

Table of Contents

Volume 2:

Compounds of Groups 7-3 (Mn..., Cr..., V..., Ti..., Sc..., La..., Ac...)

2.10	Product Class 10: Organometallic Complexes of Titanium	
2.10.18	Organometallic Complexes of Titanium	2011
	T. Takeda and A. Tsubouchi	
2.10.18	Organometallic Complexes of Titanium	1
2.10.18.1	Titanium-Mediated Alkenation Reactions	1
2.10.18.1.1	Method 1: Using Thioacetals as Carbene Complex Precursors	1
2.10.18.1.2	Method 2: Using Monohalides as Carbene Complex Precursors	12
2.10.18.1.3	Method 3: Using <i>gem</i> -Dichlorides as Carbene Complex Precursors	13
2.10.18.1.4	Method 4: Using 1,1-Dichloroalk-1-enes as Carbene Complex Precursors	14
2.10.18.1.5	Method 5: Using Alkenyl and Alkynyl Sulfones	15
2.10.18.2	Titanium-Mediated Alkene Metathesis	16
2.10.18.2.1	Method 1: Metathesis and Related Reactions via Titanacyclobutanes	16
2.10.18.2.1.1	Variation 1: Reaction of Titanocene Alkyldenes with Alkenes	16
2.10.18.2.1.2	Variation 2: Intramolecular Reaction of Titanocene Alkyldenes Bearing an Alkene Moiety	19
2.10.18.2.1.3	Variation 3: Reaction of Unsaturated Titanocene–Carbene Complexes with Alkenes	23
2.10.18.2.2	Method 2: Metathesis and Related Reactions via Titanacyclobutenes	27
2.10.18.2.2.1	Variation 1: Reaction of Alkenylcarbene Complexes of Titanium with Acetylene	27
2.10.18.2.2.2	Variation 2: Reaction of Titanocene Alkyldenes with Alkynes	27
2.10.18.2.2.3	Variation 3: Reaction of Titanocene Alkenylidenes with Alkynes	30
2.10.18.2.2.4	Variation 4: Reaction of Titanocene Alkyldenes with Alkynyl Sulfones	31
2.10.18.2.2.5	Variation 5: Valence Tautomerization of Alkenylcarbene Complexes	32
2.10.18.2.2.6	Variation 6: Titanium-Promoted Alkylation of Propargyl Carbonates	33

Volume 4: Compounds of Group 15 (As, Sb, Bi) and Silicon Compounds

4.4	Product Class 4: Silicon Compounds	
<hr/>		
4.4.2.5	Silenes (Update 1)	2011
		H. Ottosson and A. M. Rouf
<hr/>		
4.4.2.5	Silenes (Update 1)	37
4.4.2.5.1	Method 1: Synthesis of Silenes by Photolysis or Thermolysis of Acylpolysilanes and Derivatives	39
4.4.2.5.1.1	Variation 1: Thermolysis of Carbamoylpolsilanes	39
4.4.2.5.1.2	Variation 2: Thermal Rearrangement of Mercury Bis(acylsilanes)	40
4.4.2.5.2	Method 2: Salt Elimination Methods	41
4.4.2.5.2.1	Variation 1: Reaction of Lithium Disilenides with Acyl or Vinyl Halides	42
4.4.2.5.2.2	Variation 2: Reaction of Dilithiosilos with Ketones	43
4.4.2.5.3	Method 3: Sila-Peterson Alkenation Reactions	43
4.4.2.5.4	Method 4: Silylene–Silene and Carbene–Silene Isomerizations	45
<hr/>		
4.4.2.6	Silenes (Update 2)	2011
		H. Ottosson and J. Ohshita
<hr/>		
4.4.2.6	Silenes (Update 2)	47
4.4.2.6.1	Silenolates	47
4.4.2.6.1.1	Method 1: Synthesis of Silen-2-olates by Trimethylsilyl–Metal Exchange	51
4.4.2.6.1.1.1	Variation 1: With Germyllithium Reagents	51
4.4.2.6.1.1.2	Variation 2: With Silyllithium Reagents	51
4.4.2.6.1.1.3	Variation 3: With Potassium <i>tert</i> -Butoxide	52
4.4.2.6.2	Method 2: Synthesis of Silen-2-olates by Reaction of Bis(lithiosilyl)mercury Compounds with Acyl Chlorides	53

Volume 20:
Three Carbon—Heteroatom Bonds: Acid Halides; Carboxylic Acids and Acid Salts; Esters, and Lactones; Peroxy Acids and R(CO)OX Compounds; R(CO)X, X = S, Se, Te

20.2	Product Class 2: Carboxylic Acids	
20.2.1.2.10	Synthesis from Carboxylic Acid Derivatives	2011
	A. K. Mourad and C. Czekelius	
20.2.1.2.10	Synthesis from Carboxylic Acid Derivatives	57
20.2.1.2.10.1	Method 1: Hydrolysis of Esters	57
20.2.1.2.10.1.1	Variation 1: Nucleophile-Promoted Cleavage	57
20.2.1.2.10.1.2	Variation 2: Hydrogenolytic Cleavage of Benzyl Esters	58
20.2.1.2.10.1.3	Variation 3: Transition-Metal-Mediated Cleavage of Allyl Esters	59
20.2.1.2.10.1.4	Variation 4: Cleavage of 2-Haloethyl Esters	61
20.2.1.2.10.1.5	Variation 5: Light-Induced Cleavage	63
20.2.1.2.10.1.6	Variation 6: Fluoride-Mediated Cleavage of Silyl Esters	64
20.2.1.2.10.1.7	Variation 7: Enzymatic Hydrolysis	65
20.2.1.2.10.2	Method 2: Hydrolysis of Hydrazides	66
20.2.1.2.10.2.1	Variation 1: Base-Mediated Hydrolysis	66
20.2.1.2.10.2.2	Variation 2: Acid-Catalyzed Hydrolysis	67
20.2.1.2.10.2.3	Variation 3: Oxidative Hydrolysis	68
20.2.1.2.10.2.4	Variation 4: Enzymatic Hydrolysis	69
20.2.1.2.10.3	Method 3: Hydrolysis of 1,1,1-Trihalides	70
20.5	Product Class 5: Carboxylic Acid Esters	
20.5.1.2.8	Synthesis from Carboxylic Acids and Derivatives	2011
	A. K. Mourad and C. Czekelius	
20.5.1.2.8	Synthesis from Carboxylic Acids and Derivatives	77
20.5.1.2.8.1	Synthesis from Carboxylic Acids	77
20.5.1.2.8.1.1	Method 1: Synthesis via Active Esters	77
20.5.1.2.8.1.1.1	Variation 1: Via Mixed Sulfonic Anhydrides	78
20.5.1.2.8.1.1.2	Variation 2: Via (Acyloxy)phosphorus Compounds	80
20.5.1.2.8.1.1.3	Variation 3: Via Esters of Electron-Deficient Alcohols or of N-Acylhydroxylamines	81
20.5.1.2.8.1.1.4	Variation 4: Via Ketene Acyl Acetals	82
20.5.1.2.8.1.2	Method 2: Oxidative Coupling	83
20.5.1.2.8.1.3	Method 3: Electrophilic Esterification	83
20.5.1.2.8.1.3.1	Variation 1: Using Alkyl Halides	83
20.5.1.2.8.1.3.2	Variation 2: Using Diazoalkanes	85
20.5.1.2.8.1.4	Method 4: Enzymatic Esterification	86

20.5.1.2.8.2	Synthesis from Carboxylic Acid Derivatives	87
20.5.1.2.8.2.1	Method 1: Synthesis from Thioesters	87
20.5.1.2.8.2.2	Method 2: Synthesis from Carboxylic Acid Hydrazides	88

Volume 27: Heteroatom Analogues of Aldehydes and Ketones

27.7	Product Class 7: Imines	
27.7.6	Imines	2011
	S. Dekeukeleire, M. D'hooghe, and N. De Kimpe	
27.7.6	Imines	93
27.7.6.1	N-Unsubstituted Imines	93
27.7.6.1.1	Synthesis of N-Unsubstituted Imines	93
27.7.6.1.1.1	Method 1: Reaction of Aldehydes and Ketones with Ammonia	93
27.7.6.1.1.2	Method 2: Synthesis from Oximes	94
27.7.6.1.1.3	Method 3: Oxidation of Primary Amines	95
27.7.6.1.1.4	Method 4: Synthesis from Nitriles	95
27.7.6.1.1.5	Method 5: Miscellaneous Procedures	97
27.7.6.2	N-Silylimines	97
27.7.6.2.1	Synthesis of N-Silylimines	97
27.7.6.2.1.1	Method 1: Reaction of Carbonyl Compounds with Lithium Hexamethyl-disilazane	97
27.7.6.2.1.2	Method 2: Reaction of Nitriles with Organometallic Reagents	98
27.7.6.3	N-Alkyl- and N-Arylimines	99
27.7.6.3.1	Synthesis of N-Alkyl- and N-Arylimines	100
27.7.6.3.1.1	Method 1: Reaction of Aldehydes or Ketones with Primary Amines	100
27.7.6.3.1.1.1	Variation 1: With Azeotropic Removal of Water	100
27.7.6.3.1.1.2	Variation 2: With Titanium(IV) Chloride	100
27.7.6.3.1.1.3	Variation 3: With Solid-Phase Lewis Acids	102
27.7.6.3.1.1.4	Variation 4: With Other Lewis Acids	102
27.7.6.3.1.1.5	Variation 5: Miscellaneous Procedures	104
27.7.6.3.1.2	Method 2: Reaction of Imidates with Organometallic Reagents	104
27.7.6.3.1.3	Method 3: Synthesis from Amides	105
27.7.6.3.1.3.1	Variation 1: By Reduction	105
27.7.6.3.1.3.2	Variation 2: By Addition of Organometallic Reagents	106
27.7.6.3.1.3.3	Variation 3: By Hydrolysis of N-Vinyl Lactams	107
27.7.6.3.1.3.4	Variation 4: Via Nitrilium Ions	107
27.7.6.3.1.3.5	Variation 5: Miscellaneous Procedures	109
27.7.6.3.1.4	Method 4: Synthesis from Oximes	109
27.7.6.3.1.5	Method 5: Synthesis from Imidoyl Halides	111
27.7.6.3.1.5.1	Variation 1: By Reduction	111

27.7.6.3.1.5.2	Variation 2:	By Substitution	112
27.7.6.3.1.5.3	Variation 3:	Via Palladium-Catalyzed Cross Coupling	112
27.7.6.3.1.5.4	Variation 4:	Via 1,3-Dipolar Cycloaddition	114
27.7.6.3.1.6	Method 6:	Oxidation of Amines	114
27.7.6.3.1.6.1	Variation 1:	Oxidative Amination of Alkenes	114
27.7.6.3.1.6.2	Variation 2:	Oxidation of Secondary Amines	114
27.7.6.3.1.7	Method 7:	Dehydrohalogenation of <i>N</i> -Haloamines	116
27.7.6.3.1.8	Method 8:	Reaction of Aldehydes and Ketones with Azides (Aza-Wittig Reaction)	118
27.7.6.3.1.9	Method 9:	Addition of Primary Amines to Alkynes	120
27.7.6.3.1.10	Method 10:	Addition of Organometallic Compounds to Nitriles	123
27.7.6.3.1.11	Method 11:	Addition/Rearrangement of Alkenic Azides	124
27.7.6.3.1.12	Method 12:	C-Alkylation of 1-Azaallyl Anions	125
27.7.6.3.1.13	Method 13:	N-Alkylation of <i>N</i> -Unsubstituted Imines	126
27.7.6.3.1.14	Method 14:	α -Halogenation of Imines	127
27.7.6.3.1.15	Method 15:	Synthesis from Enamines	129
27.7.6.3.1.16	Method 16:	Synthesis from Isocyanides	130
27.7.6.3.1.17	Method 17:	Synthesis from Alkenyl Halides	132
27.7.6.3.1.18	Method 18:	Miscellaneous Procedures	133
27.7.6.4	2 <i>H</i> -Azirines	136	
27.7.6.4.1	Synthesis of 2 <i>H</i> -Azirines	136	
27.7.6.4.1.1	Method 1:	Synthesis from Oximes and Hydrazonium Salts	136
27.7.6.4.1.2	Method 2:	Oxidation of Aziridines	137
27.7.6.4.1.3	Method 3:	Elimination from <i>N</i> -Substituted Aziridines	137
27.7.6.4.1.4	Method 4:	Synthesis from Vinyl Azides	138
27.7.6.4.1.5	Method 5:	Synthesis from Other Azirines	138
27.7.6.4.1.6	Method 6:	Miscellaneous Procedures	138
27.7.6.5	2,3-Dihydroazetes	140	
27.7.6.5.1	Synthesis of 2,3-Dihydroazetes	140	
27.7.6.5.1.1	Method 1:	Miscellaneous Procedures	140

27.8 Product Class 8: Iminium Salts

27.8.2	Iminium Salts	2011	
	S. Dekeukeleire, M. D'hooghe, and N. De Kimpe		
27.8.2	Iminium Salts	151	
27.8.2.1	Synthesis of Iminium Salts	151	
27.8.2.1.1	Method 1:	Reaction of Secondary Amines with Aldehydes or Ketones	151
27.8.2.1.2	Method 2:	Reaction of Tertiary Amines	154
27.8.2.1.3	Method 3:	Cleavage of Aminals	155
27.8.2.1.4	Method 4:	Cleavage of Hemiaminals	156
27.8.2.1.5	Method 5:	Synthesis from Aldimines and Ketimines	158
27.8.2.1.5.1	Variation 1:	By Alkylation	158

27.8.2.1.5.2	Variation 2: By Protonation	160
27.8.2.1.6	Method 6: Synthesis from Enamines	161
27.8.2.1.6.1	Variation 1: By Alkylation	161
27.8.2.1.6.2	Variation 2: By Protonation	162
27.8.2.1.6.3	Variation 3: By Halogenation	163
27.8.2.1.7	Method 7: Synthesis from Enaminones	164
27.8.2.1.8	Method 8: Cyclization of Alkenimines	166
27.8.2.1.8.1	Variation 1: Electrophile-Induced Cyclization of γ,δ -Unsaturated Imines ..	166
27.8.2.1.8.2	Variation 2: Treatment of γ,δ -Unsaturated Imines with Hydrochloric Acid ..	168
27.8.2.1.9	Method 9: Vilsmeier Formylation	168
27.8.2.1.10	Method 10: Synthesis from Other Iminium Salts	170
27.8.2.1.10.1	Variation 1: By Cycloaddition	170
27.8.2.1.10.2	Variation 2: By Anion Exchange	171
27.8.2.1.11	Method 11: Oxidation of Amino Ketene Acetals	172
27.8.2.1.12	Method 12: Organoboron Compounds as Iminium Ion Generators	172
27.8.2.1.13	Method 13: Miscellaneous Reactions	173

Volume 39: Sulfur, Selenium, and Tellurium

39.3	Product Class 3: Alkanesulfinic Acids and Acyclic Derivatives	
39.3.9	Alkanesulfinic Acids and Acyclic Derivatives	2011
	R. Kawęcki	
39.3.9	Alkanesulfinic Acids and Acyclic Derivatives	179
39.3.9.1	Alkanesulfinyl Halides	179
39.3.9.1.1	Applications of Alkanesulfinyl Halides in Organic Synthesis	179
39.3.9.1.1.1	Method 1: Synthesis of 1-(<i>tert</i> -Butylsulfonyl)aziridines	179
39.3.9.1.1.2	Method 2: Synthesis of Alkyl Sulfoxides	179
39.3.9.1.1.3	Method 3: Synthesis of Dipeptides	180
39.3.9.1.1.4	Method 4: Synthesis of (Alkylsulfonyl)allenes	181
39.3.9.2	Alkanesulfinic Acid Esters	182
39.3.9.2.1	Synthesis of Alkanesulfinic Acid Esters	182
39.3.9.2.1.1	Method 1: Reaction of Alk-2-ene-1-sulfinic Acid–Boron Trichloride Complexes with Ethers	183
39.3.9.2.1.2	Method 2: Reaction of Alkanesulfinyl Chlorides with Alcohols: Asymmetric Synthesis of Alkanesulfinic Acid Esters	184
39.3.9.3	Alkanethiosulfinic Acid Esters	185
39.3.9.3.1	Synthesis of Alkanethiosulfinic Acid Esters	185
39.3.9.3.1.1	Method 1: Synthesis from Disulfides	185
39.3.9.3.1.1.1	Variation 1: By Oxidation with 3-Chloroperoxybenzoic Acid	185
39.3.9.3.1.1.2	Variation 2: By Asymmetric Oxidation	185

39.3.9.4	Alkanesulfinamides	187
39.3.9.4.1	Synthesis of Alkanesulfinamides	187
39.3.9.4.1.1	Method 1: Reduction of <i>N</i> -Alkylidenealkanesulfinamides	187
39.3.9.4.1.1.1	Variation 1: Using Catecholborane or Lithium Triethylborohydride	187
39.3.9.4.1.1.2	Variation 2: Using Sodium Borohydride or L-Selectride	188
39.3.9.4.1.1.3	Variation 3: Using Diisobutylaluminum Hydride	191
39.3.9.4.1.1.4	Variation 4: Stereoselective Reduction–Cyclization	192
39.3.9.4.1.1.5	Variation 5: Using Diethylzinc and Nickel(II) Acetylacetone	193
39.3.9.4.1.2	Method 2: Nucleophilic Addition to <i>N</i> -Alkylidenealkanesulfinamides	194
39.3.9.4.1.2.1	Variation 1: Addition of Grignard Reagents	194
39.3.9.4.1.2.2	Variation 2: Addition of Organolithium Reagents	195
39.3.9.4.1.2.3	Variation 3: Addition of Titanium Enolates	196
39.3.9.4.1.2.4	Variation 4: Addition of Zinc Enolates	198
39.3.9.4.1.2.5	Variation 5: Addition of Zinc/Copper Enolates	200
39.3.9.4.1.2.6	Variation 6: Addition of (Trifluoromethyl)trimethylsilane	201
39.3.9.4.1.2.7	Variation 7: Addition of Silyl Nucleophiles	202
39.3.9.4.1.2.8	Variation 8: Addition of Triorganozincates	203
39.3.9.4.1.2.9	Variation 9: Addition of α -Dithiolanecarboxylates	204
39.3.9.4.1.2.10	Variation 10: Addition of Vinylaluminum Reagents	205
39.3.9.4.1.2.11	Variation 11: Allylation Using Allyl Bromide and Zinc	206
39.3.9.4.1.2.12	Variation 12: Allylation Using Allyl Bromide and Indium	208
39.3.9.4.1.2.13	Variation 13: Allylation Using Allene	210
39.3.9.4.1.2.14	Variation 14: Allylation Using Allylzinc Reagents	211
39.3.9.4.1.2.15	Variation 15: Addition of Lithium Acetyldes	213
39.3.9.4.1.2.16	Variation 16: Addition of Lithium Acetyldes in the Presence of Trimethylaluminum	214
39.3.9.4.1.2.17	Variation 17: Addition of Lithium Acetyldes in the Presence of Titanium(IV) Isopropoxide	215
39.3.9.4.1.2.18	Variation 18: Addition of Alkynylmagnesium Chlorides	216
39.3.9.4.1.2.19	Variation 19: Addition of Arylboronic Acids	217
39.3.9.4.1.2.20	Variation 20: Addition of Alkenyl(trifluoro)borates	219
39.3.9.4.1.2.21	Variation 21: Addition of Silyllithium Reagents	220
39.3.9.4.1.2.22	Variation 22: Addition of Dialkylphosphine Oxides	221
39.3.9.4.1.2.23	Variation 23: Addition of (Tributylstannyl)metals	222
39.3.9.4.1.3	Method 3: Samarium-Promoted Coupling	224
39.3.9.4.1.3.1	Variation 1: Reductive Homocoupling with Samarium(II) Iodide	224
39.3.9.4.1.3.2	Variation 2: Coupling with Nitrones	224
39.3.9.4.1.3.3	Variation 3: Coupling with Aldehydes	225
39.3.9.5	<i>N</i> -Alkylidenealkanesulfinamides	226
39.3.9.5.1	Synthesis of <i>N</i> -Alkylidenealkanesulfinamides	227
39.3.9.5.1.1	Method 1: Condensation of Alkanesulfinamides with Aldehydes and Ketones	227
39.3.9.5.1.1.1	Variation 1: Using Magnesium Sulfate	227
39.3.9.5.1.1.2	Variation 2: Using Copper(II) Sulfate	227
39.3.9.5.1.1.3	Variation 3: Using Titanium(IV) Ethoxide	228
39.3.9.5.1.1.4	Variation 4: Using Cesium Carbonate	229

39.3.9.5.1.1.5	Variation 5:	Using Potassium Hydrogen Sulfate	230
39.3.9.5.1.1.6	Variation 6:	Using Strong Bases	231
39.3.9.5.1.1.7	Variation 7:	Under Barbier-Type Conditions	232
39.3.9.5.1.1.8	Variation 8:	Using Cesium Fluoride	233
39.3.9.5.2		Applications of <i>N</i> -Alkylidenealkanesulfinamides in Organic Synthesis	234
39.3.9.5.2.1	Method 1:	Synthesis of Amines	234
39.3.9.5.2.2	Method 2:	Synthesis of Nitriles	234
39.5		Product Class 5: Alkanethiols	
39.5.2		Alkanethiols	2011
		D. Witt	
39.5.2		Alkanethiols	
39.5.2.1		Applications of Alkanethiols in Organic Synthesis	239
39.5.2.1.1	Method 1:	Synthesis of Sulfonyl Chlorides from Alkanethiols	242
39.5.2.1.2	Method 2:	Synthesis of Alkanesulfonamides from Alkanethiols	243
39.5.2.1.3	Method 3:	Synthesis of Thiosulfinates from Alkanethiols	243
39.5.2.1.4	Method 4:	Synthesis of Sulfides	244
39.5.2.1.4.1	Variation 1:	Reaction of Alkanethiols with Alkyl Halides	244
39.5.2.1.4.2	Variation 2:	Preparation of Dialkyl Sulfides by Substitution of Alcohols and Carbamates	244
39.5.2.1.4.3	Variation 3:	Ring Opening of Cyclic Ethers and Aziridines	246
39.5.2.1.4.4	Variation 4:	Addition of Alkanethiols to Simple Alkenes	247
39.5.2.1.4.5	Variation 5:	Miscellaneous Reactions for Sulfide Formation	248
39.5.2.1.5	Method 5:	Synthesis of β -Sulfido Carbonyl and Related Compounds	248
39.5.2.1.6	Method 6:	Synthesis of Alkyl Aryl Sulfides	251
39.5.2.1.7	Method 7:	Synthesis of Alkyl Vinyl Sulfides	254
39.5.2.1.7.1	Variation 1:	Coupling of Alkanethiols with Vinyl Halides	254
39.5.2.1.7.2	Variation 2:	Addition of Alkanethiols to Alkynes	257
39.5.2.1.8	Method 8:	Synthesis of Acyclic Dialkyl Disulfides	258
39.5.2.1.8.1	Variation 1:	Symmetrical Dialkyl Disulfides	258
39.5.2.1.8.2	Variation 2:	Unsymmetrical Dialkyl Disulfides	260
39.5.2.1.9	Method 9:	Synthesis of Acyclic Dialkyl Trisulfides	263
39.5.2.1.9.1	Variation 1:	Symmetrical Dialkyl Trisulfides	263
39.5.2.1.9.2	Variation 2:	Unsymmetrical Dialkyl Trisulfides	264
39.5.2.1.10	Method 10:	Synthesis of Dithioacetals and Dithioketals	266
39.5.2.1.11	Method 11:	Synthesis of O,S-Acetals	269
39.5.2.1.12	Method 12:	Synthesis of Thioesters	272
39.5.2.1.13	Method 13:	Synthesis of Thiocarbamates	275
39.5.2.1.14	Method 14:	Miscellaneous Reactions Involving Application of Alkanethiols	277

39.6	Product Class 6: Acyclic Alkanethiolates	
39.6.1.2	Alkanethiolates of Group 1, 2, and 13–15 Metals	2011
	D. Witt	
39.6.1.2	Alkanethiolates of Group 1, 2, and 13–15 Metals	281
39.6.1.2.1	Applications of Alkanethiolates of Group 13–15 Metals in Organic Synthesis	281
39.6.1.2.1.1	Applications of Arsenic Alkanethiolates	281
39.6.1.2.1.1.1	Method 1: Preparation of Sulfonium Salts	281
39.6.1.2.1.1.2	Method 2: Preparation of Unsymmetrical Dialkyl Disulfides	282
39.6.1.2.1.1.3	Method 3: Preparation of (Alkylsulfanyl)stannanes	282
39.6.1.2.1.1.4	Method 4: Preparation of Phosphonotri thioate Derivatives	282
39.6.1.2.1.1.5	Method 5: Preparation of Trialkylarsines	283
39.6.1.2.1.2	Applications of Silicon Alkanethiolates	283
39.6.1.2.1.2.1	Method 1: Preparation of O-Silyl O,S-Acetals, S,S-Acetals, and S,S-Ketals	283
39.6.1.2.1.2.2	Method 2: Preparation of S-Alkyl Thiocarboxylates	284
39.6.1.2.1.2.3	Method 3: Preparation of Dialkyl Sulfides	285
39.6.1.2.1.2.4	Method 4: Preparation of Methyl 1-Thioglycosides	289
39.6.1.2.1.2.5	Method 5: Preparation of Disulfides	289
39.6.1.2.1.2.6	Method 6: Miscellaneous Reactions of Silicon Alkanethiolates	290
39.6.1.2.1.3	Applications of Germanium Alkanethiolates	292
39.6.1.2.1.3.1	Method 1: Preparation of [(Alkylsulfanyl)alkyl]germanes	292
39.6.1.2.1.3.2	Method 2: Preparation of Phosphonodithioate Derivatives	292
39.6.1.2.1.4	Applications of Tin Alkanethiolates	293
39.6.1.2.1.4.1	Method 1: Preparation of Alkyl 1-Thioglycosides	293
39.6.1.2.1.4.2	Method 2: Preparation of Alkyl Aryl Sulfides and Alkyl Vinyl Sulfides	294
39.6.1.2.1.4.3	Method 3: Preparation of Alkyl Disulfides	295
39.6.1.2.1.4.4	Method 4: Miscellaneous Reactions of Tin Alkanethiolates	297
39.6.1.2.1.5	Applications of Lead Alkanethiolates	300
39.6.1.2.1.5.1	Method 1: Preparation of (Alkylsulfanyl)silanes	300
39.6.1.2.1.5.2	Method 2: Preparation of Trithioortho Esters	300
39.6.1.2.1.6	Applications of Boron Alkanethiolates	301
39.6.1.2.1.6.1	Method 1: Preparation of S-Alkyl Thiocarboxylates	301
39.6.1.2.1.6.2	Method 2: Preparation of Alkyl Aryl Sulfides and Alkyl Vinyl Sulfides	302
39.6.1.2.1.6.3	Method 3: Miscellaneous Reactions of Boron Alkanethiolates	304
39.6.1.2.1.7	Applications of Aluminum Alkanethiolates	306
39.6.1.2.1.7.1	Method 1: Preparation of S-Alkyl Thiocarboxylates and Related Compounds	306
39.6.1.2.1.7.2	Method 2: Preparation of β -Alkylsulfanyl-Substituted Ketones and Related Compounds	308
39.6.1.2.1.7.3	Method 3: Preparation of Alkyl Alkanimidothioates	312
39.6.1.2.1.7.4	Method 4: Miscellaneous Reactions of Aluminum Alkanethiolates	313

39.6.1.2.1.8	Applications of Indium Alkanethiolates	315
39.6.1.2.1.8.1	Method 1: Preparation of Alkyl Aryl Sulfides	315
39.6.1.2.1.9	Applications of Thallium Alkanethiolates	316
39.6.1.2.1.9.1	Method 1: Preparation of S-Alkyl Thiocarboxylates	316
39.6.1.2.2	Applications of Alkanethiolates of Group 1 and 2 Metals in Organic Synthesis	317
39.6.1.2.2.1	Applications of Lithium Alkanethiolates	317
39.6.1.2.2.1.1	Method 1: Preparation of Sulfides	317
39.6.1.2.2.1.2	Method 2: Preparation of S-Alkyl Thiocarboxylates and Related Compounds	321
39.6.1.2.2.1.3	Method 3: Miscellaneous Reactions of Lithium Alkanethiolates	323
39.6.1.2.2.2	Applications of Sodium Alkanethiolates	325
39.6.1.2.2.2.1	Method 1: Preparation of Alkyl Sulfides	325
39.6.1.2.2.2.2	Method 2: Preparation of α -Alkylsulfanyl-Substituted Carbonyl Compounds	328
39.6.1.2.2.2.3	Method 3: Preparation of S-Alkyl Thiocarboxylates and Related Compounds	331
39.6.1.2.2.2.4	Method 4: Deprotection or Removal of Functional Groups	332
39.6.1.2.2.2.5	Method 5: Miscellaneous Reactions of Sodium Alkanethiolates	334
39.6.1.2.2.3	Applications of Potassium Alkanethiolates	336
39.6.1.2.2.3.1	Method 1: Miscellaneous Reactions of Potassium Alkanethiolates	336
39.6.1.2.2.4	Applications of Cesium Alkanethiolates	338
39.6.1.2.2.4.1	Method 1: Preparation of Alkyl Sulfides	338
39.6.1.2.2.5	Applications of Halomagnesium Alkanethiolates	339
39.6.1.2.2.5.1	Method 1: Deprotection of Functional Groups	339
39.39	Product Class 39: Tellurolanes, Larger Rings, and Derivatives of Various Oxidation States	
39.39.1	Product Subclass 1: Cyclic Alkanetelluronic Acid Derivatives	2011
	T. Kimura	
39.39.1	Product Subclass 1: Cyclic Alkanetelluronic Acid Derivatives	345
39.39.2	Product Subclass 2: Cyclic Dialkyl Tellurones and Derivatives	2011
	T. Kimura	
39.39.2	Product Subclass 2: Cyclic Dialkyl Tellurones and Derivatives	347
39.39.2.1	Synthesis of Product Subclass 2	347
39.39.2.1.1	Cyclic Tellurone Derivatives	347
39.39.2.1.1.1	Method 1: Reaction of Spirodioxytelluranes with Hydrogen Peroxide ...	347

39.39.2.1.1.2	Method 2:	Reaction of 2,2-Diiodo-1,3-dihydrobenzo[c]tellurophene with Sodium Diethyldithiocarbamate and Related Compounds	348
39.39.2.1.1.3	Method 3:	Reaction of 1,1-Diiodo-1λ ⁴ -tellurane with Tetraphenyl Onium Iodides	349

Volume 40:

Amines, Ammonium Salts, Amine N-Oxides, Halo-amines, Hydroxylamines and Sulfur Analogues, and Hydrazines

40.1 Product Class 1: Amino Compounds

40.1.1.5.5 Metal-Mediated Cyclizations of Amines

J. Ipaktschi and M. R. Saidi

New

40.1.1.5.5	Metal-Mediated Cyclizations of Amines	351
40.1.1.5.5.1	Metal-Catalyzed Cycloisomerizations of N-Tethered 1,n-Enynes and 1,n-Dienes	351
40.1.1.5.5.1.1	Enyne Cycloisomerization without Skeletal Reorganization	352
40.1.1.5.5.1.1.1	Method 1: Palladium-Catalyzed Cycloisomerization to Pyrrolidine Derivatives	352
40.1.1.5.5.1.1.1.1	Variation 1: Enantioselective Cycloisomerization of 1,6-Enynes Catalyzed by Chiral Bisphosphine–Palladium Complexes	355
40.1.1.5.5.1.1.2	Method 2: Rhodium-Catalyzed 1,6-Enyne Cycloisomerization to Pyrrolidine Derivatives	357
40.1.1.5.5.1.1.2.1	Variation 1: Rhodium-Catalyzed Cycloisomerization of 1,6-Enynes to Alder-Ene-Type Products	357
40.1.1.5.5.1.1.2.2	Variation 2: Rhodium-Catalyzed Asymmetric 1,6-Enyne Cycloisomerization of Terminal Alkynes	359
40.1.1.5.5.1.1.2.3	Variation 3: Rhodium-Catalyzed Enantioselective Reductive Cyclization of 1,6-Enynes	361
40.1.1.5.5.1.1.3	Method 3: Ruthenium-Catalyzed Cycloisomerization of 1,6-Enynes	362
40.1.1.5.5.1.1.4	Method 4: Titanocene-Catalyzed Cycloisomerization of 1,6-Enynes to Pyrrolidine Derivatives	363
40.1.1.5.5.1.1.5	Method 5: Bismuth(III) Chloride Catalyzed Cycloisomerization of 1,6-Enynes	364
40.1.1.5.5.1.1.6	Method 6: Nickel-Catalyzed Reductive Cyclization of Unactivated N-Tethered 1,6-Enynes in the Presence of Organozinc Reagents	365
40.1.1.5.5.1.1.7	Method 7: Cycloisomerization of 1,6-Enynes Catalyzed by Low-Valent Iron Complexes	368
40.1.1.5.5.1.1.8	Method 8: Silver(I)-Catalyzed Cycloisomerization of 1,6-Enynes Containing Propargylic Alcohol Groups	371
40.1.1.5.5.1.1.8.1	Variation 1: Intramolecular Carbostannylation Catalyzed by Silver(I) Ions	373
40.1.1.5.5.1.1.9	Method 9: Gold(I)-Catalyzed Transformations of N-Tethered 1,6-Enynes	374
40.1.1.5.5.1.1.9.1	Variation 1: Gold(I)-Catalyzed Cycloisomerization of 1,6-Enynes to 1,4-Dienes	374
40.1.1.5.5.1.1.9.2	Variation 2: Gold(I)-Catalyzed Methoxycyclization of Enynes	375

40.1.1.5.5.1.1.9.3	Variation 3:	Gold-Catalyzed Asymmetric Hydroxycyclization	376
40.1.1.5.5.1.1.9.4	Variation 4:	Gold(I)-Catalyzed Tandem Cyclization/Friedel–Crafts-Type Addition	376
40.1.1.5.5.1.1.10	Method 10:	Enantioselective Cycloisomerization of 1,7-Enynes to Piperidine Derivatives	377
40.1.1.5.5.1.2		Enyne Cycloisomerization with Skeletal Reorganization	379
40.1.1.5.5.1.2.1	Method 1:	Gallium(III) Chloride Catalyzed Isomerization of 1,6-Enynes to Eight-Membered Rings	380
40.1.1.5.5.1.2.2	Method 2:	Rhodium-Catalyzed Asymmetric Cycloisomerization of Nitrogen-Bridged 1,6-Enynes to Bicyclo[4.1.0]hept-4-ene Derivatives	381
40.1.1.5.5.1.2.3	Method 3:	Gold(I)-Catalyzed Transformations of 1,6-Enynes with Skeletal Rearrangement	383
40.1.1.5.5.1.2.3.1	Variation 1:	Rearrangements to Piperidine Derivatives	384
40.1.1.5.5.1.2.3.2	Variation 2:	Rearrangements of N-Tethered 1,6-Enynes to 3-Azabicyclo[4.1.0]heptene Derivatives	385
40.1.1.5.5.1.2.3.3	Variation 3:	Gold(I)-Catalyzed Cycloisomerizations of Amide-Tethered 1,6-Enynes	391
40.1.1.5.5.1.2.4	Method 4:	Platinum-Catalyzed Cycloisomerization Reactions of Enynes ..	393
40.1.1.5.5.1.2.4.1	Variation 1:	Application of Axially Chiral Platinum(II) Complexes	397
40.1.1.5.5.1.2.4.2	Variation 2:	Platinum-Catalyzed Cycloisomerization of Chiral Enynes	398
40.1.1.5.5.2		Metathesis of N-Tethered Dienes and Enynes	400
40.1.1.5.5.2.1	Method 1:	Ring-Closing Metathesis of N-Tethered 1,n-Dienes	402
40.1.1.5.5.2.1.1	Variation 1:	Ring-Closing Metathesis of 1,n-Dienes in Water as Solvent ..	408
40.1.1.5.5.2.2	Method 2:	Ring-Closing Metathesis of Chiral Dienes: Synthesis of Chiral Five- to Eight-Membered Nitrogen-Containing Heterocycles ..	412
40.1.1.5.5.2.2.1	Variation 1:	Synthesis of Optically Active 2-Alkyl-Substituted 2,5-Dihydro-pyrroles	412
40.1.1.5.5.2.2.2	Variation 2:	Synthesis of Optically Active Six- to Eight-Membered Nitrogen-Containing Heterocycles	412
40.1.1.5.5.2.3	Method 3:	Ring-Rearrangement Metathesis	415
40.1.1.5.5.2.3.1	Variation 1:	Ring-Rearrangement Metathesis of Cyclopropene Derivatives ..	415
40.1.1.5.5.2.3.2	Variation 2:	Synthesis of (–)-Swainsonine by a Ruthenium-Catalyzed Ring-Closing/Ring-Opening Tandem Process	417
40.1.1.5.5.2.4	Method 4:	Asymmetric Ring-Closing Metathesis: Synthesis of Nitrogen-Containing Heterocycles	419
40.1.1.5.5.2.4.1	Variation 1:	Enantioselective Synthesis of Cyclic Amines through Molybdenum-Catalyzed Asymmetric Ring-Closing Metathesis	420
40.1.1.5.5.2.4.2	Variation 2:	Enantioselective Synthesis of Cyclic Amides through Molybdenum-Catalyzed Asymmetric Ring-Closing Metathesis	422
40.1.1.5.5.2.4.3	Variation 3:	Application of Asymmetric Ring-Closing Metathesis to the Enantioselective Synthesis of Quebrachamine	425
40.1.1.5.5.2.4.4	Variation 4:	Microwave-Induced Ring-Closing Metathesis of Dienes	428
40.1.1.5.5.2.5	Method 5:	Ring-Closing Metathesis of N-Tethered Enynes	429
40.1.1.5.5.2.5.1	Variation 1:	<i>exo</i> -Selective Enyne Ring-Closing Metathesis Promoted by Ruthenium Carbenes: Efficient Synthesis of Chiral Five-Membered Nitrogen-Containing Heterocycles	431

40.1.1.5.5.2.5.2	Variation 2:	<i>endo</i> -Selective Enyne Ring-Closing Metathesis Promoted by Stereogenic-at-Molybdenum Complexes	432
40.1.1.5.5.2.5.3	Variation 3:	Enantioselective Molybdenum-Catalyzed Ring-Closing Metathesis Reactions of Dienynes	434
40.1.1.5.5.2.5.4	Variation 4:	Ring-Closing Metathesis of Chiral Enynes; Synthesis of Six- and Seven-Membered Chiral Nitrogen-Containing Heterocycles ..	435
40.1.1.5.5.2.6	Method 6:	Tandem Enyne Ring-Closing Metathesis and Selective Hydrogenation to a Tricyclic Carbamate	436
40.1.1.5.5.2.7	Method 7:	Ruthenium-Catalyzed Tandem Ring-Opening/Ring-Closing/Cross Metathesis of Cyclopropene-Containing 1,6-Enynes and Alkenes	437
40.1.1.5.5.3		Transition-Metal-Catalyzed Cycloaddition Reactions of N-Tethered 1,n-Enynes, 1,n-Dynes, and 1,n-Dienes	438
40.1.1.5.5.3.1	Method 1:	Synthesis of Nitrogen-Containing Heterocycles by Pauson–Khand Reaction of Enynes	439
40.1.1.5.5.3.1.1	Variation 1:	Diastereoselective Pauson–Khand Reaction of Nitrogen-Containing 1,n-Enynes and 1,n-Dienes	440
40.1.1.5.5.3.1.2	Variation 2:	Asymmetric Pauson–Khand-Type Reaction Mediated by a Rhodium(I) Catalyst at Ambient Temperature	442
40.1.1.5.5.3.1.3	Variation 3:	Rhodium(I)-Catalyzed Carbonylative [5 + 2 + 1] and [3 + 2 + 1] Carbocyclization: Synthesis of Fused Cyclooctenones, Cyclohexenones, and Phenol Derivatives	444
40.1.1.5.5.3.1.4	Variation 4:	Rhodium-Catalyzed Pauson–Khand-Type Reaction Using an Alcohol as a Source of Carbon Monoxide	447
40.1.1.5.5.3.2	Method 2:	Transition-Metal-Mediated Cycloaddition and Cyclization Reactions of 2-Methylpropane-2-sulfonamide-Tethered Enyne and Diyne Substrates	449
40.1.1.5.5.3.3	Method 3:	Regio- and Enantioselective Intermolecular Rhodium-Catalyzed [2 + 2 + 2]-Cycloaddition Reactions of 1,6-Enynes	455
40.1.1.5.5.3.3.1	Variation 1:	Intramolecular Rhodium-Catalyzed [2 + 2 + 2] Cyclizations of N-Tethered 1,6-Dynes with α,β -Unsaturated Carbonyl Compounds under Microwave Irradiation	461
40.1.1.5.5.3.3.2	Variation 2:	[2 + 2 + 2] Cycloaddition of 1,6-Enynes with Electron-Deficient Ketones Catalyzed by a Cationic Rhodium(I)/H ₈ -BINAP Complex	462
40.1.1.5.5.3.3.3	Variation 3:	Cyclotrimerization of N-Tethered 1,6-Dynes with Triple Bonds: Synthesis of Chiral Aromatic Compounds	464
40.1.1.5.5.3.3.4	Variation 4:	Enantioselective Synthesis of Chiral Polycyclic Compounds with Quaternary Carbon Stereocenters by Catalytic Intramolecular Cycloaddition	467
40.1.1.5.5.3.3.5	Variation 5:	Enantioselective Synthesis of Axially Chiral N,N-Dialkylbenzamides by Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition of N-Tethered Dienes with N,N-Dialkylalkynylbenzamides	470
40.1.1.5.5.3.3.6	Variation 6:	Palladium-Catalyzed Tandem Reaction of N-Tethered 1,6-Diynyl Carbonates with 2,3-Dienoic Acids	471
40.1.1.5.5.3.4	Method 4:	Metal-Catalyzed Intramolecular Diels–Alder Reactions of Unactivated Alkynes To Give Bi- and Polycyclic Nitrogen-Containing Heterocycles	472

40.1.1.5.5.3.4.1	Variation 1:	Gold-Catalyzed [4 + 2] Cycloadditions of N-Tethered Dien-allenes	476
40.1.1.5.5.3.5	Method 5:	Sequential Platinum-Catalyzed Cycloisomerization and Cope Rearrangement of N-Tethered Dienynes	481
40.1.1.5.5.3.6	Method 6:	Rhodium-Catalyzed Intramolecular Cyclization of Cyclopropyl-Containing N-Tethered 1,6-Dienes	483
40.1.1.5.5.4		Transition-Metal-Catalyzed Cyclization/Coupling Reactions of Unsaturated Amines and Amides	485
40.1.1.5.5.4.1	Method 1:	Mizoroki–Heck Reactions of Amines and Amides	486
40.1.1.5.5.4.1.1	Variation 1:	Palladium-Catalyzed Domino Coupling/Cycloisomerization of N-Tethered 1,6-Enynes	486
40.1.1.5.5.4.2	Method 2:	Synthesis of Annulated Hexahydro-1 <i>H</i> -benzo[<i>f</i>]isoindole Derivatives	488
40.1.1.5.5.4.3	Method 3:	Synthesis of Haouamine Precursors by Cascade Mizoroki–Heck Cyclization	489
40.1.1.5.5.4.4	Method 4:	Preparation of Nitrogen-Containing Spiro-Fused Dihydroindolones by Palladium-Catalyzed Tandem Mizoroki–Heck Reaction/C–H Functionalization	490
40.1.1.5.5.5		Cross-Coupling Reactions of N-Tethered 1,6-Dienes and 1,6-Enynes	493
40.1.1.5.5.5.1	Method 1:	Palladium-Catalyzed Cycloalkylations of N-Tethered 2-Bromo-1,6-dienes with Organoboronic Acids	493
40.1.1.5.5.5.2	Method 2:	Palladium-Catalyzed Tandem Cyclization/Suzuki Coupling of N-Tethered 1,6-Enynes To Give Mono- and Bicyclic Heterocycles	494
40.1.1.5.5.5.3	Method 3:	Palladium-Mediated Cascade Cross-Coupling/Electrocyclization Approach to the Construction of Fused Bi- and Tricyclic Rings	495
Author Index			505
Abbreviations			535