

Contents

Chapter 1	Aliphatic Organosulphur Compounds Compounds with Exocyclic Sulphur Functional Groups, and their Selenium and Tellurium Analogues	1
	<i>By G. C. Barrett</i>	
1	Textbooks and Reviews	1
2	Spectroscopic and Other Physical Properties of Organosulphur, Organoselenium, and Organotellurium Compounds	2
	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
3	Thiols, Selenols, and Telluroles	8
	Preparation	8
	Reactions	10
	Thiyl and Related Selenium Radicals	13
4	Thiolesters, Selenolesters, and Tellurolesters	13
	Preparation	13
	Reactions of Thiolacids and Thiolesters, Selenolesters, and Tellurolesters	14
5	Sulphides, Selenides, and Tellurides	15
	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 α -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
 α -Thiovinyl Anions 98
 Miscellaneous α -Thiocarbanions 100
- 7 Sulphinyl and Sulphiliminyl 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 α -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
1 Di-co-ordinate Sulphur	127
Sulphinyl-amines and -amides	127
Structure	127
Preparation and Reactions	127
Sulphur Di-imides	130
Preparation and properties of (SN) _x	130
Tetrasulphur Tetranitride	131
Preparation of Other Sulphur Di-imides	131
Reactions	132
Structure	133
Thione S-Imides	133
2 Tri-co-ordinate Sulphur	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
3 Tetra-co-ordinate Sulphur	143
Sulphoximides	143
Sulphodi-imides	147
4 Selenium and Tellurium Analogues	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

1 Thioaldehydes and Selenoaldehydes	148
Synthesis	148
Transient Species	148
Mass Spectrometry	150
Molecular Orbital Calculations	150
2 Thioketones	150
Synthesis	150
Reactions	152
Spectroscopy	157
3 Thioketens and Selenoketens	158
Synthesis	158
Reactions	159
Spectroscopy	160
Part II Sulphines and Sulphenes	160
<i>By D. R. Hogg</i>	
1 Sulphines	160
2 Sulphenes	163
Part III Thioureas, Thiosemicarbazides, Thioamides, Thiono- and Dithio-carboxylic Acids, and their Selenium Analogues	165
<i>By J. K. Landquist</i>	
Reviews	165
1 Thioureas and Selenoureas	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
2 Thiosemicarbazides, Dithiocarbazates, and Thiocarbohydrazides	174
Synthesis	174
Physical Properties	174
Reactions	175

3 Thioamides and Selenoamides	177
Synthesis	177
Physical Properties	180
Reactions	182
Hydrolysis	182
Oxidation	182
Alkylation and Arylation	183
Nucleophilic Reactions of the α -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
4 Thiono- and Dithio-carboxylic Acids, their Derivatives, and their Selenium Analogues	189
Synthesis of Derivatives of Thionocarboxylic Acids	189
Synthesis of Dithiocarboxylic Acids and their Derivatives	191
Physical Properties	194
Reactions	194
5 Thio- and Dithio-carbamates	197
Synthesis	197
Physical Properties	199
Reactions	199
6 Xanthates and Trithiocarbonates	203
Preparation	203
Physical Properties	204
Reactions	204
 Chapter 4 Small-ring Compounds of Sulphur and Selenium	207
<i>By C. G. Venier</i>	
1 Thiirans (Episulphides)	207
Reviews	207
Formation	207
Reactions	210
2 Thiiran Oxides (Episulphoxides and Episulphones)	215
3 Thiiranium Ions (Episulphonium Ions)	215
4 Thiirens and Thiiren Oxides	216
5 Three-membered Rings with More than One Heteroatom	218
6 Thietans	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 <i>P. K. Claus</i>	
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^{II}-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 λ^4 -thiapentalenes and Related Systems** 299
Synthesis 299
Structural and Spectroscopic Studies 300
'Bond Switch' at π -Hypervalent Sulphur 301