheme 7

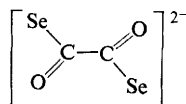
Potassium 1,2-diseleno-oxalate has been prepared by saponification of diphenyl oxalate by alcoholic  $\text{K}_2\text{Se}$ . It is very sensitive to oxygen. The ion was shown by X-ray analysis to have the *trans*-planar conformation (116).<sup>215</sup>



(114)



(115)



(116)

<sup>207</sup> F. Khouri and M. K. Kaloustian, *J. Am. Chem. Soc.*, 1979, **101**, 2249.

<sup>208</sup> R. Hoffmann and K. Hartke, *Chem. Ber.*, 1980, **113**, 919.

<sup>209</sup> S. Uemura, N. Watanabe, A. Toshimitsu, and M. Okano, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1818.

<sup>210</sup> E. P. Lebedev, V. A. Baburina, and M. D. Mizhiritskii, *Zh. Obshch. Khim.*, 1979, **49**, 1081 (*Chem. Abstr.*, 1979, **91**, 39 577).

<sup>211</sup> D. T. Lewis, *J. Chem. Soc.*, 1940, 831.

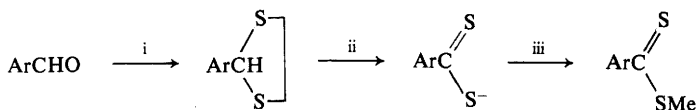
<sup>212</sup> A. Senning and K. Schank, *Acta Chem. Scand., Ser. B*, 1978, **32**, 780.

<sup>213</sup> A. Holm, L. Carlsen, and E. Larsen, *J. Org. Chem.*, 1978, **43**, 4816.

<sup>214</sup> L. A. Carpino and J. R. Williams, *J. Org. Chem.*, 1979, **44**, 1177.

<sup>215</sup> C. Matz and R. Mattes, *Z. Naturforsch., Teil. B*, 1978, **33**, 461.

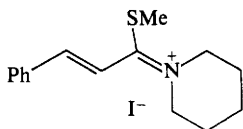
**Synthesis of Dithiocarboxylic Acids and their Derivatives.**—The preparation of thioterephthalic acid from 1,4-di(chloromethyl)benzene, sulphur, and sodium methoxide (see Vol. 5, p. 179) has been reported by another group.<sup>216</sup> In a similar reaction, the addition of chloroacetonitrile to sulphur and triethylamine in DMF, followed by alkylation, gave methyl and ethyl cyanodithioformates. These were not isolated, but they condensed when water was added, giving *E/Z* mixtures of 1,2-di(alkylmercapto)-1,2-dicyanoethylenes.<sup>217</sup> Ethylene dithioacetals from aromatic aldehydes are decomposed by sodium hydride in DMF containing HMPA, with elimination of ethylene and the liberation of an aryldithiocarboxylate anion; this may be alkylated to give the dithioester (Scheme 8).<sup>218</sup>



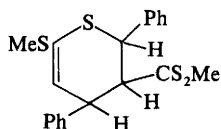
Reagents: i,  $(\text{CH}_2\text{SH})_2$ ,  $\text{H}^+$ ; ii,  $\text{NaH}$ ,  $\text{DMF}$ ,  $\text{HMPA}$ ; iii,  $\text{MeI}$

**Scheme 8**

Methyl dithiocinnamate was obtained in low yield from styrylmagnesium bromide by reaction with  $\text{CS}_2$  and methylation with  $\text{MeI}$ , and in better yield by low-temperature thiolysis of the thioimide (117). At room temperature the thiolysis was complicated by addition of  $\text{H}_2\text{S}$  to give the saturated sulphide analogous to (114). The dithiocinnamate dimerizes reversibly, by  $[4 + 2]$ cycloaddition, to form a product that was assigned the structure (118) on n.m.r. evidence.



(117)



(118)

Another stereoisomer is obtained by heating the dimer with methyl dithiocinnamate at  $125^\circ\text{C}$ . Methyl dithiocrotonate could only be isolated as its dimer.<sup>208</sup> Another approach to unsaturated dithioesters employs the addition of an unsaturated Grignard reagent to phenyl isothiocyanate, followed by methylation and thiolysis of the resulting *S*-methyl-*N*-phenylimidate. With allylic Grignard reagents, inversion occurs through attack by the isothiocyanate at the allylic position. Double bonds in the  $\beta\gamma$ -position can be moved into conjugation with the thiocarbonyl group by  $\text{NEt}_3$  catalysis.<sup>219</sup> The synthesis of dithioesters from Grignard reagents and  $\text{CS}_2$  is improved by the addition of  $\text{CuBr}$ , *i.e.* by the use of an organocopper reagent.<sup>220</sup>

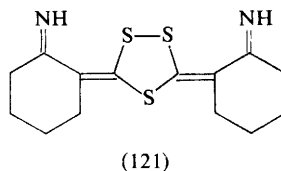
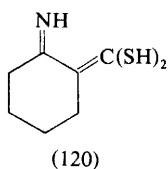
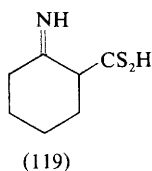
<sup>216</sup> J. M. Fabre, E. Torreilles, and L. Giral, *Tetrahedron Lett.*, 1978, 3703.

<sup>217</sup> R. Mayer, W. Thiel, and H. Viola, *Z. Chem.*, 1979, **19**, 56.

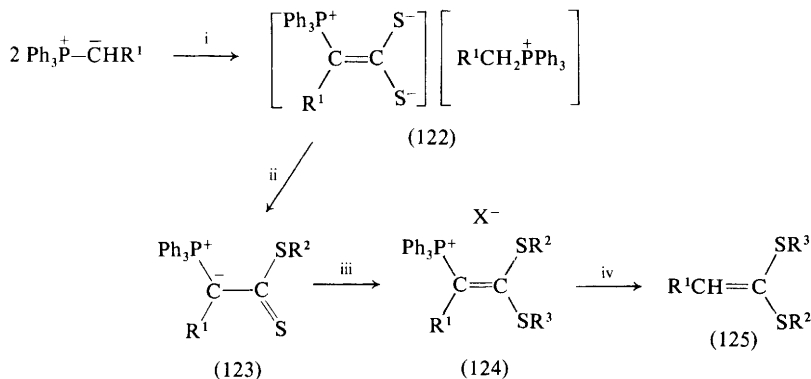
<sup>218</sup> N. C. Gonnella, M. V. Lakshmikantham, and M. P. Cava, *Synth. Commun.*, 1979, **9**, 17.

<sup>219</sup> P. Gosselein, S. Masson, and A. Thuillier, *Tetrahedron Lett.*, 1978, 2715.

<sup>220</sup> H. Westmijze, H. Kleijn, J. Meijer, and P. Vermeer, *Synthesis*, 1979, 432.



The synthesis of dithiocarboxylates by addition of  $\text{CS}_2$  to enamines or activated methylene groups is further exemplified in the pyrimidine series<sup>221–223</sup> and in the preparation of pyridinium and quinolinium zwitterions from *N*-methyl anhydrobases of 2-methyl-pyridines and -quinolines.<sup>224, 225</sup> 2-Iminocyclohexanedithiocarboxylic acid (119) has been made from cyclohexanone, excess  $\text{CS}_2$ , and aqueous ammonia. It shows more tendency to exist in the dimercaptomethylene form (120) than does the cyclopentane analogue, and on oxidation with  $\text{I}_2$  it gives the trithiole derivative (121).<sup>226</sup> Alkylidetriphenylphosphoranes that have a hydrogen atom attached to the negative carbon atom add to  $\text{CS}_2$  in a 2:1 ratio, giving phosphonium salts (122) in which the dithiocarboxylic acid component can be alkylated successively on both sulphur atoms to yield first 2-(triphenylphosphoranylidene)alkanedithioates (123) and then phosphonium salts (124) that give keten dithioacetals (125) and triphenylphosphine oxide upon alkaline hydrolysis (Scheme 9). Compounds (123) do not undergo the Wittig reaction. The adducts from  $\text{CS}_2$  and other alkylidene phosphoranes are betaines (126), from which dithiocarboxylic



Reagents: i,  $\text{CS}_2$ ; ii, alkylation,  $\text{R}^2\text{X}$ ; iii, alkylation,  $\text{R}^3\text{X}$ ; iv,  $\text{H}_2\text{O}$ ,  $\text{OH}^-$

**Scheme 9**

<sup>221</sup> H. Okuda, Y. Tominaga, Y. Matsuda, and G. Kobayashi, *Heterocycles*, 1979, **12**, 485.

<sup>222</sup> Y. Tominaga, H. Okuda, Y. Mitsuomi, Y. Matsuda, G. Kobayashi, and K. Sakemi, *Heterocycles*, 1979, **12**, 503.

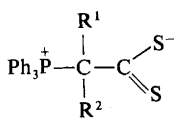
<sup>223</sup> Y. Tominaga, T. Machida, H. Okuda, Y. Matsuda, and G. Kobayashi, *Yakugaku Zasshi*, 1979, **99**, 515.

<sup>224</sup> W. O. Foye, Y. J. Lee, K. A. Shah, and J. M. Kauffman, *J. Pharm. Sci.*, 1978, **67**, 962.

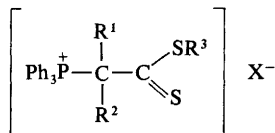
<sup>225</sup> W. O. Foye and J. M. Kauffman, *J. Pharm. Sci.*, 1979, **68**, 336.

<sup>226</sup> T. Takeshima, A. Yano, N. Fukada, Y. Hirose, and M. Muraoka, *J. Chem. Res. (S)*, 1979, 140.

esters are obtained by alkylation to the phosphonium salts (127) and removal of triphenylphosphine by electrolytic reduction.<sup>227</sup>

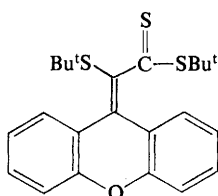


(126)

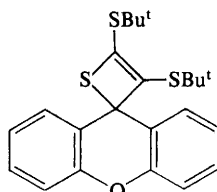


(127)

Methyl and ethyl dithioacetates, when heated with trimethyl phosphite, undergo a thio-Claisen condensation with loss of  $\text{H}_2\text{S}$ , giving *cis*- and *trans*- $\beta$ -(alkylthio)dithiocrotonic esters.<sup>228</sup> Alkylation of potassium 1,1-dithio-oxalate in water gives exclusively the *S*-monoester. A second alkyl group may be introduced, located on oxygen, by alkylating the sodium salt of the monoester in HMPA.<sup>229</sup> Dimethyl trithio-oxalate has been made by alkylating potassium trithio-oxalate in MeOH.<sup>230</sup> Irradiation of xanthenethione with bis-(*t*-butylthio)ethyne gives both an  $\alpha\beta$ -unsaturated dithioester (128) and a thiet (129), which equilibrate in solution.<sup>231</sup> With bis(methylthio)ethyne only the ester was obtained<sup>232</sup> (see Vol. 4, p. 181).



(128)



(129)

On standing in a refrigerator, dithioacetic acid forms crystals containing two trimers (1,3,5-trithian derivatives) as well as a trace of the previously reported tetramethylhexathia-adamantane. The isomers, which were not separated, regenerate monomer on distillation or chromatography.<sup>233</sup> Convenient methods for the preparation of anhydrous sodium dithiocarboxylates<sup>234</sup> and other alkali-metal salts<sup>235</sup> have been described. Exchange of sulphur between  $^{32}\text{S}$  and methyl dithiobenzoate or methyl cyclohexanedithiocarboxylate requires a basic solvent, *e.g.* pyridine, and occurs at the  $\text{C}=\text{S}$  and not the  $\text{SMe}$  position.<sup>236</sup>

<sup>227</sup> H. J. Bestmann, R. Engler, H. Hartung, and K. Roth, *Chem. Ber.*, 1979, **112**, 28.

<sup>228</sup> Z. Yoshida, S. Yoneda, T. Kawase, and M. Inaba, *Tetrahedron Lett.*, 1978, 1285.

<sup>229</sup> J. Voss and H. Gunther, *Synthesis*, 1978, 849.

<sup>230</sup> U. Niemer, K. Mennemann, and R. Mattes, *Chem. Ber.*, 1978, **111**, 2113.

<sup>231</sup> A. C. Brouwer, A. V. E. George, D. Seykens, and H. J. T. Bos, *Tetrahedron Lett.*, 1978, 4839.

<sup>232</sup> A. C. Brouwer and H. J. T. Bos, *Tetrahedron Lett.*, 1976, 209.

<sup>233</sup> G. Levesque, A. Mahjoub, and A. Thuillier, *Tetrahedron Lett.*, 1978, 3847.

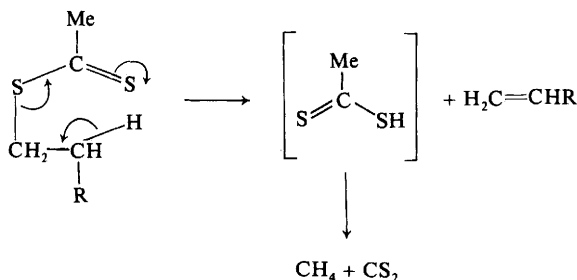
<sup>234</sup> S. Kato, K. Ito, R. Hattori, M. Mizuta, and T. Katada, *Z. Naturforsch., Teil. B*, 1978, **33**, 976.

<sup>235</sup> S. Kato, S. Yamada, H. Goto, K. Terashime, M. Mizuta, and T. Katada, *Z. Naturforsch., Teil. B*, 1980, **35**, 458.

<sup>236</sup> L. Lešetický and F. Picha, *Collect. Czech. Chem. Commun.*, 1978, **43**, 2403.

Alkyl trithioesteres [alkyl thiocarbonyldisulphides,  $R^1C(=S)SSR^2$ ] were obtained by the reaction of *t*-butylsulphenyl iodide with a metal (preferably Pb) salt of a dithio-acid,<sup>237</sup> but they are made more conveniently by the addition of  $CS_2$  to a Grignard reagent and treatment of the adduct with methyl methanethiolsulphonate,  $MeSO_2SMe$ .<sup>238</sup>

**Physical Properties.**—Further *X*-ray studies of methyl thio- and dithio-esters have confirmed previous findings (see Vol. 5, p. 180) that the ester group is almost planar, with a *Z* conformation.<sup>230,239</sup> Kinetic studies of the gas-phase pyrolysis of dithioacetates have shown that the reaction is a concerted unimolecular process, consistent with the mechanism shown in Scheme 10.<sup>240</sup>



Scheme 10

Radical anions that had been generated by the electrochemical reduction of some ( $^2H_3$ )methyl esters of mono- and di-thiobenzoic acids that were enriched in  $^{13}C$  or  $^{33}S$  were studied by e.s.r. spectroscopy. The results indicated that the radical anions are benzyl radicals, and not thiy radicals.<sup>241</sup>

**Reactions.**—2-Iminocyclopentanedithiocarboxylic acid adds to Schiff bases at room temperature to form esters (130); these cyclize to 1,3-thiazines (131), with loss of arylamine, on warming.<sup>242</sup> Similar 1,3-thiazines are readily obtained from cyclohexanone,  $CS_2$ , and ammonia.<sup>226</sup> The addition of dithio-acids to dienes goes by a concerted reaction at  $\sim 50^\circ C$  and by a free-radical mechanism at higher temperatures, the products being allyl or vinyl dithioesters and/or dithiolans, e.g. (132).<sup>243,244</sup>

A dication (133), containing a tetrathian ring, has been made by electrochemical oxidation of sodium 4-diethylaminodithiobenzoate, and also by oxidation with

<sup>237</sup> D. F. Aycock and G. R. Jurch Jr., *J. Org. Chem.*, 1979, **44**, 569.

<sup>238</sup> R. S. Sukhai and L. Brandsma, *Synthesis*, 1979, 971.

<sup>239</sup> U. Niemer and R. Mattes, *Chem. Ber.*, 1978, **111**, 2118.

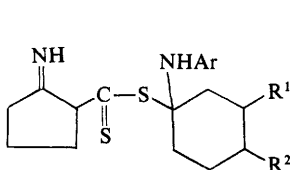
<sup>240</sup> N. Al-Awadi, D. B. Bigley, and R. E. Gabbott, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1223.

<sup>241</sup> C-P. Klages, W-D. Malmberg, and J. Voss, *J. Chem. Res. (S)*, 1979, 160.

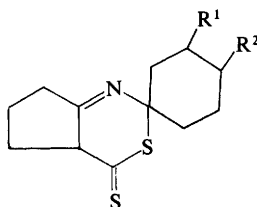
<sup>242</sup> N. Fukada, M. Kato, H. Seki, M. Kawana, and T. Takeshima, *J. Chem. Soc., Perkin Trans. 1*, 1978, 558.

<sup>243</sup> G. Levesque, A. Mahjoub, and A. Thuillier, *Colloq. Int. CNRS*, 1977, **278**, 365 (*Chem. Abstr.*, 1979, **91**, 174 492).

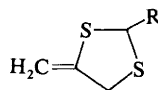
<sup>244</sup> J. C. Gressier, G. Levesque, A. Mahjoub, and A. Thuillier, *Bull. Soc. Chim. Fr., Part 2*, 1979, 355.



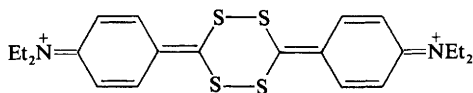
(130)



(131)



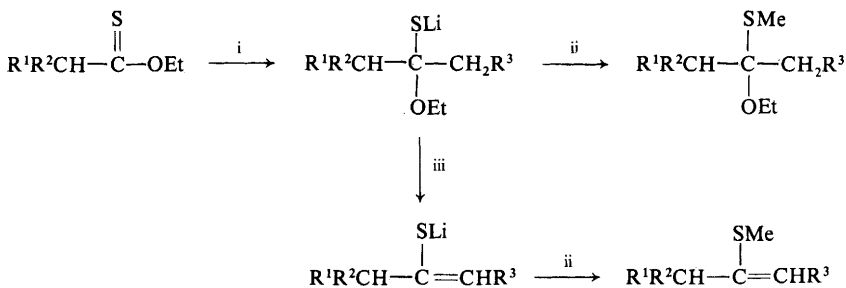
(132)



(133)

iodine.<sup>245</sup> Electroreductive alkylation of dithioesters in the presence of alkyl iodides gives dithioacetals; keten dithioacetals also are obtained from alkyl dithio-propionates.<sup>246</sup>

At  $-78\text{ }^{\circ}\text{C}$ , *O*-ethyl thioesters undergo nucleophilic addition of alkyl-lithium at the C=S group. The products may be alkylated to give monothioacetals, or converted into thioenolates by warming to room temperature with LDA (Scheme 11).<sup>247</sup> Anions generated from dithioesters with LDA have been employed as



Reagents: i,  $\text{R}^3\text{CH}_2\text{Li}$ ; ii, MeI; iii, LDA

Scheme 11

equivalents of acyl anions in reaction with electrophiles<sup>248</sup> (see also Chap. 2, Pt I, p. 95) and as intermediates for preparing keten dithioacetals.<sup>249</sup> The methyl and isopropyl esters of pent-4-enedithioic acid, when treated successively with potassium hydride and *s*-butyl-lithium, give dianions of penta-2,4-dienedithioate esters. These react with carbonyl compounds at the 5-position, affording anions that may be alkylated to give keten dithioacetals or quenched with water to give substituted

<sup>245</sup> G. Cauquis and A. Deronzier, *J. Chem. Soc., Chem. Commun.*, 1978, 809.

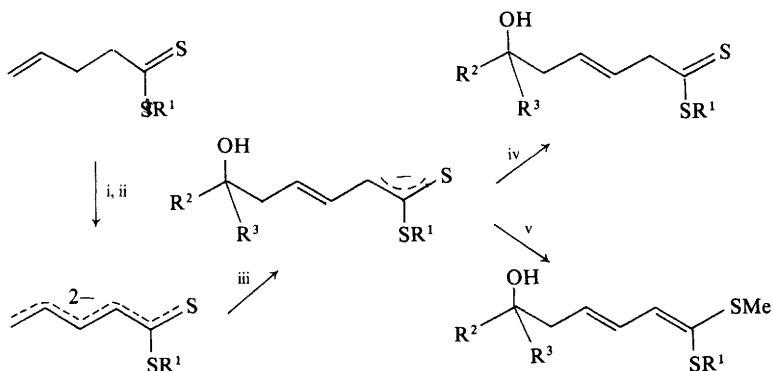
<sup>246</sup> L. Kistenbrügger and J. Voss, *Liebigs Ann. Chem.*, 1980, 472.

<sup>247</sup> L. Narasimhan, R. Sanitra, and J. S. Swenton, *J. Chem. Soc., Chem. Commun.*, 1978, 719.

<sup>248</sup> A. I. Meyers, T. A. Tait, and D. L. Comins, *Tetrahedron Lett.*, 1978, 4657.

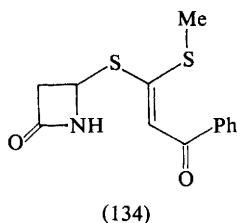
<sup>249</sup> B. Cazes and S. Julia, *Tetrahedron Lett.*, 1978, 4065.

dithioesters (Scheme 12).<sup>250</sup> The unusual keten dithioacetal (134) is made by the reaction of 4-acetoxyazetidin-2-one with methyl  $\beta$ -hydroxydithiocinnamate.<sup>251</sup>



Reagents: i, KH, at 0 °C; ii, Bu<sup>s</sup>Li, at -78 °C, TMEDA; iii, R<sup>2</sup>COR<sup>3</sup>; iv, H<sub>2</sub>O; v, MeI

Scheme 12



Thio-oxalates MeOC(S)C(S)OMe, and the more reactive MeSC(S)C(S)SMe, act as  $2\pi$  and  $4\pi$  components in cycloadditions, giving, e.g., (135; X = O) or (135; X = S) with dimethylbutadiene and (136; X = O) or (136; X = S) with phenylacetylene. Dimethyl tetrathio-oxalate is in equilibrium with its [4 + 2]cyclo-adduct dimer (137) in non-polar solvents.<sup>252</sup> Allyl, propargyl, and benzyl dithioesters react with dimethyl acylenedicarboxylate to form 1,3-dithioles, e.g. (138), with migration of the allyl, propargyl, or benzyl group.<sup>253, 254</sup> Thietanones (139) are obtained by the addition of diphenylketen to dithiobenzoic esters.<sup>255</sup> Some further meso-ionic 1,3-dithiolones (140; R = Me or thioalkyl) (see Vol. 4, p. 185) have been made by dehydration of  $\alpha$ -carboxybenzyl dithioesters RC(S)SCHPhCO<sub>2</sub>H, and their cycloaddition reactions have been investigated.<sup>256</sup>

Acyl thioacyl sulphides, R<sup>1</sup>C(S)SC(O)R<sup>2</sup>, disproportionate in the presence of

<sup>250</sup> M. Pohmakotr and D. Seebach, *Tetrahedron Lett.*, 1979, 2271.

<sup>251</sup> M. Shibuya and S. Kubota, *Heterocycles*, 1979, 12, 1315.

<sup>252</sup> K. Hartke, T. Kissel, J. Quante, and G. Henssen, *Angew. Chem., Int. Ed. Engl.*, 1978, 17, 953.

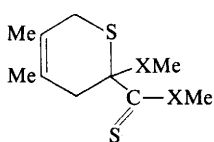
<sup>253</sup> V. N. Drozd and O. A. Popova, *Tetrahedron Lett.*, 1979, 4491.

<sup>254</sup> V. N. Drozd, *Zh. Org. Khim.*, 1979, 15, 1106 (*Chem. Abstr.*, 1979, 91, 193 229).

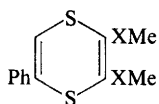
<sup>255</sup> V. N. Drozd and O. A. Popova, *Zh. Org. Khim.*, 1979, 15, 2602 (*Chem. Abstr.*, 1980, 92, 163 777).

<sup>256</sup> H. Gotthardt, O. M. Huss, and C. M. Weissshuhn, *Chem. Ber.*, 1979, 112, 1650.

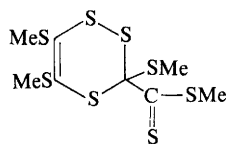




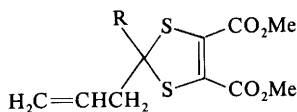
(135)



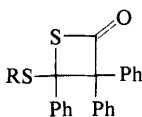
(136)



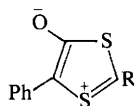
(137)



(138)



(139)



(140)

lithium alkoxides or lithium mercaptides to give bis(thioacyl) sulphides and bis(acyl) sulphides.<sup>257</sup>

Aliphatic selone esters  $RC(Se)OEt$  react with a stoichiometric amount (0.5 mol) of hydrazine to give hydrazones  $RC(OEt)=NN=C(OEt)R$ ,<sup>182</sup> and with semicarbazides and thiosemicarbazides they give 3-hydroxy- or 3-mercapto-1,2,4-triazoles.<sup>258</sup>

## 5 Thio- and Dithio-carbamates

**Synthesis.**—The chief method for the preparation of dithiocarbamates remains the reaction of  $CS_2$  with amines, sometimes in the presence of an added base, and alkylation of the dithiocarbamate ion if an ester is required. The heat of formation of diethylammonium diethyldithiocarbamate, made by this method, has been determined.<sup>259</sup> Polymeric dithiocarbamates are made from  $CS_2$  with amino-celluloses<sup>260</sup> or linear poly(iminoethylene).<sup>261</sup> Amino-acids, when treated with  $CS_2$  and alkali, and then with ethyl bromide, give dithiocarbamic esters,  $EtSCSNHCHRCO_2H$ , which are sufficiently volatile for mass spectrometry by the direct-inlet probe, without the need to esterify the carboxyl groups.<sup>262</sup> Dithiocarbamates from amino-acids have been incorporated into macrocyclic compounds which are multidentate ligands.<sup>263</sup> Cyclic amides, including 2-pyrrolidone, 2-piperidone, imidazolidin-2-one, and 2,5-dioxopiperazine, give 1-dithiocarboxylic acids and/or 1,3-bis-dithiocarboxylic acids, depending on the reaction conditions (Scheme 13), but imido-groups that are between two carbonyl groups are not attacked by  $CS_2$ .<sup>264</sup> 2-Aminopyridine methiodide reacts with  $CS_2$  and NaOH to

<sup>257</sup> S. Kato, K. Sugino, M. Mizuta, and T. Katada, *Angew. Chem.*, 1978, **90**, 718.

<sup>258</sup> V. I. Cohen, *J. Heterocycl. Chem.*, 1978, **15**, 237.

<sup>259</sup> K. J. Cavell, J. O. Hill, and R. J. Magee, *Thermochim. Acta*, 1979, **33**, 377.

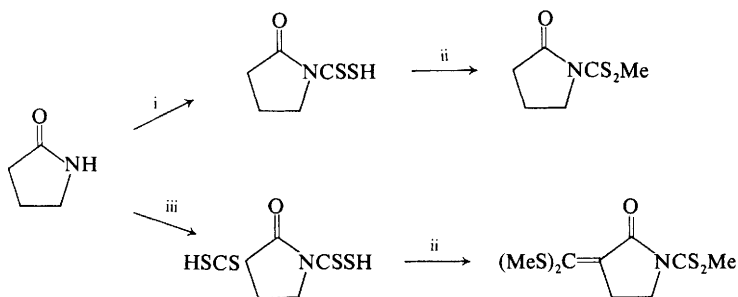
<sup>260</sup> S. Imai, M. Muroi, A. Hamaguchi, R. Matsushita, and M. Koyama, *Anal. Chim. Acta*, 1980, **113**, 139.

<sup>261</sup> K. J. Ivin and E. D. Lillie, *Makromol. Chem.*, 1978, **179**, 591.

<sup>262</sup> J. Szafranek, G. Blotny, and P. Vouros, *Tetrahedron*, 1978, **34**, 2763.

<sup>263</sup> G. Blotny and J. F. Biernat, *Pol. J. Chem.*, 1979, **53**, 689 (*Chem. Abstr.*, 1979, **91**, 123 725).

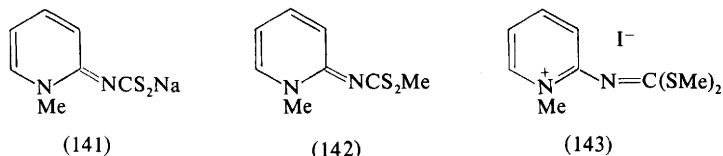
<sup>264</sup> T. Takeshima, M. Ikeda, M. Yokoyama, N. Fukada, and M. Muraoka, *J. Chem. Soc., Perkin Trans. 1*, 1979, 692.



Reagents: i,  $\text{CS}_2$ , KOH; ii, MeI; iii,  $\text{CS}_2$ , NaH

Scheme 13

give a dithiocarbamate (141), in which methylation gives successively a methyl ester (142) and a quaternized *SS*-dimethyl *N*-(2-pyridyl)dithiocarbonimidate (143).



Similar products are obtained from the methiodides of 2-aminopyrimidine and 2-aminothiazole, but 4-aminopyridine methiodide gives 1-methyl-4-thiopyridone.<sup>265</sup> Some pyridyl-alkyl esters of dithiocarbamates have been made by treatment of the sodium salts with 2-(chloromethyl)pyridine or 2-vinylpyridine,<sup>266</sup> and 6-chloro-3-pyridyl *NN*-dimethylthiocarbamate by reaction with diazotized 3-amino-6-chloropyridine.<sup>267</sup>

A second route to dithiocarbamic esters uses the reaction of isothiocyanates with thiols.<sup>266,268</sup> Cysteine and similar compounds containing mercapto- and amino-groups react with isothiocyanates through the mercapto-group at pH 4–6, giving dithiocarbamates, but, in alkaline solution (pH ~ 9), the reaction occurs at the amino-group.<sup>269</sup> The reaction of amines with aryloxythiocarbonyl chlorides,  $\text{ArOCSCl}$ , gave thiocarbamic esters of phenols.<sup>270</sup>

$\gamma$ -Aryltrithioallophanic acids,  $\text{ArNHC(S)NHCSSH}$ , are prepared by thiolysis of their allylbenzyl esters, which are made from aryl isothiocyanates and  $\text{PhCH}_2\text{SC(=NH)SCH}_2\text{CH=CH}_2$ .<sup>271</sup> Thiolysis of 2-alkoxycarbonyl-3-imino-5-methylthio-1,2,4-thiadiazolines gives *N*<sup>1</sup>-alkoxycarbonyl-*N*<sup>2</sup>-(methylthio)thiocarbonylguanidines with loss of sulphur (Scheme 14).<sup>272</sup> Thiocarbamate esters that are unsubstituted

<sup>265</sup> K. Mizuyama, Y. Tominaga, Y. Matsuda, and G. Kobayashi, *Chem. Pharm. Bull.*, 1979, **27**, 2879.

<sup>266</sup> J. Berner and K. Kirmse, *Z. Chem.*, 1978, **18**, 381.

<sup>267</sup> K. Krowicki, *Pol. J. Chem.*, 1979, **53**, 889 (*Chem. Abstr.*, 1979, **91**, 140 689).

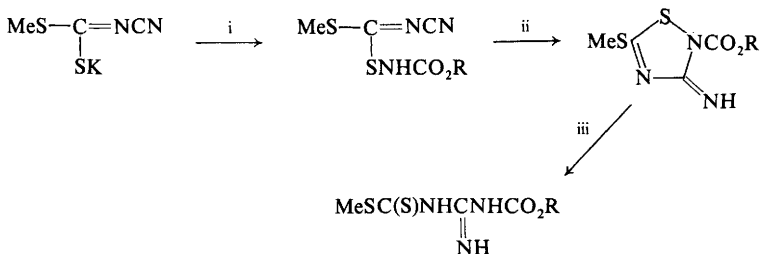
<sup>268</sup> F. Pavanetto, M. Mazza, L. Montanari, and T. Modena, *Farmaco, Ed. Sci.*, 1979, **34**, 808.

<sup>269</sup> D. Podhradský, L. Drobica, and P. Kristian, *Experientia*, 1979, **35**, 154.

<sup>270</sup> V. Konečný, S. Varkonda, and N. Kuličková, *Collect. Czech. Chem. Commun.*, 1979, **44**, 918.

<sup>271</sup> M. H. Damle, *Indian J. Chem., Sect. B*, 1979, **17**, 17 (*Chem. Abstr.*, 1980, **92**, 41 527).

<sup>272</sup> T. Fuchigami and T. Nonaka, *Chem. Lett.*, 1979, 829.



Reagents: i,  $\text{ClNHCO}_2\text{R}$ ; ii,  $\text{H}^+$ ; iii,  $\text{H}_2\text{S}$

Scheme 14

tuted on nitrogen are obtained, with other products, by prolonged treatment of alkyl or aryl thiocyanates with  $(\text{Pr}^t\text{O})_2\text{P}(\text{S})\text{SH}$  at  $20^\circ\text{C}$ .<sup>273</sup>

Sodium dialkyldithiocarbamates react with perfluoropropene both by substitution and by addition, to give  $\text{CF}_3\text{CF}=\text{CFSC}(\text{S})\text{NR}_2$  [(*E*) and (*Z*) forms] and  $\text{CF}_3\text{CHF}(\text{CF}_2)\text{SC}(\text{S})\text{NR}_2$ , respectively. Pyrolysis of the latter compounds gives quantitative yields of dialkylthiocarbamoyl fluorides.<sup>274</sup> Treatment of *N*-trimethylsilyl-amines with an excess of thiophosgene gives good yields of thiocarbamoyl chlorides of excellent purity. Bis(thiocarbamoyl) chlorides,  $\text{X}(\text{NRCSCl})_2$ , are obtained from *NN'*-bis(trimethylsilyl)diamines.<sup>275</sup>

**Physical Properties.**—The i.r. spectra of dithiocarbamate and diselenocarbamate ions have been compared.<sup>276</sup> In continuation of earlier work,<sup>277</sup> a dynamic  $^1\text{H}$  n.m.r. investigation of restricted rotation at the  $\text{N}-\text{C}-\text{X}$  bond in  $\text{H}_2\text{C}=\text{CMeCH}_2-\text{N}(\text{R})-\text{CXY}$  ( $\text{X} = \text{O}$ ,  $\text{Y} = \text{SEt}$ ; or  $\text{X} = \text{S}$ ,  $\text{Y} = \text{OPh}$ ) has been made.<sup>278</sup> Numerous dithiocarbamates, mostly metal salts and complexes, have been studied by  $^{13}\text{C}$  n.m.r. spectroscopy, and the chemical shifts of carbon in the  $\text{NCS}_2$  fragment have been correlated with the degree of  $\pi$ -bonding.<sup>279</sup> An *X*-ray crystallographic study of the fungicide Denmert (144) showed the pyridyl and benzyl groups to be in a *syn* configuration, but n.m.r. evidence showed that the *syn*- and *anti*-forms are in equilibrium in solution.<sup>280</sup>

**Reactions.**—Electrolytic oxidation of dialkylamines and  $\text{CS}_2$  in an undivided cell, with solvent extraction of the product, provides a simple preparative method for bis(dialkylthiocarbamoyl) disulphides (thiuram disulphides),<sup>281</sup> and electrolytic

<sup>273</sup> A. N. Pudovik, R. A. Cherkasov, M. G. Zimin, and R. M. Kamalov, *Zh. Obshch. Khim.*, 1978, **48**, 2645 (*Chem. Abstr.*, 1979, **90**, 137 443).

<sup>274</sup> T. Kitazume, S. Sasaki, and N. Ishikawa, *J. Fluorine Chem.*, 1978, **12**, 193.

<sup>275</sup> S. J. i Skorini and A. Senning, *Tetrahedron*, 1980, **36**, 539.

<sup>276</sup> K. N. Tantry and M. L. Shankaranarayana, *Indian J. Chem., Sect. A*, 1979, **18**, 347 (*Chem. Abstr.*, 1980, **92**, 31 345).

<sup>277</sup> E. Kleinpeter, R. Widera, and M. Mühlstädt, *J. Prakt. Chem.*, 1977, **319**, 133; *Z. Chem.*, 1977, **17**, 298.

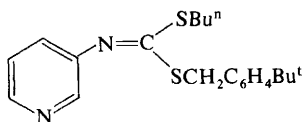
<sup>278</sup> E. Kleinpeter, R. Widera, and M. Mühlstädt, *J. Prakt. Chem.*, 1978, **320**, 279.

<sup>279</sup> H. L. M. Van Gaal, J. W. Diesveld, F. W. Pijpers, and J. G. M. Van der Linden, *Inorg. Chem.*, 1979, **18**, 3251.

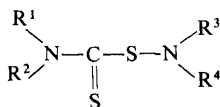
<sup>280</sup> S. Tanaka, T. Kato, S. Yamamoto, H. Yoshida, Z. Taira, and W. H. Watson, *Agric. Biol. Chem.*, 1978, **42**, 287.

<sup>281</sup> S. Torii, H. Tanaka, and K. Misima, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1575.

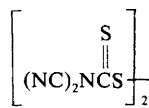
oxidation of these in the presence of amines gives the thiocarbamoylsulphenamides (145).<sup>282</sup> Oxidation of potassium dicyanimidodithioformate with iodine gives *N*-tetracyanothiuram disulphide (146).<sup>283</sup> The free acid (NC)<sub>2</sub>NCS<sub>2</sub>H has been made and its physical constants have been determined.<sup>284</sup> Thiocarbamic esters R<sup>1</sup>R<sup>2</sup>NC(O)SR<sup>3</sup> are prepared by the oxidation of dithiocarbamic esters with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and H<sub>2</sub>SO<sub>4</sub>.<sup>285</sup>



(144)

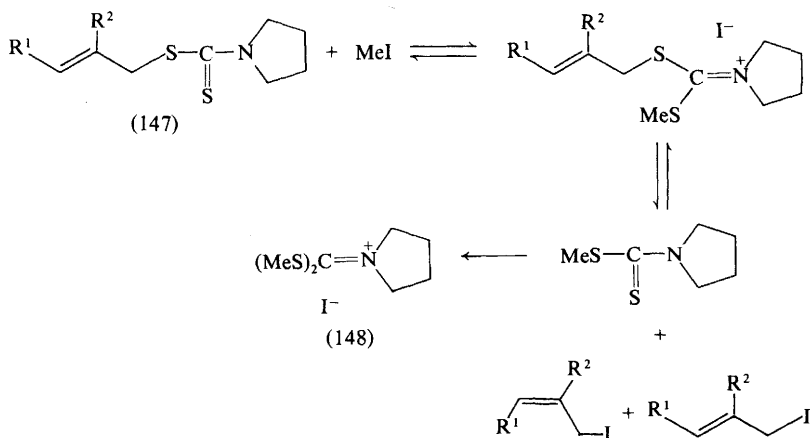


(145)



(146)

Pyrolysis of *S*-ethyl *N*-disubstituted dithiocarbamates gives ethylene, CS<sub>2</sub>, and secondary amines and/or a trisubstituted thiourea and ethanethiol.<sup>286</sup> *NNSS'*-Tetrasubstituted dithiocarbamidium iodides, obtained by *S*-alkylating dithiocarbamates, are in equilibrium with their precursors, and this equilibrium has been used in the conversion of allylic dithiocarbamates, particularly allylic 1-pyrrolidine-carbodithioates (147), into allylic iodides by treatment with methyl iodide; bis(methylthio)methylenepyrrolidinium iodide (148) is insoluble, and it precipitates from the reaction mixture (Scheme 15).<sup>287</sup> *NNSS'*-Tetramethyldithiocarbamidium iodide (149) reacts with hydroxylamine or semicarbazide with displacement of the dimethylamino-group, but with other nucleophiles, *e.g.* thiosemicarbazide or



Scheme 15

<sup>282</sup> S. Torii, H. Tanaka, and M. Ukida, *J. Org. Chem.*, 1978, **43**, 3223.

<sup>283</sup> G. Gattow and H. Hlawatschek, *Z. Anorg. Allg. Chem.*, 1979, **454**, 131.

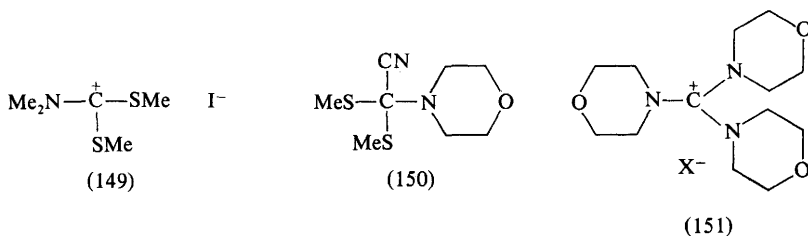
<sup>284</sup> G. Gattow and H. Hlawatschek, *Z. Anorg. Allg. Chem.*, 1979, **454**, 125.

<sup>285</sup> S. A. Staicu and D. M. Constantin, *Rom. P.* 65 590 (*Chem. Abstr.*, 1980, **92**, 58 256).

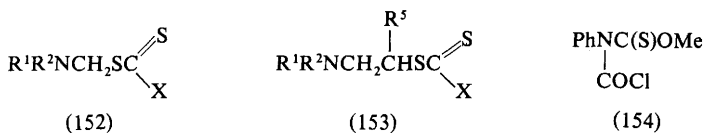
<sup>286</sup> M. S. Chande, *J. Indian Chem. Soc.*, 1979, **56**, 386 (*Chem. Abstr.*, 1979, **91**, 192 553).

<sup>287</sup> A. Sakurai, T. Hayashi, I. Hori, Y. Jindo, and T. Oishi, *Synthesis*, 1978, 370.

amines, one or both of the methylthio-groups are replaced.<sup>288</sup> The morpholine analogue of (149) loses morpholine on thiolysis, giving dimethyl trithiocarbonate, but its other reactions include addition of cyanide ion to give (150) and replacement of the methylthio-groups by morpholine, giving the guanidinium salt (151).<sup>289</sup>



S-Methyl dithiocarbamates attack the reactive methylene groups of cyanoacetamide, cyanoacetic ester, or bis(phenylsulphonyl)methane with loss of methanethiol and formation of the thioamides  $\text{R}^1\text{R}^2\text{CHC}(\text{S})\text{NR}^3\text{R}^4$ .<sup>290,291</sup> Diazomethane and phenyldiazomethane, which is more reactive, insert into dialkylaminomethyl esters of dialkylthiocarbamic acids (152;  $\text{X} = \text{NR}^3\text{R}^4$ ) or ethyl xanthic acid (152;  $\text{X} = \text{OEt}$ ), giving esters (153;  $\text{R}^5 = \text{H}$  or  $\text{Ph}$ ,  $\text{X} = \text{NR}^3\text{R}^4$  or  $\text{OEt}$ ) that have an extended alkylene chain.<sup>292</sup>



Alkali-metal salts of *O*-methyl *N*-phenylthiocarbamate are acylated on nitrogen by  $\text{COCl}_2$ , giving the carbamoyl chloride (154), but they react with benzenesulphonyl chloride to give the disulphide  $[\text{PhN}=\text{C}(\text{OMe})\text{S}]_2$ , presumably through *S*-acylation of the ambident anion and decomposition of the acyl derivative.<sup>293</sup> Treatment of *O*-ethyl *N*-monosubstituted thiocarbamates with butyl-lithium gives lithiated derivatives, which decompose to give isothiocyanates, the reaction being accelerated by  $\text{CS}_2$ .<sup>294</sup> Acylation of methyl *N*-aryldithiocarbamates with propiolactone in  $\text{Ac}_2\text{O}$  gives 4-oxo-2-thioxotetrahydro-1,3-thiazines (155) in low yield.<sup>295</sup> 2-Dialkylamino-1,3-oxathiol-2-ylum salts (156) are conveniently made by cyclizing 2-oxoalkyl dithiocarbamates (157) with dimethyl sulphate at 100–120 °C.<sup>296</sup>

<sup>288</sup> S. A. Okecha, *Chem. Ind. (London)*, 1979, 526.

<sup>289</sup> F. Stansfield and M. D. Coomassie, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2708.

<sup>290</sup> I. M. Bazavova, R. G. Dubenko, and P. S. Pel'kis, *Zh. Org. Khim.*, 1978, **14**, 195 (*Chem. Abstr.*, 1978, **88**, 152 374).

<sup>291</sup> I. M. Bazavova, E. F. Gorbenko, R. G. Dubenko, and P. S. Pel'kis, *Zh. Org. Khim.*, 1979, **15**, 1213 (*Chem. Abstr.*, 1979, **91**, 211 048).

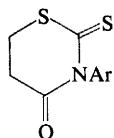
<sup>292</sup> Y. Akasaka, K. Suzuki, T. Morimoto, and M. Sekiya, *Chem. Pharm. Bull.*, 1979, **27**, 2327.

<sup>293</sup> W. Mack, *Chem. Ber.*, 1980, **113**, 165.

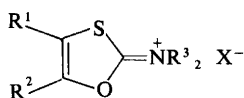
<sup>294</sup> T. Fujinami, M. Ashida, and S. Sakai, *Nippon Kagaku Kaishi*, 1978, 773 (*Chem. Abstr.*, 1978, **89**, 108 570).

<sup>295</sup> W. Hanefeld, *Arch. Pharm. (Weinheim, Ger.)*, 1979, **312**, 635.

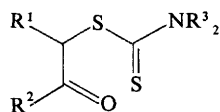
<sup>296</sup> Y. Ueno and M. Okawara, *Synthesis*, 1979, 182.



(155)

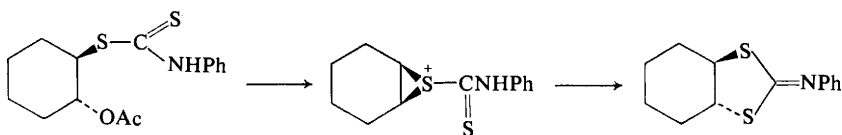


(156)



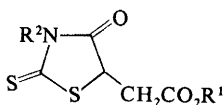
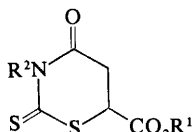
(157)

*trans*-2-(Phenylthiocarbamoylthio)cyclohexyl acetate (158) or its *S*-acetyl derivative cyclizes to *trans*-2-phenyliminoperhydro-1,3-benzodithiole in the presence of KOH in ethanol. Since there is retention of configuration, the reaction is considered to proceed *via* an episulphonium ion intermediate, as shown in Scheme 16. The *cis* analogues do not cyclize.<sup>297</sup>

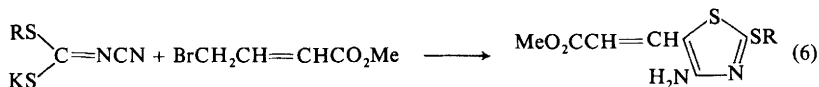


(158)

Scheme 16

(159) R<sup>1</sup> = Me or Et(160) R<sup>1</sup> = Me or Et

Several reactions leading to thiazole derivatives have been reported. Primary amines react with CS<sub>2</sub> and methyl or ethyl maleate to give rhodanilylacetaes (159), and not the expected 1,3-thiazines (160).<sup>298</sup> The potassium salts of cyanimidodithiocarbonates, when alkylated by  $\gamma$ -bromocrotonic esters or  $\gamma$ -bromocrotononitrile, give 4-aminothiazoles through attack of the cyano-group on the activated methylene group [reaction (6)]. Salts of *N*<sup>1</sup>*N*<sup>1</sup>-disubstituted *N*<sup>2</sup>-cyano-



thiourea undergo a similar ring-closure, but *N*<sup>1</sup>-monosubstituted *N*<sup>2</sup>-cyanothioureas cyclize to thiazolidines (161) by an internal Michael addition.<sup>299</sup> Some *S*<sup>1</sup>-alkyl *S*<sup>2</sup>-benzyl *N*-cyanoimidodithiocarbonates are cyclized by base to the analogous 4-aminothiazoles.<sup>300</sup> *S*-Methyl *N*-acyldithiocarbamates may be alkylated

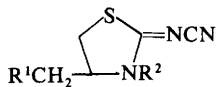
<sup>297</sup> R. C. Foster and L. N. Owen, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1208.

<sup>298</sup> W. Hanefeld and W. Hinz, *Arch. Pharm. (Weinheim, Ger.)*, 1980, **313**, 20.

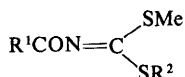
<sup>299</sup> D. Wobig, *Liebigs Ann. Chem.*, 1978, 1118.

<sup>300</sup> P. Lipka and D. Wobig, *Liebigs Ann. Chem.*, 1979, 757.

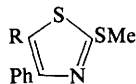
to give *N*-acyliminodithiocarbonic acid diesters (162), and when these have a reactive methylene group, e.g. (162; R<sup>1</sup> = Ph, R<sup>2</sup> = PhCH<sub>2</sub> or PhCOCH<sub>2</sub>), they cyclize to thiazoles (163; R = Ph or PhCO). Mono- and di-substitution of the diesters (162) with amines gives thioureas, guanidines, or heterocyclic compounds.<sup>301</sup>



(161)



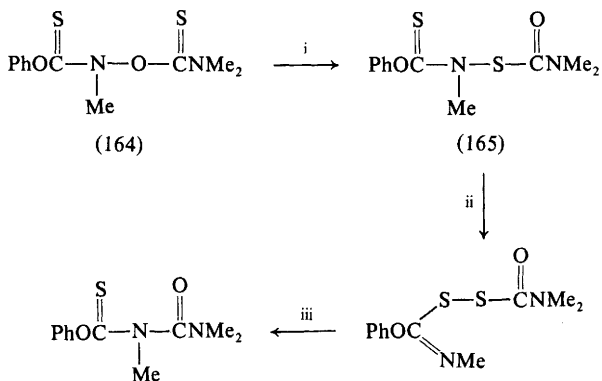
(162)



(163)

Sodium *NN*-diethyldithiocarbamate reacts with TeCl<sub>4</sub> to give Te(Et<sub>2</sub>NCS<sub>2</sub>)<sub>3</sub>Cl, which has a pentagonal-bipyramidal structure.<sup>302</sup> Some other organotellurium dithiocarbamates R<sup>1</sup><sub>2</sub>Te(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub> have been reported.<sup>303</sup>

The hydroxylamine derivative (164) is of interest since it undergoes a hetero-Cope rearrangement through the intermediate (165), which has been isolated (Scheme 17).<sup>304</sup>



Reagents: i, MeOH, at 25 °C; ii, MeOH, at 55 °C; iii, desulphurize

Scheme 17

## 6 Xanthates and Trithiocarbonates

**Preparation.**—The reaction of alcohols with CS<sub>2</sub> under strongly alkaline conditions remains the standard method for preparing xanthates (*O*-alkyl dithiocarbonates). Alkylation of xanthates to *OS*-dialkyl dithiocarbonates is conveniently done by a phase-transfer process, using an alkyl halide or an alkyl methanesulphonate,<sup>305</sup> and

<sup>301</sup> M. Augustin, M. Richter, and S. Salas, *J. Prakt. Chem.*, 1980, **322**, 55.

<sup>302</sup> W. Schnabel, K. Von Deuten, and G. Klar, *Chem.-Ztg.*, 1979, **103**, 231.

<sup>303</sup> T. N. Srivastava, R. C. Srivastava, and A. Bhargava, *Indian J. Chem., Sect. A*, 1979, **18**, 236 (*Chem. Abstr.*, 1980, **92**, 163 801).

<sup>304</sup> A. J. Lawson, *J. Chem. Soc., Chem. Commun.*, 1979, 456.

<sup>305</sup> I. Degani and R. Fochi, *Synthesis*, 1978, 365.

it may also be performed by 1-alkyl-2,4,6-triphenylpyridinium perchlorates.<sup>306</sup> *S*-Methyl dithiocarbonates of 6-*O*-tritylamylose and 6-*O*-tritylcellulose with a high degree of substitution were obtained by treating the *O*-trityl polysaccharide, dissolved in DMSO, successively with the methylsulphinyl anion, with CS<sub>2</sub>, and with methyl iodide. Oxidation of the unmethylated xanthate with nitrous acid gave dithiobis(thioformates).<sup>307</sup> Boron trifluoride etherate catalyses the rearrangement of *OS*-dialkyl dithiocarbonates to *SS*-dialkyl dithiocarbonates. The reaction was studied kinetically, and a crossover reaction between the dimethyl and diethyl esters showed that the process is intermolecular.<sup>308</sup> Some alkylthioxanthic acids (mono-esters of trithiocarbonic acid) have been made by acidification of their potassium salts.<sup>309</sup> Aryl chlorodithiocarbonates, ArSC(S)Cl, are obtained in ~20% yield from arenediazonium chlorides and CS<sub>2</sub>, with catalysis by copper or CuCl.<sup>310</sup>

**Physical Properties.**—The i.r. spectra and normal vibrations of *O*-methyl thiocarbonate, *S*-methyl dithiocarbonate, *N*-methylthiocarbamate, methyl trithiocarbonate, and similar ions have been related and compared.<sup>311</sup> Band assignments were made for the i.r. spectra of monoalkyl trithiocarbonates and for the Raman spectrum of methyl trithiocarbonate.<sup>312</sup> The mass-spectral fragmentation patterns of dialkyl trithiocarbonates have been studied.<sup>313</sup> The formation of tris(organo-thiyl)methyl radicals, R<sub>n</sub>MSC(SR<sup>1</sup>)<sub>2</sub>, by the reaction of trithiocarbonates with the transient radicals R<sub>n</sub>M• has been demonstrated by electron paramagnetic resonance studies.<sup>314</sup> A dodecant rule has been developed for predicting the relative sign of the Cotton effect of chiral xanthates at 355 nm. In the preferred conformation the hydrogen in the geminal position to the oxygen adapts a *syn* periplanar orientation towards the C=S double bond.<sup>315</sup> X-Ray crystallography of three carbohydrate xanthates showed that they have the same conformation in the crystal as that preferred in solution.<sup>316</sup>

**Reactions.**—Unsymmetrical dialkyl sulphides are obtained by the action of aqueous KOH, at 80 °C, on *OS*-dialkyl dithiocarbonates (with different alkyl groups) under phase-transfer conditions.<sup>317</sup> The reaction depends on the liberation of a mercaptan and its alkylation by the *O*-alkyl group of the diester. Ethoxythiocarbonyl derivatives of amino-acids are made by acylating the amino-acids with the stable reagent bis(ethoxythiocarbonyl) sulphide, (EtOCS)<sub>2</sub>S. This is prepared by an improved method from potassium ethylxanthate (2 mol) and ethyl chloroformate (1 mol). Esters of amino-acids are acylated by carboxymethyl

<sup>306</sup> A. R. Katritzky, U. Gruntz, N. Mongelli, and M. C. Rezende, *J. Chem. Soc., Chem. Commun.*, 1978, 133; *J. Chem. Soc., Perkin Trans. 1*, 1979, 1953.

<sup>307</sup> N. W. H. Cheetham, *Carbohydr. Res.*, 1978, **65**, 144.

<sup>308</sup> K. Komaki, T. Kawata, K. Harano, and T. Taguchi, *Chem. Pharm. Bull.*, 1978, **26**, 3807.

<sup>309</sup> D. Hoerner and G. Gattow, *Z. Anorg. Allg. Chem.*, 1978, **442**, 195.

<sup>310</sup> H. Viola and R. Mayer, *Z. Chem.*, 1979, **19**, 289.

<sup>311</sup> K. N. Tantry and M. L. Shankaranarayana, *Proc. Indian Acad. Sci., Sect. A*, 1979, **88**, 457 (*Chem. Abstr.*, 1980, **92**, 118 832).

<sup>312</sup> D. Hoerner and G. Gattow, *Z. Anorg. Allg. Chem.*, 1978, **442**, 204.

<sup>313</sup> D. Hoerner and G. Gattow, *Z. Anorg. Allg. Chem.*, 1978, **444**, 117.

<sup>314</sup> D. Forrest and K. U. Ingold, *J. Am. Chem. Soc.*, 1978, **100**, 3868.

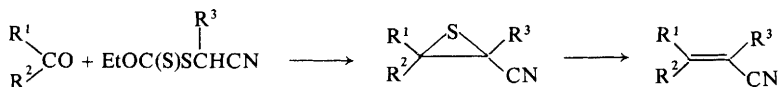
<sup>315</sup> H. Paulsen, B. Elvers, H. Redlich, E. Schüttelz, and G. Snatzke, *Chem. Ber.*, 1979, **112**, 3842.

<sup>316</sup> P. Luger, B. Elvers, and H. Paulsen, *Chem. Ber.*, 1979, **112**, 3855.

<sup>317</sup> I. Degani, R. Fochi, and V. Regondi, *Synthesis*, 1979, 178.

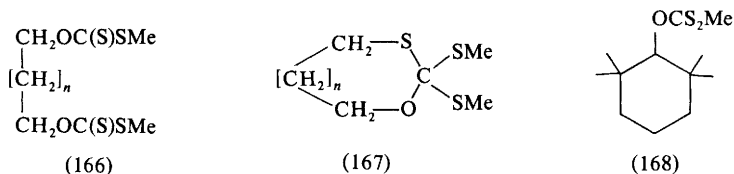


*O*-ethylxanthate,  $\text{EtOC}(=\text{S})\text{SCH}_2\text{CO}_2\text{H}$ .<sup>318</sup> *O*-Ethyl *S*-cyanomethyl dithio-carbonate condenses with ketones, under basic conditions, to give alk-2-enitriles,<sup>319</sup> as shown in Scheme 18.



Scheme 18

Thermolysis of bis-(*S*-methyl dithiocarbonates) of 1,2- and 1,3-diols (166;  $n = 0$  or 1) gives cyclic *OS*-di- or tri-methylene *SS*-dimethyl trithio-orthocarbonates (167;  $n = 0$  or 1), the C-S bond being formed preferentially at a primary carbon atom.<sup>320</sup> This reaction has been applied in the carbohydrate field.<sup>321, 322</sup> *S*-Methyl dithiocarbonates derived from suitably protected monosaccharides or amino-glycosides are reduced to deoxy-sugars by tributyltin hydride or tributyltin deuteride, the reaction being highly stereoselective.<sup>323–327</sup> Vicinal diols are converted into olefins in high yield by the reaction of their bis-(*S*-methyl dithiocarbonate) derivatives with tri-*n*-butylstannane.<sup>328</sup> Rearranged olefins are obtained from cyclohexyl xanthates, e.g. (168), with elimination of the xanthate residue, by heating with  $[\text{RhCl}(\text{PPh}_3)_3]$  or its Ir, Pd, or Pt analogue.<sup>329</sup>



1,3-Dithiole-2-thiones are obtained in good yield by alkylating sodium *t*-butyl trithiocarbonate with propargyl halides and heating the unsymmetrical ester with TFA in acetic acid (Scheme 19).<sup>330</sup>

Alkyl (and aryl) chlorodithioformates,  $\text{RSC}(\text{S})\text{Cl}$ , react with potassium toluene-*p*-thiosulphonate to give  $\text{RSC}(\text{S})\text{SSTs}$ ,  $\text{RSC}(\text{S})\text{Ts}$ , and  $[\text{RSC}(\text{S})\text{S}]_2$ , none of the expected primary product, *i.e.*  $\text{RSC}(\text{S})\text{STs}$ , being isolated.<sup>331</sup>

<sup>318</sup> G. Barany, B. W. Fulpius, and T. P. King, *J. Org. Chem.*, 1978, **43**, 2930.

<sup>319</sup> K. Tanaka, N. Ono, Y. Kubo, and A. Kaji, *Synthesis*, 1979, 890.

<sup>320</sup> A. Faure and G. Descotes, *Synthesis*, 1978, 286.

<sup>321</sup> G. Descotes and A. Faure, *Synthesis*, 1976, 449.

<sup>322</sup> A. Faure, B. Kryczka, and G. Descotes, *Carbohydr. Res.*, 1979, **74**, 127.

<sup>323</sup> D. H. R. Barton and S. W. McCombie, *J. Chem. Soc., Perkin Trans. I*, 1975, 1574.

<sup>324</sup> T. Hayashi, T. Iwaoka, N. Takeda, and E. Ohki, *Chem. Pharm. Bull.*, 1978, **26**, 1786.

<sup>325</sup> J. J. Patroni and R. V. Stick, *J. Chem. Soc., Chem. Commun.*, 1978, 449.

<sup>326</sup> J. J. Patroni and R. V. Stick, *Aust. J. Chem.*, 1979, **32**, 411.

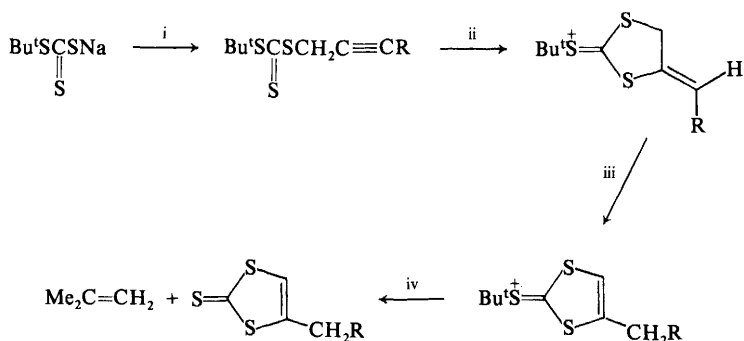
<sup>327</sup> E. M. Acton, R. N. Goerner, H. S. Uh, K. J. Ryan, D. W. Henry, C. E. Cass, and G. A. Lepage, *J. Med. Chem.*, 1979, **22**, 518.

<sup>328</sup> A. G. M. Barrett, D. H. R. Barton, and R. Bielski, *J. Chem. Soc., Perkin Trans. I*, 1979, 2378.

<sup>329</sup> R. Hamilton, T. R. B. Mitchell, J. J. Rooney, and M. A. McKervey, *J. Chem. Soc., Chem. Commun.*, 1979, 731.

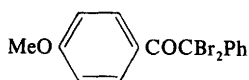
<sup>330</sup> N. F. Haley, *Tetrahedron Lett.*, 1978, 5161.

<sup>331</sup> H. C. Hansen and A. Senning, *J. Chem. Soc., Chem. Commun.*, 1979, 1135.

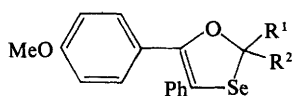


Reagents: i,  $\text{BrCH}_2\text{C}\equiv\text{CR}$ ; ii, TFA, at 25 °C; iii, 100 °C; iv, HOAc, at 100 °C

**Scheme 19**



(169)



(170)  $\text{R}^1\text{R}^2 = \text{O}$

(171)  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{COC}_6\text{H}_4\text{OMe-}p$

Potassium *O*-ethyl diselenocarbonate reacts with the dibromo-ketone (169) to give the two 1,3-oxaselenoles (170) and (171) and *O,Se*-diethyl diselenocarbonate.<sup>332</sup>

<sup>332</sup> C. Bak, K. Praefcke, and L. Henriksen, *Chem.-Ztg.*, 1978, **102**, 361.

### 1 Thiirans (Episulphides)

**Reviews**—A book on thiirans<sup>1</sup> and a review covering the reactivity of thiirans<sup>2</sup> have been published by the same authors. Thiirens,<sup>3</sup> thiiranium ions,<sup>4</sup> and thiirenium ions<sup>5</sup> have been reviewed. Small rings are among the compounds covered in a book on reactive species<sup>6</sup> and a review on the pyrolysis of sulphones.<sup>7</sup> Two reviews on heterocyclic analogues of methylenecyclopropanes have appeared,<sup>8,9</sup> and a survey of the recent literature in the area of heterocyclic compounds includes three- and four-membered rings that contain chalcogens.<sup>10</sup> For coverage of biologically active steroidal episulphides and naturally occurring episulphides, see the bibliography on page 232.

**Formation**.—The full paper showing that the compound previously reported to be 2,3-dibenzoyl-2,3-diphenylthiiran is actually 2,4,5-triphenyl-1,3-oxathiole has appeared<sup>11</sup> (see Vol. 1, p. 115 and Vol. 2, p. 102).

The preparation of thiirans by the reaction of diazo-compounds with thiocarbonyls has received widespread use.<sup>12–22</sup> In particular, a number of preparations of

<sup>1</sup> A. V. Fokin and A. F. Kolomiets, 'Khimiya Tiiranov' ('Chemistry of Thiiranes'), Nauka, Moscow, 1978.

<sup>2</sup> A. V. Fokin and A. F. Kolomiets, *Russ. Chem. Rev. (Engl. Transl.)*, 1976, **45**, 25.

<sup>3</sup> M. Torres, E. M. Lown, and O. P. Strausz, *Heterocycles*, 1978, **11**, 697.

<sup>4</sup> (a) V. N. Gogte and H. M. Modak, in 'New Trends in Heterocyclic Chemistry,' ed. R. B. Mitra, Elsevier, Amsterdam, 1979, p. 142; (b) W. A. Smit, N. S. Zefirov, I. V. Bodrikov, and M. Z. Krimer, *Acc. Chem. Res.*, 1979, **12**, 282.

<sup>5</sup> G. Capozzi, V. Lucchini, and G. Modena, *Rev. Chem. Intermed.*, 1979, **2**, 347.

<sup>6</sup> E. Block, 'Reactions of Organosulfur Compounds,' Academic Press, New York, 1978.

<sup>7</sup> F. Vogtle and L. Rossa, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 515.

<sup>8</sup> G. L'abbé, in 'Topics in Organic Sulphur Chemistry,' ed. M. Tisler, University Press, Ljubljana, Yugoslavia, 1978, Ch. 6.

<sup>9</sup> G. L'abbé, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 276.

<sup>10</sup> A. R. Katritzky and P. M. Jones, *Adv. Heterocycl. Chem.*, 1979, **25**, 303.

<sup>11</sup> U. J. Kempe, T. Kempe, and T. Norin, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1547.

<sup>12</sup> F. M. E. Abdel-Megeid, A. A. Elbarbary, and F. A. Gad, *Pol. J. Chem.*, 1979, **53**, 1877.

<sup>13</sup> M. O-oka, A. Kitamura, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 301.

<sup>14</sup> K. Friedrich and M. Zamkanci, *Chem. Ber.*, 1979, **112**, 1873.

<sup>15</sup> M. Tashiro, S. Mataka, and S. Ishi-i, *Heterocycles*, 1979, **12**, 184.

<sup>16</sup> S. Mataka, S. Ishi-i, and M. Tashiro, *J. Org. Chem.*, 1978, **43**, 3730.

<sup>17</sup> M. S. Raasch, *J. Org. Chem.*, 1979, **44**, 632.

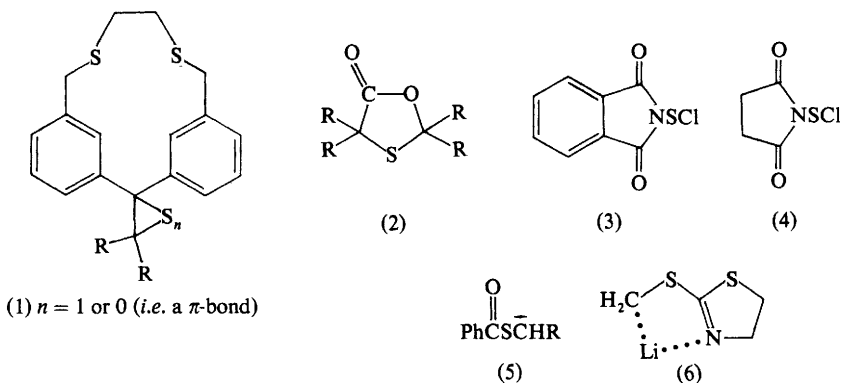
<sup>18</sup> M. Atzmueller and F. Vogtle, *Chem. Ber.*, 1979, **112**, 138.

<sup>19</sup> D. H. R. Barton, L. S. L. Choi, R. H. Hesse, and M. M. Pechet, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1166.

highly hindered thiirans and olefins have used this procedure; e.g., of (1).<sup>12</sup> Tetrasubstituted alkenes are also prepared *via* 1,3,4-thiadiazolines and hence episulphides<sup>23,24</sup> (see Vol. 5, p. 188). The flash pyrolysis of 1,3-oxathiolan-5-ones (2), related to the pyrolysis of thiadiazoline by loss of carbon dioxide rather than nitrogen, also gives thiirans stereospecifically.<sup>25,26</sup>

The conversion of oxirans into thiirans by the action of sulphur nucleophiles has been further exploited, using thiourea<sup>27-32</sup> or a thiocyanate.<sup>33-35</sup> Treatment of alkenes with (3) or (4), followed by reduction with  $\text{LiAlH}_4$ , gives thiirans in good yields in a process that provides an alternative method for the conversion of alkenes into episulphides.<sup>36</sup> Vicinal iodo-thiocyanates are converted into thiirans when treated with base.<sup>37</sup>

Conversions of aldehydes and ketones into thiirans have been reported, using the  $\alpha$ -anions of alkyl thiolbenzoates (5),<sup>38</sup> the dianions of  $\alpha$ -mercapto-esters,<sup>39</sup> and, in



<sup>20</sup> W. Friedrichsen, M. Betz, E. Buedt, H. J. Jurgens, R. Schmidt, I. Schwarz, and K. Visser, *Liebigs Ann. Chem.*, 1978, 440.

<sup>21</sup> M. D. Bachi, O. Goldberg, and A. Gross, *Tetrahedron Lett.*, 1978, 4167.

<sup>22</sup> M. A. F. Elkaschef, F. M. E. Abdel-Megeid, and A. A. Elbarbary, *Acta Chim. Acad. Sci. Hung.*, 1977, 157.

<sup>23</sup> D. J. Humphreys, C. E. Newall, G. H. Philipps, and G. A. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1978, 45.

<sup>24</sup> A. Krebs and W. Rueger, *Tetrahedron Lett.*, 1979, 1305.

<sup>25</sup> T. B. Cameron and H. W. Pinnick, *J. Am. Chem. Soc.*, 1979, **101**, 4755.

<sup>26</sup> T. B. Cameron and H. W. Pinnick, *J. Am. Chem. Soc.*, 1980, **102**, 744.

<sup>27</sup> H. Prinzbach, H. P. Boehm, S. Kagabu, V. Wessely, and H. V. Rivera, *Tetrahedron Lett.*, 1978, 1243.

<sup>28</sup> F. Haviv and B. Belleau, *Can. J. Chem.*, 1978, **56**, 2677.

<sup>29</sup> B. Kraska and L. Mester, *Tetrahedron Lett.*, 1978, 4583.

<sup>30</sup> I. L. Kuranova, E. V. Snetkova, and V. A. Gindin, *Vestn. Leningr. Univ., Fiz. Khim.*, 1978, 140 (*Chem. Abstr.*, 1978, **89**, 107 190).

<sup>31</sup> A. Hasegawa, Y. Kawai, H. Kasugai, and M. Kiso, *Carbohydr. Res.*, 1978, **63**, 131.

<sup>32</sup> T. Takigawa, M. Tominaga, K. Mori, and M. Matsui, *Agric. Biol. Chem.*, 1979, **43**, 1591.

<sup>33</sup> M. Goguelin and M. Sepulchre, *Makromol. Chem.*, 1979, **180**, 1215.

<sup>34</sup> I. M. Abdullabekov, F. Kh. Agaev, A. L. Shabanov, and M. M. Movsumzade, *Dokl. Akad. Nauk Az. SSR*, 1978, 34 (*Chem. Abstr.*, 1979, **90**, 6157).

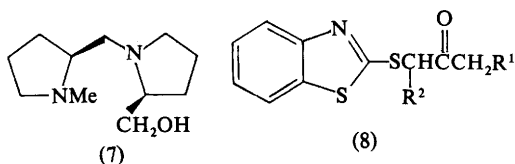
<sup>35</sup> C. A. Kingsbury, D. L. Durham, and R. Hutton, *J. Org. Chem.*, 1978, **43**, 4696.

<sup>36</sup> M. U. Bombala and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1979, 3013.

<sup>37</sup> R. C. Cambie, H. H. Lee, P. S. Rutledge, and P. D. Woodgate, *J. Chem. Soc., Perkin Trans. 1*, 1979, 765.

<sup>38</sup> D. B. Reitz, P. Beak, R. F. Farney, and L. S. Helmick, *J. Am. Chem. Soc.*, 1978, **100**, 5428.

<sup>39</sup> K. Tanaka, N. Yamagishi, R. Tanikaga, and A. Kaji, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3619.



an optically active form, using (6) in the presence of (7)<sup>40</sup> (see Vol. 4, p. 188). Also, derivatives (8) are converted into thiirans by sequential treatment with  $\text{NaBH}_4$  and  $\text{NaH}$ .<sup>41</sup>

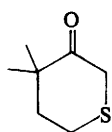
Diazotization of cysteine and its derivatives and of penicillamine and its derivatives yields thiirancarboxylic acids and esters.<sup>42</sup>

Direct addition of various forms of elemental sulphur to alkenes has been reported: of sulphur atoms (produced by photolysis of  $\text{COS}$ <sup>43</sup> or by laser irradiation of  $\text{S}_8$ <sup>44</sup>) and of cyclo-octasulphur (involving irradiation<sup>45</sup> or activation by amines<sup>46,47</sup>).

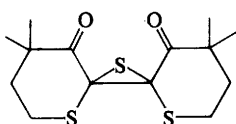
Treatment of (9) with thionyl chloride gave a 6% yield of (10), which could be desulphurized to the corresponding olefin with triphenylphosphine.<sup>48</sup>

Adamantylideneadamantene episulphide (11) was prepared by demethylation of the corresponding methyl episulphonium salt with chloride or bromide ion.<sup>49</sup>

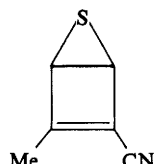
Di-*t*-butylsulphine reacts with primary Grignard reagents to give thiirans.<sup>50</sup> The



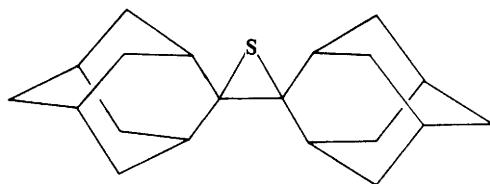
(9)



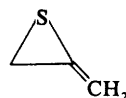
(10)



(12)



(11)



(13)

<sup>40</sup> K. Soai and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3371.

<sup>41</sup> V. Calo, L. Lopez, and G. Pesce, *Gazz. Chim. Ital.*, 1979, **109**, 703.

<sup>42</sup> C. D. Maycock and R. J. Stoodley, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1852.

<sup>43</sup> A. G. Sherwood, I. Safarik, B. Verkoczy, G. Almadi, H. A. Wiebe, and O. P. Strausz, *J. Am. Chem. Soc.*, 1979, **101**, 3000.

<sup>44</sup> D. R. Betteridge and J. T. Yardley, *Chem. Phys. Lett.*, 1979, **62**, 570.

<sup>45</sup> S. Inoue, T. Tezuka, and S. Oae, *Phosphorus Sulfur*, 1978, **4**, 219.

<sup>46</sup> J. Emsley, D. W. Griffiths, and G. J. J. Jayne, *J. Chem. Soc., Perkin Trans. 1*, 1979, 228.

<sup>47</sup> H. Kutlu, *Doga*, 1979, **3**, 71 (*Chem. Abstr.*, 1979, **91**, 211 321).

<sup>48</sup> U. Luhmann and W. Luettker, *Chem. Ber.*, 1978, **111**, 3246.

<sup>49</sup> J. Bolster and R. M. Kellogg, *J. Chem. Soc., Chem. Commun.*, 1978, 630.

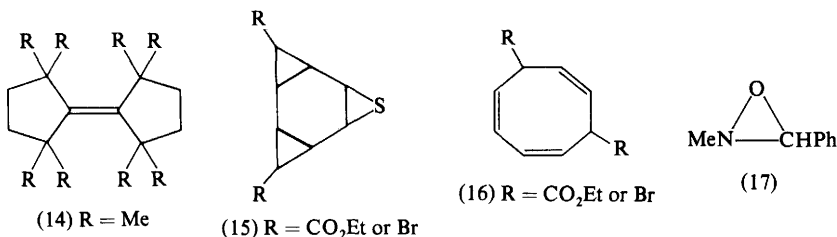
<sup>50</sup> A. Ohno, M. Uohama, K. Nakamura, and S. Oka, *J. Org. Chem.*, 1979, **44**, 2244.

'Dewar' thiophen (12) has been isolated, following irradiation of the parent thiophen.<sup>51,52</sup>

Allene episulphide (13) has been prepared, by flash vacuum pyrolysis, independently by two groups seeking cyclopropanethione.<sup>53,54</sup>

For spectroscopic information, see the bibliography on p. 232.

**Reactions.**—Desulphurization of thiirans to alkenes remains an important strategy for the preparation of hindered alkenes, *e.g.* (14),<sup>24</sup> and is the most typical thiiran reaction. Phosphines and phosphites are the reagents that are most often used.<sup>12–14, 17, 19, 20, 21, 24, 48</sup> Lithium reagents desulphurize *trans*-2,3-diphenylthiiran to (*E*)-stilbene, while the *cis*-isomer is converted into a 1 : 1 mixture of (*Z*)-stilbene and the two isomers of  $\alpha$ -mercaptostilbene.<sup>55</sup> 2-Phenylthiiran is desulphurized by  $\alpha$ -metallated isocyanides.<sup>56</sup> Thermal extrusions of sulphur include the conversion of (15) into (16),<sup>27</sup> amongst others.<sup>15, 18, 22</sup> Desulphurizations using zinc and acetic acid,<sup>23</sup> molybdenum<sup>57</sup> or palladium<sup>58</sup> complexes, and the oxaziridine (17)<sup>59</sup> have been reported.



Harder nucleophiles often react with thiirans to give a predominance of attack at carbon, with consequent cleavage of the weak carbon–sulphur bond. This strategy has been used to prepare 7-oxa-4-thia-alk-1-enes from alkoxides, thiiran, and allyl chlorides,<sup>60</sup>  $\beta$ -mercaptoethyl sulphides from thiiran and thiolate ions,<sup>61</sup> thiazines by the Cu<sub>2</sub>O-catalysed cyclization of the adducts of  $\alpha$ -lithio-isocyanides with thiirans,<sup>56</sup> tautomeric mixtures of (18) and (19) or (20) from thiiran and hydrazones,<sup>62</sup> *N*-methylpyrrolidines from bis(epithio)linoleic acid and methylamine,<sup>63</sup> and 2,4-dimethylhex-5-ene-2-thiol by addition of the Grignard reagent derived from 3-chlorobut-1-ene with 2,2-dimethylthiiran.<sup>64</sup> Methylthiiran has been found to open

<sup>51</sup> J. A. Barltrop, A. C. Day, and E. Irving, *J. Chem. Soc., Chem. Commun.*, 1979, 881.

<sup>52</sup> J. A. Barltrop, A. C. Day, and E. Irving, *J. Chem. Soc., Chem. Commun.*, 1979, 966.

<sup>53</sup> E. Jongejan, T. S. V. Buys, H. Steinberg, and T. J. De Boer, *Recl. Trav. Chim. Pays-Bas*, 1978, **97**, 214.

<sup>54</sup> E. Block, R. E. Penn, M. D. Ennis, T. A. Owens, and S. L. Yu, *J. Am. Chem. Soc.*, 1978, **100**, 7436.

<sup>55</sup> B. F. Bonini, G. Maccagnani, G. Mazzanti, and P. Piccinelli, *Tetrahedron Lett.*, 1979, 3987.

<sup>56</sup> U. Schollkopf, R. Jentsch, and K. Madawinata, *Liebigs Ann. Chem.*, 1979, 451.

<sup>57</sup> M. W. Bishop, J. Chatt, and J. R. Dilworth, *J. Chem. Soc., Dalton Trans.*, 1979, 1.

<sup>58</sup> A. L. Batch, L. S. Benner, and M. M. Olmstead, *Inorg. Chem.*, 1979, **18**, 2996.

<sup>59</sup> Y. Hata and M. Watanabe, *J. Org. Chem.*, 1980, **45**, 1691.

<sup>60</sup> A. A. Rodin, K. A. V'yunov, A. I. Ginak, and E. G. Sochilin, *Zh. Org. Khim.*, 1979, **15**, (a) p. 1272; (b) p. 2252.

<sup>61</sup> B. Bannister, *J. Chem. Soc., Perkin Trans. 1*, 1978, 967.

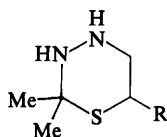
<sup>62</sup> S. M. Shevchenko and A. A. Potekhin, *Khim Geterotsikl. Soedin.*, 1978, 1569.

<sup>63</sup> I. L. Kuranova and E. V. Snetkova, *Zh. Org. Khim.*, 1978, **14**, 2460.

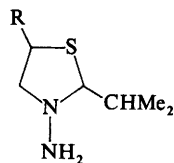
<sup>64</sup> P. K. Claus, W. Rieder, and F. W. Vierhapper, *Monatsh. Chem.*, 1978, **109**, 609.



(18)



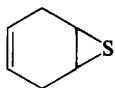
(19)



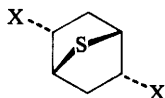
(20)

faster than methyloxiran with butylamine<sup>65</sup> or alkoxides,<sup>60</sup> even though it is less strained.

Electrophilic opening of thiirans in molecules possessing an accessible double bond leads to dihalogenated cyclic sulphides; e.g., (21) gives (22) with chlorine or (23) with bromine. The intermediacy of (24) establishes that the initial, and exclusive, attack by halogen is at sulphur.<sup>66</sup> Treatment of (21) with  $\text{SCl}_2$  gives (25), probably by a similar route.<sup>66</sup>

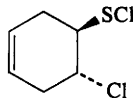


(21)

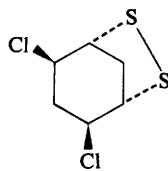


(22) X = Cl

(23) X = Br

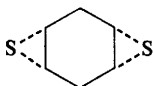


(24)

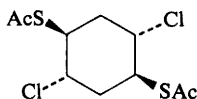


(25)

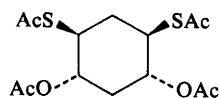
Bis(epithio)cyclohexa-1,4-diene (26) gives the *cis*-1,4-sulphur-substituted derivative (27) upon treatment with acetyl chloride, but the *cis*-1,3-sulphur-substituted derivative (28) on ring-opening with mercury(II) acetate.<sup>28</sup> Thiiran plus acetyl bromide gives 2-bromoethyl thiolacetate,<sup>67</sup> while carboxylic acid anhydrides give mixtures of 2-acyloxy-1-acylthio- and 1-acyloxy-2-acylthio-derivatives with *n*-alkyl-thiirans.<sup>68</sup> A preliminary report shows that phenyl acetate reacts with thiiran to give a low yield of 2-phenoxyethyl thiolacetate.<sup>69</sup> The rapid reaction of methylthiiran with HCl can be used as a non-basic scavenger for HCl that is produced in reactions.<sup>70</sup> Bis(epithio)linoleic acid gives tetrahydrothiophens with acids.<sup>71</sup>



(26)



(27)



(28)

<sup>65</sup> H. Kakiuchi, T. Iijima, and H. Horie, *Tetrahedron*, 1979, **35**, 303.

<sup>66</sup> P. H. McCabe and A. Stewart, *J. Chem. Soc., Chem. Commun.*, 1980, 100.

<sup>67</sup> L. Anoardi, R. Fornasier, D. Sostero, and U. Tonellato, *Gazz. Chim. Ital.*, 1978, **108**, 707.

<sup>68</sup> Y. Taguchi and Y. Suhara, *Yukagaku*, 1979, **28**, 270 (*Chem. Abstr.*, 1979, **91**, 56 719).

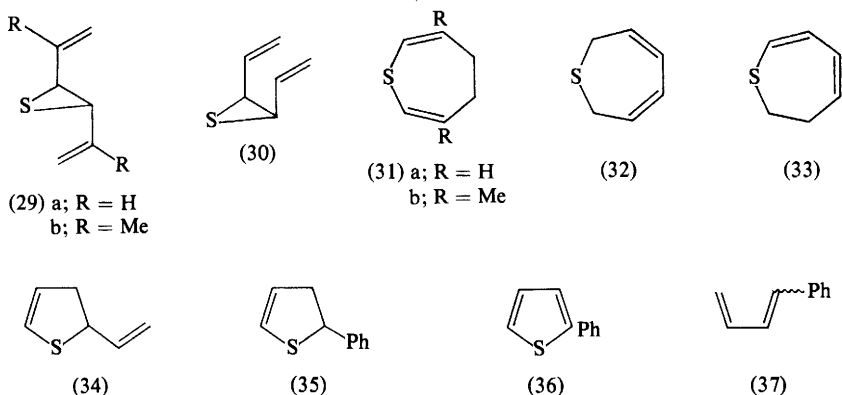
<sup>69</sup> K. Funahashi, *Chem. Lett.*, 1978, 1043.

<sup>70</sup> A. F. Kolomiets, A. V. Fokin, and A. A. Krolevets, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1468.

<sup>71</sup> I. L. Kuranova and E. V. Snetkova, *Zh. Org. Khim.*, 1978, **14**, 2165.

Treatment of episulphides with sulphuric acid in the presence of nitriles gives thiazolines,<sup>72</sup> and with acetic acid in the presence of imines gives thiazolidines.<sup>73</sup>

Two groups of workers have reported the preparation and thermolysis of the divinyl-thiirans (29) and (30).<sup>74,75</sup> At 90 °C, (29a) gives a 1:1 mixture of (31a) and (32);<sup>75</sup> at 340 °C, (29a) gives only (31a).<sup>74</sup> At 110 and 300 °C, (29b) gives only (31b), with activation parameters  $\Delta H^\ddagger = 105 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -46 \text{ e.u.}^\ddagger$  At 100 °C, (30) gives only (32), which is slowly converted into (33);<sup>75</sup> at 420 °C, (30) gives a mixture of products, (31a) (29%) and (34) (15%) being the only sulphur-containing ones.<sup>74</sup> The direct production of (31) is a Cope rearrangement, while all other products probably arise from processes involving cleavage of carbon-sulphur bonds to form radicals. At 400 °C, *cis*- and *trans*-2-phenyl-3-vinylthiiran are in equilibrium, and they react *via* a radical pathway to give (35), (36), and (37).<sup>74</sup>



Cycloaddition reactions starting from 2-iminothiirans have been reviewed,<sup>8,9</sup> new results including the addition of isocyanides to give 2,4-bis(imino)thietans<sup>76</sup> and a demonstration that (38) can react through all three combinations of terminal atoms in the intermediate (39) to give (40), (41), and (42) (Scheme 1).<sup>77</sup>

Diethylgermylene reacts with thiiran to give (43), probably *via* the intermediacy of 2,2-diethyl-2-germathietan and 3-germapentane-3-thione,<sup>78</sup> and a germaphosphine (44) is trapped by thiiran to give (45).<sup>79</sup>

The 'Dewar' thiophen (12), isolated after photolysis of the parent,<sup>52</sup> is in thermal equilibrium with the other three isomers that have the methyl and cyano-groups on adjacent carbons, as evidenced by the photochemical interconversion of the four

<sup>72</sup> M. Maguet and R. Guglielmetti, *Bull. Soc. Chim. Fr., Part 2*, 1978, 539.

<sup>73</sup> S. W. Pelletier, J. Nowacki, and N. V. Mody, *Synth. Commun.*, 1979, 9, 201.

<sup>74</sup> J. C. Pommelet and J. Chucho, *J. Chem. Res. (S)*, 1979, 56.

<sup>75</sup> M. P. Schneider and M. Schnaithmann, *J. Am. Chem. Soc.*, 1979, 101, 254.

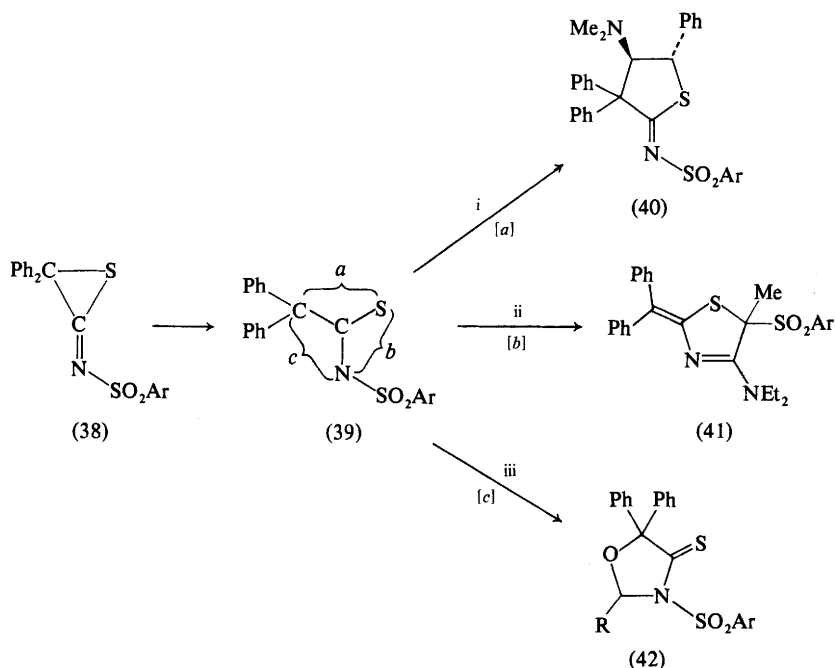
<sup>76</sup> G. L'abbé, J.-P. Dekerk, J.-P. Declercq, G. Germain, and M. Van Meerseche, *Tetrahedron Lett.*, 1979, 3213.

<sup>77</sup> G. L'abbé, J.-P. Dekerk, S. Toppet, J.-P. Declercq, G. Germain, and M. Van Meerseche, *Tetrahedron Lett.*, 1979, 1819.

<sup>78</sup> J. Barrau, M. Bouchaut, H. Lavyssiere, G. Dousse, and J. Satgé, *Helv. Chim. Acta*, 1979, 62, 152.

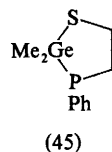
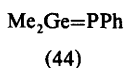
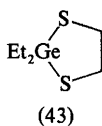
<sup>79</sup> C. Couret, J. Satgé, J. D. Andriamizaka, and J. Escudie, *J. Organomet. Chem.*, 1978, 157, C35.





Reagents: i, PhCH=CHNMe<sub>2</sub>; ii, MeC≡CNEt<sub>2</sub>; iii, RCHO

### Scheme 1



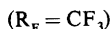
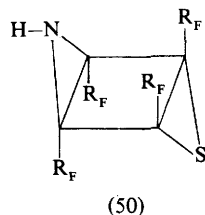
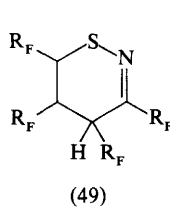
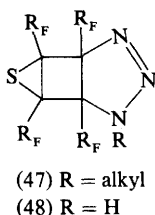
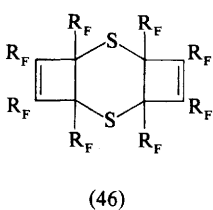
isomers. Neither of the thiophen isomers with the methyl group and the cyano-group on carbon atoms which are not formally bonded in the 'Dewar' structure is produced from (12).<sup>51</sup> This led the investigators to postulate interconversion by 'sulphur walk' around the periphery of the cyclobutene.

Further reactions of tetrakis(trifluoromethyl)-'Dewar' thiophen have been reported. The half-life for reversion to the normal thiophen is 5.1 h at 160 °C, in benzene. The isomerization occurs at room temperature in triphenylphosphine; in DMSO, a dimer (46) precipitates immediately.<sup>80</sup> Diels–Alder reactions with butadienes, furan, pyrrole, and cyclopentadiene give the expected products.<sup>81</sup> The furan adduct is converted into an oxahomocubane by photolysis, after desulphurization. Heating of the azide adduct (47) leads, after desulphurization, to pyrroles through a thiet intermediate.<sup>81</sup> Under the same conditions, the hydrazoic

<sup>80</sup> Y. Kobayashi, I. Kumadaki, A. Ohsawa, Y. Sekine, and A. Ando, *Heterocycles*, 1977, 6, 1587.

<sup>81</sup> Y. Kobayashi, A. Ando, K. Kawada, I. Kumadaki, and A. Ohsawa, *Heterocycles*, 1979, 12, 211.

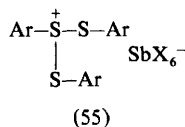
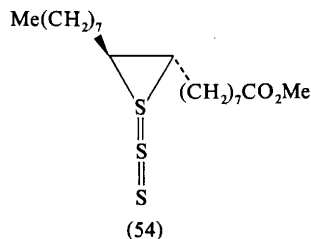
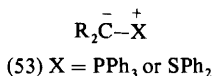
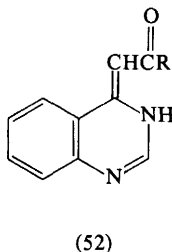
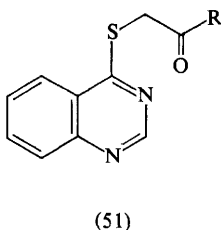
acid derivative (48) gives the 1,2-thiazine (49), but *N*-unsubstituted tetrakis-(trifluoromethyl)-'Dewar' pyrrole can be prepared by photolysis of (48) to (50), followed by desulphurization.<sup>82</sup>



Thiiran that is produced by the addition of sulphur atoms to ethylene<sup>43</sup> intramolecularly decays to vinyl mercaptan.<sup>43</sup> High-temperature pyrolysis of thiiran leads to vinyl mercaptan, thiophen, and benzothiophen under milder conditions than are necessary for the pyrolysis of dimethyl sulphide.<sup>83</sup> Its pyrolysis in chlorobenzene has also been reported.<sup>84</sup>

Thiiran reacts with arenediazonium chlorides to give 2-(arylthio)ethyl radicals.<sup>85</sup>

Thiirans have been proposed as intermediates in the reaction of sulphines with thiophilic reagents,<sup>86</sup> in the low-yield synthesis of tetracyclo[12.4.1.1<sup>3,12</sup>.1<sup>5,10</sup>]henicosanonaene,<sup>87</sup> and in the conversion of (51) into (52) by sodium ethoxide in DMF<sup>88</sup> or by concentrated sulphuric acid.<sup>89</sup>



<sup>82</sup> Y. Kobayashi, A. Ando, and I. Kumadaki, *J. Chem. Soc., Chem. Commun.*, 1978, 509.

<sup>83</sup> E. N. Deryagina, E. N. Sukhomazova, O. B. Bannikova, and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2103.

<sup>84</sup> E. N. Sukhomazova, E. N. Deryagina, and M. G. Voronkov, *Zh. Org. Khim.*, 1980, 16, 405.

<sup>85</sup> R. Kh. Freidlina, B. V. Kopylova, and L. V. Yashkina, *Tezisy Dokl. Nauchn. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei, 14th*, 1975 (publ. 1976), 114 (*Chem. Abstr.*, 1978, 89, 129 149).

<sup>86</sup> J. A. Loontjes, M. van der Leij, and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1980, 99, 39.

<sup>87</sup> W. Wagemann, M. Iyoda, H. M. Deger, J. Sombroek, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 1978, 17, 956.

<sup>88</sup> H. Singh, S. S. Narula, and C. S. Gandhi, *J. Chem. Res. (S)*, 1978, 324.

<sup>89</sup> H. Singh, C. S. Gandhi, and M. S. Bal, *Heterocycles*, 1980, 14, 3.

## 2 Thiiran Oxides (Episulphoxides and Episulphones)

Lithium reagents desulphurize *trans*-2,3-diphenylthiiran 1-oxide, but give about equal yields of *cis*-stilbene and the lithium salt of stilbene- $\alpha$ -sulphenic acid with *cis*-2,3-diphenylthiiran 1-oxide.<sup>55</sup> Decomposition of the *trans*-isomer in the presence of ylides (53) leads to small yields of sulphines.<sup>90</sup> Pyridine *N*-oxide is deoxygenated by SO.<sup>91</sup> In all these cases, kinetic measurements show that decomposition of the thiiran 1-oxide occurs independently of the substrate.

An episulphoxide intermediate has been proposed in the thiophilic reactions of sulphines<sup>86</sup> (see Chap. 3, Pt II, p. 162). The necessity of a 'pseudopericyclic' process in the isomerization of tetrakis(trifluoromethyl)-'Dewar' thiophen *S*-oxide has been questioned.<sup>92</sup> Calculations of the electronic transitions of thiiran and methylthiiran oxides have been related to their u.v. and c.d. spectra.<sup>93</sup>

Episulphones are treated in a review of the pyrolysis of sulphones.<sup>7</sup> A detailed analysis of the vibrational spectra of sulphones includes thiiran 1,1-dioxide.<sup>94</sup>

A molecular formula (54) appears in *Chemical Abstracts* as a product proposed to arise from the treatment of methyl oleate or methyl elaidate with sulphur at 140–160 °C.<sup>95</sup> No details are available to the Reporter.

## 3 Thiiranium Ions (Episulphonium Ions)

Two reviews of thiiranium ions have appeared.<sup>4</sup> The main conclusion of reference 4b is that episulphonium ions are generally not involved in reactions unless their counter-ions are very poorly nucleophilic. Additional studies supporting this point have appeared. The existence of two Ad<sub>E</sub>-2 mechanisms has been established,<sup>96,97</sup> additional examples of the reactions of nucleophiles with pre-formed thiiranium ions are reported,<sup>98,99</sup> and a new method for the preparation of thiiranium ions by the reaction of alkenes with aryl bis(aryltio)sulphonium ions (55) has been described.<sup>100,101</sup>

While there are normally two reactions of thiiranium ions with nucleophiles, namely ring-opening (with cleavage of a carbon–sulphur bond) or desulphurization to an alkene, a third reaction, *i.e.* dealkylation to (56), was reported for (57) when chloride or bromide ion was used as the nucleophile. When fluoride, iodide, azide, or

<sup>90</sup> B. F. Bonini, G. Maccagnani, G. Mazzanti, P. Pedrini, and P. Piccinelli, *J. Chem. Soc., Perkin Trans. J.*, 1979, 1720.

<sup>91</sup> B. F. Bonini, G. Maccagnani, G. Mazzanti, and P. Pedrini, *Tetrahedron Lett.*, 1979, 1799.

<sup>92</sup> J. P. Snyder and T. A. Halgren, *J. Am. Chem. Soc.*, 1980, **102**, 2861.

<sup>93</sup> G. L. Bendazzoli, P. Palmieri, G. Gottarelli, I. Moretti, and G. Torre, *Gazz. Chim. Ital.*, 1979, **109**, 19.

<sup>94</sup> J. Brunvoll and I. Hargittai, *Acta Chim. Acad. Sci. Hung.*, 1978, **96**, 337.

<sup>95</sup> D. Rankov, A. Popov, and S. Ivanov, *Symp. Pap., IUPAC Int. Symp. Chem. Nat. Prod.*, 11th, 1978, **2**, 223 (*Chem. Abstr.*, 1980, **92**, 94 151).

<sup>96</sup> I. V. Bodrikov, A. V. Borisov, L. V. Chumakov, N. S. Zefirov, and W. A. Smit, *Tetrahedron Lett.*, 1980, **21**, 115.

<sup>97</sup> I. V. Bodrikov, T. S. Ganzhenko, F. M. Sokova, and N. S. Zefirov, *Zh. Org. Khim.*, 1980, **16**, 246.

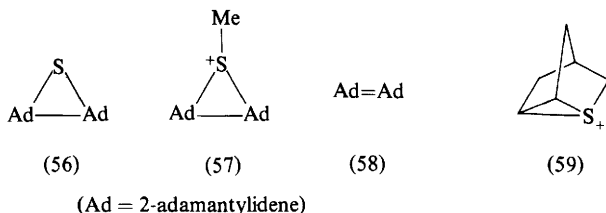
<sup>98</sup> A. S. Gybin, M. Z. Krimer, W. A. Smit, V. S. Bogdanov, and E. A. Vorob'eva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 563.

<sup>99</sup> A. S. Gybin, W. A. Smit, and M. Z. Krimer, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 927.

<sup>100</sup> A. S. Gybin, W. A. Smit, V. S. Bogdanov, M. Z. Krimer, and J. B. Kalyan, *Tetrahedron Lett.*, 1980, **21**, 383.

<sup>101</sup> A. S. Gybin, W. A. Smit, V. S. Bogdanov, and M. Z. Krimer, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1663.

methylthiolate ions or methyl-lithium were used, the alkene (58) was formed.<sup>49</sup> The episulphonium ion (59) has been observed.<sup>102</sup> The use of thiiranium ions in synthesis has received recent attention.<sup>103-106</sup> New calculations of the structures of thiiranium ions have appeared.<sup>107</sup>



Seleniranium<sup>108</sup> and selenirenium<sup>109</sup> ions have been reported. Thiirenium ions have been reviewed<sup>5</sup> and a crystal structure has been reported.<sup>110</sup>

#### 4 Thiirens and Thiiren Oxides

A review has appeared.<sup>3</sup> The preparation and observation by a second research group<sup>111</sup> of thiirens from 1,2,3-thiadiazoles by irradiation at low temperature (8 K) (see Vol. 5, p. 197) has engendered a spirited discussion of its i.r. spectrum.<sup>112,113</sup> *Ab initio* calculations of the structure and the i.r. spectrum of thiiren lead to the conclusion that thiiren is properly anti-aromatic, but cast doubt on the existence of a disputed band at 660 cm<sup>-1</sup>.<sup>114</sup> Thiirens have also been prepared by irradiation of vinylene trithiocarbonates at low temperatures<sup>115</sup> and of 1,2,3-thiadiazoles in the gas phase.<sup>116</sup> Both 4- and 5-methyl-1,2,3-thiadiazoles give (60) in the presence of hexafluorobut-2-yne.<sup>116</sup> Similarly, (61) and (62) give the same ratio of isomeric 2- or 3-methyltriphenylthiophens upon thermolysis in the presence of diphenylacetylene.<sup>117,118</sup>

A <sup>13</sup>C-labelling experiment has established firmly that (63) does *not* give (64).<sup>119</sup> Chemical labelling of benzothiadiazole (65) has established that, in the presence of

<sup>102</sup> J. Ohishi, K. Tsuneoka, S. Ikegami, and S. Akaboshi, *J. Org. Chem.*, 1978, **43**, 4013.

<sup>103</sup> W. A. J. de Loos, A. J. W. van den Berg-van Kuijk, H. M. van Iersel, J. W. de Haan, and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 53.

<sup>104</sup> T. Terasawa and T. Okada, *Heterocycles*, 1980, **14**, 99.

<sup>105</sup> F. Cooke, R. Moerck, J. Schwindeman, and P. Magnus, *J. Org. Chem.*, 1980, **45**, 1046.

<sup>106</sup> B. M. Trost, W. C. Vladuchick, and A. J. Bridges, *J. Am. Chem. Soc.*, 1980, **102**, 3548.

<sup>107</sup> (a) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, 1979, **101**, 783; (b) H. Lischka and H. J. Kohler, *Chem. Phys. Lett.*, 1979, **63**, 326.

<sup>108</sup> (a) S. Raucher, *Tetrahedron Lett.*, 1978, 2261; (b) N. Miyoshi, Y. Ohno, K. Kondo, S. Murai, and N. Sonoda, *Chem. Lett.*, 1979, 1309; (c) K. C. Nicolaou, R. L. Magolda, W. J. Sipio, W. E. Barnette, Z. Lysenko, and M. M. Joullie, *J. Am. Chem. Soc.*, 1980, **102**, 3784.

<sup>109</sup> C. N. Filer, D. Ahern, R. Fazio, and E. J. Shelton, *J. Org. Chem.*, 1980, **45**, 1313.

<sup>110</sup> R. Destro, T. Pilati, and M. Simonetta, *Nouv. J. Chim.*, 1979, **3**, 533.

<sup>111</sup> M. Torres, A. Clement, J. E. Bertie, H. E. Gunning, and O. P. Strausz, *J. Org. Chem.*, 1978, **43**, 2490.

<sup>112</sup> M. Torres, I. Safarik, A. Clement, J. E. Bertie, and O. P. Strausz, *Nouv. J. Chim.*, 1979, **3**, 365.

<sup>113</sup> A. Krantz and J. Lauren, *J. Org. Chem.*, 1979, **44**, 2730.

<sup>114</sup> B. A. Hess, jun., L. J. Schaad, and C. S. Ewig, *J. Am. Chem. Soc.*, 1980, **102**, 2507.

<sup>115</sup> M. Torres, A. Clement, H. E. Gunning, and O. P. Strausz, *Nouv. J. Chim.*, 1979, **3**, 149.

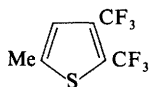
<sup>116</sup> J. Font, M. Torres, H. E. Gunning, and O. P. Strausz, *J. Org. Chem.*, 1978, **43**, 2487.

<sup>117</sup> E. Schaumann, J. Ehlers, W. R. Forster, and G. Adiwidjaja, *Chem. Ber.*, 1979, **112**, 1769.

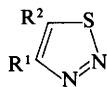
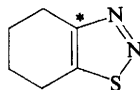
<sup>118</sup> E. Schaumann, J. Ehlers, and H. Mrotzek, *Liebigs Ann. Chem.*, 1979, 1734.

<sup>119</sup> U. Timm, H. Buhl, and H. Meier, *J. Heterocycl. Chem.*, 1978, **15**, 697.

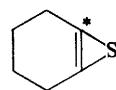
a hydrogen donor, (65) must go through a symmetric intermediate in some cases.<sup>120</sup> The effect is more noticeable in photolysis than in thermolysis. An intermediate, most probably benzothiiren, has been observed in an argon matrix at 8 K.<sup>111</sup> The photolysis of (66) to (67) is best rationalized by the intermediacy of (68).<sup>121</sup>



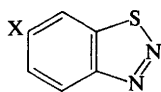
(60)

(61) R<sup>1</sup> = Ph, R<sup>2</sup> = Me(62) R<sup>1</sup> = Me, R<sup>2</sup> = Ph

(63)

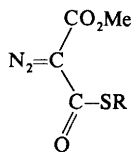


(64)

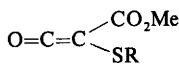


(65)

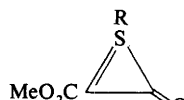
X = MeO, Cl, Me,  
or MeO<sub>2</sub>C



(66)



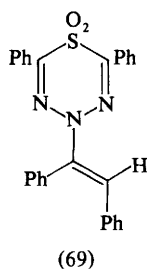
(67)



(68)

A full paper detailing the preparation and chemical properties of diphenylthiiren 1-oxide has appeared.<sup>122</sup> The reactions of thiiren 1,1-dioxides with  $\alpha$ -metallated isocyanides<sup>123,124</sup> and lithium azide<sup>125</sup> have been reported. The latter leads to a new heterocyclic system (69). Dimethyl- and diphenyl-thiiren 1,1-dioxides are reported to react with the 1,3-dipoles (70) and (71) to give (72) or (73) respectively.<sup>124</sup> In the case of (71) and diphenylthiiren 1,1-dioxide, (74) is also formed.<sup>124</sup> The Diels–Alder reaction with a diene-amine, but not the structure of the product, is mentioned in the same report.

Extensive calculations and discussions of the comparative conjugative and

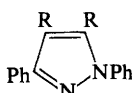


(69)

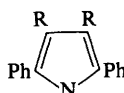


(70) X = NPh

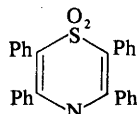
(71) X = CHPh



(72)



(73)



(74)

<sup>120</sup> R. C. White, J. Scoby, and T. D. Roberts, *Tetrahedron Lett.*, 1979, 2785.

<sup>121</sup> V. Georgian, S. K. Boyer, and B. Edwards, *J. Org. Chem.*, 1980, **45**, 1686.

<sup>122</sup> L. A. Carpino and H.-W. Chen, *J. Am. Chem. Soc.*, 1979, **101**, 390.

<sup>123</sup> Y. Yoshida, M. Komatsu, Y. Ohshiro, and T. Agawa, *J. Org. Chem.*, 1979, **44**, 830.

<sup>124</sup> Y. Yoshida, M. Uesaka, M. Komatsu, Y. Ohshiro, and T. Agawa, *Heterocycles*, 1980, **14**, 91.

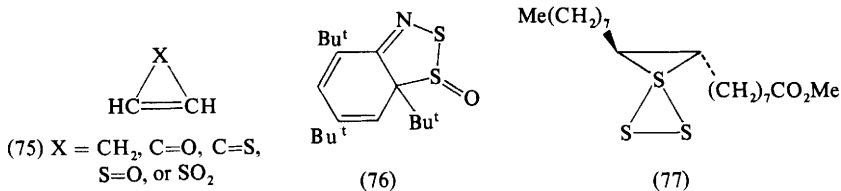
<sup>125</sup> B. B. Jarvis, G. P. Stahly, and H. L. Ammon, *Tetrahedron Lett.*, 1978, 3781.

inductive effects of C=S, C=O, S=O, and SO<sub>2</sub>, with relation to the structure and properties of (75), have been accomplished.<sup>126</sup> In the case of all except the thiiren 1,1-dioxide, the calculated energy levels have been compared to those determined by p.e. spectroscopy.<sup>127</sup>

Some of the recent papers on thiirenium ions are listed in the bibliography on page 232.

### 5 Three-membered Rings with More than One Heteroatom

Oxathiiran, oxathiiran 2-oxide, and oxathiiren<sup>128</sup> and oxathiiran 1-oxide<sup>129</sup> have been treated theoretically. An oxathiiran<sup>130</sup> and an oxathiiren<sup>131</sup> have been proposed as reaction intermediates. The first dithiiran has been implicated in the reaction of  $\alpha$ -chloroalkyl acyl disulphides with amines.<sup>132</sup> Phenylthiazirine has been observed in low-temperature photolyses<sup>133</sup> and implicated as an intermediate in the production of benzonitrile sulphide from the photolysis of a number of heterocycles.<sup>134,135</sup> A book treating thiazirines amongst other topics has appeared.<sup>136</sup> Dithiaziridines have been proposed to exist in the reactions of *N*-thiosulphinyl compounds.<sup>137</sup> 2-Imino-oxadithiirans have been proposed as first intermediates in the oxidation of *N*-thiosulphinyl compounds,<sup>138</sup> and a dithiaziridine *S*-oxide in the decomposition of (76).<sup>138</sup> A compound of the structure (77) has been proposed as a product of the reaction of methyl oleate or methyl elaidate with sulphur at 140–160 °C.<sup>95</sup> No details are available to the Reporter.



A selenacarbaborane that contains a B–C–Se three-membered ring has been prepared.<sup>139</sup>

<sup>126</sup> H. L. Hase, C. Mueller, and A. Schweig, *Tetrahedron*, 1978, **34**, 2983.

<sup>127</sup> C. Mueller, A. Schweig, and H. Vermeer, *J. Am. Chem. Soc.*, 1978, **100**, 8056.

<sup>128</sup> L. Carlsen and J. P. Snyder, *J. Org. Chem.*, 1978, **43**, 2216.

<sup>129</sup> L. Carlsen, *J. Chem. Soc., Perkin Trans. 2*, 1980, 188.

<sup>130</sup> K. Praefcke and C. Weichsel, *Liebigs Ann. Chem.*, 1980, 333.

<sup>131</sup> C. F. Ebbinghaus, P. Morrissey, and R. L. Rosati, *J. Org. Chem.*, 1979, **44**, 4697.

<sup>132</sup> A. Senning, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 941.

<sup>133</sup> A. Holm, N. Harrit, and I. Trabjerg, *J. Chem. Soc., Perkin Trans. 1*, 1978, 746.

<sup>134</sup> A. Holm and N. H. Toubro, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1445.

<sup>135</sup> A. Holm, J. J. Christiansen, and C. Lohse, *J. Chem. Soc., Perkin Trans. 1*, 1979, 960.

<sup>136</sup> A. Holm, 'On the Trail of Nitrile Sulfides, Thioacylnitrenes and Thiazirines', Oersted Institute, Copenhagen University, Denmark, 1978.

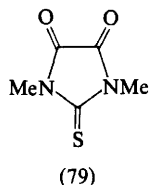
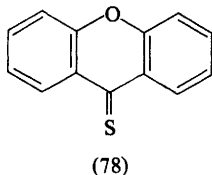
<sup>137</sup> Y. Inagaki, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2002.

<sup>138</sup> Y. Inagaki, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3615.

<sup>139</sup> G. D. Friesen, A. Barriola, and L. J. Todd, *Chem. Ind. (London)*, 1978, 631.

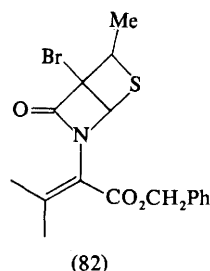
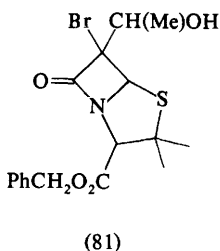
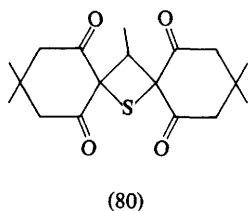
## 6 Thietans

**Formation.**—A number of thietans have been prepared in high yield from 1,3-bis(benzenesulphonates) by treatment with sulphide ion in DMSO.<sup>140</sup> The photochemical addition of (78) and (79) to cyclic alkenes gives spiro-thietans.<sup>141</sup>



Di-*t*-butyl thioketone photochemically adds to alkoxy- and cyano-substituted alkenes to give thietans, but abstracts hydrogen from simple alkenes.<sup>142</sup> Thiobenzophenone reacts with acrylonitriles to give thietans.<sup>143</sup>

Chloromethyl-oxirans react with barium hydroxide that is saturated with H<sub>2</sub>S to give 3-hydroxy-thietans.<sup>144</sup> Aldehyde-dimedone adducts give thietans (80) when treated with SCl<sub>2</sub>.<sup>145</sup> Ring-contraction of a dithiolan with tris(diethylamino)-phosphine gives a 2-propyl-thietan.<sup>146</sup> Treatment of (81) with triphenylphosphine and diethyl azodicarboxylate gives (82).<sup>147</sup>



Methylenethietans, *e.g.* (83), are prepared from quaternized 4-methyl-5-(2-chloroethyl)-1,3-thiazoles by treatment with base.<sup>148</sup> Thioxanthione adds photochemically to the terminal double bonds of hexa-2,3,4-trienes to give 3-allenyl-thietans, *e.g.* (84).<sup>149</sup>

The preparation and structure determination of a 2,4-bis(imino)thietan<sup>76</sup> and a tris(imino)thietan<sup>150</sup> have been reported.

<sup>140</sup> M. Buza, K. K. Andersen, and M. D. Pazdon, *J. Org. Chem.*, 1978, **43**, 3827.

<sup>141</sup> H. Gotthardt and S. Nieberl, *Chem. Ber.*, 1978, **111**, 1471.

<sup>142</sup> R. Rajee and V. Ramamurthy, *Tetrahedron Lett.*, 1978, 3463.

<sup>143</sup> C. C. Leung, *Diss. Abstr. Int. B*, 1979, **39**, 5938.

<sup>144</sup> F. S. Abbott and K. Haya, *Can. J. Chem.*, 1978, **56**, 71.

<sup>145</sup> S. Ito and J. Mori, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3403.

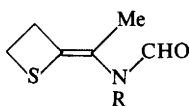
<sup>146</sup> D. R. Crump, *Tetrahedron Lett.*, 1978, 5233.

<sup>147</sup> F. DiNinno, *J. Am. Chem. Soc.*, 1978, **100**, 3251.

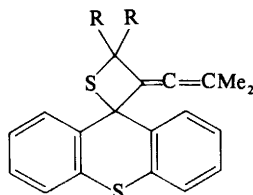
<sup>148</sup> H.-J. Federsel, J. Bergman, and U. Stenhede, *Heterocycles*, 1979, **12**, 751.

<sup>149</sup> R. G. Visser and H. J. T. Bos, *Tetrahedron Lett.*, 1979, 4857.

<sup>150</sup> G. L'abbé, L. Huybrechts, J.-P. Declercq, G. Germain, and M. Van Meerse, *J. Chem. Soc., Chem. Commun.*, 1979, 160.



(83)



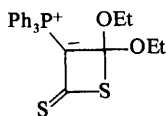
(84)

Diphenylketen cyclo-adds to thiobenzophenone<sup>151</sup> and to alkyl dithiobenzoates<sup>152</sup> to give the corresponding 2-oxothietans ( $\beta$ -thio- $\beta$ -lactones), but with *p*-anisyl  $\beta$ -styryl thioketone to give only the six-membered-ring adduct.<sup>153</sup> Azibenzil reacts with thiobenzophenone to give mostly oxathiolan, but a small amount of a tetraphenylthietanone is also formed. In the case of di-(*p*-anisyl) thioketone, a 44% yield of the 2-thietanone is reported, and has been attributed to the trapping by thioketone of di-(*p*-anisyl)keten that arises from the azibenzil.<sup>16</sup> However, no structure proof for the thietanone is provided, and the melting point of the di-(*p*-anisyl) derivative is substantially different from that reported in reference 151 for the 2-thietanone.

The di-, tri-, and tetra-methyl-3-thietanones have been prepared by the ring-closure of  $\alpha, \alpha'$ -dibromo-ketones with sulphide ion.<sup>154</sup> The stereochemistry of the dimethyl compounds was determined by reduction to the thietanols.<sup>154</sup> 3-Thietanones can also be prepared by the reaction of ketones with thionyl chloride.<sup>155</sup> The Wittig reagent (85) has been prepared.<sup>156</sup>

A bibliography on biologically active thietans is on p. 232.

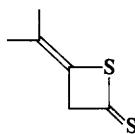
**Reactions.**—Pyrolysis of thietan at 700 °C is the best source of thioformaldehyde.<sup>157</sup> Photofragmentation of thietans, sensitized by (86), gives good yields of highly substituted olefins.<sup>158</sup> A careful study of the mercury-sensitized decomposition of thietan suggests the trimethylenethiyl biradical as the first intermediate.<sup>159</sup> Photolysis of (87) gives (88).<sup>160</sup>



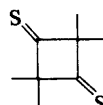
(85)



(86)



(87)



(88)

<sup>151</sup> H. Kohn, P. Charumilind, and Y. Gopichand, *J. Org. Chem.*, 1978, **43**, 4961.

<sup>152</sup> V. N. Drozd and O. A. Popova, *Zh. Org. Khim.*, 1979, **15**, 2602.

<sup>153</sup> T. Karakasa, H. Yamaguchi, and S. Motoki, *J. Org. Chem.*, 1980, **45**, 927.

<sup>154</sup> B. Fohlisch and W. Gottstein, *Liebigs Ann. Chem.*, 1979, 1768.

<sup>155</sup> J. S. Pizey and K. Symeonides, *Phosphorus Sulfur*, 1980, **8**, 1.

<sup>156</sup> H. J. Bestmann and R. W. Saalfrank, *J. Chem. Res. (S)*, 1979, 313.

<sup>157</sup> R. H. Judge and G. W. King, *J. Mol. Spectrosc.*, 1979, **74**, 175.

<sup>158</sup> H. Gotthardt and S. Nieberl, *Liebigs Ann. Chem.*, 1979, 866.

<sup>159</sup> D. R. Dice and R. P. Steer, *Can. J. Chem.*, 1978, **56**, 114.

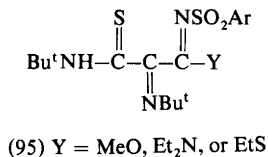
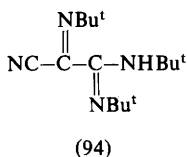
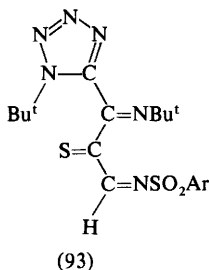
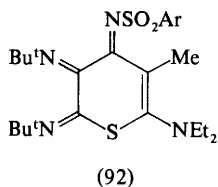
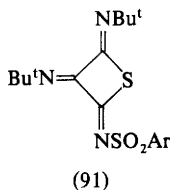
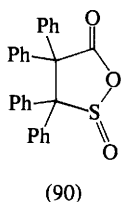
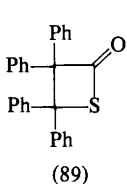
<sup>160</sup> K. Muthuramu and V. Ramamurthy, *J. Chem. Soc., Chem. Commun.*, 1980, 243.



Oxidation of simple thietans with peroxy-acids gives monoxides<sup>140,145</sup> and dioxides.<sup>144</sup> However, oxidation of tetraphenyl-2-thietanone (89) with *m*-chloroperoxybenzoic acid gives (90), which is a stable carboxylic-sulphinic acid anhydride.<sup>161</sup> Thietan dioxides are formed in the oxidation of thietans by  $\text{NaMnO}_4$ .<sup>140</sup> 2-Arylsulphonyl-3-aryl-oxaziridines oxidize sulphides (including thietans) to sulphoxides.<sup>162</sup> 3-Hydroxythietan can be oxidized to 3-thietanone, without oxidation at sulphur, with DMSO and benzoic anhydride.<sup>163</sup>

Thionyl chloride reacts with 2-phenyl-3-hydroxythietan to give 3-phenylallyl chloride rather than the expected 2-phenyl-3-chlorothietan.<sup>144</sup> Of the 3-chloro-thiacycloalkanes, 3-chlorothietan is the most reactive in both  $S_N1$  and  $S_N2$  reactions.<sup>164</sup> A substantial amount of ring-opening to allyl phenyl disulphide occurs in the reaction of 3-chlorothietan with thiophenoxide ion.<sup>164</sup> Attack at sulphur by the sulphur nucleophiles has also been suggested in the reaction of 3-thietanones with hydrogen sulphide ion;<sup>163</sup>  $\alpha$ -mercapto-ketones and their di- and tri-sulphide derivatives are the only products, with no evidence of sulphur on the  $\alpha'$ -position being found.<sup>154</sup>

Tris(imino)thietan (91) reacts with enamines to give 2-aminopyrroles,<sup>165</sup> with ynamines to give (92),<sup>165</sup> with hydrazoic acid to give the tetrazole (93),<sup>166</sup> with  $\text{NaN}_3$  to give (94),<sup>166</sup> and with  $\text{MeOH}$ ,  $\text{Et}_2\text{NH}$ , and  $\text{EtSH}$  to give the derivatives (95).<sup>166</sup> Pyrolysis of the sodium salt of the tosylhydrazone of 3-thietanone gives methylenethiiran.<sup>54</sup>



<sup>161</sup> H. Kohn, P. Charumilind, and S. H. Simonsen, *J. Am. Chem. Soc.*, 1979, **101**, 5431.

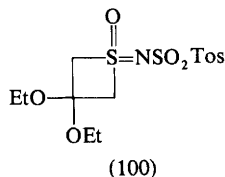
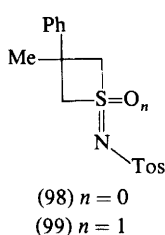
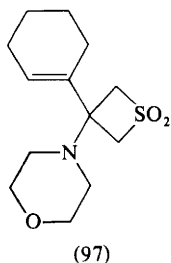
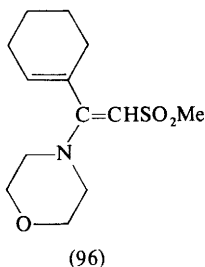
<sup>162</sup> F. A. Davis, R. Jenkins, jun., and S. G. Yocklovich, *Tetrahedron Lett.*, 1978, 5171.

<sup>163</sup> B. Fohlisch and B. Czuderna, *Phosphorus Sulfur*, 1978, **4**, 167.

<sup>164</sup> H. Morita and S. Oae, *Heterocycles*, 1977, **6**, 1593.

<sup>165</sup> G. L'abbé, L. Huybrechts, S. Toppet, J.-P. Declercq, G. Germain, and M. Van Meerse, *Bull. Soc. Chim. Belg.*, 1978, **87**, 893.

<sup>166</sup> G. L'abbé, L. Huybrechts, S. Toppet, J.-P. Declercq, G. Germain, and M. Van Meerse, *Bull. Soc. Chim. Belg.*, 1979, **88**, 297.



Neighbouring-group participation by  $\beta$ -sulphur, through thietanium ions, has been demonstrated.<sup>167</sup>

### 7 Thietan Oxides and Imides

**Formation.**—Preparation of thietan oxides by oxidation of thietans is covered in the previous section. Cycloaddition of sulphenes to electron-rich alkenes, the other important method of preparation of episulphones, has been further used for the preparation of  $\alpha$ -chloro- and  $\beta$ -amino,<sup>168</sup>  $\alpha$ -sila- and  $\beta$ -amino,<sup>169</sup> and  $\alpha$ -alkoxycarbonyl- and  $\beta$ -amino-thietan dioxides.<sup>170</sup> The sulphonyl enamine (96) can be converted into the thietan dioxide (97) by treatment with acid, a procedure that usually hydrolyses enamines to ketones.<sup>171</sup> Regeneration of (96) from (97) occurs on heating in alcoholic base.<sup>171</sup> Thiet sulphone cyclo-adds to cyclopentadiene to give the Diels–Alder adducts with an *exo/endo* ratio of 0.25.<sup>172</sup>

Thietan sulphilimines (98) can be prepared by the reaction of thietans with Chloramine T, and the corresponding sulphoximines (99) can be prepared by oxidation of the sulphilimines with  $\text{NaMnO}_4$ .<sup>140</sup> The thietan sulphoximine (100) results from the cycloaddition of an iminosulphene to 1,1-diethoxyethene.<sup>173</sup>

**Reactions.**—2,2,4,4-Tetra-acylthietan monoxides are photochemically converted into cyclopropanes.<sup>145</sup> The conformational aspects of thietan monoxides have been assessed, using lanthanide shift reagents and n.m.r. spectroscopy.<sup>174</sup>

Thiet sulphones result from thietan sulphones by elimination reactions: from sulphonates<sup>144,175</sup> and by Cope elimination.<sup>168</sup>

Photolysis of thietan dioxides is a preparatively useful synthesis of cyclopropanes, particularly since stabilization of an  $\alpha$ -carbanion by a sulphonyl group allows wide latitude for manipulation.<sup>176</sup> Thietan dioxide (101) gives (102) in 95% yield upon photolysis.<sup>145</sup> Trimethylene sulphone gives trimethylene biradicals

<sup>167</sup> E. L. Eliel, W. H. Pearson, L. M. Jewell, and A. G. Abatjoglou, *Tetrahedron Lett.*, 1980, **21**, 331.

<sup>168</sup> W. Ried and H. Bopp, *Chem. Ber.*, 1978, **111**, 1527.

<sup>169</sup> A. G. Shipov, A. V. Kisin, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1979, **49**, 1170.

<sup>170</sup> A. Etienne and B. Desmazieres, *J. Chem. Res. (S)*, 1978, 484.

<sup>171</sup> R. A. Ferri, G. Pitacco, and E. Valentin, *Tetrahedron*, 1978, **34**, 2537.

<sup>172</sup> H. D. Martin, R. Iden and H. J. Schiwiek, *Tetrahedron Lett.*, 1978, 3337.

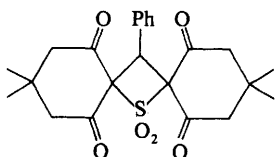
<sup>173</sup> C. R. Johnson, E. U. Jonsson, and C. C. Bacon, *J. Org. Chem.*, 1979, **44**, 2055.

<sup>174</sup> D. J. H. Smith, J. D. Finlay, C. R. Hall, and J. J. Uebel, *J. Org. Chem.*, 1979, **44**, 4757.

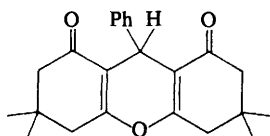
<sup>175</sup> P. Dalla Croce, P. Del Buttero, S. Maiorana, and R. Vistocco, *J. Heterocycl. Chem.*, 1978, **15**, 515.

<sup>176</sup> J. D. Finlay, D. J. H. Smith, and T. Durst, *Synthesis*, 1978, 579.

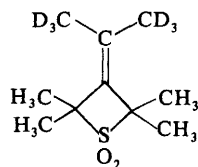
during vacuum-u.v. photolysis.<sup>177</sup> The hexamethyl-3-methylenethietan dioxide (103) gives methylenecyclopropanes with less deuterium scrambling than required of conventional trimethylenemethane intermediates.<sup>178</sup>



(101)



(102)



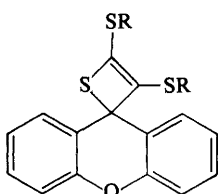
(103)

2-Phenyl-3-hydroxythietan 1,1-dioxide gives benzyl methyl sulphone with hydroxide ion, but benzyl methyl ketone with sulphuric or phosphoric acids.<sup>144</sup>

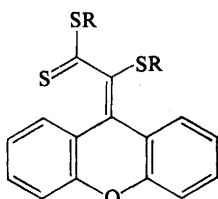
### 8 Thiet and its Derivatives

Thiets have been reviewed.<sup>179</sup>

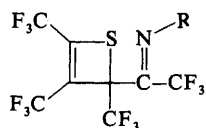
**Formation.**—Phenyl-, 2-naphthyl-, 2-thienyl-, and 2-furanyl-thiets are prepared from aryl methyl ketones, dimethylamine, and methanesulphonyl chloride.<sup>180</sup> X-Ray crystal structures establish that the compounds arising from the cycloaddition of alkynes to thioxanones are thiets, and not spiro-dihydropyrans, as originally proposed.<sup>181</sup> Additional work shows that alkynyl sulphides also give thiets with thioxanone, and that the adduct (104) is in rapid equilibrium with the open form (105) in solution, although they can be isolated separately.<sup>182,183</sup> Thiet (106) was isolated after thermolysis of a 'Dewar' thiophen-azide adduct.<sup>81</sup>



(104)



(105)



(106)

A potentially useful reaction for the large-scale preparation of benzothiet (107) has been reported. It involves the thermolysis of (108) at 700 °C and is estimated to

<sup>177</sup> A. A. Scala and I. Colon, *J. Phys. Chem.*, 1979, **83**, 2025.

<sup>178</sup> R. J. Bushby and M. D. Pollard, *Tetrahedron Lett.*, 1978, 3855.

<sup>179</sup> D. C. Dittmer, in 'New Trends in Heterocyclic Chemistry', ed. R. B. Mitra, Elsevier, Amsterdam, 1979.

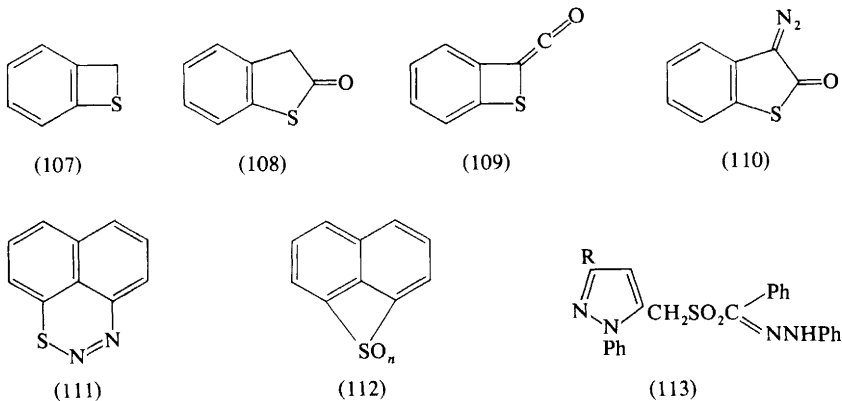
<sup>180</sup> B. H. Patwardhan, E. J. Parker, and D. C. Dittmer, *Phosphorus Sulfur*, 1979, **7**, 5.

<sup>181</sup> H. Gotthardt and O. M. Huss, *Tetrahedron Lett.*, 1978, 3617; cf. H. Gotthardt and S. Nieberl, *ibid.*, 1976, 3563.

<sup>182</sup> A. C. Brouwer, A. V. E. George, D. Seykens, and H. J. T. Bos, *Tetrahedron Lett.*, 1978, 4839.

<sup>183</sup> G. J. Verhoeckx, J. Kroon, A. C. Brouwer, and H. J. T. Bos, *Acta Crystallogr., Sect. B*, 1980, **36**, 484.

have an 80% yield.<sup>184</sup> The keten (109) is observed by p.e. spectroscopy when (110) is heated to 350 °C.<sup>184</sup> Neither thiet has a tendency to open. The thiadiazine (111) can be used as the starting material for the preparation of (112;  $n = 0, 1, \text{ or } 2$ ).<sup>185</sup>



Thiet sulphones are prepared by elimination reactions of the appropriate thietan sulphones.<sup>144, 168, 175</sup>

**Reactions.**—Condensation of thiet sulphone with 2 moles of halogeno-hydrazones,  $\text{RC}(\text{Cl})=\text{NNHPh}$ , gives isoimidazoles (113).<sup>175</sup> Cycloaddition of thiet sulphone to cyclopentadiene occurs with an *exo/endo* ratio of 0.25.<sup>172</sup> 2,4-Diphenylthiet dioxide is hydrolysed to dibenzyl sulphone with base, but rearranges to the isomeric sulphinate 3,5-diphenyl-1,2-oxathiolen 2-oxide with concentrated sulphuric acid.<sup>143</sup> Treatment of 4-phenyl-2*H*-thiet 1,1-dioxide with KOH in ethanol gives 3-ethoxy-2-phenylthietan 1,1-dioxide.<sup>144</sup>

A theoretical study concludes that the activation energy for ring-closure of an  $\alpha\beta$ -unsaturated thione to a thiet should be about 30 kJ mol<sup>-1</sup> more favourable than the closure of butadiene to cyclobutene.<sup>186</sup> Acid catalysis should increase the difference by another 45 kJ mol<sup>-1</sup>.

## 9 Dithietans, Dithiets, and their Derivatives

**1,2-Dithietans.**—1,2-Dithietan (114) is the first isolated derivative in that class. It arises by dimerization of ethyl sulphine, probably by rearrangement of a first-formed sulphenyl sulphinate<sup>187</sup> (see Chap. 3, Pt. II, p. 161).

**1,2-Dithiets.**—Two dithiets (115) and (116) have been isolated,<sup>188</sup> and more observed.<sup>189, 190</sup> Benzodithiet is trapped by dimethyl acetylenedicarboxylate to give

<sup>184</sup> R. Schulz and A. Schweig, *Tetrahedron Lett.*, 1980, **21**, 343.

<sup>185</sup> J. Nakayama, T. Fukushima, E. Seki, and M. Hoshino, *J. Am. Chem. Soc.*, 1979, **101**, 7684.

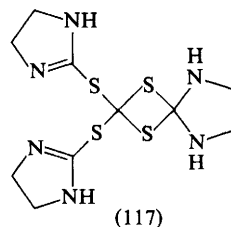
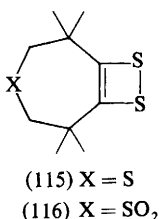
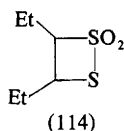
<sup>186</sup> J. P. Snyder, *J. Org. Chem.*, 1980, **45**, 1341.

<sup>187</sup> E. Block, A. A. Bazzi, and L. K. Revelle, *J. Am. Chem. Soc.*, 1980, **102**, 2490.

<sup>188</sup> A. Krebs, H. Colberg, U. Hopfner, H. Kimling, and J. Odenthal, *Heterocycles*, 1979, **12**, 1153.

<sup>189</sup> N. Jacobsen, P. de Mayo, and A. C. Weedon, *Nouv. J. Chim.*, 1978, **2**, 331.

<sup>190</sup> P. de Mayo, A. C. Weedon, and G. S. K. Wong, *J. Org. Chem.*, 1979, **44**, 1977.

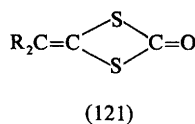
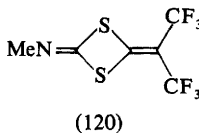
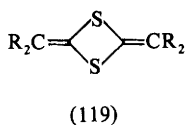
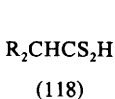


a benzo-1,4-dithiin.<sup>190</sup> Tervalent phosphorus compounds insert into the S—S bond of bis-(trifluoromethyl)dithiet.<sup>191</sup>

**Formation of 1,3-Dithietans.**—The dimerization of thiones or potential thiones is a major source of 1,3-dithietans; e.g., treatment of  $\alpha$ -chlorosulphenyl chlorides with triphenylphosphine gives derivatives of dithietan.<sup>192</sup> Monothiobenzil gives 2,4-diphenyl-2,4-dibenzoyl-1,3-dithietan on standing in solution, but can be regenerated photochemically.<sup>193</sup> Symmetrically substituted dithietans often accompany the preparation of thiones.<sup>194–196</sup> Spiro-derivatives (117) arise from ethylenethiourea and carbon disulphide in the presence of NaH in THF.<sup>197</sup>

Dithiocarboxylic acids (118) can be converted into 1,3-dithietans (119) by acid chlorides,<sup>198,199</sup> iodine,<sup>199</sup> HCl,<sup>199</sup> DCCl,<sup>200</sup> or upon standing for a long time,<sup>199</sup> and they are formally thioketen dimers. The cycloaddition of two C=S groups yields thioketen dimers<sup>118,151,201–203</sup> and (120) from methyl isothiocyanate.<sup>204</sup> Derivatives (121) are prepared by the reaction of dithiocarboxylic acids (118) with phosgene.<sup>199,205</sup>

For papers on biologically active dithietans and for spectroscopic information see the bibliography on p. 232.



<sup>191</sup> B. C. Burros, N. J. De'Ath, D. B. Denney, D. Z. Denney, and I. J. Kipnis, *J. Am. Chem. Soc.*, 1978, **100**, 7300.

<sup>192</sup> K. Oka, *J. Org. Chem.*, 1979, **44**, 1736.

<sup>193</sup> C. Bak and K. Praefcke, *Z. Naturforsch., Teil B*, 1980, **35**, 372.

<sup>194</sup> P. Metzner, J. Vialle, and A. Vibet, *Tetrahedron*, 1978, **34**, 2289.

<sup>195</sup> M. M. A. Abdel-Rahman, *Acta Chim. Acad. Sci. Hung.*, 1977, **93**, 425.

<sup>196</sup> B. S. Pedersen, S. Scheiby, N. H. Nilsson, and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 223.

<sup>197</sup> M. Yokoyama, S. Ohtuki, M. Muraoka, and T. Takeshima, *Tetrahedron Lett.*, 1978, 3823.

<sup>198</sup> M. Augustin, C. Groth, H. Kristen, K. Peseke, and C. Wiechmann, *J. Prakt. Chem.*, 1979, **321**, 205.

<sup>199</sup> E. Schaumann and F.-F. Grabley, *Liebigs Ann. Chem.*, 1979, 1715.

<sup>200</sup> T. Takeshima, A. Yano, N. Fukada, Y. Hirose, and M. Muraoka, *J. Chem. Res. (S)*, 1979, 140.

<sup>201</sup> H. Kohn, Y. Gopichand, and P. Charumilind, *J. Org. Chem.*, 1978, **43**, 4955.

<sup>202</sup> H. Boehme and P. Malcherek, *Arch. Pharm. (Weinheim, Ger.)*, 1980, **313**, 81.

<sup>203</sup> E. Schaumann and F.-F. Grabley, *Liebigs Ann. Chem.*, 1979, 1702.

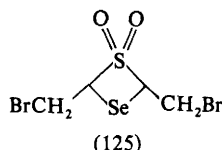
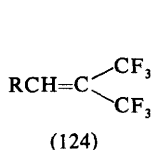
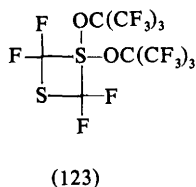
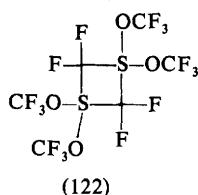
<sup>204</sup> M. S. Raasch, *J. Org. Chem.*, 1978, **43**, 2500.

<sup>205</sup> E. Schaumann, E. Kausch, and E. Rossmannith, *Liebigs Ann. Chem.*, 1978, 1543.

**Reactions of 1,3-Dithietans.**—Monothiobenzil can be generated by photolysis of its dithietan dimer.<sup>193</sup> Dithietanones (121) can be used as thioketen equivalents.<sup>199,205</sup> Tetrafluoro-1,3-dithietan reacts with oxygen atoms to give  $\text{CF}_2$ ,  $\text{SO}$ , and  $\text{CF}_2\text{S}$  as primary products,<sup>206</sup> and with trifluoromethyl hypochlorite to give (122).<sup>207</sup> With tris(trifluoromethyl)methyl hypochlorite it gives (123).<sup>208</sup> The 1,1-dioxides and the 1,1,3,3-tetroxides of tetrafluoro-, tetrachloro-, and tetrabromo-1,3-dithietans have been reported.<sup>209</sup>

Aldehydes can be converted into their hexafluoroisopropylidene derivatives (124) by reaction with triphenylphosphine and 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietan.<sup>210</sup>

**Selenium Derivatives.**—Pyrolysis of 1,2,3-selenadiazoles at 500–600 °C gives 2,4-bis(methylene)-1,3-diselenetans.<sup>211</sup> Treatment of divinyl sulphone with selenium tetrabromide gave a compound that was claimed to be (125).<sup>212</sup>



## 10 Four-membered Rings containing Sulphur and Oxygen

Calculations concerning the stabilities of 1,2-oxathietan 2-oxide,<sup>128</sup> 1,2-oxathietan-3-one and its enol,<sup>128</sup> and 1,2,3-<sup>128</sup> and 1,3,2-dioxathietans<sup>128,129</sup> have appeared.

The anhydride (126) has been prepared at 10 K by photochemical addition of  $\text{SO}_2$  to keten.<sup>213</sup> It decomposes photochemically to formaldehyde,  $\text{CO}_2$ , and sulphur. The reaction of the tetramethylcyclobutadiene– $\text{AlCl}_3$  complex with  $\text{SO}_2$  gives a new complex, which might be (127).<sup>214</sup>

The reaction of two derivatives of 5,5-diallylbarbituric acid with sulphuric acid in acetonitrile is said to give characterizable  $\beta$ -sultones.<sup>215</sup> Addition of  $\text{SO}_3$  to hexafluorobutadiene occurs in a 1,2 manner to give (128).<sup>216</sup> The double bond of (128) can be brominated to give another stable  $\beta$ -sultone. The addition is reversible above 20 °C, and (128) reacts with excess  $\text{SO}_3$  to give (129) and  $\text{SO}_2$ .<sup>216</sup>

<sup>206</sup> I. R. Slagle and D. Gutman, *Int. J. Chem. Kinet.*, 1979, **11**, 453.

<sup>207</sup> T. Kitazume and J. M. Shreeve, *Inorg. Chem.*, 1978, **17**, 2173.

<sup>208</sup> Q.-C. Mir, K. A. Laurence, R. W. Shreeve, D. P. Babb, and J. M. Shreeve, *J. Am. Chem. Soc.*, 1979, **101**, 5949.

<sup>209</sup> R. Seelinger and W. Sundermeyer, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 203.

<sup>210</sup> D. J. Barton and Y. Inouye, *Tetrahedron Lett.*, 1979, 3397.

<sup>211</sup> A. Holm, C. Berg, C. Bjerre, B. Bak, and H. Svanholt, *J. Chem. Soc., Chem. Commun.*, 1979, 99.

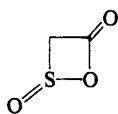
<sup>212</sup> Yu. V. Migalina, V. G. Lend'el, A. S. Koz'min, and N. S. Zefirov, *Khim. Geterotsikl. Soedin.*, 1978, **708**.

<sup>213</sup> I. R. Dunkin and J. G. MacDonald, *J. Chem. Soc., Chem. Commun.*, 1978, 1020.

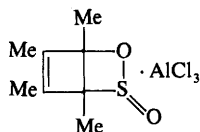
<sup>214</sup> P. B. J. Driessen and H. Hogeveen, *J. Organomet. Chem.*, 1978, **156**, 265.

<sup>215</sup> M. Konieczny and A. Radzicka, *Arch. Immunol. Ther. Exp.*, 1978, **26**, 955.

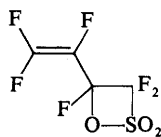
<sup>216</sup> N. B. Kaz'mina, I. L. Knunyants, G. M. Kuz'yants, E. I. Mysov, and E. P. Lur'e, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 118.



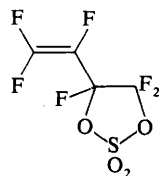
(126)



(127)



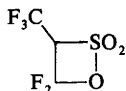
(128)



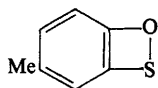
(129)

Oxathietan 1,1-dioxide (130) reacts with alcohols to give (2-fluorosulphonyl)-carboxylic esters, and with  $\text{BF}_3$  and  $\text{Et}_3\text{N}$  to give fluorosulphonyl(trifluoromethyl)keten.<sup>217</sup> The latter reaction is more efficient if the ring is first opened with  $\text{KF}$  and  $\text{HF}$ . Chloral cyclo-adds to sulphenes to give  $\beta$ -sultones.<sup>170,218</sup> 4-Trichloromethyl-1,2-oxathietan 2,2-dioxide reacts with primary and secondary amines to give  $\beta$ -hydroxy-sulphonamides.<sup>218</sup>

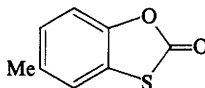
An oxathiet (131) has been observed in the low-temperature photolysis of (132).<sup>190</sup> The thermolysis of diphenylthiiren 1-oxide also yields an oxathiet.<sup>122</sup> The alkylidene sulphate (133) has been reported.<sup>219</sup>



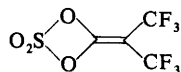
(130)



(131)



(132)



(133)

## 11 Four-membered Rings containing Sulphur and Nitrogen and/or Phosphorus

**1,2-Thiazetidines and their Derivatives.**—Carboxamides with an acidic  $\alpha$ -hydrogen react with thionyl chloride in the presence of pyridine to give 1,2-thiazetid-3-one 1-oxides (134).<sup>220</sup> *N*-Phenyl-1,2-thiazetid-3-one 1-oxide, prepared from keten and *N*-sulphonylaniline, is opened by anilines to give (135).<sup>221</sup> Thiofluorenone reacts with (136) to give, amongst other things, a small yield of (137); this is oxidized to its sulphonamide by MCPBA.<sup>222</sup>

*N*-(Alkylsulphonyl)imides (138), prepared by treating *N*-alkylsulphamoyl chlorides with  $\text{Et}_3\text{N}$ , react with enamines that bear no hydrogens  $\beta$  to the morpholino-group to give 1,2-thiazetidine 1,1-dioxides (139).<sup>223</sup> The preparations and e.s.r. spectra of two relatively stable 1,2-thiazet-2-yl radicals have been reported.<sup>224,225</sup>

<sup>217</sup> A. F. Eleev, S. I. Pletnev, G. A. Sokol'skii, and I. L. Knunyants, *Zh. Vses. Khim. O-va*, 1978, **23**, 229 [*Mendeleev Chem. J.*, 1978, **23**, No. 6, p. 45].

<sup>218</sup> W. Hanefeld and D. Kluck, *Arch. Pharm. (Weinheim, Ger.)*, 1978, **311**, 698.

<sup>219</sup> A. F. Eleev, G. A. Sokol'skii, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2360.

<sup>220</sup> L. Capuano, G. Urhahn, and A. Willmes, *Chem. Ber.*, 1979, **112**, 1012.

<sup>221</sup> J. E. Semple and M. M. Joullic, *J. Org. Chem.*, 1978, **43**, 3066.

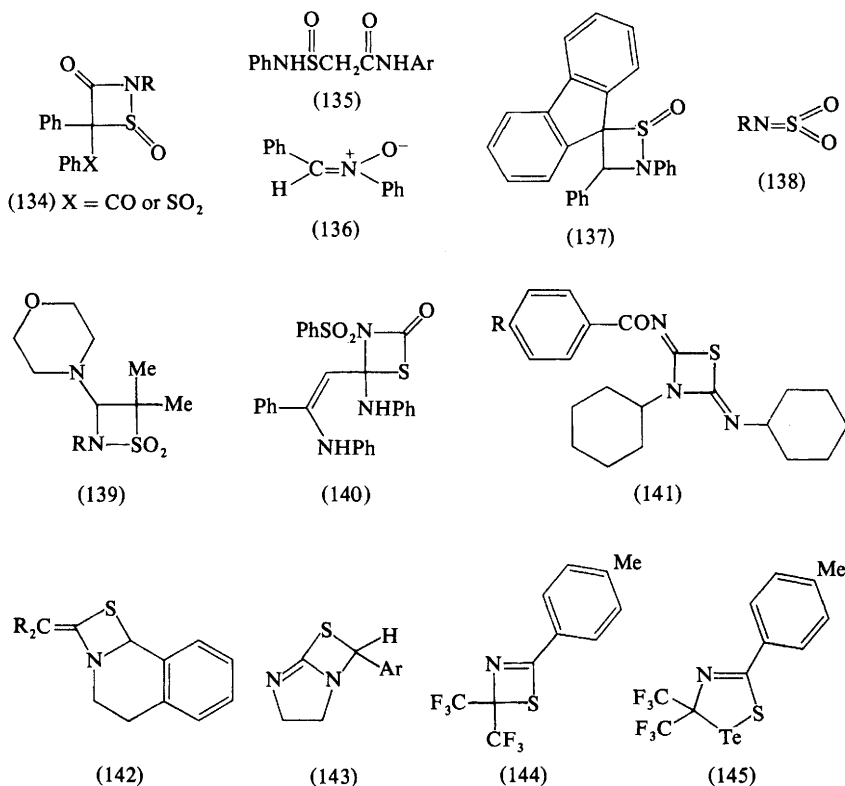
<sup>222</sup> G. Mazzanti, G. Maccagnani, B. F. Bonini, P. Pedrini, and B. Zwanenburg, *Gazz. Chim. Ital.*, 1980, **110**, 163.

<sup>223</sup> T. Nagai, T. Shingaki, M. Inagaki, and T. Ohshima, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1102.

<sup>224</sup> R. Mayer, G. Domschke, S. Bleisch, and A. Bartl, *Tetrahedron Lett.*, 1978, 4003.

<sup>225</sup> R. Mayer, S. Bleisch, G. Domschke, A. Tkac, A. Stasko, and A. Bartl, *Org. Magn. Reson.*, 1979, **12**, 532.

**1,3-Thiazetidines and their Derivatives.**—Cyclization reactions yield (140) from benzenesulphonyl isocyanate and a thioamide,<sup>226</sup> (141) from aroyl isothiocyanates and DCCI,<sup>227</sup> (142) from dihydroisoquinoline and the CS<sub>2</sub> adduct of a Wittig reagent,<sup>203</sup> and (143) from the BF<sub>3</sub>·Et<sub>2</sub>O-catalysed reaction of ethylenethiourea and aryl aldehydes.<sup>228</sup> Thiazet (144) reacts with Sb<sub>2</sub>Te<sub>3</sub>, presumably through the open thione-imine form, to give (145).<sup>229</sup> 1,3-Thiazetidines have been proposed as intermediates.<sup>205, 230</sup>



**Other Four-membered Rings containing Sulphur and Nitrogen.**—The reaction of tris(imino)sulphur derivatives with a slight excess of sulphonyl isocyanates gives eventually (146).<sup>231, 232</sup> Tris(trimethylsilylimino)sulphur reacts with *N*-(sulphinyl)-heptafluoroisopropylamine to give (147), possibly through the intermediacy of (148).<sup>232</sup> The compound (149) arises from the reaction of (150a) and (150b).<sup>232</sup>

<sup>226</sup> W. Zankowska-Jasinska and H. Borowiec, *Pol. J. Chem.*, 1978, **52**, 1683.

<sup>227</sup> O. Hritzova and P. Kristian, *Collect. Czech. Chem. Commun.*, 1978, **43**, 3258.

<sup>228</sup> M. Yokoyama and H. Monma, *Tetrahedron Lett.*, 1980, **21**, 293.

<sup>229</sup> K. Burger, R. Ottlinger, A. Proksch, and J. Firl, *J. Chem. Soc., Chem. Commun.*, 1979, 80.

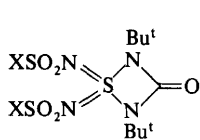
<sup>230</sup> E. Schaumann and E. Kausch, *Liebigs Ann. Chem.*, 1978, 1560.

<sup>231</sup> F.-M. Tesky, R. Mews, B. Krebs, and M. R. Udupa, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 677.

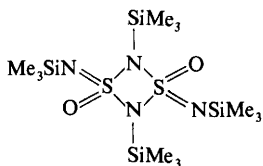
<sup>232</sup> F.-M. Tesky, R. Mews, and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 235.



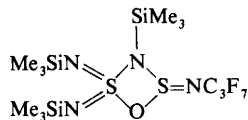
Dimer (151) is opened and stabilized by pyridine and  $S_4N_4$ .<sup>233</sup> Sulphur trioxide gives (152) with *N*-(sulphinyl)trifluoromethanesulphonamide.<sup>234</sup> Both (151) and (152) react with benzonitrile to give (153).<sup>233,234</sup> With aryl isocyanates, they give (154).<sup>234</sup> Both 1,2,3,4-dithiadiazetidines<sup>235</sup> and 1,3,2,4-dithiadiazetidines<sup>236</sup> have been proposed as reaction intermediates.



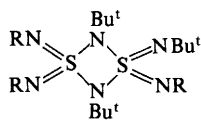
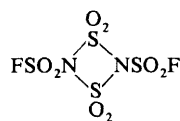
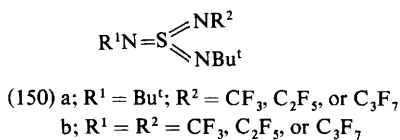
(146)



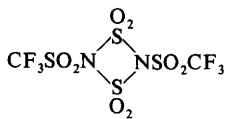
(147)



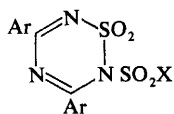
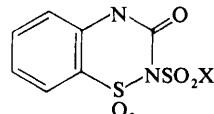
(148)

(149) R = CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>,  
or C<sub>3</sub>F<sub>7</sub>

(151)



(152)

(153) X = F or CF<sub>3</sub>

(154)

**1,3,2,4-Dithiadiphosphetans.**—2,4-Disubstituted 1,3,2,4-dithiadiphosphetan 2,4-disulphides (155) are the anhydrides of dithiophosphonic acids. They have been prepared by the reaction of (156) with  $H_2S$ .<sup>237–239</sup> The di-*t*-butyl derivative (155; R = Bu<sup>t</sup>) has been prepared from tetra-*t*-butylcyclotetraphosphine by heating with excess sulphur,<sup>240</sup> and (155; R = Ph) from bis(trifluoromethylthio)phenylphosphine and sulphur.<sup>241</sup> These anhydrides, particularly (155; R = *p*-anisyl), have been exploited for the preparation of thiocarbonyl groups from the corresponding carbonyls (replacing the more obnoxious  $P_2S_5$ ) e.g., thioketones.<sup>196</sup>

<sup>233</sup> H. W. Roesky and M. Aramaki, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 129.

<sup>234</sup> H. W. Roesky, M. Aramaki, and L. Schonfelder, *Z. Naturforsch., Teil B*, 1978, **33**, 1072.

<sup>235</sup> H. Kagami and S. Motoki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3463.

<sup>236</sup> Y. Inagaki, T. Hosogai, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 205.

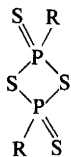
<sup>237</sup> P. S. Khokhlov, L. I. Markova, G. D. Sokolova, B. Ya. Chvertkin, S. G. Zhemchuzhin, and A. I. Ermakov, *Zh. Obshch. Khim.*, 1978, **48**, 564.

<sup>238</sup> K. D. Dzhandubayev, A. S. Sulaimanov, and B. Batyrkanova, *Zh. Obshch. Khim.*, 1978, **48**, 2037.

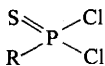
<sup>239</sup> O. N. Grishina, N. A. Andreev, and E. I. Babkina, *Zh. Obshch. Khim.*, 1978, **48**, 1321.

<sup>240</sup> M. Baudler, C. Gruner, G. F. Furstenberg, B. Kloth, F. Saykowski, and U. Oezer, *Z. Anorg. Allg. Chem.*, 1978, **446**, 169.

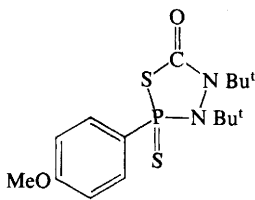
<sup>241</sup> T. Vakratsas, *Chem. Chron.*, 1978, **7**, 125 (*Chem. Abstr.*, 1979, **90**, 137 911).



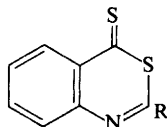
(155)



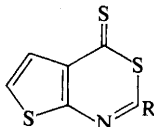
(156)



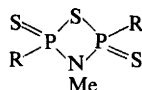
(159)



(157)



(158)

(160) R = *p*-anisyl

thioesters,<sup>242–244</sup> and thioamides.<sup>245–249</sup> Tetramethylene sulphoxide is converted into tetramethylene disulphide.<sup>250</sup> Heterocycles (157) and (158) are prepared by the reaction of the corresponding *o*-acylamino-ethoxycarbonyl derivatives with (155; R = *p*-anisyl).<sup>251,252</sup> The latter reagent also reacts with 1,2-di-*t*-butyldiaziridinone to give (159).<sup>253</sup> Grignard reagents attack the dimers at phosphorus to give derivatives of dithiophosphinic acid.<sup>254,255</sup> Dimers (155) also serve as donors of the monomer in cycloadditions.<sup>255</sup> Reactions of dimers (155) with alcohols give esters of the monomers.<sup>239</sup> The thiazadiphosphetidine (160) was prepared from (155; R = *p*-anisyl) and bis(trimethylsilyl)methylamine.<sup>256</sup>

**Four-membered Rings containing Sulphur, Nitrogen, and Phosphorus.**—The compound (160) results from the reaction of (155; R = *p*-anisyl) and (Me<sub>3</sub>Si)<sub>2</sub>NMe.<sup>256</sup> Heterocycle (161) is obtained from isocyanates and (162).<sup>257</sup> Thionyl chloride reacts with (163) to give (164).<sup>258</sup>

<sup>242</sup> B. S. Pedersen, S. Scheibye, K. Clausen, and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 293.

<sup>243</sup> R. Shabana, S. Scheibye, K. Clausen, S. O. Olesen, and S.-O. Lawesson, *Nouv. J. Chim.*, 1980, **4**, 47.

<sup>244</sup> S. Scheibye, J. Kristensen, and S.-O. Lawesson, *Tetrahedron*, 1979, **35**, 1339.

<sup>245</sup> S. Scheibye, B. S. Pedersen, and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 229.

<sup>246</sup> S. Scheibye, B. S. Pedersen, and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 299.

<sup>247</sup> H. Fritz, P. Hug, S.-O. Lawesson, E. Logemann, B. S. Pedersen, H. Sauter, S. Scheibye, and T. Winkler, *Bull. Soc. Chim. Belg.*, 1978, **87**, 525.

<sup>248</sup> H. J. Meyer, C. Nolde, I. Thomsen and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 621.

<sup>249</sup> W. Walter and T. Proll, *Synthesis*, 1979, 941.

<sup>250</sup> J. B. Rasmussen, K. A. Jorgensen, and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 307.

<sup>251</sup> K. Clausen and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, 1979, **88**, 305.

<sup>252</sup> K. Clausen and S.-O. Lawesson, *Nouv. J. Chim.*, 1980, **4**, 43.

<sup>253</sup> G. L'abbé, J. Flemal, J.-P. Declercq, G. Germain, and M. Van Meersehe, *Bull. Soc. Chim. Belg.*, 1979, **88**, 737.

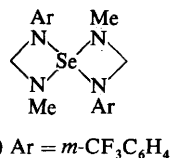
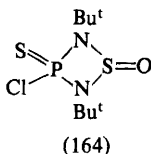
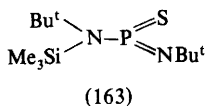
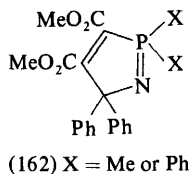
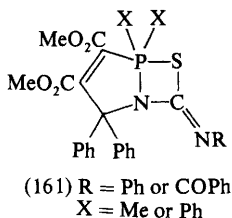
<sup>254</sup> (a) W. Kuchen, R. Uppenkamp, and K. Diemert, *Z. Naturforsch., Teil B*, 1979, **34**, 1398; (b) K. Diemert, P. Haas, and W. Kuchen, *Chem. Ber.*, 1978, **111**, 629.

<sup>255</sup> (a) J. Hogel and A. Schmidpeter, *Z. Naturforsch., Teil B*, 1979, **34**, 915; (b) W. Zeiss and A. Schmidpeter, *ibid.*, p. 1042.

<sup>256</sup> W. Zeiss, H. Henjes, D. Lux, W. Schwarz, and H. Hess, *Z. Naturforsch., Teil B*, 1979, **34**, 1334.

<sup>257</sup> A. Schmidpeter and T. von Criegern, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 443.

<sup>258</sup> O. J. Scherer, N.-T. Kulbach, and W. Glassel, *Z. Naturforsch., Teil B*, 1978, **33**, 652.



**Selenium Derivatives.**—The spiro-compound (165) is produced in 47% yield in the reaction of *m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>N(SiMe<sub>3</sub>)CON(Me)SiMe<sub>3</sub> with SeOCl<sub>2</sub>.<sup>259</sup>

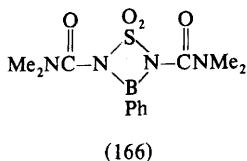
## 12 Four-membered Rings containing Sulphur and Silicon or Germanium

3,3-Diethyl-2,4-dimethyl-3-silathietan is prepared from divinyl sulphide by its reaction with diethylsilane.<sup>260</sup> Tetramethyl-2,4-disila-1,3-dithietan disproportionates with octamethyl-1,4-dithia-2,3,5,6-tetrasilacyclohexane to give hexamethyl-1,3-dithia-2,4,5-trisilacyclopentane.<sup>261</sup>

2,2-Diethyl-2-germathietan has been proposed as an intermediate in the reaction of thiiran with diethylgermylene.<sup>78</sup>

## 13 Thiadiazaboretidines

Cyclization of bis(dimethylamino)phenylborane with sulphuryl isocyanates gives (166).<sup>262</sup>



<sup>259</sup> H. W. Roesky and K. Ambrosius, *Z. Naturforsch., Teil B*, 1978, **33**, 759.

<sup>260</sup> M. G. Voronkov, S. V. Kirpichenko, T. J. Barton, V. V. Keiko, V. A. Pestunovich, and B. A. Trofimov, *Tezisy Dokl. Nauchn. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei*, 14th, 1975, 147 (*Chem. Abstr.*, 1978, **89**, 43 569).

<sup>261</sup> H. Noth, H. Fußstetter, H. Prommerening, and T. Taeger, *Chem. Ber.*, 1980, **113**, 342.

<sup>262</sup> H. W. Roesky and S. K. Mehrotra, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 599.

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 F. Kobayashi, H. Furukawa, M. Ogawa, Y. Muraoka, I. Yahara, and Y. Hayashi, *Oyo Yakuri*, 1978, **16**, 779 (*Chem. Abstr.*, 1979, **90**, 146 153)  
 K. Takeda, *Symp. Pap., IUPAC Int. Symp. Chem. Nat. Prod.*, 11th, 1978, **4** (Part 1) 464 (*Chem. Abstr.*, 1980, **92**, R34 512)  
 T. Hori, T. Miyake, K. Takeda, and J. Kato, *Prog. Cancer Res. Ther.*, 1978, **10**, 159  
 Y. Nomura, J. Yamagata, H. Kondo, K. Kanda, and K. Takenaka, *Prog. Cancer Res. Ther.*, 1978, **10**, 15  
 A. V. Kamernitskii, A. M. Ustyniuk, and T. M. A. Ngo, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 180
- Naturally occurring Episuiphides.**—R. A. Cole, *Phytochemistry*, 1978, **17**, 1563 [in autolysis of turnip, *Brassica campestris*]  
 L. N. Nixon, E. Wong, C. B. Johnson, and E. J. Birch, *J. Agric. Food Chem.*, 1979, **27**, 355 [aroma of cooking mutton]  
 M. Sakaguchi and T. Shibamoto, *Agric. Biol. Chem.*, 1979, **43**, 667, and *J. Agric. Food Chem.*, 1978, **26**, 1179 [in model system for browning of food]
- Spectroscopy.**—W. J. Broer and W. D. Weringa, *Org. Mass Spectrom.*, 1978, **13**, 232 [ $C_2H_3S^+$  ions]  
 J. L. Holmes, A. S. Blair, G. M. Weese, A. D. Osborne, and J. K. Terlouw, *Adv. Mass Spectrom., Sect. B*, 1978, **7**, 1227 [ $C_2H_4S^+$  ions]  
 G. Baykut, K.-P. Wanczek, and H. Hartmann, *Adv. Mass Spectrom., Sect. A*, 1980, **8**, 186 [thiiran spectrum and ion chemistry]  
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 M. Sakaguchi and T. Shibamoto, *Agric. Biol. Chem.*, 1979, **43**, 667 [ $C_2H_4S_2$  in model system for browning of food]  
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 J. L. Holmes, A. S. Blair, G. M. Weese, A. D. Osborne, and J. K. Terlouw, *Adv. Mass Spectrom., Sect. B*, 1978, **7**, 1227 [mass spectrum of  $C_2H_4S^+$ ]  
 H. J. Moeckel, *Fresenius' Z. Anal. Chem.*, 1979, **295**, 241 [CI mass spectrometry of thietan]  
 A. A. Scala and I. Colon, *J. Heterocycl. Chem.*, 1978, **15**, 421 [mass spectra of thietan and both oxides]  
 R. Gleiter and J. Spanget-Larsen, *Top. Current Chem.*, 1979, **86**, 139 [photoelectron spectra of thietan and a dithietan]

# Saturated Cyclic Compounds of Sulphur, Selenium, and Tellurium

BY P. K. CLAUS

## 1 Introduction

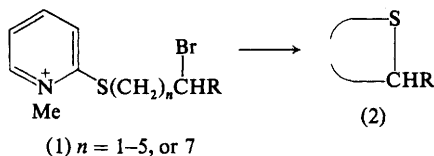
The organization of this chapter follows the lines of previous volumes, with the exception that a subsection on sulphur-containing macrocycles has been omitted.

A number of reviews on several aspects of sulphur chemistry and comprehensive books on general organic chemistry include material pertinent to this Report. Among these are various chapters of recent volumes of a well-known reference book<sup>1</sup> and of a new comprehensive book on Organic Chemistry.<sup>2</sup> A review on <sup>13</sup>C n.m.r. data of non-aromatic heterocyclic compounds includes numerous data on saturated sulphur heterocycles.<sup>3</sup> The synthesis of saturated heterocyclic rings has been summarized.<sup>4</sup> Conformations of five-membered rings have been reviewed in detail.<sup>5</sup> New tellurium heterocyclic chemistry has been summarized.<sup>1,6</sup>

## 2 Thiolans, Thians, Thiepan, Thiocans, and their Oxides, Dioxides, and Imides

**Synthesis.**—A new general synthesis of  $\alpha$ -substituted three- to nine-membered cyclic sulphides (2) has been developed:<sup>7</sup> cyclization, with NaOH, of the pyridinium salts (1), prepared by the reaction of  $\alpha,\omega$ -dihalogenoalkanes with *N*-methyl-(1*H*)-pyridine-2-thione, afforded the cyclic sulphides (2).

Several 2- and 3-substituted thiolans have been prepared by the bromination of



<sup>1</sup> 'Rodd's Chemistry of Carbon Compounds', Elsevier, Amsterdam, Vol. IV, Part E (1977), Chap. 21; Part H (1978), Chap. 40; and Part K (1979), Chap. 50, 52, 55, and 56.

<sup>2</sup> 'Comprehensive Organic Chemistry', Vol. 3, ed. D. N. Jones, and Vol. 4, ed. P. G. Sammes, Pergamon Press, London, 1979.

<sup>3</sup> E. L. Eliel and K. M. Pietrusiewicz, *Top. Carbon-13 NMR Spectrosc.*, 1979, **3**, 171.

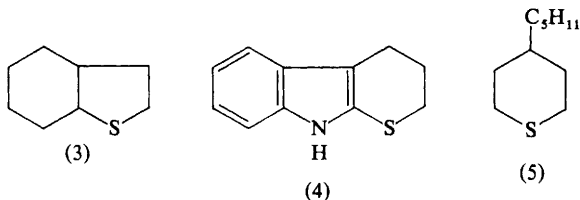
<sup>4</sup> N. F. Elmore, in 'General and Synthetic Methods' (Specialist Periodical Reports), ed. G. Pattenden, The Chemical Society, London, 1978, Vol. 1, p. 197.

<sup>5</sup> B. Fuchs, *Top. Stereochem.*, 1978, **10**, 1.

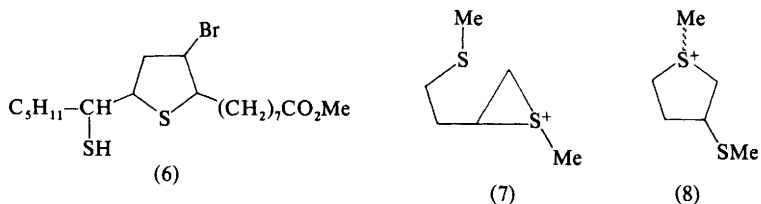
<sup>6</sup> K. J. Irgolic, *J. Organomet. Chem.*, 1978, **158**, 235, 267.

<sup>7</sup> K. Sotoya, M. Yamada, T. Takamoto, T. Sakakibara, and R. Sudoh, *Synthesis*, 1977, 884.

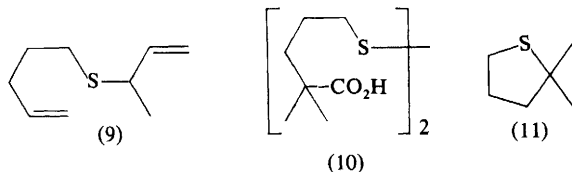
$\delta$ -methoxy-alkanols and cyclization with  $\text{Na}_2\text{S}$ .<sup>8</sup> Bicyclic *S*-heterocycles, e.g. (3), have been obtained by intramolecular electrophilic addition of thiol groups to double bonds.<sup>9</sup> The thiopyrano-indole (4) was obtained by oxidative cyclization of 3-(indol-3-yl)propanethiol.<sup>10</sup> Ultraviolet irradiation of ethylene sulphide and alkenyl-magnesium bromides gave 4-substituted thians, e.g. (5).<sup>11</sup>



Ring-opening of episulphides was also involved in the synthesis of substituted thiolans, e.g. (6).<sup>12</sup> Methylsulphenylation of but-3-enyl methyl sulphide afforded an intermediate thiiranium salt (7) that suffered intramolecular attack by the methylthio-group to give a diastereoisomeric mixture of the sulphonium salts (8).<sup>13</sup>



Photolysis of allyl pent-4-enyl sulphides such as (9) gave mixtures of five- and six-membered sulphur heterocycles *via* unsaturated thiyl radicals.<sup>14</sup> Oxidative decarboxylation of the disulphide (10), and intramolecular trapping of the intermediate carbon radical to give the thiolan (11), indicated a biochemical pathway for the formation of the C(2)–S bond of penicillins.<sup>15</sup>



<sup>8</sup> N. P. Volynskii and L. P. Shcherbakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1080 (*Chem. Abstr.*, 1979, **91**, 175 105).

<sup>9</sup> A. B. Urin, G. N. Gordadze, N. P. Volynskii, G. D. Gal'pern, and V. G. Zaikin, *Tezisy Dokl. Nauchn. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei 14th*, 1975, (publ. 1976), 56 (*Chem. Abstr.* 1978, **88**, 190 543).

<sup>10</sup> T. Hino, H. Miura, R. Murata, and M. Nakagawa, *Chem. Pharm. Bull.*, 1978, **26**, 3695.

<sup>11</sup> V. P. Krivonogov, V. I. Dronov, and R. F. Nigmatullina, *Khim. Geterotsikl. Soedin.*, 1977, 1622 (*Chem. Abstr.* 1978, **88**, 152 358).

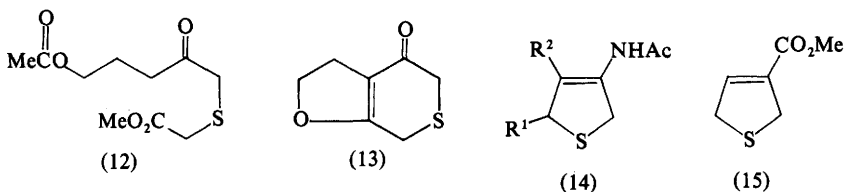
<sup>12</sup> I. L. Kuranova and E. V. Snetkova, *Zh. Org. Khim.*, 1978, **14**, 2165 (*Chem. Abstr.*, 1979, **90**, 121 320).

<sup>13</sup> M. L. Kline, N. Beutow, J. K. Khim, and M. C. Caserio, *J. Org. Chem.*, 1979, **44**, 1904.

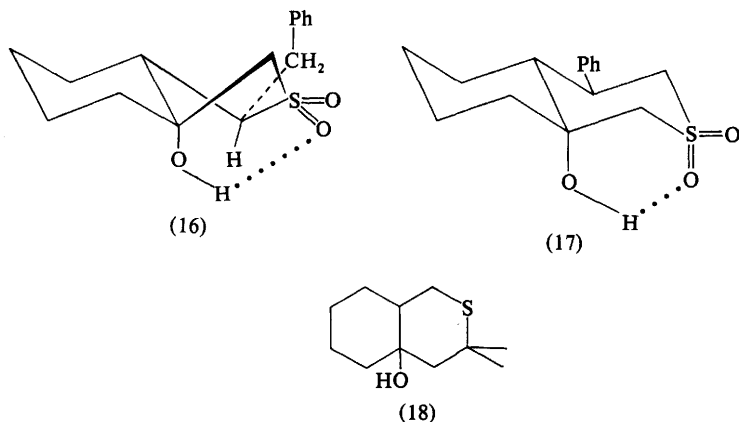
<sup>14</sup> G. Bastien and J. M. Surzur, *Bull. Soc. Chim. Fr., Part 2*, 1979, 601.

<sup>15</sup> J. E. Baldwin and T. S. Wan, *J. Chem. Soc., Chem. Commun.*, 1979, 249.

Intramolecular Claisen condensation of (12), followed by cyclization, afforded the fused  $\Delta^3$ -dihydrothiopyran-5-one (13).<sup>16</sup> A new ring-closure reaction was found by heating *N*-acetyl-*S*-( $\alpha$ -keto-alkyl)cysteines with acetic anhydride to give 2,5-dihydrothiophens (14).<sup>17</sup> 3-Methoxycarbonyl-2,5-dihydrothiophen (15), an excellent precursor to 2-methoxycarbonyl-1,3-butadiene, was synthesized by modifications of previously reported procedures.<sup>18</sup> Carbon-13 n.m.r. data for a series of 2,5-dihydrothiophens have been reported.<sup>19</sup>



The studies on cyclization of 2-(methylsulphonylalkyl)cyclohexanones have been continued,<sup>20</sup> and 2-thiahyrindane 2,2-dioxides, *e.g.* (16), and 2-thiadecalin 2,2-dioxides, *e.g.* (17), have been isolated as the main products of such cyclizations. The synthesis of the 2-thiadecalin (18), with an angular hydroxy-group in position 10, has been reported.<sup>21</sup>



Nucleophilic addition of activated methylene compounds to distyryl sulphides, sulphoxides, or sulphones stereoselectively gave the thian derivatives (19).<sup>22</sup> Analogues of the known host compound (20) have been synthesized, and their

<sup>16</sup> S. Bernasconi, C. Capellini, A. Corbella, M. Ferrari, P. Gariboldi, G. Jommi, and M. Sisti, *Gazz. Chim. Ital.*, 1979, **109**, 5.

<sup>17</sup> G. F. Field, *J. Org. Chem.* 1979, **44**, 825.

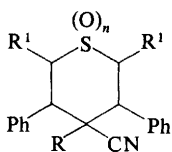
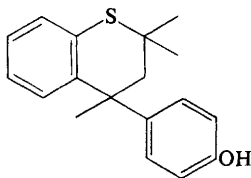
<sup>18</sup> J. M. McIntosh and R. A. Sieler, *J. Org. Chem.*, 1978, **43**, 4431.

<sup>19</sup> J. M. McIntosh, *Can. J. Chem.*, 1979, **57**, 131.

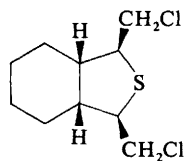
<sup>20</sup> S. Fabrisini, S. Fatutta, and A. Risaliti, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1321.

<sup>21</sup> G. V. Pavel and M. N. Tilichenko, *Zh. Org. Khim.*, 1978, **14**, 2369 (*Chem. Abstr.*, 1979, **90**, 137 626).

<sup>22</sup> O. H. Hartwig and H. Yamamura, *Liebigs Ann. Chem.*, 1977, 1500; H. Yamamura and H. H. Otto, *Arch. Pharm. (Weinheim, Ger.)*, 1978, **311**, 762.

(19)  $n = 0, 1, \text{ or } 2$ R = CN, CO<sub>2</sub>R<sup>2</sup>, or CONH<sub>2</sub>

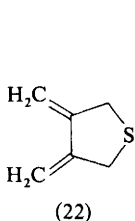
(20)



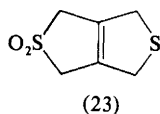
(21)

inclusion properties investigated.<sup>23</sup> Double addition of SCl<sub>2</sub> to 1,2-divinylcyclohexane afforded the *cis*-2-thiahyrindane (21).<sup>24</sup>

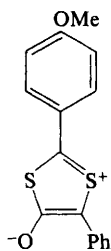
Cycloaddition reactions are particularly valuable for the construction of sulphur heterocycles, and have been intensively investigated. Thus, Diels–Alder reactions of the thiolan (22), which has an exocyclic *cis*-diene structure, and which is easily prepared from 2,3-bis(bromomethyl)buta-1,3-diene, have been studied.<sup>25</sup> Addition of SO<sub>2</sub> gave the cyclo-adduct (23). A series of dithiabicycloheptan-3-ones have been prepared by [3 + 2]cycloadditions of the cyclic thiocarbonyl ylide (24) to a variety of dipolarophiles; *e.g.*, to formaldehyde to give (25).<sup>26</sup>



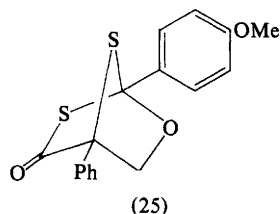
(22)



(23)



(24)



(25)

The double Diels–Alder reaction of tetrachlorothiophen 1,1-dioxide and allyl vinyl sulphide proceeded with cheletropic loss of SO<sub>2</sub> to give the hetero-isotwistene (26).<sup>27</sup> Various Diels–Alder reactions of 2*H*-thiopyran yielded *endo*-adducts, such as (27).<sup>28</sup>

Cycloadditions of thiocarbonyl compounds to dienes, or of vinyl thiocarbonyl derivatives to dienophiles, have received particular attention. Thus, Δ<sup>3</sup>-dihydrothiopyrans, *e.g.* (28), have been obtained by the addition of diphenyl thioketone to 1,3-dienes.<sup>29</sup> Oxidation of (28), followed by a vinylogous Pummerer reaction, gave the 2*H*-thiopyran (29).<sup>29</sup>

1,2-Dithiocarbonyl compounds such as dithio- or tetrathio-oxalates (30) served

<sup>23</sup> A. D. U. Hardy, J. J. McKendrick, and D. D. McNicol, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1072.

<sup>24</sup> N. N. Novitskaya, N. K. Pokonshchikova, R. G. Kantyukova, E. E. Zaev, L. M. Khalilov, and G. A. Tolstikov, *Tezisy Dokl. Nauchn. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei 14th*, 1975, (publ. 1976), 102 (*Chem. Abstr.*, 1978, **88**, 190 512).

<sup>25</sup> Y. Gaoni and S. Sadeh, *J. Org. Chem.*, 1980, **45**, 870.

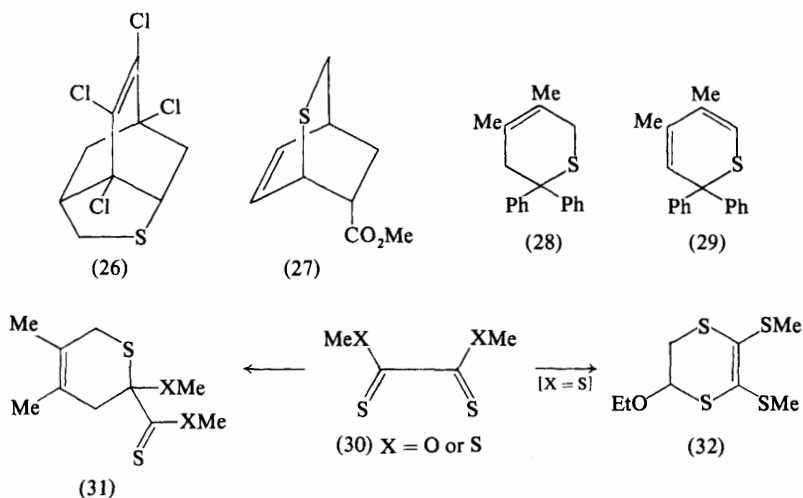
<sup>26</sup> H. Gotthardt and C. M. Weissshuhn, *Chem. Ber.*, 1976, **111**, 3029, 3037, 3171, 3178; H. Gotthardt, C. M. Weissshuhn, and B. Christl, *Liebigs Ann. Chem.*, 1979, 360.

<sup>27</sup> M. S. Raasch, *J. Org. Chem.*, 1980, **45**, 856.

<sup>28</sup> R. H. Fleming and B. M. Murray, *J. Org. Chem.*, 1979, **44**, 2280.

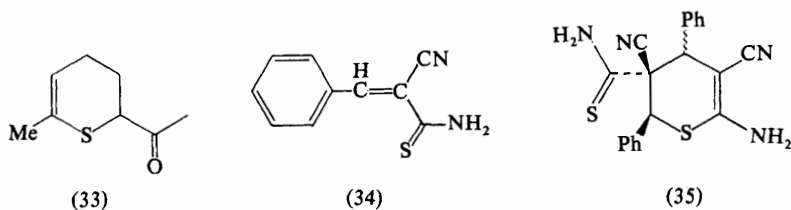
<sup>29</sup> K. Praefcke and C. Weichsel, *Liebigs Ann. Chem.*, 1979, 784; *ibid.*, 1980, 333.





in cycloadditions both as  $2\pi$  and  $4\pi$  components, yielding either  $\Delta^3$ -dihydrothiopyrans (31) or dithiin derivatives, e.g. (32)<sup>30</sup> (see also Chap. 3, Pt III, p. 196).

2-Acyl- $\Delta^2$ -dihydrothiopyrans, e.g. (33), have been obtained by Diels-Alder reactions and Cope rearrangements of intermediate 2-thioacyl- $\Delta^3$ -dihydrothiopyrans.<sup>31</sup> Certain 3-aryl-2-cyano-thioacrylamides, such as (34), dimerize in a ( $4_s + 2_s$ ) mode to give a  $\Delta^2$ -dihydrothiopyran, e.g. (35).<sup>32</sup>



The  $\alpha\beta$ -unsaturated thioketone (36), generated by thermolysis of its dimer, reacts with a variety of dienophiles to give cyclo-adducts with the  $\Delta^2$ -dihydrothiopyran structure, e.g. (37).<sup>33</sup> A similar cycloaddition has been used for the preparation of (38).<sup>34</sup>

The *o*-thioquinone methide (39), generated by the photoreaction of benzo-1,2-dithiole-3-thione with olefins, dimerizes to give a head-to-head dimer.<sup>35a</sup> Further

<sup>30</sup> K. Hartke, T. Kissel, J. Quante, and G. Henssen, *Angew. Chem.*, 1978, **90**, 1016.

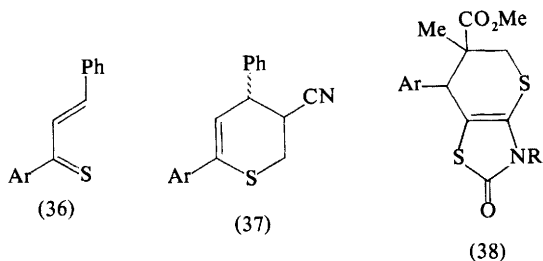
<sup>31</sup> K. B. Lipkowitz and B. P. Mundy, *Tetrahedron Lett.*, 1977, 3417; K. B. Lipkowitz, S. Scarpone, B. P. Mundy, and W. G. Bornmann, *J. Org. Chem.*, 1979, **44**, 486.

<sup>32</sup> J. S. A. Brunskill, A. De, and D. F. Ewing, *J. Chem. Soc., Perkin Trans. 1*, 1978, 629.

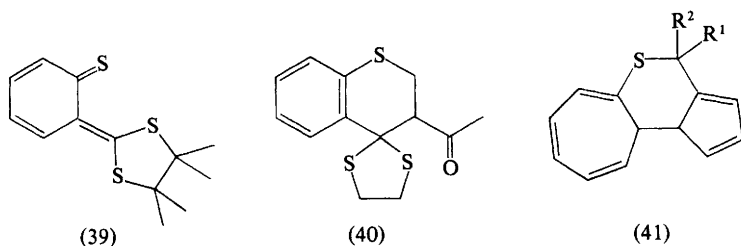
<sup>33</sup> T. Karakasa and S. Motoki, *J. Org. Chem.*, 1978, **43**, 4147; *ibid.*, 1979, **44**, 4151; T. Karakasa, H. Yamaguchi, and S. Motoki, *ibid.*, 1980, **45**, 927.

<sup>34</sup> H. Abdel Reheem Ead, N. Abdel Latif Kassab, H. Koeppel, W. D. Bloedorn, and K. D. Schleinitz, *J. Prakt. Chem.*, 1980, **322**, 155.

<sup>35</sup> (a) R. Okazaki, F. Ishii, K. Sunagawa, and N. Inamoto, *Chem. Lett.*, 1978, 51; (b) R. Okazaki, K. T. Kang, K. Sunagawa, and N. Inamoto, *ibid.*, p. 55; R. Okazaki, K. Sunagawa, K. T. Kang, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 496.

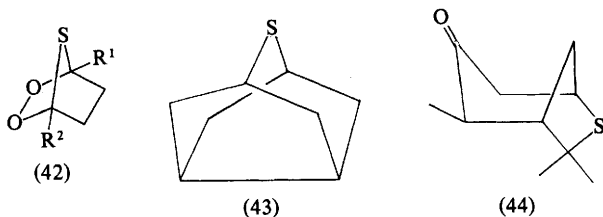


stereo- and regio-selective [4 + 2]-cycloaddition reactions of (39), e.g. to give (40), have also been investigated.<sup>35b</sup> Cycloaddition of trophothione to fulvenes afforded the cyclo-adducts (41).<sup>36</sup>



Various thiolans have been prepared by ionic hydrogenation of thiophens with  $\text{Et}_3\text{SiH}$  in the presence of acids.<sup>37</sup> Addition of singlet oxygen to alkyl-substituted thiophens, followed by reduction with di-imine, gave the bicyclic compounds (42); these are examples of the hardly known thia-ozonides.<sup>38</sup> 9-Thia-noradamantane (43) has been synthesized from cyclo-octa-2,7-dienone by a reaction sequence involving a transannular C—H carbene insertion.<sup>39</sup> A bicyclic product (44) has been obtained by the reaction of (–)-carvone with  $\text{H}_2\text{S}$ .<sup>40</sup>

Photolysis of 9-thiabicyclo[3.3.1]nonane-2,6-dione (45) gave monocyclic products, e.g. (46), by  $\alpha$ -cleavage and  $\text{C}_\alpha$ —S bond cleavage.<sup>41</sup> The 2,6-dithia-



<sup>36</sup> T. Machiguchi, M. Watanabe, and M. Hoshino, *Koen Yoshishu-Hibenzekei Hokozoku Kagaku Toronkai [oyobi] Kozo Yuki Kagaku Toronkai*, 12th, 1979, 5 (*Chem. Abstr.*, 1980, **92**, 128 670).

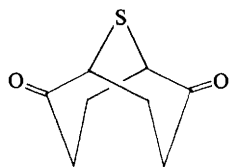
<sup>37</sup> Z. N. Parnes, Yu. I. Lyakhovetskii, M. I. Kalinkin, D. N. Kursanov, and L. I. Belen'kii, *Tetrahedron*, 1978, **34**, 1703; A. V. Anisimov, V. F. Ionova, V. S. Babaitsev, V. K. Govorek, and E. A. Viktorova, *Khim. Geterotsykl. Soedin.*, 1979, 1062 (*Chem. Abstr.*, 1980, **92**, 41 801).

<sup>38</sup> W. Adam and H. J. Eggelte, *Angew. Chem.*, 1978, **90**, 811.

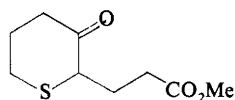
<sup>39</sup> T. Sasaki, S. Eguchi, and T. Hioki, *J. Org. Chem.*, 1978, **43**, 3808.

<sup>40</sup> M. Hargreaves, R. McDougall, and L. Rabari, *Z. Naturforsch., Teil B*, 1978, **33**, 1535.

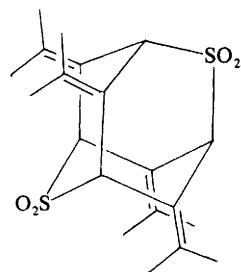
<sup>41</sup> P. H. McCabe and C. R. Nelson, *Tetrahedron Lett.*, 1978, 2819.



(45)



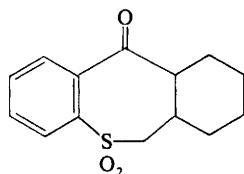
(46)



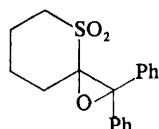
(47)

adamantane (47) has, surprisingly, been formed by the  $\text{Bu}^n\text{Li}$ -induced cyclo-dimerization of diallenyl sulphone.<sup>42</sup>

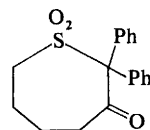
Tetrahydro-1- and -2-benzothiepins have been prepared by ring-expansion of thio- and isothio-chroman-4-ones, using ethyl diazoacetate.<sup>43</sup> Photocycloaddition of cyclohexene to 3-acetoxybenzo[*b*]thiophen 1,1-dioxide and base-catalysed hydrolytic ring-expansion of the intermediate tricyclic adduct gave (48).<sup>44</sup> Expansion of the ring was also observed in the acid-catalysed rearrangement of the  $\alpha\beta$ -epoxy-sulphone (49) to the thiepan-3-one (50). A similar ring-expansion of unsaturated sultones afforded  $\beta$ -keto-sultones.<sup>45</sup>



(48)

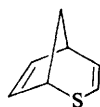


(49)

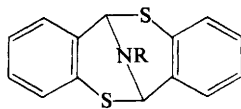


(50)

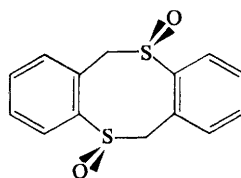
The bicyclic thia-octadiene (51) and its partially and fully saturated derivatives have been prepared by known methods.<sup>46</sup> The preparation of the dibenzodithiocins (52) and (53) has been reported.<sup>47</sup> The chiral *cis*-isomer (53) could be partially resolved.<sup>47b</sup>



(51)



(52)



(53)

<sup>42</sup> S. Braverman, D. Reisman, and M. Sprecher, *Tetrahedron Lett.*, 1979, 901.

<sup>43</sup> R. Pellicciari and B. Natalini, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1822.

<sup>44</sup> N. V. Kirby and S. T. Reid, *J. Chem. Soc., Chem. Commun.*, 1980, 150.

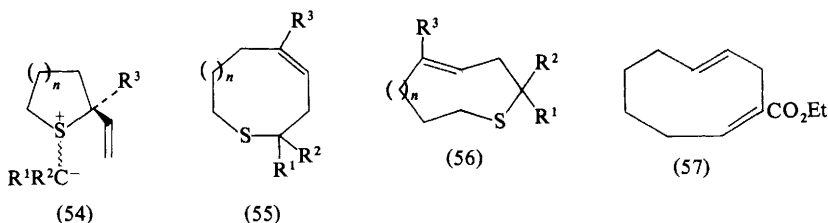
<sup>45</sup> T. Durst, K. C. Tin, F. Dereinachirtzbach, J. M. Decesare, and M. D. Ryan, *Can. J. Chem.*, 1979, 57, 258.

<sup>46</sup> P. Barraclough, S. Bilgic, and D. W. Young, *Tetrahedron*, 1979, 35, 91; P. Barraclough, S. Bilgic, J. B. Pedley, A. J. Rogers, and D. W. Young, *ibid.*, p. 99.

<sup>47</sup> (a) J. Becher, C. Dreier, and O. Simonsen, *Tetrahedron*, 1979, 35, 869; (b) M. Nogradi, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1261.

One of the most intriguing developments in the chemistry of mesocyclic heterocycles began with Vedejs' ring-expansion procedure, involving a [2,3]-sigmatropic shift of stabilized sulphonium ylides<sup>48</sup> (see Vol. 4, p. 84, and Vol. 5, p. 214). Further details of the synthesis of medium-sized sulphur and nitrogen heterocycles by the repeatable ring-expansion process have now been given.<sup>49</sup> A general method for the synthesis of 2-vinyl-substituted thiacycloalkanes has been described by Fava.<sup>50</sup> The ring-expansion procedure has been extended to the use of non-stabilized ylides.<sup>50</sup> It can be shown that ring expansion does not compete favourably with a rapid isomerization by reversible deprotonation-reprotonation at C-2, *i.e.*,  $\alpha$  to the vinyl group. Methylides (54;  $R^1 = R^2 = H$ ) that are without hydrogen at C-2 ( $R^3 = Me$ ) undergo highly stereoselective but non-stereospecific ring-enlargements: only the five-membered ylide with the carbanionic and the vinyl moieties on the same side of the ring reacted in a [2,3]-sigmatropic fashion, to give a 17:1 mixture of (*Z*)- and (*E*)-5-methylthiacyclo-oct-4-ene [(55; and (56;  $R^1 = R^2 = H$ ,  $R^3 = Me$ ,  $n = 1$ )], but both isomers of the six-membered ylide (54;  $n = 2$ ) gave exclusively (*E*)-5-methylthiacyclonon-4-ene (56;  $n = 2$ ).<sup>51</sup> The results have been rationalized in terms of conformational effects of the ground state and reactant-like transition states. The DBU-induced rearrangement of the ylide (54;  $R^1 = H$ ,  $R^2 = CO_2Et$ ,  $R^3 = H$ ,  $n = 2$ ) afforded the thiacyclononene (55;  $R^1 = R^3 = H$ ,  $R^2 = CO_2Et$ ,  $n = 2$ ), in 97% isolated yield.<sup>52</sup>

The configurational inversion of (55;  $R^1 = R^2 = R^3 = H$ ,  $n = 1$ ) to the corresponding compound (56) was achieved by applying the Whitham method of concerted fragmentation of a dioxolan derivative.<sup>53</sup> Cyclic sulphides, prepared by the repeatable ring-expansion process, could be converted into carbocycles by a Ramberg-Bäcklund extrusion of sulphur from the corresponding sulphones; *e.g.*, the formation of (57) from the sulphone derived from (56;  $R^1 = R^3 = H$ ,  $R^2 = CO_2Et$ ,  $n = 3$ ).<sup>54</sup>



Attempts to cause the conversion of cyclic sulphides, *e.g.* (58), into carbocycles, *e.g.* (59), by an anionic [2,3]-shift of the derived enolate anions failed.<sup>55</sup> After *S*-methylation, a product of a sigmatropic shift could be obtained only in the case of the six-membered ring (58), but Stevens 1,2-migrations and fragmentations to

<sup>48</sup> E. Vedejs and J. P. Hagen, *J. Am. Chem. Soc.*, 1975, **97**, 6878.

<sup>49</sup> E. Vedejs, M. J. Arco, D. W. Powell, J. M. Renga, and S. P. Singer, *J. Org. Chem.*, 1978, **43**, 4831.

<sup>50</sup> V. Ceré, C. Paolucci, S. Pollicino, E. Sandri, and A. Fava, *J. Org. Chem.*, 1978, **43**, 4826.

<sup>51</sup> V. Ceré, C. Paolucci, S. Pollicino, E. Sandri, and A. Fava, *J. Org. Chem.*, 1979, **44**, 4128.

<sup>52</sup> E. Vedejs, M. J. Arco, and J. M. Renga, *Tetrahedron Lett.*, 1978, 523.

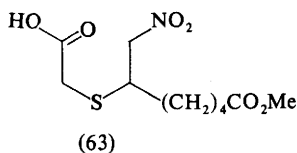
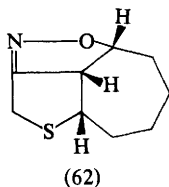
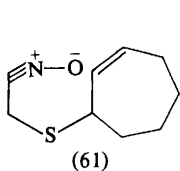
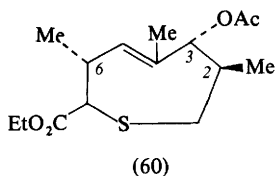
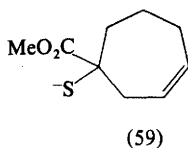
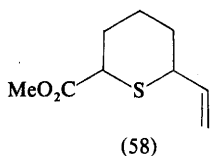
<sup>53</sup> V. Ceré, A. Guenzi, S. Pollicino, E. Sandri, and A. Fava, *J. Org. Chem.*, 1980, **45**, 261.

<sup>54</sup> E. Vedejs and S. P. Singer, *J. Org. Chem.*, 1978, **43**, 4884.

<sup>55</sup> E. Vedejs, M. J. Arnost, and J. P. Hagen, *J. Org. Chem.*, 1979, **44**, 3230.

alkanes also occurred, and these were the exclusive pathways in the case of the eight-membered derivatives. The *trans*-1-thiacyclo-oct-4-ene (60), which incorporates the C-1 to C-7 segment of a macrocyclic antibiotic with the natural stereochemistry at C-2, C-3, and C-6, has been obtained by a remarkably stereospecific cyclization of an intermediate sulphenic acid, followed by DBU-promoted [2,3]-sigmatropic ring-expansion, which transformed the stereochemistry at C-4 of the intermediate thiolanium ylide into the stereochemistry at C-6 of (60).<sup>56</sup>

The construction of saturated sulphur heterocycles was also involved in numerous contributions to the synthesis of natural products or modified natural products. Further syntheses of 'd'- or 'dl'-biotin have been reported. An intramolecular [3 + 2]-cycloaddition of the nitrile oxide (61) to give the tricyclic product (62) was the key step in a synthesis of racemic biotin, starting with cycloheptene.<sup>57</sup> A quite different approach to racemic biotin, involving only nine steps, started with a cycloaddition of chlorosulphonyl isocyanate to chromene.<sup>58</sup> In a synthesis of 'd'-biotin, the monoaldehyde of adipic acid was transformed into the heptanoate (63), which was resolved.<sup>59</sup> A sequence of thirteen steps led from 'd'-glucosamine to 'd'-biotin.<sup>60</sup> Several biotin analogues have been prepared,<sup>61</sup> and the <sup>13</sup>C n.m.r. spectrum of biotin has been studied.<sup>62</sup>



Various approaches to the synthesis of sulphur-containing prostaglandins and prostacyclins, and of thia-steroids with sulphur in ring A, B, C, or D have been

<sup>56</sup> E. Vedejs and M. J. Mullins, *J. Org. Chem.*, 1979, **44**, 2947.

<sup>57</sup> P. N. Confalone, E. D. Lollar, G. Pizzolato, and M. R. Uskokovic, *J. Am. Chem. Soc.*, 1978, **100**, 6291.

<sup>58</sup> A. Fliri and K. Hohenlohe-Oehringen, *Chem. Ber.*, 1980, **113**, 607.

<sup>59</sup> J. Vasilvskis, J. A. Gualteri, S. D. Hutchings, R. C. West, J. W. Scott, D. R. Parrish, F. T. Bizzarro, and G. F. Field, *J. Am. Chem. Soc.*, 1978, **100**, 7423.

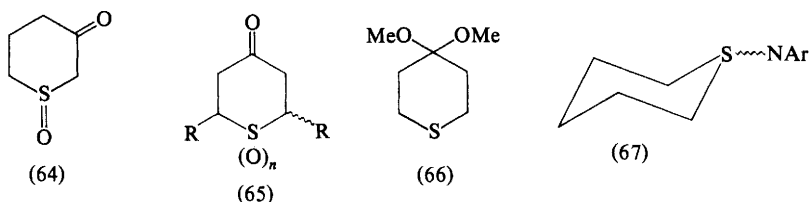
<sup>60</sup> H. Ohru, N. Sueda, and S. Emoto, *Agric. Biol. Chem.*, 1978, **42**, 865 (*Chem. Abstr.*, 1978, **89**, 59 857).

<sup>61</sup> S. D. Mikhno, T. M. Filippova, N. S. Kulachkina, I. G. Suchkova, and V. M. Berezovskii, *Zh. Org. Khim.*, 1978, **14**, 1706 (*Chem. Abstr.*, 1978, **89**, 197 247).

<sup>62</sup> H. J. Bradbury and R. N. Johnson, *J. Magn. Reson.*, 1979, **35**, 217; S. P. Singh, V. I. Stenberg, S. A. Franum, and S. S. Parmar, *Spectrosc. Lett.*, 1978, **11**, 259 (*Chem. Abstr.*, 1978, **89**, 41 785).

reported.<sup>63,64</sup> The synthesis and properties of 6-thiatetracycline have been described,<sup>65</sup> and the *X*-ray structure of 6-thiatetracycline has been determined.<sup>66</sup>

**Properties.**—Stereochemical aspects in the chemistry of saturated sulphur heterocycles are still emphasized; <sup>1</sup>H and, in particular, <sup>13</sup>C n.m.r. spectroscopy have been widely used for conformational and configurational assignments. Thus, n.m.r. studies indicated that thian-3-one, its 1-oxide (64), and its 1,1-dioxide have the chair conformation.<sup>67,68</sup> The conformational equilibria for (64) and for the 4-oxo-isomer (65; R = H, *n* = 1) and its dimethyl acetal were shown to be heavily shifted towards the axial sulphoxide conformer, compared with that for the thian 1-oxide itself.<sup>67</sup> Carbon-13 n.m.r. shift data indicated a transannular interaction between the sulphur and the carbonyl group of (64) and of its 1,1-dioxide.<sup>68</sup> The conformations of a series of 2,6-diphenylthian-4-ones (65; R = Ph, *n* = 0) and of a few thian-4-ols have been investigated by <sup>13</sup>C n.m.r. methods.<sup>69</sup> Low-temperature <sup>13</sup>C n.m.r. spectroscopy was used for a determination of the barrier to ring inversion of the ketal (66) (42.7 kJ mol<sup>-1</sup>)<sup>70</sup> and for a study of the conformational equilibria of a series of 1-imide derivatives of thian, and of some oxa- and di-thians.<sup>71</sup> In a series of thian 1-*N*-arylimides (67), which generally prefer the conformation with an equatorial S—N bond, the conformational preference was found to depend on the nature of the substituents on the aromatic ring; strongly electron-withdrawing substituents increase the percentage of the conformer with an axial S—N bond.<sup>71</sup>



Dynamic n.m.r. methods have also been used for the determination of the barrier to inversion of (68),<sup>72</sup> and of the free energy for ring inversion between the two

<sup>63</sup> J. H. Jones, J. B. Bicking, and E. J. Cragoe, Jr., *Prostaglandins*, 1979, **17**, 223 (*Chem. Abstr.*, 1979, **90**, 203 934); K. C. Nicolaou, R. L. Magolda, and W. E. Barnette, *J. Chem. Soc., Chem. Commun.*, 1978, 375; K. C. Nicolaou, S. P. Seitz, W. J. Sipio, and J. F. Blount, *J. Am. Chem. Soc.*, 1979, **101**, 3884; K. C. Nicolaou, W. E. Barnette, and R. L. Magolda, *ibid.*, 1978, **100**, 2567; K. Shimoi, Y. Arai, and M. Hayashi, *Chem. Lett.*, 1978, 1375.

<sup>64</sup> P. S. Jogdeo and G. V. Bhide, *Heterocycles*, 1977, **7**, 985; S. Kano, K. Tanaka, S. Hibino, and S. Shibuya, *J. Org. Chem.*, 1979, **44**, 1580, 1582; S. R. Ramadas and P. S. Srinivasan, *Steroids*, 1977, **30**, 213; N. Rao and L. D. Quin, *Phosphorus Sulfur*, 1979, **5**, 371; T. Terasawa and T. Okada, *Heterocycles*, 1978, **11**, 171; *ibid.*, 1980, **14**, 99; *J. Chem. Soc., Perkin Trans. I*, 1978, 576; *ibid.*, 1979, 990.

<sup>65</sup> R. Kirchlechner and W. Rogalski, *Tetrahedron Lett.*, 1980, **21**, 247; K. Irmscher, *Symp. Pap. — IUPAC Intern. Symp. Chem. Nat. Prod. 11th*, 1978, **4** (Part 1), 494 (*Chem. Abstr.*, 1980, **92**, 94 142).

<sup>66</sup> R. Prevo and J. J. Stezowski, *Tetrahedron Lett.*, 1980, **21**, 251.

<sup>67</sup> W. A. Nachtergaele, D. Tavernier, and M. J. O. Anteunis, *Bull. Soc. Chim. Belg.*, 1980, **89**, 33.

<sup>68</sup> J. A. Hirsch and A. A. Jarmas, *J. Org. Chem.*, 1978, **43**, 4106.

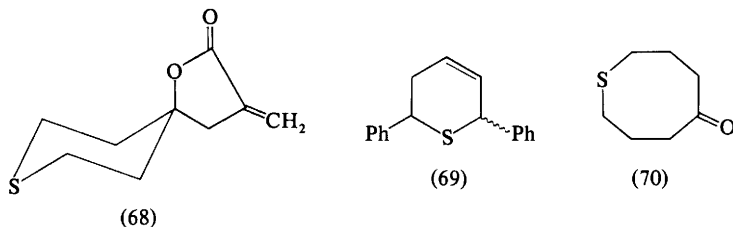
<sup>69</sup> K. Ramalingam, K. D. Berlin, R. A. Loghry, D. van der Helm, and N. Satyamurthy, *J. Org. Chem.*, 1979, **44**, 471, 477.

<sup>70</sup> R. Borsdorf, E. Kleinpeter, S. Agurakis, and H. Jancke, *J. Prakt. Chem.*, 1978, **320**, 309.

<sup>71</sup> P. K. Claus, F. W. Vierhapper, and R. L. Willer, *J. Org. Chem.*, 1979, **44**, 2863.

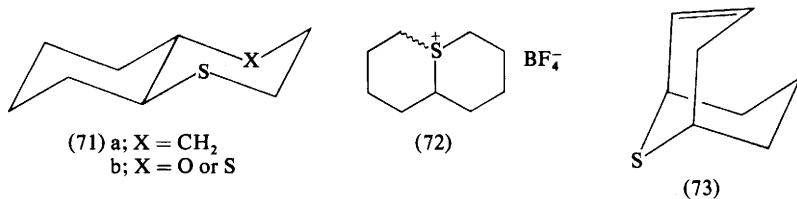
<sup>72</sup> K. Ramarajan and K. D. Berlin, *Proc. Okla. Acad. Sci.*, 1979, **59**, 70 (*Chem. Abstr.* 1980, **92**, 163 468).

half-chair forms of (35), which are about equally populated at  $-25\text{ }^{\circ}\text{C}$ .<sup>73</sup> Considering contributions from torsional interactions of the substituents, a value of about  $37\text{ kJ mol}^{-1}$  has been calculated for unsubstituted dihydrothiopyrans;<sup>73</sup> thus the introduction of a sulphur atom into a six-membered unsaturated ring increases the barrier to inversion by about  $15\text{ kJ mol}^{-1}$ . The *cis*- and *trans*-isomers of 2,6-diphenyl-5,6-dihydro-2*H*-thiopyran (69) have been found to exist in half-chair rather than in boat conformations.<sup>74</sup> Two conformational processes, with free-energy barriers of  $28.1$  and  $34.1\text{ kJ mol}^{-1}$ , respectively, and which were assigned to pseudorotation and to ring-inversion processes, were found for 1-thiacyclo-octan-5-one (70), which has been deduced to have an unsymmetrical boat-chair conformation.<sup>75</sup>



Carbon-13 n.m.r. spectra of *trans*-1-thiadecalin (71a), of 4-hetera-*trans*-1-thiadecalins (71b), and of the corresponding sulphoxides ( $\alpha$ - or  $\beta$ -oriented) and sulphones have been reported.<sup>76</sup> The *trans*- and *cis*-stereoisomers of 1-thionia-bicyclo[4.4.0]decane salts (72) were prepared, and their stereostructures assigned by  $^{13}\text{C}$  and  $^1\text{H}$  n.m.r. spectroscopy and by *X*-ray analysis.<sup>77</sup> Activation parameters for the configurational inversion of (72) and of the derived ylides were determined. The *cis*-ylide has been found to be much more stable than the *trans*-form.<sup>77</sup> Values of substituent-induced  $^{13}\text{C}$  n.m.r. chemical shifts in the 9-thiabicyclo[3.3.1]non-2-ene skeleton were evaluated by measuring the spectra of a number of derivatives (73).<sup>78</sup>

An elucidation of the structure, of the conformation, and of the configuration at sulphur of the bicyclic compounds (74) was based on  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. evidence



<sup>73</sup> J. S. A. Brunskill, A. De, and D. F. Ewing, *Org. Magn. Reson.*, 1979, **12**, 257.

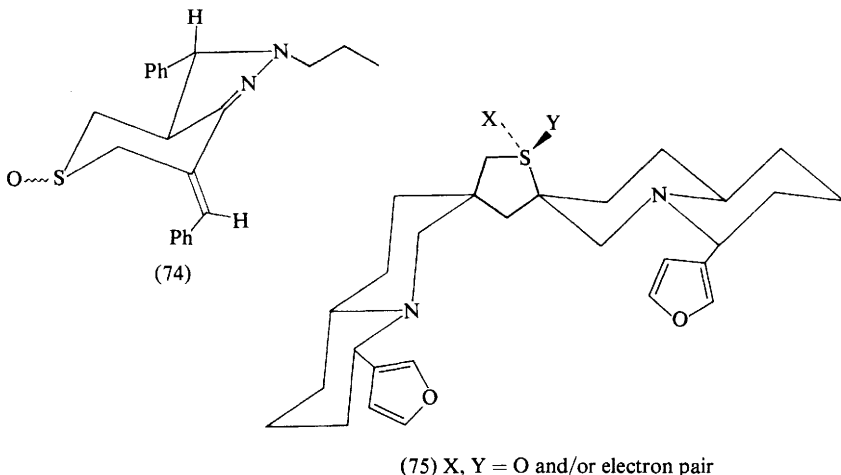
<sup>74</sup> P. M. Henrichs and C. H. Chen, *J. Org. Chem.*, 1979, **44**, 3591.

<sup>75</sup> F. A. L. Anet and M. Ghiaci, *J. Org. Chem.*, 1980, **45**, 1224.

<sup>76</sup> R. P. Rooney and S. A. Evans, *J. Org. Chem.*, 1980, **45**, 180.

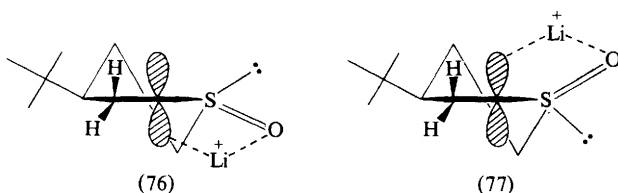
<sup>77</sup> D. M. Roush, E. M. Price, L. K. Templeton, D. H. Templeton, and C. H. Heathcock, *J. Am. Chem. Soc.*, 1979, **101**, 2971.

<sup>78</sup> J. W. de Haan, L. J. M. van de Ven, H. Vlems, M. M. E. Scheffers-Sap, H. Gillissen, and H. M. Buck, *Tetrahedron*, 1980, **36**, 799.



and *X*-ray results.<sup>79</sup> The configuration at the sulphur atom in sulphoxides of the thiaspiran alkaloids (75), extracted from *Nuphar* species, was established by ASIS and LIS methods and by analysis of S—O bond-anisotropy-induced shifts.<sup>80</sup> LIS studies have also been proven to be useful in structural investigations of sulphonium salts.<sup>81</sup> There is strong evidence that a weak complexation occurs between the lanthanide ion and the anion of the sulphonium compound, and not with the electron pair on sulphur.

On the basis of the observed coupling constants, the lithio-derivatives of *cis*- and *trans*-4-*t*-butylthian 1-oxides (76) and (77) have been proposed to exist in half-chair conformations, with a planar metallated carbon atom and the Li<sup>+</sup> held in a stable co-ordinated structure.<sup>82</sup>



The use of <sup>1</sup>H n.m.r. data for the calculation of torsional angles in 4-*t*-butylthian has been discussed.<sup>83</sup> Conformations of *cis*- and *trans*-3- and -4-acetoxy-1-methylthianium compounds were investigated by M.O. calculations, <sup>1</sup>H n.m.r.

<sup>79</sup> M. S. Puar, G. C. Rovnyak, A. I. Cohen, B. Töplitz, and J. Z. Gougoutas, *J. Org. Chem.*, 1979, **44**, 2513; G. C. Rovnyak and V. Shu, *ibid.*, p. 2518.

<sup>80</sup> J. T. Wrobel, J. Ruzskowska, and K. Wojtasiewicz, *J. Mol. Struct.*, 1978, **50**, 299.

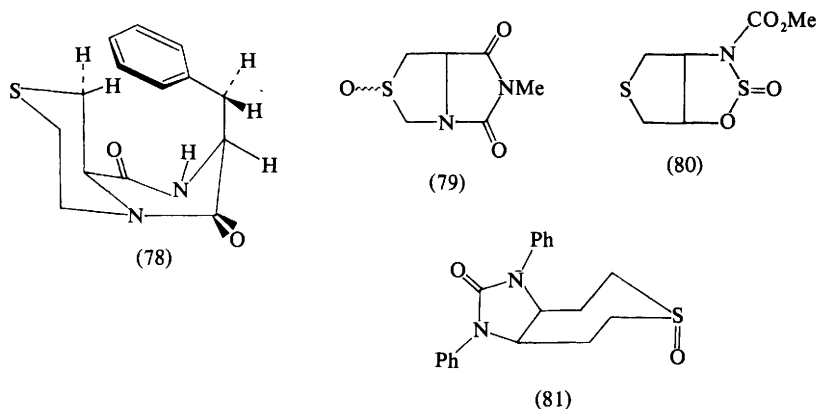
<sup>81</sup> R. L. Caret and A. N. Vennos, *J. Org. Chem.*, 1980, **45**, 361.

<sup>82</sup> G. Chassaing, R. Lett, and A. Marquet, *Tetrahedron Lett.*, 1978, 471; R. Lett and G. Chassaing, *Tetrahedron*, 1978, **34**, 2705.

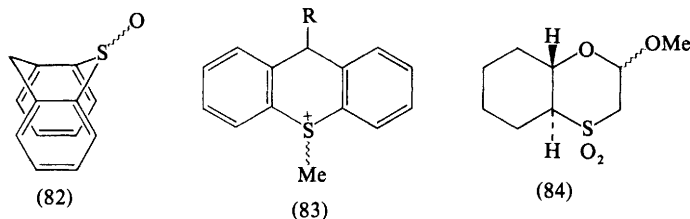
<sup>83</sup> M. Brigodiot, S. Boileau, M. C. Taieb, and H. Cheradame, *Tetrahedron*, 1979, **35**, 87.



spectroscopy, and X-ray crystallography.<sup>84</sup> The assignment of the configuration and conformation of cyclic dipeptides with sulphur-containing saturated rings, e.g. (78),<sup>85</sup> of the two isomeric sulphoxides (79) of *N*-methyl-L-thiazolidine-4-carboxylic acid hydantoin,<sup>86</sup> of the bicyclic compound (80),<sup>87</sup> and of two isomeric sulphoxides with the 8,10-diaza-4-thiabicyclo[5.3.0]decan-9-one structure, e.g. (81),<sup>88</sup> was based on n.m.r. data.



The conformations of thioxanthene *S*-oxide (82)<sup>89</sup> and of several thioxanthenium salts (83)<sup>90</sup> have been investigated. The conformation of (82) was shown to be changed from *S*-O pseudo-equatorial in weakly interacting solvents to pseudo-axial *S*-O in associating solvents such as  $\text{CF}_3\text{CO}_2\text{H}$ .<sup>89</sup> The solvent-dependent conformational free-energy of the 2-methoxy-group of (84) was determined by  $\text{BF}_3$ -catalysed equilibration.<sup>91</sup>



<sup>84</sup> H. D. Höltje, *Arch. Pharm. (Weinheim, Ger.)*, 1978, **311**, 311 (*Chem. Abstr.*, 1978, **89**, 42 136); H. D. Höltje, B. Jensen, and G. Lambrecht, *Eur. J. Med. Chem.-Chim. Ther.*, 1978, **13**, 453 (*Chem. Abstr.*, 1979, **90**, 161 938); G. Lambrecht, *Arch. Pharm. (Weinheim, Ger.)*, 1978, **311**, 636 (*Chem. Abstr.*, 1978, **89**, 107 866).

<sup>85</sup> M. J. O. Anteunis, R. Schrooten, W. A. Nachtergaele, and I. Neirinckx, *Bull. Soc. Chim. Belg.*, 1979, **88**, 684; M. J. O. Anteunis, C. Bécu, B. Liberek, and A. Kolodziejczyk, *ibid.*, p. 817.

<sup>86</sup> M. J. O. Anteunis, W. A. Nachtergaele, and M. Budesinsky, *Bull. Soc. Chim. Belg.*, 1979, **88**, 233.

<sup>87</sup> T. M. Filippova, S. D. Mikhno, N. S. Kulchikina, I. G. Suchkova, and V. M. Berezovskii, *Vopr. Stereokhim.*, 1978, **7**, 35 (*Chem. Abstr.*, 1979, **91**, 38 783).

<sup>88</sup> L. Lacombe and S. Lavielle, *Org. Magn. Reson.*, 1979, **12**, 39.

<sup>89</sup> A. L. Ternay, Jr., J. Herrmann, and B. A. Hayes, *J. Org. Chem.*, 1980, **45**, 189.

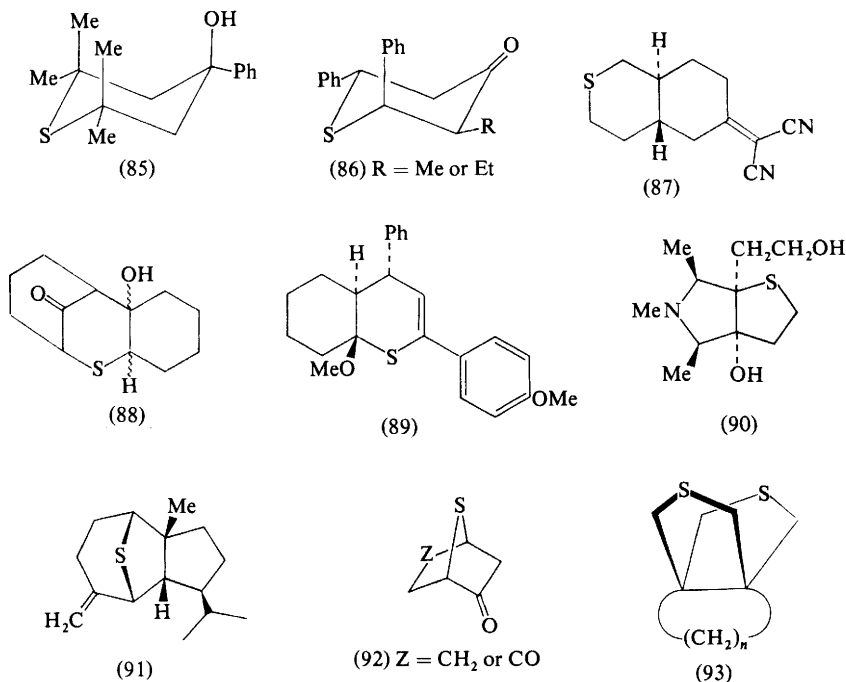
<sup>90</sup> M. Hori, T. Kataoka, H. Shimizu, and S. Ohno, *Heterocycles*, 1979, **12**, 1555.

<sup>91</sup> D. Lee, J. C. Keifer, R. P. Rooney, T. B. Garner, and S. A. Evans, *J. Org. Chem.*, 1979, **44**, 2580.

A partial conformational analysis of a series of substituted thian-4-ols, based on a study of the kinetics of acetylation, has been reported.<sup>92</sup>

The structures of several sulphur heterocycles have been determined using *X*-ray methods, including the thian-4-ol (85), which still showed a flattened chair form,<sup>92</sup> thian-4-ones, e.g. (86),<sup>69</sup> 2-chloro-4-*t*-butylthian 1-oxides,<sup>93</sup> 1-methylthiolanium iodide,<sup>94</sup> the *trans*-2-thiadecalin derivative (87),<sup>95</sup> *cis*- and *trans*-fused tricyclic compounds (88),<sup>96</sup> the bicyclic dihydrothiopyran (89),<sup>97</sup> thiochroman-4-one 1,1-dioxide,<sup>98</sup> 4-bromothiochroman 1,1-dioxide,<sup>99</sup> the degradation product from thiamine (90),<sup>100</sup> and the tricyclic sulphur-containing sesquiterpene (91).<sup>101</sup>

Spatial interactions between sulphur functional groups and carbonyl groups have been investigated by i.r. measurements on a series of thiacycloalkanones, and by



<sup>92</sup> N. Satyamurthy, R. Sivakumar, K. Ramalingam, K. D. Berlin, R. A. Loghry, and D. van der Helm, *J. Org. Chem.*, 1980, **45**, 349.

<sup>93</sup> F. Robert, *Acta Crystallogr., Sect. B*, 1977, **33**, 3480, 3484.

<sup>94</sup> F. Miyoshi, K. Tokuno, T. Watanabe, M. Matsui, and T. Ohashi, *Yakugaku Zasshi*, 1979, **99**, 924 (*Chem. Abstr.*, 1980, **92**, 41 192).

<sup>95</sup> K. Goubitz and C. H. Stam, *Cryst. Struct. Commun.*, 1978, **7**, 503.

<sup>96</sup> A. A. Usoltsev, E. S. Karaulov, M. N. Tilichenko, M. Yu. Antipin, S. G. Il'in, and Yu. T. Struchkov, *Khim. Geterotsykl. Soedin.*, 1978, 1044 (*Chem. Abstr.*, 1978, **89**, 214 799).

<sup>97</sup> S. V. Soboleva, O. A. D'yachenko, L. O. Atovmyan, V. G. Kharchenko, and S. K. Klimenko, *Zh. Strukt. Khim.*, 1978, 499 (*Chem. Abstr.*, 1978, **89**, 196 860).

<sup>98</sup> S. E. Ealick, D. van der Helm, and J. R. Baker, *Acta Crystallogr., Sect. B*, 1979, **35**, 495.

<sup>99</sup> G. D. Andreotti, G. Bocelli, and P. Sgarabotto, *Cryst. Struct. Commun.*, 1978, **7**, 543.

<sup>100</sup> K. Kamiya, Y. Wada, and M. Takamoto, *Takeda Kenkyusho Ho.*, 1979, **38**, 44 (*Chem. Abstr.*, 1980, **92**, 22 423).

<sup>101</sup> T. Yoshida, S. Muraki, and K. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1979, 512.

studying u.v. spectra of 7-thiabicyclo[2.2.1]heptan-2-one and the 2,5-dione (92).<sup>102</sup> P.e. spectra of dithiapropanes (93) indicated increasing spatial interaction between the  $3p$  lone pairs on the sulphur centres with increasing values of  $n$ .<sup>103</sup> The preferred conformation of thiolan-2-yl radicals at low temperatures is probably the envelope form, as indicated by e.s.r. studies.<sup>104</sup> Dipole moments of 1-thiaindans<sup>105</sup> and gas-phase ionization potentials, electrochemical redox potentials, and spectroscopic properties of a series of thiochroman-4-ones and thiochromones<sup>106</sup> have been determined.

**Reactions.**—The stereoselectivity of the abstraction of diastereotopic protons  $\alpha$  to trico-ordinated sulphur and the stereochemistry of electrophilic reactions at the carbanion centres of  $\alpha$ -lithio-thian 1-oxides still excite considerable interest. The rate factors for base-catalysed H–D exchange of  $\alpha$ -protons in several conformationally biased or rigid thianium cations have been measured: with increasing rigidity, the reactivity of  $H_a$  decreases, while that of  $H_e$  remains about constant.<sup>107</sup> It was proposed that the removal of  $H_a$  requires a change to a half-chair conformation in order to get the incipient lone pair at C- $\alpha$  aligned *syn* or *anti* to one of the vicinal S–C bonds.

While the methylation of  $\alpha$ -lithio-thian 1-oxides usually gave stereoselectively the  $\alpha$ -methylated isomer with the *trans* configuration, the alkylation of seven- or eight-membered 1-thiacycloalkane 1-oxides proceeded with inversed stereochemistry, and the more abundant isomer always had the *cis* configuration.<sup>108</sup> Thus the mechanistic explanation (see Vol. 5, p. 91) (based on experiments involving methylations by trimethyl phosphate<sup>82</sup>) which proposed inversion of configuration because of a sterically hindered approach by  $CH_3I$ , but retention when the electrophilic species can act as a chelating agent, does not seem to be generally applicable. A *trans* arrangement of the entering methyl and the *S*-phenyl group was always obtained in low-temperature methylations of six-membered cyclic sulphonium ylides, e.g. (94),<sup>109</sup> even if configurational inversion is necessary, while methylation of five-membered ylides was not found to be stereoselective. The Pummerer reactions of both *cis*- and *trans*-4-(*p*-chlorophenyl)thian *S*-oxide gave the *trans* product (95), but the *cis* product when an excess of DCC or 2,6-lutidine was present.<sup>110</sup> A detailed mechanism for the  $\alpha$ -halogenation of sulphoxides, particularly thian 1-oxides, has been proposed,<sup>111</sup> involving the formation of a positively charged ylide (96). Chlorination of 2,6-diphenylthian-4-one with DMF and  $POCl_3$  gave 4-chloro-2,6-diphenyl-3-formyl-2*H*-dihydrothiopyran, whereas

<sup>102</sup> R. Borsdorf and H. Remane, *J. Prakt. Chem.*, 1980, **322**, 152; M. Kobayashi and R. Gleiter, *Z. Naturforsch., Teil B*, 1978, **33**, 1057.

<sup>103</sup> I. Tabushi, Y. Tamaru, and Z. Yoshida, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1178.

<sup>104</sup> C. Gaze and B. C. Gilbert, *J. Chem. Soc., Perkin Trans. 2*, 1978, 503.

<sup>105</sup> I. U. Numanov, L. M. Kim, and I. M. Nasyrov, *Izv. Akad. Nauk Tadzh. SSR, Otd. Fiz.-Mat. Geol.-Khim. Nauch.*, 1978, 120 (*Chem. Abstr.*, 1979, **91**, 192 638).

<sup>106</sup> R. O. Loutfy, I. W. J. Still, M. Thompson, and T. S. Leong, *Can. J. Chem.*, 1979, **57**, 638.

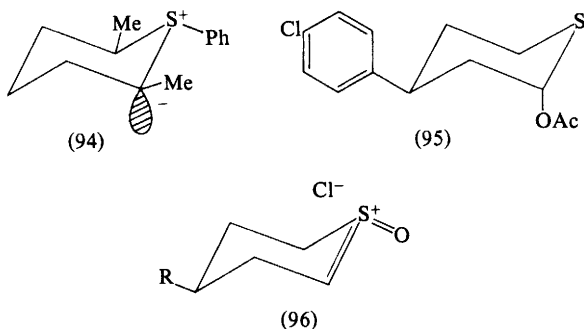
<sup>107</sup> G. Barbarella, G. Dembach, A. Garbesi, F. Bernardi, A. Bottoni, and A. Fava, *J. Am. Chem. Soc.*, 1978, **100**, 200.

<sup>108</sup> V. Ceré, S. Pollicino, E. Sandri, and A. Fava, *Tetrahedron Lett.*, 1978, 5239.

<sup>109</sup> A. Garbesi, *Tetrahedron Lett.*, 1980, **21**, 547.

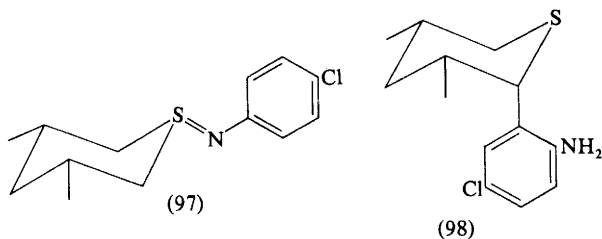
<sup>110</sup> T. Numata, O. Itoh, and S. Oae, *Tetrahedron Lett.*, 1979, 161.

<sup>111</sup> J. Klein, *Chem. Lett.*, 1979, 359.



NCS in pyridine gave 2,6-diphenyldihydro-4*H*-thiopyran-4-one.<sup>112</sup> Full details of the kinetically controlled additions of various photogenerated carbenes and nitrenes to 4-*t*-butylthian have been published.<sup>113</sup> Only *N*-aryl sulphimides with equatorial S–N bonds were obtained from conformationally mobile or rigid thians and from *cis*- and *trans*-1-thiadecalins.<sup>114</sup>

Sulphimides with axial S–N bonds have been prepared from cyclic sulphoxides with equatorial S–O bonds.<sup>114</sup> [2,3]-Sigmatropic rearrangements of configurationally and conformationally homogeneous sulphimides, *e.g.* (97), proceed with high stereospecificity to give the *cis*-rearranged product *e.g.* (98)<sup>115</sup> (see also Chap. 2, Pt III, p. 135). The reduction of thian-4-ones with hydrides has also been studied.<sup>116</sup> The acceleration of the reaction, compared to the rate observed with cyclohexanone, has been attributed to a transannular ‘through-space’ effect.<sup>116a</sup>



The influence of the sulphur functional group on the kinetics of various reactions at position 4 of thian derivatives has been studied, and participation of the electron pair on sulphur, steric approach control, and distortion of the chair conformation were considered in order to explain the observed effects.<sup>117</sup> Base-catalysed

<sup>112</sup> J. A. Van Allan, G. A. Reynolds, and C. H. Chen, *J. Heterocycl. Chem.*, 1977, **14**, 1399; C. H. Chen and G. A. Reynolds, *J. Org. Chem.*, 1979, **44**, 3144.

<sup>113</sup> D. C. Appleton, D. C. Bull, J. McKenna, J. M. McKenna, and A. R. Walley, *J. Chem. Soc., Perkin Trans. 2*, 1980, 385.

<sup>114</sup> P. K. Claus, W. Rieder, and F. W. Vierhapper, *Monatsh. Chem.*, 1978, **109**, 609, 631.

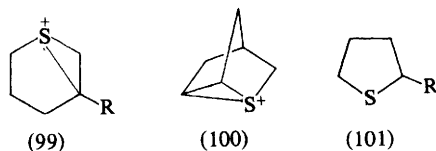
<sup>115</sup> P. K. Claus, W. Rieder, F. W. Vierhapper, and J. Bailer, *Tetrahedron*, 1979, **35**, 1373.

<sup>116</sup> (a) P. Geneste, R. Durand, I. Hugon, and C. Reminiac, *J. Org. Chem.*, 1979, **44**, 1971; (b) N. Satyamurthy and K. Ramalingam, *Indian J. Chem., Sect. B*, 1979, **17**, 62 (*Chem. Abstr.*, 1979, **91**, 123 305).

<sup>117</sup> V. Baliah and R. Jeyaraman, *Indian J. Chem., Sect. B*, 1977, **15**, 832, 852 (*Chem. Abstr.*, 1978, **88**, 88 973, 189 872); V. Baliah and K. Pandiarajan, *ibid.*, 1978, **16**, 807 (*Chem. Abstr.*, 1979, **90**, 103 269); V. Baliah, N. Bhavani, and J. Chandrasekharan, *ibid.*, 1979, **18**, 243 (*Chem. Abstr.*, 1980, **92**, 163 452); V. Baliah and N. Bhavani, *ibid.*, 1978, **16**, 776 (*Chem. Abstr.*, 1979, **90**, 186 718).

cycanoethylation of thian-4-ones and condensations of thiolan-3-ones with acrolein have been reported.<sup>118</sup> Participation of the  $\beta$ -sulphur atom in solvolysis reactions with cyclic systems has been studied intensively. The observed reactivity in solvolysis of various 3-thiacycloalkyl derivatives of different ring size was in the order  $4 > 6 > 3 \gg 5$ .<sup>119</sup> Solvolysis studies with  $\beta$ -substituted five- and six-membered thiacycloalkanes indicated an intermediate episulphonium ion (99).<sup>120</sup> The episulphonium ion (100), formed on solvolysis of a 6-substituted 2-thiabicyclo-[2.2.1]heptane, could be isolated as the perchlorate.<sup>120</sup> The unusually high *exo/endo* rate ratio found in this reaction is the highest observed for participation of  $\beta$ -S.

The 2-tetrahydrothienyl group has been suggested as an excellent protecting group for alcohols, and it is easily introduced by acetal exchange reactions between alcohols and 2-tetrahydrothienyl diphenylacetate (101; R = OCOCHPh<sub>2</sub>), pre-



pared from 2-chlorothiolan (101; R = Cl).<sup>121</sup> Reactions of phosphorus, nitrogen, and carbon nucleophiles with 2-chlorothiolan afforded 2-substituted thiolans, e.g. (101; R = Ph<sub>3</sub>P<sup>+</sup> or R<sub>2</sub>PO), which are useful as equivalents of acyl anions in subsequent Wittig–Horner reactions, and [101; R = CH(CO<sub>2</sub>Et)<sub>2</sub>]. Quenching of the anion derived from the last compound with MeI resulted in  $\alpha$ -methylation and in S-methylation with ring-opening.<sup>121</sup>

3-Tosyl-sulpholens (102) have been prepared as precursors of electron-deficient dienes.<sup>122</sup> The reaction of the bicyclic sulphone (103a) with Grignard reagents was found to produce butadienyl sulphoxides, which are interesting as synthetic intermediates. Cyclopentenones were prepared by thermal cheletropic elimination of SO<sub>2</sub> from (103b).<sup>123</sup> Miscellaneous reactions of di- and tetra-hydrothiophen 1,1-dioxides (alkylations, nitrations, displacement reactions, reactions of 2,3- and 3,4-epoxy-derivatives, Pummerer reactions, and desulphonylations) have been investigated by various groups.<sup>124</sup>

<sup>118</sup> K. Kh. Tokmurzin, *Tezisy Dokl.-Vses. Konf. Stereokhim. Konform. Anal. Org. Neftekhim. Sint. 3rd*, 1976, 83 (*Chem. Abstr.*, 1978, **88**, 169 899); S. D. Mikhno, T. M. Filippova, T. N. Polyanskaya, S. I. Peretokina, I. G. Suchkova, and V. M. Berezovskii, *Khim. Geterotsikl. Soedin.*, 1978, 1620 (*Chem. Abstr.*, 1979, **90**, 121 322).

<sup>119</sup> H. Morita and S. Oae, *Symp. Heterocycl.*, 1977, 95 (*Chem. Abstr.*, 1979, **90**, 5503).

<sup>120</sup> J. Ohishi and S. Ikegami, *Chem. Pharm. Bull.*, 1978, **26**, 3211 (*Chem. Abstr.*, 1979, **90**, 54 321); J. Ohishi, K. Tsuneoka, S. Ikegami, and S. Akaboshi, *J. Org. Chem.*, 1978, **43**, 4013.

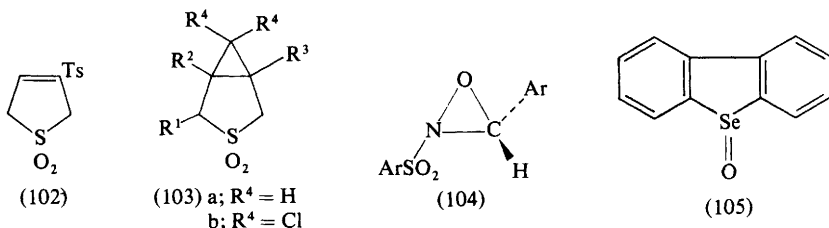
<sup>121</sup> C. G. Kruse, E. K. Poels, F. L. Jonkers, and A. van der Gen, *J. Org. Chem.*, 1978, **43**, 3548; C. G. Kruse, E. K. Poels, and A. van der Gen, *ibid.*, 1979, **44**, 2911; C. G. Kruse, A. C. V. Janse, V. Dert, and A. van der Gen, *ibid.*, p. 2916.

<sup>122</sup> K. Inomata, H. Kinoshita, H. Takemoto, Y. Murata, and H. Kotake, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3341.

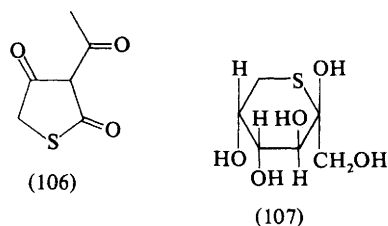
<sup>123</sup> Y. Gaoni, *Tetrahedron Lett.*, 1977, 4521.

<sup>124</sup> Only the latest publications of the various groups are given: E. M. Asatryan, A. Ts. Malkhasyan, R. T. Grigoryan, A. P. Engoyan, S. M. Mirakyan, and G. T. Martirosyan, *Arm. Khim. Zh.*, 1979, **32**, 44 (*Chem. Abstr.*, 1980, **92**, 41 672); V. M. Berestovitskaya, M. V. Titova, and V. V. Perekalin, *Zh. Org. Khim.*, 1979, **15**, 877 (*Chem. Abstr.*, 1979, **91**, 20 226); P. G. Dul'nev, *Khim. Geterotsikl. Soedin.*

(continued overleaf)



The reactivity of cyclic sulphides toward hydrogen atoms<sup>125</sup> and the isomerization and dehydrogenation of thian and other monocyclic sulphides in the presence of acid catalysts<sup>126</sup> have been studied. Among the new reagents for the oxidation of sulphides to sulfoxides was found the oxaziridine (104), which oxidizes 4-t-butylthian to give 64% of the *trans*-sulphoxide and 16% of the *cis*-isomer.<sup>127</sup> Oxidation of thian by the photochemical transfer of oxygen from the selenoxide (105) and by direct photo-oxidation was also observed.<sup>128</sup> P<sub>2</sub>S<sub>5</sub> has been used as a new mild reagent for the reduction of sulfoxides to sulphides, including cyclic derivatives.<sup>129</sup> Various base-induced photoreactions (reductive ring-cleavage, or fragmentation with rearrangement of the carbon skeleton) of the 3-(acetyl)thio-tetronic acid (106) were reported.<sup>130</sup> The reaction of four- to six-membered cyclic sulphoxides with t-butoxyl radicals gave rise to the formation of acyclic alkyl radicals by a ring-opening reaction.<sup>131</sup> A series of chromium pentacarbonyl complexes of dihydro- and tetrahydro-thiophens and of their sulphoxides, in which chromium is bonded to sulphur, have been prepared.<sup>132</sup> The rates of ring-opening and -closing and the proportion of the sugar with a free SH group have been

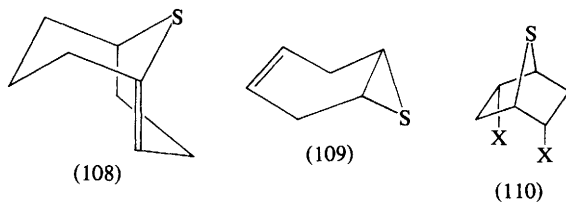


(reference 124 continued)

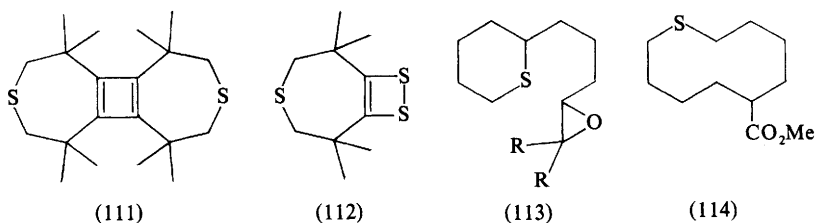
- 1979, 892 (*Chem. Abstr.*, 1979, **91**, 157 536); U. M. Dzhemilev, R. V. Kunakova, F. V. Sharipova, L. V. Spirikhin, L. M. Khalilov, E. V. Vasil'eva, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1822 (*Chem. Abstr.*, 1980, **92**, 6341); L. A. Mukhamedova and L. I. Kursheva, *Khim. Geterotsykl. Soedin.*, 1979, 613 (*Chem. Abstr.*, 1979, **91**, 107 852); N. N. Novitskaya, B. V. Flekhter, L. V. Spirikhin, and G. A. Tolstikov, *ibid.*, p. 563 (*Chem. Abstr.*, 1979, **91**, 39 234); J. Polakova, M. Palecek, and M. Prochazka, *Collect. Czech. Chem. Commun.*, 1979, **44**, 3705; F. Borg-Visse, F. A. Dawans, and E. Marechal, *Synthesis*, 1979, 817.
- <sup>125</sup> O. Horie, J. Nishino, and A. Amano, *J. Org. Chem.*, 1978, **43**, 2800.
- <sup>126</sup> A. K. Yus'kovich, T. A. Danilova, and E. A. Viktorova, *Tezisy Dokl. Nauchn. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei 14th*, 1975, (publ. 1976), 222 (*Chem. Abstr.*, 1978, **89**, 43 031).
- <sup>127</sup> F. A. Davis, R. Jenkins, Jr., and S. G. Yocklovich, *Tetrahedron Lett.*, 1978, 5171.
- <sup>128</sup> T. Tezuka, H. Suzuki, and H. Miyazaki, *Tetrahedron Lett.*, 1978, 4885; T. Tezuka, H. Miyazaki, and H. Suzuki, *ibid.*, p. 1959.
- <sup>129</sup> I. W. J. Still, S. K. Hasan, and K. Turnbull, *Can. J. Chem.*, 1978, **56**, 1423.
- <sup>130</sup> K. Saito and T. Sato, *Chem. Lett.*, 1978, 307.
- <sup>131</sup> W. B. Gara and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1708.
- <sup>132</sup> J. H. Eekhof, M. Hogeveen, and R. M. Kellogg, *J. Organomet. Chem.*, 1978, **161**, 361.

measured for several thio-sugars, e.g. for (107), by following the rates of the reactions with dipyriddy disulphides.<sup>133</sup>

The rate of hydration of the strained 9-thiabicyclononane (108)<sup>134</sup> and the halogenolysis of cyclohexa-1,4-diene monoepisulphide (109), which formed the sulphur-bridged products (110), have been studied.<sup>135</sup>



Several bi- and tri-cyclic thiapan derivatives were obtained by autoxidation of the cyclobutadiene (111) or by various reactions with strained sulphur-containing acetylenes, e.g. the dithiet (112).<sup>136</sup> The ylides derived from *cis*- and *trans*-(72) were alkylated stereoselectively at low temperatures,<sup>77</sup> and they reacted with carbonyl compounds to give ring-opened oxirans (113).<sup>77,137</sup> Reduction of the 6-methoxycarbonyl derivative of (72) afforded the ten-membered cyclic sulphide (114).<sup>77</sup>



Kinetic studies on bimolecular substitutions at the benzylic centre of (115) indicated that the cyclic structure of (115) prevents an orthogonal arrangement of nucleophile and leaving group, and thus stabilization of the transition state by conjugation with the aromatic ring.<sup>138</sup> Various reactions of thiochromanones and related compounds have been studied, including the formation of the 1-thioflavone 1-oxide (116) from the corresponding 1-thioflavanone;<sup>139</sup> the photodehydrogenation of 1-thiochroman-4-ones;<sup>140</sup> the formation of the cyclic thiol ester (117) from isothiochromane;<sup>141</sup> and the *t*-butylation of isothiochroman-4-one by lithiation,

<sup>133</sup> C. E. Grimshaw, R. L. Whistler, and W. W. Cleland, *J. Am. Chem. Soc.*, 1979, **101**, 1521.

<sup>134</sup> W. K. Chwang, A. J. Kresge, and J. R. Wiseman, *J. Am. Chem. Soc.*, 1979, **101**, 6972.

<sup>135</sup> P. H. McCabe and A. Stewart, *J. Chem. Soc., Chem. Commun.*, 1980, 100.

<sup>136</sup> A. Krebs, R. Kemper, H. Kimling, K. H. Klaska, and R. Klaska, *Liebigs Ann. Chem.*, 1979, 473; A. Krebs, H. Colberg, U. Höpfner, A. Kimling, and J. Odenthal, *Heterocycles*, 1979, **12**, 1153; H. J. Lindner and B. Klitschke, *Chem. Ber.*, 1978, **111**, 2047.

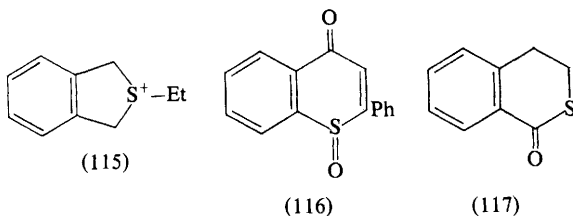
<sup>137</sup> K. Tokuno, F. Miyoshi, Y. Arata, Y. Itatani, Y. Arakawa, and T. Ohashi, *Yakugaku Zasshi*, 1978, **98**, 1005 (*Chem. Abstr.*, 1979, **90**, 6195).

<sup>138</sup> J. F. King and G. T. Y. Tsang, *J. Chem. Soc., Chem. Commun.*, 1979, 1131.

<sup>139</sup> R. Bognar, J. Balint, and M. Rakosi, *Liebigs Ann. Chem.*, 1977, 1529.

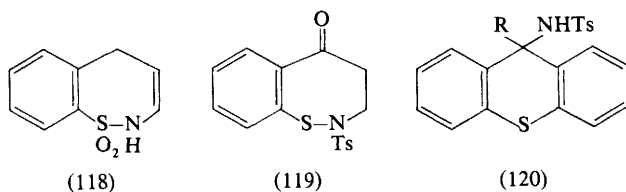
<sup>140</sup> A. Couture, A. Lablache-Combier, and T. Qu Ninh, *Tetrahedron Lett.*, 1977, 2873.

<sup>141</sup> H. Böhme and H.-J. Wilke, *Liebigs Ann. Chem.*, 1978, 1123.

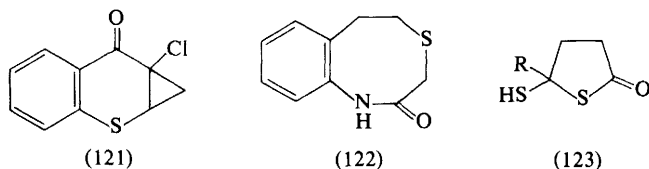


reaction with  $\text{CS}_2$  and  $\text{MeI}$ , and subsequent reaction with an excess of lithium dimethylcuprate.<sup>142</sup>

Photolysis of 2-azido-4-thiochromanone 1,1-dioxide afforded the ring-expanded product (118),<sup>143</sup> while (119) and (120) were formed by base-catalysed sulphimide rearrangements.<sup>144</sup>



The scope of the synthesis of 4-chloro-1-benzothiepins from benzothio-pyranones (121) has been extended by introducing a 5-alkyl or -aryl group *via* Grignard addition.<sup>145</sup> The ring-expansion of a 3-benzothiepinone to the 4,1-benzothiazocine (122) by a Beckmann rearrangement has been described.<sup>146</sup>



Several approaches to cyclic thio- and dithio-lactones have been described: thus, the reaction of  $\gamma$ -oxo-esters with  $\text{H}_2\text{S}$  gave 5-mercaptothiolan-2-ones (123)<sup>147</sup> (see Vol. 5, p. 249). A general approach to  $\gamma$ - and  $\delta$ -thiolactones, *e.g.* (124), involves the reaction of a bis-metallated thioacid with  $\alpha$ - or  $\beta$ -chloro-ketones and cyclization of the resulting  $\gamma$ - or  $\delta$ -chloro- $\beta$ -hydroxy-thioacids.<sup>148</sup> Reactions of cyclic lactones with the dimeric phenylthionophosphine sulphide (125) gave dithiolactones.<sup>149</sup>  $\gamma$ -Dithiolactones, *e.g.* (126), were obtained from 2-alkenyl alkanedithioates, which

<sup>142</sup> O. H. Johansen and K. Undheim, *Acta Chem. Scand., Ser. B*, 1979, **33**, 460.

<sup>143</sup> I. W. J. Still and T. S. Leong, *Can. J. Chem.*, 1980, **58**, 369.

<sup>144</sup> Y. Tamura, S. M. Bayoni, C. Mukai, and M. Ikeda, *Tetrahedron Lett.*, 1980, **21**, 533; Y. Tamura, Y. Nishikawa, C. Mukai, K. Sumoto, M. Ikeda, and M. Kise, *J. Org. Chem.*, 1979, **44**, 1684.

<sup>145</sup> V. J. Traynelis, J. A. Schield, W. A. Lindley, and D. W. H. McDowell, *J. Org. Chem.*, 1978, **43**, 3379.

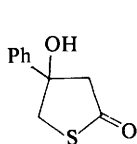
<sup>146</sup> H. Böhme and R. Malcherek, *Arch. Pharm. (Weinheim, Ger.)*, 1979, **312**, 648, 653, 714.

<sup>147</sup> J. Brunet, D. Paquer, and P. Rioult, *Phosphorus Sulfur*, 1977, **3**, 377.

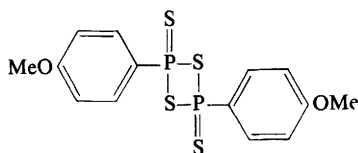
<sup>148</sup> A. M. Sarpeshkar, G. J. Gossick, and J. Wemple, *Tetrahedron Lett.*, 1979, 703.

<sup>149</sup> S. Scheibye, J. Kristensen, and S. O. Lawesson, *Tetrahedron* 1979, **35**, 1339.

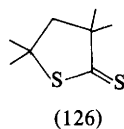




(124)



(125)

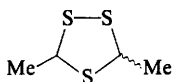


(126)

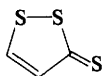
are easily prepared from Grignard reagents,  $\text{CS}_2$ , and allyl bromides, by a [3,3]-sigmatropic rearrangement and cyclization.<sup>150</sup> Dihydrodithioisocoumarin was easily obtained by a one-pot reaction, involving the  $\text{AlCl}_3$ -promoted reaction of  $\text{CS}_2$  with phenylethyl alcohol.<sup>151</sup>

### 3 Compounds containing Two or More Sulphur Atoms in the Ring

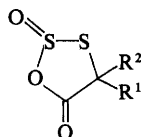
**Di- and Poly-sulphides.**—A new, simple synthesis of *dl'*- $\alpha$ -lipoic acid, using a butadiene telomer as the starting material, has been reported.<sup>152</sup> 3,5-Dimethyl-1,2,4-trithiolan (127), a constituent of processed meat, was prepared by a one-step synthesis from  $\alpha$ -chloroethanesulphenyl chloride.<sup>153</sup> The isolation of *cis*- and *trans*-3,5-diethyl-1,2,4-trithiolan from a member of the genus *Allium*,<sup>154</sup> and the separation of the *cis/trans* isomers of 3,5-dialkyl-1,2,4-trithiolans and their structural investigation by NOE measurements,<sup>155</sup> have been reported. 1,2-Dithiolans (128) (see Vol. 5, p. 306)<sup>156</sup> and cyclic trithiocarbonates have been prepared by various methods.<sup>157</sup> Reactions of  $\alpha$ -mercapto-acids with  $\text{SOCl}_2$  afforded the anhydro-sulphites (129).<sup>158</sup> 1,2-Dithian was formed by treatment of thiolan 1-oxide with the sulphur-transfer reagent (125).<sup>159</sup>



(127)



(128)



(129)

The disulphide (130) was obtained by the reaction of myrcene (7-methyl-3-methylene-octa-1,6-diene) with sulphur.<sup>160</sup> Carbon-13 n.m.r. spectra of 3-methyl-1,2-dithian and of the derived 1- and 2-monoxides, the 1,1- and

<sup>150</sup> M. Schoufs, J. Meijer, P. Vermeer, and L. Brandsma, *Synthesis*, 1978, 439.

<sup>151</sup> M. Czarniecki and R. Q. Kluttz, *Tetrahedron Lett.*, 1979, 4893.

<sup>152</sup> J. Tsuji, H. Yasuda, and T. Mandai, *J. Org. Chem.*, 1978, **43**, 3606.

<sup>153</sup> P. Dubs and M. Joho, *Helv. Chim. Acta*, 1978, **61**, 1404.

<sup>154</sup> H. Kameoka, Y. Demizu, Y. Iwase, and M. Miyazawa, *Tennen Yuki Kagobutsu Toronkai Koen Yoshishu*, 21st, 1978, 199 (*Chem. Abstr.*, 1979, **90**, 69 093); H. Kameoka and Y. Demizu, *Phytochemistry*, 1979, **18**, 1397.

<sup>155</sup> H. P. Kruse and H. Anger, *Z. Chem.*, 1980, **20**, 65.

<sup>156</sup> E. Meinetsberger, A. Schöffer, and H. Behringer, *Synthesis*, 1977, 802.

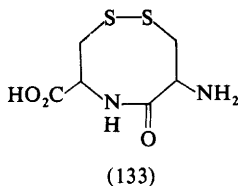
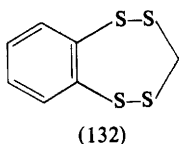
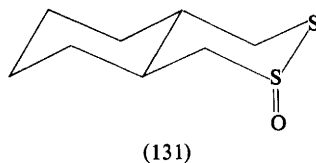
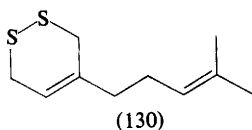
<sup>157</sup> S. Kubota, E. Taniguchi, M. Eto, and K. Maekawa, *J. Fac. Agric., Kyushu Univ.*, 1977, **22**, 1 (*Chem. Abstr.*, 1978, **88**, 74 354).

<sup>158</sup> M. Ali, S. Roy, and B. J. Tighe, *J. Appl. Chem. Biotechnol.*, 1977, **27**, 696 (*Chem. Abstr.*, 1978, **88**, 169 551).

<sup>159</sup> J. B. Rasmussen, K. A. Jörgensen, and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 307.

<sup>160</sup> T. L. Peppard and J. A. Elridge, *Chem. Ind. (London)*, 1979, 552.

2,2-dioxides,<sup>161</sup> and of some bicyclic disulphides, thiolsulphinates, and thiol-sulphonates, e.g. the *trans*-configured 2,3-dithiadecalin  $\beta$ -oxide (131),<sup>162</sup> have been reported. According to the observed  $\beta_{SO}$  effect, 1,2-dithian 1-oxide must exist exclusively in the axial conformation at ambient temperature.<sup>162</sup> Numerous preparations of meso- and macro-cyclic di-, tri-, and poly-sulphides have been reported.<sup>163</sup> Thus, a chair conformation has been assigned to the 1,2,4,5-benzotetrathiepin (132).<sup>163b</sup> The conformation of the cyclic L-cysteinyl-L-cysteine (133) has been investigated by <sup>1</sup>H n.m.r. conformational analysis and compared with the conformation in the solid state.<sup>163d</sup> Numerous macrocyclic di-, tri-, and tetra-disulphides with *m*- or *p*-cyclophane structures<sup>163f</sup> and five- to 26-membered cyclic mono- or bis-trisulphides<sup>163g</sup> have been prepared.



**1,3-Dithiolans, 1,3-Dithians, 1,4-Dithians, and 1,3,5-Trithians.**—Because of the significance of cyclic dithioacetals in organic synthesis, the efforts in investigating their chemical, physical, and structural properties are still increasing. Various di-, tri-, and tetra-alkyl-substituted 1,3-dithians have been prepared,<sup>164,165</sup> and their

<sup>161</sup> T. Takata, Y. H. Kim, S. Oae, and K. T. Suzuki, *Tetrahedron Lett.*, 1978, 4303.

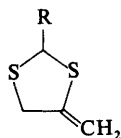
<sup>162</sup> S. W. Bass and S. A. Evans, Jr., *J. Org. Chem.*, 1980, 45, 710.

<sup>163</sup> (a) H. B. Bühl, U. Timm and H. Meier, *Chem. Ber.*, 1979, 112, 3728; (b) F. Fehér and B. Engelen, *Z. Naturforsch., Teil B*, 1979, 34, 426; (c) A. A. Mahmood and J. M. Fayadh, *Egypt. J. Chem.*, 1976, 19, 539 (*Chem. Abstr.*, 1979, 91, 157 712); (d) S. Capasso, L. Mazzarella, and T. Tancredi, *Biopolymers*, 1979, 18, 1555 (*Chem. Abstr.*, 1979, 91, 57 517); (e) R. T. Parfitt, D. E. Games, R. F. Cookson, A. C. Richards, and N. Lynaugh, *Org. Mass. Spectrom.*, 1978, 13, 341; (f) F. Bottino, S. Foti, S. Pappalardo and N. Bresciani-Pahor, *Tetrahedron Lett.*, 1979, 1171; F. Bottino, S. Foti, S. Pappalardo, P. Finocchiaro, and M. Ferrugia, *J. Chem. Soc., Perkin Trans. 1*, 1979, 198, 1712; F. Bottino and S. Pappalardo, *Heterocycles*, 1979, 12, 1331; M. S. Raasch, *J. Org. Chem.*, 1979, 44, 2629; Z. V. Todres, N. G. Furmanova, S. P. Avagyan, Yu. T. Struchkov, and D. N. Kursanov, *Phosphorus Sulfur*, 1979, 5, 309; (g) A. Kato, Y. Hashimoto, I. Otsuka, and K. Nakatsu, *Chem. Lett.*, 1978, 1219; J. Emsley, D. W. Griffiths, and R. Osborn, *J. Chem. Soc., Chem. Commun.*, 1978, 658; J. Emsley and D. W. Griffiths, *J. Chem. Res. (S)*, 1979, 251; J. Emsley, D. W. Griffiths, and G. J. J. Jayne, *J. Chem. Soc., Perkin Trans. 1*, 1979, 228; F. Fehér and B. Engelen, *Acta Crystallogr., Sect. B*, 1979, 35, 1853; F. Fehér and K. Glinka, *Z. Naturforsch., Teil B*, 1979, 34, 1031; D. N. Harpp and A. Granata, *J. Org. Chem.*, 1979, 44, 4144; H. W. Roesky, H. Zamankhan, J. W. Bats, and H. Fuess, *Angew. Chem.*, 1980, 92, 122.

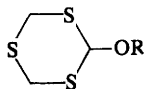
<sup>164</sup> A. V. Bogatskii, A. I. Gren, T. I. Davidenko, and A. F. Galatin, *Vopr. Stereoхим.*, 1978, 7, 24 (*Chem. Abstr.*, 1979, 91, 19 741); T. I. Davidenko, *ibid.*, 1978, 7, 20 (*Chem. Abstr.*, 1979, 91, 19 284); A. V. Bogatskii, T. I. Davidenko, A. I. Gren, and Yu. Yu. Samitov, *Zh. Org. Khim.*, 1979, 15, 2195 (*Chem. Abstr.*, 1980, 92, 93 792).

<sup>165</sup> R. Boehm, *Pharmazie*, 1978, 33, 614 (*Chem. Abstr.*, 1979, 90, 6323).

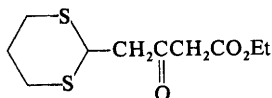
stereochemistry and spectral properties investigated.<sup>164</sup> The synthesis of 1,3-dithian-2- and -5-ones, and of 1,3-dithian-2-thiones, has been reported.<sup>166,167</sup> The reaction of  $\alpha$ -diazo-ketones with CS<sub>2</sub> afforded 1,3-dithiolans.<sup>168</sup> The addition of dithiocarboxylic acids to allenes provided an entry to the 4-alkylidene-1,3-dithiolans (134).<sup>169</sup> A variety of 2-substituted 1,3-dithians has been prepared, partially in view of their synthetic applications. Thus, 2-cyano-1,3-dithian was obtained by lithiation of 1,3-dithian, followed by isocyanide-metal exchange.<sup>170</sup> The reaction of the *N*-tosylimide of 1,3,5-trithian with alcohols and base leads to 2-alkoxy-1,3,5-trithians (135).<sup>171</sup> 2-Trimethylsilyl-1,3-dithian reacts with acid chlorides to give 2-acyl-1,3-dithians.<sup>172</sup> 2-( $\alpha$ -Keto-alkyl)-1,3-dithiolans and 1,3-dithians were obtained by addition of 1,2-dithiols to acetylenic ketones,<sup>173</sup> and by condensation of 1,3-dicarbonyl compounds with propane-1,3-dithiol,<sup>174</sup> respectively. An approach to the  $\gamma$ -(1,3-dithian-2-yl)- $\beta$ -keto-ester (136) has been found.<sup>175</sup> Full details of the synthetic applications of 2-chloro-1,3-dithian have appeared, including reactions with Grignard reagents and active-methylene compounds, and electrophilic aromatic substitutions.<sup>176</sup>



(134)



(135)



(136)

Reports have appeared on the preparation and on the Wittig-Horner reactions of (1,3-dithian-2-yl)phosphonium salts, e.g. (137).<sup>177</sup> Cyclocondensation of O(CH<sub>2</sub>SSO<sub>3</sub>Na)<sub>2</sub> with thioesters gave the 1,3,5-oxathian derivatives (138).<sup>178</sup> 1,2-Dithiols and 2-mercaptoethanols were added to CF<sub>3</sub>CN to give 1,3-dithiolans, e.g. (139), and 1,3-oxathiolans, respectively.<sup>179</sup> Several 2-ferrocenyl-1,3-dithiolans, -1,3-oxathiolans, and -1,3,5-trithians have been prepared.<sup>180</sup>

<sup>166</sup> S. Satsumabayashi, S. Motoki, and H. Takahashi, *Synthesis*, 1979, 184.

<sup>167</sup> S. Kubota, E. Taniguchi, M. Eto, and K. Maekawa, *Agric. Biol. Chem.*, 1977, **41**, 1621 (*Chem. Abstr.*, 1978, **88**, 22 766).

<sup>168</sup> P. Yates and J. A. Eenkhorn, *Heterocycles*, 1977, **7**, 961.

<sup>169</sup> G. Levesque, A. Mahjoub, and A. Thuillier, *Colloq. Int. CNRS*, 1977, **278**, 365 (*Chem. Abstr.*, 1979, **91**, 174 492).

<sup>170</sup> H. N. Khatri and H. M. Walborsky, *J. Org. Chem.*, 1978, **43**, 734.

<sup>171</sup> H. Gross and H. G. Walther, *Z. Chem.*, 1978, **18**, 62.

<sup>172</sup> P. Jutzi and O. Lorey, *Phosphorus Sulfur*, 1979, **7**, 203.

<sup>173</sup> M. N. Basyouni, M. T. Omar, and E. A. Ghali, *Synthesis*, 1980, 115; V. N. Elokhina, R. V. Karnaukhova, A. S. Nakhmanovich, I. D. Kalikhman, and M. G. Voronkov, *Zh. Org. Khim.*, 1979, **15**, 57 (*Chem. Abstr.*, 1979, **91**, 5133).

<sup>174</sup> I. Stahl, R. Manske and J. Gosselck, *Chem. Ber.*, 1980, **113**, 800.

<sup>175</sup> E. C. Taylor and J. L. La Mattina, *J. Org. Chem.*, 1978, **43**, 1200.

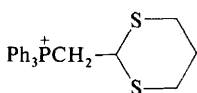
<sup>176</sup> C. G. Kruse, A. Wiseman, and A. van der Gen, *J. Org. Chem.*, 1979, **44**, 1847.

<sup>177</sup> H. J. Cristau, H. Cristol, and D. Bottaro, *Synthesis*, 1978, 826; H. J. Cristau, J. P. Vors and H. Cristol, *Tetrahedron Lett.*, 1979, 2377; B. Costisella and H. Gross, *J. Prakt. Chem.*, 1978, **320**, 128.

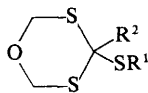
<sup>178</sup> M. G. Gadzhieva, Sh. T. Akhmedov, I. G. Alizade, and A. Z. Gumbatalieva, *Zh. Org. Khim.*, 1978, **14**, 2188 (*Chem. Abstr.*, 1979, **90**, 72 153).

<sup>179</sup> O. Glemser and J. M. Shreeve, *Inorg. Chem.*, 1979, **18**, 2319.

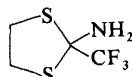
<sup>180</sup> A. Ratajczak and A. Pierko, *Rocz. Chem.*, 1977, **51**, 967 (*Chem. Abstr.*, 1978, **88**, 37 936); A. Ratajczak, *ibid.*, p. 1735 (*Chem. Abstr.*, 1978, **88**, 50 997).



(137)



(138)

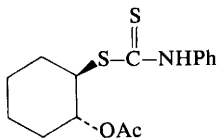


(139)

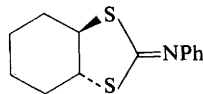
Several papers have appeared concerning new preparative pathways to cyclic keten *SS*-acetals.<sup>181</sup> Both the synthetic exploration of the chemistry of these keten dithioacetals and the synthetic aspects of dithian chemistry in general will not be covered in this Report (see Chap. 2, Pt I, p. 90).

The preparation and several reactions and spectral properties of a variety of tetra- and hexa-thia-adamantanes have been reported.<sup>182</sup>

Retention of configuration was observed in several preparations of bicyclic 1,3-dithiolans from mono- or bi-cyclic precursors that have a *cis* or a *trans* configuration.<sup>183</sup> Thus, the reaction of the *trans*-acetate (140) with KOH gave *trans*-perhydrobenzo-1,3-dithiole (141), probably *via* an intermediate thiuranium ion.



(140)



(141)

Tricyclic 1,3-dithiolanone derivatives, *e.g.* (142), were obtained by the cycloaddition of meso-ionic 1,3-dithiolones (143), which were prepared *in situ*.<sup>184</sup> 1,2-Dithiole-3-thione reacts with norbornadiene and other strained olefins to give heterodienes such as (144).<sup>185</sup> 1,3-Dithiolan-2-thione, though thermally unreactive towards acetylenes, does react photochemically to give dithioles (145).<sup>186</sup>

The chemistry of 2-alkoxy-1,3-benzodithioles has been reviewed.<sup>187</sup> A new route for the reduction of carboxylic acid derivatives is provided by their conversion into 1,3-benzodithiolium salts (146), which can be reduced in two steps to give the corresponding hydrocarbons.<sup>188</sup> The reaction of  $\alpha$ -mercapto-ketones with am-

<sup>181</sup> M. Mikolajczyk, S. Grzejszczak, A. Zatorski, M. Mlotkowska, H. Gross, and B. Costisella, *Tetrahedron*, 1978, **34**, 3081; M. Augustin and Ch. Groth, *J. Prakt. Chem.*, 1979, **321**, 215; T. Harada, Y. Tamaru, and Z. Yoshida, *Tetrahedron Lett.*, 1979, 3525; Y. Nagao, K. Seno, and E. Fujita, *ibid.*, p. 4403; M. J. Taschner and G. A. Kraus, *J. Org. Chem.*, 1978, **43**, 4235.

<sup>182</sup> G. Levesque, A. Mahjoub, and A. Thuillier, *Tetrahedron Lett.*, 1978, 3847; P. Borg, K. Olsson, and Y. Shahab, *Chem. Scr.*, 1977, **11**, 192 (*Chem. Abstr.*, 1979, **90**, 103 253); V. I. Khvostenko, E. G. Galkin, E. M. Vyrypaev, B. M. Lerman, and G. A. Tolstikov, *Khim. Geterotsikl. Soedin.*, 1978, 748 (*Chem. Abstr.*, 1979, **90**, 21 729); B. M. Lerman, L. I. Umanskaya, Z. Ya. Aref'eva and G. A. Tolstikov, *Tezisy Dokl. Nauchn. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei 14th 1975* (publ. 1976), 186 (*Chem. Abstr.*, 1978, **88**, 190 759).

<sup>183</sup> R. C. Forster and L. N. Owen, *J. Chem. Soc., Perkin Trans 1*, 1978, 822, 1208.

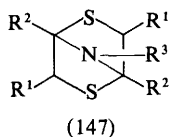
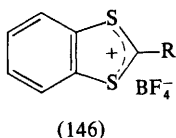
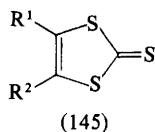
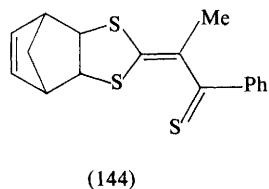
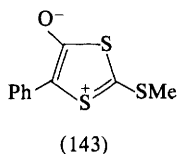
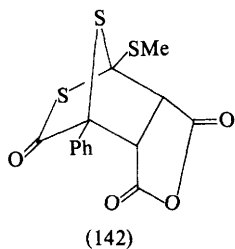
<sup>184</sup> H. Gotthardt, O. M. Huss, and C. M. Weissuhm, *Chem. Ber.*, 1979, **112**, 1650.

<sup>185</sup> V. N. Drozd and G. S. Bogomolova, *Zh. Org. Khim.*, 1977, **13**, 2012 (*Chem. Abstr.*, 1978, **88**, 37 668).

<sup>186</sup> M. Ohashi, N. Mino, N. Nakayama, and S. Yamada, *Chem. Lett.*, 1978, 1189.

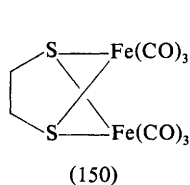
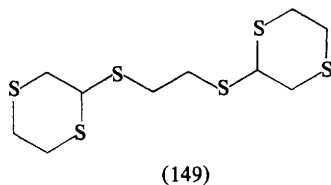
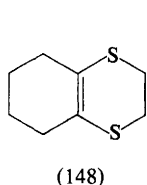
<sup>187</sup> J. Nakayama, K. Ueda, M. Hoshino, and T. Takemasa, *Synthesis*, 1977, 770.

<sup>188</sup> I. Degani and R. Fochi, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1133.



monia, primary amines, diamines, hydroxylamines, or substituted hydrazines provides a versatile synthesis of 2,5-epimino-1,4-dithians (147).<sup>189</sup>

The 1,4-dithian derivatives (148) and (149) have been isolated after the reaction of ethane-1,2-thiol with 2-chlorocyclohexanone<sup>190</sup> and  $\alpha$ -bromoacetaldehyde diethyl acetal,<sup>191</sup> respectively. A novel cleavage reaction, with the formation of complexes such as (150), was observed when 1,4-dithian reacted with  $[\text{Fe}_2(\text{CO})_9]$ .<sup>192</sup>



The protonation of 1,3-dithian in  $\text{FSO}_3\text{H}$  has been thoroughly studied.<sup>193,194</sup> At slow S-H exchange, the monoprotonated species (151) appeared to be predominantly equatorial. The formation of a hydrogen-bonded complex between 1,3-dithian and  $\text{FSO}_3\text{H}$  has been suggested in order to explain the observation that

<sup>189</sup> F. Asinger, A. Saus, and M. Bähr-Wirtz, *Liebigs Ann. Chem.*, 1979, 708.

<sup>190</sup> I. G. Mursakulov, F. F. Kerimov, N. K. Kasumov, E. A. Ramazanov, and N. S. Zefirov, *Azerb. Khim. Zh.*, 1979, 93 (*Chem. Abstr.*, 1979, 91, 56 925).

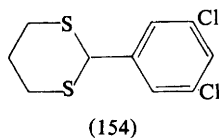
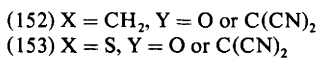
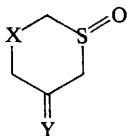
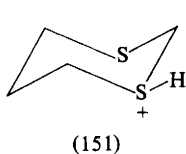
<sup>191</sup> G. Giusti, M. Ambrosio, R. Faure, G. Schembri, E. J. Vincent, and C. Feugeas, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1979, 288, 441.

<sup>192</sup> A. Shaver, P. J. Fitzpatrick, K. Steliou, and I. S. Butler, *J. Am. Chem. Soc.*, 1979, 101, 1313.

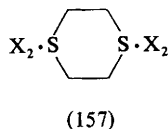
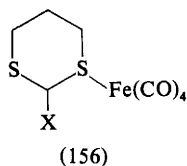
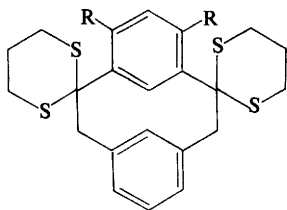
<sup>193</sup> J. B. Lambert, E. Vulgaris, S. I. Featherman, and M. Majchrzak, *J. Am. Chem. Soc.*, 1978, 100, 3269.

<sup>194</sup> J. B. Lambert, M. W. Majchrzak, and D. Stec, III, *J. Org. Chem.*, 1979, 44, 4689.

the axial and equatorial 2-protons are equivalent at 60 °C without equilibration of the 4- and 6-positions. Besides (151), a second form, probably a ring-opened sulphonium ion, was present. Similar phenomena were observed in other related heterocycles, such as 1,3-diselenan, 1,3,5-trithian, and 1,3-dithiolan.<sup>193,194</sup> Thian derivatives (152) strongly prefer the axial conformation of S—O, while the amount of the conformer in which S—O is equatorial is increased in the case of the 1,3-dithian compounds (153).<sup>195</sup> Similar steric requirements for the CH<sub>2</sub> moieties and sulphur atoms have been concluded on the basis of the similar barriers to phenyl rotation that are observed for the dithian (154) and phenylcyclohexane.<sup>196</sup>



An axial preference of the aryl moiety of spirocyclic metacyclophanes (155) has been deduced from <sup>1</sup>H n.m.r. data.<sup>197</sup> The energy barriers to ring inversion were determined for the complexes (156)<sup>198</sup> and (157).<sup>199</sup> The coalescence phenomenon observed in the spectra of the dihalogen complexes (157) was found to be due not to reversal of the 1,4-dithian ring but rather to inversion of the configuration at the sulphur atom.<sup>199</sup>



The existence of a repulsive S/S or S/O *gauche* effect has been demonstrated by *cis/trans* equilibration studies with 1,3-dithians (158).<sup>200</sup> Carbon-13 n.m.r. data have been reported for 2-X-substituted (X = Me, SiMe<sub>3</sub>, GeMe<sub>3</sub>, SnMe<sub>3</sub>, or PbMe<sub>3</sub>) and a series of methyl-substituted 1,3-dithians.<sup>198,201</sup> Incremental shifts of the carbon atoms of the ring have been used for assignments of the stereochemistry of S—O of anancomeric compounds (159).<sup>202</sup> Other spectral studies have dealt with

<sup>195</sup> K. Bergesen, B. M. Carden, and M. J. Cook, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1001.

<sup>196</sup> T. Schaefer, W. Niemczura, and W. Danchura, *Can. J. Chem.*, 1979, **57**, 355.

<sup>197</sup> E. Langer, H. Lehner, and M. J. O. Anteunis, *Monatsh. Chem.*, 1978, **109**, 719.

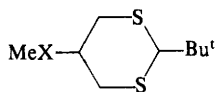
<sup>198</sup> D. J. Cane, W. A. G. Graham, and L. Vancea, *Can. J. Chem.*, 1978, **56**, 1538.

<sup>199</sup> G. Hunter, R. F. Jameson, and M. Shiralian, *J. Chem. Soc., Perkin Trans. 2*, 1978, 712.

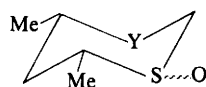
<sup>200</sup> E. L. Eliel and E. Juaristi, *J. Am. Chem. Soc.*, 1978, **100**, 6114.

<sup>201</sup> K. Pihlaja and B. Bjoerkvist, *Org. Magn. Reson.*, 1977, **9**, 533.

<sup>202</sup> M. J. O. Anteunis and L. Van Acker, *Acta Cienc. Indica, Ser. Chem.*, 1979, **5**, 57 (*Chem. Abstr.*, 1980, **92**, 146 145).

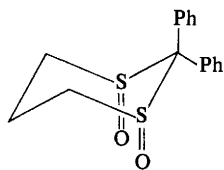


(158) X = O or S

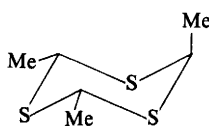
(159) Y = CH<sub>2</sub>, O, or S

the i.r. spectra of 1,3,5-trithian and of its 1-oxide,<sup>203</sup> and with the electron-impact fragmentation of 1,3,5-trithians.<sup>204</sup>

The lower-melting *cis*-1,3-dioxide of 2,2-diphenyl-1,3-dithian (160) exists in the crystal in the conformation with both sulphoxide oxygens *syn*-diaxial.<sup>205</sup> Other X-ray data have been reported on the structure of the trimethyl-1,3,5-trithian (161)<sup>206</sup> and on several 1,4-dithian derivatives.<sup>207</sup>



(160)



(161)

The high stereoselectivity exhibited by the 2-carbanions of 1,3-dithians in reactions with electrophiles evoked further investigations on the structure of the lithiated species. Proton and <sup>13</sup>C n.m.r. spectra of the 2-lithio- and 2-potassio-derivatives of 2-phenyl-1,3-dithian suggested that neither lithium-sulphur interactions nor the concomitant intimate ion-pairing, but rather an intrinsically preferred equatorial orientation of the lone pair in carbanions derived from 1,3-dithians, may be responsible for such stereoselectivity.<sup>208</sup> An X-ray analysis of the TMEDA complex of 2-lithio-2-methyl-1,3-dithian showed the complex to have the dimeric structure (162), with the two lithium atoms in equatorial positions<sup>209</sup> (see Chap. 2, Pt I, p. 89). The barriers to phenyl rotation in 2-lithio-2-phenyl-4,6-dimethyl-1,3-dithian have been discussed in terms of the formation of tight and solvent-separated ion pairs.<sup>210</sup> Exchange studies with 2,2-dimethyl-1,3-dithian, as well as *ab initio* SCF calculations, gave evidence that the polarizability of the C-S  $\alpha$ -bond at the carbanionic site accounts for the regiochemistry of C-H acidification by sulphur.<sup>211</sup> The synthetic scope of 2-lithio-2-stannyl-1,3-dithians (163) has been explored.<sup>212</sup> Tritiation of the 2-anion of 2-nonyl-1,3-dithian was involved in the synthesis of (*R*)-[1-<sup>2</sup>H, 1-<sup>3</sup>H]decane

<sup>203</sup> M. Asai and K. Noda, *Spectrochim. Acta, Part A*, 1978, **34**, 695.

<sup>204</sup> P. Wolkoff and J. L. Holmes, *Org. Mass Spectrom.*, 1978, **13**, 338.

<sup>205</sup> R. F. Bryan, F. A. Carey, and R. W. Miller, *J. Org. Chem.*, 1979, **44**, 1540.

<sup>206</sup> K. Sekido, H. Ono, T. Noguchi, and S. Hirokawa, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 3149.

<sup>207</sup> K. H. Linke and H. G. Kalker, *Z. Anorg. Allg. Chem.*, 1977, **434**, 157; M. Bukowska-Strzyzewska, W. Dobrowolska, and B. Pniowska, *Pol. J. Chem.*, 1978, **52**, 1843 (*Chem. Abstr.*, 1979, **90**, 86 606); J. Kaiser, R. Richter, L. Mögel, and W. Schroth, *Tetrahedron*, 1979, **35**, 505.

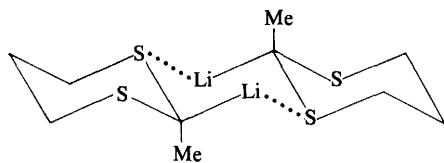
<sup>208</sup> A. G. Abatjoglou, E. L. Eliel, and L. F. Kuyper, *J. Am. Chem. Soc.*, 1977, **99**, 8262.

<sup>209</sup> R. Amstutz, D. Seebach, P. Seiler, B. Schweizer, and J. D. Dunitz, *Angew. Chem.*, 1980, **92**, 59.

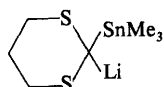
<sup>210</sup> L. F. Kuyper and E. L. Eliel, *J. Organomet. Chem.*, 1978, **156**, 245.

<sup>211</sup> W. T. Borden, E. R. Davidson, N. H. Andersen, A. D. Denniston, and N. D. Epiotis, *J. Am. Chem. Soc.*, 1978, **100**, 1604.

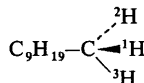
<sup>212</sup> D. Seebach, I. Willert, A. K. Beck, and B. T. Gröbel, *Helv. Chim. Acta*, 1978, **61**, 2510.



(162)



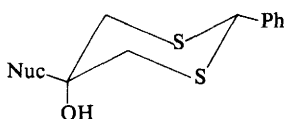
(163)



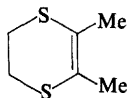
(164)

(164).<sup>213</sup> A novel synthesis of  $\alpha$ -diketones from aldehydes proceeds by the formation of the anion of the ethylene dithioacetal of the aldehyde, reaction with  $\text{Fe}(\text{CO})_5$ , alkylation, and hydrolysis.<sup>214</sup>

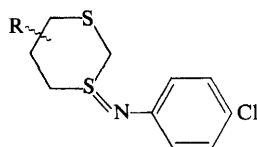
In contrast to 2-phenyl-1,3-dioxan-5-one, where nucleophiles add, regardless of their size, from the axial side of the carbonyl group, the same nucleophiles add to 2-phenyl-1,3-dithian-5-one exclusively from the equatorial side, to yield (165).<sup>215</sup> A ring-expansion reaction has been observed when 2-methyl-2-ethyl-1,3-dithiolan was brominated, giving the dithiin (166).<sup>216</sup>



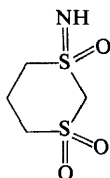
(165)



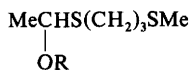
(166)



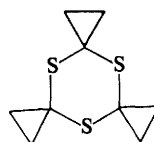
(167)



(168)



(169)



(170)

The liquid-phase oxidation of 1,3-dithian, and oxidation of alcoholic functional groups in the presence of the 1,3-dithian moiety by the Pfitzner–Moffatt reagent, has been studied.<sup>217,218</sup> Both *cis*- and *trans*-1,3-dithian 1-*N*-arylimides (167) were prepared and they rearranged with high stereospecificity.<sup>219</sup> 1,3-Dithian 1-imide 1,3,3-trioxide (168) has been obtained, in excellent yield, by the cleavage of the corresponding *N*-tosyl compound with Na and  $\text{NH}_3$ .<sup>220</sup>

<sup>213</sup> B. T. Golding, P. V. Ioannou, and I. F. Eckhard, *J. Chem. Soc., Perkin Trans. 1*, 1978, 774.

<sup>214</sup> M. Yamashita and R. Suemitsu, *J. Chem. Soc., Chem. Commun.*, 1977, 691.

<sup>215</sup> Y. M. Kobayashi, J. Lambrecht, J. C. Jochims, and U. Burkert, *Chem. Ber.*, 1978, **111**, 3442.

<sup>216</sup> G. Giusti and G. Schembri, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1978, **287**, 213.

<sup>217</sup> S. A. Agisheva, F. N. Latypova, S. S. Zlotskii, V. S. Martem'yanov, A. I. Gren, and D. L. Rakhmankulov, *Tezisy Dokl. Nauchn. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei 14th*, 1975, (publ. 1976), 176 (*Chem. Abstr.*, 1978, **88**, 189 680).

<sup>218</sup> I. Dyong, R. Hermann, and G. von Kiedrowski, *Synthesis*, 1979, 526.

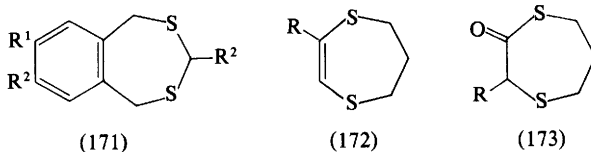
<sup>219</sup> J. Bailer, P. K. Claus, and F. W. Vierhapper, *Tetrahedron*, 1980, **36**, 901.

<sup>220</sup> R. B. Greenwald and D. H. Evans, *Synthesis*, 1977, 650.



Ring cleavage of 1,3-dithiolans and 1,3-dithians by methylthiolation,<sup>221</sup> and of *s*-trithian by treatment with bromine or with Na in liquid NH<sub>3</sub>,<sup>222</sup> has been reported. New methods for dethioacetalization of cyclic and acyclic *SS*- and *OS*-acetals included reactions with isoamyl nitrite, Tl(NO<sub>3</sub>)<sub>2</sub>, Hg(ClO<sub>4</sub>)<sub>2</sub>, nitrosonium or nitronium salts, bromodimethylsulphonium bromide, benzeneseleninic anhydride, electrochemical oxidation, or treatment of *S*-oxides with triethyloxonium salts and hydrolysis.<sup>223</sup> The reaction of 1,3-dithianonium salts with alcohols to give hemithioacetals (169) has been tested as a new method for the protection of alcohols.<sup>224</sup> The pyrolysis of 2,4,6-trimethyl-1,3,5-trithian, affording vinyl mercaptan,<sup>225</sup> and of trimeric cyclopropanethione (170), as a precursor of allene episulphide,<sup>226</sup> has been investigated. The abstraction of hydrogen at C-2 of 1,3-dithians, 1,3-dithiolans, and 1,3-oxathiolans by hydroxyl or *t*-butoxyl radicals has been studied by e.s.r. methods.<sup>227</sup>

**Medium-sized Dithiacycloalkanes.**—A convenient procedure for the preparation of 1,4-dithiepan has been given recently,<sup>228</sup> and the synthesis of various dithiepan derivatives, *i.e.* 6-benzoyl-1,4-dithiepan,<sup>229</sup> 4,7-dihydro-1,3-dithiepin,<sup>230</sup> and 2-substituted benzothiepins (171),<sup>231</sup> has been described. Dynamic <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy revealed the most stable conformation of the seven-membered ring of (171) to be a chair, on which the 2-methyl group adopts an equatorial position while the 2-methoxy-group takes the axial position.<sup>231b</sup> Several dithiepan derivatives were prepared by ring-expansion methods: dehydration of 1,3-dithian-2-ylmethanol gave



<sup>221</sup> J. K. Kim, J. K. Pau, and M. C. Caserio, *J. Org. Chem.*, 1979, **44**, 1544.

<sup>222</sup> E. Weissflog and M. Schmidt, *Phosphorus Sulfur*, 1978, **4**, 383; *ibid.*, 1979, **6**, 453.

<sup>223</sup> K. Juji, K. Ichikawa, and E. Fujita, *Tetrahedron Lett.*, 1978, 3561; E. Fujita, Y. Nagao, and K. Kaneko, *Chem. Pharm. Bull.*, 1978, **26**, 3743 (*Chem. Abstr.*, 1979, **90**, 203 915); R. A. J. Smith and D. J. Hannah, *Synth. Commun.*, 1979, **9**, 301; G. A. Olah, S. C. Narang, G. F. Salem, and B. G. B. Gupta, *Synthesis*, 1979, 273; G. A. Olah, Y. D. Vankar, M. Arvanaghi, and G. K. S. Prakash, *ibid.*, 1979, 720; D. H. R. Barton, N. J. Cussans, and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 1977, 751; Q. N. Porter and J. H. P. Utley, *J. Chem. Soc., Chem. Commun.*, 1978, 255; M. Platen and E. Steckhan, *Tetrahedron Lett.*, 1980, 511; I. Stahl, J. Apel, R. Manske, and J. Gosselck, *Angew. Chem.*, 1979, **91**, 179.

<sup>224</sup> T. A. Hase and R. Kivikari, *Synth. Commun.*, 1979, **9**, 107.

<sup>225</sup> E. N. Deryagina, M. A. Kuznetsova, O. B. Bannikova, and M. G. Voronkov, *Zh. Org. Khim.*, 1978, **14**, 2012 (*Chem. Abstr.*, 1979, **90**, 22 713).

<sup>226</sup> E. Block, R. E. Penn, M. D. Ennis, T. A. Owens, and S. L. Yu, *J. Am. Chem. Soc.*, 1978, **100**, 7436.

<sup>227</sup> V. V. Zorin, S. S. Zlotskii, V. F. Shuvalov, A. P. Moravskii, and D. L. Rakhmankulov, *Zh. Org. Khim.*, 1979, **15**, 178 (*Chem. Abstr.*, 1979, **90**, 186 034); Ch. Gaze and B. C. Gilbert, *J. Chem. Soc., Perkin Trans. 2*, 1979, 763.

<sup>228</sup> E. Weissflog, *Phosphorus Sulfur*, 1979, **6**, 489.

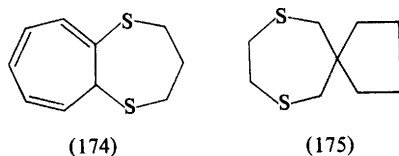
<sup>229</sup> V. I. Dronov, R. F. Nigmatullina, L. M. Khalilov, and Yu. E. Nikitin, *Zh. Org. Khim.*, 1979, **15**, 1709 (*Chem. Abstr.*, 1980, **92**, 5662).

<sup>230</sup> D. N. Harpp, K. Steliou, and B. T. Friedlander, *Org. Prep. Proced. Int.*, 1978, **10**, 133.

<sup>231</sup> (a) H. Gross, I. Keitel, and B. Costisella, *J. Prakt. Chem.*, 1978, **320**, 255; (b) F. Sauriol-Lord and M. St. Jacques, *Can. J. Chem.*, 1979, **57**, 3221.

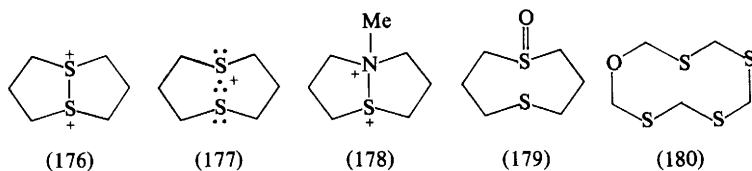
6,7-dihydro-5*H*-1,4-dithiepins (172),<sup>232</sup> while the reaction of keten *SS*-dithioacetals, derived from 1,3-dithian, with  $\text{Pb}(\text{OAc})_4$  afforded 3-alkyl-1,4-dithiepan-2-ones (173).<sup>233</sup>

Bicyclic 1,4-dithiepan, *e.g.* (174), have been obtained from tropone and dithiols.<sup>234</sup> A tetrathiapropellane<sup>235</sup> and numerous spirocyclic 1,4-dithiepan, *e.g.* (175), have been prepared.<sup>236</sup>



Oxidation of mesocyclic dithioethers<sup>237</sup> gave cyclic dithioether cations, *e.g.* (176), and cationic cyclic sulphur radicals, *e.g.* (177); these are the first long-lived, non-aromatic sulphur-containing radicals to be reported, characterized by a new S—S bond that is established by the interaction of three electrons.<sup>237b</sup> Similarly, a long-lived N—S-bonded cation radical and the dication (178) were obtained from 5-methyl-1-thia-5-azacyclo-octane (see also Chap. 2, Pt III, p. 142). Kinetic investigations on the reduction of mesocyclic sulphoxides, *e.g.* (179), indicated that there is anchimeric assistance by the transannular thioether group, with the formation of intermediate dithioether cations.<sup>237</sup>

Participation of transannular sulphur atoms has also been suggested to operate in the facile ring-opening of a dibenzodithiecin by brominolysis.<sup>238</sup> The crystal-structure determination of (180) revealed a double boat conformation, with all sulphur atoms nearly coplanar.<sup>239</sup>



<sup>232</sup> P. M. Weintraub, *J. Heterocycl. Chem.*, 1979, **16**, 1081.

<sup>233</sup> K. Hiroi and S. Sato, *Chem. Lett.*, 1979, 923.

<sup>234</sup> M. Cavazza, G. Morganti, and F. Pietra, *Tetrahedron Lett.*, 1978, 2135.

<sup>235</sup> J. Jamrozik, *J. Prakt. Chem.*, 1979, **321**, 437.

<sup>236</sup> S. Smolinski, J. Mokrosz, M. Jamrozik, and M. Kubaszek, *Monatsh. Chem.*, 1977, **108**, 885; S. Smolinski and J. Mokrosz, *Zesz. Nauk. Univ. Jagiellon, Pr. Chem.*, 1978, **23**, 7, 19 (*Chem. Abstr.*, 1979, **90**, 87 416, 87 417).

<sup>237</sup> (a) P. B. Roush and W. K. Musker, *J. Org. Chem.*, 1978, **43**, 4295; J. T. Doi and W. K. Musker, *J. Am. Chem. Soc.*, 1978, **100**, 3533; W. K. Musker, T. L. Wolford, and P. B. Roush, *ibid.*, p. 6416; W. K. Musker, A. S. Hirschon, and J. T. Doi, *ibid.*, p. 7754; G. S. Wilson, D. D. Swanson, J. T. Klug, R. S. Glass, M. D. Ryan, and W. K. Musker, *ibid.*, 1979, **101**, 1040; (b) K. D. Asmus, *Colloq. Int. CNRS*, 1977, **278**, 305 (*Chem. Abstr.*, 1979, **91**, 210 573).

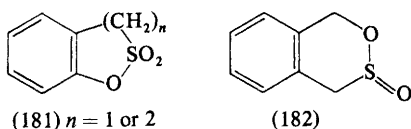
<sup>238</sup> M. K. Au, T. C. W. Mak, and T. L. Chan, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1475.

<sup>239</sup> G. Valle and G. Zanotti, *Cryst. Struct. Commun.*, 1977, **6**, 651.

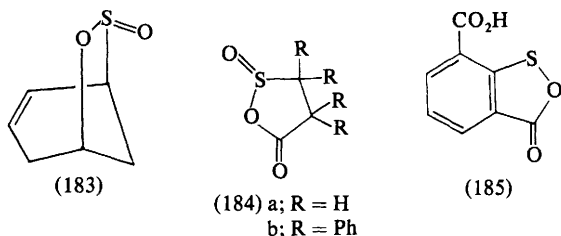
## 4 Sulphur- and Oxygen-containing Rings

**Sultenes, Sultines, and Sultones.**—Further reports have appeared on the formation of sultones from  $\text{SO}_3$  and dienes<sup>240</sup> and from the cycloaddition of  $\alpha$ -amino-methylene-ketones and sulphene.<sup>241</sup> Unusual sultone formations occurred during the reaction of a ketose derivative with mesyl chloride<sup>242</sup> and during the rearrangements of bicyclic ketones that were induced by sulphuric acid, respectively.<sup>243</sup> The kinetics of reactions of sultones (181) with nucleophiles<sup>244</sup> and the enthalpy changes accompanying their alkaline hydrolysis,<sup>245</sup> which allow an estimation of differences in ring strain between the five- and six-membered sultones, have been studied.

A further report on a  $[\pi + \pi\pi]$ -cycloaddition of a diene and  $\text{SO}_2$  has appeared:<sup>246</sup> the reaction of *o*-quinodimethane with  $\text{SO}_2$  afforded mainly the cyclic sulphinate (182), and only small amounts of the  $[n + \pi\pi]$  product were formed.



In an  $\text{SbF}_5$ -promoted cycloaddition of  $\text{SO}_2$  to cyclohexa-1,3-diene, the sultine (183) was formed, probably *via* a [1,2]-H shift in an initially generated allylic intermediate.<sup>247</sup>  $\gamma$ -Sultines have been shown to extrude  $\text{SO}_2$  thermally to give cyclopropanes when there is an aryl group at C-5.<sup>248</sup> An earlier report on a synthesis of 1,2-oxathiolan-5-one (184a) was shown to have been erroneous,<sup>249</sup> yet the first stable members of this class of mixed carboxylic-sulphinic acid anhydrides have been reported: thus treatment of a four-membered thiolactone with MCPBA gave the tetraphenyl derivative (184b), probably by a ring-expanding isomerization



<sup>240</sup> A. V. Semenovskii, E. V. Polunin, I. M. Zaks, and A. M. Moiseenkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1327 (*Chem. Abstr.*, 1979, **91**, 123 689); T. Akiyama, M. Sugihara, T. Imagawa, and M. Kawanisi, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1251; F. van der Griendt and H. Cerfontein, *Tetrahedron Lett.*, 1978, 3263.

<sup>241</sup> L. Mosti, G. Menozzi, G. Bignardi, and P. Schenone, *Farmacol. Ed. Sci.*, 1977, **32**, 794 (*Chem. Abstr.*, 1978, **88**, 62 262); L. Mosti, P. Schenone, and G. Menozzi, *J. Heterocycl. Chem.*, 1979, **16**, 177; F. Evangelisti, P. Schenone, and A. Bargagna, *ibid.*, p. 217.

<sup>242</sup> M. B. Yunker and B. Fraser-Reid, *J. Chem. Soc., Chem. Commun.*, 1978, 325.

<sup>243</sup> D. S. Brown, H. Heaney, S. V. Ley, K. G. Mason, and P. Singh, *Tetrahedron Lett.*, 1978, 3937.

<sup>244</sup> T. Deacon, C. R. Farrar, B. J. Sikkell, and A. Williams, *J. Am. Chem. Soc.*, 1978, **100**, 2525.

<sup>245</sup> E. Izbacka and D. W. Bolen, *J. Am. Chem. Soc.*, 1978, **100**, 7625.

<sup>246</sup> T. Durst and L. Tetreault-Ryan, *Tetrahedron Lett.*, 1978, 2353.

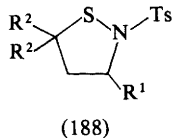
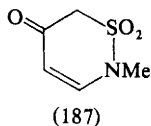
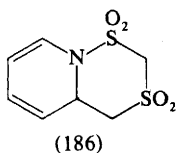
<sup>247</sup> K. S. Fongers and H. Hogeveen, *Tetrahedron Lett.*, 1979, 275.

<sup>248</sup> T. Durst, J. D. Finlay, and D. J. H. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1979, 950.

<sup>249</sup> J. G. Kasperek and G. J. Kasperek, *J. Org. Chem.*, 1978, **43**, 3393.

of the intermediate  $\alpha$ -keto-sulphoxide.<sup>250</sup> Heating of 2-(benzylsulphonyl)isophthalic acid in a mixture of acetic acid and acetic anhydride afforded the mixed anhydride (185).<sup>251</sup>

Several sultams have been prepared by cycloaddition reactions similar to those applied to the synthesis of sultones.<sup>252, 253</sup> Thus, the generation of sulphene in the presence of pyridine gave the sultam (186).<sup>252</sup> Activated dienes reacted with simple *N*-sulphonylamines, e.g. MeN=SO<sub>2</sub>, to give unsaturated sultams such as (187),<sup>254</sup> and thione *S*-imides reacted smoothly as 1,3-dipoles to give cyclic sulphenamides (188), or as dienophiles, with the formation of  $\Delta^3$ -dihydrothiopyran 1-imides.<sup>255</sup>



**1,3-Oxathiolans and 1,3- and 1,4-Oxathians.**—The attractive and repulsive *gauche* effects, including effects observed in 2-substituted 1,4-oxathians and 5-substituted 1,3-dithians, have been reviewed.<sup>256</sup>

A series of methyl-substituted 1,3-oxathians has been prepared by conventional procedures.<sup>257</sup> Details of a great number of preparative procedures for the synthesis of a variety of oxathiolan and oxathian derivatives have been published, including the synthesis of 1,3-benzoxathioles and 1,3-oxathiolans by cyclocondensation of *o*-mercaptophenol and  $\beta$ -mercaptoethanol, respectively, with acetylenic ketones,<sup>258</sup> the condensation of benzaldehyde with  $\alpha$ -monothioglycerol to give a mixture of the *cis*- and *trans*-isomers of the 1,3-oxathian (189) and of the 1,3-oxathiolan (190);<sup>259</sup> the free-radical addition of thioglycolic acid to appropriate olefins as a key step for the preparation of 1,4-oxathian- and 1,4-oxathiepan-2-ones, e.g. of (191);<sup>260</sup> cyclocondensation of orthoesters with  $\alpha$ -mercapto-carboxylic acids to give 1,3-oxathiolan-5-ones;<sup>261</sup> the synthesis of 1,4-oxathian-2-ones (192) by the reaction of chalcone epoxides with thioglycolic acid;<sup>262</sup> the electrophilic addition of SCl<sub>2</sub> to vinylic ethers, to afford mixtures of the *cis*- and *trans*-isomers of 2,6-dichloro-

<sup>250</sup> H. Kohn, P. Charumilind, and S. H. Simonsen, *J. Am. Chem. Soc.*, 1979, **101**, 5431.

<sup>251</sup> W. Walter, B. Krische, G. Adiwidjaja, and J. Voss, *Chem. Ber.*, 1978, **111**, 1685.

<sup>252</sup> J. St. Grossert, M. M. Bharadwaj, R. F. Langler, T. St. Cameron, and R. E. Cordes, *Can. J. Chem.*, 1978, **56**, 1183.

<sup>253</sup> W. E. Truce and J. P. Shepherd, *J. Am. Chem. Soc.*, 1977, **99**, 6453; T. Iwasaki, S. Kajigaeshi, and S. Kanemasa, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 229.

<sup>254</sup> J. A. Kloek and K. L. Leschinsky, *J. Org. Chem.*, 1979, **44**, 305.

<sup>255</sup> T. Saito and S. Motoki, *J. Org. Chem.*, 1979, **44**, 2493.

<sup>256</sup> E. Juaristi, *J. Chem. Educ.*, 1979, **56**, 438.

<sup>257</sup> K. Pihlaja, P. Pasanen, and J. Wähäsilta, *Org. Magn. Reson.*, 1979, **12**, 331.

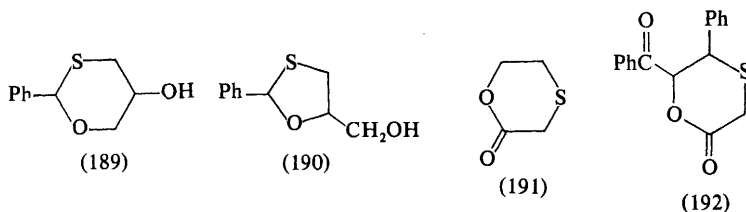
<sup>258</sup> V. N. Elokhina, A. S. Nakhmanovich, I. D. Kalikhman, and M. G. Voronkov, *Tezisy Dokl.-Vses. Konf. Khim. Atsetilena*, 5th, 1975, 298 (*Chem. Abstr.*, 1978, **88**, 170 015).

<sup>259</sup> R. Böhm, *Pharmazie*, 1978, **33**, 465.

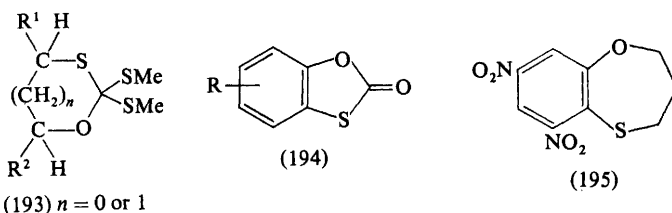
<sup>260</sup> D. I. Davies, L. Hughes, Y. D. Vankar, and J. E. Baldwin, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2476.

<sup>261</sup> Yu. A. Davidovich, L. A. Pavlova, and S. V. Rogoshin, *Zh. Org. Khim.*, 1978, **14**, 664 (*Chem. Abstr.*, 1978, **88**, 190 647).

<sup>262</sup> A. A. Hamed, A. Essawy, and M. A. Salem, *Indian J. Chem., Sect. B*, 1978, **16**, 693 (*Chem. Abstr.*, 1979, **90**, 121 517).

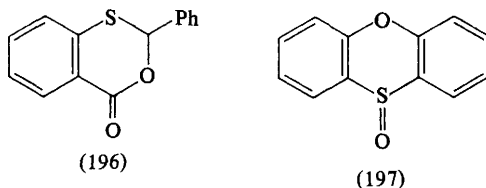


1,4-oxathians;<sup>263</sup> the formation of cyclic trithio-orthocarbonates (193) by the thermolysis of bis-(dithiocarbonates);<sup>264</sup> the preparation of 1,3-oxathiol-2-ones and of 2-substituted 1,3-oxathioles by treatment of  $\alpha$ -dibromo-ketones with potassium ethyl xanthate;<sup>265</sup> a novel synthesis of 2*H*-1,3-benzoxathiol-2-ones (194) by the HI- or pyridine-hydrochloride-induced cyclization of thiocarbamates;<sup>266</sup> and the base-catalysed cyclization and Smiles rearrangement of 3-(2,4,6-trinitrophenyl)propanol to give the benzoxathiepin (195).<sup>267</sup>



The formation of the benzoxathianone (196) by an intramolecular Pummerer reaction has been studied by a combination of <sup>18</sup>O labelling and stereoselective deuterium labelling and the use of optically active compounds.<sup>268</sup>

Conformations and chair-twist equilibria of a series of methyl-substituted 1,3-oxathians have been studied by <sup>1</sup>H n.m.r. spectroscopy.<sup>267</sup> Similarly, the conformations of various other 1,3- and 1,4-oxathians have been investigated.<sup>269</sup> Phenoxathiin sulphoxide (197) has been found to exist in the pseudo-axial conformation in both the solid state and in solution.<sup>270</sup>



<sup>263</sup> M. Schoufs, J. Meijer, and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 12.

<sup>264</sup> A. Faure and G. Descotes, *Synthesis*, 1978, 286.

<sup>265</sup> C. Bak, G. Höhne, and K. Praefcke, *Chem.-Ztg.*, 1978, **102**, 66.

<sup>266</sup> J. T. Traxler, *J. Org. Chem.*, 1979, **44**, 4971.

<sup>267</sup> V. N. Knyazev, V. N. Drozd, and V. M. Minov, *Zh. Org. Khim.*, 1978, **14**, 105 (*Chem. Abstr.*, 1978, **89**, 43 366).

<sup>268</sup> S. Wolfe, P. M. Kazmaier, and H. Auksi, *Can. J. Chem.*, 1979, **57**, 2404.

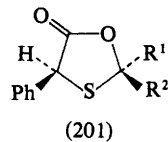
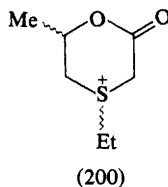
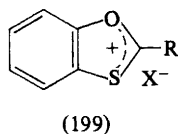
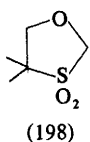
<sup>269</sup> T. Spoomaker and M. J. A. de Bie, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 15; A. I. Gren, A. M. Turyanskaya, V. I. Sidorov, and A. Weigt, *Vopr. Stereokhim.*, 1977, **6**, 87 (*Chem. Abstr.*, 1979, **90**, 186 259); A. M. Turyanskaya, *ibid.*, 1978, **7**, 68 (*Chem. Abstr.*, 1979, **91**, 38 786).

<sup>270</sup> J. S. Chen, W. H. Watson, D. Austin, and A. L. Ternay, Jr., *J. Org. Chem.*, 1979, **44**, 1989.

The configurations of several steroid 1,3-oxathiolans have been established by using a new c.d. sector rule.<sup>271</sup> Infrared and Raman spectra of thian 1-oxide and 1,4-oxathian 4-oxide, and the ionization potentials of 1,4-oxathian, have been studied.<sup>272, 273</sup>

The preparative aspects of 1,3-oxathiacycloalkane chemistry are expanding. Cleavage of 1,3-oxathiolan with  $\text{Me}_3\text{SiI}$  afforded the thioether  $\text{Me}_3\text{SiO}(\text{CH}_2)_2\text{S-CH}_2\text{I}$ , which has been found to be useful as an efficient alkylating agent.<sup>274</sup> 4,4-Dimethyl-1,3-oxathiolan 3,3-dioxide (198) offers a new equivalent of the formyl anion which readily demasks under thermal conditions. Alkylation and pyrolysis gave aldehydes in excellent yields. The reaction of the 2-lithio-derivative of (198) with ketones, followed by pyrolysis, afforded either  $\alpha$ -hydroxy-aldehydes or ring-expanded acyloins.<sup>275</sup> 2-Substituted 1,3-benzoxathiolium salts (199), readily obtainable from esters, react with alcohols to furnish good yields of esters after  $\text{Hg}^{2+}$ -promoted hydrolysis. Thus, the compounds (199) are masked esters from which the protecting group can be easily removed.<sup>276</sup>

Alkylations of 2-lithio-1,3-oxathians have been briefly studied.<sup>277</sup> The stereochemistry of the diastereoisomeric 1,4-oxathianium salts (200) has been investigated and the (6*S*)-isomers have been synthesized from ethyl (*S*)-lactate. A full account of the chemical correlation of (6*S*)-*trans*-(200) with the (+)-methylpropylsulphonium ion has been given.<sup>278</sup> Solvent and pH effects on the u.v. spectrum and the quantum yield of the photodecomposition of 1,3-oxathiolan-2-one have been investigated.<sup>279</sup> 1,3-Oxathiolan-5-ones (201) were converted into thiirans by flash vacuum pyrolysis, *via* the intermediate thiocarbonyl ylides.<sup>280</sup> The reaction proceeds by clean inversion of configuration and is assumed to involve disrotatory ring-opening followed by conrotatory ring-closure. The liquid complex of borane and 1,4-oxathian has been suggested as a new, convenient hydroborating agent.<sup>281</sup>



**Cyclic Sulphites and Sulphates.**—Major interest has still been devoted to the stereochemistry of the  $\text{S}=\text{O}$  group of cyclic sulphites. According to a systematic  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. study of a series of trimethylene sulphites that have phenyl or

<sup>271</sup> P. Welzel, I. Mütter, K. Kobert, F. J. Witteler, T. Hartwig, and G. Snatzke, *Liebigs Ann. Chem.*, 1978, 1333.

<sup>272</sup> Y. Hase and Y. Kawano, *Spectrosc. Lett.*, 1978, 11, 161 (*Chem. Abstr.*, 1978, 89, 5595).

<sup>273</sup> J. Jalonen, *Ann. Acad. Sci. Finn., Ser. A2*, 1979, 189, 88 (*Chem. Abstr.*, 1979, 91, 174 694).

<sup>274</sup> G. E. Keyser, J. D. Bryant, and J. R. Barrio, *Tetrahedron Lett.*, 1979, 3263.

<sup>275</sup> G. W. Gokel and H. M. Gerdes, *Tetrahedron Lett.*, 1979, 3375, 3379.

<sup>276</sup> G. Aimò, I. Degani, and R. Fochi, *Synthesis*, 1979, 223.

<sup>277</sup> K. Juji, M. Ueda, and E. Fujita, *J. Chem. Soc., Chem. Commun.*, 1977, 814.

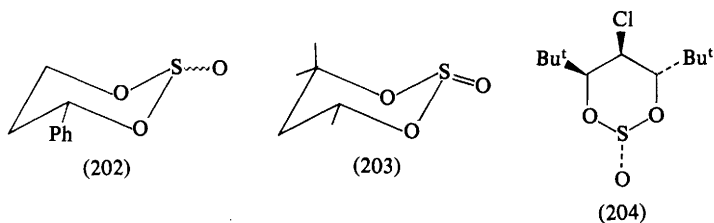
<sup>278</sup> E. Kelstrup, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1029, 1037.

<sup>279</sup> H. Chandra and K. S. Sidhu, *Indian J. Chem., Sect. B*, 1977, 158, 823 (*Chem. Abstr.*, 1978, 88, 169 301).

<sup>280</sup> T. B. Cameron and H. W. Pinnick, *J. Am. Chem. Soc.*, 1979, 101, 4755; *ibid.*, 1980, 102, 744.

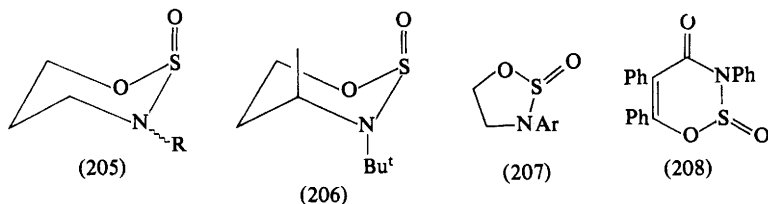
<sup>281</sup> H. C. Brown and A. K. Mandal, *Synthesis*, 1980, 153.

t-butyl groups at C-4 or at both C-4 and C-6 which are potentially *syn*-diaxial to S=O, it appears that the ring inverts to a conformation with both S=O and the bulky substituent equatorial except for *trans*-4,6-disubstituted systems, which are reluctant to adopt a chair conformation with a *syn*-diaxial orientation of the bulky substituent and sulphoxide oxygen. Twist geometries have been suggested for these latter compounds.<sup>282</sup> Both isomers of the sulphite (202) have been prepared, and the chair conformations established.<sup>282b</sup> X-Ray structures have been determined for several trimethylene sulphites:<sup>283</sup> the unusual equatorial position of the S=O group of (203) has been confirmed,<sup>283a</sup> and a twist conformation has been established for (204).<sup>283c</sup>



Cyclic sulphinamates (205), like cyclic sulphites, also prefer a chair conformation with an axial S=O group.<sup>284</sup> Substituents R on the nitrogen atom are preferentially axial. The 3-t-butyl-*cis*-4-methyl derivative (206) has been shown to prefer (in solution and in the solid state) a slightly distorted chair conformation, with nitrogen at the top of a very flattened pyramid, with axial S=O and methyl, and with the t-butyl group displaced towards the axial direction. Unlike cyclic sulphites, the chair form with equatorial S=O is rarely involved, and twist forms with a 3,6- or 1,4-axis were observed.<sup>284</sup> Carbon-13 n.m.r. spectra of the five-membered analogues (207) have also been related to the conformational situation.<sup>285</sup>

Unsaturated analogues are available by various cyclization procedures, e.g. by condensation of SOCl<sub>2</sub> with a 2-acyl-acetamide to give (208).<sup>286</sup> Other cyclizations



<sup>282</sup> (a) G. W. Buchanan, C. M. E. Cousineau, and T. C. Mundell, *Can. J. Chem.*, 1978, **56**, 2019; (b) *Tetrahedron Lett.*, 1978, 2775.

<sup>283</sup> (a) G. Petit, A. T. H. Lenstra, W. Van de Mierop, H. J. Geise, and D. G. Hellier, *Recl. Trav. Chim. Pays-Bas*, 1978, **97**, 202; (b) G. Petit, A. T. H. Lenstra, and H. J. Geise, *Bull. Soc. Chim. Belg.*, 1978, **87**, 659; (c) A. C. Carbonelle, Y. Jeannin, and F. Robert, *Acta Crystallogr., Sect. B*, 1978, **34**, 1631; (d) G. Petit, A. T. H. Lenstra, H. J. Geise, and P. Swepston, *Cryst. Struct. Commun.*, 1980, **9**, 187.

<sup>284</sup> P. Tisnes, P. Maroni, and L. Cazaux, *Org. Magn. Reson.*, 1979, **12**, 481, 490; L. Cazaux, P. Tisnes, and J. Jaud, *J. Chem. Res. (S)*, 1980, 10.

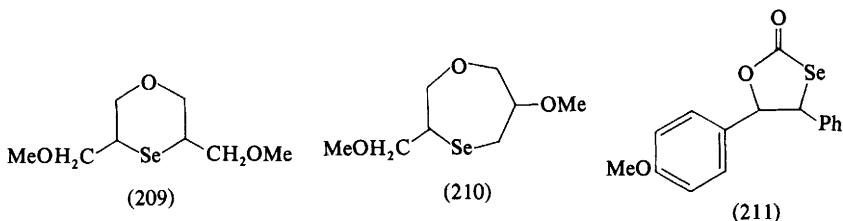
<sup>285</sup> T. Nishiyama, T. Mizuno, and F. Yamada, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 323.

<sup>286</sup> L. Capuano, G. Urhahn, and A. Willmes, *Chem. Ber.*, 1979, **112**, 1012.

with  $\text{SOCl}_2$  led to the formation of eight- to sixteen-membered cyclic sulphites.<sup>287</sup> The structures of cyclic sulphites of sugars have been established by  $^1\text{H}$  n.m.r. methods,<sup>288</sup> and the preparation of cyclic sulphite esters has been used to establish the stereochemistry, *meso* or DL, of chiral pinacols.<sup>289</sup>

Several cyclic sulphates have been obtained, by various sulphonation procedures.<sup>290</sup>

**Selenium- and Tellurium-containing Rings.**—The synthesis of selenacyclohexane from n-pentane and  $\text{SeO}_2$  was improved by using a zeolite catalyst containing rare-earth elements.<sup>291</sup> A direct formation of selenacycloalkanes, e.g. (209) and (210), by intramolecular oxyseleation of diallyl ether and other olefins with  $\text{KSeCN}$  and  $\text{CuCl}_2$  in MeOH, has been described.<sup>292</sup> The reaction of an  $\alpha$ -dibromo-ketone with the potassium salt of ethyl diselenocarbonate gave a 61% yield of the 1,3-oxaselenolan (211).<sup>293</sup>



In contrast to the less reactive 1-(vinylthio)alkynes, their sulphoxides or sulphones reacted readily with  $\text{Na}_2\text{Se}$  to give 1,4-thiaselenins (212).<sup>294</sup> Other studies dealt with the formation of 5,6-dihydro-2*H*-selenopyran,<sup>295</sup> the synthesis of optically active 8-thia- and 8-selena-derivatives of 1,1'-binaphthyls, e.g. (213),<sup>296</sup> and the formation of a tetracyclic selenium heterocycle on treatment of bicyclic selenoketals with  $\text{Bu}^n\text{Li}$ .<sup>297</sup> A product that was obtained after oxidation of dimedone with  $\text{SeO}_2$  has been identified as a tricyclic 1,3-oxaselenole.<sup>298</sup> Selena- and

<sup>287</sup> T. Nishiyama, K. Ido, and F. Yamada, *J. Heterocycl. Chem.*, 1979, **16**, 597; A. C. Guimaraes, J. B. Robert, L. Cazaux, C. Picard, and P. Tisnes, *Tetrahedron Lett.*, 1980, **21**, 1039.

<sup>288</sup> W. Reeve and S. K. Davidsen, *J. Org. Chem.*, 1979, **44**, 3430.

<sup>289</sup> Y. Wang and H. P. C. Hogenkamp, *Carbohydr. Res.*, 1979, **76**, 131.

<sup>290</sup> A. Koeberg-Telder, F. Van de Griendt, and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 1980, 358; F. Van de Griendt and H. Cerfontain, *ibid.*, p. 23; A. Nishinaga and S. Wakabayashi, *Chem. Lett.*, 1978, 913; V. L. Krasnov, N. K. Tulegenova, and I. V. Bodrikov, *Zh. Org. Khim.*, 1979, **15**, 1997 (*Chem. Abstr.*, 1980, **92**, 6509); N. B. Kaz'mina, I. L. Knunyants, G. M. Kuz'yants, E. I. Mysov, and E. P. Lur'e, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 118 (*Chem. Abstr.*, 1979, **90**, 137 784).

<sup>291</sup> E. Sh. Mamedov, S. B. Kurbanov, R. D. Mishiev, and T. N. Shaktaktinski, *Zh. Org. Khim.*, 1979, **15**, 1554 (*Chem. Abstr.*, 1979, **91**, 211 231).

<sup>292</sup> A. Toshimitsu, S. Uemura, and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1206.

<sup>293</sup> C. Bak, K. Praefcke, and L. Hendriksen, *Chem.-Ztg.*, 1978, **102**, 361.

<sup>294</sup> W. Verboom, R. S. Sukhai, and J. Meijer, *Synthesis*, 1979, 47.

<sup>295</sup> C. H. Chen, G. A. Reynolds, N. Zumbulyadis, and J. A. Van Allan, *J. Heterocycl. Chem.*, 1978, **15**, 289.

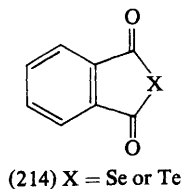
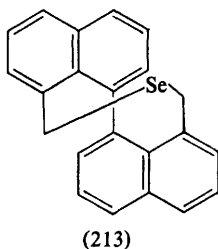
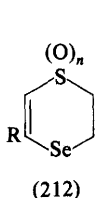
<sup>296</sup> M. M. Harris and P. K. Patel, *J. Chem. Soc., Perkin Trans. 2*, 1978, 304.

<sup>297</sup> H. M. J. Gillissen, P. Schipper, P. J. J. M. Van Ool, and H. M. Buck, *J. Org. Chem.*, 1980, **45**, 319.

<sup>298</sup> T. Laitalainen, T. Simonen, M. Klinga, and R. Kivekaes, *Finn. Chem. Lett.*, 1979, 145 (*Chem. Abstr.*, 1980, **92**, 163 902); T. Laitalainen and T. Simonen, *ibid.*, p. 147 (*Chem. Abstr.*, 1980, **92**, 58 273).

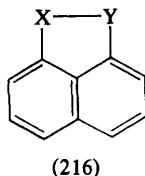
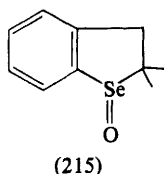
<sup>299</sup> J. Bergman and L. Engman, *Org. Prep. Proced. Int.*, 1978, **10**, 289.





tellura-phthalic anhydrides (214) were obtained by treating  $\text{NaBH}_4$  with selenium or tellurium, followed by phthaloyl chloride.<sup>299</sup>

The thermolysis of 2,2-dimethyl-2,3-dihydrobenzo[*b*]selenophen oxide (215) proceeded by *syn*-elimination of selenoxide and intramolecular addition of the intermediate benzeneselenenic acid.<sup>300</sup> Cleavage of *s*-trisenan by its reaction with bromine offers a preparative pathway to bis-(bromomethyl) selenide.<sup>301</sup> A series of naphthalene and tetracene dichalcogenides (216; X, Y = S, Se, or Te) were



prepared, and their X-ray structures, magnetic susceptibilities, Raman spectra, half-wave oxidation potentials, and their conducting complexes with inorganic anions were investigated.<sup>302</sup> X-Ray structures and the determination of the activation energy for an intramolecular ligand-reorganization process of selenuranes have been reported.<sup>303</sup> Spectral studies on saturated selenium and tellurium compounds included studies on infrared and Raman spectra and investigations of ASIS effects.<sup>304</sup> Several five- and six-membered 1,1-dihalogeno-I-tellura-compounds have been prepared, and their properties studied.<sup>305</sup>

<sup>300</sup> H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, and D. F. Wendelborn, *J. Org. Chem.*, 1978, **43**, 1697.

<sup>301</sup> E. Weissflog, *Phosphorus Sulfur*, 1980, **8**, 87.

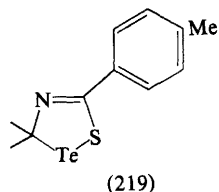
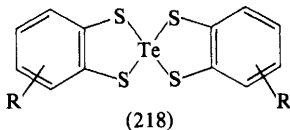
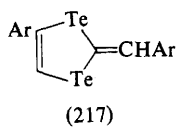
<sup>302</sup> J. Meinwald, D. Dauplaise, and J. Clardy, *J. Am. Chem. Soc.*, 1977, **99**, 7743; D. Dauplaise, J. Meinwald, J. C. Scott, H. Temkin, and J. Clardy, *Ann. N.Y. Acad. Sci.*, 1978, **313**, 382 (*Chem. Abstr.*, 1979, **91**, 157 665); O. N. Eremenko, S. P. Zolotukhin, A. I. Kotov, M. L. Khidekel, and E. B. Yagudskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1507 (*Chem. Abstr.*, 1979, **91**, 175 269).

<sup>303</sup> B. Dahlen and B. Lindgren, *Acta Chem. Scand., Ser. A*, 1979, **33**, 403; D. B. Denney, D. Z. Denney, and J. F. Hsu, *J. Am. Chem. Soc.*, 1978, **100**, 5982.

<sup>304</sup> M. G. Giorgini, G. Paliani, and R. Cataliotti, *Spectrochim. Acta, Part A*, 1977, **33**, 1083 (*Chem. Abstr.*, 1978, **89**, 59 342); J. R. Durig and W. J. Natter, *J. Chem. Phys.*, 1978, **69**, 3714; A. L. Esteban and E. Diez, *J. Magn. Reson.*, 1979, **36**, 113; A. L. Esteban and E. Diez, *J. Org. Chem.*, 1979, **44**, 3425.

<sup>305</sup> C. Knobler and R. F. Ziolo, *J. Organomet. Chem.*, 1979, **178**, 423; Yu. V. Migalina, I. M. Balog, V. G. Lendel, A. S. Koz'min, and N. S. Zefirov, *Khim. Geterotsikl. Soedin.*, 1978, 1212 (*Chem. Abstr.*, 1979, **90**, 6360); T. N. Srivastava, R. C. Srivastava, and M. Singh, *J. Organomet. Chem.*, 1978, **157**, 405; T. N. Srivastava, R. C. Srivastava, and H. B. Singh, *Indian J. Chem., Sect. A*, 1979, **18**, 71 (*Chem. Abstr.*, 1979, **91**, 193 143); T. N. Srivastava, R. C. Srivastava, and A. Bhargava, *ibid.*, p. 236 (*Chem. Abstr.*, 1980, **92**, 163 801); T. N. Srivastava, R. C. Srivastava, H. B. Singh, and M. Singh, *ibid.*, p. 367 (*Chem. Abstr.*, 1980, **92**, 110 772); R. F. Ziolo and W. H. H. Guenther, *J. Organomet. Chem.*, 1978, **146**, 245.

Treatment of sodium phenylacetylide with tellurium in DMSO gave the ditelluroles (217).<sup>306</sup> Thermolysis of the easily available spirocyclic tellurans (218) afforded cyclic bis(disulphides) in good yields.<sup>307</sup> The first heterocycles to contain sulphur, nitrogen, and tellurium, e.g. (219), have been obtained by the reaction of the intermediate 1,3-thiazabuta-1,3-dienes with  $\text{Sb}_2\text{Te}_3$ .<sup>308</sup> Proton and  $^{13}\text{C}$  n.m.r. spectra of telluran-3,5-diones have been reported.<sup>309</sup>



*Acknowledgement.* A conventional literature search has been assisted by computer, through the Lockheed search system, and a CA Current Awareness Search has been provided by the Computer Informationsdienst Graz. This work was supported by the Bundesministerium für Wissenschaft und Forschung.

<sup>306</sup> M. L. Petrov, V. Z. Laishev, and A. A. Petrov, *Zh. Org. Khim.*, 1979, **15**, 2596 (*Chem. Abstr.*, 1980, **92**, 163 912).

<sup>307</sup> B. Nakhdjavan and G. Klar, *Liebigs Ann. Chem.*, 1977, 1683.

<sup>308</sup> J. C. Dewan, W. B. Jennings, J. Silver, and M. S. Tolley, *Org. Magn. Res.*, 1978, **11**, 449.

<sup>309</sup> K. Burger, R. Ottlinger, A. Proksch, and J. Firl, *J. Chem. Soc., Chem. Commun.*, 1979, 80.

# 6

## Heteroaromatic Compounds of Sulphur, Selenium, and Tellurium

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BY M. DAVIS

### 1 Introduction

The organization of this Chapter is a radical change from the arrangement of the corresponding parts of Volume 5. This Reporter has tried to review, from the standpoint of sulphur chemistry rather than of heterocyclic chemistry, the highlights of current work which in the previous Volume comprised Chapters 6, 10, 11, 12, and 13, and parts of Chapters 7 and 8. It is not, of course, comprehensive; the main criteria used in selection were novelty, utility, and theoretical interest.

Two relevant reviews, on meso-ionic ring systems<sup>1</sup> and on selenium–nitrogen heterocycles,<sup>2</sup> have been published; and a three-part volume on 'Thiazole and Its Derivatives' has appeared.<sup>3</sup> Parts 1 and 2 of this volume are concerned with the chemistry of thiazole and substituted thiazoles, and the third part contains chapters on meso-ionic compounds, on cyanine dyes, and on selenazoles.

### 2 Theoretical and Spectroscopic Studies

**Molecular Orbital Calculations.**—The agreement between *ab initio* M.O. calculations and experimental data, usually spectroscopic, for heteroaromatic sulphur compounds is often not good. There are difficulties in deciding which M.O. terms should be included. Nevertheless, this is an active area, and some interesting results have been reported. For example, the conformations, stabilities, and charge distributions in 2- and 3-monosubstituted thiophens have been studied; the calculations show, in accord with experience, that the thienyl group prefers to act, relative to phenyl, as a  $\pi$ -electron donor or  $\sigma$ -electron acceptor, and that such electronic effects are greater at the 2- rather than at the 3-position.<sup>4</sup> The  $\pi$ -electron distributions in thiophen, selenophen, and tellurophen (1; X = S, Se, and Te, respectively) have been calculated;<sup>5</sup> and similar calculations have been used to correlate the observed magnetic circular dichroism (m.c.d.) of these rings.<sup>6</sup> The m.c.d. of thiophen is only slightly perturbed by substituents, unlike the different and

<sup>1</sup> K. T. Potts, *Lect. Heterocycl. Chem.*, 1978, **4**, 35.

<sup>2</sup> I. Lalezari and A. Shafiee, *Adv. Heterocycl. Chem.*, 1979, **24**, 109.

<sup>3</sup> 'The Chemistry of Heterocyclic Compounds', Vol. 34, ed. J. V. Metzger, Wiley-Interscience, New York, 1979.

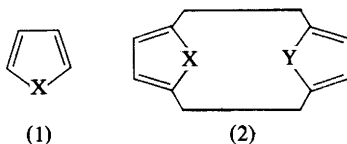
<sup>4</sup> J. Kao and L. Radom, *J. Am. Chem. Soc.*, 1979, **101**, 311.

<sup>5</sup> J. Fabian, *Z. Phys. Chem. (Leipzig)*, 1979, **260**, 81.

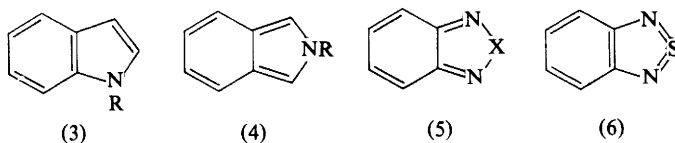
<sup>6</sup> B. Norden, R. Hakansson, P. B. Pedersen, and E. W. Thulstrup, *Chem. Phys.*, 1978, **33**, 355.

much weaker m.c.d.'s of pyrrole and furan (1; X = NH and O, respectively), which change shape considerably when the molecules are substituted.

The theoreticians have been working their way steadily towards more complex molecules, and recently thiazoles, isothiazoles, and thiadiazoles have received attention in connection with n.q.r.<sup>7</sup> or p.e.<sup>8</sup> spectroscopy. Photoelectron spectroscopy has also been used to examine the energy levels of benzo-fused derivatives of these heterocycles;<sup>9</sup> certain cyclophanes (2; X, Y = O or S) have also been examined, and the extent of through-space and through-bond interaction between the heterocyclic rings has thereby been determined.<sup>10</sup>



**Nuclear Magnetic Resonance.**—Nitrogen-14, carbon-13, and proton n.m.r. has been used to distinguish isomeric benzazoles<sup>11</sup> and thiadiazoles.<sup>12</sup> There is a large difference in nitrogen shielding, generally more than 20 p.p.m., between isomeric benzenoid (3) and *ortho*-quinonoid (4) structures, and similar differences occur in analogous sulphur compounds.<sup>11</sup> Natural-abundance <sup>15</sup>N n.m.r. spectra of such nitrogen-sulphur and nitrogen-selenium rings as 2,1,3-benzothiadiazole (5; X = S) and 2,1,3-benzoselenadiazole (5; X = Se) have been obtained, and it has been suggested that the high-field <sup>15</sup>N resonance of the benzothiadiazole can be explained by a significant resonance contribution from a sulphur di-imide form (6).<sup>13</sup>



Carbon-13 n.m.r. spectra of numerous thiazoles,<sup>14</sup> 1,2,3-thiadiazoles,<sup>15</sup> and benzothiazoles<sup>16</sup> have been reported and correlated with the electronic effects of substituents. Replacement of one or more of the phenyl groups in the cyclo-

<sup>7</sup> M. Redshaw, M. H. Palmer, and R. H. Findlay, *Z. Naturforsch., Teil A*, 1979, **34**, 220.

<sup>8</sup> G. Salmona, R. Faure, E. J. Vincent, C. Guimon, and G. Pfister-Guillouzo, *J. Mol. Struct.*, 1978, **48**, 205.

<sup>9</sup> C. Guimon, G. Pfister-Guillouzo, G. Salmona, and E. J. Vincent, *J. Chim. Phys. Phys.-Chim. Biol.*, 1978, **75**, 859; M. H. Palmer and S. M. F. Kennedy, *J. Mol. Struct.*, 1978, **43**, 33.

<sup>10</sup> F. Bernardi, A. Bottoni, F. P. Colonna, G. Distefano, U. Folli, and P. Vivarelli, *Z. Naturforsch., Teil A*, 1978, **33**, 959.

<sup>11</sup> L. Stefaniak, *Org. Magn. Reson.*, 1978, **11**, 385.

<sup>12</sup> M. Witkowski, L. Stefaniak, A. Grabowska, and G. A. Webb, *Spectrochim. Acta, Part A*, 1978, **34**, 877.

<sup>13</sup> I. Yavari, R. E. Botto, and J. D. Roberts, *J. Org. Chem.*, 1978, **43**, 2542; K. L. Williamson and J. D. Roberts, *Heterocycles*, 1978, **11**, 121.

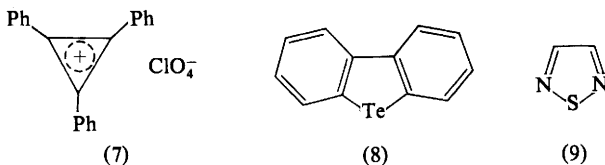
<sup>14</sup> R. Faure, J.-P. Galy, E.-J. Vincent, and J. Elguero, *Can. J. Chem.*, 1978, **56**, 46.

<sup>15</sup> J. H. Looker, N. A. Khatri, R. B. Patterson, and C. A. Kingsbury, *J. Heterocycl. Chem.*, 1978, **15**, 1383.

<sup>16</sup> S. N. Sawhney and D. W. Boykin, *J. Org. Chem.*, 1979, **44**, 1136.

propenium perchlorate (7) by 2-thienyl groups causes a shift of the absorption bands of the cyclopropenium ions to longer wavelengths, showing that 2-thienyl is more effective than phenyl in delocalizing positive charge; n.m.r. spectra and pK values support this view.<sup>17</sup>

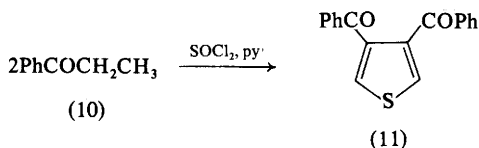
Mössbauer spectra have been reported for some tellurium heterocycles; e.g., (8).<sup>18</sup> The complete structure of 1,2,5-thiadiazole (9) has been determined by double-resonance modulation (DRM) microwave spectroscopy.<sup>19</sup>



### 3 Thiophens, Selenophens, and Tellurophens

**General.**—Recent publications include a chapter on thiophens in a comprehensive treatise;<sup>20</sup> an article on recent advances in the synthesis of benzo[*b*]thiophens;<sup>21</sup> a published plenary lecture on condensed thiophens, especially thienothiophens, selenothiophens, and related systems;<sup>22</sup> and a review on the synthesis of polycyclic thiophens from the direct insertion of heterosulphur bridges into vinylarenes, biaryls, and angularly condensed arenes.<sup>23</sup>

**Ring Synthesis and Destruction.**—One method of preparing thiophens is by inserting a sulphur atom into an acyclic precursor. The 'sulphur-transfer reagent' may be a simple inorganic compound, as illustrated by the formation of (11) from ethyl phenyl ketone (10) on treatment with pyridine and thionyl chloride.<sup>24</sup> The simplest sulphur-transfer reagent is elemental sulphur, as in the production of the thiophen (13; X = S) from 1,4-diphenyl-2,3-dibenzylbutadiene (12). The reaction of (12) with selenium dioxide affords the corresponding selenophen (13; X = Se).<sup>25</sup>



<sup>17</sup> G. Martelli, P. Spagnolo, L. Testaferri, and M. Tiecco, *Tetrahedron Lett.*, 1979, 281; cf. ref. 4.

<sup>18</sup> N. S. Dance and C. H. W. Jones, *Can. J. Chem.*, 1978, **56**, 1746.

<sup>19</sup> O. L. Stiefvater, *Z. Naturforsch., Teil A*, 1978, **33**, 1511; *ibid.*, p. 1518.

<sup>20</sup> O. Meth-Cohn in 'Comprehensive Organic Chemistry', Vol. 4, ed. P. G. Sammes, Pergamon Press, Oxford, 1979, p. 789.

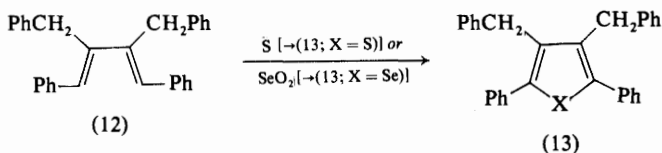
<sup>21</sup> B. Iddon, *Stud. Org. Chem. (Amsterdam)*, 1979, **3** (New Trends Heterocycl. Chem.), 250.

<sup>22</sup> V. P. Litvinov, in 'Topics in Organic Sulphur Chemistry', ed. M. Tišler, University Press, Ljubljana, 1978, p. 157.

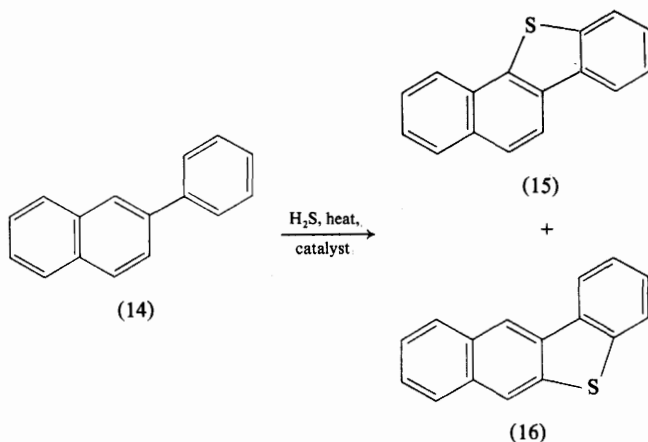
<sup>23</sup> L. H. Klemm, J. J. Karchesy, and D. R. McCoy, *Phosphorus Sulfur*, 1979, **7**, 9.

<sup>24</sup> K. Oka, *Heterocycles*, 1979, **12**, 461; see also C. M. Bonnin, P. A. Cadby, C. G. Freeman, and D. A. Ward, *Aust. J. Chem.*, 1979, **32**, 833.

<sup>25</sup> L. Lepage and Y. Lepage, *J. Heterocycl. Chem.*, 1978, **15**, 1185; similar sulphur-insertion reactions have been described by D. Nasipuri, A. Sarkar, P. K. Chakraborty, and I. De Dalal, *J. Indian Chem. Soc.*, 1978, **55**, 1232, and by K. Adachi and J. Tanaka, *Nippon Kagaku Kaishi*, 1978, 1666 (*Chem. Abstr.*, 1978, **90**, 137 605).



Hydrogen sulphide reacts reversibly with many unsaturated or aromatic hydrocarbons, in the presence of mixed oxide catalysts, to produce thiophens; these may be polycyclic, according to the complexity of the starting hydrocarbon. This reaction, which is believed to be the source of many of the sulphur compounds found in crude oil, has been studied in particular by Klemm and his co-workers, who have now published their detailed results.<sup>23,26</sup> A typical example is the formation of the isomeric benzonaphthothiophens (15) and (16) from the reaction of 2-phenylnaphthalene (14) with hydrogen sulphide over a sulphided cobaltous oxide–molybdc oxide–alumina catalyst at 450–630 °C in a flow system. Thiophens may also be obtained from aldehydes in like manner.<sup>27</sup> The kinetics and mechanism of these sulphurization reactions, and especially of the industrially important reverse reactions (hydrodesulphurization), have been examined in some detail; thiols may be intermediates.<sup>26,28</sup>



Other novel methods of synthesis of thiophens are the formation of thiophen-3-malonate esters (18; X = S) and their selenium analogues (18; X = Se) from an acyclic precursor (17) by treatment with sodium sulphide or selenide;<sup>29</sup> the synthesis of benzo[*b*]thiophens by the photocyclization of 2-(arylthio)aceto-

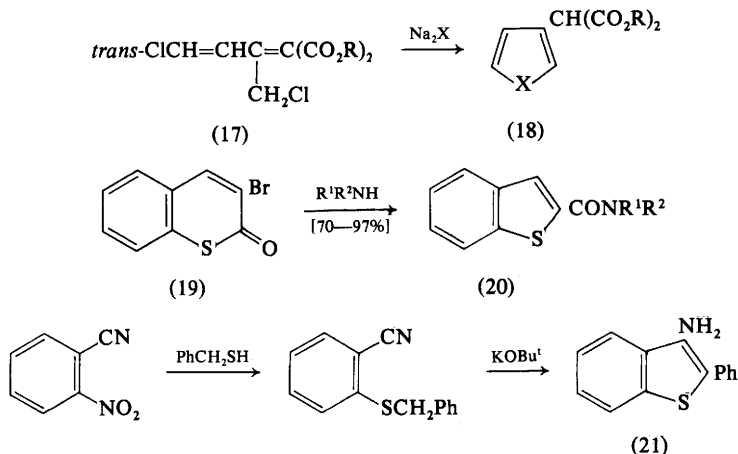
<sup>26</sup> L. H. Klemm and J. J. Karchesy, *J. Heterocycl. Chem.*, 1978, **15**, 65; *ibid.*, p. 281; L. H. Klemm, J. J. Karchesy, and R. F. Lawrence, *ibid.*, p. 417; L. H. Klemm and J. J. Karchesy, *ibid.*, p. 561; L. H. Klemm, J. J. Karchesy, and R. F. Lawrence, *ibid.*, p. 773; L. H. Klemm and R. F. Lawrence, *ibid.*, 1979, **16**, 599.

<sup>27</sup> J. Barrault, M. Guisnet, J. Lucien, and R. Maurel, *J. Chem. Res. (S)*, 1978, 207.

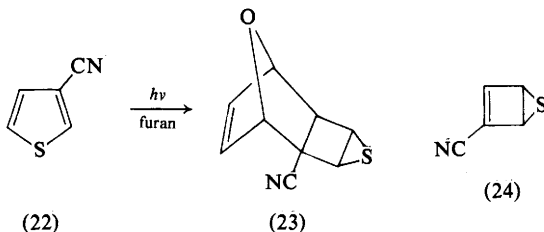
<sup>28</sup> N. K. Nag, A. V. Sapre, D. H. Broderick, and B. C. Gates, *J. Catal.*, 1979, **57**, 509; J. M. Pazos and P. Andréu, *Can. J. Chem.*, 1980, **58**, 479.

<sup>29</sup> J. P. Clayton, A. W. Guest, A. W. Taylor, and R. Ramage, *J. Chem. Soc., Chem. Commun.*, 1979, 500.

acetates;<sup>30</sup> the ring-contraction of 3-bromothiocoumarin (19) by amines, which yields benzo[*b*]thiophen-2-carboxamides (20);<sup>31</sup> or the remarkably easy preparation of 2-phenylbenzo[*b*]thiophen-3-amines (21) from 2-nitrobenzonitrile and toluene- $\alpha$ -thiol.<sup>32</sup>



Apart from hydrodesulphurization, reactions causing transformation or destruction of the thiophen ring are rather rare. Three interesting examples have been reported. In the first,<sup>33</sup> photolysis of 3-cyanothiophen (22) in furan affords the adduct (23) as the major product. 2-Cyanothiophen behaves in a similar way, and an analysis of permutation patterns has indicated that there is a mechanism involving first the 2,5-bridged compound (24) followed by a 'walk' of the sulphur atom. Anils (25) are converted into pyrroles (26) by triethyl phosphite;<sup>34</sup> a similar ring-opening by intramolecular insertion of nitrene has also been shown to occur with *o*-nitrophenyl-di-(2-thienyl)methanes.<sup>35</sup>



<sup>30</sup> T. Sasaki and K. Hayakawa, *Tetrahedron Lett.*, 1980, **21**, 1525.

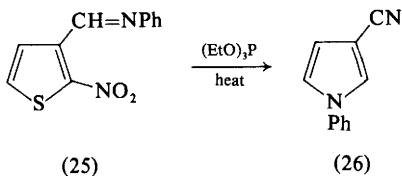
<sup>31</sup> V. L. Savel'ev, T. G. Afanas'eva, and V. A. Zagorevskii, *Khim. Geterotsikl. Soedin.*, 1978, 1340 (*Chem. Abstr.*, 1979, **90**, 38 740).

<sup>32</sup> J. R. Beck, *J. Heterocycl. Chem.*, 1978, **15**, 513.

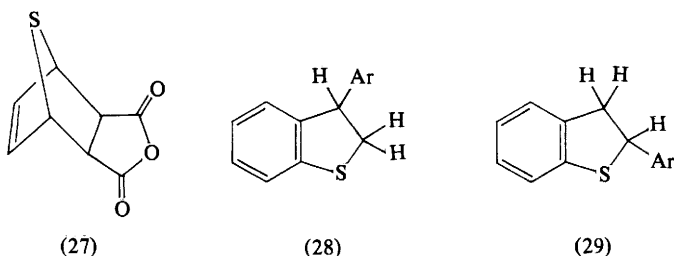
<sup>33</sup> J. A. Barltrop, A. D. Day, and E. Irving, *J. Chem. Soc., Chem. Commun.*, 1979, 881.

<sup>34</sup> V. M. Colburn, B. Iddon, H. Suschitzky, and P. T. Gallagher, *J. Chem. Soc., Chem. Commun.*, 1978, 453.

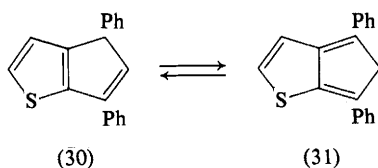
<sup>35</sup> G. Jones, C. Keates, I. Kladko, and P. Radley, *Tetrahedron Lett.*, 1979, 1445.



**Reactions and Reactivity.**—Thiophens can be induced to behave as dienes in Diels–Alder reactions at high pressure, as in the reaction between thiophen itself and maleic anhydride in dichloromethane at 100 °C and 15 kbar, which gives the adduct (27).<sup>36</sup> Aromatic hydrocarbons (ArH) can be added across the 2,3-bond of benzo[*b*]thiophens under Friedel–Crafts conditions at low temperatures, giving the adducts (28) and (29); at higher temperatures the main product is a 2-arylbenzo[*b*]thiophen.<sup>37</sup>



An unexpected finding is that 4,6-diphenyl-4*H*-cyclopenta[*b*]thiophen (30) exists in equilibrium with its 5*H*-isomer (31); the latter compound is fluorescent and possesses high Diels–Alder reactivity as a diene; surprisingly, (30) itself will react with dienophiles under mild conditions.<sup>38</sup>



Substitution reactions of thiophen derivatives have received attention recently, particularly of nitro-thiophens, in which both *ipso*- and *cine*-substitutions may occur<sup>39</sup> or in which radical chain reactions may be involved.<sup>40</sup> Isomeric bromo-

<sup>36</sup> H. Kotsuki, H. Nishizawa, S. Kitagawa, M. Ochi, N. Yamasaki, K. Matsuoka, and T. Tokoroyama, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 544.

<sup>37</sup> P. D. Clark, K. Clarke, D. F. Ewing, and R. M. Scrowston, *J. Chem. Soc., Perkin Trans. 1*, 1980, 677.

<sup>38</sup> J. Skramstad and T. Midthaug, *Acta Chem. Scand., Ser. B*, 1978, **32**, 413.

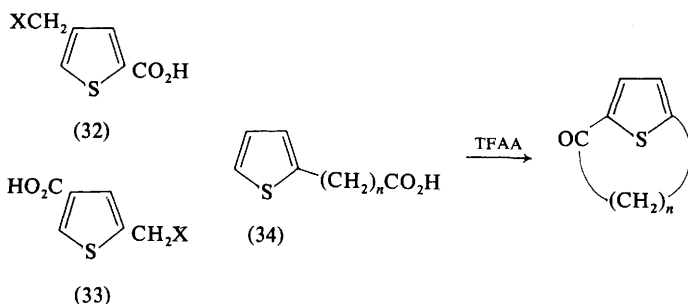
<sup>39</sup> P. Cogolli, F. Maiolo, L. Testaferri, M. Tiecco, and M. Tingoli, *J. Heterocycl. Chem.*, 1979, **16**, 1495; M. Novi, G. Guanti, F. Sancassan, and C. Dell'Erba, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1140.

<sup>40</sup> P. J. Newcombe and R. K. Norris, *Aust. J. Chem.*, 1978, **31**, 2463; *ibid.*, 1979, **32**, 2647.

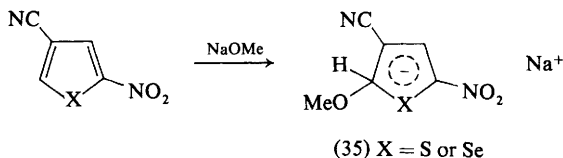


iodo-thiophens give the same mixture of products with sodium methoxide – the so-called ‘halogen-dance’.<sup>41</sup>

**Rate Data, Substituent Effects, and Hammett Relationships.**— Infrared spectroscopic measurements on the isomeric acids (32) and (33) show a good correlation between the data and the  $\sigma_1$  constants of the substituents X; with n.m.r. spectroscopy there was no good single-parameter correlation. The Hammett  $\rho$  for the series (32) was 1.5 times that for the corresponding series (33);<sup>42</sup> this Reporter suggests that the presence of only *one* hydrogen atom adjacent to the carboxyl group in (32) might permit greater coplanarity of that group, and thus greater sensitivity to electronic effects that are transmitted through the ring. Reliable rate data for the cyclization of  $\omega$ -(2-thienyl)alkanoic acids (34) have been obtained for ring sizes up to 21 (*i.e.*,  $n = 17$ ). Below a ring size of nine nuclei, the macrocyclization is exceedingly slow.<sup>43</sup>



Two groups have examined the rate and equilibrium constants for the formation of Meisenheimer complexes, *e.g.* (35), by methoxide ion with nitro-thiophens and nitro-selenophens, and they have compared the results with those of the corresponding benzene compounds.<sup>44</sup>



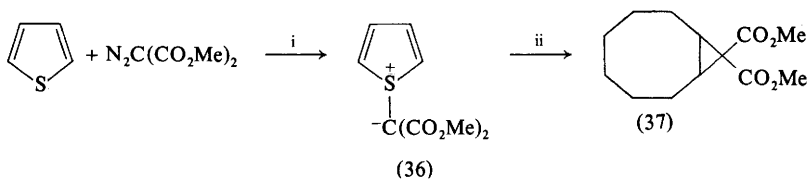
**Synthetic Uses of Thiophen Derivatives.**—The reaction between dimethyl diazomalonate and thiophen is catalysed by rhodium salts; the product is a stable ylide (36) which can be used as an equivalent of bis(methoxycarbonyl)carbene. Thus the heating of (36) with cyclo-octene under reflux affords the bicyclononane (37) in

<sup>41</sup> S. Gronowitz, A. Hallberg, and C. Glennow, *J. Heterocycl. Chem.*, 1980, **17**, 171.

<sup>42</sup> A. Perjéssy, M. Janda, and D. W. Boykin, *J. Org. Chem.*, 1980, **45**, 1366.

<sup>43</sup> C. Galli, G. Illuminati, and L. Mandolini, *J. Org. Chem.*, 1980, **45**, 311.

<sup>44</sup> D. Spinelli, G. Consiglio, and R. Noto, *J. Chem. Res. (S)*, 1978, 242; F. Terrier, A.-P. Chatrousse, and C. Paulmier, *J. Org. Chem.*, 1979, **44**, 1634.

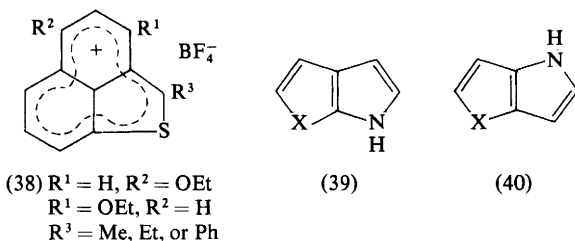


Reagents: i, Rhodium salts; ii, cyclo-octene, heat

**Scheme 1**

86% yield, as shown in Scheme 1.<sup>45</sup> Other thiophens, including benzo[*b*]thiophen, react similarly, except where electron-withdrawing substituents are present. Simple diazoketones generally produce 2-substituted thiophens rather than ylides.

**Naphthothiophens, especially Thiapseudophenalenones.**—Neidlein (see Vol. 5, p. 291) has continued his interesting work on these remarkable thiophen analogues of phenalene and phenalenium cations; a series of papers describes the synthesis and properties of compounds such as (38).<sup>46</sup>



**Thiophen Rings Fused to other Heteroaromatic Systems that do not contain Sulphur, Selenium, or Tellurium.**—Very many such annelated systems have been described, and in this section only those of particular note are mentioned. Annelation to other sulphur-, selenium-, and tellurium-containing rings is considered in a later section (p. 296).

*Thieno- and Selenolo-pyrroles.* Examples of these, *e.g.* (39; X = S or Se) and (40; X = S or Se), have been prepared by the reaction of ethyl azidoacetate with the monoaldehydes of thiophen or selenophen, followed by cyclization, hydrolysis, and decarboxylation of the product.<sup>47</sup>

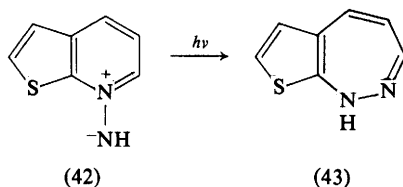
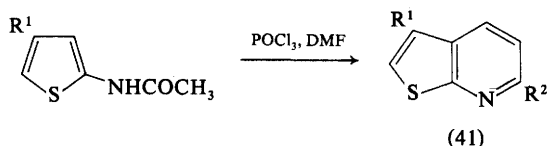
*Thienopyridines.* These have received much attention in the past few years, particularly by Klemm, who has continued his examination of all six possible

<sup>45</sup> J. Cuffe, R. J. Gillespie, and A. E. A. Porter, *J. Chem. Soc., Chem. Commun.*, 1978, 641; R. J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A. E. A. Porter, *ibid.*, 1979, 366; R. J. Gillespie and A. E. A. Porter, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2624.

<sup>46</sup> R. Neidlein and H. Seel, *Arch. Pharm. (Weinheim, Ger.)*, 1978, **311**, 324; R. Neidlein and K. F. Cepera, *Liebigs Ann. Chem.*, 1978, 627; R. Neidlein and L. Seguil-Camargo, *Arch. Pharm. (Weinheim, Ger.)*, 1978, **311**, 710; R. Neidlein, K. F. Cepera, and A. Hotzel, *ibid.*, 1978, **311**, 861; R. Neidlein and L. Seguil-Camargo, *Liebigs Ann. Chem.*, 1979, 965.

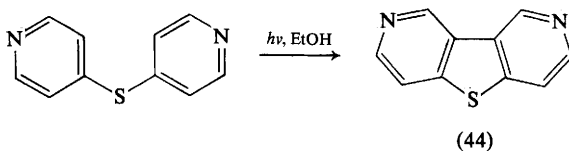
<sup>47</sup> S. Soth, M. Farnier, and C. Paulmier, *Can. J. Chem.*, 1978, **56**, 1429.

isomers.<sup>48</sup> Other workers have studied, especially, the preparation and properties of derivatives of the [2,3-*b*] isomer (41; R<sup>1</sup> = R<sup>2</sup> = H).<sup>49</sup> One versatile synthetic procedure is the Vilsmeier formylation of acetamido-thiophens, as in the preparation of the halogenated compound (41; R<sup>1</sup> = Br, R<sup>2</sup> = Cl).<sup>50</sup> Thieno[2,3-*b*]pyridinium ylide (42), prepared by *N*-amination of thieno[2,3-*b*]pyridine with hydroxylamine *O*-mesitylenesulphonate and base, undergoes ring-expansion on irradiation, producing the previously unknown thieno-1*H*-1,2-diazepines (43).<sup>51</sup> Thieno[2,3-*c*]pyridines, on similar treatment, afford mixtures of the analogous thieno-1*H*-1,3- and -3*H*-2,3-diazepines.<sup>52</sup>



Thieno[3,2-*b*]pyridines<sup>53</sup> and thieno[3,2-*c*]pyridines<sup>54</sup> have also received attention.

A simple synthesis of thieno[3,2-*c*:4,5-*c'*]dipyridine (44) by photolysis of 4,4'-thiodipyridine has been described.<sup>55</sup>



**Polythiophens and Related Systems.**—Two groups have prepared compounds containing two thiophen rings fused to medium-sized carbocycles. At the University

<sup>48</sup> L. H. Klemm and M. Bajer, *J. Heterocycl. Chem.*, 1979, **16**, 1289; and previous papers of the series.

<sup>49</sup> J. Becher, C. Dreier, E. G. Frandsen, and A. S. Wengel, *Tetrahedron*, 1978, **34**, 989; C. Corral, R. Madronero, and N. Ulecia, *Afinidad*, 1978, **35**, 129 (*Chem. Abstr.*, 1978, **89**, 129 477); K. Gewald, H. Schaefer, and K. Sattler, *Monatsh. Chem.*, 1979, **110**, 1189; P. M. Gilis, A. Haemers, and W. Bollaert, *Eur. J. Med. Chem. — Chim. Ther.*, 1978, **13**, 265 (*Chem. Abstr.*, 1978, **89**, 129 437); I. Lalezari, *J. Heterocycl. Chem.*, 1979, **16**, 603; V. I. Shvedov, T. P. Sycheva, and T. V. Sakovich, *Khim. Geterotsikl. Soedin.*, 1979, 1331 (*Chem. Abstr.*, 1979, **92**, 76 361); *ibid.*, 1979, 1336 (*Chem. Abstr.*, 1979, **92**, 94 271); *ibid.*, 1979, 1340 (*Chem. Abstr.*, 1979, **92**, 146 648).

<sup>50</sup> O. Meth-Cohn and B. Narine, *Tetrahedron Lett.*, 1978, 2045.

<sup>51</sup> T. Tsuchiya, M. Enkaku, J. Kurita, and H. Sawanishi, *Chem. Pharm. Bull.*, 1979, **27**, 2183.

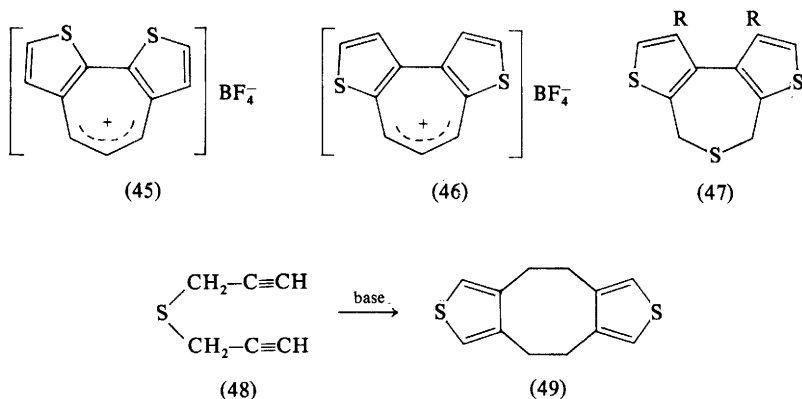
<sup>52</sup> T. Tsuchiya, M. Enkaku, and H. Sawanishi, *Heterocycles*, 1979, **12**, 1471.

<sup>53</sup> J. M. Barker, P. R. Huddleston, and A. W. Jones, *J. Chem. Res. (S)*, 1978, 393.

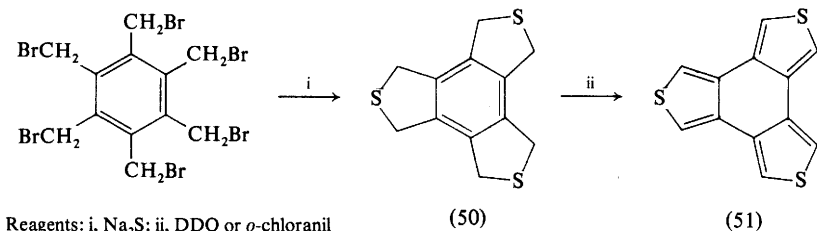
<sup>54</sup> J. P. Maffrand and R. Boigegrain, *Heterocycles*, 1979, **12**, 1479.

<sup>55</sup> J. E. Rockley and L. A. Summers, *Chem. Ind. (London)*, 1979, 666.

of Lund the dithienotropylium salts (45) and (46) have been made by standard, if lengthy, syntheses from substituted thiophens;<sup>56</sup> and a group of workers at University College London have prepared the related compound (49) by the base-catalysed rearrangement and dimerization of the diyne (48).<sup>57</sup> Derivatives of the closely related dithienothiepin (47) and its isomers have been made independently by workers at the Universities of Lund and of Dijon (France).<sup>58,59</sup> If the substituents are bulky, as in the diacid (47; R = CO<sub>2</sub>H), enantiomers are produced, but the barrier to inversion is not large.<sup>58</sup>



Benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]trithiophen (51), a 'hexaradialene', or exocyclic benzene, has been prepared by the oxidation of the trisulphide (50), as shown in Scheme 2. It is unreactive towards dienophiles and appears to be a reasonably stable aromatic system.<sup>60</sup> It would be interesting to determine the lengths of the C-C bonds of the central ring, if only to decide whether this compound (51) could be described like a 'donut' ('a hole surrounded by jam and dough'). A related molecule,



Scheme 2

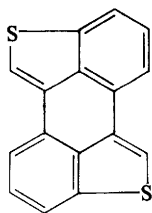
<sup>56</sup> S. Gronowitz and P. Pedaja, *Tetrahedron*, 1978, **34**, 587.

<sup>57</sup> Y. S. P. Cheng, E. Dominguez, P. J. Garratt, and S. B. Neoh, *Tetrahedron Lett.*, 1978, 691; P. J. Garratt and S. B. Neoh, *J. Org. Chem.*, 1979, **44**, 2667.

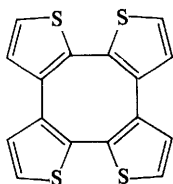
<sup>58</sup> A. Almqvist and R. Hakansson, *Chem. Scr.*, 1977, **11**, 180; *ibid.*, p. 186.

<sup>59</sup> P. Meunier, *J. Heterocycl. Chem.*, 1978, **15**, 593.

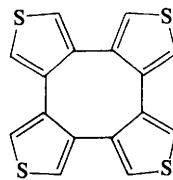
<sup>60</sup> H. Hart and M. Sasaoka, *J. Am. Chem. Soc.*, 1978, **100**, 4326.



(52)



(53)

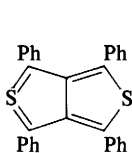


(54)

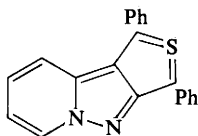
3,4:3',4'-bibenzo[*b*]thiophen (52), has been made. It is isoelectronic with perylene and, indeed, has similar physical and chemical properties.<sup>61</sup>

The tetrathiophens (53) and (54) have been synthesized, in moderate yield, by the reaction of dibromobithiophens with butyl-lithium, followed by oxidative coupling with ferric or cupric chloride.<sup>62</sup>

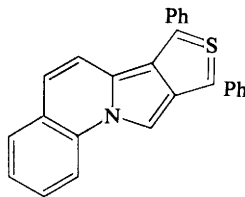
**Non-classical Thiophens.**—Thiophens which formally require quadrivalent bonding about one or more sulphur atoms are usually called 'non-classical'. Numerous examples have been described during the past decade (see Vol. 5, pp. 282–3). Tetraphenylthieno[3,4-*c*]thiophen (55) and its radical-cation and -anion have now been subjected to a detailed spectroscopic examination, and the results have been rationalized by M.O. models.<sup>63</sup> Non-classical thiophens usually need several aromatic substituents for reasonable stability; examples in which the stability is conferred, at least in part, by fusion to polycyclic nitrogen heterocycles, *e.g.* (56) and (57), have been described, but the degree of stability is not great; (57), for example, has only a transient existence.<sup>64</sup>



(55)



(56)



(57)

**Selenophens and Tellurophens.**—The mass spectrometric fragmentations of selenophen and tellurophen have been elucidated; they are analogous to that of thiophen.<sup>65</sup> An improved synthesis (Scheme 3) of tellurophen (59) has been described, starting from elemental tellurium and using 1,4-bis(trimethylsilyl)buta-

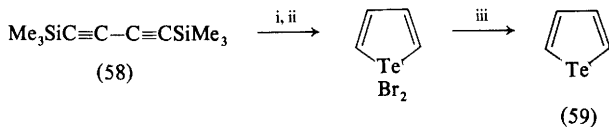
<sup>61</sup> F. Wudl, R. C. Haddon, E. T. Zellers, and F. B. Bramwell, *J. Org. Chem.*, 1979, **44**, 2491.

<sup>62</sup> T. Kauffmann, B. Greving, R. Kriegesmann, A. Mitschker, and A. Woltermann, *Chem. Ber.*, 1978, **111**, 1330.

<sup>63</sup> R. Gleiter, R. Bartetzko, G. Braehler, and H. Bock, *J. Org. Chem.*, 1978, **43**, 3893; P. Fuerderer, F. Gerson, M. P. Cava, and M. V. Lakshmikantham, *Heterocycles*, 1978, **11**, 93.

<sup>64</sup> K. T. Potts and S. Yao, *J. Org. Chem.*, 1979, **44**, 977; K. T. Potts, H. P. Youzwak, and S. J. Zurawel, Jr., *J. Org. Chem.*, 1980, **45**, 90.

<sup>65</sup> F. Fringuelli and A. Taticchi, *J. Heterocycl. Chem.*, 1978, **15**, 137.



Reagents: i,  $\text{Na}_2\text{Te}$  (from  $\text{Te} + \text{NaOH} + \text{HOCH}_2\text{SO}_2\text{Na}$ , in water); ii,  $\text{Br}_2$ ; iii,  $\text{Na}_2\text{SO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{H}_2\text{O}$

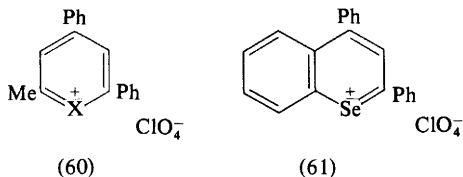
### Scheme 3

1,3-diyne (58) as the organic moiety.<sup>66</sup> Compounds in which selenophen rings are fused to benzene or naphthalene,<sup>67</sup> on to benzofurans,<sup>68</sup> or on to quinolines or carbazoles<sup>69</sup> have been prepared. The last-named compounds are the selenophen analogues of known carcinogens.

## 4 Thiopyrylium and Selenopyrylium Salts

Cyclic voltammetry has been used to measure redox potentials for two series of pyrylium and thiopyrylium salts in order to compare the electron-donating properties of oxygen and sulphur in a quantitative manner. Ionic and radical systems are more stable in the sulphur analogue in each case. The wavelength of the intramolecular charge-transfer band, and the electrochemical reduction potentials, indicate that the thiopyrylium group is more electron-withdrawing than the pyrylium one.<sup>70</sup> A similar comparison has been carried out, using the methyl-substituted salts (60;  $\text{X} = \text{O}$  or  $\text{S}$ ) and measuring the reactivity of the methyl group towards carbonyl compounds.<sup>71</sup>

The benzoseleninium salt (61) has been made by the reaction of selenoflavone with phenylmagnesium bromide, followed by perchloric acid.<sup>72</sup>



Thiopyrylium salts (62) are converted into diazo-esters (63) by the lithium salt of ethyl diazoacetate (see Scheme 4); further treatment with palladium(II) complexes produces thiepins (64), the stability of which depends on R. Remarkably, the 2-propyl compound (64;  $\text{R} = \text{CHMe}_2$ ) extrudes sulphur at  $-70^\circ\text{C}$ , yet the t-butyl analogue (64;  $\text{R} = \text{CMe}_3$ ) has a half-life of some 7 hours at  $131^\circ\text{C}$ .<sup>73</sup>

<sup>66</sup> W. Lohner and K. Praefcke, *Chem. Ber.*, 1978, **111**, 3745.

<sup>67</sup> P. Cagniant, G. Kirsch, and L. Christiaens, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1978, **287**, 333 (*Chem. Abstr.*, 1978, **90**, 87 187).

<sup>68</sup> A. Shafiee and E. Behnam, *J. Heterocycl. Chem.*, 1978, **15**, 589.

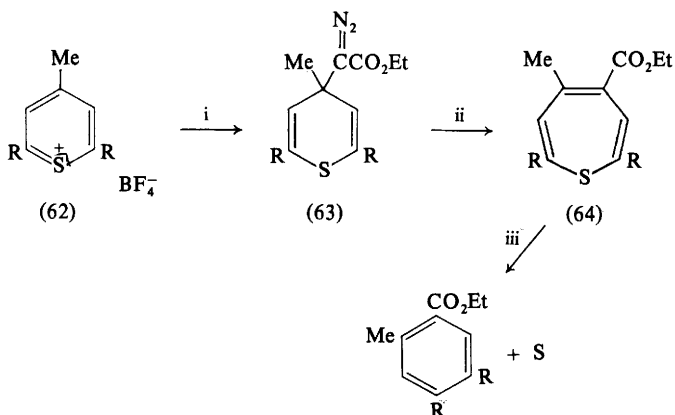
<sup>69</sup> G. Marechal, L. Christiaens, M. Renson, and P. Jacquignon, *Collect. Czech. Chem. Commun.*, 1978, **43**, 2916.

<sup>70</sup> F. D. Saeva and G. R. Olin, *J. Am. Chem. Soc.*, 1980, **102**, 299.

<sup>71</sup> R. Neidlein and I. Koerber, *Arch. Pharm. (Weinheim, Ger.)*, 1978, **311**, 236.

<sup>72</sup> R. Neidlein and I. Koerber, *Arch. Pharm. (Weinheim, Ger.)*, 1978, **311**, 170.

<sup>73</sup> S. Yano, K. Nishino, K. Nakasuji, and I. Murata, *Chem. Lett.*, 1978, 723; K. Nishino, S. Yano, Y. Kohashi, K. Yamamoto, and I. Murata, *J. Am. Chem. Soc.*, 1979, **101**, 5059.



Reagents: i,  $N_2C(Li)CO_2Et$ ; ii, palladium(II) complexes; iii, heat

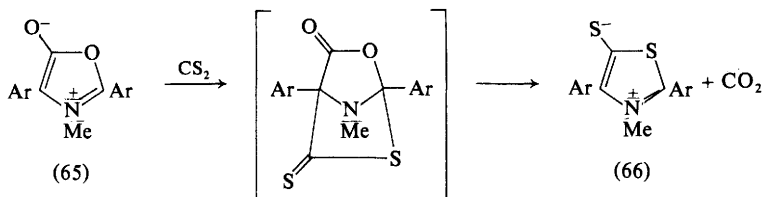
**Scheme 4**

### 5 Thiazoles and Selenazoles

**General.**—The three-part book<sup>3</sup> on thiazoles, which includes a chapter on selenazoles, has been mentioned earlier.

**Mass Spectrometry.**—Several groups have examined in detail the mass spectra of thiazoles and isothiazoles,<sup>74</sup> of benzothiazoles,<sup>75,76</sup> and of benzoselenazoles.<sup>75</sup> That thiazole and isothiazole isomerize to a common structure before fragmentation has been shown by an analysis of the abundances of metastable ions and the releases of kinetic energy.<sup>74</sup>

**Synthesis and Reactions.**—Oxazolium-5-olates (65) add carbon disulphide with high regioselectivity, and the adducts lose carbon dioxide to afford thiazolium-5-thiolates (66) in excellent yield.<sup>77</sup> The thiazolium-5-olate (67) undergoes photochemical ring-opening to give the keten (68), which can be trapped by ethanol, producing the ester (69); a competing fragmentation, yielding carbonyl sulphide, also occurs.<sup>78</sup> The reaction of *gem*-dicyano-epoxides (70) with thioamides (71) yields the corresponding thiazolium-4-olates (72)<sup>79</sup> (see Chap. 3, Pt III, p. 186).



<sup>74</sup> G. Salmona and E.-J. Vincent, *Org. Mass Spectrom.*, 1978, **13**, 119.

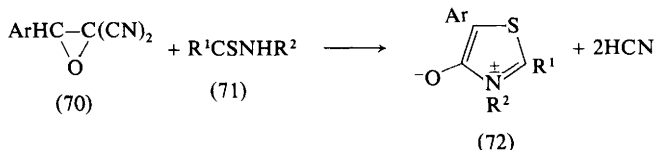
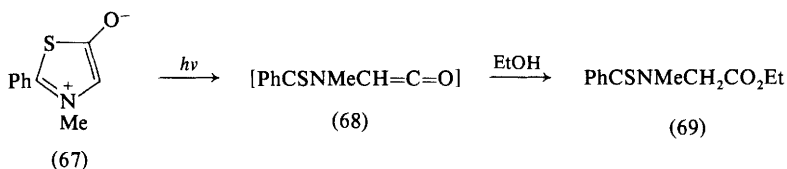
<sup>75</sup> G. Ciurduar, Z. Moldovan, and I. Oprean, *Monatsh. Chem.*, 1978, **109**, 379.

<sup>76</sup> S. Claude, R. Tabacchi, L. Duc, R. Fuchs, and K.-J. Boosen, *Helv. Chim. Acta*, 1980, **63**, 682.

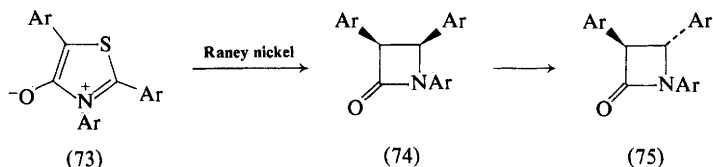
<sup>77</sup> R. Huisgen and T. Schmidt, *Liebigs Ann. Chem.*, 1978, 29.

<sup>78</sup> N. H. Toubro, B. Hansen, N. Harrit, A. Holm, and K. T. Potts, *Tetrahedron*, 1979, **35**, 229.

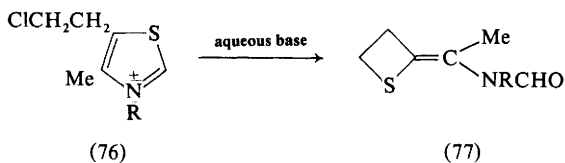
<sup>79</sup> M. Baudy, A. Robert, and A. Foucaud, *J. Org. Chem.*, 1978, **43**, 3732.



Thiazolium-4-olates (73) in which all hydrogen atoms have been replaced by aryl groups can be desulphurized by Raney nickel, yielding *cis*-lactams (74) as the sole products. On heating, these lactams (74) isomerized to the *trans*-compounds (75).<sup>80</sup>



Quaternary thiazolium salts that possess a 2-chloroethyl group, e.g. (76), are rapidly rearranged by aqueous base to thietan derivatives, e.g. (77), presumably *via* an intermediate bicyclic sulphonium salt.<sup>81</sup>



Benzothiazoles can be regarded for synthetic purposes as carbonyl equivalents, and the sequence shown in Scheme 5 illustrates the synthesis of aldehydes. Yields are almost quantitative throughout.<sup>82</sup>

**Fused Systems containing Thiazole.**—A large number of polyheterocyclic systems have been prepared, but in most cases the methods of synthesis, and the properties of the products, are straightforward extensions of earlier work; they will not, therefore, be further discussed.

The thiazolo[3,2-*a*]pyridinium structure has, however, received much attention, perhaps because it is so readily accessible. For example, the cyclization of 2-(pyridylthio)acetic acids (78) affords thiazolo[3,2-*a*]pyridinium-3-olates (79).<sup>83</sup>

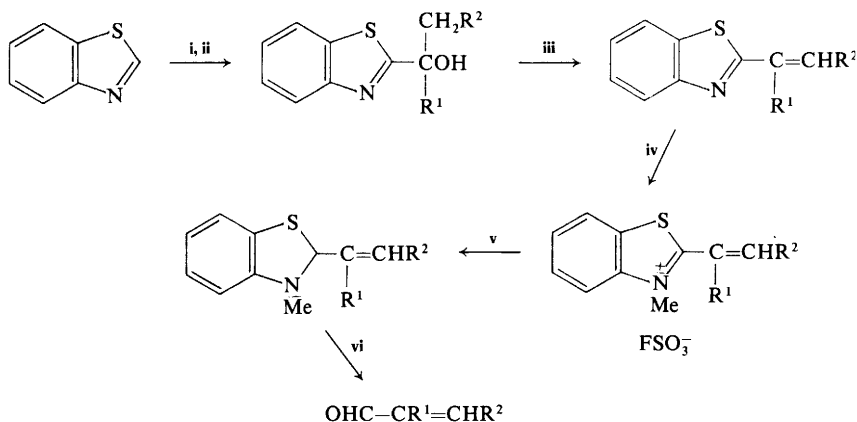
<sup>80</sup> T. Sheradsky and D. Zbaida, *Tetrahedron Lett.*, 1978, 2037.

<sup>81</sup> H. J. Federsel, J. Bergman, and U. Stenhede, *Heterocycles*, 1979, **12**, 751.

<sup>82</sup> E. J. Corey and D. L. Boger, *Tetrahedron Lett.*, 1978, 5.

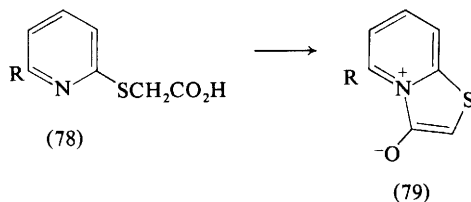
<sup>83</sup> L. T. Gorb, N. N. Romanov, E. D. Sych, and A. I. Tolmachev, *Dopov. Akad. Nauk Ukr. RSR, Ser. B*, 1978, 894 (*Chem. Abstr.*, 1978, **90**, 38 831); L. T. Gorb, N. N. Romanov, and A. I. Tolmachev, *Khim. Geterotsikl. Soedin.*, 1979, 1343 (*Chem. Abstr.*, 1979, **92**, 128 789).





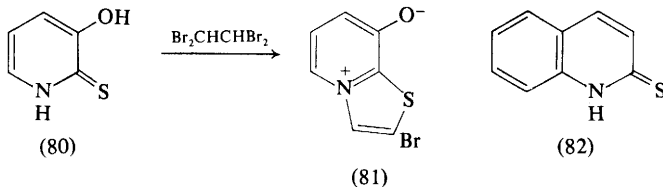
Reagents: i, BuLi; ii, R<sup>1</sup>COCH<sub>2</sub>R<sup>2</sup>; iii, P<sub>2</sub>O<sub>5</sub>, MeSO<sub>3</sub>H; iv, FSO<sub>3</sub>Me; v, NaBH<sub>4</sub>; vi, AgNO<sub>3</sub>, H<sub>2</sub>O

Scheme 5



The nucleus C-2 of the thiazole ring in these compounds is appreciably nucleophilic, and it will react readily with electrophiles, including diazonium salts and aldehydes.

In much the same way, 3-hydroxypyridine-2-thione (80) reacts with 1,1,2,2-tetrabromoethane to afford the 8-olate (81); the remaining bromine atom of (81) allows selective deuteration on C-2 and C-3 of the thiazole ring.<sup>84</sup> Other halogen compounds react with (80) in an analogous fashion;<sup>85</sup> quinoline-2-thione (82) can also be used.<sup>86</sup>



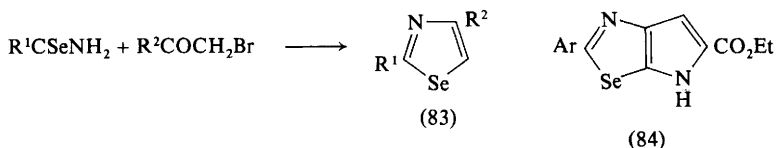
**Selenazoles.**—2,4-Disubstituted selenazoles (83) can be prepared in moderate to good yields by an extension of the Hantzsch reaction, the reaction of a halogenoketone with, in this case, a selenoamide.<sup>87</sup> Appropriate manipulation of R<sup>2</sup>

<sup>84</sup> T. Laerum, G. A. Ulsaker, and K. Undheim, *Acta Chem. Scand.*, Ser. B, 1978, **32**, 651.

<sup>85</sup> G. A. Ulsaker, T. Laerum, and K. Undheim, *Acta Chem. Scand.*, Ser. B, 1978, **32**, 460.

<sup>86</sup> K. T. Potts and D. R. Choudhury, *J. Org. Chem.*, 1978, **43**, 2700.

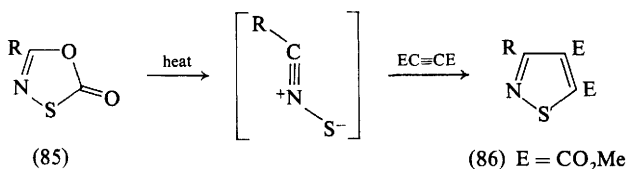
<sup>87</sup> V. I. Cohen, *Synthesis*, 1979, 66.



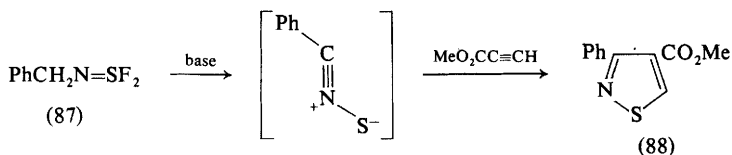
in (83) allows of the construction of an annelated pyrrole ring, thus affording the previously unknown pyrrolo[3,2-*d*]selenazole system (84).<sup>88</sup>

### 6 Isothiazoles, Isoselenazoles, and Isotellurazoles

**Synthesis.**—Several new methods for the synthesis of isothiazoles and benzisothiazoles have been reported. Nitrile sulphides are probable intermediates in one such synthesis; they are produced by the thermolysis of 1,3,4-oxathiazol-2-ones (85), and can be trapped by acetylenic dipolarophiles to give good yields of isothiazoles (86); unsymmetrical acetylenes afford a mixture of isomeric products. Isothiazolines are obtained in reasonable yields if olefinic dipolarophiles are used.<sup>89</sup>



The nitrile sulphide can also be generated from a fluorinated benzylamine derivative (87); in this case, the reaction with a monosubstituted acetylene yields predominantly the 4-substituted isothiazole (88).<sup>90</sup> These 4-substituted isothiazoles (88) have also been prepared by an alternative synthesis from 3-aminocinnamate esters.<sup>91</sup>



The thermolysis of azetidinone ( $\beta$ -lactam) disulphides (89) yields the isothiazolin-3-ones (90), amongst other products; these, in turn, can be converted (in high yield) into 3-alkyl-(or aryl)-aminoisothiazoles (91) by reaction with methyl fluorosulphonate followed by ammonia,<sup>92</sup> as shown in Scheme 6.

4-Amino-isothiazoles, e.g. (93), can be prepared (Scheme 7) from the corresponding *O*-hydroxylamine derivative (92) by reaction with toluene- $\alpha$ -thiol and cyclization of the intermediate thio-oxime.<sup>93</sup>

<sup>88</sup> A. Shafiee, A. Mazloumi, and V. I. Cohen, *J. Heterocycl. Chem.*, 1979, **16**, 1563.

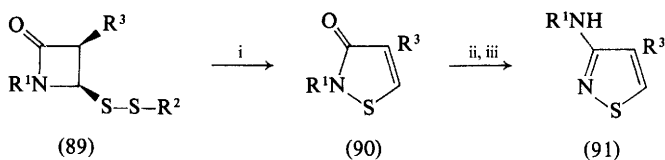
<sup>89</sup> R. K. Howe, T. A. Gruner, L. G. Carter, L. L. Black, and J. E. Franz, *J. Org. Chem.*, 1978, **43**, 3736; R. K. Howe and J. E. Franz, *ibid.*, p. 3742.

<sup>90</sup> M. J. Sanders, S. L. Dye, A. G. Miller, and J. R. Grunwell, *J. Org. Chem.*, 1979, **44**, 510.

<sup>91</sup> R. K. Howe, T. A. Gruner, L. G. Carter, and J. E. Franz, *J. Heterocycl. Chem.*, 1978, **15**, 1001.

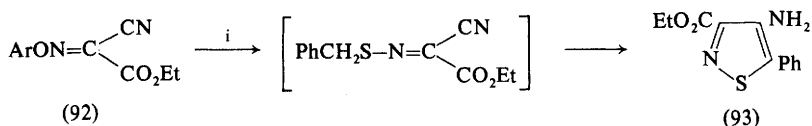
<sup>92</sup> M. Sako and Y. Maki, *Chem. Pharm. Bull.*, 1978, **26**, 1236; J. Rokach and P. Hamel, *J. Heterocycl. Chem.*, 1978, **15**, 695; J. Rokach, P. Hamel, Y. Girard, and G. Reader, *J. Org. Chem.*, 1979, **44**, 1118.

<sup>93</sup> K. Gewald and P. Bellmann, *Liebigs Ann. Chem.*, 1979, 1534.



Reagents: i, heat; ii, MeSO<sub>3</sub>F; iii, NH<sub>3</sub>

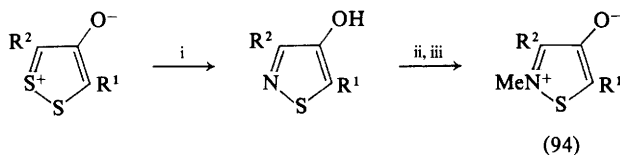
**Scheme 6**



Reagents: i, PhCH<sub>2</sub>SH

**Scheme 7**

Isothiazolium-4-olates (94) are obtained from 1,2-dithiolium-4-olates (p. 291) by successive treatment with ammonia, alkylating agents, and base,<sup>94</sup> as shown in Scheme 8.



Reagents: i, NH<sub>3</sub>; ii, Me<sub>2</sub>SO<sub>4</sub>; iii, NaOH

**Scheme 8**

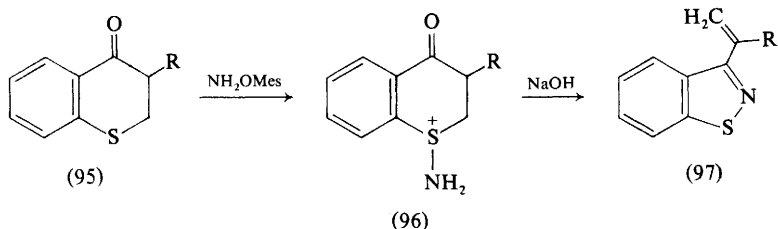
The thiochromanones (95; R = Me or Ph) react with hydroxylamine *O*-mesitylenesulphonate to yield sulphilimines (96); these, with base, rearrange to 1,2-benzisothiazoles (97).<sup>95</sup> A remarkable preparation of a 1,2-benzisothiazole (99; X = S) and of a 1,2-benzisoselenazole (99; X = Se), by the reaction of 2,1,3-benzothia-(or seleno-)diazole (98; X = S or Se) with benzyne, has been reported.<sup>96</sup> Another interesting synthesis, this time of a 2,1-benzisothiazole (102), is by the reaction of the fluorosilylated amine derivative (100) with bis(tri-methylsilyl)sulphur di-imide (101).<sup>97</sup>

<sup>94</sup> D. Barillier, *Phosphorus Sulfur*, 1978, **5**, 251; *Bull. Soc. Chim. Fr., Part 2*, 1979, 26; *Phosphorus Sulfur*, 1980, **8**, 79.

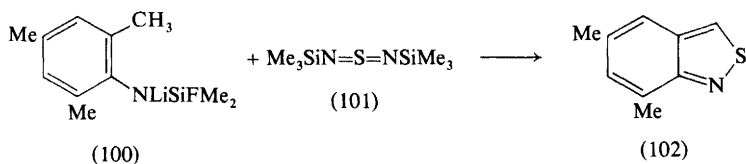
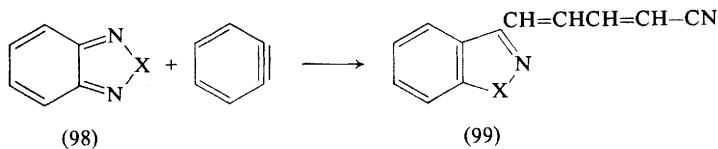
<sup>95</sup> Y. Tamura, S. M. Bayomi, C. Mukai, M. Ikeda, M. Murase, and M. Kise, *Tetrahedron Lett.*, 1980, **21**, 533.

<sup>96</sup> C. D. Campbell, C. W. Rees, M. R. Bryce, M. D. Cooke, P. Hanson, and J. M. Vernon, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1006.

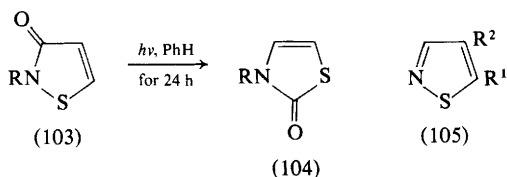
<sup>97</sup> U. Klingebiel and D. Bentmann, *Z. Naturforsch., Teil B*, 1979, **34**, 123; see also M. Davis, *ibid.*, 1980, **35**, 405.



(Mes = mesitylenesulphonate)



**Reactions.**—2-Substituted isothiazolin-3-ones (103) isomerize to 3-substituted thiazolin-2-ones (104) in high yield when irradiated in benzene. The isomerization probably involves homolysis to a biradical, which then re-cyclizes to an  $\alpha$ -lactam. Ring-expansion to the thiazolone follows.<sup>98</sup> This Reporter notes that this reaction is almost the exact converse of the thermolysis of  $\beta$ -lactam disulphides that was mentioned earlier.<sup>92</sup> Thermolysis of isothiazoles (105;  $\text{R}^1, \text{R}^2 = \text{H}$  or  $\text{Me}$ ) in the gas phase at  $590^\circ\text{C}$  yields thioketens ( $\text{RCH}=\text{C}=\text{S}$ ), and kinetic experiments showed that this decomposition is not a radical process.<sup>99</sup>



Isothiazolin-3-one 1-oxides and 1,1-dioxides (106;  $n = 1$  or  $2$ ) react with dienes to give adducts, e.g. (107;  $n = 1$  or  $2$ ), sometimes in nearly quantitative yield.<sup>100</sup>

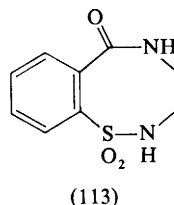
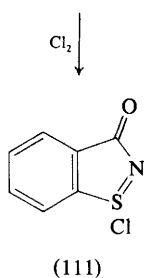
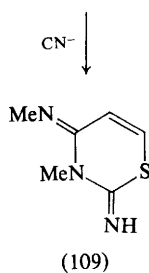
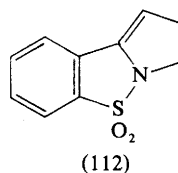
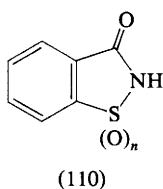
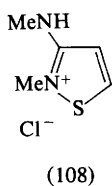
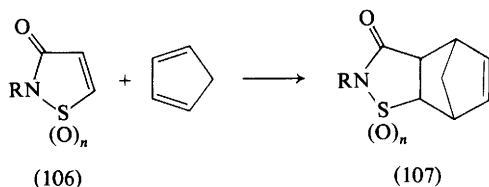
Isothiazolium chlorides (108) undergo ring-expansion when treated with cyanide ion; the product is a 1,3-thiazine (109), illustrating once again the lability of the  $\text{N}-\text{S}$  bond in isothiazolium salts.<sup>101</sup>

<sup>98</sup> J. Rokach and P. Hamel, *J. Chem. Soc., Chem. Commun.*, 1979, 786.

<sup>99</sup> G. E. Castillo and H. E. Bertorello, *J. Chem. Soc., Perkin Trans. 1*, 1978, 325.

<sup>100</sup> E. D. Weiler and J. J. Brennan, *J. Heterocycl. Chem.*, 1978, **15**, 1299.

<sup>101</sup> J. Rokach, P. Hamel, Y. Girard, and G. Reader, *Tetrahedron Lett.*, 1979, 1281.



3-Chloro-1,2-(and -2,1)-benzisothiazoles are useful synthetic intermediates, since the chlorine atom is readily displaced by nucleophiles (see Vol. 5, pp. 352, 355), and recently reported work<sup>102</sup> has extended the range of products thereby obtained. 1-Chloro-1,2-benzisothiazol-3-one (111), obtained by the chlorination of 1,2-benzisothiazolin-3-one (110;  $n = 0$ ), may also prove a useful intermediate.<sup>103</sup>

Saccharin (110;  $n = 2$ ) and its derivatives continue to be the subject of numerous papers; little has changed in regard to the carcinogenicity controversy (see Vol. 5, p. 353), but a typical example of a 'chemical' paper is one in which it is shown how saccharin may be transformed into the imidazo-fused derivative (112) or the thiadiazocine (113).<sup>104</sup>

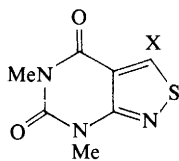
**Isothiazoles Fused to other Nitrogen-containing Heterocycles.**—In view of the ease with which, in the laboratory at least, an isothiazole ring may be fused to 'biological' nitrogen heterocycles, it is, perhaps, surprising that no naturally occurring isothiazole has yet been found. Typical recent work includes the efficient synthesis of isothiazolo[3,4-*d*]pyrimidines (114;  $X = \text{NHR}$  or  $\text{SMe}$ ),<sup>105</sup> of isothiazolo[4,5-*b*]-

<sup>102</sup> H. Boeshagen and W. Geiger, *Synthesis*, 1979, 442; *Chem. Ber.*, 1979, **112**, 3286; A. H. Albert, D. E. O'Brien, and R. K. Robins, *J. Heterocycl. Chem.*, 1978, **15**, 529.

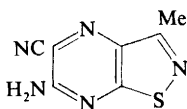
<sup>103</sup> E. S. Levchenko and T. N. Dubinina, *Zh. Org. Khim.*, 1978, **14**, 862 (*Chem. Abstr.*, 1978, **89**, 109 201).

<sup>104</sup> J. Ashby, D. Griffiths, and D. Paton, *J. Heterocycl. Chem.*, 1978, **15**, 1009.

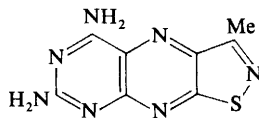
<sup>105</sup> H. Takahashi, N. Nimura, and H. Ogura, *Chem. Pharm. Bull.*, 1979, **27**, 1147; H. Okuda, Y. Tominaga, Y. Matsuda, and G. Kobayashi, *Yakugaku Zasshi*, 1979, **99**, 989 (*Chem. Abstr.*, 1979, **92**, 128 845).



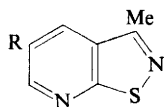
(114)



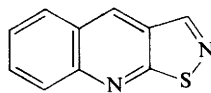
(115)



(116)



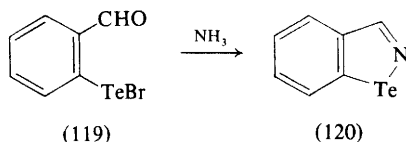
(117)



(118)

pyrazines (115) and isothiazolo[4,5-*g*]pteridines (116),<sup>106</sup> of isothiazolo[5,4-*b*]pyridines (117; R = alkyl),<sup>107</sup> and of isothiazolo[5,4-*b*]quinoline (118).<sup>108</sup>

**1,2-Benzisoselenazole and 1,2-Benzisotellurazole.**—One new synthesis<sup>96</sup> of a 1,2-benzisoselenazole has already been discussed (p. 287). 1,2-Benzisotellurazole (120) has been prepared by the cyclization of the aldehyde (119) with ammonia.<sup>109</sup> The crystal and molecular structures of (120) and of 1,2-benzisoselenazole have



been determined; the tellurium compound has anomalous physical properties (solubility, m.pt, *etc.*), and such anomalies have been attributed to the very short intermolecular Te—N bonds (2.4 Å) in the crystal; 1,2-benzisoselenazole does not have similar short Se—N bonds.<sup>110</sup>

## 7 Oxathiolium and Dithiolium Salts

**General.**—It was pointed out in the previous volume (see Vol. 5, p. 306) that much of the interest in 1,3-dithioles is a result of the discovery of electrical conductivity in tetrathiafulvalenes ('organic metals'). The charge-transfer complexes formed between tetrathiafulvalenes and bromine, iodine, or other electron sinks (TCNE, TCNQ, *etc.*) may involve the production of 1,3-ditholium ions, but discussion of this aspect is beyond the scope of this Chapter, and no attempt has been made to review the voluminous literature on this topic.

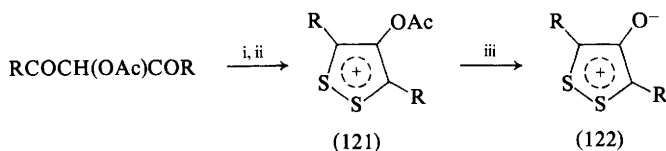
<sup>106</sup> E. C. Taylor and E. Wachsen, *J. Org. Chem.*, 1978, **43**, 4154.

<sup>107</sup> C. Skoetsch and E. Breitmaier, *Synthesis*, 1979, 370.

<sup>108</sup> I. Iijima and K. C. Rice, *J. Heterocycl. Chem.*, 1978, **15**, 1527.

<sup>109</sup> R. Weber, J. L. Piette, and M. Renson, *J. Heterocycl. Chem.*, 1978, **15**, 865.

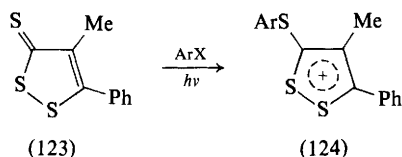
<sup>110</sup> H. Campsteyn, L. Dupont, J. Lamotte-Brasseur, and M. Vermeire, *J. Heterocycl. Chem.*, 1978, **15**, 745.



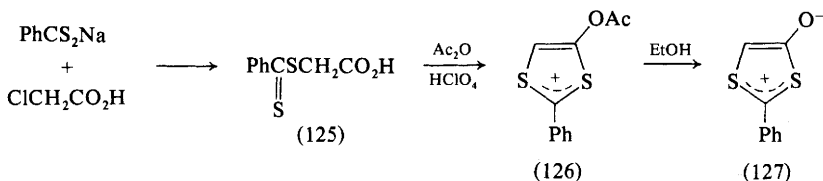
Reagents: i,  $\text{P}_4\text{S}_{10}$ ,  $\text{CS}_2$  or xylene; ii,  $\text{HClO}_4$ ; iii, py

**Scheme 9**

**Synthesis.**—3,5-Diaryl- and 3,5-dialkyl-1,2-dithiolium salts (121;  $\text{R} = \text{Ar}$  or  $\text{Bu}^t$ ) can be prepared in good yield by the sulphurization of diketones (Scheme 9). Treatment of these salts (121) with pyridine affords the corresponding 4-olates (122), which can be *O*-alkylated with iodomethane and similar compounds. With ammonia, ring scission and re-cyclization occurs, and the corresponding isothiazolium-4-olates are formed.<sup>94</sup> An unusual synthesis of 1,2-dithiolium salts (124) is by the photolysis of 1,2-dithiole-3-thiones (123) in benzene or acetonitrile, in the presence of aryl or alkenyl bromides or iodides.<sup>111</sup>



1,3-Dithiolium salts, *e.g.* (126), can be made from the dithioester (125) by reaction with acetic anhydride; in polar solvents the meso-ionic 1,3-dithiolium-4-olate (127) is readily produced. If dithiocarbamates are used as starting materials, then 2-amino-1,3-dithiolium-4-olates are formed.<sup>112</sup>



**Physical and Chemical Properties.**—It has been shown that charge-transfer complexes of 1,2-dithiolium cations with TCNQ have conductivities comparable with, but smaller than, those of analogous 1,3-dithiolium salts.<sup>113</sup>

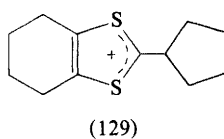
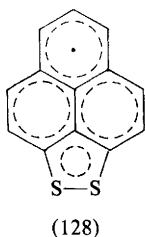
The 1,9-dithiaphenalenyl radical (128) is a stable, monomeric, coplanar species; its e.s.r. spectrum and other spectroscopic properties have been described.<sup>114</sup>

<sup>111</sup> V. N. Drozd, G. S. Bogomolova, and Yu. M. Udachin, *Zh. Org. Khim.*, 1979, **15**, 1069 (*Chem. Abstr.*, 1979, **91**, 74 509).

<sup>112</sup> H. Gotthardt and C. M. Weisshuhn, *Chem. Ber.*, 1978, **111**, 2021; *ibid.*, p. 3178.

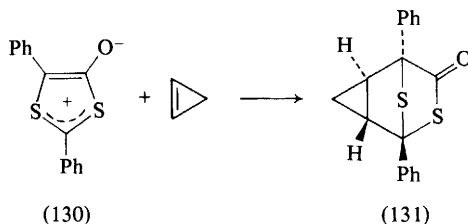
<sup>113</sup> G. Le Coustumer, J. Amzil, and Y. Mollier, *J. Chem. Soc., Chem. Commun.*, 1979, 353.

<sup>114</sup> R. C. Haddon, F. Wudl, M. L. Kaplan, J. H. Marshall, and F. B. Bramwell, *J. Chem. Soc., Chem. Commun.*, 1978, 429; R. C. Haddon, F. Wudl, M. L. Kaplan, J. H. Marshall, R. E. Cais, and F. B. Bramwell, *J. Am. Chem. Soc.*, 1978, **100**, 7629.



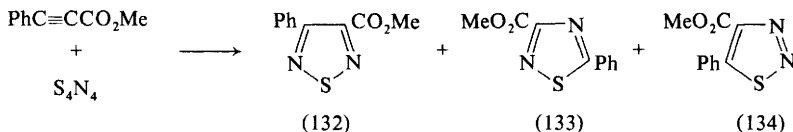
It has been pointed out that  $^{13}\text{C}$  n.m.r. spectroscopy indicates clearly that 1,3-dithiolium cations, e.g. (129), are carbenium ions that are stabilized by heteroatoms, and are not delocalized systems that involve the double bond.<sup>115</sup> The same is probably true of 1,3-dioxolium and 1,3-diselenolium ions and analogous mixed systems.

1,3-Dithiolium-4-olates (130) undergo cycloaddition reactions with cyclic olefins and with benzoquinone; the stereochemistry of the adducts, e.g. (131), depends on the particular olefin.<sup>116</sup>



## 8 Thiadiazoles and Related Compounds

**Synthesis of Thiadiazoles.**—The use of  $\text{S}_4\text{N}_4$  in the preparation of nitrogen–sulphur heterocycles (see Vol. 5, pp. 104, 345) has been extended in that it has now been shown that its reaction with, for example, methyl propiolate in toluene, under reflux, yields mainly the 1,2,5-thiadiazole (132), with lesser amounts of the 1,2,4- and 1,2,3-isomers (133) and (134), respectively. With diphenylacetylene, the yield of 3,4-diphenyl-1,2,5-thiadiazole is a remarkable 87%.<sup>117</sup> Thionyl chloride is another useful sulphur reagent, and its reaction with substituted hydrazones (135;  $\text{R}^1, \text{R}^2 = \text{alkyl, aryl, or H}$ ;  $\text{R}^3 = \text{COMe, CO}_2\text{Et, SO}_2\text{Tol, or CONH}_2$ ) gives good yields of 1,2,3-thiadiazoles (136).<sup>118</sup>



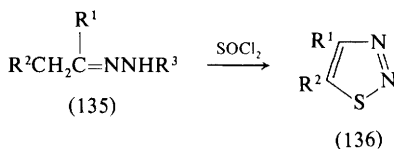
<sup>115</sup> U. Timm, U. Pluecken, H. Petersen, and H. Meier, *J. Heterocycl. Chem.*, 1979, **16**, 1303.

<sup>116</sup> H. Gotthardt, C. M. Weissshuhn, and B. Christl, *Chem. Ber.*, 1978, **111**, 3037.

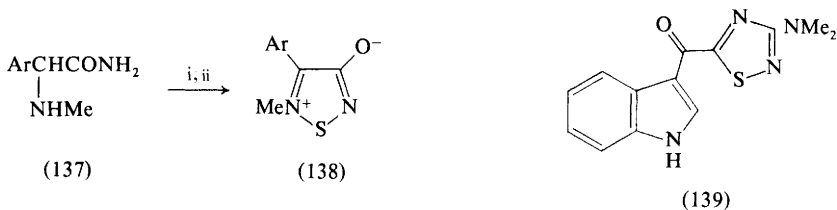
<sup>117</sup> S. Mataka, K. Takahashi, Y. Yamada, and M. Tashiro, *J. Heterocycl. Chem.*, 1979, **16**, 1009.

<sup>118</sup> H. Meier, G. Trickes, E. Laping, and U. Merkle, *Chem. Ber.*, 1980, **113**, 183.





Meso-ionic 1,2,5-thiadiazolium-4-olates (138) are obtained by the action of sulphur monochloride on the *N*-methylated amino-acid amide (137);<sup>119</sup> see Scheme 10. Several other meso-ionic thiadiazole derivatives have been reported, especially 1,2,3-thiadiazolium-4-(and -5)-olates and -thiolates.<sup>120</sup>

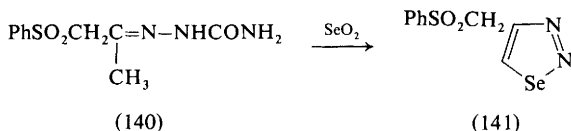


Reagents: i, S<sub>2</sub>Cl<sub>2</sub>, DMF; ii, NaHCO<sub>3</sub> (aq.)

**Scheme 10**

**The First S<sup>II</sup>-N Bond in a Natural Product?**—Dendrodoine, of which 98 mg was isolated from 2.2 tonnes of a marine tunicate, *Dendrodoa grossularia* (Styeliidae), has been shown by X-ray and spectral data to be an indole derivative of 1,2,4-thiadiazole (139).<sup>121</sup> A noteworthy feature is that, as far as this Reporter is aware, this is the first natural product with a sulphur(II)-nitrogen bond. All the other fourteen possible combinations of the five common biological elements (C, H, N, O, and bivalent S) are elaborated by living cells; only S-N has, so far, been missing.

**Synthesis of Selenadiazoles.**—One important selenium-transfer reagent is selenium dioxide, which reacts with hydrazones such as (140) to form 1,2,3-selenadiazoles (141); steroid-like compounds (142; R<sup>1</sup>, R<sup>2</sup> = H, Me, or OMe) can be made in this way,<sup>122</sup> and a similar reaction has been described in which H<sub>2</sub><sup>75</sup>SeO<sub>3</sub> was used to insert a radioactive label into a potential adrenal-imaging agent (143).<sup>123</sup>



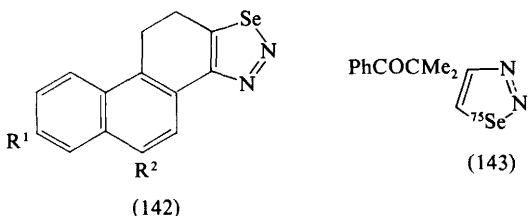
<sup>119</sup> K. Masuda, J. Adachi, and K. Nomura, *J. Chem. Soc., Chem. Commun.*, 1979, 331.

<sup>120</sup> P. Demaree, M. C. Doria, and J. M. Muchowski, *J. Heterocycl. Chem.*, 1978, **15**, 1295; K. Masuda, J. Adachi, and K. Nomura, *J. Chem. Soc., Perkin Trans. 1*, 1979, 956; *ibid.*, p. 2349.

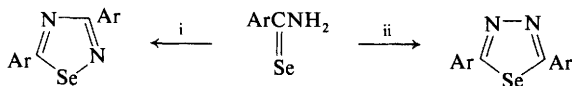
<sup>121</sup> S. Heitz, M. Durgeat, M. Guyot, C. Brassy, and B. Bachet, *Tetrahedron Lett.*, 1980, **21**, 1457.

<sup>122</sup> I. Lalezari, A. Shafiee, J. Khorrami, and A. Soltani, *J. Pharm. Sci.*, 1978, **67**, 1336; I. Lalezari, A. Shafiee, and S. Sadeghi-Milani, *J. Heterocycl. Chem.*, 1979, **16**, 1405; I. Lalezari and S. Sadeghi-Milani, *ibid.*, 1978, **15**, 501.

<sup>123</sup> R. N. Hanson and M. A. Davis, *J. Labelled Compd. Radiopharm.*, 1979, **16**, 31 (*Chem. Abstr.*, 1979, **92**, 22 436).



Aryl selenoamides react with iodine to give 3,5-diaryl-1,2,4-selenadiazoles; with hydrazine, however, the corresponding 1,3,4-selenadiazoles are formed (Scheme 11)<sup>124</sup> (see also Chap. 3, Pt III, p. 185).



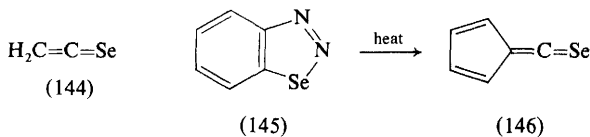
Reagents: i, I<sub>2</sub>, MeOH; ii, H<sub>2</sub>NNH<sub>2</sub>

**Scheme 11**

**Photolysis and Thermolysis of Thiadiazoles and Selenadiazoles.**—A remarkably large number of papers on the photolysis of 1,2,3-thiadiazoles, and the likely production of thiirens thereby, have appeared (see Vol. 5, pp. 197, 432).<sup>125</sup> This subject is discussed in Chapter 4 (p. 216), but it may be noted here that two groups have now isolated thiirens and recorded their spectra by low-temperature matrix techniques.<sup>126</sup>

Thermolysis of 1,2,3-selenadiazole affords only selenoketen (144) and acetylene; above 800 °C, acetylene is the only organic product. Thermolysis of 1,2,3-benzoselenadiazole (145) yields the fulvaselone (146), which was observed as an unstable red deposit on a cold finger at -196 °C; it was identified by p.e. spectroscopy.<sup>127</sup>

When 1,2,5-selenadiazoles (147) are photolysed, nitrile selenides (148) are the



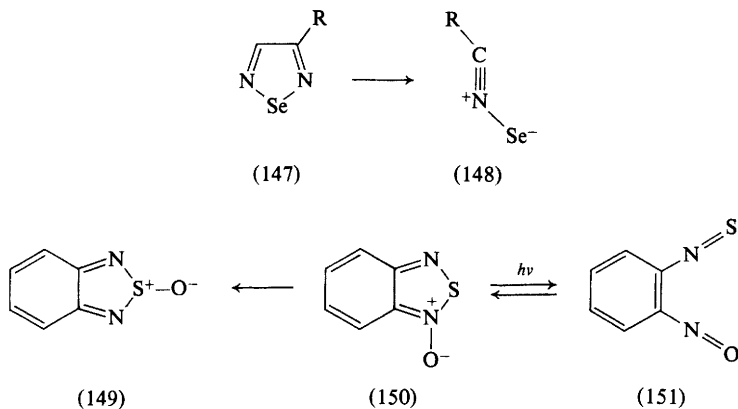
<sup>124</sup> V. I. Cohen, *Synthesis*, 1978, 768; *J. Heterocycl. Chem.*, 1979, **16**, 365.

<sup>125</sup> U. Timm, H. Buehl, and H. Meier, *J. Heterocycl. Chem.*, 1978, **15**, 697; U. Timm and H. Meier, *ibid.*, 1979, **16**, 1295; H. Buehl, U. Timm, and H. Meier, *Chem. Ber.*, 1979, **112**, 3728; H. Meier, S. Graw, U. Timm, and T. Echter, *Nouv. J. Chim.*, 1979, **3**, 715; R. C. White, J. Scooby, and T. D. Roberts, *Tetrahedron Lett.*, 1979, 2785; E. Schaumann, J. Ehlers, and H. Mrotzek, *Liebigs Ann. Chem.*, 1979, 1734.

<sup>126</sup> A. Krantz and J. Laureni, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 13; M. Torres, A. Clement, J. E. Bertie, H. E. Gunning, and O. P. Strausz, *J. Org. Chem.*, 1978, **43**, 2490; M. Torres, I. Safarik, A. Clement, J. E. Bertie, and O. P. Strausz, *Nouv. J. Chim.*, 1979, **3**, 365.

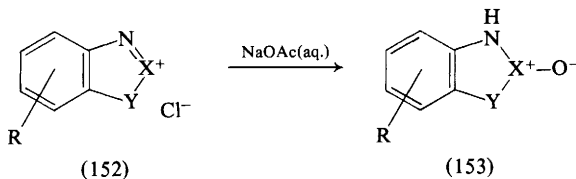
<sup>127</sup> R. Schulz and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 69.

initial products.<sup>128</sup> If 2,1,3-benzothiadiazole 1-oxide (150) is photolysed, one reaction that occurs is a reversible isomerization to 2-thionitroso-nitrosobenzene (151); irreversible isomerization to the *S*-oxide (149) is a competing reaction.<sup>129</sup>



### 9 Benzodithazolium Salts and their Selenium Analogues

A careful comparison of the rates of reaction of 1,2,3-benzodithazolium salts (152; X = Y = S) and their selenium analogues (152; X, Y = S or Se) with *p*-toluidine in acetic acid at 20 °C has shown that substitution of selenium for sulphur at X increases the rate about four-fold; substitution at Y causes only a very slight increase. This observed order of reactivity is in accord with conclusions on charge densities based on M.O. calculations and n.m.r. data.<sup>130</sup> Buffered hydrolysis of some of these salts, e.g. (152; X = Y = S, or X = Se, Y = S; R = 6-Cl), yields the corresponding *S*- or *Se*-oxide (153), in which the heterocyclic ring is no longer aromatic. Two stereoisomers of each of these oxides (153), having the N-H and X=O bonds on the same side or on opposite sides of the ring, were observed. These stereoisomers can be interconverted in acidic media.<sup>131</sup>



<sup>128</sup> C. L. Pedersen, N. Harrit, M. Poliakoff, and I. Dunkin, *Acta Chem. Scand., Ser. B*, 1977, **31**, 848; C. L. Pedersen and N. Hacker, *Tetrahedron Lett.*, 1977, 3982.

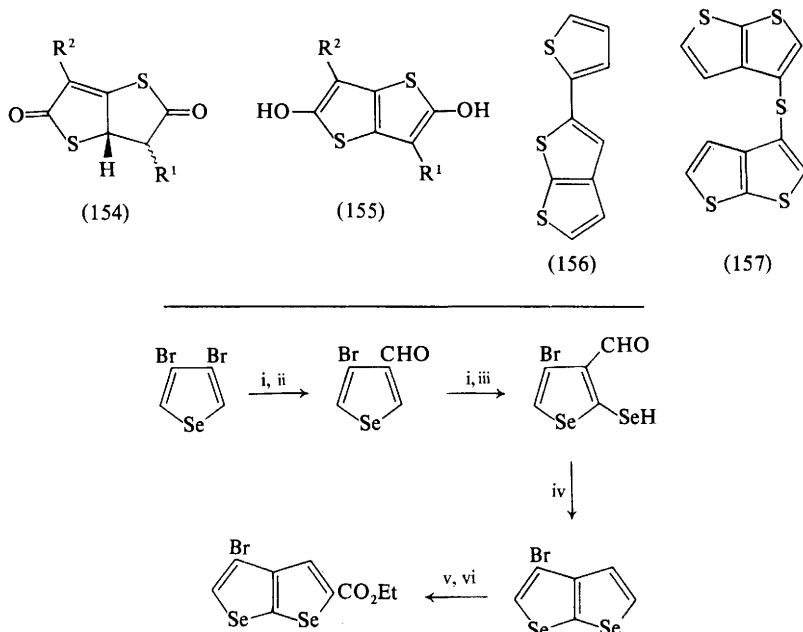
<sup>129</sup> C. L. Pedersen, C. Lohse, and M. Poliakoff, *Acta Chem. Scand., Ser. B*, 1978, **32**, 625.

<sup>130</sup> Yu. I. Akulin, M. M. Gel'mont, B. Kh. Strelets, and L. S. Efros, *Khim. Geterotsykl. Soedin.*, 1978, 912 (*Chem. Abstr.*, 1978, **90**, 54 275).

<sup>131</sup> B. Kh. Strelets, M. M. Gel'mont, Yu. I. Akulin, and L. S. Efros, *Khim. Geterotsykl. Soedin.*, 1979, 1205 (*Chem. Abstr.*, 1979, **92**, 128 024).

### 10 Compounds with Two Fused Aromatic Rings, each containing Sulphur or Selenium Atoms

**Thienothiophens and their Selenium Analogues.**—Thieno[3,4-*c*]thiophens have already been mentioned (p. 281). It has been shown that the potentially tautomeric compounds (154) exist as such, rather than as 2,5-dihydroxythieno[3,2-*b*]thiophens (155).<sup>132</sup> A number of thienylthieno[2,3-*b*]thiophens and their corresponding sulphides, *e.g.* (156), have been synthesized,<sup>133</sup> and 3-bromoselenolo[2,3-*b*]selenophen has been prepared (Scheme 12).<sup>134</sup>



Reagents: i, BuLi; ii, DMF; iii, Se; iv, BrCH<sub>2</sub>CO<sub>2</sub>Et, NaOEt; v, H<sup>+</sup>, H<sub>2</sub>O; vi, heat

**Scheme 12**

**Thienothiazoles and Selenothiazoles.**—An unusual synthesis (Scheme 13) of a thieno[2,3-*d*]thiazole (159) has been reported, the key steps of which are the formation of a dithiazolium salt (158), its hydrolysis, and the insertion of a carbon disulphide moiety, with extrusion of sulphur to form the thiazole ring.<sup>135</sup>

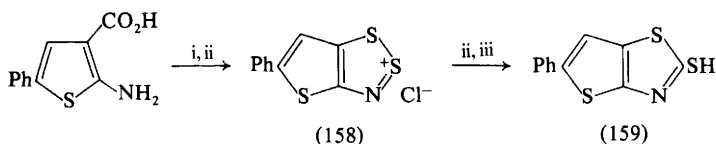
2,6-Disubstituted thieno[3,4-*d*]thiazoles (161; X = S) and selenolo[3,4-*d*]thiazoles (161; X = Se) can be prepared from the readily available thiazolyl

<sup>132</sup> L. Testaferri, M. Tiecco, P. Zanirato, and G. Martelli, *J. Org. Chem.*, 1978, **43**, 2197.

<sup>133</sup> P. Meunier, *Bull. Soc. Chim. Belg.*, 1979, **88**, 325.

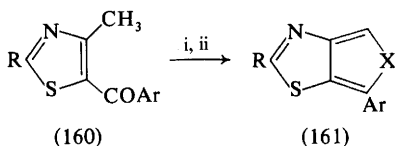
<sup>134</sup> Ya. L. Gol'dfarb, V. P. Litvinov, and I. P. Konyaeva, *Khim. Geterotsikl. Soedin.*, 1979, 1072 (*Chem. Abstr.*, 1979, **92**, 41 802).

<sup>135</sup> P. I. Abramenko, T. K. Ponomareva, and G. I. Priklonskikh, *Khim. Geterotsikl. Soedin.*, 1979, 477 (*Chem. Abstr.*, 1979, **91**, 74 518).



Reagents: i,  $S_2Cl_2$ ; ii,  $H_2O$ ; iii,  $CS_2$ ,  $NaOH$ ,  $H_2O$

**Scheme 13**



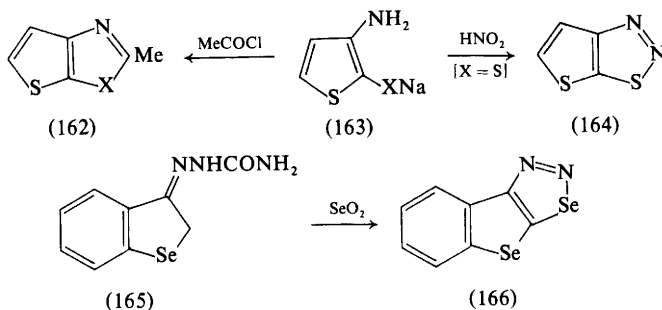
(R = H or Ph)

Reagents: i, *N*-Bromosuccinimide; ii,  $MeCSNH_2$  or  $EtCSeNEt_2$

**Scheme 14**

ketones (160) as shown in Scheme 14; a thioamide or selenoamide is used as the sulphur- or selenium-transfer reagent.<sup>136</sup>

Thieno[3,2-*d*]thiazoles (162; X = S), thieno[3,2-*d*]selenazoles (162; X = Se), and thieno[3,2-*d*]-1,2,3-thiadiazoles (164) are all easily made from the sodium salt of 3-aminothiophen-2-thiol (163; X = S) or its selenol analogue.<sup>137</sup> Benzo[*b*]selenolo[3,2-*d*]-1,2,3-selenadiazole (166) can be prepared by the cyclocondensation of the semicarbazone (165) with selenium dioxide.<sup>138</sup>

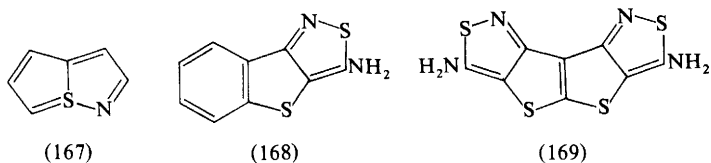


**Thienoisothiazoles.**—This seems to be an area of research in which there has suddenly been an increase in activity, judging from the number of papers published in the period under review. Examples of five of the six possible isomers have now been reported, the sole exception being thieno[2,1-*e*]isothiazole (167), which is one of the two possible ‘non-classical’ isomers.

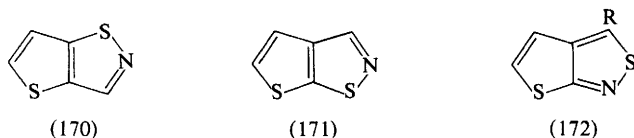
<sup>136</sup> A. Shafiee and A. Mazloumi, *J. Heterocycl. Chem.*, 1978, **15**, 1455.

<sup>137</sup> C. Paulmier, *Bull. Soc. Chim. Fr., Part 2*, 1980, 151.

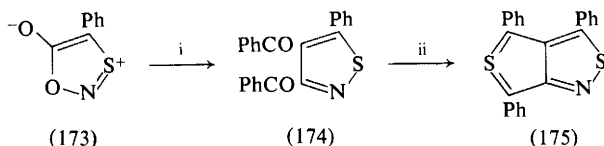
<sup>138</sup> V. P. Litvinov and I. A. Dzhusaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 478 (*Chem. Abstr.*, 1979, **90**, 203 977).



Thieno[3,2-*c*]isothiazoles, e.g. (168) or (169), have been made, the isothiazole rings being constructed by the well-tried oxidation of *o*-amino-thioamides with a peroxide.<sup>139</sup> In a chemical *tour-de-force*, a group at the University of Hull has devised elegant and efficient syntheses of thieno[2,3-*d*]isothiazoles (170), thieno[3,2-*d*]isothiazoles (171), and thieno[2,3-*c*]isothiazoles (172), in most cases obtaining the parent compound or a simple derivative. The general procedures employed include not only most of the standard methods for annelating isothiazole rings, in this case on to thiophen precursors, but also the more difficult construction of isothiazoles with substituents capable of forming a thiophen ring.<sup>140</sup> A surprising alternative synthesis of a thieno[2,3-*c*]isothiazole (172; R = CO<sub>2</sub>Et) by the reaction between phosphorus pentasulphide and ethyl 3-cyano-5,5-diethoxy-2-oxopentanoate, (EtO)<sub>2</sub>CHCH<sub>2</sub>CH(CN)COCO<sub>2</sub>Et, has been briefly reported; the structure of the product was confirmed by an alternative synthesis from an isothiazole-3-thiol.<sup>141</sup>



A heavily substituted non-classical thieno[3,4-*c*]isothiazole (175) has been prepared in almost quantitative yield by the cyclization of the dibenzoylisothiazole (174) with phosphorus pentasulphide (Scheme 15). The precursor (174) is itself synthesized, albeit in low yield, from the oxathiazolium-olate (173), by a process akin to that described earlier (p. 286).<sup>142</sup> The thiophen ring (but not the isothiazole ring) in (175) behaves as a masked ylide, and it undergoes cycloaddition reactions such as with dimethyl acetylenedicarboxylate, when the 2,1-benzisothiazole (178) is



Reagents: i, PhCOC≡CCOPh; ii, P<sub>4</sub>S<sub>10</sub>

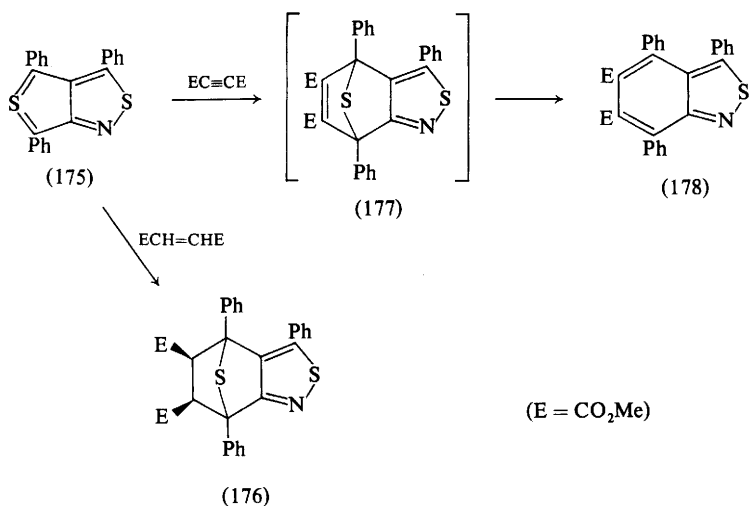
### Scheme 15

<sup>139</sup> B. Tornetta, M. A. Siracusa, G. Ronsisvalle, and F. Guerrero, *Gazz. Chim. Ital.*, 1978, **108**, 57; G. Seybold and H. Eilingsfeld, *Liebigs Ann. Chem.*, 1979, 1271.

<sup>140</sup> K. Clarke, W. R. Fox, and R. M. Scrowston, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1029.

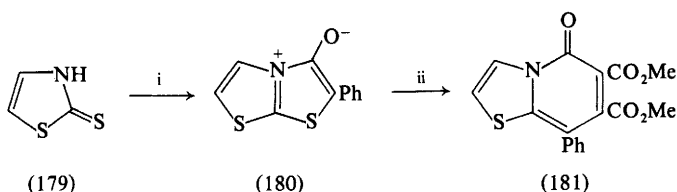
<sup>141</sup> F. C. James and D. Krebs, *Phosphorus Sulfur*, 1979, **6**, 143.

<sup>142</sup> H. Gotthardt, F. Reiter, R. Gleiter, and R. Bartetzko, *Chem. Ber.*, 1979, **112**, 260.



formed; the intermediate adduct (177) spontaneously extrudes sulphur. Dimethyl maleate and other olefinic dipolarophiles react stereospecifically, without elimination of sulphur, to give the corresponding adducts, e.g. (176), as *exo-endo* isomer pairs.<sup>143</sup>

**Meso-ionic Thiazolo[2,3-*b*]thiazoles.**—Thiazoline-2-thione (179) reacts readily with 2-bromo-2-phenylacetyl chloride in the presence of base (Scheme 16) to produce 2-phenylthiazolo[2,3-*b*]thiazolium-3-olate (180), which undergoes cycloaddition reactions with acetylenic and olefinic dipolarophiles in much the same way as (175). With dimethyl acetylenedicarboxylate, for example, the thiazolo[3,2-*a*]pyridin-5-one (181) is formed.<sup>144</sup>



Reagents: i, PhCHBrCOCl, NEt<sub>3</sub>; ii, MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me

**Scheme 16**

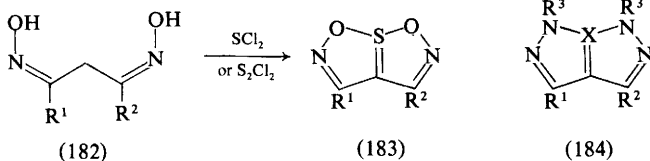
### 11 1,6-Dihetera-6aλ<sup>4</sup>-thiapentalenes and Related Systems

**Synthesis.**—A remarkably simple synthesis of 1,6-dioxo-6aλ<sup>4</sup>-thia-2,5-diazapentalenes (183) and their selenium and tellurium analogues is by the reaction

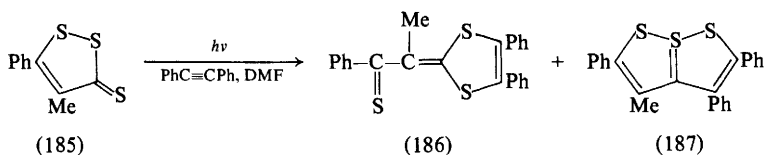
<sup>143</sup> H. Gotthardt and F. Reiter, *Chem. Ber.*, 1979, **112**, 266.

<sup>144</sup> K. T. Potts and D. R. Choudhury, *J. Org. Chem.*, 1978, **43**, 2697; K. T. Potts and S. Kanemasa, *ibid.*, 1979, **44**, 3808.

between the dioximes (182) and sulphur, selenium, or tellurium chlorides. A similar reaction works equally well with dihydrazones; the products are then the corresponding  $6a\lambda^4$ -thia-1,2,5,6-tetra-azapentalenes (184). For the selenium or tellurium analogues it may be preferable to treat the dihydrazone first with selenium or tellurium dioxide and then an appropriate halide.<sup>145</sup>

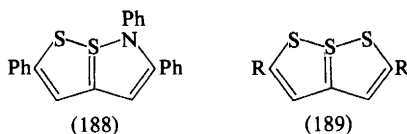


Another novel procedure is the photolysis of a mixture of the 1,2-dithiole-3-thione (185) and diphenylacetylene in DMF. The main product is the 1,3-dithiole (186), but a small yield of the 1,6,6aλ<sup>4</sup>-trithiapentalene (187) is also obtained.<sup>146</sup>



**Structural and Spectroscopic Studies.**—An X-ray crystallographic structure determination of the 1,6aλ<sup>4</sup>-dithia-6-azapentalene (188) has been completed;<sup>147</sup> gas-phase p.e. spectra of 1,6-dioxa-6aλ<sup>4</sup>-thia-2,5-diazapentalene (183; R<sup>1</sup> = R<sup>2</sup> = H) have been reported, and discussed in regard to the effect of changes of the 6a-atom on all other non-hydrogen atoms in the molecule. The observed vibrational broadening of the oxygen 1s lines is related to the observed bond lengths, within a simple model.<sup>148</sup>

Trithiapentalenyl radicals can be generated by the reaction of 1,6,6aλ<sup>4</sup>-trithiapentalenes (189; R = H or Me) with trimethylsilyl or tributylstannyl radicals. The hyperfine e.s.r. splitting of the trithiapentalenyl radicals is significantly lower than that of pentadienyl radicals, indicating considerable delocalization of unpaired spin on to sulphur.<sup>149</sup>



<sup>145</sup> M. Perrier and J. Vialle, *Bull. Soc. Chim. Fr., Part 2*, 1979, 199; *ibid.*, p. 205.

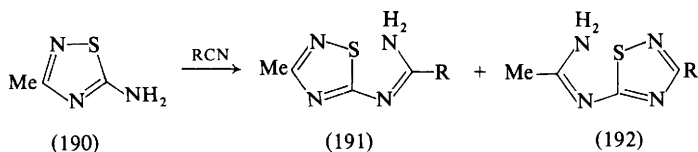
<sup>146</sup> V. N. Drozd, G. S. Bogomolova, and Yu. M. Udachin, *Zh. Org. Khim.*, 1978, **14**, 2459 (*Chem. Abstr.*, 1978, **90**, 152 052).

<sup>147</sup> M. M. Borel, A. Leclaire, G. Le Coustumer, and Y. Mollier, *J. Mol. Struct.*, 1978, **48**, 227.

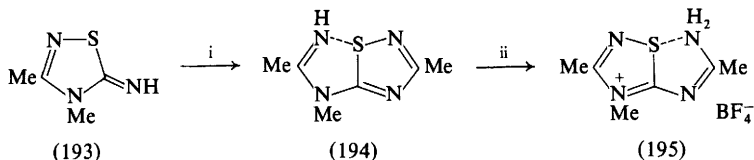
<sup>148</sup> L. J. Saethre, N. Martensson, S. Svensson, P. A. Malmquist, U. Gelius, and K. Siegbahn, *J. Am. Chem. Soc.*, 1980, **102**, 1783.

<sup>149</sup> K. U. Ingold, D. H. Reid, and J. C. Walton, *J. Chem. Soc., Chem. Commun.*, 1979, 371.





**'Bond Switch' at  $\pi$ -Hypervalent Sulphur.**—Condensation of 5-amino-3-methyl-1,2,4-thiadiazole (190) with alkyl or aryl cyanides affords an equilibrium mixture of products (191) and (192). A similar bond switch is observed when the 5-imino-1,2,4-thiadiazoline (193) is treated with the imino-ester  $\text{MeC(=NH)OEt}$ , as shown in Scheme 17. An *X*-ray analysis of the product (194) shows that the S---N and S—N bond lengths are 2.500 and 1.668 Å, respectively.<sup>150</sup> Protonation of (194) causes a reverse switch, the thermodynamically more stable salt (195) being formed.<sup>151</sup> In each case, the probable intermediates are species containing a quadricovalent sulphur atom.



Reagents: i,  $\text{MeC(=NH)OEt}$ , at 60—80 °C; ii,  $\text{HBF}_4$

**Scheme 17**

<sup>150</sup> K. Akiba, T. Kobayashi, and S. Arai, *J. Am. Chem. Soc.*, 1979, **101**, 5857; K. Akiba, S. Arai, T. Tsuchiya, Y. Yamamoto, and F. Iwasaki, *Angew. Chem.*, 1979, **91**, 176.

<sup>151</sup> K. Akiba, S. Arai, and F. Iwasaki, *Tetrahedron Lett.*, 1978, 4117.



# Author Index

---

- Aarts, A. J., 180  
Abatjoglou, A. G., 26, 222, 259  
Abbott, F. S., 219  
Abdel Latif Kassab, N., 237  
Abdel-Megeid, F. M. E., 207, 208  
Abdel-Rahman, M. M. A., 225  
Abdel Reheem Ead, H., 237  
Abdel-Wahab, A. A., 58  
Abdullabekov, I. M., 208  
Abdullaev, A. G., 32  
Abe, Y., 76  
Abramenko, P. I., 296  
Abramovitch, R. A., 74  
Abushanab, E., 50, 103  
Abu-Taha, A., 66  
Ackrell, J., 101  
Acton, E. M., 205  
Adachi, J., 293  
Adachi, K., 273  
Adachi, M., 65, 166, 179  
Adam, W., 238  
Adam, Y., 58  
Adams, J., 76  
Adiwidjaja, G., 74, 160, 171, 187, 216, 264  
Advani, B. G., 172, 184  
Adzima, L. J., 147  
Afanas'ev, M. M., 181  
Afanas'eva, T. G., 275  
Agaev, F. Kh., 208  
Agawa, T., 36, 41, 100, 217  
Agisheva, S. A., 260  
Agozzino, P., 170  
Agurakis, S., 242  
Ahern, D., 18, 216  
Ahern, T. P., 41  
Ahlers, H., 116  
Ahmad, R., 182  
Aiba, K., 62  
Aida, T., 14, 41, 136  
Aimo, G., 266  
Ainpour, P., 63  
Akaboshi, S., 216, 249  
Akasaka, T., 41, 77, 136, 137, 143, 144  
Akasaka, Y., 201  
Akatsuka, R., 153  
Akesson, B., 3  
Akgun, E., 41  
Akhmedov, S. T., 64, 255  
Akhmedova, R. S., 19  
Akhmetov, L. I., 67  
Akiba, K., 301  
Akimkina, N. F., 65  
Akita, H., 87  
Akiyama, S., 36  
Akiyama, T., 263  
Akkermann, J. M., 56  
Akulin, Yu. I., 295  
Akutagawa, K., 144  
Al-Awadi, N., 194  
Albasini, A., 7  
Alberti, A., 8  
Alberts, A. H., 90  
Alcudia, F., 5, 50  
Aleev, R. S., 23  
Ali, M., 253  
Aliiev, N. A., 16  
Alizade, I. G., 255  
Allen, R. W., 99  
Almadi, G., 209  
Almond, V., 4  
Almqvist, A., 280  
Alper, H., 10, 12, 155, 182  
Alpert, M. L., 6  
Alsaïdi, H., 17  
Altland, H. W., 177  
Altman, R. S., 131  
Amann, W., 81, 112  
Amano, A., 11, 250  
Amato, J. S., 171  
Ambrosio, M., 257  
Ambrosius, K., 132, 231  
Amer, F. A., 184  
Ames, A., 14, 22  
Amick, D. R., 87, 138  
Amin, N., 132  
Ammann, D., 178  
Ammon, H. L., 3, 217  
Amosova, S. V., 6, 26, 32, 34, 53, 170  
Amstutz, R., 89, 259  
Amzil, J., 291  
Andersen, K. K., 134, 219  
Andersen, N. H., 2, 93, 259  
Anderson, S. A., 43  
Ando, A., 213, 214  
Ando, M., 40  
Ando, T., 17  
Ando, W., 26, 34, 51, 81, 82  
Andrade, J. R., 90  
Andreani, A., 174  
Andreetti, G. D., 246  
Andreeve, N. A., 229  
Andreocci, M. V., 7  
Andréu, P., 274  
Andriamizaka, J. D., 212  
Andriyankova, L. V., 32  
Anet, F. A. L., 169, 243  
Anger, H., 253  
Ania, F., 132  
Anicich, V., 232  
Anisimov, A., 25, 238  
Ankner, K., 58  
Anksi, H., 42  
Annunziata, R., 50, 54, 144  
Anoardi, L., 211  
Anteunis, M. J. O., 242, 245, 258  
Anthonsen, T., 85  
Antipin, M. Yu., 246  
Antipov, M. A., 23, 58  
Anzai, K., 19  
Aoai, T., 18, 21  
Aoki, S., 61  
Aono, M., 83  
Aoyama, H., 154  
Aoyama, S., 100  
Aoyama, Y., 11  
Apel, J., 261  
Appel, R., 127  
Appelton, D. C., 135, 248  
Arai, S., 301  
Arai, Y., 82, 242  
Arakawa, Y., 82, 251  
Arakelyan, R. H., 172  
Araki, T., 167  
Aramaki, M., 229  
Aramaki, R., 128  
Arata, Y., 82, 251  
Araya, K., 63  
Arbuzov, B. A., 7, 41, 82, 112  
Arco, M. J., 84, 240  
Aref'eva, Z. Ya., 256  
Arigoni, D., 67  
Armitage, D. A., 63, 127  
Arnaudov, M. V., 166  
Arne, K., 95  
Arnold, Z., 42  
Arnost, M. J., 84, 240  
Aron, A. J., 157  
Arrington, C. A., 160  
Arthur, N. L., 24  
Arthur, S. D., 111  
Arumyan, N., 51  
Arvanaghi, M., 41, 45, 51, 75, 87, 261  
Asai, M., 259  
Asakura, H., 70  
Asaoka, M., 21

- Asatryan, E. M., 249  
 Ash, D. K., 78  
 Ashby, J., 289  
 Ashida, M., 201  
 Ashour, F. A., 177  
 Asinger, F., 257  
 Askari, M., 3  
 Aslam, M., 71, 164  
 Aslanov, I. A., 32  
 Asmus, K. D., 2, 13, 262  
 Assadi, F., 170  
 Assef, G., 26  
 Atkinson, J. G., 73  
 Atkinson, R. S., 63, 64  
 Atovmyan, L. O., 246  
 Attah-Poku, S. K., 14  
 Atzmuller, M., 88, 207  
 Au, M.-K., 106, 262  
 Augustin, M., 17, 46, 203, 225, 256  
 Auksi, H., 52, 265  
 Austin, D., 265  
 Avagyan, S. P., 254  
 Awad, M. A., 184  
 Awano, H., 8  
 Aycock, D. F., 194  
 Ayyangar, N. R., 74  
 Azuma, Y., 2  
 Azvedo, L. J., 131  
  
 Babaitsev, V. S., 25, 238  
 Babb, D. P., 48, 226  
 Babkina, E. I., 229  
 Babler, J. H., 55  
 Baboulene, M., 100  
 Baburina, V. A., 190  
 Bacchin, P., 6  
 Bach, R. D., 76  
 Bachtel, B., 293  
 Bachi, M. D., 62, 87, 208  
 Back, T. G., 62, 68  
 Back, T. J., 50  
 Bacon, C. C., 222  
 Badahir, M., 183  
 Baddar, F. G., 170  
 Bader, B., 40  
 Badiello, R., 13  
 Bähr-Wirtz, M., 257  
 Baer, G., 68  
 Baert, F., 175  
 Bahnemann, D., 13  
 Bailer, J., 135, 248, 260  
 Bails, G., 10, 67  
 Baiocchi, F., 11  
 Bairov, V. V., 6, 170  
 Baiwir, M., 5  
 Bajer, M., 279  
 Bak, B., 158, 226  
 Bak, C., 156, 206, 225, 265, 268  
 Baker, J. R., 246  
 Baker, N. J., 70  
 Bakker, B. H., 40  
 Bakos, V., 38  
  
 Bal, M. S., 214  
 Balaji, T., 28  
 Balaz, S., 12  
 Baldwin, J. E., 13, 234, 264  
 Baldwin, P., 37  
 Balenovic, K., 46  
 Baliah, V., 3, 7, 248  
 Balint, J., 251  
 Balog, I. M., 269  
 Balogh, M., 177  
 Balta Calleja, F. T., 132  
 Ban, Y., 49, 143  
 Banerjee, S. N., 178  
 Banister, A. J., 127, 132  
 Bankov, Y. I., 72  
 Bannikova, O. B., 24, 214, 261  
 Bannister, B., 210  
 Bannville, J., 106  
 Barabadze, Sh. Sh., 165  
 Baranovskaya, E. M., 53  
 Barany, G., 205  
 Barashenko, G. G., 147  
 Barbarella, G., 247  
 Bares, J. E., 116  
 Bargagna, A., 164, 263  
 Bargar, T., 93  
 Barillier, D., 2, 287  
 Barker, J. M., 279  
 Barltrop, J. A., 210, 275  
 Barnes, A. C., 144  
 Barnette, W. E., 57, 62, 109, 216, 242  
 Barraclough, P., 239  
 Barrau, J., 212  
 Barrault, J., 9, 274  
 Barrera, R., 53  
 Barrett, A. G. M., 205  
 Barrett, G. C., 9, 65, 79, 186  
 Barrett, J., 232  
 Barrett, P., 131  
 Barrio, J. R., 266  
 Barriola, A., 218  
 Barroeta, N., 12  
 Bartetzko, R., 281, 298  
 Bartl, A., 227  
 Bartlett, P. A., 61, 105, 111  
 Bartmess, J. E., 116  
 Barton, D. H. R., 68, 75, 140, 151, 205, 207, 261  
 Barton, D. J., 226  
 Barton, T. J., 231  
 Bartosevich, J. F., 174  
 Bartzko, R., 133  
 Bass, S. W., 5, 254  
 Bastien, G., 26, 234  
 Basu, P. K., 157  
 Basu, S. K., 91  
 Basyouni, M. N., 166, 255  
 Batch, A. L., 210  
 Bates, G. S., 45, 96  
 Bats, J. W., 132, 254  
 Batyrkanova, B., 229  
 Baudat, R., 14, 87  
  
 Baudler, M., 229  
 Baudy, M., 186, 283  
 Bauer, G., 70  
 Bauer, O. H., 182  
 Baughman, R. H., 131  
 Baukov, Yu. I., 164, 222  
 Baur, A., 165  
 Bautina, I. V., 3, 4  
 Baxter, A. J. G., 15  
 Bayer, R., 42  
 Baykut, G., 232  
 Bayley, H., 11  
 Bayomi, S. M., 60, 140, 147, 252, 287  
 Bazavova, I. M., 201  
 Bazzi, A. A., 161, 224  
 Beagley, B., 133  
 Beak, P., 15, 181, 208  
 Beauchamp, J. L., 232  
 Beaulieu, P. L., 18, 19  
 Becher, J., 239, 279  
 Beck, A. K., 28, 93, 96, 259  
 Beck, J. R., 17, 275  
 Beckert, R., 128  
 Bécu, C., 245  
 Beer, R. J. S., 157  
 Bejer, J., 172, 177  
 Begtrup, M., 186  
 Behnam, E., 282  
 Behr, H., 187  
 Behringer, H., 253  
 Beierlein, I., 178  
 Belanger, R., 13  
 Belen'kii, L. I., 238  
 Belfoure, E. L., 72  
 Belkin, Y. V., 41, 82, 112  
 Belleau, B., 208  
 Bellesia, F., 43  
 Belli, A., 188  
 Bellmann, P., 286  
 Belyaev, N. N., 19  
 Belyaev, V. A., 3  
 Benack, H., 69, 143  
 Ben-David, Y., 29, 107  
 Bendazzoli, G. L., 215  
 Benders, P. H., 166  
 Benezra, C., 55  
 Benner, L. S., 210  
 Bennett, J. E., 8  
 Bennett, P., 85  
 Bentmann, D., 132, 287  
 Bentov, N., 43  
 Benz, H., 53  
 Berdnikov, E. A., 19, 58  
 Berestovitskaya, V. M., 249  
 Beretta, M. G., 90  
 Berezovskii, V. M., 241, 245, 249  
 Berg, C., 158, 226  
 Berg, U., 181  
 Berger, M., 132  
 Berger, M. H., 100  
 Bergeron, R. J., 74  
 Bergesen, K., 258

- Bergman, A., 57  
 Bergman, J., 49, 219, 268, 284  
 Berlan, J., 56  
 Berlin, K. D., 242, 246  
 Berman, D. W., 232  
 Berman, E., 64  
 Bernard, C., 127, 131  
 Bernard, J., 179  
 Bernardi, F., 8, 160, 247, 272  
 Bernardi, R., 85  
 Bernasconi, G. F., 70  
 Bernasconi, S., 235  
 Bernauer, K., 187  
 Berner, J., 198  
 Bernstein, P. R., 111  
 Berthold, H., 71  
 Bertie, J. E., 216, 294  
 Bertorello, H., E., 158, 288  
 Beslin, P., 151  
 Besso, H., 155  
 Bestmann, H. J., 193, 220  
 Betteridge, D. R., 209  
 Betz, M., 208  
 Beutow, N., 234  
 Bewick, A., 20  
 Beyler, L., 166, 168  
 Bezverkhii, N. P., 74  
 Bharadwaj, M. M., 71, 264  
 Bhargava, A., 203, 269  
 Bhatnagar, H. L., 169  
 Bhatnagar, S., 169  
 Bhattacharjee, S. K., 19, 78  
 Bhattacharya, A. K., 77, 157  
 Bhattacharyya, A. A., 131  
 Bhavani, N., 248  
 Bhide, G. V., 242  
 Bialkowska, E., 59  
 Bicking, J. B., 242  
 Bieber, W., 183  
 Biellmann, J. F., 25, 97, 102, 103  
 Bielski, R., 205  
 Biernat, J. F., 197  
 Bigley, D. B., 27, 194  
 Bignardi, G., 263  
 Bigotto, A., 4  
 Bihari, M., 6  
 Bikbaeva, G. G., 53  
 Bilgic, S., 239  
 Bingo, N., 2  
 Binns, M. R., 37, 98  
 Birch, E. J., 232  
 Bird, P. H., 49  
 Bird, T. G. C., 109  
 Bishop, M. W., 210  
 Bittell, J. E., 10  
 Bizzarro, F. T., 241  
 Bizzigotti, G. O., 10  
 Bjerre, C., 158, 226  
 Bjoerkvist, B., 258  
 Black, L. L., 286  
 Blair, A. S., 232  
 Blais, C., 12  
 Blakely, R. L., 12  
 Blanzat, J. F., 103  
 Blatcher, P., 45, 94, 95, 96  
 Blechert, S., 1  
 Bleeker, I. P., 68  
 Bleifert, C., 73  
 Bleisch, S., 133, 227  
 Blenderman, W. G., 10  
 Block, E., 39, 61, 79, 80, 102, 160, 161, 207, 210, 224, 261  
 Block, R., 232  
 Bloedorn, W. D., 237  
 Blotny, G., 197  
 Blount, J. F., 18, 90, 242  
 Bludssus, W., 132  
 Blum, D. M., 111  
 Bocelli, G., 246  
 Bochkareva, N. N., 53  
 Bock, H., 3, 7, 150, 281  
 Bock, M. G., 87  
 Bodrikov, I. V., 2, 19, 32, 53, 65, 207, 215, 268  
 Boeckman, R. K., jun., 111  
 Boehm, H. P., 208  
 Böhm, R., 254, 264  
 Boehme, H., 16, 71, 225, 252  
 Boehmer, W., 21  
 Boekelheide, V., 82, 102  
 Boell, W., 59  
 Boeshagen, H., 289  
 Bogatskii, A. V., 167, 254  
 Bogdanov, V. S., 19, 43, 215  
 Bogel'fer, L. Ya., 167  
 Boger, D. L., 284  
 Boggia, L. M., 4  
 Boggs, J. E., 7  
 Bognar, R., 251  
 Bogomolova, G. S., 256, 291, 300  
 Bohme, H., 110  
 Bohn, R. K., 4  
 Boigegrain, R., 279  
 Boiko, V. N., 3  
 Boileau, S., 244  
 Bojes, J., 131  
 Bokel, H. H., 90  
 Boldeskul, I. E., 84, 87, 141  
 Bolen, D. W., 263  
 Bollaert, W., 279  
 Bolshakova, S. A., 26, 34  
 Bolster, J., 63, 209  
 Bombala, M. U., 208  
 Bonazzi, D., 174  
 Bond, D. L., 70  
 Bondarenko, V. A., 170  
 Bondavalli, F., 164  
 Bonifacii, M., 13  
 Bonilavri, E., 61  
 Bonina, F., 177  
 Bonini, B. F., 82, 103, 163, 210, 215, 227  
 Bonnin, C. M., 273  
 Boosen, K.-J., 283  
 Boothe, T. E., 54, 59  
 Bopp, H., 222  
 Borchers, F., 6  
 Borden, W. T., 2, 259  
 Bordwell, F. G., 116  
 Bore, J. C., 10  
 Borel, M. M., 300  
 Borg, P., 256  
 Borgen, P. C., 61, 111  
 Borg-Visse, F., 250  
 Borisov, A. V., 215  
 Bornmann, W. G., 237  
 Borovikov, Y. Y., 3, 4  
 Borovikova, G. S., 141  
 Borowiec, H., 180, 228  
 Borsdorf, F., 242, 247  
 Bos, H. J. T., 153, 193, 219, 223  
 Bossa, M., 7  
 Bottaro, D., 255  
 Bottino, F., 76, 254  
 Botto, R. E., 272  
 Bottoni, A., 247, 272  
 Bouchalová, P., 182  
 Bouchaut, M., 212  
 Boucha, J. B. S., 21  
 Boyer, S. K., 14, 217  
 Boykin, D. W., 272, 277  
 Bradbury, H. J., 241  
 Braehler, G., 281  
 Braendstroem, A., 70  
 Braentigam, I., 41  
 Bragina, I. O., 183  
 Brailion, B., 5  
 Bramwell, F. B., 232, 281, 291  
 Brand, J. C., 127  
 Brand, R. R. M., 4  
 Brandes, D., 1  
 Brandsma, L., 17, 31, 33, 38, 78, 98, 99, 194, 253, 265  
 Brandstrom, A., 70  
 Brandt, S., 41  
 Brassy, C., 293  
 Braun, M., 35, 44, 99  
 Brautigam, I., 81  
 Braverman, S., 62, 69, 108, 239  
 Bravo, P., 81, 85  
 Bregman, R., 70  
 Breitenbach, R., 86  
 Breitmaier, E., 290  
 Bren, V. A., 5  
 Brennan, J. J., 288  
 Bresciani-Pahor, N., 254  
 Brewster, A. G., 68  
 Brewster, W. D., 75  
 Bridges, A. J., 216  
 Briggs, A. G., 152  
 Brigodiot, M., 244  
 Brinck, C., 232  
 Britten-Kley, M. R., 140  
 Brocksom, T., 36  
 Broderick, D. H., 274  
 Broer, W. J., 6, 232  
 Brokaw, F. C., 82  
 Broniarz, J., 16  
 Brouwer, A. C., 153, 193, 223

- Brouwers, A. M. F., 163  
 Brown, C., 12  
 Brown, C. A., 33, 91  
 Brown, D. S., 263  
 Brown, H. C., 51, 266  
 Brownfain, D. S., 53, 85  
 Broxton, T. J., 182  
 Bruhn, F. R., 189  
 Bruhn, J., 104  
 Brule, D., 85  
 Brunet, E., 50  
 Brunet, J., 252  
 Brunskill, J. S. A., 184, 237, 243  
 Brunton, G., 8  
 Brunvoll, J., 7, 215  
 Bryan, R. F., 259  
 Bryant, J. D., 266  
 Bryantsev, B. I., 172  
 Bryce, M. R., 287  
 Buchanan, G. W., 267  
 Bucher, J. G., tert., 157  
 Buck, M. H., 126, 216, 243, 268  
 Buckley, D. J., 18  
 Buddhasukh, D., 107  
 Budenz, R., 62  
 Buder, W., 76  
 Budesinsky, M., 245  
 Budnik, L. V., 141  
 Bühl, H., 158, 216, 254, 294  
 Buedt, E., 208  
 Buerger, H., 70  
 Bukowska-Strzyzewska, M., 259  
 Bulat, A., D., 23, 58  
 Bulka, E., 175  
 Bull, D. C., 135, 248  
 Bumgardner, C. L., 111  
 Bundy, G. L., 81  
 Burger, K., 228, 270  
 Burgess, E. M., 89  
 Burghardt, D., 71  
 Burgoyne, W., 72  
 Burkert, U., 260  
 Burpitt, R. D., 71  
 Burros, B. C., 225  
 Burskii, J., 65  
 Burton, A., 45  
 Burton, D. J., 24  
 Bushby, R. J., 88, 156, 223  
 Bushkov, A. Y., 5, 49  
 Bushkov, Ya. A., 112  
 Buslaeva, G. E., 41, 82, 112  
 Butenko, G. G., 4, 8  
 Butler, D., 32  
 Butler, I. S., 257  
 Buxeraud, J., 66  
 Buys, T. S. V., 210  
 Buza, M., 134, 219  
 Bychkov, B. N., 58  
 Bychkova, T. I., 3, 58  
 Byers, L. D., 45  
 Bzhezovskii, V. M., 5, 6  
 Cabiddu, S., 90  
 Cadby, P. A., 273  
 Cadogan, J. I. G., 157  
 Cagniant, P., 282  
 Caine, D., 19  
 Cainelli, G., 65  
 Cais, R. E., 291  
 Calo, V., 209  
 Cambie, R. C., 65, 208  
 Cameron, T. B., 88, 208, 266  
 Cameron, T. S., 71, 264  
 Campaigne, E., 176  
 Campbell, C. D., 287  
 Campbell, S., 36  
 Campsteyn, H., 290  
 Cane, D. J., 258  
 Capasso, J., 12  
 Capasso, S., 254  
 Capellini, C., 235  
 Caplain, S., 76  
 Capobianco, G., 26  
 Capozzi, G., 19, 207  
 Capuano, L., 227, 267  
 Carapellucci, P. A., 76  
 Carbonelle, A. C., 267  
 Carden, B. M., 258  
 Caret, R. L., 4, 244  
 Carey, F. A., 259  
 Carkin, V. P., 147  
 Carlsen, L., 154, 157, 164, 190, 218  
 Carlson, S. C., 17, 148  
 Carnahan, E. J., 73, 82  
 Carpino, L. A., 68, 190, 217  
 Carr, R. V. C., 60  
 Carter, J. P., 128  
 Carter, L. G., 286  
 Caruso, A. J., 56  
 Caserio, M. C., 6, 43, 44, 234, 261  
 Casiglioni, M., 24  
 Casnati, G., 53  
 Cass, C. E., 205  
 Cassar, L., 177  
 Cassoux, P., 32  
 Castillo, G. E., 158, 288  
 Cataliotti, R., 269  
 Cauletti, C., 7  
 Cauquis, G., 195  
 Cava, M. C., 157  
 Cava, M. P., 22, 65, 94, 191, 281  
 Cavallini, D., 68  
 Cavanagh, R. R., 131  
 Cavazza, M., 16, 34, 40, 262  
 Cavell, K. J., 197  
 Cavrini, V., 174  
 Cawkill, E., 189  
 Cazaux, L., 267, 268  
 Cazes, B., 46, 195  
 Ceccherelli, P., 82  
 Cecon, A., 83  
 Cepera, K. F., 278  
 Ceraulo, L., 170  
 Ceré, V., 83, 84, 103, 240, 247  
 Cerfontain, H., 70, 263, 268  
 Cerkus, T. R., 19  
 Chaimovich, H., 17  
 Chakraborty, P. K., 273  
 Chalchat, J. C., 85  
 Chalkley, G. R., 143  
 Chalmers, A. A., 102  
 Chaloupka, S., 187  
 Chamberlin, A. R., 90  
 Chambers, R. G., 131  
 Chan, C. M., 46  
 Chan, D. M. T., 110  
 Chan, T. H., 14  
 Chan, T.-L., 106, 262  
 Chan, W. H., 13  
 Chande, M. S., 200  
 Chandra, H., 13, 266  
 Chandraaurin, P., 6  
 Chandrasekaran, S., 87  
 Chandrasekharan, J., 248  
 Chang, Y.-H., 111  
 Charles, S. W., 4  
 Charumilind, P., 156, 220, 221, 225, 264  
 Chasor, D. W., 50  
 Chass, D. A., 107  
 Chassaing, G., 80, 102, 244  
 Chattrouse, A.-P., 277  
 Chatt, J., 210  
 Chaudhuri, A., 19, 78  
 Chaudri, T. A., 75  
 Chaussin, R., 2, 34  
 Chaves das Neves, H. J., 15, 149  
 Cheetham, N. W. H., 204  
 Chefczynska, A., 10  
 Chen, C. H., 243, 248, 268  
 Chen, H.-W., 217  
 Chen, J. S., 265  
 Cheng, Y. S. P., 280  
 Cheradame, H., 244  
 Cherkasov, R. A., 178, 199  
 Cherkinskaya, M. L., 5  
 Cherm, L.-J., 19  
 Chernow, S. M., 70  
 Chi, Y., 58  
 Chiang, C. C., 147  
 Chien, Y.-C., 50  
 Chiericato, M., 83  
 Chikin, P. M., 131  
 Child, R. G., 82  
 Chistyakova, S. A., 178  
 Chittattu, G., 18, 21  
 Chivers, T., 131, 133  
 Chmutova, G. A., 3, 4, 5, 7  
 Chmutova, G. C., 3  
 Choi, L. S. L., 75, 151, 207  
 Cholvad, V., 5  
 Choudhari, K. G., 232  
 Choudhury, D. R., 285, 299  
 Chow, F., 24, 38, 54, 68, 91, 113, 118, 123, 269  
 Chow, Y. L., 40

- Christiaens, L., 5, 113, 282  
 Christiansen, J. J., 218  
 Christl, B., 236, 292  
 Chu, J. Y. C., 75, 149  
 Chuchani, G., 27  
 Chuche, J., 212  
 Chuit, C., 67  
 Chumakov, L. V., 65, 215  
 Chumbalov, T. K., 7  
 Chun, M. W., 60  
 Chupp, J. P., 63  
 Churkina, T. D., 5, 46  
 Chvalovsky, V., 34  
 Chvertkin, B. Ya., 229  
 Chwang, W. K., 251  
 Cimanis, A., 53  
 Cinquantini, A., 24  
 Cinquini, M., 50, 54, 59, 144  
 Cioni, M., 52  
 Cipris, D., 75  
 Cistone, F., 72  
 Ciuffarin, E., 52  
 Ciuraru, G., 283  
 Clardy, J., 93, 269  
 Claremon, D. A., 31  
 Clark, D. A., 14  
 Clark, D. R., 70  
 Clark, D. S., 65  
 Clark, G., 93  
 Clark, J. H., 20  
 Clark, M. C., 115  
 Clark, M. J., 63  
 Clark, P. D., 276  
 Clark, W. G., 131  
 Clarke, K., 276, 298  
 Claude, S., 283  
 Claus, P. K., 135, 210, 242, 248, 260  
 Clausen, K., 178, 230  
 Clayton, J. P., 274  
 Cleland, W. W., 251  
 Clement, A., 216, 294  
 Clement, B., 110  
 Cline, B. L., 152  
 Clinet, J.-C., 47  
 Clive, D. L. J., 18, 21, 44, 51, 112  
 Cobblestick, R. E., 75  
 Coe, D. E., 20  
 Cogolli, P., 17, 276  
 Cohen, A. I., 244  
 Cohen, M. L., 10, 41, 83, 112  
 Cohen, T., 44, 46, 47, 94, 96, 99, 100  
 Cohen, T. C., 95  
 Cohen, V. I., 168, 170, 180, 185, 197, 285, 286, 294  
 Colberg, H., 224, 251  
 Colburn, V. M., 275  
 Cole, R. A., 232  
 Coley, W. R., 172  
 Colle, T. H., 13  
 Collins, S., 62  
 Colombo, L., 50, 90, 103  
 Colon, I., 223, 232  
 Colonna, F. P., 160, 272  
 Colter, M. A., 126  
 Comasseto, J. V., 2, 116  
 Comins, D. L., 44, 95, 195  
 Conboy, R. J., 173  
 Confalone, P. N., 241  
 Conner, W. F., 82  
 Conrad, P. C., 61, 107  
 Consigilo, G., 277  
 Constantin, D. M., 200  
 Cook, M. J., 258  
 Cooke, F., 19, 32, 81, 216  
 Cooke, M. D., 287  
 Cookson, R. C., 33, 38, 55, 56, 99  
 Cookson, R. F., 254  
 Coomassie, M. D., 201  
 Cooper, G. K., 111  
 Corbel, B., 38  
 Corbel, B. C., 61  
 Corbella, A., 235  
 Corbet, J.-P., 55  
 Cordes, A. W., 133  
 Cordes, E. H., 46  
 Cordes, R. E., 71, 264  
 Cordt, F., 88, 156  
 Corey, E. J., 14, 36, 82, 87, 90, 126, 284  
 Corey, J. Y., 101  
 Corkins, H. G., 111, 145  
 Cornelis, A., 54  
 Corral, C., 279  
 Corrigan, M. F., 4  
 Cortez, C., 86  
 Costisella, B., 52, 255, 256, 261  
 Cottam, P. D., 50  
 Cotter, M. A., 32  
 Coulon, P., 13  
 Couret, C., 212  
 Courseille, C., 8, 127  
 Cousineau, C. M. E., 267  
 Couture, A., 76, 251  
 Covey, W. D., 70  
 Cowan, D. O., 232  
 Cowley, A. H., 48, 142  
 Cozzi, F., 50, 54, 59  
 Cragoe, E. J., jun., 242  
 Cram, D. J., 90  
 Crank, G., 75  
 Cravador, A., 44, 45, 114  
 Crawford, T. C., 86  
 Crease, A. E., 59, 67  
 Cremlyn, R. J., 71  
 Crimmin, M. J., 32  
 Cristau, H. J., 255  
 Cristol, H., 255  
 Crivello, J. V., 40  
 Croft, T. S., 19  
 Cronje, T., 71  
 Crozet, M. P., 26  
 Crump, D. R., 219, 232  
 Csizmadia, I. G., 2, 232  
 Csizmadia, V. M., 2, 19  
 Cuccovia, I. M., 17  
 Cuer, A., 5  
 Cuffe, J., 83, 278  
 Cumming, J. B., 6  
 Curini, M., 82  
 Curran, D. P., 87  
 Current, S., 18  
 Currie, J. K., 10, 182  
 Curtis, N. J., 21  
 Cussans, N. J., 68, 261  
 Czarniecki, M., 253  
 Czaderna, B., 221  
 Czech, B., 17  
 Czyzewski, J., 152  
 Dahchour, A., 67  
 Dahl, W. E., 22  
 Dahlen, B., 269  
 Dahm, D. J., 22  
 Dailey, O. D., jun., 86  
 Dalessandro, J., 72  
 Dalla Croce, P., 83, 222  
 Dalzell, H. C., 90  
 D'Amico, J. J., 22, 63  
 Damle, M. H., 167, 198  
 Dance, N. S., 4, 273  
 Danchenko, M. N., 32  
 Danchura, W., 258  
 Danheiser, R. L., 87  
 Daniel, D., 175  
 Daniewski, W. M., 44, 94, 100  
 Danilenko, V. A., 81, 82, 112  
 Danilova, T. A., 250  
 Danishefsky, S., 19, 57  
 Danyarova, M. S., 16  
 Dareshwar, G. P., 51  
 Darmadi, A., 64  
 Das, J., 126  
 Dashkevich, L. B., 178  
 da Silva Correa, C. M. M., 74  
 Daub, G. H., 73  
 Dauphin, G., 5  
 Dauplaise, D., 269  
 Daves, G. D., jun., 5, 81  
 Davidenko, T. I., 254  
 Davidovich, Yu. A., 264  
 Davidsen, S. K., 268  
 Davidson, E. R., 2, 259  
 Davidson, J. S., 178  
 Davidson, P. A., 70  
 Davies, D. I., 264  
 Davies, J., 50  
 Davis, F. A., 1, 49, 62, 64, 221, 250  
 Davis, K. R., 15  
 Davis, M., 287  
 Davis, M. A., 293  
 Davis, R., 55, 104  
 Davy, J. R., 82  
 Dawans, F. A., 250  
 Dawson, J. R., 17  
 Dawson, W. H., 5  
 Day, A. C., 210, 275  
 De, A., 184, 237, 243

- Deacon, T., 263  
 Deady, L. W., 182  
 De Alti, G., 2  
 De'Ath, N. J., 225  
 de Bie, M. J. A., 265  
 de Boer, T. J., 210  
 Decesare, J. M., 54, 61, 104, 239  
 Dechter, J. J., 5  
 Declercq, J.-P., 66, 134, 167, 184, 212, 219, 221, 230  
 Declève, P., 2  
 De Dalal, I., 273  
 Dederer, B., 133  
 Degani, I., 22, 203, 204, 256, 266  
 Deger, H. M., 214  
 Degerer, B., 127  
 Deghaidy, F. S., 232  
 Degrand, C., 60  
 De Groot, A., 19, 90  
 DeHaan, F. P., 70  
 De Haan, J. W., 216, 243  
 Dehne, H., 186  
 Dekerk, J.-P., 212  
 de Koning, H., 56  
 Delacroix, A., 68  
 Del Buttero, P., 222  
 Deleris, G., 8, 127  
 Delitsova, D. P., 128  
 Delker, G. L., 70  
 Dell'Erba, C., 276  
 de Loos, W. A. J., 216  
 Deluca, G., 128  
 DeMarco, R. A., 48  
 Demaree, P., 293  
 De Mark, B. R., 15  
 De Mayo, P., 9, 150, 152, 153, 188, 224  
 Dembach, G., 247  
 Demizu, Y., 253  
 Demyanovich, V. M., 3  
 Denis, J. N., 27, 33, 51, 102, 115  
 Denney, D. B., 225, 269  
 Denney, D. Z., 225, 269  
 Denniston, A. D., 2, 93, 259  
 Denoel, J., 5  
 De Reinach-Hirtzbach, F., 54, 104, 239  
 Dereu, N., 23  
 Derkach, N. Y., 49, 63, 112, 147  
 Deronzier, A., 195  
 Dert, V., 249  
 Deryagina, E. N., 10, 24, 44, 214, 261  
 Derzhinskii, A. R., 57  
 Desai, J. A., 172  
 Descotes, G., 205, 265  
 DesMarteau, D. D., 73  
 Desmazieres, B., 10, 67, 164, 222  
 Desseyn, H. O., 180  
 Destro, R., 216, 232  
 Detty, M. R., 11, 16, 49, 51, 75  
 Dewan, J. C., 270  
 Dewar, M. J. S., 216  
 Dhanani, M. L., 57  
 Dhar, D. N., 170  
 Dice, D. R., 220  
 Didkovskii, V. E., 3  
 Diehl, M., 132  
 Diemert, K., 230  
 Diesveld, J. W., 199  
 Dietsche, T. J., 105, 110  
 Dietzel, S., 5  
 Diez, E., 269  
 Dilbeck, G. A., 11  
 Dilk, E., 175  
 Dill, J. D., 6, 150  
 Dilworth, J. R., 210  
 Dimitriadis, E., 86  
 DiNinno, F., 152, 219  
 Dinjus, E. D., 131  
 Distefano, G., 160, 272  
 Dittmer, D. C., 223  
 Dittrich, K.-H., 42  
 Dj-Forudian, H., 66  
 Dobrikov, A. L., 23  
 Dobrodumova, E. Y., 73  
 Dobrowolska, W., 259  
 Dodd, J. H., 21, 90  
 Doi, J. T., 27, 142, 262  
 Doktorova, L. I., 3  
 Dolby, L. J., 111  
 Dombrovskii, A. V., 65  
 Dominguez, E., 280  
 Doms, G., 26  
 Domschke, G., 128, 227  
 Donnelly, J. A., 85  
 Dontsova, N. E., 17, 57  
 d'Orchymont, H., 25, 102  
 Doria, M. C., 293  
 Dormond, A., 67  
 Dorofeenko, G. N., 174  
 Dorokhava, E. M., 141  
 Doronchenkova, T. N., 172  
 Dortmund, D., 171  
 Doss, S. H., 4  
 Dossena, A., 53  
 Dostovalova, V. I., 5, 46, 74  
 Douglas, A. W., 5  
 Dousse, G., 212  
 Downes, C. P., 2  
 Downs, D. S., 131  
 Drabowicz, J., 51, 57, 69, 75  
 Dreiding, A. S., 17  
 Dreier, C., 47, 239, 279  
 Drewes, H. R., 42, 87, 138  
 Driessen, P. B. J., 226  
 Drobnica, L., 12, 198  
 Dronov, V. I., 16, 234, 261  
 Drozd, V. N., 196, 220, 256, 265, 291, 300  
 Drucker, G. E., 116  
 Dubenko, R. G., 180, 201  
 Dubinina, T. N., 141, 289  
 Dubs, P., 21, 183, 253  
 Duc, L., 283  
 Ducruix, A., 8  
 Duffy, P. F., 93  
 Dufour, R., 113  
 Duhamel, L., 80  
 Dul'nev, P. G., 249  
 Dumont, W., 24, 27, 45, 91, 102, 115, 118, 120, 121  
 Dunina, V. V., 175, 181  
 Dunitz, J. D., 89, 259  
 Dunkin, I. R., 226, 295  
 Dunogues, J., 8, 127  
 Duong, K. N. V., 59  
 Dupont, L., 290  
 Dupre, S., 68  
 Dupuis, J. W., 53  
 Durand, R., 248  
 Durgaryan, A. A., 172  
 Durgeat, M., 293  
 Durham, D. L., 208, 232  
 Durig, J. R., 269  
 Durrant, J. A., 132  
 Durst, T., 40, 54, 61, 79, 81, 104, 109, 222, 239, 263  
 Dutka, F., 16  
 Duus, F., 154, 157, 165  
 Dux, F., 72  
 Dwarakanath, K., 168, 175  
 D'Yachenko, O. A., 246  
 Dye, S. L., 137, 286  
 Dymova, S. F., 167  
 Dyong, I., 260  
 Dzhafarov, A. A., 32  
 Dzhafarov, E. F., 32  
 Dzhagatspanyan, R. V., 6  
 Dzhemilev, U. M., 10, 57, 250  
 Dzhumaeu, I. A., 297  
 Dzhundubaev, K. D., 229  
 Dzurilla, M., 173  
 Ealick, S. E., 246  
 Ebbinghaus, C. F., 218  
 Echter, T., 294  
 Eckhard, I. F., 90, 260  
 Eda, S., 36  
 Eder, U., 56, 104  
 Edward, J. T., 182  
 Edward, M., 138  
 Edwards, B., 14, 217  
 Eekhof, J. H., 250  
 Eenhorn, J. A., 255  
 Efremov, Y. A., 10  
 Efremova, G. G., 32  
 Efros, L. S., 295  
 Ege, G., 83  
 Eggelte, H. J., 238  
 Egli, H., 67  
 Egorov, Y. P., 3, 4, 141  
 Eguchi, S., 238  
 Ehlers, J., 159, 216, 294  
 Eicher, T., 155  
 Eigner, D., 13  
 Eilingsfeld, H., 298



- Einstein, F. W. B., 75  
 Eisch, J. J., 59, 107  
 El-Bahaie, S., 169  
 Elbarbary, A. A., 207, 208  
 Elbaum, C., 130  
 El Bouz, M., 45, 102  
 Eleev, A. F., 71, 227  
 Elguero, J., 272  
 Eliel, E. L., 3, 26, 86, 90, 222, 233, 258, 259  
 Elkaschef, M. A. F., 208  
 El-Khamry, A. M. A., 166  
 El-Khawaga, A. M., 58  
 Ellingsen, P. O., 60  
 Ellis, P. D., 5  
 Elman, A. R., 6  
 Elmore, N. F., 233  
 Elokхина, V. N., 255, 264  
 El-Rayyes, N. R., 170  
 Elridge, J. A., 253  
 Elsevier, C. J., 69  
 El Tabei, M. A. A. M., 60  
 Elvers, B., 204  
 Emoto, S., 40, 241  
 Emsley, J., 209, 254  
 Engberts, J. B. F. N., 7, 68, 73  
 Engelen, B., 254  
 Engler, R., 193  
 Engman, L., 49, 268  
 Engoyan, A. P., 249  
 Enkaku, M., 279  
 Ennis, M. D., 102, 210, 261  
 Epiotis, N. D., 2, 259  
 Erbea, R., 188  
 Eremenko, O. N., 269  
 Ermakov, A. I., 229  
 Ernst, L., 185  
 Erwin, R. W., 59, 110  
 Esayan, G. E., 172  
 Eschenmoser, A., 183  
 Escudié, J., 212  
 Eskenazi, C., 57  
 Esmans, E., 180  
 Espada Rios, I., 72  
 Essawy, A., 264  
 Esteban, A. L., 269  
 Etienne, A., 10, 67, 164, 222  
 Eto, M., 253, 255  
 Evangelisti, F., 164, 263  
 Evans, D. A., 85  
 Evans, D. H., 143, 260  
 Evans, S. A., jun., 5, 243, 245  
 Everhardus, R. H., 17, 33  
 Evers, R., 174  
 Eweiss, N. F., 65  
 Ewig, C. S., 216  
 Ewin, G., 186  
 Ewing, D. F., 184, 237, 243, 276  
 Exner, O., 7  
 Fabi, M. T., 27  
 Fabian, J., 2, 133, 271  
 Fabio, P. F., 82  
 Fabre, J. M., 191  
 Fabrissin, S., 235  
 Faehl, L. G., 51, 71  
 Fahsl, R., 69  
 Fainzil'berg, A. A., 40, 112  
 Fajkos, J., 85  
 Falcone, S. J., 22, 65  
 Falkenstein, K., 65  
 Fanghaenel, E., 5  
 Faragher, R., 85  
 Farberov, M. I., 58  
 Farina, R., 93  
 Farney, R. F., 15, 208  
 Farnia, G., 26  
 Farnier, M., 278  
 Farning, O., 163  
 Farrall, M. J., 40, 81  
 Farrar, C. R., 263  
 Fatutta, S., 235  
 Fauchez, J., 13  
 Faull, A. W., 66, 174  
 Faure, A., 205, 265  
 Faure, R., 257, 272  
 Fava, A., 83, 84, 103, 240, 247  
 Fawcett, A. H., 5  
 Fayadh, J. M., 254  
 Fazio, R., 18, 216  
 Featherman, S. I., 257  
 Febvay-Garot, N., 76  
 Federici, G., 68  
 Federsel, H.-J., 219, 284  
 Fedorov, S. B., 58  
 Feenan, P., 131  
 Fehér, F., 254  
 Feigon, J. F., 70  
 Fenby, D. V., 12  
 Ferrari, M., 235  
 Ferraz, H. M. C., 29, 116  
 Ferraz, J. P., 46  
 Ferreira, D., 140  
 Ferreira, J. T. B., 2  
 Ferreira, T. W., 12  
 Ferri, R. A., 222  
 Ferrugia, M., 254  
 Feshin, V. P., 5  
 Feugas, C., 257  
 Fiandanese, V., 59  
 Field, G. F., 235, 241  
 Field, L., 1, 11, 76, 79  
 Fielding, L., 131  
 Fields, R., 67  
 Fife, T. H., 15, 46  
 Figueira, R. R., 4  
 Filer, C. N., 18, 216  
 Filipenko, T. Ya., 170  
 Fillippova, T. M., 241, 245, 249  
 Finch, N., 90  
 Findlay, R. H., 272  
 Finlay, J. D., 109, 222, 263  
 Finocchiaro, P., 254  
 Fionova, V., 25  
 Firl, J., 228, 270  
 Fischer, E., 174  
 Fisk, T. E., 72  
 Fitt, J. J., 33, 98  
 Fitzpatrick, P. J., 257  
 Flaccus, R. D., 62  
 Flatow, A., 82  
 Flekhter, B. V., 250  
 Flemal, J., 230  
 Fleming, I., 19, 29  
 Fleming, M. P., 95  
 Fleming, R. H., 236  
 Flesia, E., 26  
 Fliri, A., 241  
 Floch, L., 172  
 Flowers, W. T., 21, 40, 174  
 Floyd, D., 87  
 Fochi, R., 22, 203, 204, 256, 266  
 Fohl, E. R., 76  
 Fohliisch, B., 220, 221  
 Fokin, A. V., 207, 211  
 Folli, U., 272  
 Fong, H. O., 71  
 Fongers, K. S., 263  
 Foote, C. S., 24  
 Forbus, T. R., 72  
 Ford, G. P., 216  
 Fornasier, R., 211  
 Forrest, D., 204  
 Forster, R. C., 256  
 Forster, W. R., 216  
 Fortunak, J. M., 110  
 Foster, N. G., 6  
 Foster, R. C., 202  
 Foti, S., 76, 254  
 Foucaud, A., 21, 23, 40, 48, 81, 83, 186, 283  
 Fournier, C., 5  
 Fourrey, J.-L., 25  
 Fox, M. A., 53  
 Fox, M. J., 85  
 Fox, W. B., 48  
 Fox, W. R., 298  
 Foye, W. O., 192  
 Franchi, L., 174  
 Franck-Neumann, M., 28, 54, 83, 161  
 Frandsen, E. G., 279  
 Frank, R. M., 88, 156  
 Franum, S. A., 241  
 Franz, J. E., 286  
 Fraser-Reid, B., 263  
 Frater, G., 30  
 Frazee, W. J., 17, 86  
 Frazier, K., 60, 110  
 Frechet, J. M. J., 40, 81  
 Fredga, A., 5  
 Freeman, C. G., 273  
 Freeman, F., 70  
 Freer, A., 8  
 Freidlina, R. Kh., 166, 183, 214  
 Frejd, T., 69  
 Frenkh, Y., 81  
 Freter, R., 76  
 Frickel, F., 105  
 Friedlander, B. T., 63, 65, 261

- Friedlina, R. K., 5  
 Friedman, A. J., 62  
 Friedrich, G., 189  
 Friedrich, K., 81, 112, 185, 207  
 Friedrichsen, W., 85, 208  
 Friesen, G. D., 218  
 Fringuelli, F., 150, 281  
 Fritz, H., 81, 112, 178, 230  
 Fronza, G., 81, 85  
 Fu, P. P., 86  
 Fuchigami, T., 198  
 Fuchs, B., 233  
 Fuchs, P. L., 61, 86, 107  
 Fuchs, R., 283  
 Fueno, T., 19, 34  
 Fuerderer, P., 281  
 Fuess, H., 132, 254  
 Fuji, K., 10, 45  
 Fujihara, H., 11  
 Fujii, E., 22  
 Fujiki, K., 65  
 Fujimoto, H., 133  
 Fujimoto, K., 85  
 Fujinami, T., 66, 201  
 Fujisawa, T., 105  
 Fujita, E., 10, 27, 44, 45, 51,  
   54, 90, 93, 100, 256, 261,  
   266  
 Fujita, Y., 69  
 Fujitaka, N., 98  
 Fujuki, K., 65  
 Fukada, N., 192, 194, 197, 225  
 Fukui, K., 133  
 Fukumura, M., 33, 136, 137  
 Fukushima, D., 64, 77  
 Fukushima, T., 224  
 Fulford, J. E., 53  
 Fuller, W. W., 131  
 Fullerton, T. J., 105, 110  
 Fulpius, B. W., 105  
 Funabashi, M., 90  
 Funahashi, K., 211  
 Funkschilling, P. C., 111  
 Furlani, C., 7  
 Furmanova, N. G., 254  
 Furstenberg, G. F., 229  
 Furuhashi, K., 90  
 Furukawa, H., 232  
 Furukawa, M., 68  
 Furukawa, N., 33, 41, 52, 53,  
   77, 84, 127, 136, 137, 143,  
   144  
 Furukawa, S., 83  
 Fuse, M., 33, 99  
 Fusstetter, H., 231  
  
 Gabbott, R. E., 194  
 Gad, F. A., 207  
 Gadzhiev, M. K., 17, 165  
 Gadzhieva, M. G., 255  
 Gadzhily, T. M., 49  
 Gärtner, H., 175  
 Gagarin, S. G., 7  
 Gagel, K., 138  
  
 Gaisin, R. L., 57  
 Galabov, A., 168  
 Galabov, B., 168  
 Galasso, V., 4  
 Galatin, A. F., 254  
 Galkin, E. G., 256  
 Gallacher, I. M., 39  
 Gallagher, P. T., 275  
 Galle, J. E., 59, 107  
 Galli, C., 277  
 Gallo, A. A., 11  
 Gallo, R., 17  
 Gal'pern, G. D., 234  
 Galushina, V. V., 170  
 Galy, J.-P., 272  
 Gambarotta, S., 52  
 Gambaryan, N. P., 128  
 Gambino, S., 58  
 Games, D. E., 254  
 Gandhi, C. S., 89, 183, 214  
 Gandler, J., 10  
 Gansow, O. A., 5  
 Ganyushin, L. A., 25  
 Ganzhenko, T. S., 215  
 Gaoni, Y., 236, 249  
 Gapinski, R. E., 46, 47, 94, 95  
 Gara, W. B., 250  
 Garaeva, R. N., 7  
 Garbesi, A., 82, 247  
 Garbuzov, V. G., 25  
 Garcia Fraile, A., 72  
 Garcia Martinez, A., 72  
 Garcia Ruano, J. L., 5, 50  
 Gargiulo, R. J., 11  
 Gariboldi, P., 235  
 Garito, A. F., 157  
 Garkin, V. P., 23, 49  
 Garner, T. B., 245  
 Garratt, D. G., 18, 19, 22, 49,  
   65  
 Garratt, P. J., 280  
 Garreau, R., 68  
 Garst, M. E., 40  
 Garvey, D. S., 15  
 Gasanov, F. I., 16  
 Gaset, A., 9  
 Gassmann, P. G., 21, 41, 42,  
   87, 138  
 Gates, B. C., 274  
 Gatti, R., 174  
 Gattow, G., 200, 204  
 Gaudemer, A., 59  
 Gavrilova, G. M., 5, 170  
 Gayathri-Devi, K. R., 182  
 Gaze, C., 247, 261  
 Gazizov, I. G., 3  
 Gebbing, H., 42, 69, 143  
 Geetha, P., 85  
 Geiger, W., 289  
 Geise, B., 31  
 Geise, H. J., 267  
 Geiss, K. H., 11, 90  
 Geize, G. D., 7  
 Gelius, U., 300  
  
 Gel'mont, M. M., 295  
 Gemenden, C. W., 90  
 Geneste, P., 248  
 Gennari, C., 50, 90, 103  
 George, A. V. E., 153, 193, 223  
 George, T. J., 55  
 Georgian, V., 14, 217  
 Gerdes, H. M., 109, 266  
 Gerdes, J. M., 46  
 Gerell, R., 232  
 Gerhold, J., 116  
 Gerlach, H., 15  
 Gerlach, R., 55, 105  
 Germain, G., 66, 134, 167, 184,  
   212, 219, 221, 230  
 Gerson, F., 281  
 Gewalt, K., 279, 286  
 Ghali, E. A., 255  
 Ghera, E., 29, 107  
 Ghiaci, M., 169, 243  
 Giannola, L. L., 170  
 Giddings, P. J., 18, 83  
 Gieren, A., 127, 133  
 Giese, B., 72  
 Gilbert, B. C., 77, 247, 261  
 Gilbert, E. E., 70  
 Gilbert, K., 83  
 Gilchrist, T. G., 138  
 Gilchrist, T. L., 85, 136, 139  
 Giles, J. R. G., 13  
 Gilis, P. M., 279  
 Gill, B., 77  
 Gill, W. D., 127, 131  
 Gillespie, R. J., 83, 84, 278  
 Gillissen, H. M. J., 126, 243,  
   268  
 Gilmore, C. J., 8  
 Ginak, A. I., 24, 210  
 Gindin, V. A., 208  
 Ginsburg, A., 147  
 Ginzburg, B. M., 12  
 Giordano, C., 177, 188  
 Giorgini, M. G., 269  
 Giovanninetti, G., 174  
 Giral, L., 191  
 Girard, Y., 73, 286, 288  
 Giusti, G., 257, 260  
 Gladiali, S., 26  
 Gladysz, J. A., 23  
 Glander, L., 127  
 Glass, R. S., 74, 232, 262  
 Glassel, W., 230  
 Gleason, J. G., 76  
 Gleiter, R., 133, 232, 247, 281,  
   298  
 Glemser, O., 133, 134, 147, 255  
 Glennow, C., 277  
 Glinka, K., 254  
 Gnatyuk, P. P., 165  
 Gnedin, B. G., 72  
 Goda, K., 24  
 Godinho, L. S., 149  
 Goerdeler, J., 167  
 Goerner, R. N., 205

- Götschi, E., 183  
 Gogoladze, D. D., 17  
 Gogolli, P., 17  
 Gogte, V. N., 207  
 Goguelin, M., 208  
 Gokel, G. W., 109, 266  
 Gold, P. M., 38, 91, 123  
 Goldberg, O., 62, 87, 208  
 Gol'dfarb, Ya. A., 23, 296  
 Goldhill, J., 19  
 Golding, B. T., 90, 260  
 Goldmann, S., 55, 105  
 Goldsmith, B., 72  
 Goldsmith, D., 18  
 Golida, N., 65  
 Golinski, J., 58, 111  
 Golloch, A., 127  
 Gololobov, Yu. G., 15, 32, 84  
 Golovkin, G. V., 6  
 Golovnya, R. V., 25  
 Golubeva, G. A., 189  
 Golubinskii, A. V., 7  
 Gonnella, N. C., 94, 191  
 Gopalan, R., 38, 56  
 Gopichand, Y., 156, 220, 225  
 Gorb, L. T., 284  
 Gorbenko, E. F., 180, 201  
 Gordadze, G. N., 234  
 Gordon, E. M., 64  
 Gordon, Z. L., 7  
 Gors, C., 175  
 Gossauer, A., 185  
 Gosselck, 255, 261  
 Gosselin, P., 44, 95, 191  
 Gosselink, J. W., 163  
 Gossick, G. J., 14, 252  
 Goto, H., 193  
 Goto, T., 60, 107  
 Gottarelli, G., 215  
 Gotthardt, H., 153, 154, 196,  
 219, 220, 223, 236, 256, 291,  
 292, 298, 299  
 Gottstein, W., 220  
 Goubitz, K., 246  
 Gougoutas, J. Z., 244  
 Govorek, V. K., 25, 238  
 Gowenlock, B. G., 13  
 Gowland, B. D., 109  
 Gowland, F. W., 110  
 Grabenko, A. D., 178  
 Grabley, F.-F., 38, 225  
 Grabley, S., 66, 187  
 Grabowska, A., 272  
 Graf, C., 132  
 Graf, H., 34  
 Grafing, R., 33, 98, 99  
 Graham, P. A., 177  
 Graham, W. A. G., 258  
 Gramlich, W., 54  
 Granata, A., 76, 254  
 Grandi, R., 43  
 Grapov, A. F., 167, 170  
 Gras, J. L., 87  
 Graw, S., 294  
 Gray, G. A., 5, 81  
 Gray, R. W., 17  
 Grayson, J. I., 37  
 Green, D. C., 99  
 Green, F. R., tert., 61, 105, 111  
 Green, J. C., 157  
 Greene, J. L., 54, 59  
 Greenwald, R. G., 143, 260  
 Gregory, D. C., 7  
 Grehn, L., 165, 172  
 Greiciute, D., 19, 26  
 Gren, A. I., 254, 260, 265  
 Gressier, J. C., 180, 194  
 Greve, H., 57, 60  
 Greving, B., 281  
 Grieco, P. A., 65, 116  
 Griffin, T. S., 174  
 Griffiths, D., 289  
 Griffiths, D. W., 209, 254  
 Grigoryan, R. T., 249  
 Grimaud, M., 181  
 Grimshaw, C. E., 251  
 Grishina, O. N., 229  
 Gröbel, B. T., 93, 116, 121, 259  
 Groenewegen, P., 20  
 Grohmann, I., 3  
 Gronowitz, S., 3, 5, 232, 277,  
 280  
 Gross, A., 62, 87, 208  
 Gross, H., 255, 256, 261  
 Grosserode, R. S., 91  
 Grossert, J. S., 71, 264  
 Groth, C., 46, 225, 256  
 Grotjahn, D. B., 93  
 Grue-Sorensen, G., 40  
 Gruner, C., 229  
 Gruner, T. A., 286  
 Gruntz, U., 64, 204  
 Grunwell, J. R., 137, 286  
 Gryson, J. I., 95  
 Grzejszczak, S., 10, 52, 256  
 Gschwend, H. W., 33, 79, 98  
 Gualteri, J. A., 241  
 Guanci, D. F., 173  
 Guanti, G., 103, 276  
 Guarda, M. A., 174  
 Guémas, J.-P., 156  
 Günther, W. H. H., 75, 149,  
 269  
 Guenzi, A., 240  
 Guerra, M., 8  
 Guerrero, F., 298  
 Guest, A. W., 274  
 Guglielmetti, R., 212  
 Guimaraes, A. C., 268  
 Guimon, C., 272  
 Guisnet, M., 9, 274  
 Guittet, E., 105  
 Gumbatalieva, A. Z., 255  
 Gunn, B. P., 104  
 Gunning, H. E., 216, 294  
 Gunthér, H., 193  
 Gupta, B. D., 59  
 Gupta, B. G. B., 45, 51, 261  
 Gupta, J. C., 169  
 Guryanova, E. N., 25  
 Gusarova, N. K., 32  
 Guseinov, K. Z., 16  
 Guthrie, J. P., 16  
 Gutierrez, M. C., 53  
 Gutman, D., 11, 226  
 Guyot, M., 293  
 Gybin, A. S., 19, 43, 215  
 Gyorgy, D., 27  
 Haake, M., 42, 69, 143  
 Haas, A., 47  
 Haas, P., 230  
 Habashi, K., 9  
 Hacker, N., 295  
 Haddon, R. C., 133, 232, 281,  
 291  
 Haemers, A., 279  
 Haemel, M. W., 82, 102  
 Hagen, J. P., 84, 240  
 Hagen, S., 85  
 Hagiwara, H., 33, 99  
 Haiduc, I., 127  
 Hairsine, P. W., 144  
 Hajjar, F. H., 170  
 Hakansson, R., 271, 280  
 Hakimelahi, G. H., 71  
 Halazy, S., 29, 45, 100, 114,  
 118, 119  
 Hales, N. J., 106  
 Haley, M. J., 174  
 Haley, N. F., 205  
 Halgren, T. A., 215  
 Hall, C. R., 222  
 Hall, H. T., Jun., 93  
 Hallberg, A., 277  
 Hallensleben, M. L., 4  
 Hamada, K., 4  
 Hamaguchi, A., 197  
 Hamamura, T., 36  
 Hamed, A., 264  
 Hamel, P., 149, 286, 288  
 Hamelin, J., 39  
 Hamilton, R., 205  
 Hammann, J., 131  
 Hammerschmidt, E., 183  
 Hampel, M., 71  
 Hamta, J., 60  
 Hanack, M., 60, 73, 82, 110  
 Hanafusa, F., 24  
 Hanafusa, T., 65  
 Hanai, K., 3, 4  
 Hancock, R. A., 57  
 Handrick, G. R., 90  
 Hanefeld, W., 201, 202, 227  
 Hannah, D. J., 261  
 Hansen, B., 283  
 Hansen, H. G., 78, 205  
 Hansen, M. R., 32  
 Hansen, R., 126  
 Hanson, P., 287  
 Gupta, B. D., 59  
 Hanzawa, T., 185

- Hara, S., 68  
 Harada, I., 4  
 Harada, T., 90, 184, 185, 256  
 Harano, K., 204  
 Harayama, T., 57  
 Hardinger, S. A., 111  
 Hardstaff, W. R., 71  
 Hardy, A. D., 8, 236  
 Hargittai, I., 4, 7, 215  
 Hargreaves, M., 238  
 Harhash, A. H., 184  
 Harigaya, Y., 135  
 Harmon, L. A., 59  
 Harpp, D. N., 14, 63, 65, 69,  
   76, 78, 254, 261  
 Harris, C. J., 138  
 Harris, J. F., 19  
 Harris, M. M., 268  
 Harris, W. C., 160, 232  
 Harrison, A. G., 6  
 Harrison, C. R., 65  
 Harrison, E. A., jun., 107  
 Harrit, N., 218, 283, 295  
 Hart, D. J., 85  
 Hart, H., 280  
 Hartke, K., 41, 81, 190, 196,  
   237  
 Hartmann, H., 166, 180, 232  
 Harto, S., 160  
 Hartung, H., 193  
 Hartwig, O. H., 235  
 Hartwig, T., 266  
 Harum, M. G., 163  
 Harvey, R. G., 86  
 Hasan, S. K., 51, 250  
 Hase, H. L., 218  
 Hase, T. A., 45, 261  
 Hase, Y., 266  
 Hasegawa, A., 208  
 Hasegawa, T., 154  
 Hashiguchi, S., 100  
 Hashimoto, H., 86  
 Hashimoto, K., 37, 55, 110  
 Hashimoto, Y., 254  
 Hata, H., 46  
 Hata, T., 51  
 Hata, Y., 210  
 Hatakeyama, S., 90, 93  
 Hatanaka, I., 112  
 Hatanaka, K., 16  
 Hattori, K., 9, 183, 193  
 Hauser, F. M., 21, 86  
 Haviv, F., 208  
 Haworth, D. T., 131  
 Haya, K., 219  
 Hayakawa, K., 275  
 Hayashi, J., 42, 87  
 Hayashi, M., 242  
 Hayashi, T., 65, 98, 200, 205  
 Hayashi, Y., 232  
 Hayes, B. A., 245  
 Haynes, R. K., 37, 38  
 Heal, H. G., 132  
 Heaney, H., 263  
 Heathcock, C. H., 81, 243  
 Hedstrand, D. M., 41  
 Heeshbach, D. R., 131  
 Heger, G., 168  
 Heider, W., 147  
 Heimer, N. E., 63  
 Heimgartner, H., 104, 187  
 Hein, M., 132  
 Heindel, N. D., 189  
 Heitz, S., 293  
 Helbert, M., 179  
 Heldt, W., 144  
 Hellier, D. G., 267  
 Hellner, E., 168  
 Helmick, L. S., 15, 208  
 Helquist, P., 41  
 Helwig, D., 71  
 Hendriksen, L., 268  
 Henichart, J. P., 175  
 Henjes, H., 230  
 Henkel, G., 132, 142  
 Henning, R., 95  
 Henrichs, P. M., 243  
 Henriksen, L., 206  
 Henry, D. W., 205  
 Henry, G., 25  
 Hensen, G., 196, 237  
 Herkes, F. E., 188  
 Herman, M. A., 180  
 Hermann, H., 3  
 Hermann, R., 260  
 Hermann, U., 73  
 Hermez, I., 177  
 Herrenclen-Harker, W. G., 131  
 Herrera Fernandez, A., 72  
 Herricksen, L., 47  
 Herrmann, D., 4, 21  
 Herrmann, J., 245  
 Herrmann, J. L., 100  
 Herrmann, M. H., 144  
 Herron, J. T., 24  
 Hershberger, J., 59  
 Herslof, B., 3  
 Hertenstein, H., 17  
 Hess, B. A., jun., 216  
 Hess, H., 230  
 Hesse, R. H., 75, 151, 207  
 Helsing, A., 68  
 Heuck, K., 72  
 Hevesi, L., 11, 22, 44, 45, 118  
 Hewson, A. T., 36  
 Heyder, F., 70  
 Hibbert, F., 106  
 Hibino, S., 28, 242  
 Hidaki, S., 46  
 Higashi, L. S., 8  
 Higgins, R. W., 6  
 Higuchi, T., 81  
 Hill, J. O., 186, 197  
 Hinnney, H. R., 111  
 Hino, T., 234  
 Hintzer, K., 165  
 Hinz, W., 202  
 Hioki, T., 238  
 Hirabayashi, Y., 14  
 Hirai, K., 30, 100  
 Hiraki, Y., 44  
 Hiram, M., 15  
 Hirano, S., 169  
 Hirobe, M., 75  
 Hiroi, K., 19, 20, 22, 262  
 Hirokawa, S., 259  
 Hirose, Y., 192, 225  
 Hirota, K., 71  
 Hirota, M., 57  
 Hirotsu, K., 93  
 Hirsch, J. A., 3, 242  
 Hirschon, A. S., 142, 262  
 Hlawatschek, H., 200  
 Ho, K. W., 153  
 Ho, T.-L., 24  
 Hobkirk, J., 39  
 Hodge, P., 65  
 Höhne, G., 265  
 Hölte, H. D., 245  
 Höpfner, U., 251  
 Hoerner, D., 204  
 Hoey, J. G., 85  
 Hoffman, P. G., 74  
 Hoffmann, R. W., 55, 105, 190  
 Hofmann, R. V., 72  
 Hofstetter, P., 178  
 Hogel, J., 230  
 Hogenkamp, H. P. C., 268  
 Hogeveen, H., 226, 263  
 Hogeveen, M., 250  
 Hogg, D. R., 62  
 Hogg, J. L., 15  
 Hohenlohe-Oehringen, K., 241  
 Hojo, M., 32  
 Holly, S., 16  
 Holm, A., 158, 190, 218, 226,  
   283  
 Holmes, J. L., 232, 259  
 Holt, G., 21, 40, 67  
 Holterman, H. A., 73  
 Hong, C. T., 7  
 Hopfner, U., 224  
 Hoppmann, A., 90  
 Horak, V., 75, 135, 184  
 Hordvik, A., 157  
 Hori, I., 56, 200  
 Hori, M., 81, 139, 245  
 Hori, T., 54, 138, 232  
 Horie, H., 211  
 Horie, O., 11, 250  
 Horii, T., 76  
 Horn, H., 27  
 Horner, L., 26  
 Hornfeldt, A. B., 5  
 Hortmann, A. G., 77, 157  
 Horton, D., 8  
 Hosangadi, B. C., 51  
 Hosh, L. S., 142  
 Hoshi, N., 56  
 Hoshino, M., 224, 238, 256  
 Hosogai, T., 130, 229  
 Hosoki, A., 131

- Hotzel, A., 278  
 Houssin, R., 175  
 Houston, T. L., 37, 98  
 Howe, R. K., 286  
 Hoye, T. R., 56, 100  
 Hoyer, E., 166  
 Hritzova, O., 228  
 Hsu, J. F., 269  
 Huang, S. H., 143  
 Huang, S.-L., 53, 86, 134  
 Huddleston, P. R., 279  
 Hudson, J. E., 17  
 Hudson, R. F., 12, 66  
 Huenecke, H. H., 71  
 Huffman, J. C., 105  
 Hufnal, J. M., 109  
 Hug, P., 178, 230  
 Hughes, L., 264  
 Hugon, I., 248  
 Hui, R. A. H. F., 68  
 Huisgen, R., 34, 283  
 Huisman, H. O., 56  
 Hull, R., 66, 174  
 Humphreys, D. J., 208  
 Hungerbuhler, E., 90  
 Hunter, G., 258  
 Hupe, D. J., 76  
 Hupp, J., 13  
 Huss, O. M., 196, 223, 256  
 Hussein, A. Q., 66  
 Huszthy, P., 48  
 Hutchings, S. D., 241  
 Hutchins, R. O., 72  
 Hutchins, R. R., 46, 95  
 Hutton, R., 208, 232  
 Huybrechts, L., 66, 219, 221  
 Huyser, E. S., 76  
 Hwang, K.-J., 31  
 Hyatt, J. A., 71  
  
 Ibad-Zade, A. K., 10, 16  
 Ibragimov, N. Y., 16  
 Ibrahim, N., 50  
 Ichihara, A., 96  
 Ichikawa, K., 10, 45, 261  
 Iddon, B., 273, 275  
 Iden, R., 222  
 Ido, K., 268  
 Ignatov, V. A., 63  
 Iijima, I., 290  
 Iijima, T., 211  
 Iitaka, Y., 81, 90  
 Ikeda, M., 60, 138, 140, 147,  
 197, 252, 287  
 Ikegami, S., 216, 249  
 Ila, H., 47  
 Ilchenko, A. Y., 67  
 Il'in, S. G., 246  
 Illuminati, G., 277  
 Imafuku, K., 155  
 Imagawa, T., 263  
 Imai, S., 197  
 Imanishi, T., 44  
 Imaoka, M., 27  
  
 Imazu, Y., 80  
 Imbert, J.-P., 74, 171  
 Imoto, E., 46  
 Inaba, M., 32, 193  
 Inagaki, M., 128, 227  
 Inagaki, Y., 128, 129, 130, 218,  
 229  
 Inamoto, N., 14, 24, 128, 129,  
 130, 150, 157, 207, 218, 229,  
 237  
 Inanaga, J., 29  
 Ingendoh, A., 16  
 Ingold, K. U., 204, 300  
 Inness, R. R., 54  
 Inokawa, H., 47  
 Inokawa, S., 47  
 Inomata, K., 60, 100, 111, 249  
 Inone, A., 70  
 Inoue, H., 46, 167  
 Inoue, K., 150  
 Inoue, S., 11, 138, 209  
 Inoue, T., 41  
 Inoue, Y., 24  
 Inouye, Y., 226  
 Invergo, B. J., 55  
 Ioannou, P. V., 90, 260  
 Ionova, V. F., 25, 238  
 Iqbal, J., 144  
 Iqbal, Z., 131  
 Irgolic, K. J., 2, 112, 233  
 Irie, T., 39  
 Iriuchijima, S., 51  
 Irmischer, K., 242  
 Irving, E., 210, 275  
 Ishida, M., 36  
 Ishiguro, T., 90  
 Ishihara, H., 14  
 Ishii, F., 157, 237  
 Ishii, H., 16  
 Ishi-i, S., 156, 237  
 Ishii, Y., 40  
 Ishikawa, M., 100  
 Ishikawa, N., 16, 38, 46, 199  
 Iskander, M. N., 82  
 Isobe, K., 33, 93, 99  
 Isobe, M., 60, 107  
 Isola, M., 52  
 Itabashi, K., 183  
 Itagaki, Y., 81  
 Itatani, Y., 82, 251  
 Ito, K., 16, 70, 193  
 Ito, S., 30, 98, 219  
 Ito, T., 70  
 Ito, Y., 104, 180  
 Itoh, A., 11, 16  
 Itoh, F., 232  
 Itoh, H., 53, 144  
 Itoh, M., 26  
 Itoh, O., 52, 247  
 Ivanchenko, N. M., 63  
 Ivanov, S., 215  
 Ivanov, S. N., 72  
 Ivanova, T. M., 172  
 Ivin, K. J., 5, 197  
  
 Iwai, K., 40  
 Iwama, Y., 40  
 Iwamoto, H., 90, 185  
 Iwano, Y., 30, 100  
 Iwaoko, T., 205  
 Iwasaki, F., 301  
 Iwasaki, T., 264  
 Iwase, Y., 253  
 Iwatsuki, T., 12  
 Iyer, A., 74  
 Iyoda, M., 214  
 Izawa, Y., 70  
 Izbacka, E., 263  
 Izmailskii, V. A., 3  
  
 Jackson, W. R., 37, 98  
 Jacobsen, N., 224  
 Jacobson, R. M., 86  
 Jacquignon, P., 282  
 Jadhav, M. B., 53  
 Jahn, R., 66  
 Jakobsen, H. J., 5  
 Jalonen, J., 266  
 James, C., 70  
 James, F. C., 298  
 James, S. R., 72  
 Jameson, R. F., 258  
 Jamrozik, J., 262  
 Jamrozik, M., 262  
 Jan, K. Y., 58  
 Jancke, H., 242  
 Janda, M., 277  
 Jansen, A. C. V., 249  
 Jansen, B. J. M., 19  
 Janzen, A. F., 53  
 Jarmas, A. A., 242  
 Jarvis, B. B., 217  
 Jaspers, M., 68  
 Jaud, J., 267  
 Jawdasiuk, M., 93  
 Jaworski, T., 178  
 Jayne, G. J. J., 209, 254  
 Jeannin, Y., 267  
 Jelinkova, T., 51  
 Jeminet, G., 74  
 Jencks, W. P., 46  
 Jenkins, R., 49  
 Jenkins, R., Jun., 221, 250  
 Jennings, W. B., 270  
 Jensen, B., 245  
 Jensen, H. P., 67  
 Jensen, J. L., 46  
 Jensen, K. A., 180  
 Jentsch, R., 210  
 Jewell, L. M., 26, 222  
 Jeyaraman, R., 248  
 Jezierski, A., 8  
 Jick, B. S., 23  
 Jindo, Y., 200  
 Jirackova, L., 51  
 Jo, S., 44  
 Joehims, J. C., 66, 260  
 Jørgensen, F. S., 7  
 Jørgensen, K. A., 230, 253

- Jogdeo, P. S., 242  
 Johansen, O. H., 252  
 John, D. L., 18, 83  
 Johnson, C. R., 79, 85, 105,  
   111, 127, 134, 143, 145, 146,  
   222, 232  
 Johnson, M. D., 59, 67  
 Johnson, R. A., 73  
 Johnson, R. N., 241  
 Johnston, J., 11  
 Johnston, L. J., 17  
 Joho, M., 21, 253  
 Jommi, G., 235  
 Jonczyk, A., 23, 58, 106  
 Jones, A. W., 279  
 Jones, C. H. W., 4, 273  
 Jones, D. N., 50  
 Jones, G., 275  
 Jones, I. W., 6  
 Jones, J. H., 242  
 Jones, P. M., 207  
 Jones, P. R., 4  
 Jongejan, E., 210  
 Jonkers, F. L., 249  
 Jonsson, E. U., 146, 222  
 Jonusauskas, S., 26  
 Joshi, B. C., 74  
 Jouin, P., 25  
 Joullie, M. M., 10, 18, 90, 128,  
   216, 227  
 Ju, T.-L., 77  
 Juaristi, E., 3, 258, 264  
 Judelbaum, A., 42  
 Judge, R. H., 220  
 Judkins, B. D., 63, 64  
 Jugé, S., 144  
 Juji, K., 261, 266  
 Julia, M., 1, 40, 59, 111  
 Julia, S., 46, 47, 105, 195  
 Junjappa, H., 47  
 Junker, W. R., 130  
 Jurch, G. R., jun., 194  
 Jurgens, A., 74  
 Jurgens, H. J., 208  
 Just, G., 71  
 Jutzi, P., 255  
 Jynge, K., 157  
  
 Kacher, M. L., 24  
 Kagabu, S., 208  
 Kagami, H., 229  
 Kagan, H. B., 57  
 Kagotani, M., 69, 68, 185  
 Kaiser, E. M., 79  
 Kaiser, J., 259  
 Kaji, A., 11, 43, 44, 52, 100,  
   205, 208  
 Kaji, K., 31, 37, 55, 56, 110  
 Kajigaeshi, S., 264  
 Kakimoto, M., 134, 140  
 Kakiuchi, H., 211  
 Kakudo, M., 136  
 Kakui, T., 65  
 Kalabin, G. A., 5, 6, 32, 53, 170  
 Kalabina, A. V., 58  
 Kalasinsky, V. F., 160, 232  
 Kalck, P., 9  
 Kalik, M. A., 23  
 Kalikhman, J. D., 17, 32, 34,  
   60, 172, 255, 264  
 Kalinkin, M. I., 238  
 Kalker, H. G., 259  
 Kallenberg, H., 20  
 Kaloustian, M. K., 189, 190  
 Kalyan, J. B., 43, 215  
 Kal'yan, Yu. B., 19  
 Kalyavin, V. A., 53  
 Kamalov, R. M., 199  
 Kamalyutdinova-Salikhova,  
   A. M., 8  
 Kambe, S., 65  
 Kamela, Z., 188  
 Kameoka, H., 253  
 Kamernitskii, A. V., 232  
 Kametani, F., 174  
 Kametani, T., 54  
 Kamiya, K., 246  
 Kamp, D., 82, 102  
 Kanagasabapathy, V. M., 3, 7  
 Kanal, S., 66, 170  
 Kanchuger, M. S., 45  
 Kanda, K., 232  
 Kandasamy, D., 72  
 Kandror, I. I., 5, 166, 183  
 Kaneko, K., 27, 44, 100, 131,  
   261  
 Kanemasa, S., 264, 299  
 Kang, K.-T., 157, 237  
 Kano, S., 28, 41, 102, 242  
 Kantyukova, R. G., 236  
 Kanzafarov, F. Y., 10  
 Kao, H. I., 130  
 Kao, J., 2, 271  
 Kapitanova, N. G., 7  
 Kaplan, M. L., 133, 232, 291  
 Kapovits, I., 6, 48, 127, 135  
 Karady, S., 171  
 Karakasa, T., 156, 161, 185,  
   220, 237  
 Karaulov, E. S., 246  
 Karchefski, E. M., 70  
 Karchesy, J. J., 273, 274  
 Karelov, A. A., 3  
 Kargin, Y. M., 58  
 Karlsson, S., 47  
 Karminski, W., 16  
 Karnaukhova, R. V., 255  
 Kartashev, V. R., 19  
 Kartashov, V. R., 65  
 Kaschani-Motlagh, M., 64  
 Kascheres, C., 7  
 Kashimura, S., 16, 27, 30  
 Kashurnikova, L. V., 5  
 Kasperek, G. J., 263  
 Kasperek, J. G., 263  
 Kasuga, K., 30, 100, 101  
 Kasugai, H., 208  
 Kasukhin, L. F., 84  
 Kasumov, N. K., 257  
 Katada, T., 197  
 Kataev, E. G., 19  
 Kataeva, L. M., 5  
 Kataoka, M., 36  
 Kataoka, T., 81, 139, 193, 245  
 Kato, A., 254  
 Kato, H., 133  
 Kato, J., 232  
 Kato, M., 194  
 Kato, S., 193, 197  
 Kato, T., 106, 199  
 Katritzky, A. R., 64, 189, 204,  
   207  
 Katsube, J., 12  
 Katsuhara, Y., 73  
 Katsura, Y., 63  
 Katterman, L. C. 99  
 Kauffman, J. M., 192  
 Kauffmann, T., 116, 281  
 Kaufmann, D., 29, 100  
 Kaura, A. C., 62  
 Kausch, E., 74, 167, 171, 187,  
   225, 228  
 Kaválek, J., 169  
 Kawabata, K., 44  
 Kawada, K., 213  
 Kawada, M., 26  
 Kawahara, I., 110  
 Kawai, S., 11  
 Kawai, Y., 208  
 Kawamura, S., 76  
 Kawana, M., 194  
 Kawanisi, M., 263  
 Kawano, Y., 11, 266  
 Kawasaki, T., 65, 166, 179  
 Kawase, T., 32, 155, 193  
 Kawata, T., 204  
 Kawazura, H., 130  
 Kay, D. G., 41, 52, 71  
 Kay, D. P., 144  
 Kazakova, E. I., 175, 181  
 Kazankina, E. I., 3  
 Kazmaier, P. M., 42, 52, 265  
 Kaz'mina, N. B., 226, 268  
 Keates, C., 275  
 Keats, N. G., 7  
 Kebarle, P., 6  
 Keck, G. E., 87  
 Keifer, J. C., 245  
 Keiko, V. V., 6, 17, 32, 34, 231  
 Keitel, I., 261  
 Kellner, V., 73  
 Kellogg, R. M., 41, 63, 209, 250  
 Kelstrup, E., 40, 266  
 Kempe, T., 82, 149, 207  
 Kempe, U. J., 82, 149, 207  
 Kemper, R., 251  
 Kenan, W. R., 26  
 Kende, A. S., 35, 87  
 Kende, I., 5  
 Kennedy, E. R., 85, 146  
 Kennedy, S. M. F., 272  
 Keppinger, J., 131

- Kerimov, F. F., 257  
 Kern, W., 170  
 Ketterman, L. C., 35  
 Kewley, R., 4  
 Keyser, G. E., 266  
 Khair, G. T., 232  
 Khairullin, V. K., 10  
 Khait, I., 53  
 Khalilov, L. M., 236, 250, 261  
 Khamsitthideth, S., 83  
 Khan, A. A., 182  
 Kharchenko, A. V., 141  
 Kharchenko, V. G., 246  
 Khatri, H. N., 255  
 Khatri, N. A., 270  
 Khidekel, M. L., 269  
 Khim, J. K., 234  
 Khismatova, R. B., 8  
 Khodair, A. I., 58  
 Khokhlov, P. S., 229  
 Khorrani, J., 293  
 Khouri, F., 189  
 Khudyakova, A. N., 5  
 Khurma, J. R., 12  
 Khvostenko, V. I., 256  
 Kibbel, H. U., 186  
 Kice, J. L., 51, 68, 71, 77, 163  
 Kiel, W. A., 18  
 Kielbasinski, P., 162  
 Kieszkowski, J., 65  
 Kikkawa, S., 26  
 Kikuchi, A., 40  
 Kilaas, L., 85  
 Kim, C. U., 87  
 Kim, D. G., 32  
 Kim, J. K., 43, 44, 261  
 Kim, L. M., 247  
 Kim, W. K., 72  
 Kim, Y. H., 6, 64, 67, 68, 75, 77, 78, 254  
 Kimling, H., 224, 251  
 Kimura, R., 96  
 Kimura, Y., 98  
 King, G. W., 220  
 King, J. F., 40, 71, 164, 251  
 King, R. R., 28, 51  
 King, T. P., 205  
 Kingebiel, U., 132  
 Kingsbury, C. A., 208, 232, 272  
 Kinoshita, H., 249  
 Kinoshita, M., 40, 51, 52, 63  
 Kinoshita, T., 83  
 Kipnis, I. J., 225  
 Kirby, N. V., 60, 239  
 Kirchhoff, R. A., 111, 143, 146  
 Kirchlechner, R., 242  
 Kirichenko, T. I., 167  
 Kirmse, K., 198  
 Kirpichenko, S. V., 34, 231  
 Kirsch, G., 282  
 Kise, M., 138, 140, 252, 287  
 Kiseleva, L. N., 74  
 Kishi, K., 104  
 Kishore, D., 74  
 Kisin, A. V., 164, 222  
 Kiso, M., 208  
 Kissel, T., 196, 237  
 Kistenbrügger, L., 195  
 Kister, J., 26  
 Kita, Y., 60, 65, 166, 179  
 Kitagawa, S., 178, 185, 276  
 Kitamura, A., 207  
 Kitamura, M., 60, 107  
 Kitazawa, E., 102  
 Kitazume, T., 16, 48, 199, 226  
 Kivekäs, R., 23, 268  
 Kivikari, R., 45, 261  
 Kiyokawa, H., 60  
 Kjaer, A., 40, 66  
 Klaboe, P., 4, 232  
 Klages, C.-P., 160, 194  
 Klar, G., 203, 270  
 Klaska, K. H., 251  
 Klaska, R., 251  
 Klayman, D. L., 167, 174  
 Kleemann, G., 7, 48, 80  
 Kleijn, H., 69, 191  
 Klein, H. A., 16, 44  
 Klein, J., 52, 247  
 Kleinpeter, E., 62, 199, 242  
 Klemm, L. H., 273, 274, 279  
 Klemperer, W., 131  
 Kletsko, F. P., 32  
 Klimenko, S. K., 246  
 Kline, M. L., 43, 234  
 Klinga, M., 268  
 Klingebiel, U., 287  
 Klitschke, B., 251  
 Kloek, J. A., 128, 264  
 Kloth, B., 229  
 Kluck, D., 227  
 Klug, J. T., 232, 262  
 Kouttz, R. Q., 253  
 Knapp, F. F., 7  
 Knobler, C., 269  
 Knowles, J. R., 11  
 Knunyants, I. L., 19, 26, 71, 226, 227, 268  
 Knyazev, V. N., 265  
 Kobahn, W., 132  
 Kobayashi, F., 232  
 Kobayashi, G., 46, 192, 198, 289  
 Kobayashi, K., 32, 90, 180  
 Kobayashi, M., 41, 82, 142, 247  
 Kobayashi, S., 102  
 Kobayashi, T., 42, 138, 301  
 Kobayashi, Y., 72, 213, 214  
 Kobayashi, Y. M., 260  
 Kobert, K., 266  
 Kobychhev, V. B., 5  
 Kocienski, P. J., 59, 61, 107, 110, 111  
 Kodama, M., 30, 98  
 Koeberg-Telder, A., 268  
 Koehler, M., 17  
 Köhler, S., 160  
 Koelsch, P. M., 85  
 Koennecke, A., 65  
 Koepfel, H., 237  
 Koerber, I., 282  
 Kozumi, N., 90  
 Koga, K., 90  
 Koga, O., 131  
 Kohashi, Y., 282  
 Kohler, H. J., 216  
 Kohmoto, S., 34, 82  
 Kohn, H., 156, 220, 221, 225, 264  
 Kohne, B., 5  
 Kohnke, J., 127  
 Kohout, L., 85  
 Kojima, T., 105  
 Kokubo, T., 50  
 Kolditz, L., 178  
 Kole, K. C., 27  
 Koli, S. Z., 232  
 Kollman, P., 232  
 Kolodziejczyk, A., 245  
 Kolomeitsev, A. A., 17, 19  
 Kolomiets, A. F., 207, 211  
 Kolonits, M., 7  
 Komaki, K., 204  
 Komarova, L. I., 11  
 Komatsu, M., 100, 217  
 Komina, T. V., 3  
 Komissarov, V. D., 23  
 Komissarova, E. V., 19  
 Komives, T., 16  
 Komoto, S., 51  
 Kondo, K., 2, 16, 17, 20, 169, 216, 232  
 Kondratenko, N. V., 17, 19, 40  
 Konečný, V., 198  
 Konieczny, M., 226  
 Konyaeva, I. P., 296  
 Konyushkin, L. D., 57  
 Koolpe, G. A., 33, 114, 116  
 Koosha, K., 56  
 Kopf, J., 155  
 Kopinke, F. D., 71  
 Kopylova, B. V., 166, 214  
 Koreda, M., 90  
 Kornblum, N., 17, 148  
 Korobitsyna, I. K., 81  
 Korobov, M. S., 65  
 Korshunov, S. P., 32  
 Korte, F., 183  
 Korte, H. J., 132  
 Korzhova, N. V., 32  
 Koser, G. F., 17  
 Kossai, R., 74  
 Kossoy, A. D., 7  
 Kost, A. N., 189  
 Kost, D., 64  
 Kostusyk, J. L., 47, 102  
 Kosugi, H., 33, 56, 99  
 Kosugi, K., 27  
 Kosugi, Y., 5  
 Kotake, H., 60, 100, 111, 249

- Kotov, A. I., 269  
 Kotsuki, H., 276  
 Kouri, F., 190  
 Koval, I. V., 64, 141  
 Kovaleva, L. I., 65  
 Kowalski, J., 8, 127  
 Koyama, M., 197  
 Kozawa, Y., 66  
 Kozikowski, A. P., 14, 22, 93  
 Koz'min, A. S., 226, 269  
 Kozuka, S., 40, 112, 153  
 Kral, V., 42  
 Kramer, M. J., 165  
 Krantz, A., 216, 294  
 Kraska, B., 208  
 Krasnov, V. L., 268  
 Krasnov, V. P., 23, 49, 147  
 Kraus, G. A., 60, 91, 93, 110, 256  
 Kraus, W., 128  
 Krause, D., 155  
 Krause, J. G., 74  
 Krause, W., 179  
 Krebs, S., 71  
 Krebs, A., 88, 208, 224, 251  
 Krebs, B., 132, 142, 228  
 Krebs, D., 298  
 Kremlev, M. M., 64, 74, 141  
 Kresge, A. J., 251  
 Krespan, C. G., 70  
 Kresze, G., 128, 132  
 Kreutzberger, A., 165  
 Krey, P., 186  
 Kricheldorf, H. R., 4  
 Krief, A., 22, 24, 27, 29, 33, 44, 45, 51, 91, 100, 102, 114, 115, 116, 118, 119, 120, 121, 122  
 Kriegsmann, R., 281  
 Krimer, M. Z., 2, 19, 43, 207, 215  
 Krische, B., 264  
 Krishan, K., 165  
 Krishnan, P., 73  
 Kristen, H., 46, 225  
 Kristensen, J., 230, 252  
 Kristian, P., 173, 198, 228  
 Krivonogov, V. P., 234  
 Kroeckel, W., 71  
 Krogh, J. A., 63  
 Krolevets, A. A., 211  
 Kroon, J., 223  
 Krowczynski, A., 73, 82  
 Krowicki, K., 9, 24, 198  
 Kruger, C., 85  
 Kruglick, L. I., 15  
 Kruthof, K., 69  
 Kruizinga, W. H., 41  
 Kruse, C. G., 93, 249, 255  
 Kruse, H. P., 253  
 Krutak, J. J., 71  
 Kryczka, B., 205  
 Krylov, E. N., 70  
 Krylova, A. Y., 6  
 Kubaszek, M., 262  
 Kubel, H., 167  
 Kubo, T., 4  
 Kubo, Y., 205  
 Kubota, S., 174, 175, 196, 253, 255  
 Kubota, T., 16  
 Kuchen, W., 230  
 Kuchin, A. V., 67  
 Kuchitsu, K., 7  
 Kucsman, A., 48, 127, 135  
 Kudav, N. A., 179  
 Kudyakova, R. N., 5, 32  
 Kuehle, E., 1  
 Kuenzler, R., 15  
 Kugita, K., 131  
 Kukes, S., 24  
 Kukina, M. A., 12  
 Ku'achkina, N. S., 241, 245  
 Kulaeva, L. N., 178  
 Kulbach, N.-T., 230  
 Kulibekov, M. R., 16  
 Kuličková, N., 198  
 Kuliev, A. G., 16  
 Kuliev, A. M., 16  
 Kulis, J., 26  
 Kulkowit, S., 18  
 Kumada, M., 65  
 Kumadaki, I., 72, 213, 214  
 Kumamoto, T., 17  
 Kumar, A., 47  
 Kumar, S., 165  
 Kumar, V., 49  
 Kunakova, R. V., 57, 250  
 Kunieda, N., 51, 52  
 Kunzek, H., 183  
 Kurabayashi, M., 102  
 Kuranova, I. L., 208, 210, 211, 234  
 Kurbanov, K. B., 32, 64  
 Kurbanov, S. B., 268  
 Kurita, J., 279  
 Kurobe, H., 54  
 Kuroda, Y., 3  
 Kursanov, D. N., 238, 254  
 Kursheva, L. I., 250  
 Kurth, M. J., 100  
 Kurushima, A., 76  
 Kusamran, K., 54, 107  
 Kushnarev, D. F., 5, 32  
 Kuthalingam, P., 51  
 Kutlu, H., 209  
 Kutner, W., 131  
 Kutnevich, A. M., 8  
 Kutschy, P., 173  
 Kuvaeva, E. N., 178  
 Kuwabara, K., 137  
 Kuwajima, I., 20, 22, 62, 68  
 Kuwano, H., 102  
 Kuyama, M., 110  
 Kuyper, L. F., 90, 259  
 Kuznetsova, M. A., 44, 261  
 Kuzuhara, H., 86  
 Kuz'yants, G. M., 226, 268  
 Kwart, H., 55  
 Kwon, S., 60  
 Kyandzhetsian, R. A., 112  
 Kyothi Bhasu, V. C., 168  
 Kysenko, V. P., 84  
 Kysotoku, H., 27, 30  
 Labar, D., 22, 118  
 L'abbé, G., 66, 134, 147, 164, 167, 184, 207, 212, 219, 221, 230  
 Labes, M. M., 127, 130, 131  
 Lablache-Combiér, A., 76, 251  
 Lachheim, S., 31  
 Lacombe, L., 245  
 Laengenfelder, I., 42  
 Laerum, T., 285  
 Lagain, D., 151  
 Lagerström, P. O., 70  
 Lagow, R. J., 59, 75  
 Lahara, R., 32  
 Lai, H. K., 14  
 Laidlaw, W. G., 131  
 Laishev, V. Z., 270  
 Laitalainen, T., 23, 268  
 Laitem, L., 5  
 Lajunen, L. H. J., 5  
 Lakshmikantham, M. V., 94, 157, 191, 281  
 Lal, A. R., 47, 96  
 Lal, K., 169  
 Lalezari, I., 271, 279, 293  
 Lam, J. H. W., 40  
 Lamartina, L., 170  
 La Mattina, J. L., 255  
 Lambert, J. B., 257  
 Lambeth, D., 142  
 Lambeth, D. O., 75  
 Lambrecht, G., 245  
 Lambrecht, J., 260  
 Lamm, B., 58  
 Lamm, V., 133  
 Lammerink, B. H. M., 91, 163  
 Lamotte-Brasseur, J., 290  
 Lang, S. A., jun., 82  
 Langer, E., 258  
 Langer, W., 102  
 Langler, R. F., 41, 52, 58, 71, 264  
 Lansbury, P. T., 59, 110  
 Lantseva, L. T., 19  
 Laping, E., 292  
 Laping, K., 60, 110  
 Larker, F., 39  
 Larsen, C., 63  
 Larsen, E., 180, 190  
 Larsson, E., 32  
 Latypova, F. N., 260  
 Lauer, R. F., 116  
 Launay, M., 1  
 Laurence, K. A., 226  
 Lauren, J., 216, 294  
 Lavayssière, H., 212  
 Laver, H. S., 51



- Lavielle, S., 245  
 Law, K. Y., 152  
 Lawesson, S. O., 178, 179, 225, 230, 252, 253  
 Lawrence, R. F., 274  
 Lawson, A. J., 203  
 Lazar, J., 76  
 Lazovenko, A. N., 63  
 Leach, D. N., 82  
 Lebaud, J., 2  
 Lebedev, E. P., 190  
 Leclaire, A., 300  
 Le Coustumer, G., 291, 300  
 Lee, B., 8  
 Lee, C., 18  
 Lee, D., 245  
 Lee, H. H., 65, 208  
 Lee, I., 72  
 Lee, J.-K., 181  
 Lee, S. P., 13  
 Lee, T. W. S., 68  
 Lee, Y. J., 192  
 Legyl, I., 132  
 Lehmann, E., 49  
 Lehn, J. M., 11  
 Lehner, H., 258  
 Lemarie, B., 5  
 Lemire, A. E., 53  
 Lempert, K., 27  
 Lendel, V. G., 269  
 Lenoir, D., 88, 156  
 Lenstra, A. T. H., 267  
 Lentz, D., 7  
 Lenz, W., 154  
 Leong, T. S., 10, 157, 247, 252  
 Lepage, G. A., 205  
 Lepage, L., 273  
 Lepage, Y., 273  
 Lepp, U., 177  
 Leriverend, P., 34  
 Lerman, B. M., 256  
 Leroy, R., 179  
 Leschinsky, K. L., 63, 128, 264  
 Lešetický, L., 193  
 Lester, D. J., 68  
 Lett, R., 102, 244  
 Leung, C. C., 219  
 Leung, M., 33  
 Leung, T. W., 128  
 Levason, W., 6  
 Levchenko, E. S., 63, 141, 147, 289  
 Lever, J. R., 111  
 Levesque, G., 9, 180, 193, 194, 255, 256  
 Levitan, P., 165  
 Levkovich, M. M., 65  
 Levkovskaya, G. G., 172  
 Levens, K., 6  
 Lewandowski, K., 70  
 Lewicki, J. W., 75, 149  
 Lewis, D. T., 190  
 Lewis, E. S., 13, 24, 73  
 Lewis, J., 189  
 Ley, S. V., 68, 208, 261, 263  
 Liberek, B., 245  
 Licandro, E., 83  
 Liebscher, J., 180  
 Likholobov, V. A., 51  
 Lillie, E. D., 197  
 Lim, J. K., 6  
 Lin, Y.-I., 82  
 Linden, S. M., 17  
 Lindgren, B., 269  
 Lindley, J. M., 149  
 Lindley, W. A., 252  
 Lindner, H. J., 251  
 Lindner, L. W., 61  
 Linek, E. V., 152  
 Lingman, E., 43  
 Link, H., 187  
 Linke, K. H., 259  
 Linkova, M. G., 26  
 Liotta, D., 11, 18, 32  
 Lipka, P., 202  
 Lipkowitz, K. B., 237  
 Lipshutz, B., 90  
 Lischka, H., 216  
 Liskamp, R. M. J., 44  
 Lister, D. G., 2  
 Little, R. D., 17, 61  
 Litvin, G. V., 58  
 Litvinenko, L. M., 72  
 Litvinov, V. P., 273, 296, 297  
 Liu, C.-C. A., 77  
 Liu, G. Y., 131  
 Liu, H.-J., 13, 14  
 Liu, K.-T., 50, 75  
 Liu, L. K., 7, 58  
 Llabres, G., 5  
 Lockard, J. P., 85, 146  
 Loeffler, H. G., 13  
 Logemann, E., 178, 230  
 Loghry, R. A., 242, 246  
 Lohmann, J. J., 28, 54, 83, 161  
 Lohner, W., 5, 15, 282  
 Lohse, C., 218, 295  
 Loiseau, P., 58, 179  
 Loktionova, R. A., 84  
 Lollar, E. D., 241  
 Lonchambon, G., 10, 67, 68  
 Longobardi, M., 164  
 Looker, J. H., 272  
 Loontjes, J. A., 103, 162, 214  
 Lopez, L., 209  
 Lorenz, I.-P., 165  
 Lorey, O., 255  
 Losch, R., 167  
 Lotz, S., 102  
 Loutfy, R. O., 247  
 Louw, R., 55  
 Love, P., 127, 130, 131  
 Lown, E. M., 207  
 Lu, L. D. L., 15  
 Lucchetti, J., 27, 29, 45, 91, 114, 116, 119, 121, 122  
 Lucchini, V., 2, 19, 207, 232  
 Lucien, J., 9, 274  
 Lüdersdorf, R., 6, 53  
 Lueke, H. W., 188  
 Lukacs, W., 209  
 Luger, P., 204  
 Luhmann, U., 209  
 Lukas, T. J., 10  
 Luke, H.-W., 167  
 Lukyanenko, N. G., 167  
 Lund, H., 60  
 Lundeen, M., 8  
 Lur'e, E. P., 226, 268  
 Lusch, M. J., 56  
 Lutsкая, N. V., 32, 34  
 Lux, D., 230  
 Lyakhovetskii, Yu. I., 238  
 Lyapina, T. V., 63  
 Lynaugh, N., 254  
 Lysenko, V. P., 84  
 Lysenko, Z., 18, 90, 216  
 Lythgoe, B., 61, 110, 111  
 Maak, N., 105  
 Maarsen, P. K., 70  
 McAuliffe, C. A., 2, 6  
 McCabe, P. H., 211, 238, 251  
 Maccagnani, G., 82, 103, 160, 163, 210, 215, 227  
 MacCallum, J. R., 51  
 McCaerthy, T. J., 82  
 McCleery, P., 40  
 McCollum, G. J., 116  
 McCombie, S. W., 205  
 McCoy, D. R., 273  
 McCrathren, S. S., 5  
 McCullough, F. P., 6  
 McCullough, J. J., 85  
 MacDiarmid, A. G., 131  
 Macdonald, J. E., 31  
 Macdonald, W. S., 226  
 Macdonald, J. N., 4  
 Macdonald, R. T., 75  
 McDonald, J. M., 156  
 McDougal, P. G., 20  
 McDougall, R., 238  
 McDowell, D. W. H., 252  
 McElvain, S. S., 82  
 Mach, K., 5  
 Machida, K., 3  
 Machida, T., 192  
 Machiguchi, T., 238  
 McIntosh, J. M., 235  
 Mack, W., 201  
 McKean, D. R., 17, 29, 100  
 McKendrick, J. J., 236  
 McKenna, J., 135, 248  
 McKenna, J. K., 135  
 McKenna, J. M., 248  
 McKenzie, S., 148  
 McKerver, A., 18  
 McKerver, M. A., 205  
 McKinnon, B. J., 9  
 Macklin, J. W., 131  
 McLafferty, F. W., 6, 150  
 Maclean, G., 131

- Maclean, J. A., jun., 131  
 McLelland, R. A., 33  
 McLeod, R. W., 232  
 McMonagle, D., 157  
 MacNicol, D. D., 8, 236  
 McWhinnie, W. R., 49, 75  
 Madawinata, K., 210  
 Madronero, R., 279  
 Madsen, J. O., 40  
 Maeda, Y., 66  
 Maekawa, K., 253, 255  
 Maekawa, M., 4  
 Maeshima, T., 11  
 Maffrand, J. P., 279  
 Magdesieva, N. N., 81, 82, 112  
 Magee, R. J., 197  
 Maggi, D., 85  
 Maggiulli, C. A., 187  
 Magnus, P., 19, 32, 81, 107, 216  
 Magolda, R. L., 31, 57, 216, 242  
 Maguet, M., 212  
 Mahadevappa, D. S., 53  
 Mahjoub, A., 9, 193, 194, 255, 256  
 Mahood, A. A., 254  
 Mailgoff, F. S., 7  
 Maiolo, F., 17, 276  
 Maiorana, S., 222  
 Maisuradze, G. V., 17  
 Majchrzak, M., 257  
 Mak, T. C. W., 106, 262  
 Makerov, P. V., 60  
 Maki, Y., 286  
 Makin, M. I. H., 75  
 Makosza, M., 58, 93, 111  
 Maksimenko, A. A., 40, 49, 51, 76, 112  
 Maksimenko, N. N., 72  
 Malcherek, P., 225  
 Malcherek, R., 252  
 Maletina, I. I., 71  
 Malhotra, R., 51  
 Malii, V. A., 165  
 Malkhasyan, A. Ts., 249  
 Mallamo, J. P., 56, 104  
 Mallen, D. N. B., 6  
 Malmberg, W. D., 194  
 Malmquist, P. A., 300  
 Mamedov, E. Sh., 268  
 Mamedov, F. N., 10  
 Mamedov, V. N., 16  
 Mamedov, Z. A., 64  
 Mamelov, E. S., 49, 268  
 Mancinelli, P. A., 64  
 Mancini, V., 6  
 Mancuso, A. J., 53, 85, 86  
 Manda, E., 70  
 Mandai, T., 253  
 Mandal, A. K., 51, 266  
 Mandolini, L., 277  
 Manescalchi, F., 57, 65  
 Mangini, A., 8  
 Mann, K., 24, 151  
 Mannafov, T. G., 5, 8  
 Manning, C., 85  
 Manning, W. B., 75, 184  
 Manor, H., 62, 69  
 Manske, R., 255, 261  
 Manzhos, V. K., 7  
 Maranon, J., 4  
 March, R. E., 53  
 Marchand, E., 21, 23, 48, 83  
 Marchelli, R., 53  
 Marchese, G., 59  
 Marcuzzo do Canto, M., 2  
 Marechal, E., 250  
 Marechal, G., 282  
 Maretina, I. A., 180  
 Maringgele, W., 167  
 Marini, Z. A., 41, 58  
 Marino, J. P., 35, 47, 54, 99, 102  
 Mark, H. R., jun., 131  
 Marko, V., 12  
 Markova, L. I., 229  
 Markovic, J. S., 7  
 Markovskii, L. N., 67, 87, 141  
 Maroni, P., 267  
 Marquet, A., 80, 244  
 Marshall, J. H., 232, 291  
 Martelli, G., 8, 273, 296  
 Martem'yanov, V. S., 260  
 Marten, E. H., 187  
 Martens, C., 164  
 Martens, J., 15  
 Martensson, N., 300  
 Martigny, P., 58  
 Martin, G., 12  
 Martin, G. E., 17  
 Martin, H. D., 222  
 Martin, I., 27  
 Martin, J. C., 72, 147  
 Martin, M. L., 179  
 Martin, R. P., 9  
 Martin, S. F., 79  
 Martinez, G. R., 40, 80  
 Martinez, R. I., 24  
 Martirosyan, G. T., 249  
 Marton, A. F., 16  
 Martvoñ, A., 172  
 Martynov, A. V., 17, 60  
 Maruta, M., 16  
 Maruyama, K., 37, 97  
 Maryanoff, C. A., 72  
 Masada, H., 71  
 Masamune, S., 15  
 Masaki, Y., 31, 37, 55, 56, 110  
 Masamune, T., 85  
 Mashkina, A. V., 51  
 Masilamani, D., 67  
 Mason, C. J., 174  
 Mason, K. G., 263  
 Masson, S., 44, 95, 191  
 Massy-Westropp, R. A., 86  
 Masuda, K., 293  
 Masuda, R., 32  
 Masuda, T., 52, 136  
 Masue, K., 66  
 Matsui, M., 173  
 Masure, D., 67  
 Masuyama, Y., 116  
 Mataka, S., 131, 156, 207, 292  
 Matarese, R. M., 68  
 Mathew, K., 71  
 Mathew, S. I., 184  
 Matloubi, F., 103  
 Matschiner, H., 32  
 Matsuchita, T., 3  
 Matsuda, M., 80  
 Matsuda, T., 5  
 Matsuda, Y., 19, 20, 46, 192, 198, 289  
 Matsue, H., 85  
 Matsueda, R., 62  
 Matsui, M., 208, 246  
 Matsui, S., 100  
 Matsumoto, H., 179  
 Matsumoto, M., 41, 82  
 Matsumura, H., 155  
 Matsumura, Y., 10, 16, 27, 30, 42, 87  
 Matsuoka, K., 139  
 Matsuoka, K., 276  
 Matsushita, R., 197  
 Matsuura, H., 4  
 Matsuura, Y., 136  
 Matsuyama, H., 41, 82  
 Mattes, R., 175, 190, 193, 194  
 Matteson, D. S., 45, 46, 95  
 Matthews, W. S., 116  
 Matusch, R., 24, 151  
 Matz, C., 190  
 Matz, J. R., 44, 94, 100  
 Maurel, R., 9, 274  
 Maxwell, R. J., 65  
 Maycock, C. D., 62, 209  
 Mayer, G., 144  
 Mayer, R., 2, 33, 128, 133, 165, 179, 191, 204, 227  
 Mazloumi, A., 286, 297  
 Mazza, M., 198  
 Mazzanti, G., 82, 103, 163, 210, 215, 227  
 Mazzarella, L., 254  
 Mazzei, A., 106  
 Mazzocchin, G. A., 24  
 Mazzone, G., 177  
 Meese, C. O., 181  
 Mehrotra, S. K., 231  
 Meier, H., 158, 216, 254, 292, 294  
 Meijer, E. W., 63  
 Meijer, J., 31, 69, 191, 253, 265, 268  
 Meiji, R., 127  
 Meinetsberger, E., 253  
 Meinhold, H., 62  
 Meinwald, J., 269  
 Meister, A., 127  
 Melegari, M., 7

- Melis, S., 90  
 Mellor, J. M., 20  
 Mel'nikov, N. N., 167, 170  
 Mel'nikova, L. G., 112  
 Menchen, S. M., 18, 21, 44, 51  
 Mendoza, A., 45, 46, 95  
 Mennemann, K., 193  
 Menozzi, G., 164, 263  
 Merkle, U., 292  
 Merritt, M. V., 73  
 Mertens, K. B., 8  
 Meslin, J. C., 184  
 Messinger, P., 57, 60  
 Mester, L., 208  
 Mészáros, Z., 177  
 Metcalf, B. W., 61  
 Meth-Cohn, O., 149, 273, 279  
 Metlushenko, V. P., 5  
 Metzger, J., 17, 26  
 Metzner, P., 38, 225  
 Meunier, P., 280, 296  
 Mews, R., 132, 133, 228  
 Meyer, H. J., 230  
 Meyers, A. I., 44, 95, 195  
 Michalik, M., 186  
 Michalski, J., 65  
 Micha-Screttas, M., 26, 102  
 Michelotti, E. L., 12, 73  
 Michelsen, P., 3  
 Michida, T., 63  
 Michurin, A. A., 53  
 Micic, O. I., 76  
 Miconi, F., 83  
 Midthaug, T., 276  
 Migura, W., 51, 52  
 Migalina, Yu. V., 226, 269  
 Miguel, H. T., 20  
 Mikami, K., 47, 175  
 Mikhailov, I. E., 63  
 Mikhailova, V. N., 58  
 Mikhlina, E. E., 170  
 Mikhno, S. D., 241, 245, 249  
 Mikolajczyk, M., 10, 51, 52, 57, 69, 75, 256  
 Miles, D. E., 109  
 Miles, P., 70  
 Mille, G., 26  
 Miller, A. G., 137, 286  
 Miller, J. M., 20  
 Miller, K. D., 70  
 Miller, P. K., 53  
 Miller, R. D., 7, 29, 100  
 Miller, R. F., 17  
 Miller, R. W., 259  
 Mimura, T., 31, 98  
 Minami, T., 36, 41  
 Minato, H., 41, 82, 142  
 Minkin, V. I., 2, 5, 6, 17, 23, 40, 49, 63, 65, 112, 147  
 Mino, N., 256  
 Minov, V. M., 265  
 Minyaev, R. M., 2  
 Mioskowski, C., 82, 103  
 Miotti, U., 51  
 Mir, Q. C., 48, 226  
 Mirakyan, S. M., 249  
 Mirek, J., 70  
 Mironov, G. S., 58  
 Mironova, A. A., 71  
 Mirkova, A. N., 17, 32, 34, 60, 172  
 Misawa, N., 3  
 Misco, P. F., 87  
 Misharina, T. A., 25  
 Mishiev, R. D., 268  
 Mishima, H., 102  
 Misima, K., 199  
 Misra, H. C., 170  
 Mita, N., 17  
 Mitamura, S., 104  
 Mitcham, R. V., 8  
 Mitchell, R. H., 115  
 Mitchell, T. R. B., 205  
 Mitschker, A., 281  
 Mitsuhiro, Y., 104  
 Mitsui, A., 4  
 Mitsuomi, Y., 192  
 Miura, H., 234  
 Miura, M., 27, 33, 104  
 Miura, T., 41  
 Miura, Y., 63  
 Miyake, K., 21  
 Miyake, M., 26  
 Miyake, T., 232  
 Miyano, T., 47  
 Miyashita, S., 16  
 Miyauchi, N., 4  
 Miyaura, N., 158  
 Miyazaki, H., 51, 52, 82, 250  
 Miyazaki, J., 50  
 Miyazawa, K., 137  
 Miyazawa, M., 253  
 Miyoshi, F., 82, 246, 251  
 Miyoshi, H., 49  
 Miyoshi, N., 16, 20, 22, 216  
 Mizhiritskii, M. D., 190  
 Mizoguchi, M., 42, 87  
 Mizrakh, L. I., 172  
 Mizuno, T., 267  
 Mizuta, M., 193, 197  
 Mizuyama, K., 198  
 Mlotkowska, M., 256  
 Mochizuki, H., 51  
 Mock, W. L., 68  
 Mockel, H. J., 232  
 Modak, H. M., 207  
 Modena, G., 2, 19, 207, 232  
 Modena, T., 198  
 Mody, N. V., 212  
 Moeckel, H. J., 6, 232  
 Mögel, L., 259  
 Moerck, R., 19, 32, 216  
 Moerke, W., 8  
 Mohsen, A., 177  
 Moir, M., 39  
 Moiroux, J., 24  
 Moise, C., 67  
 Moiseenkov, A. M., 110, 263  
 Mokrosz, J., 262  
 Moldovan, Z., 283  
 Mollier, Y., 291, 300  
 Mollin, J., 182  
 Monastyrnaya, N. G., 141  
 Mongelli, N., 64, 204  
 Monma, H., 173, 228  
 Monroe, B. M., 24, 38  
 Montanari, L., 198  
 Monteiro, P. M., 17  
 Montran, R., 133  
 Moody, C. J., 136  
 Moore, G. G. I., 71  
 Moore, J. H., 7  
 Moore, W. H., 71  
 Moravskii, A. P., 261  
 Morck, H., 151  
 More, K. M., 52, 104  
 Moreau, R., 58  
 Moreau, R. C., 179  
 Morel, G., 21, 23, 48, 83  
 Morel, J., 113  
 Moretti, I., 215  
 Morganti, G., 16, 34, 40, 262  
 Mori, J., 219  
 Mori, K., 63, 105, 134, 208  
 Mori, Y., 174  
 Morikawa, T., 32  
 Morimoto, T., 201  
 Morin, L., 2, 34  
 Morishita, H., 4  
 Morishita, T., 77  
 Morriset, V. M., 18  
 Morita, H., 53, 144, 221, 249  
 Moriyama, M., 143  
 Moriyama, S., 128  
 Morrissey, P., 218  
 Morrow, S. D., 111  
 Morse, R. H., 71  
 Morsum-Zade, M., 10  
 Morton, D. R., jun., 82  
 Morton, G. O., 82  
 Moskvichev, Yu. A., 58  
 Moskvina, A. F., 3  
 Moss, R. A., 10  
 Moss, S. F., 174  
 Mossman, A., 41  
 Mosti, L., 164, 263  
 Motoki, S., 78, 133, 156, 161, 185, 220, 229, 255, 264  
 Mousset, G., 58  
 Movsumzade, M. M., 208  
 Mrotzek, H., 216, 294  
 Muchowski, J. M., 293  
 Mühlstädt, M., 62, 65, 199  
 Mueller, C., 218  
 Müller, P., 74  
 Mueller, W., 69  
 Mütter, I., 266  
 Mukai, C., 138, 140, 252, 287  
 Mukaiyama, T., 27, 85, 209  
 Mukhamedova, L. A., 250  
 Mullen, D., 168  
 Muller, T., 132

- Mullins, D., 76  
 Mullins, D. F., 69  
 Mullins, M. J., 21, 84, 241  
 Mundell, T. C., 267  
 Mundy, B. P., 237  
 Murahashi, S., 17  
 Murahashi, S.-I., 10  
 Murai, A., 85  
 Murai, H., 157  
 Murai, S., 12, 16, 20, 22, 216  
 Murakami, Y., 11  
 Muraki, S., 246  
 Muramoto, Y., 70  
 Muraoka, M., 192, 197, 225  
 Muraoka, Y., 232  
 Murase, H., 85  
 Murase, M., 140, 287  
 Murata, H., 2, 4  
 Murata, I., 282  
 Murata, R., 234  
 Murata, Y., 249  
 Muroi, M., 197  
 Murphy, W. S., 93  
 Murray, B. M., 236  
 Murray-Rust, J., 84, 278  
 Murray-Rust, P., 84, 278  
 Mursakulov, I. G., 257  
 Musa, F. H., 49, 75  
 Musial, B. C., 17  
 Musker, W. K., 27, 142, 232, 262  
 Musorin, G. K., 6, 32, 53  
 Muszkat, K. A., 53  
 Muthuramu, K., 220  
 Muzychkina, R. A., 7  
 Myer, G., 130  
 Mysov, E. I., 226, 268
- Nachtergaele, W. A., 242, 245  
 Naddaka, V. I., 23, 49, 147  
 Nadir, U. K., 1, 62  
 Nag, N. K., 274  
 Nagai, T., 12, 128, 227  
 Nagano, T., 75  
 Nagao, Y., 27, 44, 54, 90, 93, 100, 256, 261  
 Nagase, H., 183  
 Nagashima, T., 34  
 Nagata, T., 46  
 Nagel, B., 4  
 Nagy-Felsobuki, E., 7  
 Naidan, G. D., 58, 65  
 Naidan, V. M., 58, 65  
 Naidu, H. M. K., 53  
 Naidu, M. S. R., 7, 60  
 Nair, M. D., 172  
 Naito, T., 87  
 Nakabayashi, T., 76  
 Nakada, M., 34  
 Nakagawa, M., 36, 234  
 Nakagawa, T., 85  
 Nakai, T., 31, 38, 46, 47, 98, 175  
 Nakajima, T., 127, 132
- Nakamura, A., 167  
 Nakamura, F., 72  
 Nakamura, K., 40, 152, 155, 163, 209  
 Nakamura, M., 153  
 Nakamura, Y., 78  
 Nakanishi, A., 105, 134  
 Nakasuji, K., 282  
 Nakata, T., 87  
 Nakatsu, K., 254  
 Nakatsuji, S., 36  
 Nakayama, A., 22  
 Nakayama, J., 224, 256  
 Nakayama, N., 256  
 Nakayama, Y., 26  
 Nakazawa, K., 22  
 Nakhdžavan, B., 276  
 Nakhmanovich, A. S., 255, 264  
 Nametkin, N. S., 12  
 Nanetti, A., 174  
 Nanjundiah, R., 54  
 Nara, N., 232  
 Narang, S. C., 45, 51, 261  
 Narasimhan, K., 85  
 Narasimhan, L., 45, 195  
 Narine, B., 279  
 Narisano, E., 50, 103  
 Narita, K., 81  
 Narula, S. P., 133  
 Narula, S. S., 214  
 Naseeri-Noori, B., 67  
 Nasipuri, D., 273  
 Naso, F., 59  
 Nasyrov, D. M., 8  
 Nasyrov, I. M., 247  
 Natalini, B., 82, 239  
 Natter, W. J., 269  
 Naumenko, R. P., 141  
 Naumov, V. A., 7  
 Naumov, Yu. I., 3  
 Nazaretyan, V. P., 71  
 Ncube, S., 94  
 Neef, G., 56, 104  
 Nefedov, V. I., 168  
 Negita, H., 4  
 Negmatullaev, K. N., 16  
 Negoro, K., 41  
 Negrebetskii, V. V., 167  
 Neidlein, R., 278, 282  
 Neirinckx, I., 245  
 Nekrasova, L. I., 6  
 Nel, M., 59  
 Nelson, C. R., 238  
 Nelson, D. J., 13  
 Nelson, S., 232  
 Nemoto, H., 54  
 Nenadovic, M. T., 76  
 Neoh, S. B., 280  
 Nesener, E., 183  
 Nesmeyanov, N. A., 53  
 Nesterenko, D. P., 177  
 Newall, C. E., 208  
 Newcombe, P. J., 276  
 Neykova, N., 168
- Neynaber, C. B., 173  
 Ngo, T. M. A., 232  
 Nichols, L. F., 127  
 Nicolau, K. C., 18, 31, 57, 62, 90, 109, 216, 242  
 Nicoud, J. F., 57  
 Nidy, E. G., 73  
 Nie, P.-L., 189  
 Nieberl, S., 153, 219, 220, 223  
 Niederprum, H., 70  
 Niegel, H., 71  
 Nielsen, C. J., 4  
 Niemczura, W., 258  
 Niemer, U., 193, 194  
 Nieses, B., 13  
 Nieuwpoort, W. C., 6  
 Nigmatullina, R. F., 16, 234, 261  
 Niki, I., 41  
 Nikitin, P. A., 5  
 Nikitin, Yu. E., 16, 53, 261  
 Nikitina, V. I., 178  
 Nikolaev, V. A., 81  
 Nikolskii, N. S., 7  
 Nilsson, N. H., 225  
 Nimgirawath, S., 54  
 Nimitz, J. S., 15  
 Nimura, N., 165, 174, 289  
 Nio, N., 96  
 Nishi, S.-I., 80  
 Nishida, M., 22  
 Nishide, K., 10  
 Nishihata, K., 57  
 Nishikawa, M., 68  
 Nishikawa, Y., 136, 138, 252  
 Nishimoto, K., 3  
 Nishimura, T., 128  
 Nishimura, Y., 82  
 Nishinaga, A., 268  
 Nishino, J., 11, 250  
 Nishino, K., 282  
 Nishio, M., 57  
 Nishio, T., 33, 50, 65, 83, 136  
 Nishiyama, H., 83, 183  
 Nishiyama, T., 267, 268  
 Nishizawa, H., 276  
 Nishizawa, K., 51, 82  
 Nitsche, M., 28, 96  
 Nitz, S., 183  
 Nivorozhkin, L. E., 49, 65  
 Nixon, L. N., 232  
 Noda, K., 259  
 Node, M., 10  
 Nogradi, M., 239  
 Noguchi, A., 4  
 Noguchi, H., 102  
 Noguchi, M., 164  
 Noguchi, T., 259  
 Noguchi, Y., 68  
 Nokami, J., 26, 69  
 Nolan, S. M., 47, 96  
 Nolde, C., 230  
 Nomura, K., 293  
 Nomura, M., 26

- Nomura, Y., 232  
 Nonaka, T., 198  
 Norden, B., 271  
 Norin, T., 82, 149, 207  
 Normant, J. F., 32, 67  
 Norris, R. K., 276  
 Nossin, P. M. M., 38  
 Noth, H., 231  
 Noto, R., 277  
 Novgorodtseva, L. A., 19  
 Novi, M., 276  
 Novitskaya, N. N., 236, 250  
 Nowacki, J., 212  
 Nowak, R., 131  
 Nozaki, H., 11, 16  
 Nozaki, K., 154  
 Nudelmann, A., 2  
 Nugent, R. M., 68  
 Numanov, I. U., 247  
 Numata, H., 133  
 Numata, T., 2, 8, 27, 51, 52, 137, 247  
 Nurekeshova, N., 17  
 Nurgatiu, V. V., 12  
 Nurullina, R. N., 8  
 Nyitrai, J., 27
- Oae, S., 6, 8, 27, 33, 41, 51, 52, 53, 63, 64, 67, 68, 69, 75, 77, 78, 84, 127, 136, 137, 143, 144, 209, 221, 247, 249, 254  
 Oakley, R. T., 131, 133  
 Obata, N., 174  
 Oberhammer, H., 7  
 Occolowitz, J. L., 7  
 Ochi, M., 276  
 Ochiai, M., 20, 51  
 Odenthal, J., 224, 251  
 Odham, G., 232  
 Odom, J. D., 5  
 Oezer, U., 229  
 Ogaard Madsen, J., 66  
 Ogasawara, K., 90, 93  
 Ogata, M., 179  
 Ogata, T., 47  
 Ogawa, M., 40, 232  
 Ogawa, S., 137  
 Ogino, K., 40  
 Ogiso, A., 102  
 Ogura, H., 42, 81, 90, 138, 165, 174, 289  
 Ogura, K., 83, 104  
 Ohashi, M., 256  
 Ohashi, T., 82, 246, 251  
 Ohishi, J., 216, 249  
 Ohki, E., 205  
 Ohkubo, K., 2  
 Ohmori, H., 173  
 Ohno, A., 152, 155, 163, 209  
 Ohno, K., 4, 183  
 Ohno, S., 81, 245  
 Ohno, Y., 20, 216  
 Ohrui, H., 86, 241  
 Ohsaku, M., 2, 4  
 Ohsawa, A., 213  
 Ohshima, T., 227  
 Ohshiro, Y., 100, 217  
 Ohtsu, M., 137  
 Ohtsuka, Y., 106  
 Ohtuki, S., 225  
 Oikawa, I., 133  
 Oishi, S., 154  
 Oishi, T., 49, 56, 87, 98, 106, 143, 200  
 Oka, K., 68, 155, 225, 273  
 Oka, S., 152, 155, 163, 209  
 Okada, T., 216, 242  
 Okamura, H., 27, 33, 38, 104  
 Okano, M., 18, 21, 44, 49, 50, 66, 80, 82, 190, 268  
 Okawara, M., 24, 60, 61, 111, 116, 134, 135, 140, 201  
 Okawara, R., 26, 69  
 Okawara, T., 68  
 Okazaki, R., 128, 129, 130, 150, 157, 207, 218, 229, 237  
 Okecha, S. A., 201  
 Okuda, H., 192, 289  
 Okuda, I., 66  
 Okuda, T., 4  
 Okuma, K., 142  
 Okumoto, H., 22, 100  
 Okuyama, T., 19, 34  
 Olah, G. A., 41, 45, 51, 75, 87, 261  
 Olavesen, A. H., 70  
 Oleinik, T. G., 64, 141  
 Olekhnovich, L. P., 63  
 Oleksyszyn, J., 169  
 Olin, G. R., 282  
 Olivato, P. R., 27  
 Ollis, W. D., 189  
 Olmstead, M. M., 210  
 Olsen, E. G., 12, 107, 115, 123  
 Olsson, K., 256  
 Omar, M. E., 177  
 Omar, M. T., 255  
 Omogbai, F., 21  
 Omote, Y., 33, 50, 65, 83, 154  
 Omura, K., 53, 85, 86  
 Ono, H., 259  
 Ono, N., 11, 44, 100, 205  
 Ono, T., 28  
 O-oka, M., 207  
 Oppenheimer, N. J., 39  
 Oppolzer, W., 109  
 Oprean, I., 283  
 Orabi, M. O. A., 67  
 Orena, M., 57  
 Origuti, S., 10  
 Orszulik, S. T., 57  
 Osamura, Y., 3  
 Osborn, R., 254  
 Osborne, A. D., 232  
 Oshima, K., 11, 16  
 Oshima, T., 128  
 Osman, A., 65, 127  
 Osokin, D. Y., 4  
 Otani, N., 66  
 Otsubo, T., 82  
 Otsuka, I., 254  
 Ottenheijm, H. C. J., 44  
 Ottlinger, R., 228, 270  
 Otto, H. H., 235  
 Ouellette, D., 44, 94  
 Owada, H., 18  
 Owen, N. L., 4, 202, 256  
 Owens, T. A., 102, 210, 261  
 Oyanagi, K., 7  
 Ozawa, S., 11, 16  
 Ozbal, H., 3
- Paaquevent, J. C., 80  
 Paddon-Row, M. N., 53  
 Padmanabhan, P. V., 62  
 Pagel, D. J., 48, 142  
 Pagnoni, U. M., 43  
 Paik, H.-N., 155  
 Pakulski, M., 65  
 Palazzo, S., 170  
 Palecek, M., 250  
 Paliani, G., 269  
 Palmer, M. H., 272  
 Palmieri, P., 2, 215  
 Pandiarajan, K., 248  
 Pangam, J. P., 38  
 Panossian, S., 177, 188  
 Pant, B. C., 49  
 Panunto, T. W., 49  
 Panunzio, M., 65  
 Panzica, R. P., 152  
 Paolucci, C., 83, 84, 240  
 Pape, J. Y., 59  
 Pappalardo, G. C., 4, 7  
 Pappalardo, S., 76, 254  
 Paquer, D., 2, 5, 34, 252  
 Paquette, L. A., 2, 60, 106  
 Parellada, R., 53  
 Parfitt, R. T., 254  
 Park, K. H., 5, 81  
 Parker, E. J., 223  
 Parker, K. A., 90  
 Parlar, H., 183  
 Parmar, S. S., 241  
 Parnandiwar, J. M., 170  
 Parnes, Z. N., 238  
 Parr, W. J. E., 4  
 Parrish, D. R., 241  
 Parsons, P. J., 33, 55, 99  
 Pasanen, P., 264  
 Pascard, C., 8  
 Passet, B. V., 23, 58  
 Pastour, P., 113  
 Patchett, A. A., 171  
 Patel, C. C., 168  
 Patel, P. K., 268  
 Paterson, I., 29  
 Paton, D., 289  
 Patron, L., 61  
 Patroni, J. J., 205  
 Patterson, R. B., 272  
 Paty, P. B., 11

- Patwardhan, B. H., 64, 223  
 Pau, J. K., 6, 44, 261  
 Paul, R. C., 131, 147  
 Paulmier, C., 64, 65, 113, 277, 278, 297  
 Paulsen, H., 204  
 Pavanetto, F., 198  
 Pavel, G. V., 235  
 Pavlova, L. A., 264  
 Pavlova, V. L., 5  
 Pawelke, G., 70  
 Payne, N. C., 9  
 Pazdon, M. D., 134, 219  
 Pazos, J. M., 274  
 Peach, M. E., 17  
 Peake, S. L., 68  
 Pearson, W. H., 26, 222  
 Pechenyuk, V. A., 178  
 Pechet, M. M., 75, 151, 207  
 Pecoraro, J. M., 52  
 Pedaja, P., 280  
 Pedersen, B. S., 178, 179, 225, 230  
 Pedersen, C. L., 130, 295  
 Pedersen, P. B., 271  
 Pedley, J. B., 239  
 Pedrini, P., 82, 215, 227  
 Pedulli, G. F., 8  
 Peel, J. B., 7  
 Peeran, S. G., 7, 60  
 Peleties, N., 113  
 Pelister, Y., 105  
 Pel'kis, P. S., 178, 180, 201  
 Pelletier, S. W., 212  
 Pellicciari, R., 82, 239  
 Pelosi, M., 59  
 Pelter, A., 94  
 Penin, Y. V., 6  
 Penn, R. E., 61, 102, 161, 210, 261  
 Peppard, T. L., 253  
 Perekalin, V. V., 249  
 Peretokina, S. I., 249  
 Perjéssy, A., 277  
 Perkins, M. J., 13  
 Perlova, T. G., 6  
 Pernak, J., 16  
 Perrier, M., 300  
 Pershin, A. D., 5  
 Pesce, G., 209  
 Peseke, K., 46, 225  
 Pestova, G. A., 165  
 Pestunovich, V. A., 231  
 Pete, J.-P., 74  
 Peters, E., 186  
 Peters, E. M., 7  
 Peterse, A. J. G. M., 90  
 Petersen, R. L., 13  
 Peterson, I., 19  
 Petit, G., 267  
 Petit, J., 68  
 Petkovic, D. M., 7  
 Petraghani, N., 21, 29, 36, 116  
 Petrašiūnas, G. L. R., 150  
 Petriashvili, K. A., 9  
 Petrov, A. A., 19, 180, 270  
 Petrov, M. L., 270  
 Petrova, R. G., 5, 46  
 Petrzilka, M., 14, 54, 87  
 Petukhova, N. P., 17, 57  
 Petz, D., 13  
 Pfab, J., 13  
 Pfeiffer, W. D., 175  
 Pfister-Guillouzo, G., 272  
 Pham, T. N., 38  
 Phatak, M. V., 74  
 Phillipps, G. H., 208  
 Phillips, L. R., 105  
 Phim, H., 61  
 Phuong, N. T. M., 74  
 Piancastelli, M. N., 7  
 Picard, C., 268  
 Piccinelli, P., 82, 103, 210, 215  
 Picha, F., 193  
 Pierini, A. B., 17  
 Pierko, A., 255  
 Piers, E., 106  
 Pietra, F., 16, 34, 40, 262  
 Pietrusiewicz, K. M., 233  
 Piette, J. L., 5, 23, 290  
 Pihlaja, K., 258, 264  
 Pijpers, F. W., 199  
 Pilati, T., 216, 232  
 Pillai, V. N. R., 62  
 Pincock, J. A., 58, 74  
 Pindur, G., 71  
 Pinnick, H. W., 67, 75, 88, 111, 208, 266  
 Pintye, J., 77  
 Piras, P. P., 90  
 Pirkle, W. H., 102  
 Pitacco, G., 222  
 Pitt, C. G., 90  
 Pitteloud, R., 54  
 Pizey, J. S., 220  
 Pizzabiocca, A., 128  
 Pizzolato, G., 241  
 Platen, M., 261  
 Pletnev, S. I., 227  
 Plieninger, H., 54  
 Pluecken, U., 292  
 Plum, H., 11, 111  
 Pniewska, B., 259  
 Pochat, F., 32, 34  
 Pociute, N., 19  
 Podhradský, D., 198  
 Poels, E. K., 93, 249  
 Pohl, S., 132, 142  
 Pohmakotr, M., 11, 46, 90, 95, 196  
 Poilblanc, R., 9  
 Poje, M., 46  
 Pokoneshchikova, N. K., 236  
 Polakova, J., 250  
 Polezhaeva, N. A., 41, 82, 112  
 Poliakoff, M., 295  
 Pollard, M. D., 88, 156, 223  
 Pollicino, S., 83, 84, 103, 240, 247  
 Polonskaya, L. Yu., 172  
 Polunin, E. V., 110, 263  
 Polyanskaya, T. N., 249  
 Pommelet, J. C., 212  
 Pon, R. T., 54  
 Ponomarchuk, M. N., 84  
 Ponomareva, T. K., 296  
 Ponsford, R. J., 15  
 Popov, A., 215  
 Popov, V. I., 4, 17, 19, 40  
 Popova, A. G., 189  
 Popova, O. A., 196, 220  
 Porskamp, P. A. T. W., 91  
 Portella, C., 74  
 Porter, A. E. A., 83, 84, 278  
 Porter, O. N., 261  
 Posner, G. H., 50, 56, 104  
 Pospisil, J., 51  
 Potapov, V. M., 3, 175, 181  
 Potekhin, A. A., 210  
 Potts, K. T., 271, 281, 283, 285, 299  
 Pouli, D., 75  
 Poulos, C. P., 21  
 Powell, D. W., 84, 240  
 Powers, D. E., 160, 232  
 Praefcke, K., 5, 6, 15, 53, 156, 206, 218, 225, 236, 265, 268, 282  
 Prakash, G. K. S., 45, 261  
 Prange, T., 8  
 Prasanna, S., 21, 86  
 Pratt, T. M., 50  
 Preti, G., 10  
 Pretsche, E., 178  
 Prevost, R., 242  
 Price, E. M., 81, 243  
 Priess, A., 5  
 Priestley, M. G., 131  
 Prikloňskikh, G. I., 296  
 Prilezhaeva, E. N., 17, 57  
 Prinzbach, H., 208  
 Pritzkow, W., 71  
 Prochazka, M., 38, 250  
 Proctor, J., 131  
 Proidakov, A. G., 5  
 Proksch, A., 228, 270  
 Proll, T., 188, 230  
 Prommerening, H., 231  
 Proni, A., 106  
 Protsailo, T. A., 8  
 Pryor, W. A., 12  
 Przystas, T. J., 46  
 Pterov, A. A., 58  
 Puar, M. S., 244  
 Puchala, C., 127  
 Pudovik, A. N., 178, 181, 199  
 Puglis, J., 72  
 Pujanek, M., 16  
 Pulcrano, M. C., 89  
 Purchitt, A. K., 74  
 Puri, J. K., 131  
 Purrington, S. T., 111  
 Pusino, A., 26

- Puszta, L., 177  
 Puusccc, J., 64  
 Pytlewski, T., 58, 106  
  
 Quante, J., 196, 237  
 Queen, A., 53  
 Quicic, S., 17  
 Quin, L. D., 242  
 Quiniou, H., 156, 184  
 Qu Ninh, T., 251  
  
 Raasch, M. S., 159, 207, 225, 236, 254  
 Rabai, J., 6, 135  
 Raban, M., 19, 64  
 Rabari, L., 238  
 Raby, C., 66  
 Rachwal, S., 70  
 Radchenko, O. A., 67, 73  
 Radeaglia, R., 5, 71  
 Radics, L., 48  
 Radley, P., 275  
 Radom, L., 271  
 Radzhabov, N. G., 3  
 Radzicka, A., 226  
 Rae, I. D., 4  
 Rafikov, S. R., 23  
 Rahman, W., 144  
 Rai, M., 165  
 Rai, R., 183  
 Raisanen, K., 5  
 Rajagopalan, T. G., 66, 170  
 Rajan, S. J., 76  
 Rajappa, S., 66, 170, 172, 184, 188  
 Rajasekharan, K. N., 169  
 Rajee, R., 153, 219  
 Rakhmankulov, D. L., 260, 261  
 Rakitin, O. A., 112  
 Rakosi, M., 251  
 Rall, K. B., 58  
 Ramadas, S. R., 242  
 Ramage, R., 274  
 Ramalingam, K., 242, 246, 248  
 Ramamurthy, V., 153, 157, 219, 220  
 Ramarajan, K., 242  
 Ramazanov, E. A., 257  
 Rambaldi, M., 174  
 Ramm, P. J., 144  
 Ramsen, C. A., 189  
 Ramsden, M. J., 77  
 Randhawa, H. S., 4  
 Rankov, D., 215  
 Rao, A. S. C. P., 146  
 Rao, C. N. R., 157  
 Rao, M. N., 132  
 Rao, N., 242  
 Rasmussen, J. B., 230, 253  
 Rasteikiene, L., 19, 26  
 Rastelli, A., 7  
 Ratajczak, A., 255  
 Raths, R. A., 86  
 Ratovelomanana, V., 46  
 Ratovskii, G. V., 3  
 Raubenheimer, H. G., 102  
 Raucher, S., 19, 31, 32, 33, 87, 114, 116, 126, 216  
 Rautenstrauch, V., 38, 97  
 Ravichandran, R., 76  
 Rayner, E. S., 17  
 Razdan, R. K., 90  
 Read, S. F. J., 131  
 Reader, G., 286, 288  
 Reamer, R. A., 171  
 Reddy, D. B., 7, 28  
 Redlich, H., 204  
 Redshaw, M., 272  
 Reed, D., 50, 103  
 Reed, J. N., 51  
 Rees, C. W., 136, 138, 139, 287  
 Reeve, W., 172, 268  
 Regen, S. L., 17  
 Regondi, V., 22, 204  
 Reich, H. J., 2, 10, 24, 38, 41, 54, 55, 68, 83, 91, 107, 112, 113, 115, 116, 118, 123, 269  
 Reich, I. L., 55  
 Reichen, W., 1  
 Reichert, J., 179  
 Reid, D. H., 148, 152, 300  
 Reid, S. T., 60, 239  
 Reiner, M. D., 53  
 Reingold, I. D., 82  
 Reisman, D., 108, 239  
 Reiss, J. A., 82  
 Reiter, F., 298, 299  
 Reitz, D. B., 15, 208  
 Reliquet, A., 156  
 Reliquet, F., 156  
 Remane, H., 247  
 Remion, J., 119  
 Reminiac, C., 248  
 Remizov, A. B., 4, 8  
 Renga, J. M., 84, 240  
 Renou, J. P., 179  
 Renson, M., 113, 282, 290  
 Renzi, G., 128  
 Reshetova, O. S., 6, 7  
 Ressler, C., 178  
 Retisnki, A. A., 5  
 Reutov, O. A., 53  
 Reutrakul, V., 54, 104, 107  
 Revelle, L. K., 61, 161, 224  
 Reynolds, G. A., 248, 268  
 Reynolds, M. A., 67, 75  
 Reynolds, R. D., 173  
 Rezhikova, K. I., 81  
 Rezende, M. C., 64, 204  
 Reziikova, I. A., 3  
 Rhee, R. P., 21  
 Ricci, G., 68  
 Ricciardi, F., 18, 90  
 Rice, K. C., 107, 290  
 Rich, D. H., 41  
 Richards, A. C., 254  
 Richter, M., 203  
 Richter, R., 259  
 Riddles, P. W., 12  
 Ried, W., 222  
 Rieder, W., 135, 210, 248  
 Rigby, J. H., 20, 100  
 Righini, A., 1, 59, 111  
 Rinaldi, M., 7  
 Rinaldi, P. L., 102  
 Rioult, P., 252  
 Risaliti, A., 235  
 Risra, R. N., 91  
 Ritchie, C. D., 10  
 Rittner, R., 27  
 Rivera, H. V., 208  
 Rivkin, B. B., 49  
 Rizvi, S. Q. A., 49  
 Robert, A., 40, 81, 186, 283  
 Robert, F., 246, 267  
 Robert, G., 127, 131  
 Robert, J. B., 268  
 Robertiello, A., 6  
 Roberts, B. P., 13, 250  
 Roberts, J. D., 4, 127, 272  
 Roberts, P. M., 15  
 Roberts, T. D., 217, 294  
 Roberts, W. E., 109  
 Robertson, A., 62  
 Robinson, J. F., 174  
 Rockley, J. E., 279  
 Rodek, E., 132  
 Rodin, A. A., 24, 210  
 Rodriguez, H. R., 79  
 Rodriguez, J., 5  
 Rodriguez, L. O., 39  
 Roedig, A., 36  
 Roellgen, P. W., 6  
 Roesky, H. W., 127, 128, 132, 229, 231, 254  
 Rössert, M., 128  
 Roessler, F., 185  
 Rogalski, W., 242  
 Rogers, A. J., 239  
 Roggero, A., 106  
 Rogic, M. M., 67  
 Rogoshin, S. V., 264  
 Rokach, J., 73, 149, 286, 288  
 Roland, D. M., 95  
 Romanov, N. N., 284  
 Romm, I. P., 25  
 Ronsisvalle, G., 298  
 Rooney, J. J., 205  
 Rooney, R. P., 243, 245  
 Rosati, R. L., 218  
 Rose, E. H., 61, 111  
 Rosenfeld, S. M., 82  
 Roskam, J. H., 90  
 Rosmus, P., 150  
 Rosnati, V., 26  
 Rossa, L., 61, 207  
 Rossi, R. A., 17  
 Rossmanith, E., 167, 225  
 Roth, B., 91  
 Roth, K., 193  
 Roth, M., 183  
 Rothenberg, S., 232

- Rotschova, J., 51  
 Rotstein, D., 72  
 Roush, D. M., 81, 243  
 Roush, P. B., 262  
 Roush, W., 86  
 Rouwette, P. H. F. M., 61  
 Rovera, A., 9  
 Rovnyak, G. C., 244  
 Rowe, J. E., 182  
 Rowson, G. P., 189  
 Roys, S., 253  
 Rozantsev, E. G., 7  
 Rozova, T. I., 3  
 Rozsondai, B., 7  
 Rozyinov, B. V., 6  
 Ruback, W., 181  
 Rubleva, I. M., 58  
 Rudenko, A. P., 8  
 Rudolf, W. D., 32  
 Rueger, W., 208  
 Ruettinger, H. H., 17, 32  
 Ruff, F., 135  
 Ruffato, V., 51  
 Ruffner, R. J., 95  
 Ruge, B., 9  
 Ruger, W., 88  
 Ruggera, M. B., 6  
 Rukhadze, E. G., 175, 181  
 Ruostesuio, P., 4, 7  
 Ruppert, I., 48, 53  
 Rusek, J. J., 107, 123  
 Russell, G. A., 52, 59, 93  
 Ruston, S., 111  
 Ruzkowska, J., 244  
 Ruther, F., 67  
 Rutledge, P. S., 65, 208  
 Ryan, D. M., 54, 65, 104, 232, 239, 262  
 Ryan, K. J., 205  
 Ryazantsev, V. A., 19  
 Rybakova, N. A., 74  
  
 Saalfrank, R. W., 220  
 Saba, A., 26  
 Sabirov, S. S., 16  
 Sachdev, H. S., 116  
 Sachdev, K., 116  
 Sachdeva, R., 10  
 Saddler, J. C., 61, 107  
 Sadeghi-Milani, S., 293  
 Sadeh, S., 236  
 Sadekov, I. D., 5, 6, 17, 40, 49, 51, 76, 112, 147  
 Sadovaya, N. K., 19  
 Saenger, W., 169  
 Saethre, L. J., 300  
 Saeva, F. D., 282  
 Safarik, I., 209, 216, 294  
 Safin, Y. A., 6  
 Safullina, N. R., 3, 4  
 Saft, M. S., 111  
 Sai, M., 10  
 St. Jacques, M., 261  
 Saito, K., 34, 250  
 Saito, T., 133, 264  
 Sakaguchi, M., 232  
 Sakai, H., 174  
 Sakai, S., 66, 201  
 Sakakibara, M., 4  
 Sakakibara, T., 14, 85, 233  
 Sakamoto, K., 138  
 Sakamoto, M., 137  
 Sakamura, S., 96  
 Sakemi, K., 46, 192  
 Sako, M., 286  
 Sakovich, T. V., 279  
 Sakuma, K., 31, 55, 56  
 Sakurai, A., 200  
 Salakhova, R. S., 49  
 Salas, S., 203  
 Salazkin, S. N., 23  
 Saldabols, N., 53  
 Salem, G. F., 45, 261  
 Salem, M. A., 264  
 Salikhova, A. M., 7  
 Salman, S. R., 4  
 Salmona, G., 272, 283  
 Salvatori, T., 106  
 Salyin, Ya. N., 168  
 Samchenko, G. V., 58  
 Samitov, Yu. Yu., 254  
 Samuels, W. D., 19  
 Sancassan, F., 276  
 Sanchez, F., 5  
 Sanchez Garcia, J. B., 72  
 Sanders, M. J., 137, 286  
 Sanders, W. J., 10  
 Sandorfy, C., 27  
 Sandoval, D. N., 71  
 Sandri, E., 83, 84, 103, 240, 247  
 Sandstrom, J., 5, 47, 181  
 Sangalov, Y. A., 10  
 Sanina, N. L., 65  
 Sanitra, R., 45, 195  
 Sapre, A. V., 274  
 Sarkar, A., 273  
 Sarpeshkar, A. M., 14, 252  
 Sartori, P., 70  
 Sarwetre, R., 67  
 Sasaki, S., 199, 238, 275  
 Sasaoka, M., 280  
 Sastry, S., 179  
 Sathyanarayana, D. N., 168, 175, 182  
 Satgé, J., 212  
 Sato, A., 102  
 Sato, H., 2, 56  
 Sato, K., 86  
 Sato, M., 157  
 Sato, R., 63  
 Sato, S., 19, 20, 22, 262  
 Sato, T., 250  
 Sato, Y., 52  
 Satsumabayashi, S., 255  
 Sattler, K., 279  
 Satyamurthy, N., 242, 246, 248  
 Satzinger, G., 144  
 Sauer, J., 3  
 Sauriol-Lord, F., 261  
 Saus, A., 257  
 Saussine, L., 59  
 Sauter, H., 178, 230  
 Savel'ev, V. L., 275  
 Savelev, V. S., 19  
 Savelova, V. A., 72  
 Savina, T. I., 48, 71  
 Savoia, D., 57  
 Sawanishi, H., 279  
 Sawhney, S. N., 272  
 Sayed, Y., 90  
 Sayer, J. M., 13  
 Saykowski, F., 229  
 Sayo, H., 63  
 Szikova, D. L., 57  
 Sazonova, O. M., 57  
 Scala, A. A., 223, 232  
 Scarbrough, R. M., 62  
 Scarlata, G., 4  
 Scarpone, S., 237  
 Schaad, L. J., 216  
 Schaefer, H., 132, 279  
 Schaefer, K., 13  
 Schaefer, T., 4, 258  
 Schank, K., 58, 69, 81, 107, 110, 190  
 Schaumann, E., 38, 66, 74, 159, 160, 167, 171, 187, 216, 225, 228, 294  
 Scheffers-Sap, M. M. E., 243  
 Scheibe, R., 168  
 Scheibye, S., 178, 225, 230, 252  
 Scheithauer, S., 165  
 Schell, F. M., 128  
 Schembri, G., 257, 260  
 Schenkel, H. K., 4  
 Schenone, P., 164, 263  
 Scherer, O. J., 230  
 Schield, J. A., 252  
 Schipper, P., 126, 268  
 Schirlin, D., 76, 80, 97  
 Schiwiek, H. J., 222  
 Schleinitz, K. D., 237  
 Schlessinger, R. H., 100  
 Schlingensief, K. H., 81  
 Schlosser, K., 47  
 Schmid, B., 33, 104  
 Schmid, E. D., 4  
 Schmid, G. H., 19, 49  
 Schmid, H., 104, 187  
 Schmidpeter, A., 230  
 Schmidt, G., 36  
 Schmidt, M., 10, 261  
 Schmidt, R., 208  
 Schmidt, R. R., 33, 104  
 Schmidt, T., 283  
 Schmidt, U., 66  
 Schmidt, W., 82  
 Schmiedel, R., 24, 151  
 Schmieder, W., 137  
 Schmitt, H.-G., 102  
 Schmitt, J. L., 25, 102



- Schmüser, W., 160  
 Schnabel, W., 203  
 Schnaithmann, M., 212  
 Schneider, J. A., 35  
 Schneider, J. K., 178  
 Schneider, M. P., 212  
 Schnieder, F., 13  
 Schoberth, W., 73, 82  
 Schöffler, A., 253  
 Schoenfeld, P., 2  
 Schoenfelder, L., 128, 229  
 Schönholzer, P., 187  
 Schollkopf, U., 210  
 Scholz, D., 13  
 Schorstein, D., 32  
 Schoufs, M., 253, 265  
 Schroeder, F., 110  
 Schroer, W.-D., 85  
 Schroeter, E. H., 17  
 Schrooten, R., 245  
 Schroth, W., 259  
 Schubert, I., 65  
 Schüttpelz, E., 204  
 Schuetz, J., 42  
 Schuknecht, C., 81  
 Schults, J., 138  
 Schulz, R., 158, 224, 294  
 Schulze, B., 65  
 Schuster, I. I., 4  
 Schwartz, A., 54  
 Schwartz, H., 6  
 Schwarz, I., 208  
 Schwarz, W., 230  
 Schweig, A., 158, 218, 224, 294  
 Schweizer, B., 89, 259  
 Schwermann, I., 68  
 Schwindeman, J., 19, 32, 216  
 Scoby, J., 217, 294  
 Scolastico, C., 90, 103  
 Scott, J. C., 269  
 Scott, J. W., 241  
 Scovill, J. P., 167, 174  
 Screttas, C. G., 26, 102  
 Scrimin, P., 19  
 Scrowston, R. M., 276, 298  
 Seagle, I. R., 11  
 Seagusa, T., 180  
 Seaton, J. C., 39  
 Sébastien, F., 179  
 Seddon, E. A., 157  
 Sedgwick, R. D., 6  
 Seebach, D., 11, 28, 46, 89, 90,  
 93, 95, 96, 102, 113, 116,  
 121, 196, 259  
 Seeber, R., 24  
 Seeger, A., 56, 104  
 Seel, F., 62  
 Seel, H., 278  
 Seelinger, R., 163, 226  
 Seff, K., 8  
 Seguil-Camargo, L., 278  
 Seifert, C. M., 82  
 Seike, S. C., 61  
 Seiler, P., 89, 259  
 Seitz, G., 24, 66, 151  
 Seitz, S. P., 18, 90, 242  
 Seki, E., 224  
 Seki, H., 194  
 Sekido, K., 259  
 Sekiguchi, A., 26, 81  
 Sekine, M., 51  
 Sekiya, M., 16, 67, 68, 201  
 Sekretär, S., 172  
 Selby, T. P., 176  
 Seleznev, A. P., 81  
 Seltzman, H. H., 90  
 Selva, A., 26  
 Semard, D., 113  
 Semmelhack, M. F., 93  
 Semenov, V. V., 40, 81, 112  
 Semenovskii, A. V., 110, 263  
 Semple, J. E., 18, 90, 128, 227  
 Senatore, L., 52  
 Sendega, R. V., 8  
 Sengupta, P., 19  
 Senning, A., 22, 78, 163, 190,  
 199, 205, 218  
 Seno, K., 54, 90, 93, 256  
 Seno, M., 136  
 Seppelt, K., 7, 48, 80  
 Sepulchre, M., 208  
 Sesin, D. F., 4  
 Setoi, H., 60, 111  
 Seuring, B., 90  
 Severin, M. G., 26  
 Severin, T., 41, 81  
 Severson, R. G., 67, 128  
 Sevrin, M., 29, 33, 115, 120  
 Seybold, G., 298  
 Seyden-Penne, J., 45, 102  
 Seyer, U., 142  
 Seykens, D., 152, 193, 223  
 Sgamellotti, A., 2  
 Sgarabotto, P., 246  
 Shabanov, A. L., 208  
 Shafiee, A., 170, 271, 282, 286,  
 293, 297  
 Shah, K. A., 192  
 Shah, S. K., 24, 54, 113, 115,  
 116, 118  
 Shahab, Y., 256  
 Shainyan, B. A., 32  
 Shankaranarayana, M. L., 199,  
 204  
 Shakhtakhtinski, T. N., 268  
 Sharipova, F. V., 57, 250  
 Sharma, R. P., 131  
 Sharma, S., 165  
 Sharnin, G. P., 12  
 Sharp, D. W. A., 20  
 Sharpless, K. B., 18, 54, 67, 69,  
 116  
 Shaver, A., 257  
 Shcherbakova, L. P., 234  
 Shchupak, G. M., 3  
 Sheinker, Yu. N., 170  
 Sheldrick, W. S., 132  
 Shelton, E. J., 18, 216  
 Shepherd, J. P., 264  
 Sherradsky, T., 284  
 Sheremet, V. I., 141  
 Shermolovich, Y. G., 87, 141  
 Sherwood, A. G., 209  
 Shevchenko, S. M., 210  
 Shevelev, S. A., 40, 81, 112  
 Shevlin, P. B., 54, 59  
 Shibamoto, T., 232  
 Shibuya, M., 196  
 Shibuya, S., 28, 41, 102, 242  
 Shigemoto, T., 137  
 Shih, Y.-J., 17  
 Shimagaki, M., 49, 143  
 Shimanouchi, T., 4  
 Shimizu, H., 81, 139, 245  
 Shimizu, K., 95  
 Shimizu, M., 20, 22, 62, 68  
 Shimoji, K., 242  
 Shimozawa, T., 129  
 Shimura, T., 70  
 Shingaki, T., 128, 227  
 Shinham, K., 64, 68, 75  
 Shipov, A. G., 72, 164, 222  
 Shirai, K., 17  
 Shiraiishi, S., 38, 137  
 Shiralian, M., 258  
 Shirley, C. F., 9  
 Shiro, Y., 4  
 Shitov, O. P., 81  
 Shlyapochnikov, V. A., 81  
 Shono, T., 10, 16, 27, 30, 42, 87  
 Shostakovskii, S. M., 7  
 Shrake, A., 147  
 Shreeve, J. M., 48, 134, 226,  
 255  
 Shreeve, R. W., 226  
 Shrimali, S. S., 74  
 Shu, V., 244  
 Shukurov, S. S., 16  
 Shuvalov, V. F., 261  
 Shvedov, V. I., 279  
 Shvetsov-Shilovskii, N. I., 177  
 Siddiqui, M. S. S., 157  
 Sidhu, K. S., 266  
 Sidorov, V. I., 265  
 Siegbahn, K., 300  
 Sieler, R. A., 235  
 Sih, C. J., 50, 103  
 Sikkel, B. J., 263  
 Silver, J., 270  
 Silbert, L. S., 65  
 Simon, A., 7  
 Simon, H., 15  
 Simon, W., 178  
 Simonen, T., 23, 268  
 Simonet, J., 58, 59, 74  
 Simonetta, M., 216, 232  
 Simonsen, O., 239  
 Simonsen, S. H., 221, 264  
 Singer, H., 8  
 Singer, S. P., 84, 106, 240  
 Singh, A., 165  
 Singh, A. K., 170

- Singh, H., 89, 165, 183, 214  
 Singh, H. B., 269  
 Singh, M., 49, 269  
 Singh, P., 263  
 Singh, R. K., 57  
 Singh, S. P., 241  
 Singhal, R. K., 74  
 Sipio, W. J., 18, 31, 90, 216, 242  
 Siracusa, M. A., 298  
 Siret, P., 87  
 Sirlin, C., 11  
 Sisti, M., 235  
 Siu, T.-W., 106  
 Sivakumar, R., 246  
 Skatova, N. N., 32  
 Skoetsch, C., 290  
 Skorini, S. J., 199  
 Skorobogatova, E. V., 19, 65  
 Skowronska, A., 65  
 Skramstad, J., 276  
 Skrypnik, Yu. G., 73  
 Skvortsova, G. G., 32  
 Slagle, I. R., 226  
 Slavinskaya, R. A., 178  
 Slebocka-Tilk, H., 69  
 Smedstad, T., 61  
 Smit, V. A., 2, 19  
 Smit, W. A., 43, 207, 215  
 Smith, A. B., 62  
 Smith, D. J. H., 109, 222, 263  
 Smith, G. A., 208  
 Smith, J. M., 6  
 Smith, K., 94  
 Smith, R. A., 65, 76, 78  
 Smith, R. A. J., 47, 96, 261  
 Smith, R. D., 130, 131  
 Smith, R. G., 148  
 Smith, Z., 232  
 Smolinski, S., 262  
 Smorada, R. L., 59  
 Snatzke, G., 204, 266  
 Snetkova, E. V., 208, 210, 211, 234  
 Snodin, D. J., 143  
 Snyder, D. M., 58  
 Snyder, J. P., 7, 164, 215, 218, 224  
 Soai, K., 209  
 Soboleva, S. V., 246  
 Soccolini, F., 26  
 Sochilin, E. G., 24, 210  
 Sokolova, G. D., 229  
 Sokol'skii, G. A., 71, 227  
 Sokova, F. M., 215  
 Solera, P. S., 90  
 Solladie, G., 103  
 Solomoichenko, T. N., 72  
 Solonki, B., 7  
 Soloveva, L. D., 3  
 Soltani, A., 293  
 Soltz, B. L., 101  
 Soma, N., 128  
 Sombroek, J., 214  
 Sonoda, N., 2, 16, 20, 22, 216  
 Sorarrain, O. M., 4  
 Sosnovsky, G., 63  
 Sostero, D., 211  
 Sotgiu, F., 90  
 Soth, S., 278  
 Sotoya, K., 233  
 Sousa, L. R., 157  
 Sousa Lobo, M. J., 15  
 Southgate, R., 15  
 Southon, I. W., 85, 139  
 Soysa, H. S. D., 51  
 Spagnolo, P., 273  
 Spalding, E. S., 41  
 Spande, T. F., 1  
 Spanget-Larsen, J., 232  
 Speckamp, W. N., 38  
 Speer, H., 33, 104  
 Speier, J. L., 10  
 Speth, D. R., 67  
 Spinelli, D., 277  
 Spirikhin, L. V., 16, 250  
 Spoomaker, T., 265  
 Spoto, G., 68  
 Sprecher, M., 108, 239  
 Sprugel, W., 138  
 Spunta, G., 160  
 Sreenivasan, R., 66, 170, 172, 188  
 Srihari, K., 170  
 Srinivasan, C., 51  
 Srinivasan, P. S., 242  
 Srivastava, R. C., 49, 203, 269  
 Srivastava, T. N., 49, 203, 269  
 Stadnichuk, M. D., 19, 58  
 Stahl, I., 255, 261  
 Stahley, G. P., 217  
 Staicu, S. A., 200  
 Stajer, G., 77  
 Stam, C. H., 246  
 Standing, D. N., 11  
 Stang, P. J., 72  
 Stansfield, F., 184, 201  
 Stark, C. J., jun., 145  
 Stark, R., 62  
 Staral, J. S., 4, 127  
 Stasko, A., 227  
 Statsyuk, V. E., 32  
 Stec, D., tert., 257  
 Steckhan, E., 261  
 Steenkan, S., 47  
 Steer, R. P., 220  
 Stefaniak, L., 272  
 Steglich, W., 13, 59  
 Steinbach, G., 105  
 Steinberg, H., 210  
 Steliou, K., 63, 69, 76, 257, 261  
 Stelter, E. D., 70  
 Stenberg, V. I., 241  
 Stenhede, U., 284  
 Stepanova, A. A., 177  
 Stephenson, L. M., 67  
 Štěrba, V., 169  
 Stevens, G., 143  
 Stewart, A., 211, 251  
 Stewart, C. D., 5  
 Steyer, C., 68  
 Stezowski, J. J., 242  
 Stick, R. V., 205  
 Stiefvater, O. L., 273  
 Still, I. W. J., 10, 24, 49, 51, 136, 143, 157, 247, 250, 252  
 Stirling, C. J. M., 2, 106  
 Stockton, A., 63  
 Stoesser, R., 3  
 Stojakovic, D. G., 127  
 Stoodley, R. J., 62, 209  
 Stoss, P., 144  
 Stowell, J. C., 79  
 Strandlund, G., 70  
 Stransky, N., 62  
 Strausz, O. P., 24, 157, 207, 209, 216, 294  
 Street, G. B., 127, 131  
 Strepe, P. E., 105, 110  
 Strelets, B. Kh., 295  
 Strijtveen, H. J. M., 103, 162  
 Strobel, M.-P., 34  
 Struchkov, Yu. T., 246, 254  
 Stufkens, D. J., 127  
 Stumbreviciute, E., 26  
 Sturdik, E., 12  
 Sturtz, G., 100  
 Tusche, D., 82  
 Su, S. S., 28, 100  
 Subramanian, K., 73, 82  
 Subramanian, L. R. S., 73, 82  
 Suchi, R., 4  
 Suchkova, I. G., 21, 245, 249  
 Suchling, C. J., 32  
 Sudoh, R., 14, 85, 233  
 Sueda, N., 86, 241  
 Suemitsu, R., 260  
 Sugawara, M., 83  
 Suggett, A., 39  
 Sugie, A., 12  
 Sugihara, H., 52  
 Sugihara, M., 263  
 Sugikawa, W., 2  
 Sugimoto, T., 50, 80, 82  
 Sugino, K., 197  
 Sugiyama, H., 66  
 Suh, I.-H., 169  
 Suhara, Y., 211  
 Sukhai, R. S., 38, 78, 194, 268  
 Sukhanov, S. V., 63  
 Sukhomazova, E. N., 24, 214  
 Sukumaran, K. B., 86  
 Sulaimanov, A. S., 229  
 Sulfanov, B. Yu., 3  
 Sum, F. W., 98  
 Sumarokova, T. N., 178  
 Sumita, M., 60, 100, 111  
 Summers, L. A., 7, 279  
 Sumoto, K., 252  
 Sunagawa, K., 157, 237  
 Sundaram, S., 73  
 Sundaramurthy, V., 170

- Sundermeyer, W., 163, 226  
 Surzur, J. M., 26, 234  
 Suschitzky, H., 149, 275  
 Sutrinso, R., 66, 151  
 Suzuki, A., 158  
 Suzuki, F., 50, 103  
 Suzuki, H., 51, 52, 65, 70, 250  
 Suzuki, K., 29, 54, 67, 68, 201  
 Suzuki, K. T., 6, 254  
 Suzuki, N., 70  
 Suzuki, R., 68  
 Suzuki, S., 131, 154  
 Svanholt, H., 158, 226  
 Svata, V., 38  
 Svensson, S., 300  
 Svoronos, P., 135  
 Swaminathan, S., 85  
 Swank, D. W., 142  
 Swanson, D. D., 232, 262  
 Swanson, S., 8  
 Swedo, R. J., 74  
 Swenton, J. C., 45, 195  
 Swebston, P., 133, 267  
 Swern, D., 53, 85, 86, 134, 143  
 Swindell, C. S., 73  
 Sych, E. D., 284  
 Sycheva, T. P., 279  
 Sydnes, L. K., 188  
 Sylvia, C. J., 4  
 Symeonides, K., 220  
 Symons, M. C. R., 13  
 Szafranek, J., 197  
 Szalaiko, U., 70  
 Szargan, R., 168  
 Szeja, W., 72  
 Szilagyi, S., 49, 143  
 Szmant, H. H., 54  
 Szymanowski, J., 16
- Tabacchi, R., 283  
 Taber, D. G., 104  
 Tabushi, I., 247  
 Tachikawa, A., 133  
 Taeger, T., 231  
 Tagaki, W., 76  
 Tagawa, J., 14  
 Tagiev, B. A., 3  
 Taguchi, T., 32, 204  
 Taguchi, Y., 211  
 Taieb, M. C., 244  
 Taira, Z., 199  
 Tait, T. A., 44, 95, 195  
 Takagi, M., 44  
 Takagi, S., 32  
 Takahaski, F., 84, 144  
 Takahashi, H., 90, 165, 174, 255, 289  
 Takahashi, K., 131, 246, 292  
 Takahashi, M., 93, 101  
 Takahashi, S., 102  
 Takahashi, T., 30, 100, 101  
 Takahashi, Y., 57  
 Takai, Y., 22  
 Takaki, K., 41
- Takamiya, N., 12  
 Takamoto, M., 246  
 Takamoto, T., 233  
 Takanashi, H., 32  
 Takano, S., 90, 93  
 Takase, T., 32  
 Takata, M., 26, 81  
 Takata, T., 6, 67, 78, 254  
 Takayanagi, H., 81, 106  
 Takeda, K., 42, 138, 165, 232  
 Takeda, N., 205  
 Takeda, R., 22, 68  
 Takeda, T., 85  
 Takeda, Y., 5  
 Takei, H., 21, 33, 38, 104  
 Takei, K., 27  
 Takemasa, T., 256  
 Takemoto, H., 249  
 Takenaka, K., 232  
 Takeshima, T., 98, 192, 194, 197, 225  
 Takeuchi, T., 5  
 Takido, T., 9, 183  
 Takigawa, T., 208  
 Takikawa, Y., 63  
 Takizawa, S., 63  
 Talaikyte, Z., 26  
 Tam, C. C., 47, 91  
 Tam, J. P., 41  
 Tamagaki, S., 112, 153  
 Tamao, K., 65  
 Tamaru, Y., 59, 68, 90, 184, 185, 247, 256  
 Tamas, J., 6  
 Tamba, M., 13  
 Tamura, Y., 60, 65, 138, 140, 147, 166, 179, 252, 287  
 Tanabe, T., 40  
 Tanaka, H., 22, 26, 100, 178, 185, 199, 200  
 Tanaka, J., 273  
 Tanaka, K., 11, 38, 43, 46, 100, 133, 205, 208, 242  
 Tanaka, S., 66, 199  
 Tanaka, T., 5  
 Tanaskov, M. M., 58  
 Tancredi, T., 254  
 Tang, H.-N., 76  
 Tang, P.-W., 50, 56, 104  
 Tangerman, A., 163  
 Tanida, H., 39  
 Tanigawa, Y., 33  
 Taniguchi, E., 253, 255  
 Tanikaga, R., 11, 43, 44, 52, 100, 208  
 Tanimoto, M., 4  
 Tanimoto, S., 44, 50, 80, 82  
 Taniyasu, S., 40  
 Tantasheva, F. R., 19  
 Tantawy, A., 165  
 Tantry, K. N., 157, 199, 204  
 Tarantelli, T., 7  
 Tarasenko, A. I., 141  
 Tarasova, O. A., 32
- Tartakovskii, V. A., 81  
 Taschner, M. J., 93, 256  
 Tashiro, M., 131, 156, 207, 292  
 Taticchi, A., 150, 281  
 Tavernier, D., 242  
 Taylor, A. J., 70  
 Taylor, A. W., 274  
 Taylor, D. R., 174  
 Taylor, E. C., 255, 290  
 Taylor, J. B., 144  
 Tazaki, M., 44  
 Tebby, J. C., 6  
 Tember-Kovaleva, T. A., 178  
 Temkin, H., 269  
 Templeton, D. H., 81, 243  
 Templeton, L. K., 81, 243  
 Terada, H., 174  
 Teranishi, A. Y., 116  
 Terasawa, T., 216, 242  
 Terashime, K., 193  
 Terayama, Y., 96  
 Ter-Gabriélyan, E. G., 128  
 Terlouw, J. K., 232  
 Ternary, L. L., jun., 245, 265  
 Terpinski, J., 178  
 Terrier, F., 277  
 Tesky, F. M., 133, 228  
 Teso Vilar, E., 72  
 Testaferri, L., 17, 273, 276, 296  
 Testoedeva, S. L., 65  
 Teterina, L. F., 32  
 Tetreault-Ryan, L., 263  
 Tezuka, T., 51, 52, 209, 250  
 Thaker, K. A., 57  
 Thamnusan, P., 54, 104  
 Thea, S., 163  
 Thi, N. P., 38  
 Thiel, W., 32, 191  
 Thielemann, C., 172, 177  
 Thijs, L., 163  
 Thind, S. S., 64  
 Thomas, E. J., 18, 83  
 Thomas, M. T., 40, 81  
 Thomas, P. J., 106  
 Thompson, M., 247  
 Thomsen, I., 230  
 Thong, P. D., 172, 177  
 Thuillier, A., 9, 44, 95, 191, 193, 194, 255, 256  
 Thulstrup, E. W., 271  
 Ticozzi, C., 81, 85  
 Tidwell, T. T., 19  
 Tiecco, M., 17, 273, 276, 296  
 Tiensripojiamam, A., 54  
 Tighe, B. J., 253  
 Tilak, B. D., 74  
 Tilhard, H.-J., 116  
 Tilichenko, M. N., 235, 246  
 Tilley, J. W., 165  
 Timm, U., 158, 216, 254, 292, 294  
 Timmerman, A., 164  
 Timofeeva, G. N., 40  
 Tin, K.-C., 54, 104, 239

- Tingoli, M., 17, 276  
 Tipping, A. E., 174  
 Tirouflet, J., 67  
 Tishchenko, N. P., 49, 112  
 Tisnes, P., 267, 268  
 Titova, M. V., 249  
 Tius, M. A., 126  
 Tkac, A., 227  
 Tobin, P. S., 91  
 Tochtermann, W., 65  
 Todd, L. J., 218  
 Todres, Z. V., 254  
 Töplitz, B., 244  
 Togo, H., 51, 137  
 Tokmurzin, K. K., 17, 249  
 Tokoroyama, T., 276  
 Tokuda, M., 26  
 Tokunaga, K., 11  
 Tokuno, K., 82, 256, 251  
 Tokura, N., 169  
 Tolchinskii, S., 180  
 Tolley, M. S., 270  
 Tolmachev, A. I., 284  
 Tolstikov, G. A., 10, 57, 67, 236, 250, 256  
 Tomchin, A. B., 177  
 Tomimatsu, Y., 137  
 Tominaga, M., 208  
 Tominaga, Y., 46, 192, 198, 289  
 Tomioka, K., 90  
 Tonellato, U., 211  
 Tong, Y.-C., 50, 75  
 Topchii, V. A., 4  
 Toppet, S., 147, 164, 212, 221  
 Torii, S., 22, 26, 100, 110, 199, 200  
 Torretta, B., 298  
 Torre, G., 215  
 Torrelles, E., 191  
 Torres, M., 207, 216, 294  
 Torres, T., 157  
 Toscano, V. G., 21  
 Toshimitsu, A., 18, 21, 66, 190, 268  
 Toubro, N. H., 218, 283  
 Tougain, P., 131  
 Townsend, L. B., 152  
 Toyoshima, K., 19, 34  
 Trabjerg, I., 218  
 Trach, S. S., 87, 141  
 Traore, U., 73  
 Trave, R., 43  
 Traxler, J. T., 265  
 Traynelis, V. J., 252  
 Treger, W., 138  
 Trend, J. E., 54, 269  
 Trenholm, J. E., 52  
 Treptow, W., 72  
 Treutmann, W., 168  
 Triassi, I., 69  
 Trickett, G., 292  
 Trimder, R. W., 131  
 Tröger, W., 41  
 Trötsch, C., 175  
 Trofimov, B. A., 5, 6, 26, 32, 34, 53, 170, 231  
 Trost, B. M., 1, 20, 29, 32, 33, 79, 82, 100, 105, 106, 110, 111, 216  
 Trsic, M., 131  
 Truce, W. E., 56, 58, 59, 73, 264  
 True, N. S., 4  
 Trufem, C., 27  
 Trzhtsinskaya, B. V., 32  
 Tsai, L.-Y., 28, 100  
 Tsai, M. C., 189  
 Tsang, G. T. Y., 40, 251  
 Tsarenko, S. V., 165  
 Tsay, Y.-H., 85  
 Tschmutova, G. A., 5  
 Tseimakh, I. D., 49  
 Tselinskii, I. V., 73  
 Tsetlina, E. O., 34  
 Tsubata, K., 10  
 Tsuchihashi, G.-I., 1, 51, 83, 104  
 Tsuchiya, H., 49, 143  
 Tsuchiya, L., 36  
 Tsuchiya, S., 136  
 Tsuchiya, T., 72, 279, 301  
 Tsuge, O., 164, 188  
 Tsuji, J., 30, 100, 101, 253  
 Tsukube, H., 167  
 Tsumaki, H., 82  
 Tsunekawa, M., 147  
 Tsuneoka, K., 216, 249  
 Tsuno, Y., 3  
 Tuchinda, P., 107  
 Tulegenova, N. K., 268  
 Tull, R. J., 171  
 Tung, C. C., 22  
 Turchin, K. F., 170  
 Turley, J. C., 17  
 Turnbull, K., 24, 51, 136, 250  
 Turner, A. G., 131  
 Turner, E. S., 13  
 Turyanskaya, A. M., 265  
 Twedde, N. J., 157  
 Twine, C. E., jun., 90  
 Tyka, R., 169  
 Tyurin, V. D., 12  
 Uchino, M., 67, 68  
 Uda, H., 33, 56, 99  
 Uda, M., 174, 175  
 Udachin, Yu. M., 291, 300  
 Udupa, M. R., 228  
 Uebel, J. J., 4, 222  
 Ueda, A., 4, 63  
 Ueda, C., 173  
 Ueda, K., 256  
 Ueda, M., 266  
 Uemura, S., 18, 21, 49, 66, 190, 268  
 Ueno, N., 131  
 Ueno, Y., 60, 61, 111, 116, 201  
 Uesaka, M., 217  
 Ugnen, D., 1, 111  
 Uh, H. S., 205  
 Ujjainwalla, M., 49, 65  
 Ukida, M., 200  
 Ulbrecht, V., 133  
 Ulecia, N., 279  
 Uliss, D. B., 90  
 Ulsaker, G. A., 285  
 Ultee, W., 55  
 Umanskaya, L. I., 256  
 Umezawa, S., 72  
 Undavia, N. K., 57  
 Undheim, K., 60, 252, 285  
 Uneme, H., 11, 100  
 Uneyama, K., 77, 110  
 Untch, K. G., 55, 104  
 Uohama, M., 152, 163, 209  
 Uppenkamp, R., 230  
 Urano, S., 188  
 Urhahn, G., 227, 267  
 Urin, A. B., 234  
 Usachev, A. I., 40, 49, 112  
 Uskokovic, M. R., 241  
 Usol'tsev, A. A., 246  
 Usov, V. A., 9  
 Usova, T. L., 34  
 Ustynyuk, A. M., 232  
 Usuki, M., 65  
 Utley, J. H. P., 261  
 Uyehara, T., 106  
 Valentin, E., 222  
 Valkov, P. G., 63  
 Valle, G., 262  
 Vampa, G., 7  
 Van Acker, L., 258  
 Van Allan, J. A., 248, 268  
 Van Asch, A., 134, 167  
 Vancea, L., 258  
 Van de Mierop, W., 267  
 van der Berg-van Kuijk, A. J. W., 216  
 van der Gen, A., 20, 93, 249, 255  
 van der Griendt, F., 263, 268  
 van der Helm, D., 242, 246  
 van der Leij, M., 91, 103, 160, 162, 214  
 Van der Linden, J. G. M., 199  
 Vanderpool, S. H., 73  
 Van Der Puy, M., 116  
 van de Ven, L. J. M., 243  
 Van Dijk, L. A., 69  
 Van Ende, D., 24, 45, 114, 115, 120  
 van Erkelens, P. A. E., 166  
 van Fossen Bravo, R., 7  
 Van Gaal, H. L. M., 199  
 Van Gemert, B., 73  
 Vanier, N. R., 116  
 van Iersel, H. M., 216  
 Vankar, Y. D., 41, 45, 51, 75, 87, 261, 264

- van Koten, G., 163  
 Van Leusen, A. M., 58, 61  
 Van Meerssche, M., 66, 134, 167, 184, 212, 219, 221, 230  
 Van Ool, P. J. J. M., 126, 268  
 Varkonda, S., 198  
 Vasella, A., 67  
 Vasil'ev, A. F., 170  
 Vasil'ev, V. V., 87, 141  
 Vasil'eva, E. V., 250  
 Vasileva, M. A., 3, 58  
 Vasilevskis, J., 241  
 Vassilev, G., 168  
 Vasyanina, M. A., 10  
 Vaya, J., 62  
 Vazeux, M., 5  
 Vdovenko, S. I., 3, 4  
 Vedejs, E., 40, 80, 84, 106, 240, 241  
 Veenstra, G. E., 103, 162, 163  
 Veenstra, L., 111, 145  
 Veltz, J. N., 68  
 Vendrova, O. E., 3  
 Venduchick, W. C., 29  
 Venier, C. G., 54, 77  
 Venkatasubban, K. S., 15  
 Venkatasubramanian, N., 73  
 Vennos, A. N., 4, 244  
 Venzo, A., 83  
 Verboom, W., 31, 268  
 Verbruggen, A., 147  
 Vercini, C. A., 40  
 Vereshchagin, A. N., 7, 8  
 Verhoeckx, G. J., 223  
 Verhoeven, T. R., 106, 110  
 Verkoczy, B., 209  
 Verkruisje, H. D., 98  
 Verma, K. V., 169  
 Verma, R. D., 131  
 Verma, V. K., 183  
 Vermeer, H., 218  
 Vermeer, P., 69, 191, 253  
 Vermeersch, G., 76  
 Vermeire, M., 290  
 Vernon, J. M., 287  
 Vernon, W. D., 5  
 Verpeaux, J.-N., 1, 59  
 Vessiere, R., 85  
 Vialle, J., 38, 151, 225, 300  
 Vianello, E., 26  
 Vibet, A., 225  
 Vicens, J. J., 103  
 Vidugiriene, V., 26  
 Vierhapper, F. W., 135, 210, 242, 248, 260  
 Viertler, H., 27  
 Vikane, O., 4  
 Viktorova, E. A., 25, 238, 250  
 Vildavskaya, A. I., 58  
 Vijloen, H. W., 102  
 Vilkov, L. V., 7  
 Villadsen, B., 5  
 Villsmaier, E., 41, 42, 138  
 Vincent, E. J., 257, 272, 283  
 Vinkler, E., 76, 77  
 Vinokurova, R. I., 5  
 Viola, H., 32, 179, 191, 204  
 Virin, L. I., 6  
 Visser, K., 208  
 Visser, R. G., 153, 219  
 Vistocco, R., 222  
 Vitkovskii, V. Yu., 6, 17, 53  
 Vivarelli, P., 272  
 Vizgert, R. V., 72  
 Vladuchick, W. C., 100, 216  
 Vlasova, N. N., 26, 32, 34  
 Vlems, H., 243  
 Vögtle, F., 61, 88, 183, 207  
 Voelter, W., 27  
 Vogel, E., 214  
 Voigt, J., 183  
 Volka, K., 175, 182  
 Volkhonskii, M. G., 51  
 Volkmann, R. A., 65  
 Volkov, A. N., 5, 32  
 Volkov, N. D., 71  
 Voloshchuk, V. G., 49, 112  
 Volpe, P., 24  
 Volynskii, N. P., 234  
 von Criegern, T., 230  
 Von Deuten, K., 203  
 von Kiedrowski, G., 260  
 Vorob'eva, E. A., 19, 215  
 Voronkov, M. G., 5, 9, 10, 17, 24, 26, 32, 34, 44, 60, 172, 214, 231, 255, 261, 264  
 Voronov, V. K., 32  
 Vors, J. P., 255  
 Voss, J., 160, 189, 193, 194, 195, 264  
 Vouros, P., 197  
 Vrieze, K., 163  
 Vtyurina, N. N., 3, 4  
 Vulson, S. G., 8  
 Vulgaris, E., 257  
 Vyrypaev, E. M., 256  
 V'yunov, K. A., 24, 210  
 Wachsen, E., 290  
 Wachtmeister, C. A., 57  
 Wada, Y., 246  
 Wade, L. G., 46  
 Wade, P. A., 111  
 Wähäsilta, J., 264  
 Wagemann, W., 214  
 Wagner, H. U., 42  
 Wahab, A., 174  
 Wakabayashi, S., 268  
 Wake, S., 74  
 Wakui, T., 78  
 Walborsky, H. M., 255  
 Walclawek, W., 127  
 Walek, W., 5  
 Walker, K. A. M., 21  
 Walker, M. L., 48, 142  
 Walley, A. R., 135, 248  
 Walter, W., 4, 167, 181, 182, 187, 188, 230, 264  
 Walther, D., 131  
 Walther, H. G., 255  
 Walton, D. J., 20  
 Walton, J. C., 300  
 Wambsgans, A., 146  
 Wan, T. S., 13, 234  
 Wanczek, K.-P., 232  
 Wander, J. D., 8  
 Wang, H.-C., 70  
 Wang, N., 28  
 Wang, N.-Y., 100  
 Wang, P. C., 18, 90  
 Wang, Y., 268  
 Ward, D. A., 273  
 Ward, M. A., 54  
 Warren, S., 2, 37, 45, 79, 94, 95, 96  
 Wartew, G. A., 12  
 Wartski, L., 45, 102  
 Wasmuth, D., 90  
 Watabe, T., 47  
 Watabe, Y., 14  
 Watanabe, H., 232  
 Watanabe, K., 51  
 Watanabe, M., 17, 83, 210, 238  
 Watanabe, N., 190  
 Watanabe, T., 246  
 Watanabe, Y., 26, 27  
 Waterhouse, I., 61, 110  
 Watson, W. H., 199, 265  
 Wattanasin, S., 93  
 Wawer, A., 12  
 Webb, G. A., 272  
 Weber, A., 110  
 Weber, H., 175  
 Weber, J. L., 155  
 Weber, L., 85, 105  
 Weber, R., 6, 290  
 Weber, W. P., 51  
 Webster, R. G., 148  
 Weedon, A. C., 150, 224  
 Weese, G. M., 232  
 Wegener, W., 3  
 Wegmann, H., 59  
 Weiber, L., 110  
 Weichsel, C., 218, 236  
 Weigel, L. O., 87, 90  
 Weigt, A., 265  
 Weiler, E. D., 288  
 Weiler, L., 98  
 Weingate, P., 69  
 Weinreb, S. M., 21, 90  
 Weinstock, L. M., 171  
 Weintraub, P. M., 262  
 Weisenfeld, R. B., 44, 46, 47, 94, 99, 100  
 Weissflog, E., 10, 261, 269  
 Weissshuhn, C. M., 196, 236, 256, 291, 292  
 Welch, S. C., 146  
 Welzel, P., 266  
 Wemple, J., 14, 52, 104, 252  
 Wendelborn, D. F., 54, 269  
 Wendelin, W., 170

- Wengel, A. S., 279  
 Wenkert, E., 12, 73  
 Wennerbeck, I., 5  
 Wenschuh, E., 68, 69  
 Wenska, G., 188  
 Weringa, W. D., 6, 232  
 Werndl, R., 17  
 Werner, F., 58, 110  
 Wessely, V., 208  
 West, B. O., 4  
 West, R. C., 241  
 Westmijze, H., 69, 191  
 Wetter, H., 22, 98  
 Wetz, U., 42  
 Weyerstahl, P., 90  
 Whaley, T. W., 73  
 Wheeler, D. M. S., 91  
 Whistler, R. L., 251  
 White, E. J., 13  
 White, R. C., 217, 294  
 Whiting, E. J., jun., 147  
 Whiting, M. C., 143  
 Wiaux-Zamar, C., 128  
 Widera, R., 199  
 Widmer, J., 17  
 Wiebe, H. A., 209  
 Wiechmann, C., 46, 225  
 Wigfield, D. C., 54  
 Wildeman, J., 58, 61, 111  
 Wildman, T. A., 4  
 Wilke, H.-J., 251  
 Wilcott, M. R., 54  
 Willcox, A., 184  
 Willer, R. L., 135, 242  
 Willert, I., 93, 259  
 Williams, A., 163, 263  
 Williams, D. J., 173  
 Williams, D. L., 90  
 Williams, J. R., 68  
 Williams, L., 17  
 Williamson, J. R., 190  
 Williamson, K. L., 272  
 Willmes, A., 227, 267  
 Wilshire, C., 75, 151  
 Wilson, D. R., 8  
 Wilson, G. S., 232, 262  
 Wilson, J. M., 76  
 Wilson, S. R., 91, 105  
 Winkler, G., 65  
 Winkler, T., 178, 230  
 Winter, M. R. C., 2  
 Wiriyachitra, P., 22  
 Wiseman, A., 255  
 Wiseman, J. R., 251  
 Witanowski, M., 272  
 Withers, G. P., 65  
 Witt, M., 132  
 Witteler, F. J., 266  
 Wladislaw, B., 27  
 Wobig, D., 202  
 Woessner, W. D., 90  
 Woggon, W.-D., 67  
 Wojcicki, A., 67, 128  
 Wojtasiewicz, K., 244  
 Wolf, H., 131  
 Wolf, S., 61  
 Wolfe, S., 42, 52, 76, 80, 265  
 Wolff, C., 65  
 Wolff, T., 34  
 Wolford, T. L., 262  
 Wolkoff, P., 259  
 Wollenberg, R. H., 15  
 Wollowitz, S., 54, 55, 269  
 Wolmershaeuser, G., 131  
 Woltermann, A., 116, 281  
 Wong, C. K., 18  
 Wong, E., 232  
 Wong, G. S. K., 224  
 Wong, S. C., 182  
 Wong, V. K., 23  
 Woo, S.-M., 163  
 Wood, G. P., 16  
 Woodgate, P. D., 65, 208  
 Wrigglesworth, R., 32  
 Wrobel, J. T., 244  
 Wudl, F., 232, 281, 291  
 Wynberg, H., 11, 63  
 Wynne, K. J., 173  
 Yagudskii, E. B., 269  
 Yagupolskii, L. M., 17, 19, 40, 48, 67, 71  
 Yahara, I., 232  
 Yahner, J. A., 17  
 Yakavleva, V. N., 51  
 Yakhontov, L. N., 170  
 Yaktapour, M., 73  
 Yamabe, T., 133  
 Yamada, F., 267, 268  
 Yamada, H., 30, 98  
 Yamada, K., 130  
 Yamada, M., 14, 233  
 Yamada, S., 193, 256  
 Yamada, Y., 131  
 Yamadera, T., 82  
 Yamagata, H., 51  
 Yamagata, J., 232  
 Yamagishi, N., 11, 100, 208  
 Yamaguchi, H., 10, 220, 237  
 Yamaguchi, M., 29  
 Yamaichi, A., 91  
 Yamamoto, G., 2, 64  
 Yamamoto, K., 82, 282  
 Yamamoto, M., 60  
 Yamamoto, S., 199  
 Yamamoto, T., 134, 135, 140  
 Yamamoto, Y., 37, 97, 301  
 Yamamura, H., 235  
 Yamamura, M., 17  
 Yamasaki, N., 276  
 Yamashita, M., 47, 104, 260  
 Yamauchi, K., 40  
 Yamawaki, J., 17  
 Yamazaki, C., 176  
 Yamigawa, S., 56  
 Yan, C. F., 19  
 Yanagi, T., 158  
 Yanagisawa, K., 17  
 Yandovskii, V. N., 73  
 Yano, A., 192, 225  
 Yano, S., 282  
 Yano, T., 10  
 Yano, Y., 76  
 Yao, S., 281  
 Yardley, J. T., 209  
 Yarkova, E. G., 3, 4  
 Yaroshenko, L. P., 141  
 Yashkina, L. V., 214  
 Yasuda, G., 138  
 Yasuda, H., 253  
 Yasui, S., 155  
 Yasumura, T., 75  
 Yasuoka, T., 173  
 Yatagai, H., 37, 97  
 Yates, K., 19  
 Yates, P., 255  
 Yavari, I., 4, 127, 272  
 Yeo, K. S., 24  
 Yeroushalmi, S., 19  
 Yocklovich, S. G., 49, 221, 250  
 Yokata, T., 24  
 Yokomatsu, T., 28, 41, 102  
 Yokoo, S.-I., 30, 98  
 Yokoyama, M., 173, 197, 225, 228  
 Yokoyama, T., 133  
 Yokoyama, Y., 116  
 Yoneda, S., 32, 155, 193  
 Yonemitsu, T., 71  
 Yoshida, H., 47, 199  
 Yoshida, T., 72, 246  
 Yoshida, Z., 32, 59, 68, 155, 184, 185, 193, 217, 247, 256  
 Yoshida, Z.-I., 90  
 Yoshifuji, M., 14, 24, 93  
 Yoshihara, M., 11  
 Yoshikawa, K., 75  
 Yoshimura, J., 86, 90  
 Yoshimura, T., 84, 136, 137, 144  
 Yoshino, K., 131  
 Yoshioka, T., 128  
 Young, D. R., 142  
 Young, D. W., 239  
 Youzwak, H. P., 281  
 Yu, C. C., 147  
 Yu, S. L., 102, 210, 261  
 Yunamoto, T., 24  
 Yunker, M. B., 263  
 Yurchenko, L. G. 19  
 Yurev, V. P., 67  
 Yurevich, V. P., 58  
 Yus'kovich, A. K., 250  
 Zabelaite-Miskiniene, V., 26  
 Zabirow, N. G., 178  
 Zabolotnaya, T. G., 141  
 Zaby, G., 36  
 Zaev, E. E., 16, 236  
 Zagorevskii, V. A., 275  
 Zaikin, V. G., 234  
 Zajac, W. W., 3

- Zakharyan, R. Z., 7  
 Zaks, I. M., 263  
 Zamankhan, H., 254  
 Zamkanej, M., 185, 207  
 Zanello, P., 24  
 Zanirato, P., 296  
 Zankowska-Jasinska, W., 180,  
 188, 228  
 Zanutti, G., 262  
 Zaripov, N. M., 7  
 Zarubin, M. Y., 8  
 Zaslavskii, V. G., 72  
 Zatorski, A., 10, 52, 256  
 Zbaida, D., 284  
 Zefrov, N. S., 2, 19, 65, 87,  
 141, 207, 215, 226, 257, 269  
 Zeifman, Y. V., 19, 128  
 Zeinalov, A. M., 10  
 Zeiss, W., 230  
 Zellers, E. T., 281  
 Zerby, G. A., 109  
 Zerner, B., 12  
 Zetkin, V. I., 6  
 Zhdanov, R. I., 7  
 Zhdanov, Y. A., 63  
 Zhdanova, M. P., 174  
 Zhemchuzhin, S. G., 229  
 Zhusupova, G. E., 7  
 Zieba, U., 188  
 Ziegler, D. M., 169  
 Ziegler, F. E., 46, 47, 91  
 Ziegler, J. M., 181  
 Zilch, H., 185  
 Zima, G., 11, 18, 32  
 Ziman, S. D., 176  
 Zimin, M. G., 178, 181, 199  
 Zimmerer, S., 42, 138  
 Ziolo, R. F., 8, 269  
 Zlotchenko, S. I., 141  
 Zlotskii, S. S., 260, 261  
 Zolotukhin, S. P., 269  
 Zontova, V. N., 167, 170  
 Zorin, V. V., 261  
 Zumbulyadis, N., 268  
 Zurawel, S. J., 281  
 Zvezdina, E. A., 174  
 Zwanenburg, B., 91, 103, 160,  
 162, 163, 214, 227





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