

Volume 33: Ene–X Compounds (X = S, Se, Te, N, P)

	Preface	V
	Volume Editor's Preface	VII
	Table of Contents	XIII
	Introduction	
	G. A. Molander	1
33.1	Product Class 1: Alk-1-enyl Sulfur Compounds	
33.1.1	Product Subclass 1: Alk-1-enesulfonic Acids and Derivatives	
	J. C. Carretero and R. G. Arrayás	13
33.1.2	Product Subclass 2: Alk-1-enyl Sulfones	
	J. C. Carretero and R. G. Arrayás	19
33.1.3	Product Subclass 3: S-Alk-1-enylsulfoximides	
	J. C. Carretero and R. G. Arrayás	51
33.1.4	Product Subclass 4: Alk-1-enesulfinic Acids and Derivatives	
	J. C. Carretero and R. G. Arrayás	59
33.1.5	Product Subclass 5: Alk-1-enyl Sulfoxides, Sulfimides, and Related Compounds	
	J. C. Carretero and R. G. Arrayás	65
33.1.6	Product Subclass 6: Alk-1-enethiols	
	J. Drabowicz, P. Kielbasiński, and M. Mikołajczyk	101
33.1.7	Product Subclass 7: Metal Alk-1-enethiolates	
	J. Drabowicz, P. Kielbasiński, and M. Mikołajczyk	109
33.1.8	Product Subclass 8: Alk-1-enyl Sulfides	
	J. Drabowicz, P. Kielbasiński, and M. Mikołajczyk	113
33.1.9	Product Subclass 9: Alk-1-enylsulfonium Salts	
	J. Drabowicz, P. Kielbasiński, and M. Mikołajczyk	169
33.1.10	Product Subclass 10: Alk-1-enesulfenic Acid Derivatives	
	J. Drabowicz, P. Kielbasiński, and M. Mikołajczyk	177
33.1.11	Product Subclass 11: Alk-1-enyl Disulfides	
	J. Drabowicz, P. Kielbasiński, and M. Mikołajczyk	183

33.1.12	Product Subclass 12: Thietes and Derivatives	
	E. Block	187
33.1.13	Product Subclass 13: 2,3-Dihydrothiophenes and Derivatives	
	E. Block	203
33.1.14	Product Subclass 14: 3,4-Dihydro-2H-thiopyrans and Derivatives	
	E. Block	235
33.1.15	Product Subclass 15: 2,3,4,5-Tetrahydrothiepins, Larger Rings, and Derivatives	
	E. Block	259
33.2	Product Class 2: Alk-1-enyl Selenium Compounds	
	D. Avilov and D. Dittmer	275
33.3	Product Class 3: Alk-1-enyl Tellurium Compounds	
	D. Avilov and D. Dittmer	303
33.4	Product Class 4: Alk-1-enyl Nitrogen Compounds	
33.4.1	Product Subclass 1: 1-Nitroalkenes	
	N. Ono	337
33.4.2	Product Subclass 2: 1-Nitrosoalkenes	
	H.-U. Reissig and R. Zimmer	371
33.4.3	Product Subclass 3: N-Alk-1-enyliminosulfur Compounds	
	H.-U. Reissig and R. Zimmer	391
33.4.4	Product Subclass 4: Alk-1-enediazonium Salts, Alkeneazoxy, and Alkeneazo Compounds	
	395
33.4.5	Product Subclass 5: N-Alk-1-enyliminophosphorus Compounds	
	H.-U. Reissig and R. Zimmer	397
33.4.6	Product Subclass 6: Enamines	
	T. Sammakia, J. A. Abramite, and M. F. Sammons	405
33.4.7	Product Subclass 7: Enammonium Salts	
	T. Sammakia, J. A. Abramite, and M. F. Sammons	443
33.4.8	Product Subclass 8: N-Silylenamines	
	S. J. Collier	451
33.4.9	Product Subclass 9: N-Borylenamines	
	S. J. Collier	475

33.4.10	Product Subclass 10: N-Haloenamines S. J. Collier	487
33.4.11	Product Subclass 11: N-Alk-1-enylhydroxylamines S. J. Collier	493
33.4.12	Product Subclass 12: N-Alk-1-enylaminosulfur Compounds S. J. Collier	503
33.4.13	Product Subclass 13: Alk-1-enylhydrazines S. J. Collier and M. D. McLaws	521
33.4.14	Product Subclass 14: Alk-1-enyl Azides S. J. Collier	541
33.4.15	Product Subclass 15: N-Alk-1-enylaminophosphorus Compounds S. J. Collier	565
33.4.16	Product Subclass 16: 1,2-Dihydroazetes and Derivatives P. Jubault, E. Leclerc, and J.-C. Quirion	577
33.4.17	Product Subclass 17: 2,3-Dihydro-1H-pyrroles and Derivatives P. Jubault, E. Leclerc, and J.-C. Quirion	583
33.4.18	Product Subclass 18: 1,2-Dihydropyridines, 1,4-Dihydropyridines, and Derivatives J.-C. Quirion, E. Leclerc, and P. Jubault	601
33.4.19	Product Subclass 19: 1,2,3,4-Tetrahydropyridines and Derivatives J.-C. Quirion	629
33.4.20	Product Subclass 20: 2,3,4,5-Tetrahydro-1H-azepines, Larger Rings, and Derivatives J.-C. Quirion, E. Leclerc, and P. Jubault	659
33.5	Product Class 5: Alk-1-enyl Phosphorus Compounds	
33.5.1	Product Subclass 1: Alk-1-enylphosphonic Acids and Derivatives A. C. Gaumont and M. Gulea	665
33.5.2	Product Subclass 2: Alk-1-enylphosphinic Acids and Derivatives A. C. Gaumont and M. Gulea	695
33.5.3	Product Subclass 3: Alk-1-enylphosphine Oxides and Derivatives A. C. Gaumont and M. Gulea	701
33.5.4	Product Subclass 4: Alk-1-enylphosphines A. C. Gaumont and M. Gulea	711

33.5.5	Product Subclass 5: Alk-1-enylphosphonium Salts A. C. Gaumont and M. Gulea	725
33.5.6	Product Subclass 6: P-Heteroatom-Substituted Alk-1-enylphosphines A. C. Gaumont and M. Gulea	731
33.5.7	Product Subclass 7: 1,2-Dihydrophosphetes and Derivatives Gy. Keglevich and H. Szelke	737
33.5.8	Product Subclass 8: 2,3-Dihydro-1H-phospholes and Derivatives Gy. Keglevich and H. Szelke	745
33.5.9	Product Subclass 9: 1,2,3,4-Tetrahydrophosphinines and Derivatives Gy. Keglevich and H. Szelke	759
33.5.10	Product Subclass 10: 1,4-Dihydrophosphinines and Derivatives Gy. Keglevich and H. Szelke	765
	Keyword Index	773
	Author Index	817
	Abbreviations	861

Table of Contents

Introduction

G. A. Molander

Introduction	1
---------------------------	---

33.1 Product Class 1: Alk-1-enyl Sulfur Compounds

33.1.1 Product Subclass 1: Alk-1-enesulfonic Acids and Derivatives

J. C. Carretero and R. G. Arrayás

33.1.1	Product Subclass 1: Alk-1-enesulfonic Acids and Derivatives	13
33.1.1.1	Synthesis of Product Subclass 1	13
33.1.1.1.1	Method 1: Synthesis from 2-Chloroalkanesulfonic Acid Derivatives	13
33.1.1.1.2	Method 2: Condensations of the Carbanions of Sulfonic Acid Derivatives with Carbonyl Compounds	14
33.1.1.1.2.1	Variation 1: Aldol-Type Condensations and Related Processes	14
33.1.1.1.2.2	Variation 2: Wadsworth–Emmons Alkenation Reactions	15
33.1.1.1.3	Method 3: Cyclic Alk-1-enesulfonic Esters and Sulfonamides by Metathesis Reactions	16
33.1.1.1.4	Methods 4: Miscellaneous Syntheses of Alk-1-enesulfonic Acid Derivatives from Other Sulfur Compounds	17

33.1.2 Product Subclass 2: Alk-1-enyl Sulfones

J. C. Carretero and R. G. Arrayás

33.1.2	Product Subclass 2: Alk-1-enyl Sulfones	19
33.1.2.1	Synthesis of Product Subclass 2	19
33.1.2.1.1	Method 1: Sulfonylation of Nucleophilic Alkenyl Reagents	19
33.1.2.1.2	Method 2: Condensation of Sulfonyl Carbanions with Carbonyl Compounds	20
33.1.2.1.2.1	Variation 1: Aldol-Type Condensation and Dehydration	20
33.1.2.1.2.2	Variation 2: Knoevenagel Condensation of Activated Sulfones	22
33.1.2.1.2.3	Variation 3: Condensation of Sulfinyl(sulfonyl)methanes with Aldehydes	23
33.1.2.1.2.4	Variation 4: Horner–Wadsworth–Emmons Alkenation of α -Sulfonyl Phosphonates	24
33.1.2.1.2.5	Variation 5: Peterson Alkenation of α -Silylalkyl Sulfones	26
33.1.2.1.3	Method 3: Sulfonylation of Alkenes Followed by Elimination	28
33.1.2.1.3.1	Variation 1: Chlorosulfonylation of Alkenes, Followed by Sulfur Oxidation and Elimination	28
33.1.2.1.3.2	Variation 2: Sulfonomercuration of Alkenes Followed by Demercuration	29
33.1.2.1.3.3	Variation 3: Selenosulfonylation of Alkenes Followed by Selenium Oxidation	30

33.1.2.1.3.4	Variation 4:	Iodosulfonylation of Alkenes Followed by Dehydroiodination	31
33.1.2.1.4	Method 4:	Sulfonylation of Alkynes	33
33.1.2.1.5	Method 5:	Functionalization of Alk-1-ynyl Sulfones	34
33.1.2.1.5.1	Variation 1:	Addition Reactions	35
33.1.2.1.5.2	Variation 2:	Cycloaddition Reactions	37
33.1.2.1.6	Method 6:	Oxidation of Alk-1-enyl Sulfides and Sulfoxides	37
33.1.2.1.7	Method 7:	Functionalization of Allyl Sulfones and Derivatives	38
33.1.2.1.8	Method 8:	Functionalization of Simple Alk-1-enyl Sulfones	40
33.1.2.1.8.1	Variation 1:	α -Functionalization	40
33.1.2.1.8.2	Variation 2:	Heck Reaction	42
33.1.2.1.8.3	Variation 3:	Cross-Metathesis Reactions	43
33.1.2.1.8.4	Variation 4:	Diels–Alder Reactions of Dienyl Sulfones	44
33.1.2.1.8.5	Variation 5:	Substitution of β -Functionalized Alk-1-enyl Sulfones	45
33.1.3	Product Subclass 3: S-Alk-1-enylsulfoximides		
	J. C. Carretero and R. G. Arrayás		
33.1.3	Product Subclass 3: S-Alk-1-enylsulfoximides		51
33.1.3.1	Synthesis of Product Subclass 3		51
33.1.3.1.1	Method 1:	Condensation of Sulfonimidoyl Carbanions with Carbonyl Compounds	51
33.1.3.1.1.1	Variation 1:	Aldol-Type Condensations of α -Sulfonimidoyl Carbanions and the Dehydration of the Intermediate β -Hydroxylated Sulfoximides	52
33.1.3.1.1.2	Variation 2:	Peterson and Wadsworth–Emmons Alkenation Reactions	54
33.1.3.1.2	Method 2:	Imination of Alk-1-enyl Sulfoxides	55
33.1.3.1.3	Method 3:	Functionalization of Simple S-Alk-1-enyl- and S-Alk-2-enylsulfoximides	56
33.1.4	Product Subclass 4: Alk-1-enesulfinic Acids and Derivatives		
	J. C. Carretero and R. G. Arrayás		
33.1.4	Product Subclass 4: Alk-1-enesulfinic Acids and Derivatives		59
33.1.4.1	Synthesis of Product Subclass 4		59
33.1.4.1.1	Method 1:	Reaction of Allenes and Alkynes with Sulfur Dioxide	59
33.1.4.1.2	Method 2:	Oxidative Fragmentation of Alk-1-enyl Benzyl Sulfoxides	60
33.1.4.1.3	Method 3:	S-Oxidation of Isothiazol-3(2H)-ones	61
33.1.5	Product Subclass 5: Alk-1-enyl Sulfoxides, Sulfimides, and Related Compounds		
	J. C. Carretero and R. G. Arrayás		
33.1.5	Product Subclass 5: Alk-1-enyl Sulfoxides, Sulfimides, and Related Compounds		65
33.1.5.1	Synthesis of Product Subclass 5		66

33.1.5.1.1	Method 1:	Sulfinylation of Nucleophilic Alkenyl Reagents	66
33.1.5.1.1.1	Variation 1:	Sulfinylation with Menthyl 4-Toluenesulfinate	66
33.1.5.1.1.2	Variation 2:	Sulfinylation with Other Enantiopure Sulfinylating Reagents	67
33.1.5.1.2	Method 2:	Condensations of Sulfinyl Carbanions (and Related Species) with Carbonyl Compounds	69
33.1.5.1.2.1	Variation 1:	Aldol-Type Condensations and Dehydrations	69
33.1.5.1.2.2	Variation 2:	Mannich-Type Reactions	72
33.1.5.1.2.3	Variation 3:	Knoevenagel-Type Condensations	73
33.1.5.1.2.4	Variation 4:	Wadsworth–Emmons Alkenation	75
33.1.5.1.2.5	Variation 5:	Wittig and Horner–Wittig Reactions	79
33.1.5.1.2.6	Variation 6:	Peterson Alkenation	80
33.1.5.1.3	Method 3:	Conversions of Alkynes into Alkenyl and Allenyl Sulfoxides	81
33.1.5.1.3.1	Variation 1:	Additions of Sulfenic Acids to Alkynes	82
33.1.5.1.3.2	Variation 2:	Reactions of Sulfenyl Chlorides with Propargylic Alcohols	83
33.1.5.1.4	Method 4:	Addition Reactions to Alkynyl Sulfoxides	84
33.1.5.1.5	Method 5:	Oxidation of Alkenyl Sulfides	86
33.1.5.1.6	Method 6:	Functionalization of Alkenyl Sulfoxides and Derivatives	88
33.1.5.1.6.1	Variation 1:	α -Functionalization	88
33.1.5.1.6.2	Variation 2:	The Heck Reaction	90
33.1.5.1.6.3	Variation 3:	The Stille and Other Palladium-Catalyzed Cross-Coupling Reactions	92
33.1.5.1.6.4	Variation 4:	Synthesis from Other Alkenyl Sulfoxides	93

33.1.6 Product Subclass 6: Alk-1-enethiols

J. Drabowicz, P. Kielbasiński, and M. Mikołajczyk

33.1.6	Product Subclass 6: Alk-1-enethiols	101	
33.1.6.1	Synthesis of Product Subclass 6	101	
33.1.6.1.1	Method 1:	Reaction of Alkenes with Elemental Sulfur	101
33.1.6.1.2	Method 2:	C–S Bond Cleavage of Alkenyl Sulfides	101
33.1.6.1.3	Method 3:	Reaction of <i>E</i> -Alkenyl(phenyl)- λ^3 -iodanes with Thioamides	102
33.1.6.1.4	Method 4:	Reaction of Haloalkenes with Hydrogen Sulfide	102
33.1.6.1.5	Method 5:	Retro-Diels–Alder Reactions of 9,10-Ethano-9,10-dihydroanthracene-11-thiols	103
33.1.6.1.6	Method 6:	Pyrolysis of 1,2-Ethanedithiol or Thiirane	103
33.1.6.1.7	Method 7:	Addition of Hydrogen Sulfide to Alkynes	103
33.1.6.1.8	Method 8:	Enethiolization of Thiocarbonyl Compounds	104

33.1.7 Product Subclass 7: Metal Alk-1-enethiolates

J. Drabowicz, P. Kielbasiński, and M. Mikołajczyk

33.1.7	Product Subclass 7: Metal Alk-1-enethiolates	109	
33.1.7.1	Synthesis of Product Subclass 7	109	
33.1.7.1.1	Method 1:	Alkali Metal Cleavage of Alk-1-enyl Alkyl Sulfides	109
33.1.7.1.2	Method 2:	Hydrolysis of Alk-1-enyl Thiolacetates	109

33.1.7.1.3	Method 3:	Transformations of Thiiranes and Thiirane S-Oxides	110
33.1.7.1.4	Method 4:	Deprotonation of Thiocarbonyl Compounds	111
33.1.8	Product Subclass 8: Alk-1-enyl Sulfides		
	J. Drabowicz, P. Kiełbasiński, and M. Mikołajczyk		
<hr/>			
33.1.8	Product Subclass 8: Alk-1-enyl Sulfides		113
33.1.8.1	Synthesis of Product Subclass 8		113
33.1.8.1.1	Synthesis of Acyclic Alk-1-enyl Sulfides		113
33.1.8.1.1.1	Method 1:	Alkylation of Alk-1-enethiolates	113
33.1.8.1.1.2	Method 2:	Transformations of 1-Haloalkenes and Their Analogues	114
33.1.8.1.1.2.1	Variation 1:	Nucleophilic Substitution by Thiolate Anions and Their Analogues	114
33.1.8.1.1.2.2	Variation 2:	Reactions of 1-Bromoalkenes with Trialkylstannyl Sulfides	115
33.1.8.1.1.2.3	Variation 3:	Reactions with Copper Thiolates	116
33.1.8.1.1.2.4	Variation 4:	Palladium-Catalyzed Reactions with Thiolanes and Their Equivalents	116
33.1.8.1.1.2.5	Variation 5:	Photochemical Reactions between 1-Bromoalk-1-enes and Sulfides	119
33.1.8.1.1.2.6	Variation 6:	Using Alk-1-enylmercury(II) Halides	119
33.1.8.1.1.2.7	Variation 7:	Using Alk-1-enyltributylstannanes	120
33.1.8.1.1.2.8	Variation 8:	Using (Trimethylsilyloxy)alkenes	121
33.1.8.1.1.3	Method 3:	Syntheses from Alkyl Sulfides	121
33.1.8.1.1.3.1	Variation 1:	Dehydrohalogenation of Haloalkyl Sulfides	121
33.1.8.1.1.3.2	Variation 2:	Manganese(IV) Oxide Promoted Reactions of Sulfides with Acetyl Chloride	125
33.1.8.1.1.3.3	Variation 3:	Peterson Reactions of α -Silyl Derivatives	125
33.1.8.1.1.3.4	Variation 4:	Decarboxylation of 2-(Methylsulfanyl)propanoic Acid	127
33.1.8.1.1.4	Method 4:	Syntheses from Dithioacetals and Trithioorthoformates	128
33.1.8.1.1.4.1	Variation 1:	Reactions with Sulfenyl Chlorides	128
33.1.8.1.1.4.2	Variation 2:	Copper- or Lewis Acid Mediated Cleavages of Sulfides	129
33.1.8.1.1.4.3	Variation 3:	Stereoselective Reduction of Ketene Dithioacetals	129
33.1.8.1.1.4.4	Variation 4:	Phosphite-Mediated Elimination Reactions	130
33.1.8.1.1.4.5	Variation 5:	From Trithioorthoformates	130
33.1.8.1.1.5	Method 5:	Aldol Condensations of Sulfides Bearing an Electron-Withdrawing α -Substituent	131
33.1.8.1.1.6	Method 6:	Syntheses via Organophosphorus Reagents	131
33.1.8.1.1.6.1	Variation 1:	From Phosphorus Ylides	131
33.1.8.1.1.6.2	Variation 2:	Wadsworth–Emmons–Horner Reactions	132
33.1.8.1.1.7	Method 7:	Synthesis from Alkyl Sulfoxides	134
33.1.8.1.1.7.1	Variation 1:	Pummerer-Type Rearrangement of α -Chloroalkyl Sulfoxides	134
33.1.8.1.1.7.2	Variation 2:	Iodotrimethylsilane-Induced Elimination–Deoxygenation of Sulfoxides	135
33.1.8.1.1.8	Method 8:	Deoxygenation of Alk-1-enyl Sulfoxides	135
33.1.8.1.1.9	Method 9:	Synthesis from Alkynyl Sulfides	136
33.1.8.1.1.9.1	Variation 1:	Reduction of Alkynyl Sulfides	136

33.1.8.1.1.9.2	Variation 2:	Hydroboration of Alkynyl Sulfides	137
33.1.8.1.1.9.3	Variation 3:	Tantalum-Mediated Additions to Alkynyl Sulfides	137
33.1.8.1.1.9.4	Variation 4:	Stereoselective Addition of Grignard Reagents to Alkynyl Sulfides	138
33.1.8.1.1.9.5	Variation 5:	Addition of Organocopper Reagents to Alkynyl Sulfides	138
33.1.8.1.1.10	Method 10:	Addition of Thiols or Their Derivatives to Alkynes	139
33.1.8.1.1.10.1	Variation 1:	Free-Radical Additions	139
33.1.8.1.1.10.2	Variation 2:	Addition of Thiolates to Alkynes	141
33.1.8.1.1.10.3	Variation 3:	Metal-Catalyzed Addition of Thiols and Their Borabicyclo Derivatives to Alkynes	143
33.1.8.1.1.10.4	Variation 4:	Addition of Sulfenyl Halides or Sulfenamides to Alkynes	147
33.1.8.1.1.11	Method 11:	Ring Opening of Epoxy Sulfides	149
33.1.8.1.1.12	Method 12:	Reaction of Benzynes with Thiiranes	151
33.1.8.1.1.13	Method 13:	Reaction of <i>N</i> -Tosylsulfimides with Potassium <i>tert</i> -Butoxide	151
33.1.8.1.2		Synthesis of Cyclic Alk-1-enyl Sulfides	151
33.1.8.1.2.1	Method 1:	Reaction of Chlorotropylium Salts with Thiols	152
33.1.8.1.2.2	Method 2:	Alkylation of Cycloalk-1-ene-1-thiolates	152
33.1.8.1.2.3	Method 3:	Dehydrochlorination of Cyclic Sulfides	152
33.1.8.1.2.3.1	Variation 1:	Chlorosulfonylation–Dehydrochlorination of Cycloalkenes	152
33.1.8.1.2.3.2	Variation 2:	Addition of Thiols to Cycloalk-2-enones, Followed by Chlorination–Dehydrochlorination of the Adducts	153
33.1.8.1.2.4	Method 4:	Synthesis from Cycloalkanones and Dithioacetals or Thiols	154
33.1.8.1.2.5	Method 5:	Pummerer Reaction of Cyclic Sulfoxides	155
33.1.8.1.2.6	Method 6:	Intramolecular Cyclization of Sulfines Derived from <i>S</i> -Unsaturated Dithioesters	156
33.1.8.1.2.7	Method 7:	Intramolecular Trapping Reactions of Enethiols Functionalized by a Silyl Group	157
33.1.8.1.3		Synthesis of Polyenyl Sulfides	157
33.1.8.1.3.1	Method 1:	Sulfanylbuta-1,3-dienes via Elimination Reactions	157
33.1.8.1.3.1.1	Variation 1:	Elimination of a Thiol from Bis(dithioacetals)	157
33.1.8.1.3.1.2	Variation 2:	Removal of Methanol from Aryl 4,4-Dimethoxybut-2-enyl Sulfides	158
33.1.8.1.3.1.3	Variation 3:	Extrusion of Sulfur Dioxide from 3-Sulfanyl-2,5-dihydrothiophene 1,1-Dioxides	160
33.1.8.1.3.1.4	Variation 4:	Flash-Vacuum Pyrolysis of Sulfur-Containing Cyclic Derivatives	160
33.1.8.1.3.1.5	Variation 5:	Elimination Reactions of Aryl 2-Chlorobut-3-enyl Sulfides	161
33.1.8.1.3.1.6	Variation 6:	Elimination Reactions of 2-Methyl-4-sulfanylbut-3-en-2-ols	161
33.1.8.1.3.2	Method 2:	Addition of Thiols to But-1-en-3-yne	162
33.1.8.1.3.3	Method 3:	Reduction of (1 <i>E</i>)-But-1-en-3-ynyl Ethyl Sulfides	163
33.1.8.1.3.4	Method 4:	Base-Catalyzed Ring-Opening Reactions of Sulfur-Containing Heterocycles	163
33.1.8.1.3.5	Method 5:	Horner–Wittig Reaction of Alkenyl Phosphine Oxides Functionalized with a Phenylsulfanyl Substituent	165

33.1.9	Product Subclass 9: Alk-1-enylsulfonium Salts J. Drabowicz, P. Kiełbasiński, and M. Mikołajczyk	
33.1.9	Product Subclass 9: Alk-1-enylsulfonium Salts	169
33.1.9.1	Synthesis of Product Subclass 9	169
33.1.9.1.1	Method 1: Dehydrohalogenation of (2-Haloalkyl)sulfonium Salts	169
33.1.9.1.2	Method 2: S-Alkylation of Alk-1-enyl Sulfides	172
33.1.9.1.3	Method 3: Synthesis from Dithioacetals	173
33.1.9.1.4	Method 4: Synthesis from Alkenes	173
33.1.9.1.5	Method 5: Synthesis from Sulfonium Ylides Stabilized by a Phosphoryl Substituent	174
33.1.10	Product Subclass 10: Alk-1-enesulfenic Acid Derivatives J. Drabowicz, P. Kiełbasiński, and M. Mikołajczyk	
33.1.10	Product Subclass 10: Alk-1-enesulfenic Acid Derivatives	177
33.1.10.1	Synthesis of Product Subclass 10	177
33.1.10.1.1	Method 1: Alk-1-enesulfonyl Chlorides by Chlorination of Enethiols or Alk-1-enyl Sulfides	177
33.1.10.1.2	Method 2: Alk-1-enesulfonyl Chlorides from Allenes and Sulfur Dichloride	178
33.1.10.1.3	Method 3: Alk-1-enesulfonyl Chlorides from Alkynes and Sulfur Dichloride	178
33.1.10.1.4	Method 4: Alkenesulfenamides by Addition of Amidosulfonyl Chlorides to Alkynes	179
33.1.10.1.5	Method 5: Alk-1-enesulfenamides from Alk-1-enesulfenate Anions	180
33.1.10.1.6	Method 6: Alk-1-enesulfenic Acids by the Enethiolization of Sulfoxines	181
33.1.11	Product Subclass 11: Alk-1-enyl Disulfides J. Drabowicz, P. Kiełbasiński, and M. Mikołajczyk	
33.1.11	Product Subclass 11: Alk-1-enyl Disulfides	183
33.1.11.1	Synthesis of Product Subclass 11	183
33.1.11.1.1	Method 1: Sulfonylation of Alkenethiolate Anions	183
33.1.11.1.2	Method 2: Addition of Nucleophiles to Sulfoxines	185
33.1.12	Product Subclass 12: Thietes and Derivatives E. Block	
33.1.12	Product Subclass 12: Thietes and Derivatives	187
33.1.12.1	Synthesis of Product Subclass 12	188
33.1.12.1.1	Synthesis by Ring-Closure Reactions	188
33.1.12.1.1.1	Method 1: Reaction of Sulfoxines and Ynamines or Ketene O,N-Acetals	188
33.1.12.1.1.2	Method 2: Photocycloaddition of Thiones to Alkynes	189
33.1.12.1.1.3	Method 3: Reaction of a Perfluorinated Alkene and <i>tert</i> -Butanethiol	190

33.1.12.1.1.4	Method 4: Electrocyclic Ring Closure of Enethiones	191
33.1.12.1.2	Synthesis by Ring Transformation	191
33.1.12.1.2.1	Method 1: Ring Enlargement of Diazothiiranimes	191
33.1.12.1.2.2	Method 2: Ring Enlargement of Thiirenes	192
33.1.12.1.2.2.1	Variation 1: Reaction of a Sulfonium Ylide with Diphenylthiirene Dioxide	192
33.1.12.1.2.2.2	Variation 2: From an <i>S</i> -Methylthiirenium Ion	192
33.1.12.1.2.3	Method 3: Ring Contraction of Thiophene 1,1-Dioxides	192
33.1.12.1.2.4	Method 4: Synthesis from Thiophenones	193
33.1.12.1.3	Elimination Reactions from Thietanes	194
33.1.12.1.3.1	Method 1: Cope and Hofmann Eliminations	194
33.1.12.1.3.2	Method 2: Elimination of a Hydrogen Halide or Ethanol	195
33.1.12.1.4	Synthesis by Substituent Modification	197
33.1.12.1.4.1	Substitution of Hydrogen	197
33.1.12.1.4.1.1	Method 1: Addition and Elimination of Halogen	197
33.1.12.1.4.2	Substitution of Halogens	197
33.1.12.1.4.2.1	Method 1: Michael Addition	197
33.1.12.1.4.3	Modification of Substituents	197
33.1.12.1.4.3.1	Method 1: Enolization/Acylation of Thietan-3-one Derivatives	197
33.1.12.1.4.3.2	Method 2: Double-Bond Isomerization	198
33.1.12.1.4.3.3	Method 3: Hydrogenation of 2-Methylenethietes	198
33.1.12.1.4.3.4	Method 4: [4 + 2] and [2 + 2] Cycloadditions of 2-Methylenethietes	198
33.1.12.1.5	Addition Reactions	199
33.1.12.1.5.1	Method 1: <i>S</i> -Alkylation Using Methyl Trifluoromethanesulfonate	199
33.1.12.1.5.2	Method 2: <i>S</i> -Oxidation Using Monoperoxyphthalic Acid	199
33.1.12.2	Applications of Product Subclass 12 in Organic Synthesis	200
33.1.12.2.1	Method 1: Ring Opening to Propenethial <i>S,S</i> -Dioxides and Subsequent Cycloaddition or Rearrangement	200
33.1.13	Product Subclass 13: 2,3-Dihydrothiophenes and Derivatives E. Block	
33.1.13	Product Subclass 13: 2,3-Dihydrothiophenes and Derivatives	203
33.1.13.1	Synthesis of Product Subclass 13	204
33.1.13.1.1	Synthesis by Ring-Closure Reactions	204
33.1.13.1.1.1	Method 1: Reaction of Zirconacycles with Sulfur Monochloride	204
33.1.13.1.1.2	Method 2: Reaction of 1-(1-Adamantylcarbonylmethyl)pyridinium Bromide with (Arylmethylene)cyanothioacetamides	204
33.1.13.1.1.3	Method 3: 1,3-Dipolar Cycloaddition of Mesoionic Thiazolium-4-olates to Nitroalkenes	205
33.1.13.1.1.4	Method 4: Heating Dialk-1-enyl Disulfides	205
33.1.13.1.1.5	Method 5: Enethiolization of ω -Halothioacylsilanes	206
33.1.13.1.1.6	Method 6: Synthesis from But-3-ynethiols and Derivatives	206

33.1.13.1.1.6.1	Variation 1:	Using Base or Hexacarbonylchromium Catalysis	206
33.1.13.1.1.6.2	Variation 2:	From Halocyclizations	207
33.1.13.1.1.7	Method 7:	Synthesis from 4,4-Dihalobut-3-enethiols	208
33.1.13.1.1.7.1	Variation 1:	From 3-(Difluoromethylene)-2-methyl-6-phenylhexane-1-thiol	208
33.1.13.1.1.7.2	Variation 2:	From 4,4-Dibromo-3-methylbut-3-ene-1-thiol	208
33.1.13.1.1.8	Method 8:	Synthesis from 5-Substituted Pentan-2-ones	208
33.1.13.1.1.8.1	Variation 1:	From 5-Sulfanylated Pentan-2-ones or 5-Bromopentan-2-ones	208
33.1.13.1.1.8.2	Variation 2:	From O-Ethyl S-(4-Oxobutyl) Dithiocarbonates	209
33.1.13.1.1.9	Method 9:	Intramolecular Michael Additions	210
33.1.13.1.1.10	Method 10:	Cyclization of α -Phosphonovinyl Radicals	210
33.1.13.1.1.11	Method 11:	Base-Induced Cyclizations of Alkynyl Benzyl Sulfides	211
33.1.13.1.1.12	Method 12:	Intramolecular Wittig Reactions of Thioesters	212
33.1.13.1.1.13	Method 13:	Intramolecular Titanocene(II)-Promoted Alkenations of Thioesters	212
33.1.13.1.1.14	Method 14:	Photocyclization of Bis(2-phenylvinyl) Sulfide	213
33.1.13.1.2	Synthesis by Ring Transformation		214
33.1.13.1.2.1	Method 1:	Formal Exchange of Ring Members with Retention of Ring Size	214
33.1.13.1.2.2	Method 2:	Light-Induced Ring Contraction of 1,2-Dithiins	214
33.1.13.1.2.3	Method 3:	Electrocyclic Ring Closure of Thionins	215
33.1.13.1.3	Synthesis by the Elimination Reactions of Thiolanes		215
33.1.13.1.3.1	Method 1:	Synthesis from 2-Acetoxy- and 2-(Benzoyloxy)tetrahydrothiophenes	215
33.1.13.1.3.2	Method 2:	Synthesis from 2- or 3-Hydroxy-, 3-Bromo-, or 2-(Alkylsulfanyl)tetrahydrothiophenes	216
33.1.13.1.3.3	Method 3:	Bamford–Stevens Elimination of the Tosylhydrazone of Dihydrothiophen-3(2 <i>H</i>)-one	217
33.1.13.1.4	Synthesis by Substituent Modification		218
33.1.13.1.4.1	Substitution of Hydrogen or Metals		218
33.1.13.1.4.1.1	Method 1:	Lithiation of 2,3-Dihydrothiophene and Its Reactions with Electrophiles	218
33.1.13.1.4.1.2	Method 2:	Replacement of Tin by Hydroxyalkyl Groups	218
33.1.13.1.4.2	Substitution of Heteroatoms		219
33.1.13.1.4.2.1	Method 1:	Nucleophilic Substitutions of 3-Bromo-2,3-dihydrothiophene 1,1-Dioxide	219
33.1.13.1.4.2.2	Method 2:	Substitution of a Trifluoromethylsulfonyloxy Group by a Metal	220
33.1.13.1.4.3	Addition Reactions		221
33.1.13.1.4.3.1	Method 1:	Reduction of Thiophenes	221
33.1.13.1.4.3.1.1	Variation 1:	Birch Reduction	221
33.1.13.1.4.3.1.2	Variation 2:	Samarium(II) Iodide Mediated Double Electrophilic Reduction	221
33.1.13.1.4.3.2	Method 2:	Dimerization of 2,3-Dihydrothiophene and Its 1,1-Dioxide	222
33.1.13.1.4.3.3	Method 3:	Addition Reactions Involving Thiophene 1-Oxides	223
33.1.13.1.4.3.3.1	Variation 1:	Dihydrodiol Formation or Oxidation/Dimerization	223
33.1.13.1.4.3.4	Method 4:	Nucleophilic Additions to Thiophene 1-Oxides or 1,1-Dioxides	224

33.1.13.1.4.3.5	Method 5:	Electrophilic Additions to Thiophene 1,1-Dioxides	225
33.1.13.1.4.3.6	Method 6:	Diels–Alder Additions	226
33.1.13.1.4.3.7	Method 7:	Ylide Formation	226
33.1.13.1.4.3.8	Method 8:	Oxidation of the Sulfur Atom	227
33.1.13.1.4.3.9	Method 9:	Sulfilimine Formation	227
33.1.13.1.4.4		Modification of Substituents	228
33.1.13.1.4.4.1	Method 1:	Reduction of the Sulfoxide Group	228
33.1.13.1.4.4.2	Method 2:	4,5-Dihydro-2-thienyl 2-Trifluoromethanesulfonate by Enolization of Thiophen-2(3 <i>H</i>)-one	228
33.1.13.1.4.4.3	Method 3:	Isomerization of 2,5-Dihydrothiophenes	228
33.1.13.1.4.4.4	Method 4:	Base-Catalyzed Isomerization of 2,5-Dihydrothiophene 1,1-Dioxides	229
33.1.13.2		Applications of Product Subclass 13 in Organic Synthesis	229
33.1.13.2.1	Method 1:	Use as a Protecting Group for Alcohols	229
33.1.13.2.2	Method 2:	Nickel-Catalyzed Replacement of a Vinylic C–S Bond with a C–C Bond	230
33.1.13.2.3	Method 3:	Aromatization of 2,3-Dihydrothiophenes	230
33.1.13.2.4	Method 4:	Photoisomerism of 2,3-Dihydrothiophenes to 2-Alkylidenetetrahydrothiophenes	230
33.1.13.2.5	Method 5:	Conversion of 2,3-Dihydrothiophenes into 6-Oxo-2-thiabicyclo[3.2.0]heptane-4-carboxylic Acids	230
33.1.13.2.6	Method 6:	[2 + 2]-Photochemical Cycloadditions to 2,3-Dihydrothiophene 1,1-Dioxide	231
33.1.13.2.7	Method 7:	3,4-Dihydro-2 <i>H</i> -thiopyrans from 2,3-Dihydrothiophenium Methylides	232
33.1.14		Product Subclass 14: 3,4-Dihydro-2<i>H</i>-thiopyrans and Derivatives E. Block	
33.1.14		Product Subclass 14: 3,4-Dihydro-2<i>H</i>-thiopyrans and Derivatives	235
33.1.14.1		Synthesis of Product Subclass 14	235
33.1.14.1.1		Synthesis by Ring-Closure Reactions	235
33.1.14.1.1.1	Method 1:	Synthesis from 1,5-Diketones and Hydrogen Sulfide/ Hydrogen Chloride, Phosphorus Pentasulfide, or Hexamethyldisilathiane	236
33.1.14.1.1.2	Method 2:	Synthesis from 1,4-Dien-3-ones and 1-En-4-yn-3-ones by Michael Addition	237
33.1.14.1.1.3	Method 3:	Synthesis from Propenethial	238
33.1.14.1.1.4	Method 4:	Synthesis from Propenethial <i>S,S</i> -Dioxide	239
33.1.14.1.1.5	Method 5:	Synthesis from Other Enethiones	239
33.1.14.1.1.6	Method 6:	Synthesis from Benzothietes	242
33.1.14.1.1.7	Method 7:	Double Michael Additions of Malonate Anions to Alk-1-enyl Alk-1-ynyl Sulfones	242
33.1.14.1.1.8	Method 8:	Combination of Enones and Two Three-Atom Fragments	243
33.1.14.1.1.9	Method 9:	Photolysis of Pent-4-ynethiol	243

33.1.14.1.1.10	Method 10:	Synthesis from ω -Halothioacysilanes	243
33.1.14.1.1.11	Method 11:	Synthesis from 3-Methyl-6-sulfanylhexan-2-ones	244
33.1.14.1.1.12	Method 12:	Synthesis from a 5,5-Dibromopent-4-enethiol or a 5,5-Dibromopent-4-enyl Sulfide	244
33.1.14.1.1.13	Method 13:	Synthesis from 1-(Arenesulfonyl)-5-iodobut-1-enyl Methyl Sulfides	244
33.1.14.1.1.14	Method 14:	Thermal Rearrangement of Prop-2-ynyl Vinyl Sulfide	245
33.1.14.1.1.15	Method 15:	Cope Rearrangement of Thiocarbonyl Compounds	245
33.1.14.1.1.16	Method 16:	Electrocyclic Ring Closure of (3 <i>E</i> ,5 <i>Z</i>)-1,1,1,7,7,7-Hexafluoro- 3,4,5-tris(trifluoromethyl)hepta-3,5-diene-2-thione	246
33.1.14.1.1.17	Method 17:	Cyclization of <i>S</i> -Allyl α -Phosphonovinyl Radicals	246
33.1.14.1.2	Synthesis by Ring Transformation		247
33.1.14.1.2.1	Method 1:	Ring Enlargement of Acyldihydrothiophenes	247
33.1.14.1.2.2	Method 2:	Ring Enlargement of 4,5-Dihydrothiophenium and Thiophenium 1-Methylides	248
33.1.14.1.3	Synthesis from Dihydro- and Tetrahydrothiopyrans		248
33.1.14.1.3.1	Method 1:	Rearrangement and/or Elimination Reactions	248
33.1.14.1.4	Synthesis by Substituent Modification		250
33.1.14.1.4.1	Substitution of Hydrogen		250
33.1.14.1.4.1.1	Method 1:	Lithiation of 3,4-Dihydro-2 <i>H</i> -thiopyrans, 2 <i>H</i> -Thiopyrans, and 4 <i>H</i> -Thiopyrans	250
33.1.14.1.4.2	Substitution of Metals		250
33.1.14.1.4.2.1	Method 1:	Replacement of Lithium by Organostannyl and Organosilyl Groups	250
33.1.14.1.4.3	Addition Reactions		250
33.1.14.1.4.3.1	Method 1:	Dimerization of 3,4-Dihydro-2 <i>H</i> -thiopyran	250
33.1.14.1.4.3.2	Method 2:	Oxidation of the Sulfur Atom	251
33.1.14.1.4.3.3	Method 3:	Sulfilimine Formation	251
33.1.14.1.4.4	Modification of Substituents		251
33.1.14.1.4.4.1	Method 1:	Enolization of Dihydrothiopyranones	251
33.1.14.1.4.4.2	Method 2:	Cationic Interconversion of 4 <i>H</i> -Thiopyrans into 2 <i>H</i> -Thiopyrans	252
33.1.14.1.4.4.3	Method 3:	Base-Induced Conversions of 2 <i>H</i> -Thiopyrans into 4 <i>H</i> -Thiopyrans	252
33.1.14.1.4.4.4	Method 4:	Photochemical Conversion of a 2 <i>H</i> -Thiopyran into a 4 <i>H</i> -Thiopyran	254
33.1.14.2	Applications of Product Subclass 14 in Organic Synthesis		254
33.1.14.2.1	Method 1:	Nickel-Catalyzed Replacement of a Vinylic C—S Bond with a C—C Bond	254
33.1.14.2.2	Method 2:	Synthesis of Thiopyrylium Salts	255
33.1.14.2.3	Method 3:	Synthesis of 4-Methylene-2,6-diphenyl-4 <i>H</i> -thiopyrans	255
33.1.14.2.4	Method 4:	Synthesis of Chiral Auxiliaries for Corey–Chaykovsky Epoxidation	255
33.1.14.2.5	Method 5:	Protecting Group for Alcohols	256

33.1.15	Product Subclass 15: 2,3,4,5-Tetrahydrothiepins, Larger Rings, and Derivatives	
	E. Block	
<hr/>		
33.1.15	Product Subclass 15: 2,3,4,5-Tetrahydrothiepins, Larger Rings, and Derivatives	259
33.1.15.1	Synthesis of Product Subclass 15	259
33.1.15.1.1	Synthesis by Ring-Closure Reactions	259
33.1.15.1.1.1	Method 1: Synthesis from 1,6-Bis(acylsilanes)	259
33.1.15.1.1.2	Method 2: Cyclopalladation of Benzyl Methyl Sulfide	259
33.1.15.1.1.3	Method 3: Synthesis from Diphenylthiirene 1,1-Dioxide and 1-Cyclohex-1-enylpyrrolidine	260
33.1.15.1.1.4	Method 4: Synthesis from 1-(Arylsulfonyl)-6-halopent-1-enyl Methyl Sulfides	260
33.1.15.1.1.5	Method 5: Synthesis from ω -Halothioacylsilanes	260
33.1.15.1.1.6	Method 6: Synthesis of a 1,2-Dihydro-2-benzothiepin by Cathodic Reduction of a Benzyl Dithiopivaloate	261
33.1.15.1.2	Synthesis by Ring Transformation	262
33.1.15.1.2.1	Method 1: Ring Enlargement of Three-Membered Rings	262
33.1.15.1.2.2	Method 2: Ring Enlargement of Five-Membered Rings	263
33.1.15.1.2.2.1	Variation 1: Two-Carbon-Atom Ring Expansion with Dimethyl Acetylenedicarboxylate	263
33.1.15.1.2.2.2	Variation 2: [2,3]-Sigmatropic Rearrangements of Ylides Obtained from 1-[(Ethoxycarbonyl)methyl]-2-ethynylthiacycloalkanes	263
33.1.15.1.2.3	Method 3: Ring Enlargement of Six-Membered Rings	264
33.1.15.1.2.3.1	Variation 1: Two-Carbon-Atom Ring Expansion with Dimethyl Acetylenedicarboxylate	264
33.1.15.1.2.3.2	Variation 2: Reaction of 6-Acyl-3,6-dihydro-2 <i>H</i> -thiopyrans with Zinc/Chlorotrimethylsilane	265
33.1.15.1.2.3.3	Variation 3: [2,3]-Sigmatropic Rearrangements of 1-[(Ethoxycarbonyl)methyl]-2-ethynylthiepane Sulfonium Ylides	265
33.1.15.1.2.3.4	Variation 4: Rearrangement of Bicyclic Sulfonium Ylides	266
33.1.15.1.2.3.5	Variation 5: Pyrolyses of Sulfoxides	266
33.1.15.1.2.4	Method 4: Ring Enlargement of Seven-Membered Rings	267
33.1.15.1.2.4.1	Variation 1: [2,3]-Sigmatropic Rearrangement of 1-[(Ethoxycarbonyl)methyl]-2-ethynylthiocane Sulfonium Ylides	267
33.1.15.1.3	Elimination Reactions Leading to Thiacyclohept-2-enes, Thiacyclooct-2-enes, and Related Systems	267
33.1.15.1.3.1	Method 1: Ring-Opening Reactions of Thiaoxabicyclo[3.2.1]octanes and Thiaoxabicyclo[3.3.1]nonanes	267
33.1.15.1.3.2	Method 2: Pummerer Reactions	269
33.1.15.1.4	Synthesis by Substituent Modification	270
33.1.15.1.4.1	Substitution of Hydrogen	270
33.1.15.1.4.1.1	Method 1: Lithiation of 2,3,4,5-Tetrahydrothiepin 1-Oxide	270
33.1.15.1.4.1.2	Method 2: Allylic Bromination of 4,5-Dihydrothiepin 1,1-Dioxide	270

33.1.15.1.4.2	Substitution of Metals	270
33.1.15.1.4.2.1	Method 1: Replacement of Lithium by Alkyl and Hydroxyalkyl Groups	270
33.1.15.1.4.3	Addition Reactions	271
33.1.15.1.4.3.1	Method 1: Oxidation of the Sulfur Atom	271
33.2	Product Class 2: Alk-1-enyl Selenium Compounds	
	D. Avilov and D. Dittmer	
33.2	Product Class 2: Alk-1-enyl Selenium Compounds	275
33.2.1	Product Subclass 1: Alk-1-enyl Selenones	275
33.2.1.1	Synthesis of Product Subclass 1	275
33.2.1.1.1	Method 1: Oxidation of Alk-1-enyl Selenides	275
33.2.2	Product Subclass 2: Alk-1-enyl Selenoxides	276
33.2.2.1	Synthesis of Product Subclass 2	276
33.2.2.1.1	Method 1: Oxidation of Alk-1-enyl Selenides	276
33.2.3	Product Subclass 3: Alk-1-eneselenols	277
33.2.3.1	Synthesis of Product Subclass 3	277
33.2.3.1.1	Method 1: Reaction of Divinyl Diselenides with Tributyltin Hydride	277
33.2.4	Product Subclass 4: Metal Alk-1-eneselenolates	277
33.2.4.1	Synthesis of Product Subclass 4	278
33.2.4.1.1	Method 1: Reaction of Metal Complexes with 1,2,3-Selenadiazoles	278
33.2.4.1.2	Method 2: Addition of Metal Complexes Containing Selenium Ligands to Alkynes	279
33.2.4.1.3	Method 3: Exchange of Selenolate Ligands in Metal Complexes	279
33.2.4.1.4	Methods 4: Other Methods	280
33.2.5	Product Subclass 5: Alk-1-enyl Selenides	280
33.2.5.1	Synthesis of Product Subclass 5	281
33.2.5.1.1	Method 1: Coupling of Organoselenenyl Halides or Diorgano Diselenides with Alk-1-enyl Heteroatom Derivatives	281
33.2.5.1.1.1	Variation 1: Reaction of Organoselenenyl Halides with Alk-1-enylmagnesium Halides	281
33.2.5.1.1.2	Variation 2: Reaction of Areneselenenyl Halides and Related Compounds with Alk-1-enylzirconocenes	282
33.2.5.1.1.3	Variation 3: Reaction of an Areneselenenyl Halide with Vinylboronic Acids and Esters	282
33.2.5.1.1.4	Variation 4: Reaction of Areneselenenyl Halides with Alk-1-enyl(trialkyl)stannanes and Related Reactions	283
33.2.5.1.1.5	Variation 5: Reaction of Areneselenenyl Halides and Related Compounds with Alk-1-enyllithiums	283
33.2.5.1.2	Method 2: Coupling of Metal Selenides or Metal Alkane- or Arene-selenolates with Alk-1-enyl Heteroatom Derivatives and Related Reactions	283

33.2.5.1.3	Method 3:	Addition–Elimination of Organoselenium Compounds to Alkenes	284
33.2.5.1.3.1	Variation 1:	Addition–Elimination of Organoselenenyl Halides and Related Compounds	285
33.2.5.1.3.2	Variation 2:	Addition–Elimination of Selenols	285
33.2.5.1.4	Method 4:	Wittig, Horner–Wadsworth–Emmons, and Related Reactions of Selenium Precursors with Carbonyl Compounds	286
33.2.5.1.5	Method 5:	Addition of Selenium Compounds to Alkynes	287
33.2.5.1.5.1	Variation 1:	Addition of Selenols	287
33.2.5.1.5.2	Variation 2:	Addition of Arene- or Alkaneselenenyl Halides, Selenosulfonates, and Related Compounds	288
33.2.5.1.5.3	Variation 3:	Addition of Diselenides	289
33.2.5.1.5.4	Variation 4:	Addition of Other Compounds Containing a Selenium–Heteroatom Bond	290
33.2.5.1.5.5	Variations 5:	Other Variations	291
33.2.5.1.6	Method 6:	Addition of Selenium Compounds to Allenes	291
33.2.5.1.7	Method 7:	Addition to Alk-1-ynylselenium Compounds	291
33.2.5.1.7.1	Variation 1:	Addition to Alk-1-ynyl Selenides	291
33.2.5.1.7.2	Variation 2:	Addition to Metal Alk-1-yneselenolates	294
33.2.5.1.8	Method 8:	Double Bond Shift of Allyl Selenides and Related Reactions	295
33.2.5.1.9	Methods 9:	Other Methods	295
33.2.6	Product Subclass 6: Alk-1-enylselenium Salts		295
33.2.6.1	Synthesis of Product Subclass 6		295
33.2.6.1.1	Method 1:	Alkylation of Alken-1-yl Selenides	295
33.2.6.1.2	Method 2:	Addition of Nucleophiles to Alk-1-ynylselenium Salts	296
33.2.7	Product Subclass 7: Alk-1-enyl Polyselenides		296
33.2.7.1	Synthesis of Product Subclass 7		296
33.2.7.1.1	Method 1:	Oxidation of Metal Alk-1-eneselenolates	297
33.3	Product Class 3: Alk-1-enyl Tellurium Compounds		
	D. Avilov and D. Dittmer		
33.3	Product Class 3: Alk-1-enyl Tellurium Compounds		303
33.3.1	Product Subclass 1: Alk-1-enyl-λ^6-tellanes		303
33.3.1.1	Synthesis of Product Subclass 1		303
33.3.1.1.1	Method 1:	Substitution of Pentaaryltellurium Trifluoromethanesulfonates	303
33.3.2	Product Subclass 2: Alk-1-enyl Telluroxides		304
33.3.2.1	Synthesis of Product Subclass 2		304
33.3.2.1.1	Method 1:	Addition of Benzenetelluranyl Trifluoromethanesulfonate to Alkynes	304
33.3.2.1.2	Method 2:	Oxidation of Alk-1-enyl Tellurides	304
33.3.3	Product Subclass 3: Alk-1-enyl-λ^4-tellanes		305

33.3.3.1	Synthesis of Product Subclass 3	305
33.3.3.1.1	Method 1: Metal–Tellurium Exchange	305
33.3.3.1.2	Method 2: Addition of Halogens to Alk-1-enyl Tellurides	305
33.3.3.1.3	Method 3: Addition of Tellurium(IV) Halides or Organotellurium Trihalides to Alkynes	306
33.3.3.1.4	Method 4: Exchange of Groups on Tellurium in Alk-1-enyl- λ^4 -tellanes	307
33.3.3.2	Applications of Product Subclass 3 in Organic Synthesis	308
33.3.4	Product Subclass 4: Alk-1-enyl Tellurides	308
33.3.4.1	Synthesis of Product Subclass 4	308
33.3.4.1.1	Method 1: Coupling of Organotellurenyl Halides or Diorganoditellanes with Alk-1-enyl Anions or Radical Equivalents	308
33.3.4.1.1.1	Variation 1: Reaction of Organotellurenyl Halides with Grignard Reagents	309
33.3.4.1.1.2	Variation 2: Reaction of Organotellurenyl Halides with Alkynylboranes or Vinylaluminum Compounds	309
33.3.4.1.1.3	Variation 3: Reaction of Organotellurenyl Halides with Alk-1-enyl Zirconocenes	310
33.3.4.1.1.4	Variation 4: Reaction of Organotellurenyl Halides and Derivatives with Alk-1-enyl Cuprates or Alk-1-enyl Mercury Derivatives	311
33.3.4.1.1.5	Variation 5: Reaction of 1,2-Bis[(Z)-2-lithiovinyl]benzene Derivatives and [(1Z,3Z)-1-Lithio-4-(2-lithiophenyl)buta-1,3-dienyl]- (trimethyl)silane with Tellurium Tetrachloride	312
33.3.4.1.1.6	Variation 6: Intramolecular Baylis–Hillman Reactions of Organotellurenyl Bromides	313
33.3.4.1.2	Method 2: Alkylation of Alk-1-enyltelluride Anions	313
33.3.4.1.3	Method 3: Displacement Reactions on Alk-1-enyl Derivatives by Telluride Anions	314
33.3.4.1.4	Method 4: Wittig and Related Reactions	315
33.3.4.1.5	Method 5: Addition of Tellurium Compounds to Alkynes or Allenes	316
33.3.4.1.5.1	Variation 1: Addition of Tellurols and Metal Tellurides	316
33.3.4.1.5.2	Variation 2: Addition of Organotellurenyl Halides and Amides	318
33.3.4.1.5.3	Variation 3: Free-Radical Additions of Tellurium Species	319
33.3.4.1.5.4	Variation 4: Addition of Iron–Telluride Complexes	320
33.3.4.1.6	Method 6: Reductions of Tellurium Compounds	320
33.3.4.1.6.1	Variation 1: Reduction of Alk-1-enyl Telluroxides	320
33.3.4.1.6.2	Variation 2: Reduction of Alk-1-enyltellurium Halides	321
33.3.4.1.6.3	Variation 3: Reduction of Alk-1-enylditellanes	322
33.3.4.1.6.4	Variation 4: Reduction of Alkynyl Tellurides	322
33.3.4.1.7	Method 7: Additions to Alkynyl Tellurides	322
33.3.4.1.8	Method 8: Modifications of Existing Alk-1-enyl Tellurium Species	323
33.3.4.1.8.1	Variation 1: Addition Reactions to the C=C Bond of Alk-1-enyl Tellurides	323
33.3.4.1.8.2	Variation 2: Replacement or Modification of Substituents on the C=C Bond of Alk-1-enyl Tellurides	324
33.3.4.1.9	Methods 9: Other Methods	326
33.3.4.2	Applications of Product Subclass 4 in Organic Synthesis	327
33.3.5	Product Subclass 5: Alk-1-enyltelluronium Salts	328
33.3.5.1	Synthesis of Product Subclass 5	328

33.3.5.1.1	Method 1:	Alkylation of Alk-1-enyl Tellurides	328
33.3.5.1.2	Method 2:	Displacement of Stannanes, Boronic Acids, and Iodophenyl Groups	328
33.3.6	Product Subclass 6: Dialk-1-enylditellanes		329
33.3.6.1	Synthesis of Product Subclass 5		329
33.3.6.1.1	Method 1:	Oxidation of Alk-1-enyl Metal Tellurides	329
33.3.6.1.2	Methods 2:	Other Methods	329
33.4	Product Class 4: Alk-1-enyl Nitrogen Compounds		
33.4.1	Product Subclass 1: 1-Nitroalkenes		
	N. Ono		
33.4.1	Product Subclass 1: 1-Nitroalkenes		337
33.4.1.1	Synthesis of Product Subclass 1		337
33.4.1.1.1	Method 1:	Nitration of Alkenes	337
33.4.1.1.1.1	Variation 1:	Nitration of Vinylsilanes or Vinylstannanes	342
33.4.1.1.1.2	Variation 2:	Nitration of α,β -Unsaturated Carboxylic Acids	343
33.4.1.1.2	Method 2:	Oxidation of Oximes and Amines	344
33.4.1.1.3	Method 3:	Elimination Reactions of β -Substituted Nitro Compounds	345
33.4.1.1.3.1	Variation 1:	Dehydration of β -Nitro Alcohols	346
33.4.1.1.3.2	Variation 2:	Elimination of Acids from β -Nitro Esters	350
33.4.1.1.3.3	Variation 3:	Elimination of HX from β -Nitro Halides	353
33.4.1.1.3.4	Variation 4:	Wittig-Type Reaction	354
33.4.1.1.3.5	Variation 5:	Elimination from β -Nitro Sulfides and Sulfoxides	355
33.4.1.1.3.6	Variation 6:	Elimination from α -Nitro Selenoxides and β -Nitro Selenoxides	356
33.4.1.1.4	Method 4:	Synthesis from α -Nitro Ketones	357
33.4.1.1.4.1	Variation 1:	Synthesis of β -Nitroenamines and β -Nitrovinyl Sulfides	359
33.4.1.1.5	Method 5:	Addition–Elimination Reactions of Nitroalkenes	360
33.4.1.1.5.1	Variation 1:	Using Carbon Nucleophiles	360
33.4.1.1.5.2	Variation 2:	Using Heteroatom Nucleophiles	365
33.4.2	Product Subclass 2: 1-Nitrosoalkenes		
	H.-U. Reissig and R. Zimmer		
33.4.2	Product Subclass 2: 1-Nitrosoalkenes		371
33.4.2.1	Synthesis of Product Subclass 2		371
33.4.2.1.1	Method 1:	Nitrosation Reactions	371
33.4.2.1.1.1	Variation 1:	Nitrosation of Alkenes	371
33.4.2.1.1.2	Variation 2:	Nitrosation of Alkynes	372
33.4.2.1.1.3	Variation 3:	Nitrosation of Allenes	372
33.4.2.1.2	Method 2:	Elimination Reactions	372
33.4.2.1.2.1	Variation 1:	Dehydrohalogenation of α -Halooximes	372

33.4.2.1.2.2	Variation 2:	Elimination of Trialkylsilanol from Silyl Nitronates	373
33.4.2.1.2.3	Variation 3:	Elimination of Nitrous Acid	374
33.4.2.1.2.4	Variation 4:	Elimination of Sulfuric Acid	374
33.4.2.1.3	Method 3:	Thermolysis Reactions	375
33.4.2.1.4	Method 4:	Photolysis Reactions	375
33.4.2.1.5	Method 5:	Reductions of Nitroalkenes	376
33.4.2.1.5.1	Variation 1:	Electrochemical Reduction	376
33.4.2.1.5.2	Variation 2:	Reduction with Phosphorus Compounds	376
33.4.2.1.6	Method 6:	Oxidation Reactions	377
33.4.2.1.7	Method 7:	Ring-Opening Reactions	377
33.4.2.1.7.1	Variation 1:	From Epoxides	377
33.4.2.1.7.2	Variation 2:	From Isoxazoles	378
33.4.2.1.8	Method 8:	Isomerization Reactions	378
33.4.2.1.9	Method 9:	Skeletal Rearrangement Reactions	379
33.4.2.1.10	Method 10:	Alkylations of Oximes	379
33.4.2.1.11	Method 11:	Derivatization of Stable Nitrosoalkenes	380
33.4.2.2		Applications of Product Subclass 2 in Organic Synthesis	381
33.4.2.2.1	Method 1:	Reactions with Nucleophiles	381
33.4.2.2.2	Method 2:	Synthesis of α,β -Unsaturated Oximes	382
33.4.2.2.3	Method 3:	[4 + 2] Cycloadditions	383
33.4.2.2.4	Method 4:	Electrocyclic Ring-Closure Reactions	385
33.4.3		Product Subclass 3: <i>N</i>-Alk-1-enyliminosulfur Compounds	
		H.-U. Reissig and R. Zimmer	
33.4.3		Product Subclass 3: <i>N</i>-Alk-1-enyliminosulfur Compounds	391
33.4.3.1		Synthesis of Product Subclass 3	391
33.4.3.1.1	Method 1:	Reaction of β -Alkoxy Michael Acceptors with Sulfoximides and Sulfodiimines	391
33.4.3.1.1.1	Variation 1:	Reactions with Sulfoximides	391
33.4.3.1.1.2	Variation 2:	Reactions with Sulfodiimines	392
33.4.3.1.2	Method 2:	Reaction of Alkynes with Dialkylsulfoxonium Salts	392
33.4.3.1.3	Method 3:	Reaction of Ethyl Bromoacetate with Sulfoximides	393
33.4.3.1.4	Method 4:	Reaction of 4-Amino-1,2-dihydropyrazol-3-one with Thionyl Chloride	393
33.4.4		Product Subclass 4: Alk-1-enediazonium Salts, Alkeneazoxy, and Alkeneazo Compounds	
33.4.4		Product Subclass 4: Alk-1-enediazonium Salts, Alkeneazoxy, and Alkeneazo Compounds	395

33.4.5	Product Subclass 5: <i>N</i>-Alk-1-enyliminophosphorus Compounds H.-U. Reissig and R. Zimmer	
<hr/>		
33.4.5	Product Subclass 5: <i>N</i>-Alk-1-enyliminophosphorus Compounds	397
33.4.5.1	Synthesis of Product Subclass 5	397
33.4.5.1.1	Method 1: Reactions of β -Alkoxy Michael Acceptors with Triphenylphosphine Imide	397
33.4.5.1.2	Method 2: Reactions of Azides with Triarylphosphines and Triorganyl Phosphites	397
33.4.5.1.2.1	Variation 1: With Triarylphosphines	398
33.4.5.1.2.2	Variation 2: With Triorganyl Phosphites	398
33.4.5.1.3	Method 3: Reactions of Nitriles with Triarylphosphines	399
33.4.5.1.4	Method 4: Reactions of Heterocycles Bearing β -Acceptor-Substituted Enamine Moieties with Triarylphosphines	399
33.4.5.1.5	Method 5: Elimination Reactions of (α -Azidoalkyl)benzotriazoles	400
33.4.5.2	Applications of Product Subclass 5 in Organic Synthesis	400
33.4.5.2.1	Method 1: Aza-Wittig Reactions	400
33.4.5.2.2	Method 2: Synthesis of Heterocycles	401
33.4.6	Product Subclass 6: Enamines T. Sammakia, J. A. Abramite, and M. F. Sammons	
<hr/>		
33.4.6	Product Subclass 6: Enamines	405
33.4.6.1	Synthesis of Product Subclass 6	405
33.4.6.1.1	Method 1: Condensation of a Ketone or Aldehyde with an Amine	405
33.4.6.1.1.1	Variation 1: Via Benzotriazole Aminals	406
33.4.6.1.1.2	Variation 2: Using Azeotropic Removal of Water	408
33.4.6.1.1.3	Variation 3: By the Action of Protic Acid Catalysis	409
33.4.6.1.1.4	Variation 4: By the Action of Molecular Sieves as Catalysts and Desiccants	410
33.4.6.1.1.5	Variation 5: By the Action of Calcium Chloride as a Desiccant	411
33.4.6.1.1.6	Variation 6: By the Action of Titanium(IV) Chloride as a Promoter	412
33.4.6.1.1.7	Variation 7: By the Action of Boron Trifluoride–Diethyl Ether Complex as a Catalyst	413
33.4.6.1.2	Method 2: Oxidative Amination	414
33.4.6.1.3	Method 3: Cross-Coupling Reactions	415
33.4.6.1.3.1	Variation 1: Of Bromides	416
33.4.6.1.3.2	Variation 2: Of Chlorides	418
33.4.6.1.3.3	Variation 3: Of Sulfonates	419
33.4.6.1.4	Method 4: Substitution and Addition–Elimination Reactions	420
33.4.6.1.5	Method 5: Elimination of Hydrogen	421
33.4.6.1.5.1	Variation 1: Dehydrogenation	421
33.4.6.1.5.2	Variation 2: Transfer Dehydrogenation	421
33.4.6.1.6	Method 6: Elimination of a Metal Hydroxide	422
33.4.6.1.7	Method 7: Addition of Hydrogen	422
33.4.6.1.7.1	Variation 1: Reduction of Enamides	422

33.4.6.1.7.2	Variation 2:	Dissolving Metal Reduction of Aromatic Amines	423
33.4.6.1.8	Method 8:	Hydroamination	423
33.4.6.1.9	Method 9:	Addition of Organometallic Reagents to Nitriles	426
33.4.6.1.10	Method 10:	Hydroaminomethylation	428
33.4.6.1.11	Method 11:	Isomerization	429
33.4.6.1.12	Method 12:	Wittig Reaction of Amides	432
33.4.6.1.13	Method 13:	Horner–Wittig Reaction of Ketones and Aldehydes	433
33.4.6.1.14	Method 14:	Alkylidenation of Carbonyl Groups via Titanium Carbenes	434
33.4.6.1.14.1	Variation 1:	Using Dialkyltitanocenes	435
33.4.6.1.14.2	Variation 2:	Using Tebbe’s Reagent	436
33.4.6.1.14.3	Variation 3:	Takai Alkylidenation	436
33.4.6.1.14.4	Variation 4:	Alkylidenation of Amides with Thioacetals Using a Titanium(II) Complex	437
33.4.7	Product Subclass 7: Enammonium Salts		
	T. Sammakia, J. A. Abramite, and M. F. Sammons		
<hr/>			
33.4.7	Product Subclass 7: Enammonium Salts		
33.4.7.1	Synthesis of Product Subclass 7		
33.4.7.1.1	Method 1:	Alkylation of Enamines	443
33.4.7.1.2	Method 2:	Conjugate Addition/Elimination	444
33.4.7.1.3	Method 3:	Alkylation/Elimination	445
33.4.7.1.4	Method 4:	Copper-Catalyzed S _N 2’ Substitution of Propargyl Chlorides	445
33.4.7.1.5	Method 5:	Elimination of a Hydrogen Halide or Water	446
33.4.7.1.6	Method 6:	Addition of Trialkylammonium Salts to Activated Alkynes	447
33.4.7.1.7	Method 7:	Cyclopropyliminium Ion Rearrangement	447
33.4.8	Product Subclass 8: N-Silylenamines		
	S. J. Collier		
<hr/>			
33.4.8	Product Subclass 8: N-Silylenamines		
33.4.8.1	Synthesis of Product Subclass 8		
33.4.8.1.1	Method 1:	Synthesis from Imines	453
33.4.8.1.1.1	Variation 1:	Direct Silylation of Imines or Enamines	453
33.4.8.1.1.2	Variation 2:	Other Approaches Involving Imines	458
33.4.8.1.2	Method 2:	Synthesis from Nitriles	460
33.4.8.1.2.1	Variation 1:	Nucleophilic Attack on Nitriles	460
33.4.8.1.2.2	Variation 2:	Other Approaches Involving Nitriles	466
33.4.8.1.3	Method 3:	Isomerization Reactions	467
33.4.8.1.4	Methods 4:	Miscellaneous Methods	469

33.4.9	Product Subclass 9: <i>N</i>-Borylenamines S. J. Collier	
<hr/>		
33.4.9	Product Subclass 9: <i>N</i>-Borylenamines	475
33.4.9.1	Synthesis of Product Subclass 9	477
33.4.9.1.1	Method 1: Direct Borylation of Imines (or Enamines)	477
33.4.9.1.2	Method 2: Synthesis from 1,2-Azaborolium Salts	480
33.4.9.1.3	Method 3: Synthesis from Other <i>N</i> -Borylenamines	481
33.4.9.1.4	Methods 4: Miscellaneous Procedures	483
33.4.10	Product Subclass 10: <i>N</i>-Haloenamines S. J. Collier	
<hr/>		
33.4.10	Product Subclass 10: <i>N</i>-Haloenamines	487
33.4.10.1	Synthesis of Product Subclass 10	487
33.4.10.1.1	Method 1: Halogenation of Enamides	487
33.4.10.1.2	Method 2: <i>N</i> -Halopyridinones and Related Compounds by Direct Halogenation	488
33.4.11	Product Subclass 11: <i>N</i>-Alk-1-enylhydroxylamines S. J. Collier	
<hr/>		
33.4.11	Product Subclass 11: <i>N</i>-Alk-1-enylhydroxylamines	493
33.4.11.1	Synthesis of Product Subclass 11	494
33.4.11.1.1	Method 1: Conjugate Addition Reactions of Hydroxylamines	494
33.4.11.1.1.1	Variation 1: With Alkenes	494
33.4.11.1.1.2	Variation 2: With Alkynes	496
33.4.11.1.2	Method 2: Synthesis from Hydroxylamines and Aldehydes or Ketones	498
33.4.11.1.3	Methods 3: Miscellaneous Methods	500
33.4.12	Product Subclass 12: <i>N</i>-Alk-1-enylaminosulfur Compounds S. J. Collier	
<hr/>		
33.4.12	Product Subclass 12: <i>N</i>-Alk-1-enylaminosulfur Compounds	503
33.4.12.1	Synthesis of Product Subclass 12	504
33.4.12.1.1	Method 1: Synthesis from Imines and Enamines and Electrophilic Sulfur Agents	504
33.4.12.1.2	Method 2: Synthesis from <i>N</i> -Sulfonylimines and Related Compounds ...	505
33.4.12.1.2.1	Variation 1: Through Deprotonation and Quenching of <i>N</i> -Sulfonyl- and <i>N</i> -Sulfinylimines	505
33.4.12.1.2.2	Variation 2: Through Nucleophilic Attack on <i>N</i> -Sulfonylimines	506
33.4.12.1.3	Method 3: Synthesis from Primary and Secondary Sulfonamides	509
33.4.12.1.4	Method 4: Synthesis through 1,2-Elimination Reactions of Amines	511
33.4.12.1.5	Method 5: Synthesis through Cross-Coupling Reactions	512

33.4.12.1.6	Method 6: Synthesis by Isomerization and Rearrangement	515
33.4.12.1.7	Methods 7: Miscellaneous Methods	517
33.4.13	Product Subclass 13: Alk-1-enylhydrazines S. J. Collier and M. D. McLaws	
33.4.13	Product Subclass 13: Alk-1-enylhydrazines	521
33.4.13.1	Synthesis of Product Subclass 13	524
33.4.13.1.1	Method 1: Synthesis from Hydrazines and Carbonyl Compounds	524
33.4.13.1.1.1	Variation 1: Monosubstituted or N,N-Disubstituted Hydrazines	524
33.4.13.1.1.2	Variation 2: N,N'-Disubstituted Hydrazines or Trisubstituted Hydrazines	526
33.4.13.1.2	Method 2: Synthesis by Conjugate Addition	528
33.4.13.1.2.1	Variation 1: Of Hydrazines to Alkynes	528
33.4.13.1.2.2	Variation 2: Of Hydrazines to β -Substituted Alkenes	530
33.4.13.1.3	Methods 3: Miscellaneous Methods	534
33.4.14	Product Subclass 14: Alk-1-enyl Azides S. J. Collier	
33.4.14	Product Subclass 14: Alk-1-enyl Azides	541
33.4.14.1	Synthesis of Product Subclass 14	544
33.4.14.1.1	Method 1: Condensation of Arylaldehydes with α -Azido-Esters	544
33.4.14.1.2	Method 2: 1,2-Elimination Reactions	549
33.4.14.1.3	Method 3: 1,4-Addition Reactions	553
33.4.14.1.4	Methods 4: Miscellaneous Methods	556
33.4.15	Product Subclass 15: N-Alk-1-enylaminophosphorus Compounds S. J. Collier	
33.4.15	Product Subclass 15: N-Alk-1-enylaminophosphorus Compounds	565
33.4.15.1	Synthesis of Product Subclass 15	565
33.4.15.1.1	Method 1: Synthesis from Imines or Enamines and Phosphorus Electrophiles	565
33.4.15.1.2	Method 2: Synthesis from Phosphamides and Aldehydes	567
33.4.15.1.3	Method 3: Synthesis from N-Allylphosphoric Triamides	569
33.4.15.1.4	Method 4: Synthesis from Nitriles	571
33.4.15.1.5	Methods 5: Miscellaneous Methods	572
33.4.16	Product Subclass 16: 1,2-Dihydroazetes and Derivatives P. Jubault, E. Leclerc, and J.-C. Quirion	
33.4.16	Product Subclass 16: 1,2-Dihydroazetes and Derivatives	577
33.4.16.1	Synthesis of Product Subclass 16	577
33.4.16.1.1	Synthesis by Ring-Closure Reactions	577

33.4.16.1.1.1	Method 1:	Addition of Amines to a Perfluoroenone	577
33.4.16.1.1.2	Method 2:	Addition of Amines to Hexafluoropropene Trimers	578
33.4.16.1.1.3	Method 3:	[2 + 2] Cycloaddition between an Imine and a Ketene Aminal	579
33.4.16.1.2		Elimination Reactions from Azetidines	579
33.4.16.1.2.1	Method 1:	Elimination of a Methanesulfonate Group	579
33.4.16.1.2.1.1	Variation 1:	Synthesis of <i>N</i> -Acyl-1,2-dihydroazetes	579
33.4.16.1.2.1.2	Variation 2:	Synthesis of <i>N</i> -Mesityl- and <i>N</i> -Nitro-1,2-dihydroazetes	580
33.4.16.1.2.2	Method 2:	1,2-Photoaromatization Reaction of an Azabicyclohexane-Type Diels–Alder Adduct	580
33.4.16.1.3		Synthesis by Substituent Modification	581
33.4.16.1.3.1		Addition Reactions	581
33.4.16.1.3.1.1	Method 1:	Addition of Malonate Derivatives to Azetes	581
33.4.17		Product Subclass 17: 2,3-Dihydro-1<i>H</i>-pyrroles and Derivatives P. Jubault, E. Leclerc, and J.-C. Quirion	
33.4.17		Product Subclass 17: 2,3-Dihydro-1<i>H</i>-pyrroles and Derivatives	583
33.4.17.1		Synthesis of Product Subclass 17	583
33.4.17.1.1		Synthesis by Ring-Closure Reactions	583
33.4.17.1.1.1	Method 1:	Addition/Cyclization of Sulfonamide Anions with Alkynyliodonium Trifluoromethanesulfonates	583
33.4.17.1.1.2	Method 2:	Iodocyclization of Alk-3-ynylsulfonamides	584
33.4.17.1.1.3	Method 3:	Palladium-Catalyzed Cyclization of α -Propargyl α -Amino Esters	585
33.4.17.1.1.4	Method 4:	Ring-Closing Metathesis of <i>N</i> -Alk-3-enyl- <i>N</i> -alk-1-ynylsulfonamides	585
33.4.17.1.1.5	Method 5:	Ring-Closing Metathesis of <i>N</i> -Alk-3-enylenamines	586
33.4.17.1.2		Elimination Reactions from Pyrrolidines	587
33.4.17.1.2.1	Method 1:	Reduction of Lactams Followed by Elimination	587
33.4.17.1.2.2	Method 2:	Dehydration of Pyrrolidin-3-ols	591
33.4.17.1.3		Synthesis by Substituent Modification	592
33.4.17.1.3.1	Method 1:	Heck Reactions of 2,3-Dihydropyrroles	592
33.4.17.1.3.2	Method 2:	Isomerizing Heck Reactions of 2,5-Dihydropyrroles	593
33.4.17.1.3.3	Method 3:	Coupling Reactions of Lactam-Derived Alkenyl Trifluoromethanesulfonates	595
33.4.18		Product Subclass 18: 1,2-Dihydropyridines, 1,4-Dihydropyridines, and Derivatives J.-C. Quirion, E. Leclerc, and P. Jubault	
33.4.18		Product Subclass 18: 1,2-Dihydropyridines, 1,4-Dihydropyridines, and Derivatives	601
33.4.18.1		Synthesis of Product Subclass 18	601

33.4.18.1.1	Synthesis by Ring-Closure Reactions	601
33.4.18.1.1.1	Method 1: Three-Component Hantzsch Synthesis	601
33.4.18.1.1.1.1	Variation 1: Classical Hantzsch Reaction	601
33.4.18.1.1.1.2	Variation 2: Microwave Activation	602
33.4.18.1.1.1.3	Variation 3: Miscellaneous Approaches	603
33.4.18.1.1.1.4	Variation 4: Solid-Phase Hantzsch Synthesis	604
33.4.18.1.1.2	Method 2: Addition/Cyclization of Nitrogen Nucleophiles to Dicarbonyl Compounds	605
33.4.18.1.1.2.1	Variation 1: Condensation of Amines with Dialdehydes	605
33.4.18.1.1.2.2	Variation 2: Condensation of Amides with Dialdehydes	606
33.4.18.1.1.2.3	Variation 3: Condensation of Ammonia with 1,5-Diketones	606
33.4.18.1.1.3	Method 3: Aza-Diels–Alder Reaction of 1-Azadienes	607
33.4.18.1.1.4	Method 4: Asymmetric Two-Component Hantzsch Reaction	609
33.4.18.1.1.5	Method 5: 6π -Electrocyclization of 1-Azatrienes	610
33.4.18.1.2	Synthesis by Ring Transformation	611
33.4.18.1.2.1	Method 1: Rearrangement of a 3,6,7-Triazatricyclo[3.2.1.0 ^{2,4}]octane Derivative	611
33.4.18.1.2.2	Method 2: Radical Deoxygenation of 3-Azatricyclo[2.2.1.0 ^{2,6}]- heptan-5-ols	612
33.4.18.1.3	Synthesis by Substituent Modification	612
33.4.18.1.3.1	Addition Reactions	612
33.4.18.1.3.1.1	Method 1: Hydride Reductions	612
33.4.18.1.3.1.2	Method 2: Dissolving-Metal Reductions	614
33.4.18.1.3.1.3	Method 3: Dithionite Reductions	615
33.4.18.1.3.1.4	Method 4: Addition of Grignard Reagents	615
33.4.18.1.3.1.5	Method 5: Addition of Organotin Reagents	617
33.4.18.1.3.1.6	Method 6: Addition of Organocopper and Organocuprate Reagents	618
33.4.18.1.3.1.7	Method 7: Addition of Enolates and Enol Ethers	620
33.4.18.1.3.1.8	Method 8: Addition of Other Carbon Nucleophiles	621
33.4.18.1.3.1.9	Method 9: Asymmetric Addition of Nucleophiles to Pyridinium Salts	622
33.4.18.1.3.1.9.1	Variation 1: Chirality on the Nitrogen Atom	622
33.4.18.1.3.1.9.2	Variation 2: Addition to Chiral Nicotinic Acid Derivatives	624
33.4.18.1.3.1.9.3	Variation 3: Catalytic Asymmetric Reissert Reaction	625
33.4.19	Product Subclass 19: 1,2,3,4-Tetrahydropyridines and Derivatives J.-C. Quirion	
33.4.19	Product Subclass 19: 1,2,3,4-Tetrahydropyridines and Derivatives	629
33.4.19.1	Synthesis of Product Subclass 19	629
33.4.19.1.1	Synthesis by Ring-Closure Reactions	629
33.4.19.1.1.1	Method 1: [4+2]-Cycloaddition Reactions of 1-Azabutadienes	630
33.4.19.1.1.1.1	Variation 1: Cyclization of <i>N</i> -Acyl-2-cyano-1-azabutadienes	630
33.4.19.1.1.1.2	Variation 2: Cyclization of <i>N</i> -Phenyl-2-cyano-1-azabutadienes	631
33.4.19.1.1.1.3	Variation 3: Cyclization of 2-Cyano- <i>N</i> -(ethoxycarbonyl)-1-azabutadienes	632

33.4.19.1.1.2	Method 2:	Photochemical Cycloaddition of 3-Aminopropenals and Alkenes	632
33.4.19.1.1.3	Method 3:	Cyclization/Isomerization of δ -Chloroimines	633
33.4.19.1.1.3.1	Variation 1:	In Situ Preparation of δ -Chloroimines	633
33.4.19.1.1.3.2	Variation 2:	Cyclization after Isolation of δ -Chloroimines	633
33.4.19.1.1.3.3	Variation 3:	Nucleophile-Induced Cyclization of δ -Chloroimines	634
33.4.19.1.1.4	Method 4:	Intramolecular Cyclization of Aminoaldehydes and Derivatives	635
33.4.19.1.1.4.1	Variation 1:	Intramolecular Cyclization of Amino Acetals	635
33.4.19.1.1.4.2	Variation 2:	Intramolecular Cyclization of an Amide and an Aldehyde or Acetal	636
33.4.19.1.1.4.3	Variation 3:	Intramolecular Cyclization of Carbamates and Aldehydes	637
33.4.19.1.1.4.4	Variation 4:	Intramolecular Condensation of Tosylamines and Acetals	638
33.4.19.1.1.5	Method 5:	Palladium-Induced Intramolecular Cyclization of an ω -Alkenic Tosylamide	639
33.4.19.1.1.6	Method 6:	Transition-Metal-Catalyzed Cyclization	639
33.4.19.1.1.6.1	Variation 1:	Platinum-Mediated Cycloisomerization of Ene-Ynamides	639
33.4.19.1.1.6.2	Variation 2:	Ring-Closing Metathesis of Ene-Ynamides	640
33.4.19.1.1.6.3	Variation 3:	Ring-Closing Metathesis of Ene-Enamides	640
33.4.19.1.1.7	Method 7:	Intramolecular Cyclization of Enamino Esters, Ketones, or Sulfones	641
33.4.19.1.1.7.1	Variation 1:	Cyclization Involving a Halogen Leaving Group	641
33.4.19.1.2		Synthesis by Transformation of a Cyclic Substrate	643
33.4.19.1.2.1	Method 1:	Reduction/Elimination of a Lactam	643
33.4.19.1.2.1.1	Variation 1:	Reduction of Unsaturated Lactams	643
33.4.19.1.2.2	Method 2:	Elimination of a Phenylselenanyl Group	644
33.4.19.1.2.3	Method 3:	Hydrogenation of Pyridine, Pyridinium Salts, and Dihydropyridines	644
33.4.19.1.2.4	Method 4:	Hydride Reduction of Pyridines and Dihydropyridines	646
33.4.19.1.2.5	Method 5:	Addition Reactions to 2,3-Dihydropyridinium Salts	647
33.4.19.1.2.5.1	Variation 1:	Addition of Organometallic Compounds	648
33.4.19.1.2.5.2	Variation 2:	Addition of Alcohols, Thiols, and Amines	649
33.4.19.1.2.5.3	Variation 3:	Addition of β -Dicarbonyl Anions	650
33.4.19.1.2.6	Method 6:	2-Carbamylation of 1,4-Dihydropyridines	650
33.4.19.1.3		Functionalization of 1,2,3,4-Tetrahydropyridines	651
33.4.19.1.3.1	Method 1:	Carboxymethylation of Substituted Vinyl Trifluoromethanesulfonates	652
33.4.19.1.3.2	Method 2:	Suzuki Reactions of Vinyl Trifluoromethanesulfonates	653
33.4.19.1.3.3	Method 3:	Functionalization of Boronates	654
33.4.19.1.3.4	Method 4:	Coupling Reactions of Vinyl Phosphates	655

33.4.20	Product Subclass 20: 2,3,4,5-Tetrahydro-1H-azepines, Larger Rings, and Derivatives	
	J.-C. Quirion, E. Leclerc, and P. Jubault	
<hr/>		
33.4.20	Product Subclass 20: 2,3,4,5-Tetrahydro-1H-azepines, Larger Rings, and Derivatives	659
33.4.20.1	Synthesis of Product Subclass 20	659
33.4.20.1.1	Synthesis by Ring-Closure Reactions	659
33.4.20.1.1.1	Method 1: Rhodium-Catalyzed Alkene–Allene Carbocyclization	659
33.4.20.1.2	Elimination Reactions	660
33.4.20.1.2.1	Method 1: Elimination Reactions of 2-Hydroxyazepanes and Derivatives	660
33.4.20.1.3	Synthesis by Substituent Modification	660
33.4.20.1.3.1	Method 1: Hydrodesulfurization of a Thiolactam-Derived Enol Ether	660
33.4.20.1.3.2	Method 2: Coupling Reactions of Lactam-Derived Vinyl Trifluoromethanesulfonates	661
33.4.20.1.3.3	Method 3: Reduction and Suzuki Coupling Reactions of Lactam-Derived Vinyl Phosphates	662
33.5	Product Class 5: Alk-1-enyl Phosphorus Compounds	
<hr/>		
33.5.1	Product Subclass 1: Alk-1-enylphosphonic Acids and Derivatives	
	A. C. Gaumont and M. Gulea	
<hr/>		
33.5.1	Product Subclass 1: Alk-1-enylphosphonic Acids and Derivatives	665
33.5.1.1	Synthesis of Product Subclass 1	665
33.5.1.1.1	Method 1: Hydrophosphorylation of Alkynes	665
33.5.1.1.1.1	Variation 1: Metal-Catalyzed Hydrophosphorylation	665
33.5.1.1.1.2	Variation 2: Base-Catalyzed Hydrophosphorylation	666
33.5.1.1.2	Method 2: P–C Bond Formation from Dialkyl Phosphonates or Trialkyl Phosphites and Vinyl Halides	667
33.5.1.1.2.1	Variation 1: Michaelis–Arbuzov-Type Reaction	668
33.5.1.1.2.2	Variation 2: Metal-Catalyzed Reaction of Dialkyl Phosphonates and Vinyl Halides	668
33.5.1.1.3	Method 3: Wittig–Horner-Type Alkenation	669
33.5.1.1.3.1	Variation 1: Deprotonation of Methylenebis(phosphonates)	669
33.5.1.1.3.2	Variation 2: Halogen–Lithium Exchange from (Halomethyl)phosphonates	671
33.5.1.1.3.3	Variation 3: Synthesis from (Dialkoxyphosphoryl)phosphoniomethanides	672
33.5.1.1.4	Method 4: Peterson-Type Alkenylation	673
33.5.1.1.4.1	Variation 1: Synthesis from (1-Silylalkyl)phosphonates	673
33.5.1.1.4.2	Variation 2: Synthesis from Alkylphosphonates by In Situ Silylation	673
33.5.1.1.4.3	Variation 3: Synthesis from Bis-silylated Methylphosphonates	674
33.5.1.1.5	Method 5: Other Alkenation Reactions	675
33.5.1.1.5.1	Variation 1: Synthesis from α -Stannylated Carbanions	675

33.5.1.1.5.2	Variation 2:	Synthesis from α -Sulfinyl Carbanions	676
33.5.1.1.6	Method 6:	Knoevenagel-Type Reactions	677
33.5.1.1.6.1	Variation 1:	Using an Aldehyde and a Base–Titanium(IV) Chloride System	677
33.5.1.1.6.2	Variation 2:	Using Bis-aminals and α -Haloacetic Acids	678
33.5.1.1.6.3	Variation 3:	Using Aldehydes and Tributylarsine	679
33.5.1.1.7	Method 7:	Mannich-Type Reaction	679
33.5.1.1.8	Method 8:	Oxidative Elimination of Sulfonyl or Selenyl Moieties	680
33.5.1.1.9	Method 9:	Elimination from β -Heteroatom-Substituted Alkylphosphonates	680
33.5.1.1.9.1	Variation 1:	Dehydrohalogenation	680
33.5.1.1.9.2	Variation 2:	Dehydration	681
33.5.1.1.9.3	Variation 3:	Elimination of Nitrous Acid	681
33.5.1.1.10	Method 10:	Hydrogenation of Alk-1-ynylphosphonates	682
33.5.1.1.11	Method 11:	1,4-Addition of Nucleophiles to Alk-1-ynylphosphonates	683
33.5.1.1.12	Method 12:	Synthesis from Organometallic Intermediates Generated from Alk-1-ynylphosphonates	683
33.5.1.1.12.1	Variation 1:	Synthesis from (Borylalk-1-enyl)phosphonates	684
33.5.1.1.12.2	Variation 2:	Synthesis from (Phosphorylalk-1-enyl)copper(I) Compounds	685
33.5.1.1.12.3	Variation 3:	Synthesis from (Tellanylalk-1-enyl)phosphonates	686
33.5.1.1.12.4	Variation 4:	Synthesis from Zirconacyclic and Titanacyclic Phosphonates	686
33.5.1.1.13	Method 13:	Modification of the Existing Double Bond in Alk-1-enylphosphonates	688
33.5.1.1.13.1	Variation 1:	Metal-Catalyzed Cross-Coupling Reactions	689
33.5.1.1.13.2	Variation 2:	Alkene Cross Metathesis	690
33.5.1.1.14	Method 14:	Transformation of Alk-1-enylphosphonates into the Corresponding Phosphonic Acids	690
33.5.1.1.14.1	Variation 1:	Acidic Hydrolysis	691
33.5.1.1.14.2	Variation 2:	Using Bromotrimethylsilane	691
33.5.2	Product Subclass 2: Alk-1-enylphosphinic Acids and Derivatives		
	A. C. Gaumont and M. Gulea		
33.5.2	Product Subclass 2: Alk-1-enylphosphinic Acids and Derivatives		695
33.5.2.1	Synthesis of Product Subclass 2		695
33.5.2.1.1	Method 1:	Hydrophosphinylation of Alkynes	695
33.5.2.1.2	Method 2:	Synthesis from Alkylphosphonochloridoates and Vinylic Organometallic Compounds	696
33.5.2.1.3	Method 3:	Metal-Catalyzed Phosphorus–Carbon Cross-Coupling Reactions	697
33.5.2.1.4	Method 4:	Alkenylation Reactions	698
33.5.2.1.5	Method 5:	Elimination from β -Heteroatom-Substituted Alkylphosphinic Esters	699

33.5.3 Product Subclass 3: Alk-1-enylphosphine Oxides and Derivatives

A. C. Gaumont and M. Gulea

33.5.3	Product Subclass 3: Alk-1-enylphosphine Oxides and Derivatives	701
33.5.3.1	Synthesis of Product Subclass 3	701
33.5.3.1.1	Method 1: Hydrophosphinylation of Alkynes	701
33.5.3.1.2	Method 2: Metal-Catalyzed Phosphorus–Carbon Cross-Coupling Reaction	702
33.5.3.1.3	Method 3: Alkenation Reactions	703
33.5.3.1.4	Method 4: Elimination from α -Oxygenated Alkylphosphine Oxides	704
33.5.3.1.4.1	Variation 1: From (1-Hydroxyalkyl)phosphine Oxides	704
33.5.3.1.4.2	Variation 2: From (1,2-Epoxyalkyl)phosphine Oxides	704
33.5.3.1.5	Method 5: Elimination from β -Heteroatom-Substituted Alkylphosphine Oxides	705
33.5.3.1.6	Method 6: Nucleophilic 1,4-Addition to Alk-1-ynylphosphine Oxides	705
33.5.3.1.7	Method 7: Synthesis from Organometallic Intermediates Generated from Alk-1-ynylphosphine Oxides	706
33.5.3.1.8	Method 8: Modification of an Existing Double Bond	707
33.5.3.1.9	Method 9: Oxidation of Alk-1-enylphosphines	708
33.5.3.1.10	Method 10: Acidic Hydrolysis of <i>P</i> -Alk-1-enylphosphinous Amides	709

33.5.4 Product Subclass 4: Alk-1-enylphosphines

A. C. Gaumont and M. Gulea

33.5.4	Product Subclass 4: Alk-1-enylphosphines	711
33.5.4.1	Synthesis of Product Subclass 4	711
33.5.4.1.1	Method 1: Hydrophosphination of Alkynes with Primary or Secondary Phosphines	711
33.5.4.1.1.1	Variation 1: Hydrophosphination under Basic Conditions	712
33.5.4.1.1.2	Variation 2: Radical-Catalyzed Hydrophosphination	713
33.5.4.1.1.3	Variation 3: Thermal Hydrophosphination	714
33.5.4.1.1.4	Variation 4: Metal-Catalyzed Hydrophosphination	714
33.5.4.1.2	Method 2: Metal-Catalyzed Phosphorus–Carbon Cross-Coupling Reactions	716
33.5.4.1.2.1	Variation 1: Palladium-Catalyzed Phosphorus–Carbon Cross-Coupling Reactions	716
33.5.4.1.2.2	Variation 2: Nickel-Catalyzed Phosphorus–Carbon Cross-Coupling Reactions	718
33.5.4.1.3	Method 3: Reaction between Halophosphines and Vinylic Organometallic Derivatives	719
33.5.4.1.4	Method 4: Reduction of Phosphorus Compounds	720
33.5.4.1.4.1	Variation 1: Reduction of Phosphonates and Phosphinates	720
33.5.4.1.4.2	Variation 2: Reduction of Chlorophosphines	721
33.5.4.1.5	Methods 5: Miscellaneous Methods	722

33.5.5	Product Subclass 5: Alk-1-enylphosphonium Salts A. C. Gaumont and M. Gulea	
<hr/>		
33.5.5	Product Subclass 5: Alk-1-enylphosphonium Salts	725
33.5.5.1	Synthesis of Product Subclass 5	725
33.5.5.1.1	Method 1: Alkenylation of Tertiary Phosphines	725
33.5.5.1.1.1	Variation 1: Nucleophilic Addition of Triphenylphosphine to Activated Alkynes	725
33.5.5.1.1.2	Variation 2: Metal-Catalyzed Addition of Triphenylphosphine to Alkynes	726
33.5.5.1.2	Method 2: Modification of Phosphoranes or Phosphonium Salts	727
33.5.5.1.2.1	Variation 1: Addition–Elimination Reactions of Phosphoranes	727
33.5.5.1.2.2	Variation 2: Elimination–Addition from Vinylidene Bisphosphonium Salts	727
33.5.5.1.3	Methods 3: Miscellaneous Methods	728
33.5.6	Product Subclass 6: P-Heteroatom-Substituted Alk-1-enylphosphines A. C. Gaumont and M. Gulea	
<hr/>		
33.5.6	Product Subclass 6: P-Heteroatom-Substituted Alk-1-enylphosphines ...	731
33.5.6.1	Synthesis of Product Subclass 6	731
33.5.6.1.1	Method 1: Alk-1-enyl(amino)phosphines by Vinylation of Halophosphines	731
33.5.6.1.1.1	Variation 1: Synthesis from Amino(chloro)phosphines	731
33.5.6.1.1.2	Variation 2: Synthesis from Amino(chloro)phosphines Generated In Situ	732
33.5.6.1.2	Method 2: Alk-1-enylphosphonous Diamides by Reaction between Enamines, Phosphorus Trihalides, and Amines	733
33.5.6.1.3	Method 3: Alk-1-enylphosphonous Dihalides by the Reaction of Phosphorus Trihalides and Organometallic Derivatives	734
33.5.6.1.4	Method 4: Alk-1-enyl(halo)phosphines by the Reaction of Tungsten–Phosphinidene Complexes and Chloroalkenes	734
33.5.7	Product Subclass 7: 1,2-Dihydrophosphetes and Derivatives Gy. Keglevich and H. Szelke	
<hr/>		
33.5.7	Product Subclass 7: 1,2-Dihydrophosphetes and Derivatives	737
33.5.7.1	Synthesis of Product Subclass 7	737
33.5.7.1.1	Synthesis by Ring-Closure Reactions	737
33.5.7.1.1.1	Method 1: Ring-Fused 1,2-Dihydrophosphetes by Cycloaddition of 1,2-Thiaphospholes and Ynamines	737
33.5.7.1.1.2	Method 2: A 1-Imino-1,2-dihydro-1 λ^5 -phosphet-1-amine by Cyclo- addition of an Imino(methylene)phosphorane and an Acetylene	738
33.5.7.1.1.3	Method 3: A 1-Imino-1,2-dihydro-1 λ^5 -phosphet-1-amine by Ring Closure of a Phosphabuta-1,3-diene Effected by an Azide	739
33.5.7.1.1.4	Method 4: Phosphetium Salts of Ring-Fused 1,2-Dihydrophosphetes by Ring Closure of (Arylmethylene)chlorophosphoranes	739

33.5.7.1.1.5	Method 5:	Synthesis of a 2-Methylene-1,2-dihydrophosphete via a Zirconium-Containing Tricyclic 1,2-Dihydrophosphete	740
33.5.7.1.2	Synthesis by Ring Transformation		740
33.5.7.1.2.1	Method 1:	Ring Expansion of Cycloprop-2-enylidene phosphines with Azides	740
33.5.7.1.2.2	Method 2:	1,2-Dihydrophosphetes by Titanium–Phosphorus Exchange of a Titanacyclobutene	741
33.5.7.1.2.3	Method 3:	A 1,2-Dihydrophosphete 1-Oxide by Ring Contraction of a 2,3-Dihydro-1,2-thiaphosphole Using Ethanol	742
33.5.8	Product Subclass 8: 2,3-Dihydro-1H-phospholes and Derivatives		
	Gy. Keglevich and H. Szelke		
33.5.8	Product Subclass 8: 2,3-Dihydro-1H-phospholes and Derivatives		745
33.5.8.1	Synthesis of Product Subclass 8		745
33.5.8.1.1	Synthesis by Ring-Closure Reactions		745
33.5.8.1.1.1	Method 1:	1-Alkoxy-2,3-dihydro-1H-phospholes via McCormack Cycloaddition of Phosphorous Acid Derivatives and Buta-1,3-dienes	745
33.5.8.1.1.1.1	Variation 1:	Reaction of Phosphorus Trihalides and Buta-1,3-dienes Followed by Reaction with Alcohols	745
33.5.8.1.1.1.2	Variation 2:	Reaction of a Dichlorophosphite and a Buta-1,3-diene	746
33.5.8.1.1.2	Method 2:	1-Chloro-4-methyl-2,3-dihydro-1H-phospholes by Reduction of the Phosphorus Trichloride–Isoprene McCormack Cycloadduct	747
33.5.8.1.1.3	Method 3:	1-Phenyl-2,3-dihydro-1H-phosphole 1-Oxides by McCormack Reaction of Dichloro(phenyl)phosphine and Buta-1,3-dienes Followed by Hydrolysis	747
33.5.8.1.1.4	Method 4:	1-Substituted 2,3-Dihydro-1H-phosphole 1-Oxides by Cyclization of Benzylphosphine Oxides and α,β -Unsaturated Ketones	748
33.5.8.1.1.5	Method 5:	1-Phenyl-2,3-dihydro-1H-phospholes by Intramolecular Cyclization of But-3-enylchloro(phenyl)phosphines	749
33.5.8.1.2	Synthesis by Double-Bond Rearrangement of 2,5-Dihydro-1H-phosphole Derivatives		749
33.5.8.1.2.1	Method 1:	1-Methyl-2,3-dihydro-1H-phosphole 1-Oxides and Sulfides by Acid- or Base-Catalyzed Isomerization	749
33.5.8.1.2.2	Method 2:	A 5-(Diphenylphosphoryl)-2,3-dihydro-1H-phosphole 1-Oxide by Isomerization with Substitution of a 2,5-Dihydro-1H-phosphole 1-Oxide	750
33.5.8.1.2.3	Method 3:	Annulated 2,3-Dihydro-1H-phospholes by Isomerization with Substitution of 2,5-Dihydro-1H-phospholes Followed by Ring Closure	750
33.5.8.1.2.4	Method 4:	3-Aryl-2,3-dihydro-1H-phosphole 1-Oxides by Isomerization with Arylation of 2,5-Dihydro-1H-phosphole 1-Oxides	751

33.5.8.1.2.5	Method 5:	3-Bromo-1-phenyl-2,3-dihydro-1 <i>H</i> -phosphole 1-Oxide by Isomerization with Bromination of 1-Phenyl-2,5-dihydro-1 <i>H</i> -phosphole 1-Oxide	751
33.5.8.1.2.6	Method 6:	4-Methoxy-1-methyl-2,3-dihydro-1 <i>H</i> -phosphole 1-Oxide by Isomerization with Chloro Substitution of 3-Chloro-1-methyl-2,5-dihydro-1 <i>H</i> -phosphole 1-Oxide	752
33.5.8.1.3	Synthesis by Elimination Reactions		752
33.5.8.1.3.1	Method 1:	2,3-Dihydro-1 <i>H</i> -phosphole 1-Oxides by Base-Catalyzed Rearrangement of 6-Oxa-3-phosphabicyclo[3.1.0]hexanes	752
33.5.8.1.3.2	Method 2:	A 3-Substituted 2,3-Dihydro-1 <i>H</i> -phosphole 1-Oxide by Reaction of a 6-Oxa-3-phosphabicyclo[3.1.0]hexane with a Malonic Ester Derivative	753
33.5.8.1.3.3	Method 3:	A 2,3-Dihydro-1 <i>H</i> -phosphole 1-Oxide by Dehydration of a 2,3,4,5-Tetrahydro-1 <i>H</i> -phosphol-2-ol 1-Oxide	753
33.5.8.1.4	Synthesis by Double-Bond Rearrangement of Phosphole Derivatives		754
33.5.8.1.4.1	Method 1:	3-Methylene-2,3-dihydro-1 <i>H</i> -phosphole Sulfides by Isomerization of 3-Methyl-1 <i>H</i> -phosphole 1-Sulfides	754
33.5.8.1.4.2	Method 2:	3-Methylene-2,3-dihydro-1 <i>H</i> -phosphole 1-Oxides by Thallium Ethoxide Mediated Conversion of 1-Benzyl-3-methyl-1 <i>H</i> -phospholium Salts	754
33.5.8.1.5	Synthesis of Fused 2,3-Dihydro-1 <i>H</i> -phospholes by Cyclopropanation of 1 <i>H</i> -Phospholes		755
33.5.8.1.5.1	Method 1:	2-Phosphabicyclo[3.1.0]hex-3-ene 2-Oxides by Cyclopropanation of 1 <i>H</i> -Phospholes with Diazomethane	755
33.5.8.1.5.2	Method 2:	A 2-Phosphabicyclo[3.1.0]hex-3-ene 2-Oxide by Intramolecular Cyclopropanation of a 1-(Iodomethyl)phospholium Salt	756
33.5.8.1.5.3	Method 3:	2-Phosphabicyclo[3.1.0]hex-3-ene 2-Sulfides by Cyclopropanation of 1 <i>H</i> -Phosphole 1-Sulfides with Ethyl Diazoacetate	756
33.5.9	Product Subclass 9: 1,2,3,4-Tetrahydrophosphinines and Derivatives Gy. Keglevich and H. Szelke		
33.5.9	Product Subclass 9: 1,2,3,4-Tetrahydrophosphinines and Derivatives		759
33.5.9.1	Synthesis of Product Subclass 9		759
33.5.9.1.1	Synthesis by Ring-Closure Reactions		759
33.5.9.1.1.1	Method 1:	1,2,3,4-Tetrahydrophosphinines by Cycloaddition of an In Situ Formed Phosphabuta-1,3-diene and Unsaturated Esters	759
33.5.9.1.1.2	Method 2:	A 1,2,3,4-Tetrahydrophosphinine 1-Oxide by Cyclization of a Diallylphosphine Oxide with Isomerization	759
33.5.9.1.2	Synthesis by Double-Bond Rearrangement of Tetrahydrophosphinines		760
33.5.9.1.2.1	Method 1:	1,2,3,4-Tetrahydrophosphinines via Bromination of the Corresponding 1,2,3,6-Tetrahydrophosphinines	760

33.5.9.1.3	Synthesis by Selective Saturation	761
33.5.9.1.3.1	Method 1: A 1,2,3,4-Tetrahydrophosphinine 1-Oxide by Hydrogenation of a 1,2-Dihydrophosphinine 1-Oxide	761
33.5.9.1.3.2	Method 2: A 4-(Dichloromethylene)-1,2,3,4-tetrahydrophosphinine 1-Oxide via Hydroboration of the Corresponding 1,4-Dihydrophosphinine 1-Oxide	761
33.5.9.1.3.3	Method 3: A 1,2,3,4-Tetrahydrophosphinin-4-one 1-Oxide by Hydrolysis of a λ^5 -Phosphinine	761
33.5.10	Product Subclass 10: 1,4-Dihydrophosphinines and Derivatives Gy. Keglevich and H. Szelke	
33.5.10	Product Subclass 10: 1,4-Dihydrophosphinines and Derivatives	765
33.5.10.1	Synthesis of Product Subclass 10	765
33.5.10.1.1	Synthesis by Ring-Closure Reactions	765
33.5.10.1.1.1	Method 1: 1,4-Dihydrophosphinines by Reaction of 1,4-Diynes with Arylphosphines	765
33.5.10.1.1.2	Method 2: 1,4-Dihydrophosphinines by Reaction of Dilithiated Penta-1,4-dienes with Dichlorophosphines	766
33.5.10.1.2	Synthesis by Ring Transformation	766
33.5.10.1.2.1	Method 1: A Biphosphinin-4(1 <i>H</i>)-ylidene 1,1'-Dioxide by Photolysis of a 2-Phosphabicyclo[3.1.0]hexane Oxide	766
33.5.10.1.3	Synthesis from λ^5 -Phosphinines and λ^3 -Phosphinines	767
33.5.10.1.3.1	Method 1: 1,4-Dihydrophosphinine 1-Oxides by Isomerization of λ^5 -Phosphinines	767
33.5.10.1.3.2	Method 2: A 1,4-Dihydrophosphinine 1-Oxide via the Chlorination of a λ^3 -Phosphinine	767
33.5.10.1.3.3	Method 3: A 4-Methylene-1,4-dihydrophosphinine 1-Oxide by a Lewis Acid Catalyzed Rearrangement of a 4-Methyl- λ^5 -phosphinine	768
33.5.10.1.3.4	Method 4: 4-Methylene-1,4-dihydrophosphinine 1-Oxides via Enolization of a λ^5 -Phosphinine-4-carbaldehyde	768
33.5.10.1.3.5	Method 5: A 1',4'-Dihydro-2,4'-biphosphinine by Special Reaction of a λ^3 -Phosphinine in the Presence of Lithium 2,2,6,6-Tetramethylpiperidide	769
33.5.10.1.4	Synthesis by Substituent Modification	770
33.5.10.1.4.1	Method 1: A Biphosphinin-4(1 <i>H</i>)-ylidene 1,1'-Dioxide by Coupling of Two Units of a Phosphinin-4(1 <i>H</i>)-one 1-Oxide	770
	Keyword Index	773
	Author Index	817
	Abbreviations	861