

**Volume 22:
Three Carbon–Heteroatom Bonds: Thio-, Seleno-, and
Tellurocarboxylic Acids and Derivatives; Imidic Acids
and Derivatives; Ortho Acid Derivatives**

	Preface	V
	Table of Contents	IX
22	Introduction	
	André B. Charette	1
22.1	Product Class 1: Thiocarboxylic Acids and Derivatives	
22.1.1	Product Subclass 1: α-Substituted Sulfur Ylides	
	V. K. Aggarwal, J. Richardson, and C. L. Winn	11
22.1.2	Product Subclass 2: Thioacyl Halides	
	R. S. Glass	75
22.1.3	Product Subclass 3: Thiocarboxylic O-Acid Esters	
	R. S. Glass	85
22.1.4	Product Subclass 4: Dithiocarboxylic Acid Esters	
	R. S. Glass	109
22.1.5	Product Subclass 5: Selenothiocarboxylic Se-Acid Esters	
	R. S. Glass	133
22.1.6	Product Subclass 6: Tellurothiocarboxylic Te-Acid Esters	
	R. S. Glass	139
22.1.7	Product Subclass 7: Thioamides	
	H. Lebel	141
22.2	Product Class 2: Selenocarboxylic Acids and Derivatives	
	T. Wirth	181
22.3	Product Class 3: Tellurocarboxylic Acids and Derivatives	
	T. Murai	213
22.4	Product Class 4: Imidic Acids and Derivatives	
22.4.1	Product Subclass 1: Carbon-Substituted Iminium Salts	
	S. Cicchi and F. M. Cordero	221
22.4.2	Product Subclass 2: C-Heteroatom-Substituted Nitrones, Other Dipoles	
	F. M. Cordero and S. Cicchi	267
22.4.3	Product Subclass 3: Imidoyl (Imino) Halides	
	N. Nakajima and M. Ubukata	331
22.4.4	Product Subclass 4: Imidates	
	N. Nakajima and M. Ubukata	343

22.4.5	Product Subclass 5: Thioimidates and Their Derivatives N. Nakajima and M. Ubukata	361
22.4.6	Product Subclass 6: Selenoimidates (Imidoselenoates) and Derivatives N. Nakajima and M. Ubukata	367
22.4.7	Product Subclass 7: Telluroimidates (Imidotelluroates) and Derivatives N. Nakajima and M. Ubukata	375
22.4.8	Product Subclass 8: <i>N</i>-Alkyl-, <i>N</i>-Aryl-, and <i>N</i>-Hetaryl-Substituted Amidines (Imidamides) K. Ostrowska and A. Kolasa	379
22.4.9	Product Subclass 9: Amidines (Imidamides) <i>N</i>-Substituted by Metals, Halogens, Oxygen, and Other Heteroatoms K. Ostrowska and A. Kolasa	489
22.5	Product Class 5: 2-Functionalized Alkylidenephosphines R. A. Aitken	565
22.6	Product Class 6: 2-Functionalized Arsaalkenes and α-Functionalized Arsonium Ylides R. A. Aitken	601
22.7	Product Class 7: Ortho Acid Derivatives	
22.7.1	Product Subclass 1: Trihalomethyl Compounds G. K. S. Prakash and J. Hu	617
22.7.2	Product Subclass 2: Ortho Esters and Halogenated Derivatives H. Lebel and M. Grenon	669
22.7.3	Product Subclass 3: Trithioortho Esters and Halogenated Derivatives H. Lebel and M. Grenon	749
22.7.4	Product Subclass 4: Triselenoortho Esters and Halogenated Derivatives H. Lebel and M. Grenon	775
22.7.5	Product Subclass 5: Tritelluroortho Esters and Halogenated Derivatives H. Lebel and M. Grenon	789
22.7.6	Product Subclass 6: Ortho Amides (Alkane-1,1,1-triamines) W. Kantlehner	795
22.7.7	Product Subclass 7: Tris(diorganophosphino)methanes and Derivatives W. Kantlehner	843
	Keyword Index	851
	Author Index	887
	Abbreviations	945

Table of Contents

22	Introduction André B. Charette	
22	Introduction	1
22.1	Product Class 1: Thiocarboxylic Acids and Derivatives	
22.1.1	Product Subclass 1: α-Substituted Sulfur Ylides V. K. Aggarwal, J. Richardson, and C. L. Winn	
22.1.1	Product Subclass 1: α-Substituted Sulfur Ylides	11
22.1.1.1	Synthesis of Product Subclass 1	13
22.1.1.1.1	Silicon-, Tin-, and Germanium-Substituted Sulfur Ylides	13
22.1.1.1.1.1	Method 1: Deprotonation of Sulfonium and Sulfoxonium Salts	14
22.1.1.1.1.2	Method 2: Hydrogen Atom Substitution of Lesser Functionalized Sulfur Ylides	15
22.1.1.1.1.2.1	Variation 1: Hydrogen Atom Substitution Using Chloro(methyl)silanes, -germanes, and -stannanes	15
22.1.1.1.1.3	Method 3: Synthesis from Carbenes	16
22.1.1.1.1.3.1	Variation 1: Transition-Metal-Catalyzed Decomposition of Diazo Compounds	17
22.1.1.1.1.4	Method 4: 1,3-Elimination Reactions	18
22.1.1.1.1.4.1	Variation 1: Thermolysis of [Bromo(trimethylsilyl)methyl] [(Trimethylsilyl)methyl] Sulfides	18
22.1.1.1.1.5	Method 5: Modification of Existing Ylides	18
22.1.1.1.2	Halogen-Substituted Sulfur Ylides	19
22.1.1.1.2.1	Method 1: Deprotonation of Sulfonium and Sulfoxonium Salts	19
22.1.1.1.2.2	Method 2: Hydrogen Atom Substitution of Lesser Functionalized Sulfur Ylides	21
22.1.1.1.2.2.1	Variation 1: Replacement with a Halogen Atom	21
22.1.1.1.2.2.2	Variation 2: Replacement with Other Functional Groups	22
22.1.1.1.2.3	Method 3: Synthesis from Carbenes	22
22.1.1.1.2.3.1	Variation 1: By Reaction with Dihalocarbenes	22
22.1.1.1.2.3.2	Variation 2: From Monohalocarbenes	25
22.1.1.1.3	Oxygen-Substituted Sulfur Ylides	25
22.1.1.1.4	Sulfur-Substituted Sulfur Ylides	26
22.1.1.1.4.1	Method 1: Deprotonation of Sulfonium and Sulfoxonium Salts	27
22.1.1.1.4.2	Method 2: Hydrogen Atom Substitution of Lesser Functionalized Sulfur Ylides	29
22.1.1.1.4.2.1	Variation 1: With Sulfur-Based Electrophiles	29
22.1.1.1.4.2.2	Variation 2: With Carbon-Based Electrophiles	31
22.1.1.1.4.3	Method 3: Synthesis from Carbenes	31
22.1.1.1.4.3.1	Variation 1: Photolytic Decomposition of Diazo Compounds	31

22.1.1.1.4.3.2	Variation 2:	Thermolysis of Diazo Compounds	32
22.1.1.1.4.3.3	Variation 3:	Metal-Catalyzed Decomposition of Diazo Compounds	32
22.1.1.1.4.3.4	Variation 4:	By Transylidation	32
22.1.1.1.4.3.5	Variation 5:	From Other Carbene Sources	35
22.1.1.1.4.4	Method 4:	Reaction of C—H Acidic Compounds with Sulfonium Salts Bearing a Leaving Group	35
22.1.1.1.4.5	Method 5:	Addition of Sulfoxides to 1-[(Trifluoromethyl)sulfonyl]alkynes	37
22.1.1.1.4.6	Method 6:	Hydrolysis of Tetrathiafulvenium Salts	37
22.1.1.1.5		Selenium-Substituted Sulfur Ylides	38
22.1.1.1.5.1	Method 1:	Reaction of “Onium” Salts with Activated Sulfoxides or Selenoxides	38
22.1.1.1.5.1.1	Variation 1:	From Sulfoxides	38
22.1.1.1.5.1.2	Variation 2:	From Selenoxides	39
22.1.1.1.6		Nitrogen-Substituted Sulfur Ylides	39
22.1.1.1.6.1	Method 1:	Deprotonation of Sulfonium and Sulfoxonium Salts	40
22.1.1.1.6.2	Method 2:	Hydrogen Atom Substitution of Lesser Functionalized Sulfur Ylides	40
22.1.1.1.6.3	Method 3:	Reaction of Sulfides with Dibromo(nitro)acetonitrile	41
22.1.1.1.6.4	Method 4:	Synthesis from Carbenes	41
22.1.1.1.6.4.1	Variation 1:	By Transylidation	41
22.1.1.1.6.5	Method 5:	Reaction of Activated Sulfoxides with C—H Acidic Compounds	42
22.1.1.1.7		Phosphorus-Substituted Sulfur Ylides	44
22.1.1.1.7.1	Method 1:	Deprotonation of Sulfonium and Sulfoxonium Salts	44
22.1.1.1.7.1.1	Variation 1:	α -Phosphorus(III)-Substituted Sulfonium Ylides	44
22.1.1.1.7.1.2	Variation 2:	α -Phosphorus(V)-Substituted Sulfonium Ylides	45
22.1.1.1.7.2	Method 2:	Hydrogen Atom Substitution of Lesser Functionalized Sulfur Ylides	45
22.1.1.1.7.2.1	Variation 1:	α -Phosphorus(III)-Substituted Sulfur Ylides	46
22.1.1.1.7.2.2	Variation 2:	α -Phosphorus(V)-Substituted Ylides	46
22.1.1.1.7.3	Method 3:	Synthesis from Carbenes	48
22.1.1.1.7.3.1	Variation 1:	α -Phosphorus(III)-Substituted Sulfur Ylides	48
22.1.1.1.7.3.2	Variation 2:	α -Phosphorus(V)-Substituted Sulfur Ylides	48
22.1.1.1.7.4	Method 4:	Reaction of C—H Acidic Compounds with Sulfonium Salts Bearing a Leaving Group	49
22.1.1.1.7.4.1	Variation 1:	Phosphorus(III)-Substituted Sulfonium Ylides	49
22.1.1.1.7.4.2	Variation 2:	Phosphorus(V)-Substituted Sulfonium Ylides	50
22.1.1.1.7.5	Method 5:	Alkylation of α -(Alkylsulfanyl) Phosphorus Ylides	50
22.1.1.1.7.6	Method 6:	Synthesis by Modification of a Heteroatom Once Attached	50
22.1.1.2		Applications of Product Subclass 1 in Organic Synthesis	51
22.1.1.2.1		Silicon-, Tin-, and Germanium-Substituted Sulfur Ylides	51
22.1.1.2.1.1	Method 1:	Reactions with Carbonyl Compounds	52
22.1.1.2.1.2	Method 2:	Reactions with Electron-Deficient Alkenes	52
22.1.1.2.1.3	Method 3:	Rearrangement Reactions	52
22.1.1.2.1.4	Method 4:	Cycloaddition Reactions	55

22.1.1.2.2	Halogen-Substituted Sulfur Ylides	56
22.1.1.2.2.1	Method 1: 1,3-Electrocyclization Reactions	56
22.1.1.2.2.2	Method 2: Preparation of α -Hydroxy Aldehydes and Acetals	57
22.1.1.2.2.3	Method 3: Rearrangement Reactions	58
22.1.1.2.3	Sulfur-Substituted Sulfur Ylides	59
22.1.1.2.3.1	Method 1: Rearrangement Reactions	60
22.1.1.2.3.2	Method 2: Reactions with Aldehydes	60
22.1.1.2.3.3	Method 3: Reactions with Electron-Deficient Alkenes	61
22.1.1.2.3.4	Method 4: Cycloreversion Reactions	62
22.1.1.2.3.5	Method 5: Hydrolysis Reactions	63
22.1.1.2.4	Selenium-Substituted Sulfur Ylides	64
22.1.1.2.4.1	Methods 1: Miscellaneous Applications	64
22.1.1.2.5	Nitrogen-Substituted Sulfur Ylides	64
22.1.1.2.5.1	Methods 1: Miscellaneous Applications	64
22.1.1.2.6	Phosphorus-Substituted Sulfur Ylides	66
22.1.1.2.6.1	Method 1: Reactions with Aldehydes	66
22.1.1.2.6.2	Method 2: Reaction with Electron-Deficient Alkenes	67
22.1.1.2.6.3	Method 3: Rearrangement Reactions	68
22.1.1.2.6.4	Methods 4: Miscellaneous Applications	68
22.1.2	Product Subclass 2: Thioacyl Halides R. S. Glass	
22.1.2	Product Subclass 2: Thioacyl Halides	75
22.1.2.1	Synthesis of Product Subclass 2	76
22.1.2.1.1	Method 1: Sulfuration	76
22.1.2.1.2	Method 2: Dehalogenation of Haloalkanesulfonyl Chlorides	76
22.1.2.1.3	Method 3: By Substitution of Dithiocarboxylic Acids	77
22.1.2.1.4	Method 4: By Nucleophilic Substitution of Thiophosgene	77
22.1.2.1.5	Method 5: By C–S Cleavage of α -Thioether Cations	78
22.1.2.2	Applications of Product Subclass 2 in Organic Synthesis	79
22.1.2.2.1	Method 1: Acyl Nucleophilic Substitution	79
22.1.2.2.2	Method 2: Reductive Dimerization	79
22.1.2.2.3	Method 3: Friedel–Crafts Thioacylation	80
22.1.2.2.4	Method 4: Cycloaddition Reactions	81
22.1.2.2.5	Method 5: Oxidation	81
22.1.3	Product Subclass 3: Thiocarboxylic O-Acid Esters R. S. Glass	
22.1.3	Product Subclass 3: Thiocarboxylic O-Acid Esters	85
22.1.3.1	Synthesis of Product Subclass 3	85
22.1.3.1.1	Method 1: Thioacylation of Alcohols	85

22.1.3.1.1.1	Variation 1:	Thioacylation of Alcohols with Thioaroyl Chlorides	86
22.1.3.1.1.2	Variation 2:	Thioacylation of Alcohols with Nitro(thioacyl)benzotriazoles	86
22.1.3.1.2	Method 2:	Thionation of Esters	87
22.1.3.1.2.1	Variation 1:	By Thionation of Esters with Lawesson's Reagent	87
22.1.3.1.2.2	Variation 2:	By Microwave Irradiation with Lawesson's Reagent	88
22.1.3.1.2.3	Variation 3:	With Phosphorus Pentasulfide and Hexamethyldisiloxane	89
22.1.3.1.3	Method 3:	Thiolysis of Imino Ethers	90
22.1.3.1.3.1	Variation 1:	From Carboxamides	90
22.1.3.1.3.2	Variation 2:	From Nitriles	91
22.1.3.1.4	Method 4:	Alkoxythiocarboxylation of Enolates	92
22.1.3.1.5	Method 5:	Elimination of Monothioacetal Derivatives	93
22.1.3.1.5.1	Variation 1:	Photochemical Elimination	93
22.1.3.1.5.2	Variation 2:	Thermolysis of Thiosulfates	94
22.1.3.2	Applications of Product Subclass 3 in Organic Synthesis		94
22.1.3.2.1	Method 1:	Thioacylation	94
22.1.3.2.2	Method 2:	Nucleophilic Addition	95
22.1.3.2.2.1	Variation 1:	Redox Glycosidation	95
22.1.3.2.2.2	Variation 2:	Organometallic Addition and Methylation	97
22.1.3.2.3	Method 3:	Synthesis of Heterocycles	98
22.1.3.2.4	Method 4:	Enolate Reactions	98
22.1.3.2.4.1	Variation 1:	Claisen Rearrangement	98
22.1.3.2.4.2	Variation 2:	Aldol Addition	99
22.1.3.2.4.3	Variation 3:	Michael Addition	100
22.1.3.2.4.4	Variation 4:	Horner–Emmons Reaction	100
22.1.3.2.5	Method 5:	Cycloaddition Reactions	101
22.1.3.2.5.1	Variation 1:	Diels–Alder 2π -Components	101
22.1.3.2.5.2	Variation 2:	Diels–Alder 4π -Components	102
22.1.3.2.5.3	Variation 3:	1,3-Dipolar Cycloaddition Reactions	102
22.1.3.2.5.4	Variation 4:	Photochemical [2 + 2] Cycloaddition	103
22.1.3.2.6	Method 6:	Reductive Desulfurization	103
22.1.3.2.6.1	Variation 1:	Reductive Desulfurization with Triphenyltin Hydride	103
22.1.3.2.6.2	Variation 2:	Reductive Desulfurization with Tributyltin Hydride	104
22.1.3.2.7	Method 7:	Reductive Dimerization	105
22.1.3.2.8	Method 8:	Barton–McCombie Deoxygenation of Secondary Alcohols	105
22.1.3.2.9	Method 9:	Fluorinative Desulfurization	106

22.1.4 Product Subclass 4: Dithiocarboxylic Acid Esters

R. S. Glass

22.1.4	Product Subclass 4: Dithiocarboxylic Acid Esters		109
22.1.4.1	Synthesis of Product Subclass 4		109
22.1.4.1.1	Method 1:	Thioacylation of Thiols	109
22.1.4.1.2	Method 2:	Thionation of Carboxylic Acids	110
22.1.4.1.3	Method 3:	Thiolysis of Imino Thioethers	111
22.1.4.1.4	Method 4:	Dithiocarboxylation	112
22.1.4.1.4.1	Variation 1:	Dithiocarboxylation of Grignard Reagents	112
22.1.4.1.4.2	Variation 2:	Dithiocarboxylation of Sulfone α -Carbanions	113

22.1.4.1.4.3	Variation 3:	Dithiocarboxyalkylation	114
22.1.4.1.5	Method 5:	Friedel–Crafts Alkyldithiocarboxylation	115
22.1.4.1.6	Method 6:	Bromination of Tin Dithiocarboxylates	116
22.1.4.1.7	Method 7:	Reaction of Dithiocarboxylates with Halophosphines, Thiophosphinic Chloride, and Selenophosphinic Chloride	116
22.1.4.1.8	Method 8:	Acylation of Dithiophosphoric Acids	117
22.1.4.1.9	Method 9:	Amination of Arenedithiocarboxylates	118
22.1.4.2	Applications of Product Subclass 4 in Organic Synthesis		118
22.1.4.2.1	Method 1:	Thioacylation	118
22.1.4.2.1.1	Variation 1:	Aminolysis of Dithioesters	118
22.1.4.2.1.2	Variation 2:	Aminolysis of <i>S</i> -Thioacyl Dithiophosphates	119
22.1.4.2.1.3	Variation 3:	Synthesis of Thiohydroxamic Acids	120
22.1.4.2.2	Method 2:	Addition of Organometallic Reagents	120
22.1.4.2.2.1	Variation 1:	Carbophilic Addition of Grignard Reagents	120
22.1.4.2.2.2	Variation 2:	Thiophilic Addition of Grignard Reagents	121
22.1.4.2.3	Method 3:	Synthesis of 5-Aryl-1,4,2-dithiazolium Salts	122
22.1.4.2.4	Method 4:	Synthesis of Penems	123
22.1.4.2.5	Method 5:	Enethiolates and Ketene Dithioacetals	123
22.1.4.2.5.1	Variation 1:	<i>S</i> -Alkylation and <i>S</i> -Silylation of Enethiolates	124
22.1.4.2.5.2	Variation 2:	Aldol Addition	125
22.1.4.2.5.3	Variation 3:	Addition to Imines	125
22.1.4.2.5.4	Variation 4:	Addition to Azodicarboxylates	126
22.1.4.2.5.5	Variation 5:	Michael Addition	127
22.1.4.2.6	Method 6:	Cycloaddition Reactions	128
22.1.4.2.6.1	Variation 1:	Diels–Alder Cycloaddition Reactions	128
22.1.4.2.6.2	Variation 2:	1,3-Dipolar Cycloaddition with Diazomethane	129
22.1.4.2.6.3	Variation 3:	1,3-Dipolar Cycloaddition with Phenyl Azide	130
22.1.4.2.7	Method 7:	Oxidation	130
22.1.5	Product Subclass 5: Selenothiocarboxylic Se-Acid Esters		
	R. S. Glass		
22.1.5	Product Subclass 5: Selenothiocarboxylic Se-Acid Esters		133
22.1.5.1	Synthesis of Product Subclass 5		133
22.1.5.1.1	Method 1:	Thioacylation of Areneselenolates	133
22.1.5.1.1.1	Variation 1:	Thioacylation with Thioacyl Chlorides	133
22.1.5.1.1.2	Variation 2:	Thioacylation with Bis(thioacyl) Sulfides	133
22.1.5.1.2	Method 2:	Reaction of Thiocarboxylic <i>O</i> -Acid Esters with Dialkylaluminum Alkaneselenolates	134
22.1.5.1.3	Method 3:	Se-Alkylation of Selenothioates	134
22.1.5.1.4	Method 4:	Sulfuration of a Selanylamine	135
22.1.5.2	Applications of Product Subclass 5 in Organic Synthesis		135
22.1.5.2.1	Method 1:	Thioacylation	135
22.1.5.2.2	Method 2:	Alkylation of Enethiolates	135
22.1.5.2.3	Method 3:	Oxidation	136

22.1.6	Product Subclass 6: Tellurothiocarboxylic Te-Acid Esters R. S. Glass	
22.1.6	Product Subclass 6: Tellurothiocarboxylic Te-Acid Esters	139
22.1.6.1	Synthesis of Product Subclass 6	139
22.1.6.1.1	Method 1: Thionation of Telluroesters	139
22.1.7	Product Subclass 7: Thioamides H. Lebel	
22.1.7	Product Subclass 7: Thioamides	141
22.1.7.1	Synthesis of Product Subclass 7	142
22.1.7.1.1	Method 1: Sulfurization of Amides by Tetraphosphorus Decasulfide	142
22.1.7.1.1.1	Variation 1: With Sodium Carbonate as an Activator	143
22.1.7.1.1.2	Variation 2: With Ultrasonic Irradiation	144
22.1.7.1.1.3	Variation 3: With Hexamethyldisiloxane	145
22.1.7.1.2	Method 2: Sulfurization of Amides	146
22.1.7.1.2.1	Variation 1: With Lawesson's Reagent	146
22.1.7.1.2.2	Variation 2: With Belleau's Reagent	149
22.1.7.1.3	Method 3: Thioamidation of Carboxylic Acids	151
22.1.7.1.4	Method 4: Thiolytic of Imidoyl Chlorides	151
22.1.7.1.4.1	Variation 1: With Hexamethyldisilathiane	151
22.1.7.1.4.2	Variation 2: With Benzyltriethylammonium Tetrathiomolybdate	152
22.1.7.1.5	Method 5: Thiolytic of Pyridinium Imidates	153
22.1.7.1.6	Method 6: Thiolytic of Dihydrooxazoles	155
22.1.7.1.7	Method 7: Thiolytic of Amidines	155
22.1.7.1.8	Method 8: Thiolytic of Nitriles	156
22.1.7.1.8.1	Variation 1: With Hydrogen Sulfide	156
22.1.7.1.8.2	Variation 2: With Ammonium Sulfide	157
22.1.7.1.8.3	Variation 3: With Sodium Trimethylsilanethiolate	157
22.1.7.1.8.4	Variation 4: With Thioacetic Acid	158
22.1.7.1.8.5	Variation 5: With Phosphorus Decasulfide	159
22.1.7.1.8.6	Variation 6: With Diethyl Dithiophosphate	160
22.1.7.1.9	Method 9: Addition of Nucleophiles to Isothiocyanates	160
22.1.7.1.9.1	Variation 1: Addition of Enamines	161
22.1.7.1.9.2	Variation 2: Addition of Ketene Acetals	161
22.1.7.1.9.3	Variation 3: Addition of Enolates	162
22.1.7.1.9.4	Variation 4: Addition of Grignard Reagents	163
22.1.7.1.9.5	Variation 5: Addition of Organolithium Reagents	163
22.1.7.1.9.6	Variation 6: Addition of Trimethyl(trifluoromethyl)silane	163
22.1.7.1.9.7	Variation 7: Via Friedel–Crafts Procedures	164
22.1.7.1.9.8	Variation 8: Via Organosamarium Complexes	165
22.1.7.1.9.9	Variation 9: Via Radical Cyclization	165
22.1.7.1.10	Method 10: Addition of Nucleophiles to Thiocarbamoyl Chlorides	166
22.1.7.1.11	Method 11: Addition of Nucleophiles to Thiuram Monosulfides	167
22.1.7.1.12	Method 12: Thioacylation of Amines	167
22.1.7.1.12.1	Variation 1: With <i>O</i> -Alkyl Thiocarboxylates	167

22.1.7.1.12.2	Variation 2:	With Dithiocarboxylates	168
22.1.7.1.12.3	Variation 3:	With Carbon Disulfide	169
22.1.7.1.13	Method 13:	Transamidation of Thioamides	169
22.1.7.1.13.1	Variation 1:	With Thioacylated Benzotriazoles	170
22.1.7.1.13.2	Variation 2:	With Thioacylated Benzimidazolones	171
22.1.7.1.13.3	Variation 3:	With Thioacylated <i>N</i> -Phthalimides	171
22.1.7.1.14	Method 14:	Synthesis from Ketones by the Willgerodt–Kindler Reaction	172
22.2	Product Class 2: Selenocarboxylic Acids and Derivatives		
	T. Wirth		
22.2	Product Class 2: Selenocarboxylic Acids and Derivatives		
22.2.1	Product Subclass 1: Selenocarboxylic Acids with Selenium in Higher Oxidation States		
22.2.2	Product Subclass 2: Selenocarbonyl Halides		
22.2.2.1	Synthesis of Product Subclass 2		
22.2.2.1.1	Method 1:	Reaction of Bis(perfluoroalkylselanyl)mercury(II) Compounds with Lewis Acids	182
22.2.2.1.2	Method 2:	Synthesis by Flash-Vacuum Pyrolysis	183
22.2.3	Product Subclass 3: Chalcosenocarboxylic Acids		
22.2.3.1	Synthesis of Product Subclass 3		
22.2.3.1.1	Method 1:	Reaction of Imidates	183
22.2.3.1.1.1	Variation 1:	With Hydrogen Selenide	183
22.2.3.1.1.2	Variation 2:	With Sodium Hydrogen Selenide	184
22.2.3.1.2	Method 2:	Reaction of Ketene Acetals with Hydrogen Selenide	185
22.2.3.1.3	Method 3:	Reaction of Alkyneselenolates and Alkyneselenols	186
22.2.3.1.4	Method 4:	Reaction of Chromium–Carbene Complexes with Selenium	187
22.2.3.1.5	Method 5:	Reaction of Esters and Ortho Esters	188
22.2.3.1.6	Method 6:	Reactions with Carbon Diselenide	188
22.2.3.1.7	Method 7:	Synthesis by Transesterification or Isomerization	189
22.2.3.2	Applications of Product Subclass 3 in Organic Synthesis		
22.2.3.2.1	Method 1:	Reaction with Nucleophiles	190
22.2.3.2.2	Method 2:	Reaction with Electrophiles	191
22.2.4	Product Subclass 4: Selenoamides		
22.2.4.1	Synthesis of Product Subclass 4		
22.2.4.1.1	Method 1:	Reaction of Amides	191
22.2.4.1.1.1	Variation 1:	With Phosphorus Pentaselenide	191
22.2.4.1.1.2	Variation 2:	With Hexamethyldisilaselene	192
22.2.4.1.1.3	Variation 3:	With Selenium and Diisobutylaluminum Hydride	193
22.2.4.1.1.4	Variation 4:	With Cyclic Phosphorus-Containing Reagents	193
22.2.4.1.2	Method 2:	Reaction of Nitriles	194
22.2.4.1.2.1	Variation 1:	With Elemental Selenium and Carbon Monoxide	194
22.2.4.1.2.2	Variation 2:	With Elemental Selenium and Sodium Borohydride	195
22.2.4.1.2.3	Variation 3:	With Aluminum Selenide	195

22.2.4.1.2.4	Variation 4:	With Hexamethyldisilaselenane	196
22.2.4.1.3	Method 3:	Reaction of Amidines or Amidinium Salts	197
22.2.4.1.3.1	Variation 1:	Reaction of Imines	197
22.2.4.1.3.2	Variation 2:	Reaction via Chloroiminium Salts	197
22.2.4.1.3.3	Variation 3:	Reaction via Imidothiocarbamates	199
22.2.4.1.4	Method 4:	Reaction of Alkyneselenolates or Alkyneselenols	199
22.2.4.1.4.1	Variation 1:	Reaction of Alkyneselenolates Synthesized from Alkynes	200
22.2.4.1.4.2	Variation 2:	Reaction of Alkyneselenolates Synthesized from 1,2,3-Selenadiazoles	200
22.2.4.1.5	Method 5:	Reaction of Isoselenocyanates	201
22.2.4.1.5.1	Variation 1:	With Alcohols	201
22.2.4.1.5.2	Variation 2:	With Amines	202
22.2.4.1.6	Method 6:	Synthesis by Transesterification	203
22.2.4.1.6.1	Variation 1:	From <i>O</i> -Alkyl Selenoates or <i>S</i> -Alkyl Selenothioates	203
22.2.4.1.6.2	Variation 2:	From Triselenocarbonates	204
22.2.4.1.7	Method 7:	Synthesis via α -Amino-Substituted Diphenylphosphine Oxide Anions	204
22.2.4.1.8	Method 8:	Synthesis via Cycloreversion of Oxaselenazines	205
22.2.4.1.9	Method 9:	Reaction of 1,1-Dihaloalkanes with Elemental Selenium	206
22.2.4.1.10	Method 10:	Synthesis from Ynamines	207
22.2.4.1.10.1	Variation 1:	Using Elemental Selenium	207
22.2.4.1.10.2	Variation 2:	Using Metal Complexes of Selenocarbonyl Compounds	207
22.2.4.2	Applications of Product Subclass 4 in Organic Synthesis		208
22.2.4.2.1	Method 1:	Reaction with Nucleophiles	208
22.2.4.2.2	Method 2:	Reaction with Electrophiles	208

22.3 Product Class 3: Tellurocarboxylic Acids and Derivatives

T. Murai

22.3	Product Class 3: Tellurocarboxylic Acids and Derivatives		213
22.3.1	Product Subclass 1: Tellurocarbonyl Halides		213
22.3.1.1	Synthesis of Product Subclass 1		213
22.3.1.1.1	Method 1:	Elimination of a Fluorostannane from a Tellanylstannane	213
22.3.2	Product Subclass 2: Tellurocarboxylic <i>O</i>-Acids and <i>O</i>-Esters		214
22.3.2.1	Synthesis of Product Subclass 2		214
22.3.2.1.1	Method 1:	Addition of Sodium Telluride to Oxoiminium Salts	214
22.3.3	Product Subclass 3: Telluroformamides		215
22.3.3.1	Synthesis of Product Subclass 3		216
22.3.3.1.1	Method 1:	Reaction of a Dialuminum Telluride with Formamides	216
22.3.3.1.1.1	Variation 1:	Reaction of Tellurium and Diisobutylaluminum Hydride with Formamides	216
22.3.3.2	Applications of Product Subclass 3 in Organic Synthesis		217
22.3.3.2.1	Method 1:	Reaction of a Telluroformamide with Pentacarbonyl- chromium–Pyridine Complex	217

22.3.4	Product Subclass 4: Telluroamides	217
22.3.4.1	Synthesis of Product Subclass 4	217
22.3.4.1.1	Method 1: Reaction of a Sulfanyliminium Salt with Hydrogen Telluride ..	217
22.3.4.1.2	Method 2: Reaction of a Dialuminum Telluride with a Cyclic Amide	218
22.3.4.1.3	Method 3: Reaction of Selanyliminium Salt with Lithium Aluminum Hydride and Elemental Tellurium	218
22.4	Product Class 4: Imidic Acids and Derivatives	
22.4.1	Product Subclass 1: Carbon-Substituted Iminium Salts S. Cicchi and F. M. Cordero	
22.4.1	Product Subclass 1: Carbon-Substituted Iminium Salts	221
22.4.1.1	Synthesis of Product Subclass 1	221
22.4.1.1.1	Halomethaniminium Salts	221
22.4.1.1.1.1	Method 1: Halogenation of Amides	222
22.4.1.1.1.2	Method 2: Reaction of (Dichloromethylene)dimethylammonium Chloride	224
22.4.1.1.1.3	Methods 3: Additional Methods	226
22.4.1.1.2	Alkoxyethaniminium Salts	227
22.4.1.1.2.1	Method 1: Reaction of Other Methaniminium Salts	227
22.4.1.1.2.1.1	Variation 1: Reaction of Alcohols with Trifluoromethanesulfonic Anhydride–Amide Adducts	227
22.4.1.1.2.1.2	Variation 2: Reaction of Alcohols with the Benzoyl Chloride–Dimethylformamide Adduct	228
22.4.1.1.2.1.3	Variation 3: Reaction of Alcohols with <i>N</i> -Acylamidinium Salts	229
22.4.1.1.2.1.4	Variation 4: Reaction of Oximes with <i>N</i> -Acylamidinium Salts	230
22.4.1.1.2.2	Method 2: Reaction of Nitrilium Salts	230
22.4.1.1.2.2.1	Variation 1: With Aromatic Aldehydes	230
22.4.1.1.2.2.2	Variation 2: With α,β -Unsaturated Carbonyl Compounds	231
22.4.1.1.2.3	Method 3: <i>O</i> -Alkylation of Amides and Lactams	232
22.4.1.1.2.3.1	Variation 1: With Methyl Sulfonates	232
22.4.1.1.2.3.2	Variation 2: With Dimethyl Sulfate	233
22.4.1.1.2.3.3	Variation 3: With Sulfonium Salts	233
22.4.1.1.2.3.4	Variation 4: With Oxonium Salts	234
22.4.1.1.2.3.5	Variation 5: With Haloalkanes	236
22.4.1.1.2.4	Method 4: <i>N</i> -Alkylation of Imidates	237
22.4.1.1.2.4.1	Variation 1: With Alkyl Sulfonates and Dialkyl Sulfates	237
22.4.1.1.2.4.2	Variation 2: With Haloalkanes	238
22.4.1.1.2.5	Method 5: Electrochemical Oxidation of <i>N,N</i> -Disubstituted Amides	240
22.4.1.1.2.6	Method 6: Ring Expansion of Cyclic Ketones by Reaction with β - and γ -Hydroxy Azides	240
22.4.1.1.2.7	Method 7: Reaction of Alkoxyethaniminium Salts	241
22.4.1.1.3	(Alkylsulfanyl)methaniminium Salts	242
22.4.1.1.3.1	Method 1: Reaction of (Sulfonyloxy)methaniminium Salts with Thiols ..	242
22.4.1.1.3.2	Method 2: <i>S</i> -Alkylation of <i>N,N</i> -Disubstituted Thioamides	243

22.4.1.1.3.2.1	Variation 1:	With (Alk-1-enyl)- λ^3 -iodanes	243
22.4.1.1.3.2.2	Variation 2:	With Alkyl Sulfonates and Dialkyl Sulfates	244
22.4.1.1.3.2.3	Variation 3:	With Oxonium Salts	245
22.4.1.1.3.2.4	Variation 4:	With Haloalkanes	246
22.4.1.1.3.2.5	Variation 5:	Reaction of N-Unsubstituted Thioamides with Aziridines	247
22.4.1.1.3.3	Method 3:	N-Alkylation of Thioimidates with Haloalkanes	248
22.4.1.1.4	Amidinium Salts		249
22.4.1.1.4.1	Method 1:	Reaction of Carboxylic Acid Derivatives with Secondary Amines	249
22.4.1.1.4.1.1	Variation 1:	Reaction of Ortho Esters with Secondary Amines	249
22.4.1.1.4.1.2	Variation 2:	Reaction of Oxonium Salts with Secondary Amines	251
22.4.1.1.4.2	Method 2:	Reaction of Other Methaniminium Salts with Secondary Amines	251
22.4.1.1.4.2.1	Variation 1:	Reaction of Chloromethaniminium Salts	252
22.4.1.1.4.2.2	Variation 2:	Reaction of Alkoxyethaniminium Salts	254
22.4.1.1.4.3	Method 3:	Reaction of Acyl Chlorides with Carbon Monoxide and Imines	255
22.4.1.1.4.4	Method 4:	Cycloaddition of Keteniminium Trifluoromethanesulfonates with Imines	255
22.4.1.1.4.5	Method 5:	Reaction of Nitrilium Salts with Amides and Aminolysis of the Adducts	256
22.4.1.1.4.6	Method 6:	Electrophilic Addition to 1,1-Bis(dialkylamino)alk-1-enes	257
22.4.1.1.4.7	Method 7:	Electrophilic Addition to <i>N'</i> -Thioacyl- and <i>N'</i> -Selenoacylamidines	258
22.4.1.1.4.8	Method 8:	S-Alkylation of Alkyl 3,3-Diaminoprop-2-ene(dithioates)	259
22.4.1.1.4.9	Method 9:	N-Alkylation of Amidines	259
22.4.1.1.4.10	Method 10:	Oxidation of Ethylenetetramines	261
22.4.1.1.4.11	Methods 11:	Additional Methods	262
22.4.2	Product Subclass 2: C-Heteroatom-Substituted Nitrones, Other Dipoles		
	F. M. Cordero and S. Cicchi		
22.4.2	Product Subclass 2: C-Heteroatom-Substituted Nitrones, Other Dipoles		267
22.4.2.1	Synthesis of Product Subclass 2		267
22.4.2.1.1	C-Chloro-Substituted Nitrones		267
22.4.2.1.1.1	Method 1:	Substitution of Aldonitrones	267
22.4.2.1.1.2	Method 2:	Alkylation of 2-Chloroquinoline 1-Oxide	268
22.4.2.1.1.3	Method 3:	Rearrangement of α -Chloro Nitroso Compounds	268
22.4.2.1.2	C-Oxygen-Substituted Nitrones		269
22.4.2.1.2.1	Method 1:	Substitution of C-Chloronitrones	270
22.4.2.1.2.2	Method 2:	Oxidation of N,N-Disubstituted Hydroxylamines	270
22.4.2.1.2.3	Method 3:	Oxidation of Aldonitrones	271
22.4.2.1.2.4	Method 4:	Hydrolysis of 2,2-Dimethoxy-1-phenylethanone Oxime	272
22.4.2.1.2.5	Method 5:	Condensation of Hydroxylamine	273
22.4.2.1.2.5.1	Variation 1:	Condensation of β -Hydroxyamino Alcohols with Ortho Esters	273
22.4.2.1.2.5.2	Variation 2:	Condensation with Amide Acetals	275
22.4.2.1.2.6	Method 6:	Alkylation of Hydroxamic Acids	275

22.4.2.1.2.7	Method 7:	Isomerization of Oxaziridines	277
22.4.2.1.2.8	Method 8:	Acid-Promoted Rearrangement of Nitroso Acetals	279
22.4.2.1.3		C-Sulfonyl- or C-Sulfonyl-Substituted Nitrones	280
22.4.2.1.3.1	Method 1:	Substitution of C-Cyanonitrones	280
22.4.2.1.3.2	Method 2:	Substitution of C-Alkoxynitrones	280
22.4.2.1.3.3	Method 3:	Demethylation of 1-Methoxypyrrolidine-2-thiones	282
22.4.2.1.3.4	Method 4:	N-Alkylation of Oximes	282
22.4.2.1.3.5	Method 5:	Reaction of Thiazolidin-4-ones with Nitrosobenzene	283
22.4.2.1.3.6	Method 6:	Reaction of Nitroalkenes with Ynamines	284
22.4.2.1.3.7	Method 7:	Intramolecular Condensation of an S-Alkyl 4-(Hydroxyamino)butanethioate	285
22.4.2.1.3.8	Method 8:	Alkylation of Thiohydroxamic Acid Derivatives	286
22.4.2.1.3.8.1	Variation 1:	Alkylation of Thiohydroxamic Acid with Alkyl Iodides	286
22.4.2.1.3.8.2	Variation 2:	Reaction of 1-Methoxypyrrolidine-2-thiones with Iodotrimethylsilane	288
22.4.2.1.3.9	Method 9:	Isomerization of a Four-Membered Cyclic Nitron	289
22.4.2.1.4		C-Nitrogen-Substituted Nitrones	289
22.4.2.1.4.1	Method 1:	Substitution of Aldonitrones	289
22.4.2.1.4.2	Method 2:	Substitution of C-Methoxynitrones	291
22.4.2.1.4.3	Method 3:	Oxidation of N,N-Disubstituted Hydroxylamines	292
22.4.2.1.4.4	Method 4:	Dehydrogenation of 2-Amino-N ² -hydroxybenzimidamides	298
22.4.2.1.4.5	Method 5:	Oxidation of Imidamides	299
22.4.2.1.4.6	Method 6:	Oxidation of Imidazolidines	303
22.4.2.1.4.7	Method 7:	Condensation of N-(2-Aminoethyl)hydroxylamines with Ortho Esters	304
22.4.2.1.4.8	Method 8:	Condensation of N-Substituted Hydroxylamines with N-Aryl-Substituted Imidates	305
22.4.2.1.4.9	Method 9:	Condensation of Amino-Substituted N ² -Hydroxyimidamides with Aldehydes	306
22.4.2.1.4.9.1	Variation 1:	Condensation of 2-Amino-N ² -hydrobenzimidamides with Aldehydes	306
22.4.2.1.4.9.2	Variation 2:	Condensation of 3-Amino-N ² -hydroxypropanimidamide and Aldehydes	308
22.4.2.1.4.10	Method 10:	Condensation of 2-(Hydroxyamino)propan-1-one Oximes with Glyoxal Derivatives	310
22.4.2.1.4.11	Method 11:	Reaction of N-Substituted Hydroxylamines with Alkyl Cyanofornates	311
22.4.2.1.4.12	Method 12:	Reactions with Nitroso Compounds	312
22.4.2.1.4.12.1	Variation 1:	Reaction of Nitroso Compounds with N-Methyleneamines	312
22.4.2.1.4.12.2	Variation 2:	Reaction of Nitroso Compounds with (Aryl)(arylamino)acetonitrile	313
22.4.2.1.4.12.3	Variation 3:	Reaction of Nitroso Compounds with Nitrile Oxides or Nitrile Imides	313
22.4.2.1.4.13	Method 13:	Reductive Cyclization of Nitroalkyl Cyanides	315
22.4.2.1.4.13.1	Variation 1:	Reductive Cyclization of 3-, 4-, and 5-Nitroalkyl Cyanides	315
22.4.2.1.4.13.2	Variation 2:	Electrochemical Reduction of 4- and 5-Nitroalkyl Cyanides	317

22.4.2.1.5	C-Phosphorus-Substituted Nitrones	319
22.4.2.1.5.1	Method 1: Substitution of Aldonitrones	319
22.4.2.1.5.2	Method 2: Oxidation of N,N-Disubstituted Hydroxylamines	320
22.4.2.1.6	C-Heteroatom-Substituted Azomethine Ylides	321
22.4.2.1.6.1	Method 1: Synthesis of C-Oxygen- or C-Sulfur-Substituted Azomethine Ylides	321
22.4.2.1.6.1.1	Variation 1: Desilylation of Iminium Salts	321
22.4.2.1.6.1.2	Variation 2: Photochemical Transformation of 2,3-Dihydroisoxazoles	322
22.4.2.1.6.1.3	Variation 3: Rhodium-Catalyzed Transformation of 1-(1-Acylpyrrolidin-2-yl)-2-diazoethanones	323
22.4.2.1.6.2	Method 2: Synthesis of C-Nitrogen-Substituted Azomethine Ylides	324
22.4.2.1.6.2.1	Variation 1: Deprotonation of 1,3-Dialkyl-4,5-dihydro-1 <i>H</i> -imidazolium Bromides	324
22.4.2.1.6.2.2	Variation 2: Nucleophilic Addition to Oxazolium Salts	326
22.4.2.1.7	C-Heteroatom-Substituted Azomethine Imides	326
22.4.2.1.7.1	Method 1: Condensation of Hydrazino Alcohols with Ortho Esters	326
22.4.3	Product Subclass 3: Imidoyl (Imino) Halides N. Nakajima and M. Ubukata	
22.4.3	Product Subclass 3: Imidoyl (Imino) Halides	331
22.4.3.1	Synthesis of Product Subclass 3	331
22.4.3.1.1	Method 1: Oxidation of Aldimines	331
22.4.3.1.2	Method 2: Halogenation of Amides	331
22.4.3.1.2.1	Variation 1: By Halogenating Reagents	331
22.4.3.1.2.2	Variation 2: By Phosphorus-Containing Reagents	333
22.4.3.1.3	Method 3: Addition of Perfluoroalkyl Iodides to Isocyanides	334
22.4.3.1.4	Methods 4: Miscellaneous Methods	334
22.4.3.2	Applications of Product Subclass 3 in Organic Synthesis	335
22.4.3.2.1	Reactions with Nucleophiles	335
22.4.3.2.1.1	Method 1: Alcohol Additions	335
22.4.3.2.1.2	Method 2: Thiol Additions	336
22.4.3.2.1.3	Method 3: Amine Additions	337
22.4.3.2.1.4	Method 4: Addition Reactions with Other Nucleophiles	337
22.4.3.2.1.4.1	Variation 1: Hydride and Organometallic Additions	337
22.4.3.2.1.4.2	Variation 2: Internal Nucleophile Additions	338
22.4.3.2.2	Reactions with Electrophiles	338
22.4.3.2.2.1	Method 1: Reactions with Palladium Complexes (Heck Reaction, Carbonylation, and Cross Coupling)	339
22.4.3.2.2.2	Method 2: Iodine–Metal Exchange Reactions	340
22.4.3.2.3	Radical Reactions	340
22.4.3.2.3.1	Method 1: Synthesis of Heterocyclic Compounds	340

22.4.4	Product Subclass 4: Imidates N. Nakajima and M. Ubukata	
<hr/>		
22.4.4	Product Subclass 4: Imidates	343
22.4.4.1	Synthesis of Product Subclass 4	344
22.4.4.1.1	Method 1: Reaction of Imidoyl Chlorides by Base-Catalyzed Coupling ...	344
22.4.4.1.2	Method 2: Conversion of Amides	344
22.4.4.1.2.1	Variation 1: By Alkylation	344
22.4.4.1.2.2	Variation 2: By Acylation	346
22.4.4.1.3	Method 3: Reaction of Ortho Esters with Amines	346
22.4.4.1.4	Method 4: Coupling of Nitriles and Isocyanides with Alcohols	346
22.4.4.1.4.1	Variation 1: Acid-Catalyzed Coupling (Pinner Synthesis)	347
22.4.4.1.4.2	Variation 2: Base-Catalyzed Coupling	347
22.4.4.1.4.3	Variation 3: Palladium-Catalyzed Reaction	349
22.4.4.1.5	Method 5: Synthesis from Metal Complexes and Organometallics	349
22.4.4.2	Applications of Product Subclass 4 in Organic Synthesis	350
22.4.4.2.1	Method 1: Introduction of Nitrogen Functionality by [3,3]-Sigmatropic Rearrangement	351
22.4.4.2.1.1	Variation 1: Thermal Conditions	351
22.4.4.2.1.2	Variation 2: Metal-Catalyzed Conditions and Asymmetric [3,3]-Sigmatropic Rearrangement	352
22.4.4.2.2	Method 2: Glycosylation	353
22.4.4.2.3	Method 3: Protection Reaction	354
22.4.4.2.4	Method 4: Cyclization	355
22.4.4.2.5	Method 5: Synthesis of Heterocyclic Compounds	356
22.4.5	Product Subclass 5: Thioimidates and Their Derivatives N. Nakajima and M. Ubukata	
<hr/>		
22.4.5	Product Subclass 5: Thioimidates and Their Derivatives	361
22.4.5.1	Synthesis of Product Subclass 5	361
22.4.5.1.1	Method 1: Coupling of Imidoyl Halides	361
22.4.5.1.2	Method 2: Conversion of Thioamides	362
22.4.5.1.2.1	Variation 1: By Alkylation	362
22.4.5.1.2.2	Variation 2: By Acylation	362
22.4.5.1.3	Method 3: Coupling of Nitriles and Isocyanides with Thiols	363
22.4.5.1.3.1	Variation 1: Acid-Catalyzed Coupling	363
22.4.5.1.3.2	Variation 2: Base-Catalyzed Coupling	363
22.4.5.1.4	Method 4: Beckmann Rearrangement	364
22.4.5.2	Applications of Product Subclass 5 in Organic Synthesis	364
22.4.5.2.1	Method 1: Metalation	364
22.4.5.2.2	Method 2: Synthesis of Heterocyclic Compounds	365

22.4.6	Product Subclass 6: Selenoimidates (Imidoselenoates) and Derivatives N. Nakajima and M. Ubukata	
<hr/>		
22.4.6	Product Subclass 6: Selenoimidates (Imidoselenoates) and Derivatives	367
22.4.6.1	Synthesis of Product Subclass 6	367
22.4.6.1.1	Method 1: Conversion of Selenoamides	367
22.4.6.1.2	Method 2: Coupling of Lithiated Hydrocarbons with Selenium and Isocyanate	368
22.4.6.1.3	Method 3: Reactions of Organometallic Compounds	369
22.4.6.2	Applications of Product Subclass 6 in Organic Synthesis	370
22.4.6.2.1	Method 1: Cyclization of Ene Radicals	370
22.4.6.2.2	Method 2: Use as Acyl Radical Synthons	371
22.4.7	Product Subclass 7: Telluroimidates (Imidotelluroates) and Derivatives N. Nakajima and M. Ubukata	
<hr/>		
22.4.7	Product Subclass 7: Telluroimidates (Imidotelluroates) and Derivatives	375
22.4.7.1	Synthesis of Product Subclass 7	375
22.4.7.1.1	Method 1: Displacement of Chloride from Imidoyl Chlorides	375
22.4.7.1.2	Method 2: Reaction of Acyl Tellurides with Isocyanides	375
22.4.7.2	Applications of Product Subclass 7 in Organic Synthesis	376
22.4.7.2.1	Method 1: Photolysis and Indole Derivatives Synthesis	376
22.4.8	Product Subclass 8: <i>N</i>-Alkyl-, <i>N</i>-Aryl-, and <i>N</i>-Hetaryl-Substituted Amidines (Imidamides) K. Ostrowska and A. Kolasa	
<hr/>		
22.4.8	Product Subclass 8: <i>N</i>-Alkyl-, <i>N</i>-Aryl-, and <i>N</i>-Hetaryl-Substituted Amidines (Imidamides)	379
22.4.8.1	Synthesis of Product Subclass 8	379
22.4.8.1.1	From Nitriles and Isocyanides	379
22.4.8.1.1.1	Method 1: Addition of Nitrogen Bases to Nitriles	379
22.4.8.1.1.1.1	Variation 1: Addition of Stoichiometric Amounts of Alkali Metal Amides	381
22.4.8.1.1.1.2	Variation 2: Addition of Amines in the Presence of Alkylolithium or Grignard Reagents	383
22.4.8.1.1.1.3	Variation 3: Addition of Silylimines	385
22.4.8.1.1.1.4	Variation 4: Addition of Ammonia or Amines to Nitriles Substituted with Electron-Withdrawing Groups	386
22.4.8.1.1.2	Method 2: Addition of Ammonia and Its Derivatives to Nitriles via Heterosubstituted Imines (The Pinner Method)	386
22.4.8.1.1.2.1	Variation 1: Modifications of the Classical Pinner Method (via Imidates)	392
22.4.8.1.1.2.2	Variation 2: Modifications of the Classical Pinner Method (via Thioimidates)	395

22.4.8.1.1.3	Method 3:	N-Substituted and N ¹ ,N ¹ -Disubstituted Amidines by Addition of an Amine to a Nitrile Activated by a Lewis Acid ···	396
22.4.8.1.1.4	Method 4:	Variouly Substituted Amidines via Nitrilium Salts ·······	400
22.4.8.1.1.5	Method 5:	Reaction of Nitriles with Azides in the Presence of Samarium(II) Iodide ···········	402
22.4.8.1.1.6	Method 6:	Reaction of Nitriles with Nitroarenes in the Presence of Metals or Metal Salts ···········	403
22.4.8.1.1.7	Method 7:	Cyclic Amidines by Treatment with Catalytic Hydrogen Sulfide, Sulfur, Phosphorus Pentasulfide, or Carbon Disulfide ·	404
22.4.8.1.1.8	Method 8:	Synthesis from Isocyanides ···········	405
22.4.8.1.2	From Cumulenes ···········		411
22.4.8.1.2.1	Method 1:	Synthesis from Isoselenocyanates, Isothiocyanates, or Isocyanates ···········	411
22.4.8.1.2.1.1	Variation 1:	Addition of Amines to Benzimidoyl Isoselenocyanates, Isothiocyanates, or Isocyanates ···········	411
22.4.8.1.2.1.2	Variation 2:	1,3-Dipolar Cycloaddition of Isothiocyanates or Isocyanates ··	412
22.4.8.1.2.1.3	Variation 3:	Semicyclic Amidines Starting from Isothiocyanates or Isocyanates and α - or β -Amino Cyanides ···········	413
22.4.8.1.2.1.4	Variation 4:	Cycloaddition of Isothiocyanates with α - or β -Hydroxy Cyanides ···········	415
22.4.8.1.2.1.5	Variation 5:	Addition of N,N-Disubstituted Amides to Isocyanates ·······	416
22.4.8.1.2.2	Method 2:	Synthesis from Carbodiimides ···········	418
22.4.8.1.2.2.1	Variation 1:	Addition of Various Carbon Nucleophiles to Carbodiimides ··	418
22.4.8.1.2.2.2	Variation 2:	Reduction of Carbodiimides ···········	419
22.4.8.1.2.3	Method 3:	Addition of Amines to Ketenimines ···········	419
22.4.8.1.3	From Carboxylic Acids and Carboxylic Acid Esters ···········		422
22.4.8.1.3.1	Method 1:	Synthesis from Carboxylic Acids ···········	422
22.4.8.1.3.1.1	Variation 1:	Reaction of Carboxylic Acids with Amines Promoted by Polyphosphoric Acid Trimethylsilyl Ester ···········	422
22.4.8.1.3.1.2	Variation 2:	Cyclic Amidines from Carboxylic Acids and Diamines ·······	423
22.4.8.1.3.2	Method 2:	Synthesis from Carboxylic or Dithiocarboxylic Acid Esters ····	424
22.4.8.1.4	From Ortho Esters, Dialkyl(dialkoxymethyl)amines, and <i>tert</i> -Butoxybis(dimethylamino)methane ···········		425
22.4.8.1.4.1	Method 1:	Synthesis from Ortho Esters by Condensation with Amines ··	425
22.4.8.1.4.2	Method 2:	Synthesis from Dialkyl(dialkoxymethyl)amines and <i>tert</i> -Butoxybis(dimethylamino)methane ···········	427
22.4.8.1.4.2.1	Variation 1:	Condensation of Dialkyl(dialkoxymethyl)amines and <i>tert</i> -Butoxybis(dimethylamino)methane ···········	427
22.4.8.1.4.2.2	Variation 2:	Cyclic Amidines by the Reaction of Dialkyl(dialkoxymethyl)amines with Diamines ···········	429
22.4.8.1.5	From Thioamides and Amides ···········		429
22.4.8.1.5.1	Method 1:	Synthesis from Thioamides ···········	429
22.4.8.1.5.1.1	Variation 1:	Reaction of Thioamides with Ammonia or Amines in the Presence of Mercury(II) Oxide or Mercury(II) Salts ·········	431

22.4.8.1.5.1.2	Variation 2:	Reaction of Thioamides Activated by Meerwein's Salt with Amines	432
22.4.8.1.5.2	Method 2:	Synthesis from Amides	434
22.4.8.1.5.2.1	Variation 1:	Amination of Amides via O-Silylated Imidates	435
22.4.8.1.5.2.2	Variation 2:	Amination of Amides via O-Sulfonylated Imidates	435
22.4.8.1.5.2.3	Variation 3:	Amination of Amides via O-Phosphorylated Imidates	437
22.4.8.1.5.2.4	Variation 4:	Reaction of Amides with Activated Amines	438
22.4.8.1.5.2.5	Variation 5:	Reaction of Amides with Azides Using Trisubstituted Phosphines as Activating Agent	438
22.4.8.1.6		From Imidoyl Chlorides	439
22.4.8.1.6.1	Method 1:	Synthesis from Imidoyl Chlorides and Ammonia or Amines ..	439
22.4.8.1.6.2	Method 2:	Synthesis from The Vilsmeier Reagent and Amines or Amides	442
22.4.8.1.7		From Thioimidates and Imidates	444
22.4.8.1.7.1	Method 1:	Synthesis from Amines and Thioimidates or Their Salts	444
22.4.8.1.7.2	Method 2:	Synthesis from Imidates	446
22.4.8.1.7.3	Method 3:	Synthesis from Alkoxyiminium Salts Obtained from Imidates ..	447
22.4.8.1.8		From Amidines	450
22.4.8.1.8.1	Method 1:	Transamination of Amidines	450
22.4.8.1.8.2	Method 2:	Alkylation of Amidines	452
22.4.8.1.8.3	Method 3:	Acylation of Amidines	455
22.4.8.1.8.4	Method 4:	Urea and Thiourea Derivatives of Amidines from Isocyanates or Isothiocyanates	457
22.4.8.1.9		Miscellaneous Syntheses	457
22.4.8.1.9.1	Method 1:	Oxidation of Aminals	457
22.4.8.1.9.2	Method 2:	Reduction of Amidoximes	458
22.4.8.1.9.3	Method 3:	Reduction of Various Compounds with the 1,3-Diaza Skeleton	460
22.4.8.1.9.4	Method 4:	Synthesis from Reagents with a Good Leaving Group	461
22.4.8.1.9.5	Method 5:	Decomposition of Various Nitrogen Heterocyclic Rings	462
22.4.8.1.9.6	Method 6:	Other Methods	464
22.4.9		Product Subclass 9: Amidines (Imidamides) N-Substituted by Metals, Halogens, Oxygen, and Other Heteroatoms K. Ostrowska and A. Kolasa	
22.4.9		Product Subclass 9: Amidines (Imidamides) N-Substituted by Metals, Halogens, Oxygen, and Other Heteroatoms	489
22.4.9.1		Synthesis of Product Subclass 9	489
22.4.9.1.1		N-Silylated, N,N-Disilylated, N,N'-Disilylated, and N,N,N'-Trisilylated Amidines	489
22.4.9.1.1.1	Method 1:	Silylation of Amidines	489
22.4.9.1.1.2	Method 2:	Synthesis from Silylated Nitrogen Compounds	490
22.4.9.1.1.3	Method 3:	Synthesis from Non-Silylated or Silylated Carbodiimides	490
22.4.9.1.2		N-Germanyl, N-Stannyl, N-Plumbyl, N-Arsenyl, and N-Antimonyl Amidines	491
22.4.9.1.2.1	Method 1:	Synthesis from Amidines	491

22.4.9.1.3	Boron-Substituted Amidines	492
22.4.9.1.3.1	Method 1: Synthesis from Amidines and Various Boron Compounds	492
22.4.9.1.4	<i>N</i> -Haloamidines	493
22.4.9.1.4.1	Method 1: N^1, N^1, N^2 -Trifluoroimidamides from Amidines and Fluorine with Sodium Fluoride as Catalyst	493
22.4.9.1.4.2	Method 2: Dehydrofluorination of <i>N,N,N',N'</i> -Tetrafluoroalkane-1,1-diamines	493
22.4.9.1.4.3	Method 3: <i>N</i> -Fluoroamidines from Imidoyl Fluorides and Amines	494
22.4.9.1.4.4	Method 4: <i>N</i> -Chloroamidines from Amidines and Hypochlorites or Chlorine in the Presence of Aqueous Sodium Hydrogen Carbonate	495
22.4.9.1.4.5	Method 5: Synthesis from Amidines and <i>N</i> -Chlorosuccinimide	496
22.4.9.1.4.6	Method 6: Synthesis from Amidines by the Action of Fluorine in Aqueous Potassium Chloride	496
22.4.9.1.4.7	Method 7: <i>N</i> -Bromoamidines from Amidines and Bromine in Acetic Acid or Sodium Hypobromite	496
22.4.9.1.4.8	Method 8: <i>N</i> -Iodoamidines from Amidines and Iodine in the Presence of Sodium Hydroxide, Potassium Iodide, or Nitrogen Iodide ..	497
22.4.9.1.5	Amidoximes (<i>N</i> -Hydroxylated Amidines)	497
22.4.9.1.5.1	Method 1: Addition of Hydroxylamine to Nitriles	497
22.4.9.1.5.2	Method 2: Addition of Ammonia or Amines to Nitrile Oxides	498
22.4.9.1.5.3	Method 3: Cycloaddition of Nitrile Oxides to Imines, Cyanates, Isocyanates, and Related Compounds	499
22.4.9.1.5.4	Method 4: Reactions of <i>N</i> -Hydroxyimidoyl Chlorides with Ammonia or Amines	500
22.4.9.1.5.5	Method 5: Reactions of Imidoyl Chlorides with Hydroxylamine, <i>O</i> -Substituted, or <i>N</i> -Substituted Hydroxylamines	501
22.4.9.1.5.6	Method 6: Hydroxyamination of Amidines	502
22.4.9.1.5.7	Method 7: Reactions of Amides or Thioamides with Hydroxylamine	502
22.4.9.1.5.8	Methods 8: Other Procedures	504
22.4.9.1.6	Carbohydroximinohydrazides	504
22.4.9.1.6.1	Method 1: Synthesis from Nitrile Oxides and Hydrazine Derivatives	504
22.4.9.1.6.2	Method 2: Synthesis from <i>N</i> -Hydroxy or <i>N</i> -Amino Imidoyl Chlorides	505
22.4.9.1.6.3	Method 3: Transaminations with Hydroxylamine or Hydrazine Derivatives	506
22.4.9.1.6.4	Methods 4: Other Procedures	506
22.4.9.1.7	<i>N</i> -Sulfanylamidines	507
22.4.9.1.7.1	Method 1: Direct Sulfanylation of Amidines	507
22.4.9.1.7.2	Methods 2: Other Procedures	508
22.4.9.1.8	<i>N</i> -Sulfonylamidines	509
22.4.9.1.8.1	Method 1: Cycloaddition Reactions of Arylsulfonyl Isocyanates, Sulfuryl Chloride Isocyanate, or <i>N</i> -Sulfinylsulfonamides	509
22.4.9.1.8.2	Method 2: Cycloaddition of Arylsulfonyl Azides and Thioamides, Enamines, or Enaminones	510
22.4.9.1.8.3	Method 3: Synthesis from Ortho Esters or (Dialkoxyethyl)dialkylamines	511

22.4.9.1.8.4	Method 4:	Synthesis from N-Thioacylated or N-Acyated Sulfonamides or Amides	512
22.4.9.1.8.5	Method 5:	Synthesis from Sulfonylimidoyl Chlorides and Amines or from Imidoyl Chlorides and Sulfonamides	513
22.4.9.1.8.6	Method 6:	Synthesis from Imidates or N-Sulfonylated Imidates	514
22.4.9.1.8.7	Method 7:	Synthesis from Amidines and Sulfonyl Chlorides	515
22.4.9.1.8.8	Methods 8:	Other Procedures	516
22.4.9.1.9	<i>N''</i> -Sulfanyl, <i>N''</i> -Sulfinyl, <i>N''</i> -Sulfonyl, or <i>N''</i> -Selayl Carboximidohydrazides		517
22.4.9.1.9.1	Method 1:	General Procedures for the Synthesis of <i>N''</i> -Sulfanyl, <i>N''</i> -Sulfinyl, or <i>N''</i> -Selayl Carboximidohydrazides	518
22.4.9.1.9.2	Method 2:	Synthesis of <i>N''</i> -Sulfonyl Carboximidohydrazides	519
22.4.9.1.10		Carboximidohydrazides and Carbohydrazonamides	520
22.4.9.1.10.1	Method 1:	Addition of Hydrazine to Nitriles	520
22.4.9.1.10.2	Method 2:	1,2- or 1,3-Addition Reactions of Nitrilimines	522
22.4.9.1.10.3	Method 3:	Synthesis from Isocyanates or Isothiocyanates and Hydrazine Derivatives	523
22.4.9.1.10.4	Method 4:	Synthesis from 4-Phenyl-1,2,4-triazole-3,5-dione or Dialkyl Azodicarboxylate	525
22.4.9.1.10.5	Method 5:	Synthesis from Carboxylic Acid Thioamides and Amides	526
22.4.9.1.10.6	Method 6:	Synthesis from Imidoyl or Hydrazonoyl Chlorides by Nucleophilic Substitution	527
22.4.9.1.10.7	Method 7:	Synthesis from Thioimidates and Hydrazines or Hydrazones	528
22.4.9.1.10.8	Method 8:	Synthesis from Imidates and Various Hydrazine Derivatives	529
22.4.9.1.10.9	Methods 9:	Other Procedures	530
22.4.9.1.11		Carbohydrazonohydrazides	531
22.4.9.1.11.1	Method 1:	Synthesis from Carboxylic, Thiocarboxylic, Dithiocarboxylic Acids, Carboxylates, or Ortho Esters	531
22.4.9.1.11.2	Method 2:	Synthesis from Carboxylic Acid Hydrazides	533
22.4.9.1.11.3	Method 3:	Synthesis from Hydrazonoyl Halides	533
22.4.9.1.11.4	Method 4:	Synthesis from Imidates, <i>N</i> -Amino Imidates, or Their Salts and Hydrazine Derivatives	535
22.4.9.1.11.5	Methods 5:	Other Procedures	536
22.4.9.1.12		Formazans	536
22.4.9.1.12.1	Method 1:	Synthesis from Aryldiazonium Salts by Azo Coupling with Aryl Hydrazones	536
22.4.9.1.12.2	Method 2:	Synthesis from Aryldiazonium Salts by Azo Coupling with Active Methylene Compounds	538
22.4.9.1.12.3	Method 3:	Synthesis from Hydrazonoyl Halides	539
22.4.9.1.12.4	Method 4:	Synthesis from Various Heterocycles by Their Decomposition or Transformation	540
22.4.9.1.12.5	Methods 5:	Other Procedures	541
22.4.9.1.13		Amidines Substituted with a Group Containing a Trivalent Phosphorus Atom	541
22.4.9.1.13.1	Method 1:	Synthesis from Amidines and Chloro Derivatives of Phospholanes	541

22.4.9.1.13.2	Method 2:	Synthesis from Silylated or Lithiated Amidines and Phosphorus(III) Chlorides	542
22.4.9.1.13.3	Methods 3:	Other Procedures	542
22.4.9.1.14		Amidines Substituted with a Group Containing a Pentavalent Phosphorus Atom	542
22.4.9.1.14.1	Method 1:	Synthesis from Amides, Imidoyl Chlorides, Imidates, or Thioimidates	542
22.4.9.1.14.2	Method 2:	Synthesis from Amidines or <i>N</i> -Chloroamidines	544
22.4.9.1.14.3	Methods 3:	Other Procedures	545
22.4.9.1.15		Highly Substituted Amidines	546
22.5		Product Class 5: 2-Functionalized Alkylidenephosphines R. A. Aitken	
22.5		Product Class 5: 2-Functionalized Alkylidenephosphines	565
22.5.1		Product Subclass 1: 2-Halophosphaalkenes [(2-Halomethylene)phosphines]	565
22.5.1.1		Synthesis of Product Subclass 1	565
22.5.1.1.1	Method 1:	Synthesis from (2,4,6-Tri- <i>tert</i> -butylphenyl)phosphine with a Haloform and Potassium Hydroxide	565
22.5.1.1.2	Method 2:	Synthesis from Dichloro(2,4,6-tri- <i>tert</i> -butylphenyl)phosphine with a Haloform and Butyllithium	566
22.5.1.1.3	Method 3:	Lithiation of (Chloromethylene)(2,4,6-tri- <i>tert</i> -butylphenyl)phosphine Followed by Alkylation	567
22.5.1.1.4	Method 4:	Lithium–Halogen Exchange of a (Dihalomethylene)(2,4,6-tri- <i>tert</i> -butylphenyl)phosphine Followed by Protonation	568
22.5.1.1.5	Method 5:	Lithium–Halogen Exchange of a (Dihalomethylene)(2,4,6-tri- <i>tert</i> -butylphenyl)phosphine Followed by Alkylation	568
22.5.1.1.6	Method 6:	Synthesis from [Bis(trimethylsilyl)methylene](2,4,6-tri- <i>tert</i> -butylphenyl)phosphine with Bromine and Sodium Methoxide	569
22.5.1.1.7	Method 7:	Synthesis from a Dihalo(halomethyl)phosphine with Sodium Hexamethyldisilazanide	570
22.5.1.1.8	Method 8:	Thermolysis of (Pentafluoroethyl)(trimethylstannyl)phosphines	570
22.5.1.1.9	Method 9:	Photolytic Ring Opening of a Diphosphirane	571
22.5.1.1.10	Method 10:	Synthesis from Alkylidynephosphines with Benzeneselenenyl Chloride	572
22.5.2		Product Subclass 2: 2-Alkoxy-, 2-(Alkylsulfanyl)-, and 2-(Alkylselenanyl)phosphaalkenes (2-Substituted Methylene phosphines)	573
22.5.2.1		Synthesis of Product Subclass 2	573
22.5.2.1.1	Method 1:	Synthesis from Potassium Phosphide with an Alkyl or Aryl Benzoate	573
22.5.2.1.2	Method 2:	Reaction of Lithium Phosphide with an Alkyl Formate	574
22.5.2.1.3	Method 3:	Synthesis from Lithium Phosphide and an Acid Chloride Followed by Protonation with Tetrafluoroboric Acid	574

22.5.2.1.4	Method 4:	Synthesis from Bis(trimethylsilyl)phosphine and Pivaloyl Chloride	575
22.5.2.1.5	Method 5:	Synthesis from Bis(trimethylsilyl)phosphine and Pivaloyl Chloride Followed by Treatment with Methyllithium and Chlorotrimethylsilane	576
22.5.2.1.6	Method 6:	Synthesis from Bis(trimethylsilyl)phosphine with Two Equivalents of Pivaloyl Chloride	576
22.5.2.1.7	Method 7:	Synthesis from (2,4,6-Tri- <i>tert</i> -butylphenyl)phosphine and Oxalyl Chloride	577
22.5.2.1.8	Method 8:	Synthesis from (1,2-Dioxoethane-1,2-diyl)bis[(2,4,6-tri- <i>tert</i> -butylphenyl)phosphine] and Methyllithium with Pivaloyl Chloride	578
22.5.2.1.9	Method 9:	Synthesis from <i>tert</i> -Butyl(2,2-dimethylpropanoyl)phosphine with Triethylamine and an Electrophile	578
22.5.2.1.10	Method 10:	Synthesis from a Metalated Acylphosphine and an Electrophile	579
22.5.2.1.11	Method 11:	Synthesis from Tris(trimethylsilyl)phosphine and an Acid Chloride	580
22.5.2.1.12	Method 12:	Reaction of Lithium Bis(trimethylsilyl)phosphide with an Acid Chloride	581
22.5.2.1.13	Method 13:	Reaction of an Alkylbis(trimethylsilyl)phosphine with an Acid Chloride	581
22.5.2.1.14	Method 14:	Synthesis from Lithium (<i>tert</i> -Butyldimethylsilyl)(2,4,6-tri- <i>tert</i> -butylphenyl)phosphide and Benzoyl Chloride	583
22.5.2.1.15	Method 15:	Synthesis from [2,2-Dimethyl-1-(trimethylsiloxy)propylidene]-(trimethylsilyl)phosphine and Hexachloroethane	583
22.5.2.1.16	Method 16:	Synthesis from [2,2-Dimethyl-1-(trimethylsiloxy)propylidene]-(trimethylsilyl)phosphine and a Diazo Compound	584
22.5.2.1.17	Method 17:	Thermolysis of 4,5-Dihydro-3 <i>H</i> -1,2,4-diazaphospholes	585
22.5.2.1.18	Method 18:	Reaction of a (Hydroxyalkyl)phosphine with (1 <i>Z</i>)-2,2-Dimethyl- <i>N</i> -(4-tolyl)propanimidoyl Chloride	586
22.5.2.1.19	Method 19:	Isomerization of (1-Ethoxyvinyl)phosphines	586
22.5.2.1.20	Method 20:	Lithium–Halogen Exchange of (<i>E</i>)-[Bromo(phenylsulfanyl)methylene](2,4,6-tri- <i>tert</i> -butylphenyl)phosphine Followed by Reaction with Methanol	587
22.5.2.1.21	Method 21:	Lithium–Halogen Exchange of (<i>E</i>)-[Bromo(phenylsulfanyl)methylene](2,4,6-tri- <i>tert</i> -butylphenyl)phosphine Followed by Oxidative Coupling	588
22.5.2.1.22	Method 22:	Reaction of an Alkylidynephosphine with Benzeneselenenyl Fluoride	588
22.5.3	Product Subclass 3: 2-Aminophosphaalkenes [(2-Aminomethylene)phosphines]		588
22.5.3.1	Synthesis of Product Subclass 3		589
22.5.3.1.1	Method 1:	Reaction of an Arylphosphine with an Amide Dimethyl Acetal	589
22.5.3.1.2	Method 2:	Reaction of Potassium Phosphide with an Ethoxyiminium Tetrafluoroborate	589
22.5.3.1.3	Method 3:	Reaction of a Bis(trimethylsilyl)phosphine with Dimethylformamide	590

22.5.3.1.4	Method 4:	Reaction of a Lithium (Trimethylsilyl)phosphide with Dimethylformamide	591
22.5.3.1.5	Method 5:	Reaction of (Phenyl)[bis(trimethylsilyl)]phosphine with an Imidoyl Chloride	591
22.5.3.1.6	Method 6:	Reaction of a Chloroiminium Chloride with Tris(trimethylsilyl)phosphine	592
22.5.3.1.7	Method 7:	Reaction of a Chloroiminium Chloride with Lithium Phenyl(triphenylstannyl)phosphide	592
22.5.3.1.8	Method 8:	Synthesis from a Lithium Phosphide and a Nitrile Followed by Protonation	593
22.5.3.1.9	Method 9:	Synthesis from a Lithium Phosphide with Acetonitrile Followed by Silylation	594
22.5.3.1.10	Method 10:	Synthesis from (2,2-Dimethylpropylidene)phosphine and a Thioketone S-Imide	594
22.5.3.1.11	Method 11:	Reaction of a 2-Chloro-1-ethylquinolinium Tetrafluoroborate with Tris(hydroxymethyl)phosphine	594
22.5.3.1.12	Method 12:	Reaction of a 1-Alkyl-2-chloroquinolinium Salt with Tris(trimethylsilyl)phosphine	595
22.5.3.1.13	Method 13:	Reaction of 2-Chloro-1-methylquinolinium Tetrafluoroborate with Sodium Dicyanophosphide Followed by Sodium Diethyl Phosphite	595
22.5.3.1.14	Method 14:	Reaction of Phosphamethinecyanine Tetrafluoroborates with Sodium Dicyanophosphide	596
22.5.3.1.15	Method 15:	[2 + 2] Cycloaddition of Tri- <i>tert</i> -butylazete and a Phosphaalkyne	596
22.5.3.1.16	Method 16:	Diels–Alder Reaction of [(Diisopropylamino)methylidene]phosphine	597
22.5.3.1.17	Method 17:	Synthesis from [2,2-Dimethyl-1-[phenyl(trimethylsilyl)amino]propylidene]phenylphosphine and Benzoyl Chloride	598
22.5.3.1.18	Method 18:	Synthesis from (2,3-Di- <i>tert</i> -butylcycloprop-2-en-1-ylidene)-(mesityl)phosphine and an Ynamine	598

22.6 Product Class 6: 2-Functionalized Arsaalkenes and α -Functionalized Arsonium Ylides

R. A. Aitken

22.6	Product Class 6: 2-Functionalized Arsaalkenes and α-Functionalized Arsonium Ylides	601
22.6.1	Product Subclass 1: 2-Haloarsaalkenes	601
22.6.1.1	Synthesis of Product Subclass 1	601
22.6.1.1.1	Method 1: Lithium–Halogen Exchange of a [(2,2-Dibromo)methylene]arsine Followed by Methanolysis ..	601
22.6.2	Product Subclass 2: 2-Alkoxyarsaalkenes	602
22.6.2.1	Synthesis of Product Subclass 2	602

22.6.2.1.1	Method 1:	Reaction of Bis(trimethylsilyl)arsines and Pivaloyl Chloride Followed by Thermal Rearrangement	602
22.6.2.1.2	Method 2:	Reaction of 2,4,6-Trimethylbenzoyl Chloride and Lithium Arsenide–1,2-Dimethoxyethane Complex in a 1:2 Ratio	603
22.6.2.1.3	Method 3:	Reaction of 2,4,6-Trimethylbenzoyl Chloride and Lithium Arsenide–Tetrahydrofuran Complex in a 2:3 Ratio	604
22.6.3	Product Subclass 3: 2-Aminoarsalkenes		605
22.6.3.1	Synthesis of Product Subclass 3		605
22.6.3.1.1	Method 1:	Reaction of Phenylbis(trimethylsilyl)arsine and an Imidoyl Chloride	605
22.6.3.1.2	Method 2:	Reaction of Phenylbis(trimethylsilyl)arsine and Dimethylformamide	605
22.6.3.1.3	Method 3:	Reaction of a Lithium Trimethylsilylarsenide and Dimethylformamide	606
22.6.3.1.4	Method 4:	Reaction of (2,4-Di- <i>tert</i> -butyl-6-methylphenyl)arsine and an Amide Dimethyl Acetal	606
22.6.3.1.5	Method 5:	Reaction of Tris(trimethylsilyl)arsine and a 1-Alkyl-2-chloroquinolinium Tetrafluoroborate	607
22.6.4	Product Subclass 4: α-Sulfur- and Selenium-Substituted Arsonium Ylides		607
22.6.4.1	Synthesis of Product Subclass 4		607
22.6.4.1.1	Method 1:	Reaction of a Stabilized Arsonium Ylide and Benzenesulfonyl Chloride	607
22.6.4.1.2	Method 2:	Reaction of Triphenyl(phenylsulfonylmethyl)arsonium Iodide with Triethylamine and Acetyl Chloride	608
22.6.4.1.3	Method 3:	Reaction of Triphenylarsine Oxide with Dimethyl(2-oxo-2-phenylethyl)sulfonium Tetraphenylborate and Acetic Anhydride	608
22.6.4.1.4	Method 4:	Reaction of [2-(4-Bromophenyl)-2-oxoethylidene]triphenylarsonane and Phenylsulfine	609
22.6.4.1.5	Method 5:	Reaction of [(Ethoxycarbonyl)methylene]triphenylarsonane and Phenylsulfonyl Chloride	610
22.6.4.1.6	Method 6:	Reaction of a Stabilized Arsonium Ylide with Benzeneselenenyl Iodide	610
22.6.4.1.6.1	Variation 1:	With No Added Base	610
22.6.4.1.6.2	Variation 2:	In the Presence of Triethylamine	611
22.6.4.1.7	Method 7:	Reaction of Triphenyl[(phenylselenyl)methyl]arsonium Iodide with Triethylamine and Acetyl Chloride	611
22.6.4.1.8	Method 8:	Reaction of (2-Oxo-2-phenylethyl)triphenylarsonium Tetrafluoroborate and Diphenyl Selenoxide in the Presence of Dicyclohexylcarbodiimide	612
22.6.4.2	Applications of Product Subclass 4 in Organic Synthesis		613
22.6.4.2.1	Method 1:	Reaction of Triphenyl[(phenylsulfonyl)methyl]arsonium Iodide with Butyllithium	613

22.6.5	Product Subclass 5: α-Nitroarsonium Ylides	614
22.6.5.1	Synthesis of Product Subclass 5	614
22.6.5.1.1	Method 1: Reaction of Dichloro(triphenyl)arsorane with (Nitromethyl)benzene and Triethylamine	614
22.6.5.1.2	Method 2: Reaction of Triphenylarsine Oxide with Nitromethane and Phosphorus Pentoxide	614
22.6.5.1.3	Method 3: Reaction of Triphenylarsine Oxide with Nitromethane and Acetic Anhydride	615
22.7	Product Class 7: Ortho Acid Derivatives	
22.7.1	Product Subclass 1: Trihalomethyl Compounds G. K. S. Prakash and J. Hu	
22.7.1	Product Subclass 1: Trihalomethyl Compounds	617
22.7.1.1	Synthesis of Product Subclass 1	617
22.7.1.1.1	Compounds Containing a Trifluoromethyl Group	617
22.7.1.1.1.1	Nucleophilic Trifluoromethylation and Perfluoroalkylation	618
22.7.1.1.1.1.1	Method 1: Reaction of Trimethyl(trifluoromethyl)silane and Other Organosilicon Reagents	618
22.7.1.1.1.1.1.1	Variation 1: Fluoride-Induced Chemoselective Nucleophilic Trifluoromethylation and Perfluoroalkylation	619
22.7.1.1.1.1.1.2	Variation 2: Stereoselective Nucleophilic Trifluoromethylation with Trimethyl(trifluoromethyl)silane	621
22.7.1.1.1.1.1.3	Variation 3: Trifluoromethylation and Perfluoroalkylation by Copper(I)-Mediated Oxidative Addition	622
22.7.1.1.1.1.2	Method 2: Reaction of Trifluoromethane and Other Polyfluoroalkanes ..	623
22.7.1.1.1.1.3	Method 3: Reaction of Hemiaminals of Trifluoroacetaldehyde	624
22.7.1.1.1.1.3.1	Variation 1: Using the Silylated Morpholino Hemiaminal of Trifluoroacetaldehyde	625
22.7.1.1.1.1.3.2	Variation 2: Using Silylated and Non-Silylated Piperazino Hemiaminals of Trifluoroacetaldehyde	625
22.7.1.1.1.1.4	Method 4: Reaction of 2,2,2-Trifluoro-1-phenylethanone and Its Adduct	626
22.7.1.1.1.1.5	Method 5: Reaction of Trifluorohalomethanes and Perfluorohaloalkanes	627
22.7.1.1.1.1.6	Method 6: Reaction of Trifluoroacetic Acid and Trifluoromethanesulfinic Acid Derivatives	628
22.7.1.1.1.1.7	Method 7: Reaction of Phenyl Trifluoromethyl Sulfide, Sulfoxide, or Sulfone	629
22.7.1.1.1.1.8	Method 8: Reaction of Fluorinated Organometallic Reagents	630
22.7.1.1.1.2	Electrophilic Trifluoromethylation or Perfluoroalkylation	631
22.7.1.1.1.2.1	Method 1: Reaction of Aryl(perfluoroalkyl)iodonium Salts	631
22.7.1.1.1.2.2	Method 2: Reaction of Aryl(polyfluoroalkyl)iodonium Salts	632
22.7.1.1.1.2.3	Method 3: Reaction of 5-(Perfluoroalkyl)dibenzothiophenium, 5-(Perfluoroalkyl)dibenzoselenophenium, and 5-(Perfluoroalkyl)dibenzotellurophenium Salts	632

22.7.1.1.1.3	Trifluoromethylation and Polyfluoroalkylation via Fluorinated Radical Species	633
22.7.1.1.1.3.1	Method 1: Addition to Unsaturated Systems	633
22.7.1.1.1.3.2	Method 2: Substitution Reactions	634
22.7.1.1.1.4	Other Methods	635
22.7.1.1.1.4.1	Method 1: Halogen-Exchange Reactions	635
22.7.1.1.1.4.2	Method 2: Reaction of Trifluoroacetic Acid Derivatives with Organometallic Compounds	635
22.7.1.1.1.4.3	Method 3: Reaction of Sulfur Tetrafluoride and Related Reagents	636
22.7.1.1.1.4.4	Method 4: Reaction of Hydrogen Fluoride and Amine Complexes	636
22.7.1.1.1.4.5	Method 5: Electrochemical Fluorination	637
22.7.1.1.1.4.6	Method 6: Perfluorination Reactions with Elemental Fluorine	638
22.7.1.1.1.4.7	Method 7: Electrophilic Fluorination of (2,2-Difluorovinyl)oxy)silanes	638
22.7.1.1.2	Compounds Containing a Trichloromethyl Group	639
22.7.1.1.2.1	Method 1: Reaction of Trimethyl(trichloromethyl)silane	639
22.7.1.1.2.2	Method 2: Reaction of Chloroform with Base	640
22.7.1.1.2.3	Method 3: Reaction of Carbon Tetrachloride with a Lewis Acid	640
22.7.1.1.2.4	Method 4: Reaction of Carbon Tetrachloride with a Reducing Agent	641
22.7.1.1.2.5	Method 5: Halogen-Exchange Reactions Using Metal Chlorides	642
22.7.1.1.2.6	Method 6: Use of Phosphorus Pentachloride as the Chlorinating Agent	642
22.7.1.1.2.7	Method 7: Reaction of Elemental Chlorine	643
22.7.1.1.2.8	Method 8: Reaction of Trichloroacetic Acid and Its Derivatives	643
22.7.1.1.2.9	Method 9: Reaction of Chloral	644
22.7.1.1.3	Compounds Containing a Tribromomethyl or Triiodomethyl Group	645
22.7.1.1.3.1	Method 1: Reaction of Elemental Bromine or Iodine	645
22.7.1.1.3.2	Method 2: Reaction of Tribromomethane with Base	645
22.7.1.1.3.3	Method 3: Reaction of Tribromoacetic Acid and Its Derivatives	646
22.7.1.1.3.4	Method 4: Reaction of Carbon Tetrabromide with a Reducing Agent	647
22.7.1.1.3.5	Method 5: Reaction of <i>N</i> -Bromosuccinimide	647
22.7.1.1.3.6	Method 6: Halogen-Exchange Reactions	648
22.7.1.1.4	Compounds Containing the Chlorodifluoromethyl, Bromodifluoromethyl, or Difluoroiodomethyl Group	648
22.7.1.1.4.1	Method 1: Reaction of (Chlorodifluoromethyl)trimethylsilane and Related Compounds	648
22.7.1.1.4.2	Method 2: Radical Reactions with Elemental Halogens	649
22.7.1.1.4.3	Method 3: Reaction of an <i>N</i> -Halosuccinimide	650
22.7.1.1.4.4	Method 4: Halogen-Exchange Reactions	650
22.7.1.1.4.5	Method 5: Electrophilic Halogenation of (2,2-Difluorovinyl)oxy)silanes	651
22.7.1.1.4.6	Method 6: Reaction of Difluorohaloacetic Acid Derivatives	651
22.7.1.1.5	Compounds Containing a Dichlorofluoromethyl, Dibromofluoromethyl, or Fluorodiiodomethyl Group	652
22.7.1.1.5.1	Method 1: Halogen-Exchange Reactions	652
22.7.1.1.5.2	Method 2: Reaction of Dichlorofluoromethane with a Base	653
22.7.1.1.5.3	Method 3: Reaction of Trichlorofluoromethane	653
22.7.1.1.5.4	Method 4: Reaction of Dichlorofluoromethanesulfonyl Acetate and Trifluoroacetate	654

22.7.1.1.5.5	Method 5:	Reaction of (2,2-Dichlorocyclopropyl)methanol or 2,2-(Dibromocyclopropyl)methanol with Pyridinium Poly(hydrogen fluoride)	654
22.7.1.1.5.6	Method 6:	Reaction of the Lithium or Zinc Carbenoid Generated from Tribromofluoromethane	655
22.7.1.1.5.7	Method 7:	Electrochemical Fluorination	656
22.7.1.1.6		Compounds Containing a Bromochlorofluoromethyl, Bromofluoroiodomethyl, or Chlorofluoroiodomethyl Group	656
22.7.1.1.6.1	Method 1:	Halogen-Exchange Reactions	656
22.7.1.1.6.2	Method 2:	Reaction of Elemental Halogens	657
22.7.1.1.6.3	Method 3:	Reaction of Dibromochlorofluoromethane and Sodium Dithionite	657
22.7.1.1.6.4	Method 4:	Electrophilic Halogenation or Halofluorination	658
22.7.1.1.7		Compounds Containing a Bromodichloromethyl, Dichloroiodomethyl, Dibromochloromethyl, Dibromoiodomethyl, Chloroiodomethyl, or Bromodiiodomethyl Group	658
22.7.1.1.7.1	Method 1:	Electrophilic Halogenation of Alkenes with Halogens	659
22.7.1.1.7.2	Method 2:	1,2-Addition of Alkenes to Alkyl Hypohalites	659
22.7.1.1.7.3	Method 3:	Reaction of Bromodichloromethane or Dibromochloromethane with a Base	660
22.7.1.1.7.4	Method 4:	Halogen-Exchange Reactions	660
22.7.1.1.7.5	Method 5:	Halogenation of Enolates Generated In Situ	661
22.7.1.1.8		Compounds Containing the Bromochloroiodomethyl Group	662
22.7.1.1.8.1	Method 1:	Reaction of Bromochloroiodomethane and Base	662
22.7.1.1.8.2	Method 2:	Halogen-Exchange Reactions	662
22.7.2	Product Subclass 2: Ortho Esters and Halogenated Derivatives		
	H. Lebel and M. Grenon		
22.7.2	Product Subclass 2: Ortho Esters and Halogenated Derivatives		
22.7.2.1	Synthesis of Product Subclass 1		
22.7.2.1.1	α,α -Dihalogenated Ethers and α -Halogenated Acetals		
22.7.2.1.1.1	Method 1:	Halogenation of Ethers	670
22.7.2.1.1.2	Method 2:	Halogen Substitution Reactions	671
22.7.2.1.1.2.1	Variation 1:	Preparation of α,α -Difluoro Ethers from α,α -Difluoro- α -haloalkanes	672
22.7.2.1.1.2.2	Variation 2:	Preparation of Ortho Esters from Trihaloalkanes	673
22.7.2.1.1.3	Method 3:	Alcoholysis of α,α -Difluorinated Alkenes	674
22.7.2.1.1.4	Method 4:	Oxidative Fluorodesulfurization of Thiocarboxylic <i>O</i> -Acid Esters	676
22.7.2.1.1.4.1	Variation 1:	Fluorination with (Diethylamino)sulfur Trifluoride	676
22.7.2.1.1.4.2	Variation 2:	Fluorination with Bromine Trifluoride	677
22.7.2.1.1.5	Method 5:	Halogenation of Esters and Anhydrides	678
22.7.2.1.1.6	Method 6:	Oxidative Fluorodesulfurization of 5,6-Dihydro-4 <i>H</i> -1,3-dithiin-1-ium Salts	679

22.7.2.1.1.7	Method 7:	Halogenation of Acetals	680
22.7.2.1.1.8	Method 8:	Electrochemical Oxidation of 2-Chloro-5,6-dihydro-1,4-dioxin	682
22.7.2.1.1.9	Method 9:	Reactions of 3,4,5,6-Tetrachlorobenzo-1,2-quinone with Benzyl Halides	682
22.7.2.1.2	Ortho Esters		683
22.7.2.1.2.1	Method 1:	Electrochemical Oxidation of Acetals to Ortho Esters	683
22.7.2.1.2.2	Method 2:	Photoinduced Electron Transfer between Tetrachlorobenzo-1,4-quinone and Benzodioxoles	685
22.7.2.1.2.3	Method 3:	Alcoholysis of Cyclopropanone Ketals	685
22.7.2.1.2.4	Method 4:	Elimination/Intramolecular Cyclization of Selenoglycosides ..	687
22.7.2.1.2.5	Method 5:	Nucleophilic Substitution Reactions on Orthocarbonates	688
22.7.2.1.2.6	Method 6:	Nucleophilic Substitution Reactions on Cyano Ortho Esters ..	689
22.7.2.1.2.7	Method 7:	Alcoholysis of Amide Acetals	690
22.7.2.1.2.8	Method 8:	Alcoholysis of Activated Amides	691
22.7.2.1.2.9	Method 9:	Nucleophilic Addition to Trialkoxycarbenium Salts	693
22.7.2.1.2.10	Method 10:	Alcoholysis of Dialkoxycarbenium Salts	693
22.7.2.1.2.11	Method 11:	Alcoholysis of Nitriles	695
22.7.2.1.2.12	Method 12:	Alcoholysis of Imidic Esters	696
22.7.2.1.2.13	Method 13:	Alcoholysis of Ketene Acetals	696
22.7.2.1.2.14	Method 14:	Transition-Metal-Catalyzed Reactions of Ketene Acetals with α -Diazo Ketones	698
22.7.2.1.2.15	Method 15:	[4 + 2] Cycloadditions of Ketene Acetals with α,β -Unsaturated Carbonyl Compounds	700
22.7.2.1.2.16	Method 16:	[4 + 2] Cycloadditions of Ketene Acetals with Acetylketene or Formylketene	702
22.7.2.1.2.17	Method 17:	[2 + 2] Cycloadditions of Ketene Acetals with Carbonyl Compounds	703
22.7.2.1.2.18	Method 18:	Transition-Metal-Catalyzed Reactions of 1,1-Diethoxyethene with α -Dicarbonyl Compounds	705
22.7.2.1.2.19	Method 19:	Alcoholysis of Alkoxyalkynes	706
22.7.2.1.2.20	Method 20:	Reactions of Lactones with Alkylating Reagents and Alcohols	707
22.7.2.1.2.21	Method 21:	Acid-Catalyzed Reactions of Lactones with Diols	708
22.7.2.1.2.22	Method 22:	Trimethylsilyl Trifluoromethanesulfonate Catalyzed Reactions of Lactones with Diols and Methoxytrimethylsilane	709
22.7.2.1.2.23	Method 23:	Reactions of Esters with Epoxides	711
22.7.2.1.2.24	Method 24:	Lewis Acid Mediated Rearrangements of Epoxy Esters	712
22.7.2.1.2.25	Method 25:	Transition-Metal-Catalyzed Rearrangements of Epoxy Esters .	713
22.7.2.1.2.26	Method 26:	Lewis Acid Catalyzed Rearrangements of Oxetane Esters	714
22.7.2.1.2.27	Method 27:	Synthesis from Dithioesters and Dialkoxydibutylstannanes ...	715
22.7.2.1.2.28	Method 28:	Preparation of Carbohydrate Ortho Esters from O-Acylglycosyl Derivatives	716
22.7.2.1.2.28.1	Variation 1:	From O-Acylglycosyl Halides	717
22.7.2.1.2.28.2	Variation 2:	From O-Acylglycosyl Trichloroimidates	719
22.7.2.1.2.29	Method 29:	[2 + 2] Electrocyclic Ring Opening of 2,2-Dimethoxycyclobutenones	720
22.7.2.1.2.30	Method 30:	[3 + 2] Cycloadditions of Carbonyl Ylides with Carbonyl Compounds	721

22.7.2.1.2.31	Method 31:	Cycloadditions of Methylene-cyclopropanone Ketals with Carbonyl Compounds	723
22.7.2.1.2.32	Method 32:	Claisen Rearrangement of Phenols with 3,3,3-Triethoxypropene	726
22.7.2.1.2.33	Method 33:	Alcoholysis of α,α -Dialkoxycyclopropyl Esters	727
22.7.2.1.2.34	Method 34:	Alcoholysis of α,α -Dihalocyclopropyl Ketones	728
22.7.2.1.2.35	Method 35:	Exchange of Alkoxy Groups by the Reactions of Ortho Esters with Alcohols (Transorthoesterification)	728
22.7.2.1.2.35.1	Variation 1:	Reactions with Diols	729
22.7.2.1.2.35.2	Variation 2:	Reactions with Triols	730
22.7.2.1.2.35.3	Variation 3:	Alcoholysis of Trithioortho Esters	732
22.7.2.1.2.36	Method 36:	The Wittig Reaction	733
22.7.2.1.2.37	Method 37:	Additions of Anions Containing an Ortho Ester Fragment	735
22.7.2.1.2.37.1	Variation 1:	Addition of the Anion of 1-Ethynyl-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane to Various Electrophiles	735
22.7.2.1.2.37.2	Variation 2:	Addition of the Anion of (<i>E</i>)-1-(2-Iodovinyl)-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane to Various Electrophiles	736
22.7.2.1.2.38	Method 38:	Transition-Metal-Catalyzed Coupling Reactions	737
22.7.2.1.2.39	Method 39:	Preparation of 3,3,3-Triethoxypropene and 3,3,3-Triethoxypropyne	738
22.7.2.1.2.39.1	Variation 1:	Preparation of 3,3,3-Triethoxypropyne	739
22.7.2.1.2.39.2	Variation 2:	Preparation of 3,3,3-Triethoxypropene	740

22.7.3 Product Subclass 3: Trithioortho Esters and Halogenated Derivatives

H. Lebel and M. Grenon

22.7.3	Product Subclass 3: Trithioortho Esters and Halogenated Derivatives	749
22.7.3.1	Synthesis of Product Subclass 3	749
22.7.3.1.1	α -Halogenated Dithioacetals and α,α -Dihalogenated Sulfides	749
22.7.3.1.1.1	Method 1: Halogenation of Sulfides	749
22.7.3.1.1.1.1	Variation 1: Fluorination of Sulfides	749
22.7.3.1.1.1.2	Variation 2: Electrolytic Fluorination of Sulfides	751
22.7.3.1.1.1.3	Variation 3: Chlorination of Sulfides	752
22.7.3.1.1.1.4	Variation 4: Bromination of Sulfides	753
22.7.3.1.1.2	Method 2: Halogen Substitution Reactions of α,α -Difluoro- α -haloalkanes	754
22.7.3.1.1.2.1	Variation 1: Substitution by Thiolates	754
22.7.3.1.1.2.2	Variation 2: Substitution by Thiocyanates	755
22.7.3.1.1.3	Method 3: Oxidative Desulfurization–Fluorination of Trithioortho Esters To Give α,α -Difluoro Sulfides	756
22.7.3.1.1.4	Method 4: Oxidative Desulfurization–Fluorination of Dithioesters To Give α,α -Difluoro Sulfides	757
22.7.3.1.1.5	Method 5: Halogenation of Dithioacetals	758
22.7.3.1.1.5.1	Variation 1: Chlorination of Dithioacetals with <i>N</i> -Chlorosuccinimide	759
22.7.3.1.1.5.2	Variation 2: Chlorination of Dithioacetals with Sulfuryl Chloride	759
22.7.3.1.1.6	Method 6: Halogenation of Ketene Dithioketals	760
22.7.3.1.2	Trithioortho Esters	761

22.7.3.1.2.1	Method 1:	Thionation of Dithioacetals with Disulfides	761
22.7.3.1.2.2	Method 2:	Transorthoesterification of Ortho Esters with Thiols	762
22.7.3.1.2.3	Method 3:	Sulfur–Metal Exchange of Thioorthocarbonates	762
22.7.3.1.2.4	Method 4:	From Disubstituted Trithiocarbonates by Nucleophilic Addition at the Sulfur Atom of the Thione Group	763
22.7.3.1.2.4.1	Variation 1:	Addition of Organolithium Reagents to Trithiocarbonates	763
22.7.3.1.2.4.2	Variation 2:	Addition of Allylsilanes to Trithiocarbonates	765
22.7.3.1.2.5	Method 5:	From Disubstituted Trithiocarbonates by Reaction with Thiocarbonyl Ylides	765
22.7.3.1.2.6	Method 6:	From Tris(methylsulfanyl)carbenium Salts	766
22.7.3.1.2.7	Method 7:	Thiolysis of Ketene Dithioacetals	768
22.7.3.1.2.8	Method 8:	Addition of Tris(alkylsulfanyl)methanes and Tris(arylsulfanyl)methanes	769
22.7.3.1.2.8.1	Variation 1:	Additions to Alkyl Halides	770
22.7.3.1.2.8.2	Variation 2:	1,2-Addition to Aldehydes and Ketones	771
22.7.3.1.2.8.3	Variation 3:	1,4-Addition to α,β -Unsaturated Carbonyl Compounds	771

22.7.4 Product Subclass 4: Triselenoortho Esters and Halogenated Derivatives

H. Lebel and M. Grenon

22.7.4	Product Subclass 4: Triselenoortho Esters and Halogenated Derivatives	775	
22.7.4.1	Synthesis of Product Subclass 4	776	
22.7.4.1.1	Method 1:	Dimerization of Selenocarbonyl Fluorides	776
22.7.4.1.2	Method 2:	Halogen Exchange of 2,4-Difluoro-2,4-bis(perfluoroalkyl)- 1,3-diselenetanes	778
22.7.4.1.3	Method 3:	Alkylation of Aldehydes with Benzeneselenenyl Bromide	778
22.7.4.1.4	Method 4:	Selenation of Diselenanes with Diselenides	779
22.7.4.1.5	Method 5:	Halogen Substitution Reactions	780
22.7.4.1.5.1	Variation 1:	From Bromoform and Carbon Tetrabromide	780
22.7.4.1.5.2	Variation 2:	From Dichloromethyl Methyl Ether	781
22.7.4.1.6	Method 6:	Transorthoesterification of Ortho Esters	782
22.7.4.1.6.1	Variation 1:	Lewis Acid Catalyzed Transorthoesterification of Ortho Esters	782
22.7.4.1.6.2	Variation 2:	Transorthoesterification of Ortho Esters with Tris(methylselenanyl)borane	783
22.7.4.1.7	Method 7:	Metalation of Selenoorthocarbonates	784
22.7.4.1.8	Method 8:	Reduction of Tris(alkylselenanyl)carbenium Salts	785
22.7.4.1.9	Method 9:	Acid-Mediated Condensation of Benzeneselenol	785
22.7.4.1.10	Method 10:	Addition of Tris(alkylselenanyl)methanes and Tris(arylselenanyl)methanes	786

22.7.5	Product Subclass 5: Tritelluroortho Esters and Halogenated Derivatives H. Lebel and M. Grenon	
<hr/>		
22.7.5	Product Subclass 5: Tritelluroortho Esters and Halogenated Derivatives	789
22.7.5.1	Synthesis of Product Subclass 5	789
22.7.5.1.1	Method 1: Dimerization of Tellurocarbonyl Fluorides	789
22.7.5.1.2	Method 2: Halogen Exchange of 2,4-Difluoro-2,4-bis(perfluoroalkyl)-1,3-ditelluretanes	790
22.7.5.1.3	Method 3: Preparation of Tris(aryltellanyl)carbenium Ions	791
22.7.6	Product Subclass 6: Ortho Amides (Alkane-1,1,1-triamines) W. Kantlehner	
<hr/>		
22.7.6	Product Subclass 6: Ortho Amides (Alkane-1,1,1-triamines)	795
22.7.6.1	Synthesis of Product Subclass 6	795
22.7.6.1.1	Method 1: Substitution of Cyano Groups	795
22.7.6.1.2	Method 2: Substitution of Halogens	796
22.7.6.1.2.1	Variation 1: Substitution of Fluorine and Sulfur Groups in Disulfides	800
22.7.6.1.2.2	Variation 2: Other Substitutions	800
22.7.6.1.3	Method 3: Substitution of Amine Derivatives	805
22.7.6.1.4	Method 4: Substitution of Alkoxy Groups	807
22.7.6.1.4.1	Variation 1: Substitution of Alkoxy and Amino Groups	810
22.7.6.1.5	Method 5: Substitution of Alkylsulfanyl Groups	812
22.7.6.1.6	Method 6: Reactions of Guanidinium Salts	813
22.7.6.1.6.1	Variation 1: With Metal Hydrides	813
22.7.6.1.6.2	Variation 2: With Organometallic Compounds	815
22.7.6.1.7	Method 7: Reaction of Pyrimidinium Salts with Amines	818
22.7.6.1.8	Method 8: Reaction of Tetrazolium Salts with Ammonia	819
22.7.6.1.9	Method 9: Reaction of Isocyanates	819
22.7.6.1.9.1	Variation 1: With Nucleophilic Carbenes	819
22.7.6.1.9.2	Variation 2: With Amides	820
22.7.6.1.9.3	Variation 3: With Amidines	820
22.7.6.1.9.4	Variation 4: With Triethylsilane	822
22.7.6.1.9.5	Variation 5: With Bis(dialkylamino)acetonitriles	822
22.7.6.1.10	Method 10: Reaction of Tetraaminoethenes with NH-Acidic Compounds	823
22.7.6.1.11	Method 11: Reaction of Azoalkenes with CH ₂ -Acidic Compounds	825
22.7.6.1.12	Method 12: Modification of Existing Ortho Amides	827
22.7.6.1.12.1	Variation 1: Transamination Reactions	827
22.7.6.1.12.2	Variation 2: N-Metalation, N-Acylation, and N-Sulfonylation	828
22.7.6.1.12.3	Variation 3: N-Alkylation	828
22.7.6.1.12.4	Variation 4: N-Dealkylation	829
22.7.6.1.12.5	Variation 5: Transformation of Carbonyl or Thiocarbonyl Groups into Methylene Groups	830
22.7.6.1.12.6	Variation 6: Sulfurization of Carbonyl Groups	831
22.7.6.1.12.7	Variation 7: Alteration of More Remote Functional Groups	831
22.7.6.1.13	Method 13: Cycloaddition Reactions	831
22.7.6.1.14	Methods 14: Other Methods	833

22.7.7	Product Subclass 7: Tris(diorganophosphino)methanes and Derivatives W. Kantlehner	
<hr/>		
22.7.7	Product Subclass 7: Tris(diorganophosphino)methanes and Derivatives	843
22.7.7.1	Synthesis of Product Subclass 7	843
22.7.7.1.1	Method 1: Alkylation of Lithium Tris(dimethylphosphino)methanides	843
22.7.7.1.2	Method 2: Phosphorylation of Lithium Bis(diorganophosphino)methanides	844
22.7.7.1.3	Method 3: Phosphorylation of [Diphenyl(thiophosphoryl)]methyllithium	846
22.7.7.1.4	Method 4: Synthesis of Phosphorylated Methanes by Addition of Oxygen, Sulfur, Selenium, and Azides	846
22.7.7.1.5	Method 5: Synthesis of Phosphonium Iodides	848
	Keyword Index	851
	Author Index	887
	Abbreviations	945