
**Volume 27:
Heteroatom Analogues of Aldehydes and Ketones**

	Preface	V
	Volume Editor's Preface	VII
	Table of Contents	XI
	Introduction	
	A. Padwa	1
27.1	Product Class 1: Sulfur Ylides	
	V. Aggarwal and J. Richardson	21
27.2	Product Class 2: Alkylidenesulfonium Salts or α-Sulfanyl Carbocations	
	C. O. Kappe	105
27.3	Product Class 3: Thioaldehyde and Thioketone S,S-Dioxides and Oxyimides (Sulfenes and Derivatives)	
	B. Zwanenburg	123
27.4	Product Class 4: Thioaldehyde and Thioketone S-Oxides and S-Imides (Sulfines and Derivatives)	
	B. Zwanenburg	135
27.5	Product Class 5: Thioaldehydes	
	S. J. Collier	177
27.6	Product Class 6: Thioketones	
	M. J. Dabdoub	215
27.7	Product Class 7: Imines	
	K. Abbaspour Tehrani and N. De Kimpe	245
27.8	Product Class 8: Iminium Salts	
	K. Abbaspour Tehrani and N. De Kimpe	313
27.9	Product Class 9: N-Acylimines	
	L. Fišera	349
27.10	Product Class 10: N-Acyliminium Salts	
	R. A. Pilli and G. B. Rosso	375
27.11	Product Class 11: Azomethine Ylides	
	W. Eberbach	441

X	Overview	
27.12	Product Class 12: N-Haloimines Jie Jack Li	499
27.13	Product Class 13: Nitrones and Cyclic Analogues P. Merino	511
27.14	Product Class 14: Nitronic Acids and Their Derivatives Jie Jack Li	581
27.15	Product Class 15: Oximes M. Yamane and K. Narasaka	605
27.16	Product Class 16: Azines D. M. Wilson and Y. Zhang	649
27.17	Product Class 17: Hydrazones S. Kim and J.-Y. Yoon	671
27.18	Product Class 18: Hydrazonium Compounds Y. Zhang and D. M. Wilson	723
27.19	Product Class 19: Azomethine Imines J. G. Schantl	731
27.20	Product Class 20: N-Nitroimines and N-Nitrosoimines Jie Jack Li	825
27.21	Product Class 21: Diazo Compounds H. Heydt	843
27.22	Product Class 22: Alkylidenephosphines E. Niecke, A. Ruban, and M. Raab	937
27.23	Product Class 23: Alkylidenephosphonium Salts E. Niecke, A. Ruban, and M. Raab	969
27.24	Product Class 24: Alkylidenephosphoranes R. Schobert and G. J. Gordon	973
	Keyword Index	1071
	Author Index	1105
	Abbreviations	1169

Table of Contents

	Introduction	
	A. Padwa	
	Introduction	1
27.1	Product Class 1: Sulfur Ylides	
	V. Aggarwal and J. Richardson	
27.1	Product Class 1: Sulfur Ylides	21
27.1.1	Product Subclass 1: Thiocarbonyl Ylides	23
27.1.1.1	Synthesis of Product Subclass 1	24
27.1.1.1.1	Method 1: By Deprotonation of Sulfonium Salts	24
27.1.1.1.2	Method 2: By 1,3-Elimination Reactions	25
27.1.1.1.2.1	Variation 1: Thermal Decomposition of Bis[(trimethylsilyl)methyl] Sulfoxides	26
27.1.1.1.2.2	Variation 2: 1,3-Elimination of Halotrimethylsilanes	26
27.1.1.1.3	Method 3: By Extrusion of Nitrogen from 2,5-Dihydro-1,3,4-thiadiazoles ·	27
27.1.1.1.3.1	Variation 1: Extrusion of Nitrogen from Stable 2,5-Dihydro-1,3,4-thia- diazoles	28
27.1.1.1.3.2	Variation 2: Extrusion of Nitrogen from 2,5-Dihydro-1,3,4-thiadiazoles Generated In Situ from Thiocarbonyl Compounds and Diazo Compounds	28
27.1.1.1.4	Method 4: By Addition of Carbenes and Carbenoids to Thiocarbonyl Compounds	29
27.1.1.1.4.1	Variation 1: By Reaction with Dihalocarbenes	29
27.1.1.1.4.2	Variation 2: Generation of Carbenes by Metal-Catalyzed Decomposition of Diazo Compounds	30
27.1.1.1.4.3	Variation 3: Generation of Thiocarbonyl Ylides from Phenyliodonium Ylides	31
27.1.1.2	Applications of Product Subclass 1 in Organic Synthesis	31
27.1.1.2.1	Method 1: Synthesis of Five-Membered Sulfur-Containing Heterocycles by 1,3-Dipolar Cycloaddition	32
27.1.1.2.1.1	Variation 1: From Thiocarbonyl Ylides Generated by Deprotonation of Sulfonium Salts	32
27.1.1.2.1.2	Variation 2: From Thiocarbonyl Ylides Generated by 1,3-Elimination of Halotrimethylsilane	34
27.1.1.2.1.3	Variation 3: From Thiocarbonyl Ylides Generated by Cycloreversion of 2,5-Dihydro-1,3,4-thiadiazoles	35
27.1.1.2.2	Method 2: Synthesis of Sulfides, Thioacetals, Dithioacetals, and Thioaminals from 1,3-Addition Reactions of Thiocarbonyl Ylides	37
27.1.1.2.2.1	Variation 1: From Thiocarbonyl Ylides Generated by Cycloreversion of 2,5-Dihydro-1,3,4-thiadiazoles	38

27.1.1.2.3	Method 3:	Synthesis of Thiiranes by 1,3-Electrocyclization Reactions of Thiocarbonyl Ylides	38
27.1.1.2.3.1	Variation 1:	From Thiocarbonyl Ylides Generated by Extrusion of Nitrogen from 2,5-Dihydro-1,3,4-thiadiazoles	39
27.1.1.2.3.2	Variation 2:	From Thiocarbonyl Ylides Generated by Addition of Carbenes to Thiocarbonyl Compounds	40
27.1.1.2.3.3	Variation 3:	By Transition-Metal-Catalyzed Decomposition of Diazo Compounds	40
27.1.1.2.4	Method 4:	Synthesis of 1,3-Oxathiole Derivatives by 1,5-Electrocyclization Reactions of Thiocarbonyl Ylides	42
27.1.2	Product Subclass 2: Sulfoxonium Ylides		42
27.1.2.1	Synthesis of Product Subclass 2		43
27.1.2.1.1	Method 1:	By Deprotonation of Sulfoxonium Salts	43
27.1.2.1.1.1	Variation 1:	In Organic Solvents	43
27.1.2.1.1.2	Variation 2:	In a Biphasic System	44
27.1.2.1.2	Method 2:	By Hydrogen Atom Substitution of Existing Sulfoxonium Ylides	44
27.1.2.1.2.1	Variation 1:	Synthesis of Carbonyl-Stabilized Sulfoxonium Ylides	45
27.1.2.1.2.2	Variation 2:	Synthesis of Thiocarbonyl-Stabilized Sulfoxonium Ylides	46
27.1.2.1.2.3	Variation 3:	Synthesis of Imide- and Imine-Stabilized Sulfoxonium Ylides	46
27.1.2.1.2.4	Variation 4:	Synthesis of Aryl- or Hetaryl-Stabilized Sulfoxonium Ylides	47
27.1.2.1.2.5	Variation 5:	Synthesis of Cyano-Stabilized Sulfoxonium Ylides	47
27.1.2.1.2.6	Variation 6:	Synthesis of Vinyl-Stabilized Sulfoxonium Ylides	48
27.1.2.1.3	Method 3:	Reaction of Sulfoxides with Carbenes	48
27.1.2.1.3.1	Variation 1:	Carbenes Generated from Transition-Metal-Catalyzed Decomposition of Diazo Compounds	49
27.1.2.1.4	Method 4:	Sulfoxonium Ylides from Sulfoximides	49
27.1.2.2	Applications of Product Subclass 2 in Organic Synthesis		50
27.1.2.2.1	Method 1:	Reactions with Aldehydes and Ketones	50
27.1.2.2.1.1	Variation 1:	In Organic Solvents	51
27.1.2.2.1.2	Variation 2:	Under Solvent-Free Conditions	52
27.1.2.2.2	Method 2:	Reaction with Imines	52
27.1.2.2.2.1	Variation 1:	In Organic Solvents	52
27.1.2.2.2.2	Variation 2:	Under Solvent-Free Conditions	53
27.1.2.2.3	Method 3:	Reaction with Electron-Deficient Alkenes	54
27.1.2.2.3.1	Variation 1:	In Organic Solvents	55
27.1.2.2.3.2	Variation 2:	In the Solid Phase	56
27.1.2.2.4	Method 4:	Reaction with Aromatic Compounds	57
27.1.2.2.5	Method 5:	Reaction with Weakly Acidic Heteroatoms: Methylation of R ¹ XH	57
27.1.2.2.6	Method 6:	Ring Expansion of Epoxides and Aziridines	58
27.1.3	Product Subclass 3: Sulfonium Ylides		59
27.1.3.1	Synthesis of Product Subclass 3		59
27.1.3.1.1	Method 1:	By Deprotonation of Sulfonium Salts	59
27.1.3.1.1.1	Variation 1:	In Organic Solvents	60

27.1.3.1.1.2	Variation 2:	Under Solid–Liquid Phase-Transfer Conditions	62
27.1.3.1.1.3	Variation 3:	In a Biphasic Medium	63
27.1.3.1.2	Method 2:	By Hydrogen Atom Substitution of an Existing Sulfonium Ylide	63
27.1.3.1.2.1	Variation 1:	Replacement with Alkyl Groups	64
27.1.3.1.3	Method 3:	Substitution of Groups on Sulfonium Salts	64
27.1.3.1.3.1	Variation 1:	From Triarylsulfonium Salts	65
27.1.3.1.3.2	Variation 2:	From Alkoxy- or Aminosulfonium Salts	65
27.1.3.1.4	Method 4:	Nucleophilic Attack on Vinyl- and Buta-1,3-dienyl-Substituted Dimethylsulfonium Salts	66
27.1.3.1.5	Method 5:	By Reaction of Sulfides with Carbenes and Carbenoids	67
27.1.3.1.5.1	Variation 1:	Transition-Metal-Catalyzed Decomposition of Diazo Compounds	67
27.1.3.1.5.2	Variation 2:	By Reaction with Dihalocarbenes	69
27.1.3.1.5.3	Variation 3:	Transylidation Reactions	69
27.1.3.1.5.4	Variation 4:	Reaction with Zinc Carbenoids	70
27.1.3.1.6	Method 6:	Desilylation of α -Silyl Sulfonium Salts	70
27.1.3.2		Applications of Product Subclass 3 in Organic Synthesis	70
27.1.3.2.1	Method 1:	Reaction of Sulfonium Ylides with Aldehydes and Ketones	70
27.1.3.2.1.1	Variation 1:	With Ylides Formed by Deprotonation	73
27.1.3.2.1.2	Variation 2:	With Ylides Formed by Reaction with Carbenes	76
27.1.3.2.1.3	Variation 3:	With Ylides Formed by Desilylation	77
27.1.3.2.1.4	Variation 4:	With Ylides Formed by Nucleophilic Attack on Vinylsulfonium Salts	78
27.1.3.2.2	Method 2:	Reaction of Sulfonium Ylides with Ketenes	80
27.1.3.2.3	Method 3:	Reaction of Sulfonium Ylides with Imines	80
27.1.3.2.3.1	Variation 1:	With Ylides Formed by Deprotonation of Sulfonium Salts	81
27.1.3.2.3.2	Variation 2:	With Ylides Formed by Reactions with Carbenes	82
27.1.3.2.4	Method 4:	Reaction of Sulfonium Ylides with Michael Acceptors	83
27.1.3.2.4.1	Variation 1:	With Ylides Formed by Deprotonation	85
27.1.3.2.4.2	Variation 2:	With Ylides Formed from Carbenes	86
27.1.3.2.5	Method 5:	Reactions with Alkynes	88
27.1.3.2.6	Method 6:	α' , β -Elimination Reactions	88
27.1.3.2.7	Method 7:	Rearrangement Reactions of Sulfonium Ylides	88
27.1.3.2.8	Method 8:	Miscellaneous Applications	92
27.1.4		Product Subclass 4: Cyclic Conjugated Sulfoxonium Ylides (1λ^4-Thiopyran 1-Oxides)	93
27.1.4.1		Synthesis of Product Subclass 4	93
27.1.4.1.1	Method 1:	From Dimethylsulfoxonium Alk-2-enylides	93
27.1.4.1.2	Method 2:	From 1,3-Diketones and Sulfoxonium Ylides	94
27.1.4.1.3	Method 3:	From Other 1 λ^4 -Thiopyran 1-Oxides	94
27.1.4.1.4	Method 4:	Miscellaneous Methods	95
27.1.5		Product Subclass 5: Cyclic Conjugated Sulfonium Ylides (1λ^4-Thiopyrans)	95
27.1.5.1		Synthesis of Product Subclass 5	96
27.1.5.1.1	Method 1:	By Deprotonation of 2 <i>H</i> -Thiopyrylium Salts	96

27.1.5.1.2	Method 2: Formation by Nucleophilic Addition of Alkylolithium Reagents to Thiopyrylium Salts	96
27.1.5.2	Applications of Product Subclass 5 in Organic Synthesis	97
27.1.5.2.1	Method 1: Reactions with Electrophilic Alkynes	97
27.1.5.2.2	Method 2: Rearrangements	98
27.2	Product Class 2: Alkylidenesulfonium Salts or α-Sulfanyl Carbocations C. O. Kappe	
27.2	Product Class 2: Alkylidenesulfonium Salts or α-Sulfanyl Carbocations ...	105
27.2.1	Synthesis of Product Class 2	106
27.2.1.1	Method 1: Alkylation of Thioketones	106
27.2.1.2	Method 2: α -Halo Elimination from α -Halo Sulfides	106
27.2.1.3	Method 3: α -Alkoxy or α -Alkylamino Elimination from O,S- or N,S-Acetals	107
27.2.1.4	Method 4: α -Alkylsulfanyl Elimination from Dithioacetals	107
27.2.1.4.1	Variation 1: Using Dimethyl(methylsulfanyl)sulfonium Tetrafluoroborate	108
27.2.1.4.2	Variation 2: Using Copper(I) Trifluoromethanesulfonate	110
27.2.1.5	Method 5: Protonation of Vinyl Sulfides	110
27.2.1.6	Method 6: Pummerer Rearrangement of Sulfoxides	111
27.2.1.6.1	Variation 1: Acetic Anhydride Promoted Reaction	112
27.2.1.6.2	Variation 2: Trifluoroacetic Anhydride Promoted Reaction	113
27.2.1.6.3	Variation 3: 4-Toluenesulfonic Acid Promoted Reaction	116
27.2.1.6.4	Variation 4: Trimethylsilyl Trifluoromethanesulfonate Promoted Reaction	117
27.2.1.6.5	Variation 5: O-Silylated Ketene Acetal Promoted Reaction	118
27.3	Product Class 3: Thioaldehyde and Thioketone S,S-Dioxides and Oxyimides (Sulfenes and Derivatives) B. Zwanenburg	
27.3	Product Class 3: Thioaldehyde and Thioketone S,S-Dioxides and Oxyimides (Sulfenes and Derivatives)	123
27.3.1	Product Subclass 1: Thioaldehyde and Thioketone S,S-Dioxides (Sulfenes)	123
27.3.1.1	Synthesis of Product Subclass 1	123
27.3.1.1.1	Method 1: Dehydrohalogenation of Alkanesulfonyl Halides	123
27.3.1.1.2	Method 2: Elimination of Chlorotrimethylsilane from Trimethylsilylmethanesulfonyl Chloride	124
27.3.1.1.3	Method 3: Cope Rearrangement of Allyl Vinyl Sulfones	124
27.3.1.1.4	Method 4: Ring Opening of Thiete 1,1-Dioxides	125
27.3.1.1.5	Method 5: Reaction of Diazoalkanes with Sulfur Dioxide	125
27.3.1.1.6	Methods 6: Miscellaneous Methods	126
27.3.1.2	Applications of Product Subclass 1 in Organic Synthesis	126
27.3.1.2.1	Method 1: In Situ Trapping with Enamines	126
27.3.1.2.2	Method 2: In Situ Cycloaddition with Vinyl Ethers	127

27.3.1.2.3	Method 3:	In Situ Trapping with Ketene Acetals	128
27.3.1.2.4	Method 4:	In Situ Trapping with Ketene <i>N,N</i> -Acetals and Ketene <i>O,N</i> -Acetals	128
27.3.1.2.5	Method 5:	In Situ Trapping with Carbonyl Compounds	129
27.3.1.2.6	Method 6:	In Situ Trapping with Imines	129
27.3.1.2.7	Method 7:	In Situ Trapping with Ynamines	129
27.3.1.2.8	Method 8:	In Situ Trapping with Nitrones	130
27.3.1.2.9	Method 9:	In Situ Trapping with β -Oxo Enamines and β -Thioxo Enamines	130
27.3.1.2.10	Method 10:	In Situ Trapping with 1-(Dialkylamino)-1,3-dienes	131
27.3.1.2.11	Method 11:	In Situ Trapping with Sulfonium Ylides	131
27.3.1.2.12	Method 12:	In Situ Trapping with Cyclopentadiene	132
27.3.1.2.13	Method 13:	Preparation of Thiirane 1,1-Dioxides	133
27.3.2	Product Subclass 2: Thioaldehyde and Thioketone Oxyimides (Sulfene Imides)		133
27.3.2.1	Synthesis of Product Subclass 2		133
27.3.2.1.1	Method 1:	Dehydrohalogenation of Sulfonimidoyl Chlorides	133
27.3.2.2	Applications of Product Subclass 2 in Organic Synthesis		134
27.3.2.2.1	Method 1:	In Situ Trapping with Ketene Acetals	134
27.4	Product Class 4: Thioaldehyde and Thioketone S-Oxides and S-Imides (Sulfines and Derivatives) B. Zwanenburg		
27.4	Product Class 4: Thioaldehyde and Thioketone S-Oxides and S-Imides (Sulfines and Derivatives)		135
27.4.1	Product Subclass 1: Thioaldehyde and Thioketone S-Oxides (Sulfines)		137
27.4.1.1	Synthesis of Product Subclass 1		137
27.4.1.1.1	Method 1:	Alkenation of Sulfur Dioxide with a Phosphonium Ylide (Wittig Reaction)	137
27.4.1.1.1.1	Variation 1:	Phosphonium Ylides with <i>N</i> -Sulfinylaniline	138
27.4.1.1.2	Method 2:	Alkenation of Sulfur Dioxide with α -Silyl Carbanions	138
27.4.1.1.2.1	Variation 1:	α -Silyl Carbanions from Vinylsilanes	140
27.4.1.1.3	Method 3:	Oxidation of Thiones	142
27.4.1.1.4	Method 4:	Thioaldehyde S-Oxides from Thioacylsilanes	144
27.4.1.1.5	Method 5:	Dehydrochlorination of Sulfinyl Chlorides	146
27.4.1.1.5.1	Variation 1:	α -Oxo Sulfines from Active Methylene Compounds and Thionyl Chloride	146
27.4.1.1.5.2	Variation 2:	α -Oxo Sulfines from Silyl Enol Ethers and Thionyl Chloride	149
27.4.1.1.6	Method 6:	Elimination of Phthalimide from <i>N</i> -Phthaloyl Sulfinamides	152
27.4.1.1.7	Method 7:	Elimination of Chloroform from Trichloromethyl Sulfoxides	152
27.4.1.1.8	Method 8:	In Situ Generation of Sulfines by Retro-hetero-Diels–Alder Reactions	153
27.4.1.1.9	Methods 9:	Miscellaneous Methods	155
27.4.1.1.9.1	Variation 1:	Reaction of Sulfur Monoxide with Diazoalkanes and Ylides	155

27.4.1.1.9.2	Variation 2:	Sulfines by a Wolff Rearrangement of Sulfinyl Carbenes	155
27.4.1.1.9.3	Variation 3:	Sulfines by Singlet Oxygen Oxidation of Thiophenes	156
27.4.1.1.9.4	Variation 4:	Sulfines by Dehydrosilylation of Silyl Sulfinates	156
27.4.1.1.9.5	Variation 5:	Synthesis of α -Disulfines from 1,2-Dithietes	157
27.4.1.1.9.6	Variation 6:	Synthesis of Chlorosulfines from Alkanesulfonyl Chlorides	158
27.4.1.2		Applications of Product Subclass 1 in Organic Synthesis	158
27.4.1.2.1	Method 1:	1,3-Dipolar Cycloaddition Reactions with Sulfines	158
27.4.1.2.2	Method 2:	Sulfines as 1,3-Dipoles	161
27.4.1.2.3	Method 3:	Diels–Alder Reactions	163
27.4.1.2.4	Method 4:	Inverse-Electron-Demand Diels–Alder Reactions of α -Oxo Sulfines	165
27.4.1.2.5	Method 5:	Thiophilic Addition Reactions	166
27.4.2		Product Subclass 2: Thioketone S-Imides	167
27.4.2.1		Synthesis of Product Subclass 2	167
27.4.2.1.1	Method 1:	<i>N</i> -Sulfinyl-Substituted Sulfonamide with Phosphonium Ylides	167
27.4.2.1.2	Method 2:	<i>N</i> -Sulfinylanilines with α -Silyl Carbanions	168
27.4.2.1.3	Method 3:	Sulfines with (Trimethylsilyl)amines	168
27.4.2.1.4	Method 4:	Thiocarbonyl Compounds with Chloroamines	169
27.4.2.1.5	Method 5:	α -Chloro Sulfonyl Chloride with Amines	172
27.4.2.2		Applications of Product Subclass 2 in Organic Synthesis	172
27.4.2.2.1	Method 1:	Diels–Alder Reactions	173
27.4.2.2.2	Method 2:	1,3-Dipolar Cycloaddition Reactions	173
27.5		Product Class 5: Thioaldehydes S. J. Collier	
27.5		Product Class 5: Thioaldehydes	177
27.5.1		Synthesis of Product Class 5	180
27.5.1.1	Method 1:	Synthesis from Aldehydes	180
27.5.1.1.1	Variation 1:	By Using Hydrogen Sulfide and Acid	180
27.5.1.1.2	Variation 2:	By Using Metal and Metalloid Sulfides	182
27.5.1.1.3	Variation 3:	Via Phosphorus Sulfides	186
27.5.1.2	Method 2:	Photofragmentation of Phenacyl Sulfides	187
27.5.1.3	Method 3:	1,2-Elimination Reactions	190
27.5.1.3.1	Variation 1:	From Sodium Thiosulfate <i>S</i> -Esters (Bunte Salts)	191
27.5.1.3.2	Variation 2:	From Thiosulfinates	192
27.5.1.3.3	Variation 3:	Via Sulfonyl Chlorides	194
27.5.1.3.4	Variation 4:	Via <i>N</i> -(Alkylsulfonyl)phthalimide Derivatives	196
27.5.1.3.5	Variation 5:	Other 1,2-Eliminations	196
27.5.1.4	Method 4:	Synthesis by Cycloreversion Reactions	198
27.5.1.4.1	Variation 1:	Retro-Diels–Alder Reactions	198
27.5.1.4.2	Variation 2:	Other Cycloreversion Reactions	201
27.5.1.5	Method 5:	Modified Vilsmeier Reactions	202
27.5.1.6	Method 6:	Synthesis from Acetals and Dihalomethyl Species	203

27.5.1.7	Method 7:	Reaction of Carbanions and Thioformate Esters	205
27.5.1.8	Method 8:	Synthesis from Phosphorus Ylides	207
27.5.1.9	Methods 9:	Miscellaneous Syntheses	208
27.6	Product Class 6: Thioketones		
	M. J. Dabdoub		
27.6	Product Class 6: Thioketones		
27.6.1	Synthesis of Product Class 6		
27.6.1.1	Method 1:	Direct Transformation of Ketones	216
27.6.1.1.1	Variation 1:	By Reaction with Hydrogen Sulfide and an Acid	216
27.6.1.1.2	Variation 2:	By Reaction with Phosphorus-Based Reagents	218
27.6.1.1.3	Variation 3:	By Reaction with Lawesson's Reagent and Derivatives	219
27.6.1.1.4	Variation 4:	By Reaction with Silicon-Based Reagents	221
27.6.1.1.5	Variation 5:	By Reaction with Hexaorganyldistannathianes or Bis(triorganoaluminum) Sulfides	222
27.6.1.2	Method 2:	Synthesis from Ketimine Anions	223
27.6.1.3	Method 3:	Synthesis from Hydrazones	224
27.6.1.3.1	Variation 1:	By Reaction with Sulfur Monochloride	224
27.6.1.3.2	Variation 2:	By Reaction with Sulfur Dichloride	226
27.6.1.3.3	Variation 3:	By Thermal Decomposition of (Triphenylphosphoranylidene)-hydrazones in the Presence of Elemental Sulfur	226
27.6.1.4	Method 4:	Synthesis from 1,3-Dithiolanes or Ketals	227
27.6.1.5	Method 5:	Retro-Diels–Alder Reaction	229
27.6.1.5.1	Variation 1:	Reaction of Diels–Alder Adducts in the Presence of a Suitable Unsaturated Compound	229
27.6.1.5.2	Variation 2:	Flash-Vacuum Thermolysis of Diels–Alder Adducts	230
27.6.1.5.3	Variation 3:	Thermolysis of Thioketone Dimers	232
27.6.1.6	Method 6:	Synthesis from Noncarbonyl Precursors	233
27.6.1.6.1	Variation 1:	From Halides via Bunte Salts	233
27.6.1.6.2	Variation 2:	By Reaction of 1,1-Dihalides with Potassium <i>O</i> -Ethyl Dithiocarbonate	234
27.6.1.6.3	Variation 3:	By Reaction of Alkyl Halides with Elemental Sulfur, Mediated by Cesium Carbonate	235
27.6.1.6.4	Variation 4:	By Reaction of Alkyl Halides with Elemental Sulfur, Mediated by 1,8-Diazabicyclo[5.4.0]undec-7-ene	236
27.6.1.6.5	Variation 5:	By Elimination Reactions of Phthalimido Derivatives	237

27.7	Product Class 7: Imines K. Abbaspour Tehrani and N. De Kimpe	
27.7	Product Class 7: Imines	245
27.7.1	Product Subclass 1: N-Unsubstituted Imines	245
27.7.1.1	Synthesis of Product Subclass 1	246
27.7.1.1.1	Method 1: Reaction of Aldehydes and Ketones with Ammonia	246
27.7.1.1.2	Method 2: From Oximes	248
27.7.1.1.3	Method 3: Oxidation of Primary Amines	249
27.7.1.1.4	Method 4: Dehydrohalogenation of <i>N</i> -Haloamines	249
27.7.1.1.5	Method 5: From Nitriles	250
27.7.1.1.6	Methods 6: Miscellaneous Procedures	251
27.7.2	Product Subclass 2: N-Silylimines	252
27.7.2.1	Synthesis of Product Subclass 2	253
27.7.2.1.1	Method 1: Reaction of Aldehydes with Lithium Disilazanides	253
27.7.2.1.2	Method 2: Dehydrohalogenation of <i>N</i> -Silylated <i>N</i> -Haloamines and Dehydrocyanation of <i>N</i> -Silylated α -Amino Cyanides	254
27.7.2.1.3	Method 3: Reaction of Nitriles with Organometallic Reagents	255
27.7.2.2	Applications of Product Subclass 2 in Organic Synthesis	255
27.7.3	Product Subclass 3: N-Alkyl- and N-Arylimines	256
27.7.3.1	Synthesis of Product Subclass 3	256
27.7.3.1.1	Method 1: Reaction of Aldehydes and Ketones with Primary Amines	256
27.7.3.1.1.1	Variation 1: With Azeotropic Removal of Water	257
27.7.3.1.1.2	Variation 2: With Titanium(IV) Chloride	258
27.7.3.1.1.3	Variation 3: With Solid-Phase Lewis Acids	260
27.7.3.1.1.4	Variation 4: With Other Lewis Acids	261
27.7.3.1.1.5	Variation 5: With <i>N,N</i> -Bis(dichloroaluminio)aniline	262
27.7.3.1.1.6	Variation 6: With <i>N,N</i> -Bis(trimethylsilyl)amines	263
27.7.3.1.2	Method 2: Reaction of Imidates with Organometallic Reagents	264
27.7.3.1.3	Method 3: From Amides	265
27.7.3.1.3.1	Variation 1: By Reduction	265
27.7.3.1.3.2	Variation 2: By Addition of Organometallic Reagents	266
27.7.3.1.3.3	Variation 3: By Hydrolysis of <i>N</i> -Vinyl Lactams	268
27.7.3.1.3.4	Variation 4: Via Nitrilium Ions	269
27.7.3.1.4	Method 4: From Oximes	269
27.7.3.1.5	Method 5: From Imidoyl Chlorides	271
27.7.3.1.5.1	Variation 1: By Reduction	271
27.7.3.1.5.2	Variation 2: By Substitution	272
27.7.3.1.5.3	Variation 3: Via Palladium-Catalyzed Cross Coupling	274
27.7.3.1.6	Method 6: Oxidation of Amines	275
27.7.3.1.6.1	Variation 1: Oxidative Amination of Alkenes	275
27.7.3.1.6.2	Variation 2: Oxidation of Secondary Amines	276
27.7.3.1.7	Method 7: Dehydrohalogenation of <i>N</i> -Haloamines	279

27.7.3.1.8	Method 8:	Reaction of Aldehydes and Ketones with Azides (Aza-Wittig Reaction)	281
27.7.3.1.9	Method 9:	Addition of Primary Amines to Alkynes	283
27.7.3.1.10	Method 10:	Addition of Organometallic Compounds to Nitriles	285
27.7.3.1.11	Method 11:	Addition/Rearrangement of Alkenic Azides	286
27.7.3.1.12	Method 12:	From Other Alkyl Azides	288
27.7.3.1.13	Method 13:	C-Alkylation of 1-Azaallyl Anions with Alkyl Halides	289
27.7.3.1.14	Method 14:	N-Alkylation of N-Unsubstituted Imines	292
27.7.3.1.15	Method 15:	Halogenation of Imines	293
27.7.3.1.16	Method 16:	From Enamines	294
27.7.4	Product Subclass 4: 2H-Azirines		296
27.7.4.1	Synthesis of Product Subclass 4		296
27.7.4.1.1	Method 1:	From Oximes and Hydrazone Salts	296
27.7.4.1.2	Method 2:	Oxidation of Aziridines	297
27.7.4.1.3	Method 3:	Elimination from N-Substituted Aziridines	298
27.7.4.1.4	Method 4:	Rearrangement of Isoxazoles	299
27.7.4.1.5	Method 5:	Pyrolysis or Photolysis of Vinyl Azides	299
27.7.4.1.6	Method 6:	From Other Azirines	300
27.7.5	Product Subclass 5: 2,3-Dihydroazetes		301
27.7.5.1	Synthesis of Product Subclass 5		301
27.7.5.1.1	Method 1:	Photochemical Isomerization of Pyridines	301
27.7.5.1.2	Method 2:	Rearrangement of Azidocyclopropanes	301
27.7.5.1.3	Methods 3:	Miscellaneous Procedures	302
27.8	Product Class 8: Iminium Salts K. Abbaspour Tehrani and N. De Kimpe		
27.8	Product Class 8: Iminium Salts		313
27.8.1	Synthesis of Product Class 8		314
27.8.1.1	Method 1:	Reaction of Secondary Amines with Aldehydes or Ketones ..	314
27.8.1.1.1	Variation 1:	Complex Salts of Secondary Amines	316
27.8.1.1.2	Variation 2:	Silylated Secondary Amines	318
27.8.1.1.3	Variation 3:	O-Alkylation with Lewis Acids	319
27.8.1.1.4	Variation 4:	Reaction of a Sulfinylmethaniminium Salt with Aldehydes and Ketones	320
27.8.1.2	Method 2:	From Hydrazones	321
27.8.1.3	Method 3:	Hydride Abstraction of Tertiary Amines	322
27.8.1.3.1	Variation 1:	With Mercury(II) Acetate	322
27.8.1.3.2	Variation 2:	With Carbenium Ions	323
27.8.1.4	Method 4:	Elimination of Cyanide from α -Aminocarbonitriles	323
27.8.1.5	Method 5:	Cleavage of Aminals	324
27.8.1.5.1	Variation 1:	With Acid Chlorides	324
27.8.1.5.2	Variation 2:	With Hydrogen Halides	325
27.8.1.5.3	Variation 3:	With Iodotrimethylsilane	325

27.8.1.5.4	Variation 4:	With Inorganic Acid Halides or Anhydrides	326
27.8.1.6	Method 6:	Cleavage of Hemiaminals	326
27.8.1.7	Method 7:	Cleavage of Acetals	329
27.8.1.8	Method 8:	Fragmentation of Halomethylammonium Halides	329
27.8.1.9	Method 9:	Decarbonylation of α -Amino Acids	330
27.8.1.10	Method 10:	From Aldimines and Ketimines	330
27.8.1.10.1	Variation 1:	By Alkylation	330
27.8.1.10.2	Variation 2:	By Protonation	333
27.8.1.11	Method 11:	From Enamines	333
27.8.1.11.1	Variation 1:	By Alkylation	333
27.8.1.11.2	Variation 2:	By Protonation at Carbon	334
27.8.1.11.3	Variation 3:	By Halogenation	335
27.8.1.12	Method 12:	From Enaminones	336
27.8.1.13	Method 13:	Electrophile-Induced Cyclization of Alk-4-enamines and Oximes	337
27.8.1.14	Method 14:	Addition of Nitrilium Salts to Pyrroles and Indoles	339
27.8.1.15	Method 15:	Vilsmeier Formylation	339
27.8.1.15.1	Variation 1:	Of Alkenes	339
27.8.1.15.2	Variation 2:	Of Aromatic Compounds	340
27.8.1.15.3	Variation 3:	Of Carbonyl Compounds	341
27.8.1.16	Method 16:	From Other Iminium Salts	342
27.8.1.16.1	Variation 1:	By Cycloaddition	342
27.8.1.16.2	Variation 2:	By Anion Exchange	343
27.8.1.16.3	Variation 3:	Miscellaneous Reactions	344

27.9 Product Class 9: *N*-Acylimines

L. Fišera

27.9	Product Class 9: <i>N</i>-Acylimines	349
27.9.1	Product Subclass 1: Stable <i>N</i>-Acylimines	349
27.9.1.1	Synthesis of Product Subclass 1	349
27.9.1.1.1	Method 1: Reaction of Imidic Acid Esters with Acid Chlorides	349
27.9.1.1.2	Method 2: Reaction of <i>N</i> -Silylimines with Acid Chlorides	350
27.9.1.1.3	Method 3: Thermal Dehydromethoxylation of <i>N,O</i> -Acetals	350
27.9.1.1.4	Method 4: Elimination of Hydrogen Chloride from <i>N</i> -(1-Chloroalkyl)amides	351
27.9.1.1.5	Method 5: From Alkylamides by Condensation with Triethoxymethane	351
27.9.1.1.5.1	Variation 1: By Condensation with Dimethylformamide Dimethyl Acetal	352
27.9.1.1.5.2	Variation 2: By Condensation with (Diethoxymethyl)triethylammonium Tetrafluoroborate	353
27.9.1.1.6	Method 6: From 1-Acyl-1,2-dihydroazetes	353
27.9.1.1.7	Method 7: Fluorenyl-Assisted N–N Bond Cleavage of Pyrazolidinediones	353
27.9.1.2	Applications of Product Subclass 1 in Organic Synthesis	354
27.9.1.2.1	Method 1: Synthesis of 1,1-Bisacylaminoalkanes	354
27.9.1.2.2	Method 2: Synthesis of Substituted Alkylamides	354

27.9.1.2.3	Method 3:	Synthesis of Malonamides and Dihydropyrimidinediones	355
27.9.1.2.4	Method 4:	Synthesis of Enantiopure β -Amidoaldehydes	356
27.9.1.2.5	Method 5:	Synthesis of Trifluoromethylated Dipeptides	357
27.9.1.2.6	Method 6:	<i>N</i> -Acylimines as Dienes in Diels–Alder Cycloaddition Reactions	358
27.9.1.2.6.1	Variation 1:	Synthesis of 6-Alkoxy-5,6-dihydro-1,3-oxazines	358
27.9.1.2.6.2	Variation 2:	Synthesis of Enantiopure 6-Alkoxy-5,6-dihydro-1,3-oxazines	359
27.9.1.2.7	Method 7:	<i>N</i> -Acylimines as Dienophiles in Diels–Alder Cycloaddition Reactions	359
27.9.1.2.8	Method 8:	Taxol A-Ring Side Chain	359
27.9.1.2.9	Method 9:	Functionalization of Penicillins at C6	360
27.9.2	Product Subclass 2: <i>N</i>-Acylimines Generated In Situ		361
27.9.2.1	Synthesis of Product Subclass 2		361
27.9.2.1.1	Method 1:	<i>N</i> -Acyl Hemiaminals as <i>N</i> -Acylimine Equivalents	361
27.9.2.1.2	Method 2:	From Bisurethanes of Aldehydes	361
27.9.2.1.3	Method 3:	Elimination Reactions of <i>N</i> -Acyl α -Substituted Amines	361
27.9.2.1.4	Method 4:	Elimination Reactions of α -Amidoalkyl Phenyl Sulfones	362
27.9.2.1.4.1	Variation 1:	Immobilization of <i>N</i> -Acylimines	362
27.9.2.1.5	Method 5:	Radical-Based Methodology from <i>N</i> - <i>tert</i> -Butyl- <i>N</i> -(methoxyalkyl)benzamides	363
27.9.2.2	Applications of Product Subclass 2 in Organic Synthesis		363
27.9.2.2.1	Method 1:	Allylic Primary Amines from <i>N</i> -Acylimine Equivalents	364
27.9.2.2.1.1	Variation 1:	Propargylic Primary Amines	364
27.9.2.2.2	Method 2:	Synthesis of β -Amino Ketones	365
27.9.2.2.3	Method 3:	Synthesis of α -Amino Acids	366
27.9.2.2.4	Method 4:	Synthesis of β -Amino Acid Esters	367
27.9.2.2.5	Method 5:	Synthesis of Six-Membered Cyclic Carbamates from Immobilized <i>N</i> -Acylimines	367
27.9.2.2.6	Method 6:	Synthesis of 1,2,3,4-Tetrahydronaphthalen-1-amines	368
27.9.2.2.6.1	Variation 1:	Synthesis of (\pm)-Sertraline	369
27.9.2.2.7	Method 7:	Alkylcarbamates from <i>N</i> -Acyl Hemiaminals	369
27.9.2.2.7.1	Variation 1:	Alkylcarbamates from Bisurethanes of Aldehydes	370
27.9.2.2.7.2	Variation 2:	Asymmetric Synthesis of Alkylcarbamates	370
27.9.2.2.8	Method 8:	Synthesis of α -Amido Ketones	371
27.9.2.2.9	Method 9:	Synthesis of Chiral <i>N</i> -Acetylaminines	371
27.10	Product Class 10: <i>N</i>-Acyliminium Salts R. A. Pilli and G. B. Rosso		
27.10	Product Class 10: <i>N</i>-Acyliminium Salts		375
27.10.1	Synthesis of Product Class 10		377
27.10.1.1	From Acyclic Precursors		377
27.10.1.1.1	Method 1:	<i>N</i> -Acylation of Imines	377
27.10.1.1.2	Method 2:	Reaction of Aldehydes with Amides, Imides, or Carbamates	381

27.10.1.1.3	Method 3:	Reduction of <i>N</i> -Acylimidates	383
27.10.1.1.4	Method 4:	α -Oxidation of <i>N</i> -Acyl Compounds	384
27.10.1.1.4.1	Variation 1:	Electrochemical Oxidation	385
27.10.1.1.4.2	Variation 2:	Oxidative Decarboxylation	388
27.10.1.1.5	Method 5:	Glycine Cation Equivalents	389
27.10.1.1.6	Methods 6:	Miscellaneous Methods	391
27.10.1.2		From Cyclic Precursors	392
27.10.1.2.1	Method 1:	<i>N</i> -Acylation of Imines, Pyridines, and Related Compounds	392
27.10.1.2.2	Method 2:	Reactions of Aldehydes and Ketones with Amides	396
27.10.1.2.3	Method 3:	Pummerer Reaction of Amido Sulfoxides	399
27.10.1.2.4	Method 4:	Reduction of <i>N</i> -Acylcarbamates and Partial Reduction of Cyclic Imides	402
27.10.1.2.5	Method 5:	Addition of Organometallic Reagents to <i>N,N</i> -Diacyl Compounds	411
27.10.1.2.6	Method 6:	α -Oxidation of <i>N</i> -Acyl Compounds	414
27.10.1.2.6.1	Variation 1:	Electrochemical Oxidation	414
27.10.1.2.6.2	Variation 2:	Oxidative Decarboxylation	417
27.10.1.2.6.3	Variation 3:	Chemical Oxidation	419
27.10.1.2.6.4	Variation 4:	Enamide Protonation and Oxidation	421
27.10.1.2.7	Methods 7:	Miscellaneous Methods	423
27.10.2		Applications of Product Class 10 in Organic Synthesis	424
27.10.2.1	Method 1:	Total Syntheses of Natural Products	424
27.11		Product Class 11: Azomethine Ylides	
		W. Eberbach	
27.11		Product Class 11: Azomethine Ylides	441
27.11.1		Synthesis of Product Class 11	442
27.11.1.1	Method 1:	Thermal and Photochemical C—C Bond Cleavage of Aziridines	442
27.11.1.2	Method 2:	Ring Cleavage of 2,3-Dihydrooxazoles	442
27.11.1.3	Method 3:	Ring Cleavage of 2,3-Dihydroisoxazoles	443
27.11.1.4	Method 4:	Cycloreversion of Oxazolidines	445
27.11.1.5	Method 5:	Cycloreversion of Dihydro-1,2,4-triazoles	446
27.11.1.6	Method 6:	Cyclization of Diaryl-, Arylvinyl-, and Divinylamines	446
27.11.1.7	Method 7:	Prototropic Rearrangement	446
27.11.1.8	Method 8:	Synthesis by Silyl Migration in <i>N</i> -(Trimethylsilylmethyl)imines and <i>N</i> -(Trimethylsilylmethyl)amides	448
27.11.1.9	Method 9:	Synthesis of <i>N</i> -Metalated Azomethine Ylides	449
27.11.1.10	Method 10:	By Deprotonation of Iminium Salts	450
27.11.1.11	Method 11:	By Desilylation of Iminium Salts	453
27.11.1.12	Method 12:	By Destannylation of Iminium Salts	454
27.11.1.13	Method 13:	By Decarboxylation of Iminium Salts	455
27.11.1.14	Method 14:	Dehydration of Tertiary Amine <i>N</i> -Oxides	456
27.11.1.15	Method 15:	By Reaction of Tetracyanoethene Oxide with Imines	457

27.11.1.16	Method 16:	By Addition of Carbenes and Carbenoids to Imines	458
27.11.1.17	Methods 17:	Miscellaneous Routes	459
27.11.2		Applications of Product Class 11 in Organic Synthesis	459
27.11.2.1	Method 1:	Dimerization To Form Piperazines	459
27.11.2.2	Method 2:	Cyclization of Conjugated Systems	459
27.11.2.2.1	Variation 1:	1,3-Electrocyclization	459
27.11.2.2.2	Variation 2:	1,5-Electrocyclization	460
27.11.2.2.3	Variation 3:	1,7-Electrocyclization	462
27.11.2.3	Method 3:	1,4-Hydrogen Shift and Cyclocondensation To Form Pyrroles and Indolizines	465
27.11.2.4	Method 4:	Cycloaddition to Alkenes and Alkynes	466
27.11.2.4.1	Variation 1:	Cycloaddition of Aziridine-Derived Azomethine Ylides	467
27.11.2.4.2	Variation 2:	Cycloaddition of 2,3-Dihydrooxazole-Derived Azomethine Ylides	471
27.11.2.4.3	Variation 3:	Cycloaddition of Azomethine Ylides from 1,2-Prototropic Rearrangements	473
27.11.2.4.4	Variation 4:	Cycloaddition of N-Metalated Azomethine Ylides	475
27.11.2.4.5	Variation 5:	Cycloaddition of Azomethine Ylides Derived from Iminium Salts by Deprotonation	476
27.11.2.4.6	Variation 6:	Cycloaddition of Azomethine Ylides Derived from Amines and Carbonyl Derivatives	477
27.11.2.4.7	Variation 7:	Cycloaddition of Azomethine Ylides Derived from Iminium Salts by Desilylation	479
27.11.2.4.8	Variation 8:	Cycloaddition of Azomethine Ylides Derived from Decarboxylation of Iminium Salts	481
27.11.2.4.9	Variation 9:	Cycloaddition of Azomethine Ylides Synthesized by Other Routes	486
27.11.2.5	Method 5:	Cycloaddition to Hetero Multiple Bonds	487
27.11.2.6	Method 6:	Cycloaddition with Asymmetric Induction	489
27.12		Product Class 12: N-Haloimines Jie Jack Li	
27.12		Product Class 12: N-Haloimines	499
27.12.1		Synthesis of Product Class 12	499
27.12.1.1		Without C—C Bond Cleavage	499
27.12.1.1.1	Method 1:	From 4-Aminophenol and Sodium Hypochlorites	500
27.12.1.1.2	Method 2:	From <i>N,N'</i> -Bis(benzylidene)arylmethanediamines and <i>tert</i> -Butyl Hypochlorite	501
27.12.1.1.3	Method 3:	From Aldehydes or Ketones and Chloroamine	502
27.12.1.1.4	Method 4:	From Dehydrohalogenation of Alkyldihaloamines	503
27.12.1.1.5	Method 5:	From Imines	504
27.12.1.1.6	Method 6:	From Silyl Imines	505
27.12.1.1.7	Method 7:	From Nitriles and Grignard Reagents	506

27.12.1.2	With C—C Bond Cleavage	506
27.12.1.2.1	Method 1: Oxidative Decarboxylation of Amino Acids	506
27.12.2	Applications of Product Class 12 in Organic Synthesis	507
27.12.2.1	Method 1: Gibbs Reaction	507
27.12.2.2	Method 2: Neber Rearrangement	509
27.13	Product Class 13: Nitrones and Cyclic Analogues P. Merino	
27.13	Product Class 13: Nitrones and Cyclic Analogues	511
27.13.1	Synthesis of Product Class 13	512
27.13.1.1	Method 1: Synthesis by Oxidation	513
27.13.1.1.1	Variation 1: Of Secondary Amines	513
27.13.1.1.2	Variation 2: Of Imines	516
27.13.1.1.3	Variation 3: Of Hydroxylamines	516
27.13.1.2	Method 2: Synthesis by Condensation of <i>N</i> -Alkylhydroxylamines	519
27.13.1.2.1	Variation 1: With Aldehydes	520
27.13.1.2.2	Variation 2: With Ketones	522
27.13.1.3	Method 3: Synthesis by <i>N</i> -Alkylation of Oximes	524
27.13.1.4	Method 4: Synthesis by Ring-Closure Reactions	525
27.13.1.5	Methods 5: Miscellaneous Methods	529
27.13.2	Applications of Product Class 13 in Organic Synthesis	530
27.13.2.1	Method 1: 1,3-Dipolar Cycloadditions	530
27.13.2.1.1	Variation 1: With Heteroatomic Multiple Bonds	531
27.13.2.1.2	Variation 2: With Alkynes	532
27.13.2.1.3	Variation 3: With Cumulenes	535
27.13.2.1.4	Variation 4: With Heterocumulenes	536
27.13.2.1.5	Variation 5: With Alkenes	537
27.13.2.1.6	Variation 6: Intramolecular Cyclizations	542
27.13.2.1.7	Variation 7: Enantioselective Catalysis	545
27.13.2.2	Method 2: Nucleophilic Additions	550
27.13.2.2.1	Variation 1: Of <i>sp</i> -Nucleophiles	550
27.13.2.2.2	Variation 2: Of <i>sp</i> ² -Nucleophiles	552
27.13.2.2.3	Variation 3: Of <i>sp</i> ³ -Nucleophiles	555
27.13.2.2.4	Variation 4: Of Enolates	558
27.13.2.2.5	Variation 5: Allylation	564
27.13.2.2.6	Variation 6: Reduction (Hydride Addition)	564
27.13.2.2.7	Variation 7: Phosphorus Nucleophiles	566
27.13.2.3	Method 3: Metal Complex Formation	567
27.13.2.4	Method 4: Rearrangements	568
27.13.2.5	Method 5: Spin-Trapping	569

27.14	Product Class 14: Nitronic Acids and Their Derivatives Jie Jack Li	
27.14	Product Class 14: Nitronic Acids and Their Derivatives	581
27.14.1	Product Subclass 1: Nitronic Acids	581
27.14.1.1	Synthesis of Product Subclass 1	581
27.14.1.1.1	Method 1: Acidification of Nitronate Salts	581
27.14.1.1.2	Method 2: Michael Addition to Nitroalkenes	582
27.14.1.1.3	Method 3: Reaction of a Nitroalkane and Formaldehyde	583
27.14.1.1.4	Method 4: Reaction of 1-Methyl-5-nitropyrimidin-2(1 <i>H</i>)-one and Primary Amines	584
27.14.1.2	Applications of Product Subclass 1 in Organic Synthesis	584
27.14.1.2.1	Method 1: The Nef Reaction	584
27.14.2	Product Subclass 2: Nitronate Salts	585
27.14.2.1	Synthesis of Product Subclass 2	585
27.14.2.1.1	Method 1: Reaction of Nitroalkanes with Base	585
27.14.2.2	Applications of Product Subclass 2 in Organic Synthesis	585
27.14.2.2.1	Method 1: Nitroaldol Reaction (The Henry Reaction)	585
27.14.2.2.2	Method 2: Michael Addition of a Nitronate	586
27.14.2.2.3	Method 3: Ozonolysis of a Sodium Nitronate Salt To Give a Ketone	587
27.14.3	Product Subclass 3: Nitronic Esters	588
27.14.3.1	Synthesis of Product Subclass 3	588
27.14.3.1.1	Method 1: Alkylation of a Nitronate Salt	588
27.14.3.2	Applications of Product Subclass 3 in Organic Synthesis	589
27.14.3.2.1	Method 1: Tandem [4+2]/[3+2] Cycloadditions	589
27.14.4	Product Subclass 4: Silyl Nitronates	590
27.14.4.1	Synthesis of Product Subclass 4	590
27.14.4.1.1	Method 1: O-Silylation of Bidentate Nitronate Ions	590
27.14.4.1.1.1	Variation 1: With Chlorotrialkylsilane	591
27.14.4.1.1.2	Variation 2: With Trimethylsilyl Trifluoromethanesulfonate	593
27.14.4.1.1.3	Variation 3: With <i>N,O</i> -Bis(trimethylsilyl)acetamide	594
27.14.4.1.2	Method 2: Reaction of 1-Nitroalk-1-enes with Allylsilanes	594
27.14.4.2	Applications of Product Subclass 4 in Organic Synthesis	595
27.14.4.2.1	Method 1: Conversion into Nitro Alcohols via the Henry Reaction	595
27.14.4.2.2	Method 2: Conversion into 2-(Trialkylsiloxy)isoxazolidines	597
27.14.4.2.3	Method 3: Conversion into an Aldehyde or a Ketone	600
27.14.4.2.4	Method 4: Conversion into Oximes	601

27.15	Product Class 15: Oximes M. Yamane and K. Narasaka	
27.15	Product Class 15: Oximes	605
27.15.1	Synthesis of Product Class 15	605
27.15.1.1	Method 1: Condensation of Carbonyl Compounds and Hydroxylamine ..	605
27.15.1.2	Method 2: By Nitrosation	607
27.15.1.2.1	Variation 1: Electrophilic Nitrosation of Active Methylene Compounds ..	607
27.15.1.2.2	Variation 2: Electrophilic Nitrosation of Alkenes	608
27.15.1.2.3	Variation 3: Radical Nitrosation	609
27.15.1.3	Method 3: By Oxidation of Amino Compounds	610
27.15.1.3.1	Variation 1: Oxidation of Hydroxylamines	610
27.15.1.3.2	Variation 2: Oxidation of Primary Amines	611
27.15.1.4	Method 4: By Reduction of Nitro and Nitroso Compounds	611
27.15.1.4.1	Variation 1: Reduction of Nitroalkanes	612
27.15.1.4.2	Variation 2: Reduction of Conjugated Nitroalkenes	613
27.15.1.4.3	Variation 3: Reduction of <i>gem</i> -Chloronitroso Compounds	614
27.15.1.5	Methods 5: Additional Methods	614
27.15.2	Applications of Product Class 15 in Organic Synthesis	615
27.15.2.1	Method 1: Formal Substitution with Cleavage of the O—N Bond	616
27.15.2.1.1	Variation 1: Via Oxidative Addition to Transition Metals	616
27.15.2.1.2	Variation 2: With Nucleophiles	617
27.15.2.1.3	Variation 3: Via Radical Intermediates	620
27.15.2.2	Method 2: Formal Elimination	623
27.15.2.2.1	Variation 1: Generation of 1,3-Dipoles	623
27.15.2.2.2	Variation 2: Conversion into Nitriles	624
27.15.2.2.3	Variation 3: Regeneration of Carbonyl Compounds	626
27.15.2.3	Method 3: Addition Reactions	627
27.15.2.3.1	Variation 1: Reduction to Primary Amines	627
27.15.2.3.2	Variation 2: Reduction to Hydroxylamines	628
27.15.2.3.3	Variation 3: With Radicals	629
27.15.2.3.4	Variation 4: With Carbon Nucleophiles	629
27.15.2.4	Method 4: Rearrangements	631
27.15.2.4.1	Variation 1: Beckmann Rearrangement	631
27.15.2.4.2	Variation 2: Neber Reaction	634
27.15.2.5	Method 5: Reactions with Retention of the Oxime Moiety	635
27.15.2.5.1	Variation 1: <i>E/Z</i> -Isomerization	635
27.15.2.5.2	Variation 2: α -Alkylation	636
27.15.2.6	Methods 6: Additional Reactions	637

27.16	Product Class 16: Azines D. M. Wilson and Y. Zhang	
27.16	Product Class 16: Azines	649
27.16.1	Synthesis of Product Class 16	649
27.16.1.1	Method 1: Monosubstituted Azines from the Reaction of Hydrazones with Formaldehyde	649
27.16.1.2	Method 2: Geminally Disubstituted Azines from the Reaction of Hydrazones with Formaldehyde	650
27.16.1.3	Method 3: 1,4-Disubstituted Azines	651
27.16.1.3.1	Variation 1: From the Reaction of Hydrazine with Aldehydes	651
27.16.1.3.2	Variation 2: From Diazoalkane Dimerization	652
27.16.1.3.3	Variation 3: Imine Hydrazinolysis	654
27.16.1.4	Method 4: Trisubstituted Azines from the Reaction of Hydrazones with Aldehydes	654
27.16.1.5	Method 5: Tetrasubstituted Azines	655
27.16.1.5.1	Variation 1: From Ketone Dimerization with Hydrazine	655
27.16.1.5.2	Variation 2: Reaction of Hydrazones with Ketones	656
27.16.1.5.3	Variation 3: Diazoalkane Dimerization	657
27.16.1.5.4	Variation 4: Azine Iminolysis	658
27.16.2	Applications of Product Class 16 in Organic Synthesis	659
27.16.2.1	Method 1: Oxidation and Reduction	659
27.16.2.2	Method 2: Addition Reactions	660
27.16.2.3	Method 3: Formation of Organometallic Complexes	663
27.16.2.4	Method 4: Intramolecular Cyclization Reactions	664
27.16.2.5	Method 5: Cycloaddition Reactions	665
27.16.2.6	Method 6: Cleavage with Nucleophiles: Hydrolysis and Iminolysis	665
27.17	Product Class 17: Hydrazones S. Kim and J.-Y. Yoon	
27.17	Product Class 17: Hydrazones	671
27.17.1	Product Subclass 1: N-Unsubstituted Hydrazones	672
27.17.1.1	Synthesis of Product Subclass 1	672
27.17.1.1.1	Method 1: Synthesis from Aldehydes and Ketones	672
27.17.1.1.1.1	Variation 1: From <i>N,N</i> -Dimethylhydrazones	674
27.17.1.1.2	Method 2: Synthesis from Diazo Compounds	674
27.17.1.2	Applications of Product Subclass 1 in Organic Synthesis	675
27.17.1.2.1	Method 1: Wolff–Kishner Reduction	675
27.17.1.2.2	Method 2: Synthesis of Nitrogen Heterocycles	676
27.17.1.2.3	Method 3: Synthesis of Diazo Compounds and Alkynes	677

27.17.2	Product Subclass 2: N-Monosubstituted Hydrazones	678
27.17.2.1	Synthesis of Product Subclass 2	678
27.17.2.1.1	Method 1: Synthesis from Aldehydes and Ketones	678
27.17.2.1.1.1	Variation 1: From Masked Aldehydes	679
27.17.2.1.2	Method 2: Synthesis from Activated Enol Ethers and Enamines	680
27.17.2.1.3	Method 3: Synthesis from Active Methylene and Methinyl Compounds ..	681
27.17.2.1.3.1	Variation 1: From Enamines	682
27.17.2.1.3.2	Variation 2: From Ketene Silyl Acetals	683
27.17.2.1.4	Method 4: Synthesis from Ketones, Esters, and Tertiary Amide Enolates	684
27.17.2.2	Applications of Product Subclass 2 in Organic Synthesis	685
27.17.2.2.1	Method 1: Fischer Indole Synthesis of <i>N</i> -Arylhydrazones	686
27.17.2.2.2	Method 2: <i>N</i> -Substituted Dihydropyrazoles via 1,3-Dipolar Cycloadditions	687
27.17.2.2.3	Method 3: <i>N</i> - <i>tert</i> -Butylhydrazones as Acyl Anion Equivalents	689
27.17.2.2.4	Method 4: Ene Reactions of Aldehyde <i>N</i> - <i>tert</i> -Butyl- and <i>N</i> -Phenylhydrazones	690
27.17.3	Product Subclass 3: N,N-Disubstituted Hydrazones	690
27.17.3.1	Synthesis of Product Subclass 3	690
27.17.3.1.1	Method 1: Synthesis from Aldehydes and Ketones	691
27.17.3.1.1.1	Variation 1: From Hindered Ketones and <i>N</i> -Dimethylaluminum- <i>N,N'</i> -dimethylhydrazide	691
27.17.3.1.2	Method 2: Synthesis from Azido Compounds	693
27.17.3.1.2.1	Variation 1: From (Trichloromethyl)arenes	694
27.17.3.1.3	Method 3: Palladium-Catalyzed Arylation of <i>N</i> -Unsubstituted Hydrazones	694
27.17.3.1.4	Method 4: <i>N</i> -Alkylation of <i>N</i> -Arylhydrazones	695
27.17.3.1.5	Method 5: Synthesis via Nucleophilic Additions to Other Hydrazones ..	696
27.17.3.2	Applications of Product Subclass 3 in Organic Synthesis	697
27.17.3.2.1	Method 1: Alkylation of Hydrazone Anions	697
27.17.3.2.2	Method 2: Organometallic Additions to Hydrazones; Primary Amine Synthesis	700
27.17.3.2.3	Method 3: Acylation of Hydrazones	701
27.17.3.2.4	Method 4: Reduction of Hydrazones	702
27.17.3.2.5	Method 5: Conversion of <i>N,N</i> -Dialkylhydrazones into Nitriles	703
27.17.4	Product Subclass 4: N-Sulfonylated Hydrazones	704
27.17.4.1	Synthesis of Product Subclass 4	704
27.17.4.1.1	Method 1: Synthesis from Aldehydes and Ketones	705
27.17.4.1.2	Method 2: Synthesis from <i>N</i> -Unsubstituted Hydrazones	705
27.17.4.2	Applications of Product Subclass 4 in Organic Synthesis	706
27.17.4.2.1	Method 1: Synthesis of Diazoalkanes	706
27.17.4.2.2	Method 2: Synthesis of Alkenes	707
27.17.4.2.2.1	Variation 1: Synthesis of Vinylolithiums	710

27.17.4.2.3	Method 3:	Fragmentation of α,β -Epoxyated Tosylhydrazones	711
27.17.4.2.4	Method 4:	Reduction of Tosylhydrazones	712
27.17.4.2.5	Method 5:	Nucleophilic Additions to Tosylhydrazones	713
27.17.4.2.5.1	Variation 1:	Conversion of Arylsulfonylhydrazones into Nitriles	717
27.18	Product Class 18: Hydrazonium Compounds		
	Y. Zhang and D. M. Wilson		
27.18	Product Class 18: Hydrazonium Compounds 723		
27.18.1	Product Subclass 1: 1,1,1-Trialkyl-2-alkylidenehydrazinium Compounds 723		
27.18.1.1	Synthesis of Product Subclass 1 723		
27.18.1.1.1	Method 1:	Alkylation of Hydrazone Compounds	723
27.18.1.1.2	Method 2:	Reaction of Carbonyl Compounds with Hydrazines	725
27.18.1.2	Applications of Product Subclass 1 in Organic Synthesis 725		
27.18.1.2.1	Method 1:	Synthesis of Azirines	725
27.18.1.2.2	Method 2:	Synthesis of Aziridines	726
27.18.1.2.3	Method 3:	Synthesis of Pyrroles	726
27.18.1.2.4	Method 4:	Synthesis of 1,2,4-Oxadiazoles	727
27.18.1.2.5	Method 5:	Synthesis of Nitriles	727
27.18.2	Product Subclass 2: 1,2,2-Trialkyl-1-alkylidenehydrazinium Compounds 728		
27.18.2.1	Synthesis of Product Subclass 2 728		
27.18.2.1.1	Method 1:	Alkylation of Hydrazone Compounds	728
27.18.2.1.2	Method 2:	Reaction of Carbonyl Compounds and Hydrazines	728
27.18.2.2	Applications of Product Subclass 2 in Organic Synthesis 729		
27.18.2.2.1	Method 1:	Nucleophilic Additions to Hydrazonium Compounds	729
27.19	Product Class 19: Azomethine Imines		
	J. G. Schantl		
27.19	Product Class 19: Azomethine Imines 731		
27.19.1	Product Subclass 1: Acyclic Azomethine Imines 732		
27.19.1.1	Synthesis of Product Subclass 1 732		
27.19.1.1.1	Method 1:	In Situ Generation from Hydrazones Followed by [3+2] Cycloaddition	732
27.19.1.1.1.1	Variation 1:	Reaction of Aryl- and Hetarylhydrazones with Alkenic and Acetylenic Dipolarophiles	732
27.19.1.1.1.2	Variation 2:	Reaction of Tosylhydrazone with a Diazonium Ion	738
27.19.1.1.1.3	Variation 3:	Reaction of Arylhydrazones with In Situ Generated Cyanic Acid and Thiocyanic Acid	738
27.19.1.1.1.4	Variation 4:	Reaction of Benzaldehyde Phenylhydrazone with 1-Methylene-1 <i>H</i> -pyrrolium Ion	740

27.19.1.1.1.5	Variation 5:	Intramolecular [3 + 2] Cycloaddition of 2-(Allyloxy)- and 2-(Prop-2-ynyl)benzaldehyde Hydrazones	740
27.19.1.1.1.6	Variation 6:	Intramolecular [3 + 2] Cycloaddition of Hetarene-carbaldehyde Phenylhydrazones	741
27.19.1.1.1.7	Variation 7:	Intramolecular [3 + 2] Cycloaddition of Hetarene-carbaldehyde Tosylhydrazones	743
27.19.1.1.1.8	Variation 8:	Reaction of Dihydropyrrole-Substituted α -Oxo Esters and Acylhydrazines Followed by Intramolecular [3 + 2] Cycloaddition	746
27.19.1.1.2	Method 2:	In Situ Generation from Enehydrazine Followed by [3 + 2] Cycloaddition	747
27.19.1.1.3	Method 3:	In Situ Generation From 1,2-Disubstituted Hydrazine Derivatives by Condensation with Carbonyl Compounds	748
27.19.1.1.3.1	Variation 1:	Reaction of 1,4-Disubstituted Semicarbazide with a (Hemi)acetal	748
27.19.1.1.3.2	Variation 2:	Reaction of <i>N</i> -Alkylcarbazates with (Het)arene-carbaldehydes Followed by Intermolecular [3 + 2] Cycloaddition	750
27.19.1.1.3.3	Variation 3:	Reaction of 3-Benzylcarbazate with Aldehydes	751
27.19.1.1.3.4	Variation 4:	Reaction of <i>N</i> -Benzylhydrazide with a (Hemi)acetal	753
27.19.1.1.3.5	Variation 5:	Reaction of 2-(Allyloxy)-Substituted Benzaldehyde with 1-Methyl-2-phenylhydrazine	754
27.19.1.1.3.6	Variation 6:	Reaction of a 2-(Allylsulfanyl)-Substituted Hetarene-carbaldehyde with <i>N'</i> -Methyl-2-phenylacetohydrazide	755
27.19.1.1.3.7	Variation 7:	Reaction of a δ,ϵ -Unsaturated Aldehyde with Ethyl 3-Benzylcarbazate	756
27.19.1.1.4	Method 4:	In Situ Generation from 1,2-Disubstituted Hydrazines by Condensation with a Carbene	756
27.19.1.1.4.1	Variation 1:	Reaction of 1,2-Disubstituted Hydrazines and Dichlorocarbene Followed by [3 + 2] Cycloaddition	756
27.19.1.1.5	Method 5:	Reaction of Diazenes with Diazoalkanes	757
27.19.1.1.5.1	Variation 1:	Reaction of Diazocyanides with Diaryldiazomethanes; Azomethine Imine Trimerization	757
27.19.1.1.6	Method 6:	Oxidation of <i>N,N,N'</i> -Trisubstituted Hydrazines Followed by [3 + 2] Cycloaddition	758
27.19.1.1.6.1	Variation 1:	Catalytic Dehydrogenation of Acyclic Trisubstituted Hydrazines	758
27.19.1.1.6.2	Variation 2:	Electrochemical Oxidation of Acyclic Trisubstituted Hydrazines	759
27.19.1.1.7	Method 7:	1,3-Dipole Metathesis of 1,2-Diaryldiazene-1-ium-1-oxides	759
27.19.1.1.8	Method 8:	In Situ Generation by 1,4-Silatropic Shift of α -Silylnitrosamines and α -Silylnitrosamides Followed by [3 + 2] Cycloaddition	761
27.19.2	Product Subclass 2: Azomethine Imines with C—N Incorporated in a Ring		762
27.19.2.1	Synthesis of Product Subclass 2		762
27.19.2.1.1	Method 1:	<i>N</i> -Alkylation of Hydrazones and Hydrazines	762
27.19.2.1.1.1	Variation 1:	Intramolecular Michael Addition of Hydrazone Followed by [3 + 2] Cycloaddition	762

27.19.2.1.1.2	Variation 2:	N-Acylation of 1,2-Substituted Hydrazine Followed by Intermolecular [3 + 2] Cycloaddition	762
27.19.2.1.2	Method 2:	Deprotonation of <i>N</i> -Amino-Substituted Heterocycles	763
27.19.2.1.2.1	Variation 1:	Deprotonation of <i>N</i> -Aminopyridinium and <i>N</i> -Amino-isoquinolinium Salts Followed by [3 + 2] Cycloaddition	764
27.19.2.1.3	Method 3:	Catalytic Dehydrogenation of <i>N</i> -Phenyl-3,4-dihydro-isoquinolin-2(1 <i>H</i>)-amine Followed by [3 + 2] Cycloaddition	770
27.19.2.1.4	Method 4:	Alkylation of Diazene by Intramolecular Attack on a Carbenoid	770
27.19.2.1.5	Method 5:	Nonclassical “Criss-Cross” Reaction: [3 + 2] Cycloaddition of Dialkyl and Diphenyl Azodicarboxylates and Diphenylketenes; [3 + 2] Cycloaddition of Resulting Azomethine Imine	771
27.19.2.1.6	Method 6:	Nonclassical “Criss-Cross” Reaction: [3 + 2] Cycloaddition of Azoalkenes with Thiocyanic Acid; [1,4]- <i>H</i> Shift of Resulting Azomethine Imine or [3 + 2] Cycloaddition with Thiocyanic Acid	773
27.19.2.1.7	Method 7:	Base-Induced Partial Reversion of a Nonclassical “Criss-Cross” Product to Generate an Enehydrazine Followed by Reaction with Dipolarophiles	776
27.19.2.1.8	Method 8:	Ring Transformation	778
27.19.2.1.8.1	Variation 1:	Reaction of 1,3,4-Oxadiazol-2(3 <i>H</i>)-one with 2 <i>H</i> -Azirene	778
27.19.2.1.8.2	Variation 2:	Exchange of One Ring Heteroatom in OIium Rings (Five-Membered Heterocycles with Positive Charge) with the Nitrogen Atom of Monosubstituted Hydrazines	778
27.19.2.1.9	Method 9:	1,5-Electrocyclization of 1,2-Diaza-1,3,5-heterotrienes	779
27.19.2.1.9.1	Variation 1:	Oxidation of 1,2-Bis(hydrazones): Formation of 1,2,3-Triazol-1-ium-1-imides	780
27.19.2.1.9.2	Variation 2:	Cyclization of 3-Hydrazonoprop-2-enylthiocyanates: Formation of Isothiazol-2-ium-2-imides	780
27.19.3	Product Subclass 3: Azomethine Imines with N–N Incorporated in a Ring		783
27.19.3.1	Synthesis of Product Subclass 3		783
27.19.3.1.1	Method 1:	Intramolecular <i>N</i> -Alkylation of Hydrazone by Dehydrohalogenation of (Haloacyl)hydrazones	783
27.19.3.1.1.1	Variation 1:	Dehydrohalogenation of (β -Haloacyl)hydrazones To Form 3-Oxo-1-methylenepyrazolidin-1-ium-2-ides and Photoreversible Transformation	787
27.19.3.1.2	Method 2:	Condensation of 1,2-Disubstituted Hydrazine Derivatives with Carbonyl Compounds	788
27.19.3.1.2.1	Variation 1:	Condensation of the Hydrazine Moiety of 1,2-Diazetidinium Tosylates with Carbonyl Compounds	788
27.19.3.1.2.2	Variation 2:	Condensation of the Hydrazide Moiety of Pyrazolidin-3-ones with Carbonyl Compounds	790
27.19.3.1.2.3	Variation 3:	Reaction of the Hydrazide Moiety in Pyrazolidin-3-ones with Alkynes	799
27.19.3.1.2.4	Variation 4:	Condensation of the Hydrazide Moiety of Six-Membered Rings with Carbonyl Compounds	801

27.19.3.1.3	Method 3:	Chlorination of 1,2,4-Triazolidine-3,5-dione Followed by Base-Induced Dehydrohalogenation of the <i>N</i> -Chlorohydrazide Moiety	804
27.19.3.1.4	Method 4:	Reaction of a Diazene with a Carbene	805
27.19.3.1.4.1	Variation 1:	Reaction of 2,5-Dihydro-1,3,4-oxadiazole with Carbenes Followed by Cycloelimination	805
27.19.3.1.4.2	Variation 2:	Reaction of Halocarbenes with Cyclic Diazenes Followed by Intramolecular [3 + 2] Cycloaddition	806
27.19.3.1.4.3	Variation 3:	Reaction of a 3 <i>H</i> -1,2,4-Triazole-3,5(4 <i>H</i>)-dione with Benzo[<i>c</i>]furan	807
27.19.3.1.5	Method 5:	Reaction of a Diazene with a Diazoalkane	807
27.19.3.1.5.1	Variation 1:	Reaction of 3 <i>H</i> -1,2,4-Triazole-3,5(4 <i>H</i>)-diones with Diaryl Diazoalkanes	807
27.19.3.1.6	Method 6:	Classical “Criss-Cross” Reaction (Tandem [3 + 2] Cycloaddition): Reaction of Azines with Two Molecules of Dipolarophile	811
27.19.3.1.6.1	Variation 1:	Reaction of Aldazine or Ketazine with Cyanic or Thiocyanic Acid To Give Tetrahydro-1 <i>H</i> ,5 <i>H</i> -1,2,4-triazolo[1,2- <i>a</i>][1,2,4]triazole-1,5-diones or the Corresponding 1,5-Dithiones	811
27.19.3.1.6.2	Variation 2:	Reaction of Hexafluoroacetone Azine with Alkenes or Alkynes To Give an Azomethine Imine (1:1 Cycloadduct) and/or “Criss-Cross” (Heterobicyclic) Product (1:2 Cycloadduct)	812
27.19.3.1.6.3	Variation 3:	1,5-Electrocyclization of Allenylazine (Intramolecular “Criss-Cross” Cycloaddition)	813
27.19.3.1.7	Method 7:	Ring Transformation	814
27.19.3.1.7.1	Variation 1:	Cycloreversion (Electrocyclic Ring Opening) of 2,3-Dihydro-1 <i>H</i> ,5 <i>H</i> -pyrazolo[1,2- <i>a</i>]pyrazole, [3 + 2] Cycloaddition, and [3 + 2] Cycloelimination (1,3-Dipole Metathesis)	814
27.19.3.1.7.2	Variation 2:	Thermally Induced [3 + 2] Cycloelimination of Phenyl Isocyanate from 1-Methylene-3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-ium-2-ide Followed by [3 + 2] Cycloaddition To Give 1-Methylene-5-oxo-1 <i>H</i> -pyrazol-1-ium-2-ides	815
27.19.3.1.7.3	Variation 3:	Azomethine Imines Generated from the Diaziridine Ring in 1,5-Diazabicyclo[3.1.0]hexanes; Reaction with Diphenylpropenone	817
27.19.3.1.8	Method 8:	Transformation of Oxo Azomethine Imines into Thioxo Azomethine Imines	819
27.19.4	Product Subclass 4: Azomethine Imines with All Three Atoms Embedded in a Ring		819
27.19.4.1	Synthesis of Product Subclass 4		819
27.19.4.1.1	Method 1:	<i>N</i> -Alkylation of Fused 1,2,4-Triazinones	819
27.19.4.1.2	Method 2:	Ring Transformation	820
27.19.4.1.2.1	Variation 1:	Thermally or Acid-Induced Ring Enlargement of an Azomethine Imine with an Exocyclic Terminal Nitrogen into the Isomer with All Three Atoms in the Ring	820

27.20	Product Class 20: <i>N</i>-Nitroimines and <i>N</i>-Nitrosoimines Jie Jack Li	
27.20	Product Class 20: <i>N</i>-Nitroimines and <i>N</i>-Nitrosoimines	825
27.20.1	Product Subclass 1: <i>N</i>-Nitroimines	825
27.20.1.1	Synthesis of Product Subclass 1	826
27.20.1.1.1	Method 1: Nitrosation of Oximes	826
27.20.1.1.1.1	Variation 1: Sodium Nitrite and Protic Acids	826
27.20.1.1.1.2	Variation 2: Nitrosyl Halides	828
27.20.1.1.1.3	Variation 3: Fuming Nitric Acid	828
27.20.1.1.2	Method 2: Nitrosation of Alkenes Using Nitrosyl Fluoride	829
27.20.1.1.3	Method 3: From Imines Using Acetic Anhydride, Ammonium Chloride, and Nitric Acid	831
27.20.1.1.4	Method 4: Reaction of Nitroamines with Aldehydes	831
27.20.1.2	Applications of Product Subclass 1 in Organic Synthesis	832
27.20.1.2.1	Method 1: Halogenation	832
27.20.1.2.2	Method 2: Knoevenagel Condensation	832
27.20.1.2.3	Method 3: Reduction To Form <i>N</i> -Nitroamines	833
27.20.1.2.4	Method 4: Thermal Rearrangement to Alkynes or Allenes	834
27.20.1.2.5	Method 5: Exchange with Nucleophiles	834
27.20.1.2.5.1	Variation 1: Aminolysis with Ammonia; Imine Synthesis	835
27.20.1.2.5.2	Variation 2: Exchange with Hydrazine; Hydrazone Synthesis	835
27.20.1.2.5.3	Variation 3: Imine Formation from <i>N</i> -Nitroimines and Primary Amines ...	835
27.20.1.2.5.4	Variation 4: Enamine Formation from <i>N</i> -Nitroimines and Secondary Amines	836
27.20.1.2.6	Method 6: Cycloaddition To Form Pyrrolidine	836
27.20.2	Product Subclass 2: <i>N</i>-Nitrosoimines	837
27.20.2.1	Synthesis of Product Subclass 2	838
27.20.2.1.1	Method 1: Nitrosation of Ketimines	838
27.20.2.1.1.1	Variation 1: With Nitrosyl Chloride	838
27.20.2.1.1.2	Variation 2: With Dinitrogen Tetroxide	838
27.20.2.1.1.3	Variation 3: With Sodium Nitrite and Protic Acids	839
27.20.2.1.2	Method 2: Nitrosation of Organometallic Ketimines with Nitrosyl Chloride	840
27.20.2.2	Applications of Product Subclass 2 in Organic Synthesis	840
27.20.2.2.1	Method 1: Reduction To Form Diazo Compounds	840

27.21	Product Class 21: Diazo Compounds H. Heydt	
27.21	Product Class 21: Diazo Compounds	843
27.21.1	Synthesis of Product Class 21	844
27.21.1.1	Method 1: Diazo Compounds by Diazo Transfer (Regitz Diazo Transfer) ·	844
27.21.1.1.1	Variation 1: To Activated Methylene Compounds	844
27.21.1.1.2	Variation 2: To Activated Methine Compounds	850
27.21.1.2	Method 2: Diazo Compounds by Diazotization Reactions	853
27.21.1.2.1	Variation 1: Of Heteroaromatic Compounds	853
27.21.1.2.2	Variation 2: Of 1,3-Dicarbonyl Compounds	853
27.21.1.2.3	Variation 3: Of Primary Amines	854
27.21.1.2.4	Variation 4: Of <i>N</i> -Alkyltriphenylphosphine Imides	857
27.21.1.3	Method 3: Diazo Compounds by Oxidation of Oximes (Forster Reaction)	857
27.21.1.4	Method 4: Diazo Compounds by Oxidation of Hydrazones	858
27.21.1.5	Method 5: Diazo Compounds by Elimination of Hydroxy Anions from Diazenolates (Diazotates)	862
27.21.1.5.1	Variation 1: Generation of Diazenolates from <i>N</i> -[[Alkyl(nitroso)amino]- methyl]carboxamides and the Corresponding Carbamates ··	862
27.21.1.5.2	Variation 2: Generation of Diazenolates from <i>N</i> -Alkyl- <i>N</i> -nitrosocarboxamides	863
27.21.1.5.3	Variation 3: Generation of Diazenolates from <i>N</i> -Alkyl- <i>N</i> -nitrosocarbamates	865
27.21.1.5.4	Variation 4: Generation of Diazenolates from 1-Alkyl-1-nitrosoureas ····	867
27.21.1.5.5	Variation 5: Generation of Diazenolates from 1-Alkyl-3-nitro-1-nitrosoguanidine	869
27.21.1.5.6	Variation 6: Generation of Diazenolates from <i>N</i> -Alkyl- <i>N</i> -nitroso-4-toluenesulfonamides	870
27.21.1.5.7	Variation 7: Generation of Diazenolates from β-[Alkyl(nitroso)amino] Ketones or Sulfones	871
27.21.1.6	Method 6: Diazo Compounds by Elimination Reactions of Sulfinates from <i>N</i> -Sulfonylhydrazones (Bamford–Stevens Reaction) ····	872
27.21.1.7	Method 7: Diazo Compounds by Elimination of Tosylamides from 1-Tosylpentaz-2-enes	884
27.21.1.8	Method 8: Diazo Compounds by Elimination of Hexaethylphosphorimidic Triamide from 1-[Tris(diethylamino)phosphoranylidene]- pentaz-2-enes	884
27.21.1.9	Method 9: Diazo Compounds by Rearrangement Reactions	885
27.21.1.9.1	Variation 1: Of 3 <i>H</i> -Diazirines	885
27.21.1.9.2	Variation 2: Of 4,5-Dihydro-3 <i>H</i> -pyrazoles	886
27.21.1.9.3	Variation 3: Of 3 <i>H</i> -Pyrazoles	887
27.21.1.9.4	Variation 4: Of 2,5-Dihydro-1,3,4-oxadiazoles	888
27.21.1.9.5	Variation 5: Of 4,5-Dihydro-1 <i>H</i> -1,2,3-triazoles	888
27.21.1.9.6	Variation 6: Of 4,4,4-Triphenyl-4,5-dihydro-3 <i>H</i> -1,2,3,4-triazaphospholes ·	890
27.21.1.9.7	Variation 7: Of 1,2,3-Triazoles	890

27.21.1.10	Method 10:	Diazo Compounds by Substitution Reactions at the Diazo Carbon Atom	892
27.21.1.10.1	Variation 1:	By Metalation and Transmetalation	893
27.21.1.10.2	Variation 2:	By Halogenation Reactions	896
27.21.1.10.3	Variation 3:	By Nitration Reactions	896
27.21.1.10.4	Variation 4:	By Alkylation Reactions	897
27.21.1.10.5	Variation 5:	By Arylation Reactions	906
27.21.1.10.6	Variation 6:	By Acylation Reactions	906
27.21.1.11	Method 11:	Diazo Compounds by Cleavage Reactions	913
27.21.1.12	Method 12:	Diazo Compounds by Additional Methods	915
27.21.2		Applications of Product Class 21 in Organic Synthesis	916
27.21.2.1	Method 1:	Carbenes and Carbenoids from Diazo Compounds	916
27.21.2.1.1	Variation 1:	Dimerization, Oligomerization, and Polymerization Reactions of Carbenes Including Alkenation Reactions	917
27.21.2.1.2	Variation 2:	The Wolff Rearrangement and Related Rearrangement Reactions	918
27.21.2.1.3	Variation 3:	Insertion Reactions into Various X–H Bonds	918
27.21.2.1.4	Variation 4:	Formation of Ylides (e.g., Carbonyl Ylides)	920
27.21.2.1.5	Variation 5:	Cyclopropanation and Related Reactions	920
27.21.2.2	Method 2:	Carbenium Ions from Diazo Compounds	921
27.21.2.3	Method 3:	Cycloaddition Reactions of Diazo Compounds	921
27.22		Product Class 22: Alkylidenephosphines E. Niecke, A. Ruban, and M. Raab	
27.22		Product Class 22: Alkylidenephosphines	937
27.22.1		Product Subclass 1: Alkylidenephosphines with a P–H or P–Si Bond	938
27.22.1.1		Synthesis of Product Subclass 1	938
27.22.1.1.1	Method 1:	Condensation Reactions of Tris(trimethylsilyl)phosphine or Its Lithium Salt with Acyl Chlorides	938
27.22.1.1.2	Method 2:	Condensation Reaction of Tris(trimethylsilyl)phosphine with Bis(dialkylamino)difluoromethanes	939
27.22.1.1.3	Method 3:	Condensation Reaction of Lithium Bis(trimethylsilyl)-phosphide and a (Methylsulfanyl)carbenium Iodide	940
27.22.1.1.4	Method 4:	Silyl–Hydrogen Exchange Reactions from <i>P</i> -(Trimethylsilyl)-Substituted Alkylidenephosphines with Alcohols or Silanols	940
27.22.2		Product Subclass 2: P-Halo-Substituted Alkylidenephosphines	941
27.22.2.1		Synthesis of Product Subclass 2	941
27.22.2.1.1	Method 1:	Condensation Reaction of Phosphorus Trichloride and Tris(trimethylsilyl)methylithium	941
27.22.2.1.2	Method 2:	Dehydrohalogenation of Bis(trimethylsilyl)methyl-, Diarylmethyl-, or [Aryl(trimethylsilyl)methyl]dihalo-phosphines with Base	942
27.22.2.2		Applications of Product Subclass 2 in Organic Synthesis	943

27.22.3	Product Subclass 3: Alkylidenephosphines with a P–O, P–S, P–N, or P–P Bond	944
27.22.3.1	Synthesis of Product Subclass 3	944
27.22.3.1.1	Method 1: Substitution Reactions of <i>P</i> -Halo-Substituted Alkylidene-phosphines with Alcohols, Sulfanyls, and Secondary Amines and Phosphines in the Presence of Base	944
27.22.3.1.2	Method 2: Substitution Reactions of <i>P</i> -Halo-Substituted Alkylidene-phosphines with Alkoxides, Thiolates, Amides, and Phosphides of Group 1	944
27.22.3.1.3	Method 3: Elimination Reactions of <i>P</i> -Heterosubstituted Organophosphines Containing Active α -Protons	945
27.22.4	Product Subclass 4: Alkylidenephosphines with a P–C Bond	945
27.22.4.1	Synthesis of Product Subclass 4	946
27.22.4.1.1	Method 1: 1,2-Elimination of Hydrogen Halides or Halosilanes from Dihalophosphines	946
27.22.4.1.2	Method 2: Condensation Reactions of Organo(trimethylsilyl)phosphines or Primary Arylphosphines with Dichloromethane, Nitriles, Aldehydes, Ketones, Their Nitrogen Analogues, or Difluoromethanediamines	947
27.22.4.1.3	Method 3: 1,2-Addition Reactions of Bis(trimethylsilyl)phosphines with Acid Chlorides, Imidoyl Chlorides, or Various Heterocumulenes, Followed by 1,3-Silotropic Isomerization	949
27.22.4.1.4	Method 4: 1,2-Addition of Grignard Reagents or Organolithium Compounds to Alkylidene-phosphines	950
27.22.4.1.5	Method 5: Substitution Reactions of <i>P</i> -Halo- or <i>P</i> -Aminoalkylidene-phosphines with Organolithium or Grignard Reagents	952
27.22.4.1.6	Method 6: By Substitution Reactions of (Dichloromethylene)-(2,4,6-tri- <i>tert</i> -butylphenyl)phosphine	953
27.22.4.1.7	Method 7: By Photochemical, Thermal, or Anionic Ring Opening of Diphosphiranes	955
27.22.4.2	Applications of Product Subclass 4 in Organic Chemistry	956
27.22.5	Product Subclass 5: Phosphaallene Derivatives	956
27.22.5.1	Synthesis of Product Subclass 5	956
27.22.5.1.1	Method 1: Condensation Reactions of Phosphaketenes, Aryl(dichloro)phosphines, or Aryl(diethynyl)phosphines	957
27.22.5.1.1.1	Variation 1: From Aryl(trimethylsilyl)phosphides and Ketenes	957
27.22.5.1.1.2	Variation 2: From Aryl(dichloro)phosphines with Monolithiated Allenes	957
27.22.5.1.1.3	Variation 3: From Aryl(diethynyl)phosphines and Organolithium Reagents	958
27.22.5.1.2	Method 2: Wittig Reaction of Phosphaketenes with Phosphoranyl Ylides	959
27.22.5.1.3	Method 3: By Metal-Catalyzed Prototropic Isomerization	959
27.22.6	Product Subclass 6: Diphosphirenes and Diphosphetes	961
27.22.6.1	Synthesis of Product Subclass 6	961

27.22.6.1.1	Method 1:	Addition Reactions of Iminophosphines, Phosphinocarbenes, or Phosphinediyls to Alkylidynephosphines	961
27.22.6.1.2	Method 2:	Condensation Reactions of Alkylidenephosphines with Boron Trifluoride in the Presence of Base	962
27.22.6.1.3	Method 3:	Condensation Reactions of Alkylidynephosphines with Perfluorinated Alkylidenephosphines	962
27.22.6.1.4	Method 4:	Hydrostannylation of Alkylidynephosphines To Give Stannyl-1,2-dihydro-1,3-diphosphetes	963
27.23	Product Class 23: Alkylidenephosphonium Salts		
	E. Niecke, A. Ruban, and M. Raab		
27.23	Product Class 23: Alkylidenephosphonium Salts		969
27.23.1	Synthesis of Product Class 23		969
27.23.1.1	Method 1:	1,2-Addition of an Electrophile to a Nucleophilic Phosphinocarbene	969
27.23.1.2	Method 2:	Halide Abstraction from Halo(alkylidene)phosphoranes with Lewis Acids	970
27.23.2	Applications of Product Class 23 in Organic Synthesis		970
27.24	Product Class 24: Alkylidenephosphoranes		
	R. Schobert and G. J. Gordon		
27.24	Product Class 24: Alkylidenephosphoranes		973
27.24.1	Product Subclass 1: C-Heteroatom-Substituted Alkylidenephosphoranes		974
27.24.1.1	Synthesis of Product Subclass 1		975
27.24.1.1.1	Method 1:	From Other Alkylidenephosphoranes	975
27.24.1.1.1.1	Variation 1:	By Metalation	975
27.24.1.1.1.2	Variation 2:	By Halogenation	977
27.24.1.1.1.3	Variation 3:	By Sulfonation and Selenation	978
27.24.1.1.1.4	Variation 4:	By Silylation	979
27.24.1.1.2	Method 2:	From Phosphonium Salts	981
27.24.1.1.2.1	Variation 1:	By Dehydrohalogenation	981
27.24.1.1.2.2	Variation 2:	By Dehalogenation	982
27.24.1.1.3	Method 3:	From Phosphines	983
27.24.1.2	Applications of Product Subclass 1 in Organic Synthesis		984
27.24.1.2.1	Method 1:	Synthesis of Enol Ethers from and Homologation of Aldehydes and Ketones with α -Alkoxyated Phosphoranes	984
27.24.1.2.2	Method 2:	Corey–Fuchs Synthesis of Alkynes	986
27.24.2	Product Subclass 2: C-Carbon-Substituted Alkylidenephosphoranes		987
27.24.2.1	Synthesis of Product Subclass 2		987
27.24.2.1.1	Method 1:	From Other Alkylidenephosphoranes	988

27.24.2.1.1.1	Variation 1:	By Replacement of Ylidic α -Hydrogen Atoms by Alkylation	988
27.24.2.1.1.2	Variation 2:	By Replacement of Ylidic α -Hydrogen Atoms through Arylation or Acylation	989
27.24.2.1.1.3	Variation 3:	By Reactions with Electron-Poor Alkenes and Alkynes	991
27.24.2.1.1.4	Variation 4:	By Replacement of a Hetero Substituent on the Ylidic Carbon Atom with a Carbon Residue	992
27.24.2.1.1.5	Variation 5:	By Addition Across the $C^{\alpha}=C^{\beta}$ Bond of Cumulated Ylides	994
27.24.2.1.2	Method 2:	From Quaternary Phosphonium Salts	995
27.24.2.1.2.1	Variation 1:	By Dehydrohalogenation	997
27.24.2.1.2.2	Variation 2:	By Pyrolytic Elimination	1000
27.24.2.1.2.3	Variation 3:	By Addition of Nucleophiles	1001
27.24.2.1.2.4	Variation 4:	By Electrochemical Reduction	1002
27.24.2.1.3	Method 3:	From Tertiary Phosphines	1003
27.24.2.1.3.1	Variation 1:	By Addition to Carbenes	1003
27.24.2.1.3.2	Variation 2:	By Addition to Activated Multiple Bonds	1003
27.24.2.2		Applications of Product Subclass 2 in Organic Synthesis	1005
27.24.2.2.1	Method 1:	Synthesis of Carbonyl Compounds	1005
27.24.2.2.1.1	Variation 1:	Hydrolysis of Acyl Ylides	1005
27.24.2.2.1.2	Variation 2:	Oxidation of Ylides	1006
27.24.2.2.1.3	Variation 3:	Reactions of Ylides with Nitriles	1007
27.24.2.2.2	Method 2:	Synthesis of Alkynes	1009
27.24.2.2.2.1	Variation 1:	Wittig–Trippett Pyrolysis of Acyl Ylides	1009
27.24.2.2.2.2	Variation 2:	Flash-Vacuum Pyrolysis of Acyl Ylides	1010
27.24.2.2.3	Method 3:	Synthesis of Alkenes by Reactions Other Than Wittig Procedures	1011
27.24.2.2.3.1	Variation 1:	Reaction of Ylides with Carbenes and Carbene Complexes	1011
27.24.2.2.3.2	Variation 2:	Allenes from the Reactions of Stabilized Ylides with Acyl Halides	1014
27.24.2.2.3.3	Variation 3:	Cycloalkenones from Hydrolysis of Bis[(triphenylphosphoranylidene)acyl] Compounds	1016
27.24.2.2.4	Method 4:	Alkenes by Wittig Alkenation of Carbonyl Compounds	1018
27.24.2.2.4.1	Variation 1:	Wittig Alkenation with Lithium Salt Free Ylides	1019
27.24.2.2.4.2	Variation 2:	Wittig Alkenation with Instant Ylides	1021
27.24.2.2.4.3	Variation 3:	In Situ Generation of Ylides with Oxiranes	1022
27.24.2.2.4.4	Variation 4:	Directed Stereoselective Alkenation Procedures	1023
27.24.2.2.4.5	Variation 5:	Cycloalkenes by Intramolecular Wittig Alkenation	1027
27.24.2.2.4.6	Variation 6:	Wittig Alkenation with Polymer-Bound Ylides	1033
27.24.2.2.4.7	Variation 7:	Wittig Alkenation under Phase-Transfer Conditions	1036
27.24.2.2.5	Method 5:	Synthesis of Cycloalkanes	1037
27.24.2.2.5.1	Variation 1:	Intramolecular S_N Reactions of ω -Halogenated Ylides	1037
27.24.2.2.5.2	Variation 2:	Cyclopropanes from Ylides and Epoxides	1039
27.24.2.2.5.3	Variation 3:	Cyclopropanes from Reactive Ylides and α,β -Unsaturated Carbonyl Compounds	1040
27.24.2.2.5.4	Variation 4:	Cyclopropanes from Ester Ylides and <i>cis</i> - γ -Hydroxyenones or 1,2-Dioxins	1040

27.24.3	Product Subclass 3: Phosphacumulene Ylides	1042
27.24.3.1	Synthesis of Product Subclass 3	1043
27.24.3.1.1	Method 1: From Phosphonium Methylides	1043
27.24.3.1.1.1	Variation 1: (Triphenylphosphoranylidene)thio ketene and -ketenimines, and Allenylidene Ylides by Addition to 1,1-Dichloro(hetero)- alkenes	1043
27.24.3.1.1.2	Variation 2: (Phosphoranylidene)ketenimines by Addition to Isothiocyanates	1045
27.24.3.1.2	Method 2: From Phosphonium Alkoxy carbonyl- and Alkyldithiocarbonylmethylides	1046
27.24.3.1.2.1	Variation 1: (Triphenylphosphoranylidene)ketene and (Triphenyl- phosphoranylidene)thio ketene by Elimination with Sodium Hexamethyldisilazanide	1046
27.24.3.1.2.2	Variation 2: (Triphenylphosphoranylidene)ketene Acetals by O-Alkylation/Deprotonation	1047
27.24.3.1.3	Method 3: Pyrolysis of Disilylated Ester Ylides	1049
27.24.3.2	Applications of Product Subclass 3 in Organic Synthesis	1050
27.24.3.2.1	Method 1: Syntheses with Acyl Ylides Obtained from Addition of Acidic Compounds to Cumulated Ylides	1050
27.24.3.2.1.1	Variation 1: α,β -Unsaturated Esters (or Amides) by a Three-Component Reaction of Alcohols (or Amines), Aldehydes, and (Triphenylphosphoranylidene)ketene	1050
27.24.3.2.1.2	Variation 2: Macrolides from ω -Hydroxy Aldehydes	1051
27.24.3.2.1.3	Variation 3: Five- and Six-Membered Carbo- and Heterocycles from Cumulated Ylides and Carbonyl Compounds Bearing Acidic Functional Groups	1052
27.24.3.2.1.4	Variation 4: Five- to Seven-Membered Heterocycles from Triphenyl- (phosphoranylidene)ketene and Hydroxy/Amino Esters	1053
27.24.3.2.1.5	Variation 5: Oxazol-2(3H)-ones and 1,3,4-Oxadiazoles from (Triphenyl- phosphoranylidene)ketene and Amides/Hydrazides	1054
27.24.3.2.2	Method 2: Syntheses of <i>E</i> - α,β -Unsaturated Ketones by Tandem Grignard/Wittig Alkenation Reactions of (Triphenyl- phosphoranylidene)ketene	1056
27.24.3.2.3	Method 3: Synthesis of Carbocycles and Heterocycles by Cycloaddition Reactions	1057
	Keyword Index	1071
	Author Index	1105
	Abbreviations	1169

