

Table of Contents

Introduction

R. L. Danheiser

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

23.1 Product Class 1: Ketene

T. T. Tidwell

23.1	Product Class 1: Ketene	15
	T. T. Tidwell	
23.1.1	Synthesis of Product Class 1	18
23.1.1.1	Method 1: Ketene from Acetic Acid, Acid Anhydrides, and Esters	19
23.1.1.2	Method 2: Dehydrohalogenation of Acetyl Halides	19
23.1.1.2.1	Variation 1: Ionization of Acetyl Halides to Acylium Ions and Deprotonation	21
23.1.1.3	Method 3: Pyrolysis of Ketene Dimer	22
23.1.1.4	Method 4: Photolysis of Cyclobutanones and Thermolysis	22
23.1.1.5	Method 5: Dehalogenation of Haloacetyl Halides	23
23.1.1.6	Method 6: Pyrolysis of Acetone	24
23.1.1.7	Method 7: Wolff Rearrangement of Diazoacetaldehyde	24
23.1.1.8	Method 8: Elimination from Alkynyl Ethers	25
23.1.2	Applications of Product Class 1 in Organic Synthesis	26
23.1.2.1	Method 1: Nucleophilic Addition to Ketene	26
23.1.2.1.1	Variation 1: Enol Acetates from the Reaction of Ketene with Aldehydes and Ketones	28
23.1.2.2	Method 2: Electrophilic and Radical Additions to Ketene	29
23.1.2.3	Method 3: Dimerization by [2 + 2] Cycloaddition	32
23.1.2.4	Method 4: [2 + 2] Cycloaddition of Ketene with Alkenes and Dienes	32
23.1.2.5	Method 5: [2 + 2] Cycloaddition of Ketene with Alkynes	34
23.1.2.6	Method 6: [2 + 2] Cycloaddition of Ketene with Imines	35
23.1.2.7	Method 7: [2 + 2] and [4 + 2] Cycloaddition of Ketene with Carbonyl Groups	36
23.1.2.7.1	Variation 1: β -Hydroxy Esters by Titanium Alkoxide Induced Addition of Carbonyl Compounds to Ketene	42
23.1.2.8	Method 8: [2 + 2] Cycloaddition of Ketene with Azobenzenes	42
23.1.2.9	Method 9: [2 + 1] Cycloaddition of Ketene with Sulfur Dioxide	43
23.1.2.10	Method 10: [2 + 1] Cycloaddition of Ketene with Diazomethane	44
23.1.2.11	Method 11: [4 + 2] Cycloaddition of Ketene with Heterodienes	44
23.1.2.12	Method 12: Wittig Reaction of Ketene with a Chiral Phosphorane	45
23.1.2.13	Method 13: Dimetal Ketenides from Ketene and Metal Salts	45
23.1.2.14	Method 14: Decarbonylation of Ketene	46

23.2	Product Class 2: Silylketenes D. M. George and R. L. Danheiser	
23.2	Product Class 2: Silylketenes	53
23.2.1	Product Subclass 1: Silyl-Substituted Aldoketenes	54
23.2.1.1	Synthesis of Product Subclass 1	54
23.2.1.1.1	Method 1: Dehydrohalogenation of Acyl Halides	54
23.2.1.1.2	Method 2: Dehydration of Silylacetic Acids	55
23.2.1.1.3	Method 3: Thermolysis of 1-Alkoxy-2-silylacetylenes	55
23.2.1.1.4	Method 4: 1,3-Silyl Shift of (Trimethylsiloxy)acetylene	57
23.2.1.1.5	Method 5: Thermolysis of Silylacetic Anhydrides	57
23.2.1.2	Applications of Product Subclass 1 in Organic Synthesis	58
23.2.1.2.1	Method 1: [2 + 2] Cycloadditions Leading to β -Lactones	58
23.2.1.2.2	Method 2: [2 + 2] Cycloadditions Leading to β -Lactams	64
23.2.1.2.3	Method 3: [2 + 2] Cycloadditions Leading to Cyclobutanones	65
23.2.1.2.4	Method 4: Formation of Allenes via Wittig Reaction with Phosphorus Ylides	65
23.2.1.2.5	Method 5: Formation of Ketenimines via Reaction with Iminophosphoranes	66
23.2.1.2.6	Method 6: Formation of Cyclopropanones and Cyclobutanones via Reaction with Diazo Compounds	67
23.2.1.2.7	Method 7: Formation of α -Silyl Ketones	68
23.2.1.2.8	Method 8: Formation of 2 <i>H</i> -1-Benzopyran-2-ones from Phenols	70
23.2.1.2.9	Method 9: (Trimethylsilyl)acetylation of Alcohols and Amines	71
23.2.2	Product Subclass 2: (Silyl)(trialkylmetal)ketenes	72
23.2.2.1	Synthesis of Product Subclass 2	72
23.2.2.1.1	Method 1: Elimination from (Silyl)(trialkylmetal)acetates	72
23.2.2.1.2	Method 2: Trapping of Lithium 2-Lithioacetylen-1-olate Generated from 2-Phenyl-2,3-dihydrofurans or 3-Phenylisoxazoles	72
23.2.2.1.3	Method 3: Carbonylation and Trapping of Lithiated Diazo(trimethyl- silyl)methane	73
23.2.2.1.4	Method 4: Lithiation of (Trialkylsilyl)ketenes and Trapping with Chlorosilanes	74
23.2.2.1.5	Method 5: Synthesis of Bis(silyl)ketenes from Other Bis(silyl)ketenes via Potassium 2-Silylacetylen-1-olates	74
23.2.3	Product Subclass 3: (Aryl)- and (Alkyl)silylketenes	76
23.2.3.1	Synthesis of Product Subclass 3	76
23.2.3.1.1	Method 1: 1,3-Silyl Shift of 1-(Siloxy)alk-1-yne	76
23.2.3.1.2	Method 2: Wolff Rearrangement of α -Diazo- α -silyl Ketones	77
23.2.3.1.2.1	Variation 1: By Thermolysis	77
23.2.3.1.2.2	Variation 2: By Photolysis	77
23.2.3.1.2.3	Variation 3: By Metal Catalysis	78
23.2.3.2	Applications of Product Subclass 3 in Organic Synthesis	79
23.2.3.2.1	Method 1: [2 + 2] Cycloadditions Leading to β -Lactones	79

23.2.3.2.2	Method 2: [4 + 1] Annulation Leading to 1,3-Dihydro-2 <i>H</i> -inden-2-ones ...	80
23.2.4	Product Subclass 4: Silyl(vinyl)ketenes	84
23.2.4.1	Synthesis of Product Subclass 4	84
23.2.4.1.1	Method 1: Dehydrohalogenation of α -Silyl- α,β -unsaturated Acid Chlorides	84
23.2.4.1.2	Method 2: Wolff Rearrangement of α -Diazo- α -silyl α',β' -Unsaturated Ketones	85
23.2.4.1.3	Method 3: Electrocyclic Ring Opening of 2-Silylcyclobut-2-enones	86
23.2.4.1.4	Method 4: Reaction of Bis(silyl)acetylenes with Chromium–Carbene Complexes	87
23.2.4.2	Applications of Product Subclass 4 in Organic Synthesis	88
23.2.4.2.1	Method 1: Formation of Cyclohexenones and Phenols by [4 + 2] Cycloadditions	88
23.2.4.2.2	Method 2: Formation of 5,6-Dihydro-2 <i>H</i> -pyran-2-ones and 5,6-Dihydropyridin-2(1 <i>H</i>)-ones by [4 + 2] Cycloadditions	89
23.2.4.2.3	Method 3: Formation of Cyclopent-2-en-1-ones by [4 + 1] Annulation	91
23.2.5	Product Subclass 5: Miscellaneous Silylketenes	96
23.2.5.1	Synthesis of Product Subclass 5	96
23.2.5.1.1	Method 1: Synthesis of Bromo(trialkylsilyl)ketenes by Dehydrohalogenation	96
23.2.5.1.2	Method 2: Synthesis of Alkoxy(triarylsilyl)ketenes from Pentacarbonyl Complexes	96
23.2.5.1.3	Methods 3: Miscellaneous Reactions	96
23.3	Product Class 3: Halogen-Substituted Ketenes T. T. Tidwell	
<hr/>		
23.3	Product Class 3: Halogen-Substituted Ketenes	101
23.3.1	Product Subclass 1: Fluoro- and Difluoroketenes	104
23.3.1.1	Synthesis of Product Subclass 1	105
23.3.1.1.1	Method 1: Fluoroketene by Pyrolysis of Fluoroacetic Anhydride	105
23.3.1.1.2	Method 2: Fluoroketene by Dehydrochlorination of Fluoroacetyl Chloride	105
23.3.1.1.3	Method 3: Difluoroketene from 1,1,2-Trifluoro-2-(trifluoromethoxy)-ethene	107
23.3.1.1.4	Method 4: Difluoroketene by Photolysis of Perfluorocyclobutanone	107
23.3.1.1.5	Method 5: Difluoroketene by Dehalogenation of Bromo(difluoro)acetyl Chloride with Zinc	108
23.3.1.1.6	Method 6: Acyl(fluoro)ketenes by Thermolysis of α -Fluorodioxinones ...	108
23.3.1.1.7	Method 7: Fluoro(pentafluoroethyl)ketene by Fluoride-Induced Dephosphorylation	109
23.3.1.1.8	Method 8: Difluoroketene by Photoisomerization/Oxygenation of Difluoroacetylene	110
23.3.1.1.9	Method 9: Fluoro(1,2,3,4,4-pentafluorobuta-1,3-dienyl)ketene from Perfluorocyclohexa-2,4-dienone	110
23.3.1.2	Applications of Product Subclass 1 in Organic Synthesis	111

23.3.1.2.1	Method 1:	Cyclobutanones by [2 + 2] Cycloaddition of Fluoroketenes with Alkenes	111
23.3.1.2.2	Method 2:	β -Lactams by [2 + 2] Cycloaddition of Fluoroketenes with Imines	113
23.3.2	Product Class 2: Chloro- and Dichloroketenes		113
23.3.2.1	Synthesis of Product Subclass 2		114
23.3.2.1.1	Method 1:	Alkyl(chloro)ketenes by Dehydration of Carboxylic Acids	115
23.3.2.1.2	Method 2:	Chloroketenes by Dehydrochlorination of Chloroalkanoyl Halides	116
23.3.2.1.2.1	Variation 1:	Chloroketene by Pyrolytic Dehydrochlorination of Chloroacetyl Chloride	118
23.3.2.1.2.2	Variation 2:	Substituted Chloroketenes by Dehydrochlorination of 2-Chloroacyl Chlorides	119
23.3.2.1.3	Method 3:	Dichloroketene by Photolysis of a Cyclic Carbonate	119
23.3.2.1.4	Method 4:	Dichloroketene by Dehalogenation of Trichloroacetyl Halides with Zinc	119
23.3.2.1.4.1	Variation 1:	Chloroketenes by Dechlorination of 2-Chloroacyl Chlorides with Diphenyl(trimethylsilyl)phosphine	124
23.3.2.1.5	Method 5:	Chloro(cyano)ketene by Thermolysis of 4-Azido-3-chloro-5-methoxyfuran-2(5H)-one	125
23.3.2.2	Applications of Product Subclass 2 in Organic Synthesis		126
23.3.2.2.1	Method 1:	Cyclobutanones by [2 + 2] Cycloadditions of Chloroketenes with Alkenes and Dienes	126
23.3.2.2.2	Method 2:	Methylenecyclobutanones by [2 + 2] Cycloaddition of Chloroketenes with Allenes	137
23.3.2.2.3	Method 3:	Cyclobutanones by [2 + 2] Cycloaddition of Chloroketenes with Alkynes	138
23.3.2.2.4	Method 4:	β -Lactams by [2 + 2] Cycloaddition of Chloroketenes with Imines	140
23.3.2.2.4.1	Variation 1:	β - and δ -Lactams by [2 + 2]- and [4 + 2]-Cycloaddition Reactions of Chloroketenes with Vinylic Imines	141
23.3.2.2.4.2	Variation 2:	γ -Lactams and γ -Lactones by [3 + 2] Cycloaddition of Dichloroketene with <i>N</i> -Vinylsulfimides	143
23.3.2.2.5	Method 5:	β -Lactones by [2 + 2] Cycloaddition of Chloroketenes with Carbonyl Compounds	146
23.3.2.2.6	Method 6:	γ -Lactones from Dichloroketene with Vinyl Sulfoxides	148
23.3.2.2.6.1	Variation 1:	γ -Lactones from Dichloroketene with Chiral Vinyl Sulfoxides	149
23.3.2.2.7	Method 7:	Thioesters by Ketene-Claisen Reaction of Dichloroketene with Allyl Sulfides	150
23.3.2.2.8	Method 8:	A Macrocyclic Lactone by the Ketene-Claisen Reaction of Dichloroketene with a Vinyltetrahydropyran	151
23.3.2.2.9	Method 9:	γ -Lactones and Lactams by the Reactions of Dichloroketene with Three-Membered Heterocycles	152
23.3.2.2.9.1	Variation 1:	A Lactam by the Reaction of Dichloroketene with a Vinylaziridine	153

23.3.2.2.9.2	Variation 2: Ketene Acetals from Cycloaddition of Chloro(cyano)ketene with 2-Phenyloxirane	154
23.3.3	Product Subclass 3: Bromo- and Iodoketenes	154
23.3.3.1	Synthesis of Product Subclass 3	154
23.3.3.1.1	Method 1: Bromo- and Iodoketenes by Dehydrochlorination of Haloacetyl Chlorides	154
23.3.3.1.1.1	Variation 1: Bromoketene by Dehydrochlorination of Bromoacetyl Chloride with a Strong Stoichiometric Base and a Shuttle Base	156
23.3.3.1.2	Method 2: Bromoketene by Pyrolysis of 2-Bromocyclobutanone	157
23.3.3.1.3	Method 3: Bromoketenes by Dehalogenation of Haloacetyl Halides	157
23.3.3.1.3.1	Variation 1: Dibromoketene by Triphenylphosphine-Induced Elimination from Trimethylsilyl Tribromoacetate	158
23.3.3.1.4	Method 4: An Aryl(bromo)ketene from a 3-Aryloxirane-2,2-dicarbonitrile	158
23.3.3.2	Applications of Product Subclass 3 in Organic Synthesis	159
23.3.3.2.1	Method 1: Cyclobutanones by [2 + 2] Cycloaddition of Bromoketenes with Alkenes or Dienes	159
23.3.3.2.1.1	Variation 1: Cyclohex-2-en-1-ones by [4 + 2] Cycloaddition of Bromo(vinyl)ketenes with Enamines	160
23.3.3.2.2	Method 2: β - and δ -Lactams by Cycloaddition of Bromoketenes with Imines	161
23.3.3.2.3	Method 3: [3 + 2] Cycloaddition of Aryl(bromo)ketenes with Pyridiniumolate Betaines	161
23.3.3.2.4	Method 4: Chiral Aryl(halo)acetates by Stereoselective Addition of Chiral Alcohols to Bromo- and Iodoketenes	162
23.3.3.2.5	Method 5: A Chiral Bromo(chloro)acetate by Stereoselective Chlorination of Bromoketene	163
23.3.3.2.6	Method 6: Mixed Dimerization of Bromo(<i>tert</i> -butyl)ketenes with <i>tert</i> -Butylketene	163
23.4	Product Class 4: Oxygen-Substituted Ketenes C. Palomo, M. Oiarbide, and J. M. Aizpurua	
23.4	Product Class 4: Oxygen-Substituted Ketenes	169
23.4.1	Synthesis of Product Class 4	170
23.4.1.1	Method 1: Elimination Reactions of Carboxylic Acids or Their Derivatives	170
23.4.1.1.1	Variation 1: Dehydration of Carboxylic Acids by Activating Reagents	170
23.4.1.1.2	Variation 2: Dehydrohalogenation of Carboxylic Acid Chlorides with Tertiary Amines in Solution	172
23.4.1.1.3	Variation 3: Dehydrohalogenation of Carboxylic Acid Chlorides with Solid-Supported Bases	174
23.4.1.2	Method 2: Photolysis of Metal–Carbene Complexes	177
23.4.1.3	Method 3: Dirhodium Tetraacetate Catalyzed Decomposition of α -Diazo Anhydrides	179
23.4.1.4	Methods 4: Miscellaneous Methods	181
23.4.2	Applications of Product Class 4 in Organic Synthesis	181

23.4.2.1	Method 1:	[2 + 2]-Cycloaddition Reactions Leading to Cyclobutanones, β -Lactones, and β -Lactams	181
23.4.2.1.1	Variation 1:	With Alkenes, Enol Ethers, or Enecarbamates	181
23.4.2.1.2	Variation 2:	With Aldehydes or Ketones	187
23.4.2.1.3	Variation 3:	With Imines	189
23.4.2.2	Method 2:	Lewis Acid Catalyzed [3,3]-Sigmatropic Bellus–Claisen Rearrangements	194
23.5	Product Class 5: Sulfur- and Selenium-Substituted Ketenes		
	C. Palomo, J. M. Aizpurua, I. Ganboa, and E. Gómez-Bengoa		
23.5	Product Class 5: Sulfur- and Selenium-Substituted Ketenes		
23.5.1	Product Subclass 1: Sulfur-Substituted Ketenes		
23.5.1.1	Synthesis of Product Subclass 1		
23.5.1.1.1	Method 1:	Elimination Reactions of Carboxylic Acids and Their Derivatives	200
23.5.1.1.1.1	Variation 1:	Dehydration of Carboxylic Acids	200
23.5.1.1.1.2	Variation 2:	Dehydrohalogenation of Acyl Halides	201
23.5.1.1.2	Method 2:	Wolff Rearrangement of Diazo Compounds	203
23.5.1.1.2.1	Variation 1:	Photochemical Wolff Rearrangement	203
23.5.1.1.2.2	Variation 2:	Thermal Wolff Rearrangement	204
23.5.1.1.2.3	Variation 3:	Metal-Catalyzed Wolff Rearrangement	205
23.5.1.1.3	Method 3:	Photolysis of Metal–Carbene Complexes	205
23.5.1.1.4	Method 4:	Fragmentation of Cyclobutene-1,2-diones	206
23.5.1.1.5	Methods 5:	Miscellaneous Preparations	207
23.5.1.2	Applications of Product Subclass 1 in Organic Synthesis		
23.5.1.2.1	Method 1:	[2 + 2]-Cycloaddition Reactions	208
23.5.1.2.1.1	Variation 1:	Reaction with Alkenes and Alkynes Leading to Cyclobutanones and Cyclobutenones	208
23.5.1.2.1.2	Variation 2:	Reaction with Imines Leading to β -Lactams	212
23.5.1.2.2	Method 2:	Formation of Allenes by Wittig Alkenation	214
23.5.2	Product Subclass 2: Selenium-Substituted Ketenes		
23.5.2.1	Synthesis of Product Subclass 2		
23.5.2.1.1	Method 1:	Dehydrohalogenation of Acyl Chlorides	215
23.5.2.1.2	Method 2:	Reactions of Silver Ketenide	217
23.5.2.2	Applications of Product Subclass 2 in Organic Synthesis		
23.5.2.2.1	Method 1:	[2 + 2]-Cycloaddition Reactions Leading to β -Lactams	217
23.6	Product Class 6: Nitrogen- and Phosphorus-Substituted Ketenes		
	C. Palomo and J. M. Aizpurua		
23.6	Product Class 6: Nitrogen- and Phosphorus-Substituted Ketenes		
23.6.1	Product Subclass 1: Nitrogen-Substituted Ketenes		
23.6.1.1	Synthesis of Product Subclass 1		

23.6.1.1.1	Method 1:	Elimination Reactions of α -Amino Acids or Their Derivatives	222
23.6.1.1.2	Method 2:	Photolysis of Metal–Carbene Complexes	224
23.6.1.2		Applications of Product Subclass 1 in Organic Synthesis	227
23.6.1.2.1	Method 1:	Addition of Nitrogen- or Oxygen-Nucleophiles	227
23.6.1.2.2	Method 2:	Cycloaddition Reactions with Alkenes Leading to Cyclobutanones	229
23.6.1.2.3	Method 3:	Cycloaddition Reactions with Imines or Hydrazones Leading to β -Lactams	230
23.6.1.2.4	Method 4:	Lewis Acid Catalyzed Bellus–Claisen Rearrangement	233
23.6.2		Product Subclass 2: Phosphorus-Substituted Ketenes	234
23.6.2.1		Synthesis of Product Subclass 2	235
23.6.2.1.1	Method 1:	Elimination Reactions of α -Phosphorylcarboxylic Acid Derivatives	235
23.6.2.1.2	Method 2:	Wolff Rearrangement of α -Diazo- β -oxophosphonates	238
23.6.2.1.3	Method 3:	Dehydroalkoxylation of α -Triarylphosphoranylidene Esters	239
23.6.2.1.4	Method 4:	Thermolysis of Phosphinoethynyl Ethers	240
23.7		Product Class 7: Alkylideneketenes	
		W. F. Austin, J. J. Kowalczyk, G. B. Dudley, and R. L. Danheiser	
23.7		Product Class 7: Alkylideneketenes	245
23.7.1		Product Subclass 1: Substituted Methyleneketenes	245
23.7.1.1		Synthesis of Product Subclass 1	245
23.7.1.1.1	Method 1:	Elimination from Carboxylic Acid Derivatives	245
23.7.1.1.2	Method 2:	Cycloreversion Reactions	246
23.7.1.1.3	Method 3:	Thermolysis of Alkylidene Derivatives of Meldrum's Acid	247
23.7.1.1.4	Method 4:	Dehalogenation of 2-Bromoacryloyl Chlorides	248
23.7.1.1.5	Method 5:	Alkenation of Carbonyl Compounds with Phosphorylideneketenes	248
23.7.1.2		Applications of Product Subclass 1 in Organic Synthesis	249
23.7.1.2.1	Method 1:	[2 + 2] Cycloadditions Leading to Cyclobutane-1,3-diones or α -Alkylidene-Substituted β -Lactones	249
23.7.1.2.2	Method 2:	Generation of Vinylidenes by Thermolysis or Photolysis	251
23.7.1.2.3	Method 3:	Rearrangements Triggering Cyclization Reactions	252
23.7.2		Product Subclass 2: Carbon Suboxide	253
23.7.2.1		Synthesis of Product Subclass 2	253
23.7.2.1.1	Method 1:	Elimination from Malonic Acid Derivatives	253
23.7.2.1.2	Method 2:	Thermolysis of <i>O,O</i> -Diacetyltartaric Anhydride	254
23.7.2.1.3	Method 3:	Dehalogenation of Dibromomalonyl Chloride	254
23.7.2.2		Applications of Product Subclass 2 in Organic Synthesis	255
23.7.2.2.1	Method 1:	Reaction with Nucleophiles Leading to Malonic Acid Derivatives	255
23.7.2.2.2	Method 2:	Generation of Oxovinylidene by Photolysis	256

23.8	Product Class 8: Cyanoketenes H. W. Moore	
<hr/>		
23.8	Product Class 8: Cyanoketenes	259
23.8.1	Synthesis of Product Class 8	259
23.8.1.1	Method 1: Synthesis from 3-Azidocyclobut-3-ene-1,2-diones	260
23.8.1.2	Method 2: Synthesis from 2,5- and 2,6-Diazidobenzo-1,4-quinones	261
23.8.1.3	Method 3: Synthesis from 4-Azido-3-halo-5-methoxyfuran-2(5 <i>H</i>)-ones ..	263
23.8.1.4	Method 4: Synthesis of Cyano(trimethylsiloxy)ketene via a Retro-Diels–Alder Reaction	266
23.8.1.5	Method 5: Synthesis of the Parent Cyanoketene	267
23.9	Product Class 9: Acylketenes G. Kollenz and S. Ebner	
<hr/>		
23.9	Product Class 9: Acylketenes	271
23.9.1	Product Subclass 1: Monoalkanoylketenes and Formylketenes	272
23.9.1.1	Synthesis of Product Subclass 1	272
23.9.1.1.1	Method 1: Ruthenium(VIII) Oxide Oxidation of an Acylallene	272
23.9.1.1.2	Method 2: Dehydrochlorination of Acid Chlorides	272
23.9.1.1.3	Method 3: Flash-Vacuum Pyrolysis	273
23.9.1.1.3.1	Variation 1: Of β -Oxo Esters	273
23.9.1.1.3.2	Variation 2: Of 4 <i>H</i> -1,3-Dioxin-4-ones and a 4 <i>H</i> -1,3-Oxazin-4-one	273
23.9.1.1.3.3	Variation 3: Of Furan-2,3-diones	275
23.9.1.1.4	Method 4: Thermolysis Reactions	276
23.9.1.1.4.1	Variation 1: Of β -Oxo Esters	276
23.9.1.1.4.2	Variation 2: Of 4 <i>H</i> -1,3-Dioxin-4-ones	276
23.9.1.1.4.3	Variation 3: Of 5-Acyl-2,2-dimethyl-1,3-dioxane-4,6-diones	280
23.9.1.1.4.4	Variation 4: Of 4-Ethoxybut-3-yn-2-one	281
23.9.1.1.4.5	Variation 5: Of 2-Diazo-1,3-dicarbonyl Compounds	281
23.9.1.1.5	Method 5: Photolysis of 2-Diazo-1,3-dicarbonyl Compounds	281
23.9.1.1.6	Method 6: [4 + 2] Dimerization of Dipivaloylketene	282
23.9.1.2	Applications of Product Subclass 1 in Organic Synthesis	283
23.9.1.2.1	Method 1: Cycloaddition Reactions	283
23.9.1.2.2	Method 2: Addition of Nucleophiles	284
23.9.2	Product Subclass 2: α-(Oxomethylene)cycloalkanones	285
23.9.2.1	Synthesis of Product Subclass 2	285
23.9.2.1.1	Method 1: Dehydrochlorination of Acid Chlorides	285
23.9.2.1.2	Method 2: Flash-Vacuum Pyrolysis of Cyclic β -Oxo Esters	286
23.9.2.1.3	Method 3: Thermolysis Reactions	286
23.9.2.1.3.1	Variation 1: Of a Fused 4 <i>H</i> -1,3-Dioxin-4-one	287
23.9.2.1.3.2	Variation 2: Of Cyclic 2-Diazo-1,3-diketones	288
23.9.2.1.4	Method 4: Photolysis of Cyclic 2-Diazo-1,3-diketones	290

23.9.3	Product Subclass 3: α-(Oxomethylene)cycloalkanones	291
23.9.3.1	Synthesis of Product Subclass 3	291
23.9.3.1.1	Method 1: Thermolysis Reactions	291
23.9.3.1.1.1	Variation 1: Of Salicylic Acid Derivatives	291
23.9.3.1.1.2	Variation 2: Of Fused Furan-2,3-diones	292
23.9.3.1.1.3	Variation 3: Of 2-Diazo-1 <i>H</i> -indene-1,3(2 <i>H</i>)-dione	293
23.9.3.1.2	Method 2: Photolysis Reactions	293
23.9.3.1.2.1	Variation 1: Of 2-Phenyl-4 <i>H</i> -1,3-benzodioxin-4-one	293
23.9.3.1.2.2	Variation 2: Of 2,3-Benzodioxin-1,4-dione	293
23.9.3.1.2.3	Variation 3: Of Fused 2-Diazo-1,3-diketones	294
23.9.3.1.3	Method 3: Addition of Alkynes to Carbon Suboxide	295
23.9.4	Product Subclass 4: α-(Oxomethylene)heterocycloalkanones	296
23.9.4.1	Synthesis of Product Subclass 4	296
23.9.4.1.1	Method 1: Thermolysis of a Furo[3,4- <i>d</i>]-1,3-dioxinone	296
23.9.4.1.2	Method 2: Photolysis Reactions	297
23.9.4.1.2.1	Variation 1: Of 5-Diazo-2,2-dimethyl-1,3-dioxane-4,6-dione	297
23.9.4.1.2.2	Variation 2: Of 3-Diazo-1-methylquinoline-2,4(1 <i>H</i> ,3 <i>H</i>)-dione	298
23.9.5	Product Subclass 5: Dialkanoylketenes	299
23.9.5.1	Synthesis of Product Subclass 5	299
23.9.5.1.1	Method 1: Flash-Vacuum Pyrolysis of 5- <i>tert</i> -Butyl-4-pivaloylfuran-2,3-dione	299
23.9.5.2	Applications of Product Subclass 5 in Organic Synthesis	300
23.9.5.2.1	Method 1: Cycloaddition Reactions	300
23.9.5.2.2	Method 2: Addition of Nucleophiles	301
23.9.6	Product Subclass 6: Monoaroylketenes	302
23.9.6.1	Synthesis of Product Subclass 6	302
23.9.6.1.1	Method 1: Thermolysis Reactions	302
23.9.6.1.1.1	Variation 1: Of β -Oxo Esters	302
23.9.6.1.1.2	Variation 2: Of 4 <i>H</i> -1,3-Dioxin-4-ones and 1,3-Dioxane-4,6-diones	302
23.9.6.1.1.3	Variation 3: Of Furan-2,3-diones	303
23.9.6.1.1.4	Variation 4: Of 2-Diazo-1,3-diketones	305
23.9.6.1.2	Method 2: Photolysis Reactions	310
23.9.6.1.2.1	Variation 1: Of 5-Phenylfuran-2,3-dione	310
23.9.6.1.2.2	Variation 2: Of 2-Diazo-1,3-diketones	310
23.9.6.1.2.3	Variation 3: Of a Mesoionic Compound	311
23.9.7	Product Subclass 7: Diaroylketenes	311
23.9.7.1	Synthesis of Product Subclass 7	311
23.9.7.1.1	Method 1: Flash-Vacuum Pyrolysis of 4-Benzoyl-5-phenylfuran-2,3-dione	311
23.9.7.1.2	Method 2: Thermolysis of 4-Benzoyl-5-phenylfuran-2,3-dione	312
23.9.8	Product Subclass 8: Carboxyketenes	314
23.9.8.1	Synthesis of Product Subclass 8	314

23.9.8.1.1	Method 1: Flash-Vacuum Pyrolysis of 5-Alkylidene-2,2-dimethyl-1,3-dioxane-4,6-diones	314
23.9.9	Product Subclass 9: (Alkoxy carbonyl)ketenes	315
23.9.9.1	Synthesis of Product Subclass 9	315
23.9.9.1.1	Method 1: Dehydrochlorination of Acid Chlorides	315
23.9.9.1.2	Method 2: Thermolysis Reactions	316
23.9.9.1.2.1	Variation 1: Of Acid Derivatives	316
23.9.9.1.2.2	Variation 2: Of 6-Methoxy-4 <i>H</i> -1,3-dioxin-4-ones	317
23.9.9.1.2.3	Variation 3: Of a Pyrrolo[1,2- σ]quinoxalinetriene	317
23.9.9.1.2.4	Variation 4: Of Dimethyl Diazomalonate	317
23.9.9.1.3	Method 3: Photolysis of 2-Diazo-1,3-dicarbonyl Compounds	318
23.9.9.2	Applications of Product Subclass 9 in Organic Synthesis	318
23.9.9.2.1	Method 1: Cycloaddition Reactions	318
23.9.9.2.2	Method 2: Addition of Nucleophiles	319
23.9.10	Product Subclass 10: Acyl(alkoxy carbonyl)ketenes	319
23.9.10.1	Synthesis of Product Subclass 10	319
23.9.10.1.1	Method 1: Flash-Vacuum Pyrolysis of Methyl 2- <i>tert</i> -Butyl-4,5-dioxo-4,5-dihydrofuran-3-carboxylate	319
23.9.10.1.2	Method 2: Thermolysis Reactions	320
23.9.10.1.2.1	Variation 1: Of 4 <i>H</i> -1,3-Dioxin-4-ones	320
23.9.10.1.2.2	Variation 2: Of Ethyl 4,5-Dioxo-2-phenyl-4,5-dihydrofuran-3-carboxylate	321
23.9.10.2	Applications of Product Subclass 10 in Organic Synthesis	322
23.9.10.2.1	Method 1: Cycloaddition Reactions	322
23.9.10.2.2	Method 2: Addition of Amines	323
23.9.11	Product Subclass 11: Bis(alkoxy carbonyl)ketenes	324
23.9.11.1	Synthesis of Product Subclass 11	324
23.9.11.1.1	Method 1: Thermolysis of 2-Diazo-3-oxosuccinates	324
23.9.11.1.2	Method 2: Photolysis of 2-Diazo-1,3-dicarbonyl Compounds	324
23.9.11.1.3	Method 3: Reaction of Tetraethoxyallene with Phosgene	325
23.9.11.2	Applications of Product Subclass 11 in Organic Synthesis	325
23.9.11.2.1	Method 1: Preparation of Allenetetracarboxylates	325
23.9.11.2.2	Method 2: Cycloaddition Reactions	326
23.9.11.2.3	Method 3: Ring Transformations of Five-Membered Heterocycles	326
23.9.12	Product Subclass 12: (Chloro carbonyl)ketenes	327
23.9.12.1	Synthesis of Product Subclass 12	327
23.9.12.1.1	Method 1: Dehydrochlorination of Malonyl Chlorides	327
23.9.12.2	Applications of Product Subclass 12 in Organic Synthesis	329
23.9.12.2.1	Method 1: Cycloaddition Reactions	329
23.9.12.2.2	Method 2: Condensation Reactions	330
23.9.13	Product Subclass 13: Fluorinated Acylketenes	333
23.9.13.1	Synthesis of Product Subclass 13	333

23.9.13.1.1	Method 1:	Thermolysis Reactions	333
23.9.13.1.1.1	Variation 1:	Of (Trifluoromethyl)malonic Acid Derivatives	333
23.9.13.1.1.2	Variation 2:	Of Fluorinated 4 <i>H</i> -1,3-Dioxin-4-ones	334
23.9.13.1.2	Method 2:	Transformation of Fluorinated Alkenes and Alkynes	335
23.9.13.1.2.1	Variation 1:	By Reaction with Sulfur Trioxide	335
23.9.13.1.2.2	Variation 2:	With Lewis Acid Catalysis	336
23.9.13.1.3	Method 3:	Photolysis of Methyl 2-Diazo-4,4,4-trifluoroacetoacetate	337
23.9.13.2	Applications of Product Subclass 13 in Organic Synthesis		337
23.9.13.2.1	Method 1:	Cycloaddition Reactions	337
23.9.13.2.2	Method 2:	Electrophilic Substitution Reactions	338
23.9.13.2.3	Method 3:	Addition of Nucleophiles	339
23.9.14	Product Subclass 14: Acyl(phosphoryl)ketenes and Acyl(trialkylmetal)ketenes		341
23.9.14.1	Synthesis of Product Subclass 14		341
23.9.14.1.1	Method 1:	Transformation of [Dialkoxy(bromo)phosphoranylidene]malonates	341
23.9.14.1.2	Method 2:	Photolysis or Thermolysis of Methyl 2-Diazo-3-(diisopropoxyphosphoryl)-3-oxopropanoate	341
23.9.14.1.3	Method 3:	Addition of Organometallic Compounds to Carbon Suboxide	341
23.9.14.1.4	Method 4:	Transformation of Functionalized Ethoxyacetylenes	342
23.10	Product Class 10: Imidoylketenes		
	G. Kollenz		
23.10	Product Class 10: Imidoylketenes		351
23.10.1	Product Subclass 1: N-Unsubstituted and N-Alkyl-Substituted Imidoylketenes		351
23.10.1.1	Synthesis of Product Subclass 1		351
23.10.1.1.1	Method 1:	Pyrolysis Reactions	352
23.10.1.1.1.1	Variation 1:	Flash-Vacuum Pyrolysis of Meldrum's Acid Derivatives	352
23.10.1.1.1.2	Variation 2:	Flash-Vacuum Pyrolysis of Pyrrole-2,3-diones	353
23.10.1.1.1.3	Variation 3:	Thermolysis of 3-Aminoacrylates	353
23.10.1.1.2	Method 2:	Reaction of 1-Aminopyridinium Iodide with 2,3-Diphenylcycloprop-2-en-1-one	354
23.10.1.1.3	Method 3:	Extrusion of Sulfur from Isothiazol-5(2 <i>H</i>)-ones	355
23.10.2	Product Subclass 2: (N-Acylimidoyl)ketenes		356
23.10.2.1	Synthesis of Product Subclass 2		356
23.10.2.1.1	Method 1:	Pyrolysis of 3-(Acylamino)acrylates	356
23.10.2.1.2	Method 2:	Reaction of Pyridinium Ylides with 2,3-Diphenylcycloprop-2-en-1-one	357
23.10.2.1.3	Method 3:	Reaction of Di- <i>tert</i> -butoxyacetylene with Benzoyl Isocyanate	357
23.10.3	Product Subclass 3: (N-Arylimidoyl)ketenes		358
23.10.3.1	Synthesis of Product Subclass 3		358
23.10.3.1.1	Method 1:	Thermolysis Reactions	359

23.10.3.1.1.1	Variation 1:	Flash-Vacuum Pyrolysis of Meldrum's Acid Derivatives	359
23.10.3.1.1.2	Variation 2:	Pyrolysis of 1-Aryl-1 <i>H</i> -pyrrole-2,3-diones	360
23.10.3.1.1.3	Variation 3:	Flash-Vacuum Pyrolysis of 1-Aryl-1 <i>H</i> -1,2,3-triazoles	362
23.10.3.1.1.4	Variation 4:	Thermolysis of <i>N</i> -Arylketenimines	363
23.10.3.1.1.5	Variation 5:	Thermolysis of Mesoionic Compounds	364
23.10.3.1.2	Method 2:	Extrusion of Sulfur from Isothiazol-5(2 <i>H</i>)-ones	364
23.10.4	Product Subclass 4: <i>N</i>-Hetaryl-Substituted Imidoylketenes		365
23.10.4.1	Synthesis of Product Subclass 4		365
23.10.4.1.1	Method 1:	Pyrolysis Reactions	365
23.10.4.1.1.1	Variation 1:	Flash-Vacuum Pyrolysis of 1-(1 <i>H</i> -Pyrazol-5-yl)-1 <i>H</i> -1,2,3-triazoles	365
23.10.4.1.1.2	Variation 2:	Flash-Vacuum Pyrolysis of Meldrum's Acid Derivatives	366
23.10.4.1.2	Method 2:	Lithiation of Isoxazol-5(2 <i>H</i>)-ones	366
23.10.5	Product Subclass 5: Acyl(imidoyl)ketenes		367
23.10.5.1	Synthesis of Product Subclass 5		367
23.10.5.1.1	Method 1:	Thermolysis Reactions of Pyrrole-2,3-diones and Furan-2,3-diones	367
23.10.5.1.1.1	Variation 1:	In the Solid State	367
23.10.5.1.1.2	Variation 2:	In Solution	368
23.10.6	Product Subclass 6: <i>N</i>-Unsubstituted 6-(Oxomethylene)cyclohexa-2,4-dien-1-imines		372
23.10.6.1	Synthesis of Product Subclass 6		372
23.10.6.1.1	Method 1:	Thermolysis of 1,2,3-Benzotriazin-4(3 <i>H</i>)-ones	372
23.10.6.1.2	Method 2:	Reactions of 3,2,1-Benzoxathiazin-4(1 <i>H</i>)-one 2-Oxide	373
23.10.7	Product Subclass 7: <i>N</i>-Substituted 6-(Oxomethylene)cyclohexa-2,4-dien-1-imines		374
23.10.7.1	Synthesis of Product Subclass 7		374
23.10.7.1.1	Method 1:	Photolysis Reactions of 1,2,3-Benzotriazin-4(3 <i>H</i>)-ones	375
23.10.7.1.2	Method 2:	Thermolysis Reactions	376
23.10.7.1.2.1	Variation 1:	Of a 3,2,1-Benzoxathiazin-4(1 <i>H</i>)-one 2-Oxide	376
23.10.7.1.2.2	Variation 2:	Of 2,1-Benzisothiazol-3(1 <i>H</i>)-ones	377
23.10.7.1.2.3	Variation 3:	Of 1-Phenyl-1 <i>H</i> -indole-2,3-dione	377
23.10.7.1.3	Method 3:	Ring Opening of 2,1-Benzisoxazol-1-ium Salts	377
23.11	Product Class 11: Alk-1-ynylketenes		
	H. W. Moore		
23.11	Product Class 11: Alk-1-ynylketenes		381
23.11.1	Synthesis of Product Class 11		381
23.11.1.1	Method 1:	Retro-Diels–Alder Reactions	381
23.11.1.2	Method 2:	Thermolysis of 1-Alkoxyalk-1-ynes	384
23.11.1.3	Method 3:	Alk-1-ynyl(cyano)ketenes from 2,5-Di(alk-1-ynyl)-3,6-diazidobenzo-1,4-quinones	385
23.11.1.4	Methods 4:	Additional Methods for the Generation of Alk-1-ynylketenes	389

23.12	Product Class 12: Aryl- and Hetarylketenes	
	T. T. Tidwell	
<hr/>		
23.12	Product Class 12: Aryl- and Hetarylketenes	391
23.12.1	Product Subclass 1: Monoarylketenes	392
23.12.1.1	Synthesis of Product Subclass 1	393
23.12.1.1.1	Method 1: Monoarylketenes by Dehydration of Arylacetic Acids	393
23.12.1.1.2	Method 2: Monoarylketenes from Arylacetic Anhydrides	393
23.12.1.1.2.1	Variation 1: Arylketene by Decarboxylation of Arylmalonic Acids	394
23.12.1.1.3	Method 3: Monoarylketenes from Arylacetate Esters	394
23.12.1.1.4	Method 4: Monoarylketenes by Dehydrohalogenation of Arylacetyl Chlorides	395
23.12.1.1.4.1	Variation 1: Monoarylketenes by Dehydrochlorination Using a Shuttle Procedure with a Kinetic Base and a Stoichiometric Base	396
23.12.1.1.5	Method 5: Monoarylketenes by Dehalogenation of Arylhaloacetyl Halides	399
23.12.1.1.6	Method 6: Monoarylketenes by Wolff Rearrangement of α -Diazo Ketones	400
23.12.1.1.6.1	Variation 1: Metal-Catalyzed Wolff Rearrangement	401
23.12.1.1.6.2	Variation 2: Monoarylketenes by Microwave and Ultrasound-Enhanced Wolff Rearrangement	403
23.12.1.1.6.3	Variation 3: Monoarylketenes by Photochemical Wolff Rearrangement	404
23.12.1.1.6.4	Variation 4: Phenylketene by Wolff-Type Rearrangement of a Sulfur Ylide	405
23.12.1.1.7	Method 7: Monoarylketenes from Ynols and Ynolates	405
23.12.1.1.8	Method 8: Monoarylketenes by Oxidation of Arylacetylenes	406
23.12.1.1.8.1	Variation 1: Monoarylketenes by Oxidation of Lithium Arylacetylides	407
23.12.1.1.8.2	Variation 2: Monoarylketenes by Ruthenium-Catalyzed Alkyne Oxygenation	408
23.12.1.1.9	Method 9: Monoarylketenes from Metal–Carbene Complexes	409
23.12.1.2	Applications of Product Subclass 1 in Organic Synthesis	410
23.12.1.2.1	Method 1: Esters and Amides by Addition of Nucleophiles to Monoarylketenes	410
23.12.1.2.2	Method 2: Ketones and Vinyl Ethers by Addition of Carbon Electrophiles	410
23.12.1.2.3	Method 3: <i>N</i> -Aroyloxyamines by Aminoxyl Radical Addition to Monoarylketenes	411
23.12.1.2.4	Method 4: Cyclobutanones by [2 + 2] Cycloaddition with Alkenes and Dienes	412
23.12.1.2.5	Method 5: Cyclobutenones by [2 + 2] Cycloaddition of Monoarylketenes with Alkynes	414
23.12.1.2.6	Method 6: β -Lactams by [2 + 2] Cycloaddition of Monoarylketenes with Imines	416
23.12.1.2.6.1	Variation 1: Pyrimidinones by [4 + 2] Cycloaddition of Monoarylketenes with 1,3-Diazabuta-1,3-dienes	418
23.12.1.2.7	Method 7: 2-Arylacetate Derivatives by [4 + 2] Cycloaddition of <i>o</i> -Chloranil with Ketene Enolates	419
23.12.1.2.8	Method 8: Carbene Formation by Decarbonylation of Monoarylketenes	419
23.12.2	Product Subclass 2: Alkyl(aryl)- and Aryl(vinyl)ketenes	420
23.12.2.1	Synthesis of Product Subclass 2	421

23.12.2.1.1	Method 1:	Alkyl(aryl)ketenes by Elimination from 2-Arylalkanoate Esters	421
23.12.2.1.2	Method 2:	Alkyl(aryl)ketenes by Dehydrohalogenation of 2-Arylalkanoyl Chlorides	423
23.12.2.1.3	Method 3:	Alkyl(aryl)ketenes by Dehalogenation of 2-Aryl-2-haloalkanoyl Halides	423
23.12.2.1.4	Method 4:	Alkyl(aryl)ketenes by Wolff Rearrangement of α -Diazo Ketones	424
23.12.2.1.5	Method 5:	Alkyl(aryl)ketenes by Decarboxylation of Malonic Acids	425
23.12.2.1.6	Method 6:	Aryl(vinyl)ketenes by Cyclobutenone Ring Opening	425
23.12.2.1.7	Method 7:	Aryl(vinyl)ketenes from Metal–Carbene Complexes	426
23.12.2.1.8	Method 8:	Alkyl(aryl)ketenes by [4 + 2] Cycloadditions of Cyclic Diazines	427
23.12.2.2	Applications of Product Subclass 2 in Organic Synthesis		428
23.12.2.2.1	Method 1:	2-Arylalkanoic Acid Derivatives by Stereoselective Esterification of Alkyl(aryl)ketenes	428
23.12.2.2.1.1	Variation 1:	Chiral 2-Arylalkanoate Esters by Catalytic Stereoselective Addition of Methanol to Alkyl(aryl)ketenes	431
23.12.2.2.1.2	Variation 2:	Chiral 2-Arylalkanoate Enol Esters by Catalytic Stereoselective Esterification of Alkyl(aryl)ketenes with Aldehydes	433
23.12.2.2.1.3	Variation 3:	Chiral 2-Arylalkanamides by Stereoselective Amination of Alkyl(aryl)ketenes	434
23.12.2.2.2	Method 2:	Ketones and Vinyl Esters and Ethers by Addition of Carbon Nucleophiles to Ethyl(phenyl)ketene	436
23.12.2.2.3	Method 3:	Divinyl Ketone Formation by Iridium–Alkyne Complex Addition to Methyl(phenyl)ketene with Double C–H Activation	438
23.12.2.2.4	Method 4:	Lactones and Cycloalkanones by Electrophilic Addition to Alkyl(aryl)ketenes	438
23.12.2.2.5	Method 5:	Allenyl Ketones and Esters by Wittig-Type Reactions of Alkyl(aryl)ketenes	439
23.12.2.2.6	Method 6:	Cyclobutanones by [2 + 2] Cycloaddition of Methyl(phenyl)ketene with Alkenes and Dienes	440
23.12.2.2.6.1	Variation 1:	Cyclobutanones by Intramolecular [2 + 2] Cycloaddition of Aryl(pent-4-enyl)ketenes	441
23.12.2.2.7	Method 7:	Naphthol Formation by Intramolecular Cyclization of an Alkyl(aryl)ketene with an Alkynyl Group	441
23.12.2.2.8	Method 8:	β -Lactone Formation by Intramolecular Cycloaddition of an Alkyl(aryl)ketene with a Carbonyl Group	442
23.12.2.2.9	Method 9:	Succinic Anhydrides by Oxidation of Alkyl(aryl)ketenes	442
23.12.2.2.10	Method 10:	Aminoxy Radical Substituted Polymers from Alkyl(aryl)ketenes	442
23.12.3	Product Subclass 3: Diarylketenes		443
23.12.3.1	Synthesis of Product Subclass 3		444
23.12.3.1.1	Method 1:	Diarylketenes by Dehydration of Diarylacetic Acids	444
23.12.3.1.2	Method 2:	Diarylketenes by Dehydrochlorination of Diarylacetyl Chlorides	445
23.12.3.1.3	Method 3:	Diarylketenes by Dehalogenation of Diarylhaloacetyl Halides	446

23.12.3.1.4	Method 4:	Diarylketenes by Pyrolysis of Diarylketene Acetals	448
23.12.3.1.5	Method 5:	Diarylketenes by Wolff Rearrangement of α -Diazo Ketones	448
23.12.3.1.5.1	Variation 1:	Diarylketenes by Photochemical Wolff Rearrangement of α -Diazo Ketones	449
23.12.3.1.6	Method 6:	Diarylketenes by Oxidation of Diarylacetylenes	449
23.12.3.2	Applications of Product Subclass 3 in Organic Synthesis		450
23.12.3.2.1	Method 1:	Diarylacetic Acid Derivatives by Nucleophilic Additions to Diarylketenes	450
23.12.3.2.2	Method 2:	Alcohols, Aldehydes, Ketones, and Enol Derivatives by Addition of Hydrogen, Carbon, and Silicon Nucleophiles and Electrophiles to Diarylketenes	450
23.12.3.2.2.1	Variation 1:	Cyclopropanones by Diazoalkane Addition to Diarylketenes	453
23.12.3.2.3	Method 3:	Aminoxy Esters from Aminoxy Radical Addition to Diarylketenes	454
23.12.3.2.4	Method 4:	Allenes by Wittig Reactions	454
23.12.3.2.4.1	Variation 1:	Ketenimines by Aza-Wittig Reaction of Diarylketenes	455
23.12.3.2.5	Method 5:	Cyclobutanones and Other Products by Cycloaddition Reactions with Alkenes and Dienes	455
23.12.3.2.6	Method 6:	[2 + 2] and [2 + 2 + 2] Cycloadditions with Alk-1-ynyl Ethers	459
23.12.3.2.7	Method 7:	β -Lactams by [2 + 2] Cycloaddition with Imines	459
23.12.3.2.7.1	Variation 1:	δ -Lactams by [4 + 2] Cycloaddition with Chiral 2-Vinyl-4,5-dihydrothiazoles	461
23.12.3.2.8	Method 8:	β -Lactones by [2 + 2] Cycloaddition with Carbonyl Groups	462
23.12.3.2.8.1	Variation 1:	γ -Lactone Formation by Diarylketene Reaction with Carbonyl Compounds	463
23.12.3.2.9	Method 9:	Polyesters by Oxidation of Diarylketenes	463
23.12.3.2.10	Method 10:	Diarylacetylenes by Deoxygenation of Diarylketenes	464
23.12.3.2.11	Method 11:	Carbenes and Carbocations by Decarbonylation of Diarylketenes	464
23.12.4	Product Subclass 4: Fulvenones		465
23.12.4.1	Synthesis of Product Subclass 4		466
23.12.4.1.1	Method 1:	Fulvenones by Elimination from Esters	466
23.12.4.1.2	Method 2:	Fulvenones by Dehydrochlorination of Acyl Chlorides	466
23.12.4.1.3	Method 3:	Fulvenones by Dehalogenation of 2-Haloacyl Halides	467
23.12.4.1.4	Method 4:	Fulvenones by Wolff Rearrangement of α -Diazo Ketones	468
23.12.4.1.4.1	Variation 1:	Azafulvenones by Wolff Rearrangement and Other Routes	470
23.12.4.1.4.2	Variation 2:	Pentafulvenone by Photochemical Wolff-like Rearrangement of 2-Halophenols	471
23.12.4.2	Applications of Product Subclass 4 in Organic Synthesis		472
23.12.4.2.1	Method 1:	Pyridinium Zwitterions from Pentafulvenones	472
23.12.4.2.2	Method 2:	Cyclobutanones by [2 + 2] Cycloaddition with Alkenes and Dienes	472
23.12.5	Product Subclass 5: Hetarylketenes		473
23.12.5.1	Synthesis of Product Subclass 5		473
23.12.5.1.1	Method 1:	Hetarylketenes by Ester Elimination of Hetarylacetates	473

23.12.5.1.2	Method 2:	Hetarylketenes by Dehydrochlorination of Hetarylacetyl Chlorides	473
23.12.5.1.2.1	Variation 1:	Hetarylketenes by Dehydrochlorination Using a Shuttle Procedure with a Kinetic Base, and a Stoichiometric Base	475
23.12.5.1.3	Method 3:	Hetarylketenes by Thermal Decarbonylation of Furan-2,3-diones	475
23.12.5.1.4	Method 4:	Hetarylketenes by Wolff Rearrangement of α -Diazo Ketones ..	476
23.12.5.1.4.1	Variation 1:	Hetarylketenes by Rhodium-Catalyzed Wolff Rearrangement of α -Diazo Ketones	478
23.12.5.1.4.2	Variation 2:	Hetarylketenes by Wolff Rearrangement and [2 + 2] Cycloaddition with Alkynes	478
23.12.5.1.4.3	Variation 3:	Hetarylketenes by Wolff-like Rearrangements of Triazoles and Other Substrates	479
23.12.5.1.5	Method 5:	Hetarylketenes by Carbene Carbonylation	481
23.12.5.1.6	Method 6:	Hetarylketenes from Chromium–Carbene Complexes	481
23.12.5.2		Applications of Product Subclass 5 in Organic Synthesis	482
23.12.5.2.1	Method 1:	Esters and Amides by Addition of Nucleophiles to Hetarylketenes	482
23.12.5.2.2	Method 2:	Imidazo[4,5-c]isoxazole Formation by Cyclization of Hetarylketenes	482
23.12.6		Product Subclass 6: Ferrocenylketenes	483
23.12.6.1		Synthesis of Product Subclass 6	483
23.12.6.1.1	Method 1:	Ferrocenylketene by Activation of Ferrocenylacetic Acid	483
23.12.6.1.2	Method 2:	Ferrocenylketenes by Wolff Rearrangement of α -Diazo Ketones	485
23.13		Product Class 13: Alkenylketenes	
		R. L. Danheiser, G. B. Dudley, and W. F. Austin	
23.13		Product Class 13: Alkenylketenes	493
23.13.1		Product Subclass 1: Vinylketenes	494
23.13.1.1		Synthesis of Product Subclass 1	494
23.13.1.1.1	Method 1:	Elimination from Carboxylic Acid Derivatives	494
23.13.1.1.2	Method 2:	Wolff Rearrangement of α' -Diazo- α,β -unsaturated Ketones ..	498
23.13.1.1.3	Method 3:	Electrocyclic Ring Opening of Cyclobutenones	501
23.13.1.2		Applications of Product Subclass 1 in Organic Synthesis	504
23.13.1.2.1	Method 1:	[2 + 2] Cycloadditions Leading to 4-Alkenylcyclobutanones ...	506
23.13.1.2.1.1	Variation 1:	Intermolecular Cycloadditions	507
23.13.1.2.1.2	Variation 2:	Intramolecular Cycloadditions	512
23.13.1.2.2	Method 2:	[2 + 2] Cycloadditions Leading to β -Lactams	520
23.13.2		Product Subclass 2: 1,3-Dienylketenes and (2-Arylvinyll)ketenes	522
23.13.2.1		Synthesis of Product Subclass 2	522
23.13.2.1.1	Method 1:	Elimination from Carboxylic Acid Derivatives	525
23.13.2.1.2	Method 2:	Wolff Rearrangement of 1,3-Dienyl α' -Diazo Ketones	526

23.13.2.1.3	Method 3:	Electrocyclic Ring Opening of Cyclobutenones	527
23.13.2.1.3.1	Variation 1:	Electrocyclic Ring Opening of 4-Alkenyl- and 4-Arylcyclobutenones	528
23.13.2.1.3.2	Variation 2:	Electrocyclic Ring Opening of 2-(1,3-Dienyl)cyclobutenones and 2-(2-Arylvinyl)cyclobutenones	530
23.13.2.1.4	Method 4:	Electrocyclic Ring Opening of 6,6-Disubstituted Cyclohexa-2,5-dien-1-ones	531
23.13.2.2	Applications of Product Subclass 2 in Organic Synthesis		533
23.13.2.2.1	Method 1:	Six-Electron Electrocyclizations Leading to Phenols	533
23.13.2.2.1.1	Variation 1:	Of Ketenes from the Elimination of Carboxylic Acid Derivatives	534
23.13.2.2.1.2	Variation 2:	Of Ketenes Generated by the Electrocyclic Ring Opening of Cyclobutenones	539
23.13.2.2.1.3	Variation 3:	Of Ketenes Generated by Electrocyclic Ring Opening of 4-Hydroxycyclobutenones	547
23.13.3	Product Subclass 3: Alk-1-en-3-ynylketenes		555
23.13.3.1	Synthesis of Product Subclass 3		556
23.13.3.1.1	Method 1:	Elimination from Carboxylic Acid Derivatives	556
23.13.3.1.2	Method 2:	Wolff Rearrangement of Diazo Ketones	557
23.13.3.1.3	Method 3:	Electrocyclic Ring Opening of 4-Alkynylcyclobutenones	558
23.13.3.2	Applications of Product Subclass 3 in Organic Synthesis		559
23.13.3.2.1	Method 1:	Cyclizations Leading to Quinones	559
23.14	Product Class 14: Alkyl- and Cycloalkylketenes T. T. Tidwell		
<hr/>			
23.14	Product Class 14: Alkyl- and Cycloalkylketenes		569
23.14.1	Product Subclass 1: Monoalkylketenes		571
23.14.1.1	Synthesis of Product Subclass 1		571
23.14.1.1.1	Method 1:	Dehydration of Alkanoic Acids	572
23.14.1.1.1.1	Variation 1:	Dehydration of Carboxylic Acids Using Mukaiyama's Reagent	572
23.14.1.1.2	Method 2:	Pyrolysis of Alkanoic Anhydrides	574
23.14.1.1.2.1	Variation 1:	From Alkanoic Anhydrides under Perkin Conditions	575
23.14.1.1.3	Method 3:	Michael Addition and Elimination Reaction of Alkanoate Esters	575
23.14.1.1.3.1	Variation 1:	Ester Pyrolysis	576
23.14.1.1.4	Method 4:	Dehydrohalogenation of Alkanoyl Chlorides	577
23.14.1.1.4.1	Variation 1:	Dehydrochlorination Using a Shuttle Procedure with a Kinetic Base and a Stoichiometric Base	577
23.14.1.1.5	Method 5:	Synthesis from Cycloalkanones and Hexa-1,5-dien-3-ones ...	579
23.14.1.1.5.1	Variation 1:	Photolysis of Cyclobutanones	581
23.14.1.1.5.2	Variation 2:	Photolysis of Cyclohexanones	582
23.14.1.1.5.3	Variation 3:	Photolysis of Hexa-1,5-dien-3-ones	583
23.14.1.1.6	Method 6:	Dehalogenation of 2-Haloalkanoyl Halides	583
23.14.1.1.7	Method 7:	Wolff Rearrangement of Diazo Ketones	585
23.14.1.1.7.1	Variation 1:	Metal-Catalyzed Wolff Rearrangement	585
23.14.1.1.7.2	Variation 2:	Ultrasound-Assisted Wolff Rearrangement	586

23.14.1.1.7.3	Variation 3:	Microwave-Enhanced Wolff Rearrangement	587
23.14.1.1.7.4	Variation 4:	Photochemical Wolff Rearrangement	587
23.14.1.1.8	Method 8:	Thermolysis of Alkynyl Ethers	588
23.14.1.1.9	Method 9:	Synthesis from Ynolates (The Kowalski Homologation)	590
23.14.1.2	Applications of Product Subclass 1 in Organic Synthesis		590
23.14.1.2.1	Method 1:	Allenyl Esters by Wittig Reactions of Monoalkylketenes	590
23.14.1.2.2	Method 2:	Alkanoic Acid Derivatives by Addition of Heteroatom Nucleophiles to Monoalkylketenes	592
23.14.1.2.2.1	Variation 1:	Alkanoic Acid Derivatives by the Arndt–Eistert Chain Elongation	592
23.14.1.2.2.2	Variation 2:	β -Amino Acid Derivatives by the Arndt–Eistert Reaction	593
23.14.1.2.2.3	Variation 3:	β -Amino Acid Esters by Kowalski Homologation of Esters	595
23.14.1.2.2.4	Variation 4:	Aldols via Boron Enolates from the Addition of Sulfur Nucleophiles to Monoalkylketenes	596
23.14.1.2.2.5	Variation 5:	γ -Lactams by Intramolecular Cyclization of Monoalkylketenes with Nitrogen Nucleophiles	597
23.14.1.2.2.6	Variation 6:	Amides by Allylic Amine Addition and Aza-Claisen Rearrangement	598
23.14.1.2.3	Method 3:	2-Halo Esters by Addition of Electrophilic Halogenating Agents to Monoalkylketenes	599
23.14.1.2.4	Method 4:	Ketones and Vinyl Ethers by Addition of Carbon Nucleophiles to Monoalkylketenes	600
23.14.1.2.5	Method 5:	Trifluoromethyl Ketones and Oxo Esters by Acylation of Monoalkylketenes with Trifluoroacetic Anhydride	601
23.14.1.2.6	Method 6:	3-Methylene- β -lactones by Dimerization of Monoalkylketenes	601
23.14.1.2.7	Method 7:	Cyclobutanones by [2 + 2] Cycloaddition of Monoalkylketenes with Alkenes and Dienes	603
23.14.1.2.7.1	Variation 1:	Polycyclic Ketones by Intramolecular [2 + 2] Cycloaddition of Monoalkylketenes with Alkenyl Groups	606
23.14.1.2.8	Method 8:	β -Lactams by [2 + 2] Cycloaddition of Monoalkylketenes with Imines	608
23.14.1.2.9	Method 9:	β -Lactones by [2 + 2] Cycloaddition of Monoalkylketenes with Aldehydes	609
23.14.1.2.10	Method 10:	γ -Lactones by Intramolecular [3 + 2] Cyclization of Ketenes to Cyclobutanones	611
23.14.1.2.11	Method 11:	Cyclopropanones by [2 + 1] Cycloaddition of Monoalkylketenes with Diazoalkanes	612
23.14.1.2.12	Method 12:	2-Hydroxyalkanoates by [4 + 2] Cycloaddition of <i>o</i> -Chloranil with Ketene Enolates	613
23.14.2	Product Subclass 2: Dialkylketenes and (Oxomethylene)cycloalkanes		613
23.14.2.1	Synthesis of Product Subclass 2		614
23.14.2.1.1	Method 1:	Dehydration of Dialkylalkanoic Acids	614
23.14.2.1.2	Method 2:	Pyrolysis of 2-Alkylalkanoic Anhydrides	615
23.14.2.1.2.1	Variation 1:	Decarboxylation of Dialkylmalonic Anhydrides	616
23.14.2.1.3	Method 3:	Elimination Reactions of 2-Alkylalkanoate Ester Enolates	617

23.14.2.1.3.1	Variation 1:	Elimination from Ester Enolates Formed by Michael Addition to Acrylates	619
23.14.2.1.4	Method 4:	Dehydrochlorination of 2-Alkylalkanoyl Halides	620
23.14.2.1.5	Method 5:	Pyrolysis of Ketene Dimers	625
23.14.2.1.6	Method 6:	Dehalogenation of 2-Haloalkanoyl Halides	628
23.14.2.1.6.1	Variation 1:	Dehalogenation of 2-Haloalkanoyl Halides with Other Metals	629
23.14.2.1.7	Method 7:	Wolff Rearrangement of Diazo Ketones	630
23.14.2.1.7.1	Variation 1:	Photochemical Wolff Rearrangement of Diazo Ketones	632
23.14.2.1.7.2	Variation 2:	Ultrasound-Enhanced Wolff Rearrangement	634
23.14.2.1.7.3	Variation 3:	Photochemical Wolff Rearrangement of α -Oxo Ketenes	635
23.14.2.1.8	Method 8:	Oxygenation of a Dialkylthioketene	635
23.14.2.2		Applications of Product Subclass 2 in Organic Synthesis	635
23.14.2.2.1	Method 1:	Carbenes by Decarbonylation of Dialkylketenes	635
23.14.2.2.2	Method 2:	Carboxylic Acid Derivatives by Nucleophilic Addition to Dialkylketenes	636
23.14.2.2.2.1	Variation 1:	Carboxylic Anhydrides and Derivatives by Electrophilic Addition to Dialkylketenes	637
23.14.2.2.2.2	Variation 2:	Esters and Free Radicals by Radical Addition to Dialkylketenes	638
23.14.2.2.3	Method 3:	Ketones and Vinyl Ethers by Addition of Carbon Nucleophiles to Dialkylketenes	639
23.14.2.2.4	Method 4:	Cyclobutane-1,3-diones by Dimerization of Dialkylketenes ..	642
23.14.2.2.4.1	Variation 1:	Cyclobutane-1,3-diones by Mixed Dimerization of Dialkylketenes with <i>tert</i> -Butyl(cyano)ketene	643
23.14.2.2.5	Method 5:	Cyclobutanones and Cyclobutenones by [2 + 2] Cycloaddition of Dialkylketenes with Alkenes, Dienes, Allenes, or Alkynes ..	644
23.14.2.2.5.1	Variation 1:	Bicyclo[n.2.0]alkanones by Intramolecular [2 + 2] Cycloaddition with Alkenyl Groups	649
23.14.2.2.6	Method 6:	β -Lactams by [2 + 2] Cycloaddition of Dialkylketenes with Imines	653
23.14.2.2.6.1	Variation 1:	Malonimides by [2 + 2] Cycloaddition of Dialkylketenes with Isocyanates	654
23.14.2.2.7	Method 7:	β -Lactones by [2 + 2] Cycloaddition of Dialkylketenes with Aldehydes	655
23.14.2.2.7.1	Variation 1:	β -Lactones by Asymmetric [2 + 2] Cycloaddition of Dimethylketene with Chiral Aldehydes	655
23.14.2.2.8	Method 8:	Cyclopropanones by [2 + 1] Cycloaddition of Dialkylketenes with Diazoalkanes	656
23.14.2.2.9	Method 9:	Polymerization of Dialkylketenes	657
23.14.3		Product Subclass 3: Cyclopropylketene, (Cycloprop-2-enyl)ketene, and Oxiranylketene	658
23.14.3.1		Synthesis of Product Subclass 3	658
23.14.3.1.1	Method 1:	Elimination from Cyclopropylacetates	658
23.14.3.1.2	Method 2:	Dehydrohalogenation of Cyclopropylacetyl Halides	659
23.14.3.1.3	Method 3:	Wolff Rearrangements of Diazo Ketones	659
23.14.3.1.3.1	Variation 1:	(Cycloprop-2-enyl)ketene by Wolff Rearrangement	661
23.14.3.1.3.2	Variation 2:	Oxiranylketenes by Wolff Rearrangement	662

23.14.3.1.4	Method 4:	Photochemical Rearrangement of 5,5-Dimethylcyclopent-2-enone	662
23.14.3.1.4.1	Variation 1:	Photolysis of Cyclopentadienones	662
23.14.3.2		Applications of Product Subclass 3 in Organic Synthesis	663
23.14.3.2.1	Method 1:	Bicyclooctadienones and Cycloheptadienones from Cyclopropylketenes by Cope Rearrangement	663
23.14.4		Product Subclass 4: (Fluoroalkyl)ketenes	665
23.14.4.1		Synthesis of Product Subclass 4	666
23.14.4.1.1	Method 1:	Dehydration of Fluoroalkanoic Acids	666
23.14.4.1.2	Method 2:	Dehalogenation of 2-Haloacyl Halides	666
23.14.4.1.3	Method 3:	Wolff Rearrangement of Diazo Ketones	667
23.14.4.1.3.1	Variation 1:	Bis(trifluoromethyl)ketene by Wolff-Type Rearrangement upon Oxidation of an Alkyne	667
23.14.4.1.4	Method 4:	Hydrolysis of a Perfluoroalkene	668
23.14.4.1.5	Method 5:	Acyl(trifluoromethyl)ketenes by Cleavage of a 1,3-Dioxin-4-one	668
23.14.4.2		Applications of Product Subclass 4 in Organic Synthesis	668
23.14.4.2.1	Method 1:	Fluoroalkyl Cyclobutanones, Cyclobutenones, and Derivatives by [2 + 2]-Cycloaddition Reactions of (Fluoroalkyl)ketenes	668
23.14.4.2.2	Method 2:	(Trifluoromethyl)malonates by Nucleophilic Additions to a (Trifluoromethyl)ketene	671
23.15		Product Class 15: Bisketenes T. T. Tidwell	
23.15		Product Class 15: Bisketenes	679
23.15.1		Product Subclass 1: 1,2-Bisketenes	681
23.15.1.1		Synthesis of Product Subclass 1	681
23.15.1.1.1	Method 1:	1,2-Bisketenes by Thermal Ring Opening of Cyclobutene-1,2-diones	682
23.15.1.1.1.1	Variation 1:	Stabilized 1,2-Bisketenes by Thermal Ring Opening of Cyclobutene-1,2-diones	683
23.15.1.1.2	Method 2:	1,2-Bisketenes by Photochemical Ring Opening of Cyclobutene-1,2-diones	684
23.15.1.1.3	Method 3:	Metal-Complexed 1,2-Bisketene	687
23.15.1.1.4	Method 4:	1,2-Bisketenes by Wolff Rearrangement of Bis(diazo ketones)	687
23.15.1.2		Applications of Product Subclass 1 in Organic Synthesis	688
23.15.1.2.1	Method 1:	Acids, Esters, and Amides by Nucleophilic Additions to 1,2-Bisketenes	688
23.15.1.2.1.1	Variation 1:	(Carboxy)ketenes and Succinic Anhydrides by Water Addition to 1,2-Bisketenes	691
23.15.1.2.2	Method 2:	Diamides by Amine Addition to 1,2-Bisketenes	692
23.15.1.2.2.1	Variation 1:	Carbamoyl-Substituted Esters by Successive Amine and Alcohol Addition	692

23.15.1.2.2.2	Variation 2:	A Cyclic Carbamoyl Ester by Addition of an Amino Alcohol to a 1,2-Bisketene	693
23.15.1.2.3	Method 3:	A Fumaroyl Bromide by Bromine Addition to a 1,2-Bisketene	693
23.15.1.2.4	Method 4:	Maleic Anhydride Formation by Aminoxyl Radical Addition to a 1,2-Bisketene	694
23.15.1.2.5	Method 5:	Furanone Formation by Dimerization of 1,2-Bisketenes	694
23.15.1.2.6	Method 6:	Naphthofuranones by [4+2] Cycloaddition of 1,2-Bisketenes with Pendant Alkenes	695
23.15.1.2.7	Method 7:	Cyclopropenes and Quinones by [2+1] and [4+2] Cycloaddition of 1,2-Bisketenes with Alkynes	695
23.15.1.2.8	Method 8:	A β -Lactone by [2+2] Cycloaddition of a 1,2-Bisketene with Acetaldehyde	697
23.15.1.2.9	Method 9:	Cyclopentenediones by [4+1] Cycloaddition of 1,2-Bisketenes with Carbenes and Diazoalkanes	697
23.15.1.2.10	Method 10:	Cyclopropenones and Alkynes by Photolysis of 1,2-Bisketenes	697
23.15.2	Product Subclass 2: 1,3- and Higher Bisketenes		699
23.15.2.1	Synthesis of Product Subclass 2		699
23.15.2.1.1	Method 1:	A Bisketene by Dehydration of a Dicarboxylic Acid	699
23.15.2.1.2	Method 2:	A Bisketene by Elimination from a Bis(isopropenyl) Ester	700
23.15.2.1.3	Method 3:	Bisketenes by Dehydrochlorination of Dicarboxylic Acid Chlorides	701
23.15.2.1.3.1	Variation 1:	Bisketenes by Dehydrochlorination of Dicarboxylic Acid Chlorides by a Shuttle Procedure with a Kinetic Base and a Stoichiometric Base	702
23.15.2.1.3.2	Variation 2:	1,4-Bis(oxovinyl)benzenes by Dehydrochlorination	705
23.15.2.1.4	Method 4:	Bisketenes by Ring Opening of Benzo-1,2-quinones	705
23.15.2.1.5	Method 5:	Bisketenes by Wolff Rearrangement of Bis(diazo ketones)	706
23.15.2.1.6	Method 6:	Bis- and Tris(oxovinyl)silanes by Thermolysis of (Ethoxyethyl)silanes	707
23.15.2.1.7	Method 7:	A 1,5-Bisketene by [4+2] Cycloaddition of Norbornadiene with a 1,3,4-Oxadiazine Followed by Nitrogen Elimination	710
23.15.2.1.8	Method 8:	A Bis(allenylketene) from a Bis(methylenecyclobutenone)	710
23.15.2.2	Applications of Product Subclass 2 in Organic Synthesis		711
23.15.2.2.1	Method 1:	Esters and Amides by Addition of Nucleophiles to Bisketenes	711
23.15.2.2.1.1	Variation 1:	Polyamides and Polyesters from Bisketenes and Diamines or Diols	711
23.15.3	Product Subclass 3: Bis(oxomethylene)cyclohexanes and -cyclohexadienes		712
23.15.3.1	Synthesis of Product Subclass 3		713
23.15.3.1.1	Method 1:	Bis(oxomethylene)cyclohexanes and -cyclohexadienes by Dehydrochlorination of Dicarboxylic Acid Chlorides	713
23.15.3.1.2	Method 2:	Bis(oxomethylene)cyclohexadienes by Dehalogenation of Terephthaloyl Halides	714
23.15.3.1.3	Method 3:	1,2-Bis(oxomethylene)cyclohexane by Ring Opening of a Cyclobutene-1,2-dione	714

23.15.3.1.4	Method 4:	5,6-Bis(oxomethylene)cyclohexa-1,3-diene by Ring Opening of a Cyclobutene-1,2-dione	715
23.15.3.1.4.1	Variation 1:	5,6-Bis(oxomethylene)cyclohexa-1,3-diene by Thermal Nitrogen Loss from Phthalazine-1,4-dione	716
23.15.3.1.5	Method 5:	5,6-Bis(oxomethylene)cyclohexa-1,3-diene by Cyclophane Cleavage	716
23.15.3.1.6	Method 6:	Bis(oxomethylene)cycloalkanes by Double Wolff Rearrangement	716
23.15.3.2	Applications of Product Subclass 3 in Organic Synthesis		717
23.15.3.2.1	Method 1:	Esters and Amides by Addition of Nucleophiles to Bisketenes	717
23.15.3.2.2	Method 2:	[4 + 2] Cycloadditions of 1,2-Bisketenes with Alkenes and Benzoquinones	718
23.15.3.2.3	Method 3:	Spiro[cyclopropane-1,1'(3'H)-isobenzofuran]-3'-ones by Cycloaddition of a 1,2-Bisketene with Alkenes	719
23.15.3.2.4	Method 4:	A 1,3,5-Oxathiazine by [4 + 2] Cycloaddition of a Bisketene with an Isocyanate	721
23.15.3.2.5	Method 5:	Benzyne by Photochemical Decarbonylation of 5,6-Bis(oxomethylene)cyclohexa-1,3-diene	721
23.15.3.2.5.1	Variation 1:	A Bicyclic Enyne by Photochemical Decarbonylation of a Bisketene	721
23.15.3.2.6	Method 6:	Polymerization of a 1,4-Bisketene by [2 + 2] Cyclodimerization	722
23.15.4	Product Subclass 4: Other Bisketenes		722
23.15.4.1	Synthesis of Product Subclass 4		722
23.15.4.1.1	Method 1:	Bis(acylketenes) by Thermolysis of Bis(dioxinones) and Bis(Meldrum's acid) Derivatives	722
23.15.4.1.2	Method 2:	A Tris(acylketene) by Thermolysis of a Triester	726
23.15.4.1.3	Method 3:	A Bis(acylketene) by Carbon Dioxide Addition to a Dinydiamine	726
23.15.4.1.4	Method 4:	Bis(acylketenes) by Wolff Rearrangement of Bis(diazo) Tetraketones	727
23.15.4.1.4.1	Variation 1:	Cyclic Bis(acylketene) Formation by a Wolff-Type Rearrangement	727
23.15.4.1.5	Method 5:	Bis(dienylketenes) by Photolysis of Bis(cyclohexadienones)	728
23.15.4.1.6	Method 6:	A Bis(oxovinyl)platinum Complex by Addition of a Ketene to an (Oxovinyl)platinum Complex	729
23.15.4.1.7	Method 7:	Bis(ketenechromium) Complexes from Bis(alkylidenechromium) Complexes	730
23.16	Product Class 16: Sulfur, Selenium, and Tellurium Analogues of Ketenes C. Spanka and E. Schaumann		
23.16	Product Class 16: Sulfur, Selenium, and Tellurium Analogues of Ketenes		735
23.16.1	Product Subclass 1: Thioketenes		735
23.16.1.1	Synthesis of Product Subclass 1		736
23.16.1.1.1	Method 1:	Sulfuration of Ketenes	736

23.16.1.1.2	Method 2:	Synthesis from Dithiocarboxylates	738
23.16.1.1.3	Method 3:	Elimination Reactions of Ketene <i>S,X</i> -Acetals	739
23.16.1.1.4	Method 4:	Synthesis by Cycloreversion	740
23.16.1.1.4.1	Variation 1:	[2 + 2] Cycloreversion of 2,4-Bis(alkylidene)-1,3-dithietanes (Thioketene Dimers) or 4-Alkylidene-1,3-dithietan-2-ones	740
23.16.1.1.4.2	Variation 2:	[3 + 2] Cycloreversion of 2-Alkylidene-1,3-dithiolane Derivatives	742
23.16.1.1.4.3	Variation 3:	1,2,3-Thiadiazoles as Stable Thioketene Precursors (Thio-Wolff Rearrangement)	746
23.16.1.1.5	Method 5:	Treatment of Alkylidenephosphanes with Carbon Disulfide	750
23.16.1.1.6	Method 6:	Thioketenes via Alkynyl Sulfides	751
23.16.1.1.6.1	Variation 1:	Protonation or Silylation of Alk-1-ynethiolates Followed by [1,3]-Hydrogen/Silicon Shift	753
23.16.1.1.6.2	Variation 2:	Thia-Cope Rearrangement of Alkynyl Allyl Sulfides	754
23.16.1.1.7	Methods 7:	Other Methods	758
23.16.2	Product Subclass 2: Cumulated Thioketenes and Their Derivatives		760
23.16.2.1	Synthesis of Product Subclass 2		760
23.16.2.1.1	Method 1:	Synthesis of Alkylidenethioketenes	760
23.16.2.1.2	Method 2:	Synthesis of (Arylimino)thioketenes	761
23.16.2.1.3	Method 3:	Synthesis of Carbon Sub sulfide (Propadienedithione)	762
23.16.3	Product Subclass 3: Thioketene S-Oxides		764
23.16.3.1	Synthesis of Product Subclass 3		764
23.16.3.1.1	Method 1:	Direct Oxidation of Thioketenes	764
23.16.3.1.2	Method 2:	[3 + 2] Cycloreversion of 1,3-Dithiolane 1,1,3-Trioxides	765
23.16.3.1.3	Method 3:	Retro-Diels–Alder Reaction	765
23.16.4	Product Subclass 4: Selenoketenes		766
23.16.4.1	Synthesis of Product Subclass 4		766
23.16.4.1.1	Method 1:	Rearrangement of Alkynyl Selenides	767
23.16.4.1.2	Method 2:	[3,3]-Sigmatropic Rearrangement of Alkynyl Allyl Selenides (Selena-Cope Rearrangement)	769
23.16.4.1.3	Method 3:	Nitrogen Extrusion from 1,2,3-Selenadiazoles	772
23.16.5	Product Subclass 5: Telluroketenes		776
23.17	Product Class 17: Ketenimines		
	H. Perst		
23.17	Product Class 17: Ketenimines		781
23.17.1	Product Subclass 1: Monoketenimines		783
23.17.1.1	Synthesis of Product Subclass 1		783
23.17.1.1.1	Synthesis by Formation of the C=C Bond		784
23.17.1.1.1.1	Method 1:	Dehydrocyanation of Imidoyl Cyanides	784
23.17.1.1.1.2	Method 2:	Dehydration of Carboxamides by Oxophilic Reagents in the Presence of Tertiary Amines	785

23.17.1.1.1.2.1	Variation 1:	Using Triphenylphosphine–Carbon Tetrachloride–Triethylamine	787
23.17.1.1.1.2.2	Variation 2:	Using Triphenylphosphine–Bromine–Triethylamine	788
23.17.1.1.1.2.3	Variation 3:	Using Diphosgene–Triethylamine	791
23.17.1.1.1.3	Method 3:	β -Elimination from Imidocarboxylic Acid Derivatives	793
23.17.1.1.1.3.1	Variation 1:	Dehydrohalogenation of Imidoyl Halides	793
23.17.1.1.1.3.2	Variation 2:	Dehalogenation of α -Haloimidoyl Halides	795
23.17.1.1.1.3.3	Variation 3:	β -Elimination from Imidocarboxylic Acid Esters	796
23.17.1.1.1.4	Method 4:	β -Elimination from Other Precursors via Imidocarboxylic Acid Derivatives Formed In Situ	798
23.17.1.1.1.4.1	Variation 1:	From Oximes	798
23.17.1.1.1.4.2	Variation 2:	From 2,2-Dihaloaziridines	799
23.17.1.1.1.5	Method 5:	Elimination of Hydrogen Sulfide from Thioamides	801
23.17.1.1.1.5.1	Variation 1:	From Thioamides via Imidoyl Chlorides	801
23.17.1.1.1.5.2	Variation 2:	From Methyl Imidothioesters	802
23.17.1.1.1.6	Method 6:	Connective Alkene Formation by Reaction of Phosponium Ylides or Related Reagents with Azaheterocumulenes	804
23.17.1.1.1.6.1	Variation 1:	Ketenimines from Wittig Reaction of Alkylidenetriphenyl- phosphoranes with Isocyanates	804
23.17.1.1.1.6.2	Variation 2:	Reaction of Alkylidenephosphoranes with Isothiocyanates or Carbodiimides	808
23.17.1.1.1.6.3	Variation 3:	Horner–Wittig Reaction of Isocyanates with Carbanions Derived from Diethyl Phosphonates	809
23.17.1.1.1.7	Method 7:	Cycloreversion	809
23.17.1.1.1.8	Method 8:	Cheletropic Reactions (Sulfur Extrusion from 2,5-Dihydroisothiazol-5-imines)	811
23.17.1.1.1.9	Method 9:	Addition of Isocyanides to Carbenes	812
23.17.1.1.1.10	Method 10:	Addition of Isocyanides to Suitable Carbon Fragments in the Coordination Sphere of Transition–Metal Complexes ...	814
23.17.1.1.1.10.1	Variation 1:	Addition of Carbenes to Transition Metal–Isocyanide Complexes	814
23.17.1.1.1.10.2	Variation 2:	Addition of Isocyanides to Transition Metal–Carbene Complexes	815
23.17.1.1.1.10.3	Variation 3:	Rearrangement of a Transition Metal–Isocyanide Complex ...	816
23.17.1.1.1.10.4	Variation 4:	Palladium-Assisted Reactions of Isocyanides with Alkyl Chlorides	817
23.17.1.1.1.11	Method 11:	Addition of Isocyanides to Alkynes	818
23.17.1.1.1.12	Method 12:	Addition of Isocyanides to Cyclopropene Derivatives	820
23.17.1.1.1.13	Method 13:	Iminocarbene–Ketenimine Rearrangement	821
23.17.1.1.1.13.1	Variation 1:	Photochemical Transformation of 2-(Cyanoimino)-1-diazoal- kanes	821
23.17.1.1.1.13.2	Variation 2:	Thermal or Photochemical Transformation of 1-Aryl-1,2,3-triazoles and 1 <i>H</i> -Benzotriazoles	822
23.17.1.1.2	Synthesis by	Formation of the C=N Bond	824
23.17.1.1.2.1	Method 1:	Dehydrocyanation of α -Cyanoenamines	825
23.17.1.1.2.2	Method 2:	Dehydrohalogenation of α -Haloenamines	826
23.17.1.1.2.3	Method 3:	Eliminations from Ketene <i>N,S</i> -Acetals	828

23.17.1.1.2.4	Method 4:	Connective Imine Formation by Aza-Wittig Reaction of Iminophosphoranes or Related Compounds with Ketenes	831
23.17.1.1.2.4.1	Variation 1:	With Preformed Iminophosphoranes and Preformed Ketenes	831
23.17.1.1.2.4.2	Variation 2:	With Preformed Iminophosphoranes and In Situ Generated Ketenes	833
23.17.1.1.2.4.3	Variation 3:	With In Situ Generated Iminophosphoranes and Preformed Ketenes	833
23.17.1.1.2.4.4	Variation 4:	Reaction of N-Substituted Diethyl Phosphoramidate Anions with Ketenes	837
23.17.1.1.2.5	Method 5:	Connective Imine Formation by the Reaction of Thioketenes with Sulfur Diimides	838
23.17.1.1.2.6	Method 6:	Deprotonation and Ring Opening of Isoxazolium Salts	839
23.17.1.1.2.7	Method 7:	Cycloreversion	840
23.17.1.1.2.8	Method 8:	Cheletropic Reactions	840
23.17.1.1.2.9	Method 9:	Thermolysis of Vinyl Azides	843
23.17.1.1.2.10	Method 10:	Photolysis of Vinyl Azides or Aryl Azides	844
23.17.1.1.3	Synthesis by Formation of the C=C and C=N Bonds		845
23.17.1.1.3.1	Method 1:	Addition–Elimination Reactions with Nitriles	845
23.17.1.1.3.1.1	Variation 1:	Via Nitrilium Ions and Subsequent Deprotonation at the β -Carbon Atom	845
23.17.1.1.3.1.2	Variation 2:	Via Nitrile Anions and Subsequent Addition of Electrophiles to the Nitrogen Atom	846
23.17.1.1.3.1.3	Variation 3:	Addition of Trialkyl Phosphites to α -Halo Nitriles and Elimination of Haloalkanes	849
23.17.1.1.3.2	Method 2:	1,4-Addition to α,β -Unsaturated Nitriles	851
23.17.1.1.3.3	Method 3:	[2,3]-Sigmatropic Rearrangement of 1-Cyanoalkyl Methylene-sulfur Ylides	852
23.17.1.2	Applications of Product Subclass 1 in Organic Synthesis		854
23.17.1.2.1	Method 1:	Addition of Protic Nucleophiles and Related Compounds	854
23.17.1.2.2	Method 2:	[2 + 2]-Cycloaddition Reactions of Ketenimines	856
23.17.1.2.2.1	Variation 1:	With Alkenes or Alkynes	856
23.17.1.2.2.2	Variation 2:	With Carbonyl Compounds	858
23.17.1.2.2.3	Variation 3:	With Thiocarbonyl Compounds	859
23.17.1.2.2.4	Variation 4:	With Imines	861
23.17.1.2.2.5	Variation 5:	With N=X Systems	862
23.17.1.2.2.6	Variation 6:	With Heterocumulenes	864
23.17.1.2.3	Method 3:	[3 + 2]-Cycloaddition Reactions of Ketenimines	865
23.17.1.2.3.1	Variation 1:	With 1,3-Dipoles	865
23.17.1.2.3.2	Variation 2:	With Three-Membered Heterocycles	867
23.17.1.2.3.3	Variation 3:	Via Intramolecular Reactions of C-(Aziridin-1-ylimino)ketenimines	869
23.17.1.2.4	Method 4:	[4 + 2]-Cycloaddition Reactions Using Ketenimines as Dienophiles	870
23.17.1.2.5	Method 5:	[4 + 2]-Cycloaddition Reactions Using Ketenimines as 1,3-Dienes	871
23.17.1.2.5.1	Variation 1:	From a 1,3-Diene Formed by the Ketenimine C=C Bond and a Suitable C-Substituent	874

23.17.1.2.5.2	Variation 2:	From a 1,3-Diene Formed by the Ketenimine C=C Bond and a C-Aryl Substituent; Intramolecular [4 + 2]-Cycloaddition Reactions	877
23.17.1.2.5.3	Variation 3:	From a 1,3-Diene Formed by the Ketenimine C=N Bond and a Suitable N-Substituent	879
23.17.1.2.5.4	Variation 4:	From a 1,3-Diene Formed by the Ketenimine C=N Bond and an N-Aryl Substituent	882
23.17.1.2.6	Method 6:	Rearrangements of Ketenimines	884
23.17.1.2.7	Method 7:	Reactions with Loss of the N-Substituent	885
23.17.1.2.7.1	Variation 1:	Thermal Cleavage	885
23.17.1.2.7.2	Variation 2:	Addition–Elimination Reactions of N-Silyl- or N-Stannylketenimines	886
23.17.1.2.7.3	Variation 3:	Alk-2-enitriles from C,C,N-Tris(trimethylsilyl)ketenimine and Aldehydes	888
23.17.2	Product Subclass 2: Bisiminopropa-1,2-dienes		889
23.17.2.1	Synthesis of Product Subclass 2		889
23.17.2.1.1	Method 1:	Thermolysis of Isoxazonoketene N,S-Acetals	889
	Keyword Index		899
	Author Index		1013
	Abbreviations		1049