

---

**Volume 23:  
Three Carbon–Heteroatom Bonds:  
Ketenes and Derivatives**

	<b>Preface</b> .....	V
	<b>Table of Contents</b> .....	IX
	<b>Introduction</b>	
	R. L. Danheiser .....	1
<b>23.1</b>	<b>Product Class 1: Ketene</b>	
	T. T. Tidwell .....	15
<b>23.2</b>	<b>Product Class 2: Silylketenes</b>	
	D. M. George and R. L. Danheiser .....	53
<b>23.3</b>	<b>Product Class 3: Halogen-Substituted Ketenes</b>	
	T. T. Tidwell .....	101
<b>23.4</b>	<b>Product Class 4: Oxygen-Substituted Ketenes</b>	
	C. Palomo, M. Oiarbide, and J. M. Aizpurua .....	169
<b>23.5</b>	<b>Product Class 5: Sulfur- and Selenium-Substituted Ketenes</b>	
	C. Palomo, J. M. Aizpurua, I. Ganboa, and E. Gómez-Bengoa .....	199
<b>23.6</b>	<b>Product Class 6: Nitrogen- and Phosphorus-Substituted Ketenes</b>	
	C. Palomo and J. M. Aizpurua .....	221
<b>23.7</b>	<b>Product Class 7: Alkylideneketenes</b>	
	W. F. Austin, J. J. Kowalczyk, G. B. Dudley, and R. L. Danheiser .....	245
<b>23.8</b>	<b>Product Class 8: Cyanoketenes</b>	
	H. W. Moore .....	259
<b>23.9</b>	<b>Product Class 9: Acylketenes</b>	
	G. Kollenz and S. Ebner .....	271
<b>23.10</b>	<b>Product Class 10: Imidoalkylketenes</b>	
	G. Kollenz .....	351
<b>23.11</b>	<b>Product Class 11: Alk-1-ynylketenes</b>	
	H. W. Moore .....	381
<b>23.12</b>	<b>Product Class 12: Aryl- and Hetarylketenes</b>	
	T. T. Tidwell .....	391
<b>23.13</b>	<b>Product Class 13: Alkenylketenes</b>	
	R. L. Danheiser, G. B. Dudley, and W. F. Austin .....	493
<b>23.14</b>	<b>Product Class 14: Alkyl- and Cycloalkylketenes</b>	
	T. T. Tidwell .....	569

<b>23.15</b>	<b>Product Class 15: Bisketenes</b>	
	T. T. Tidwell .....	679
<b>23.16</b>	<b>Product Class 16: Sulfur, Selenium, and Tellurium Analogues of Ketenes</b>	
	C. Spanka and E. Schaumann .....	735
<b>23.17</b>	<b>Product Class 17: Ketenimines</b>	
	H. Perst .....	781
	<b>Keyword Index</b> .....	899
	<b>Author Index</b> .....	1013
	<b>Abbreviations</b> .....	1049

## Table of Contents

### Introduction

R. L. Danheiser

<b>Introduction</b> .....	1
---------------------------	---

### 23.1 Product Class 1: Ketene

T. T. Tidwell

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

<b>23.2</b>	<b>Product Class 2: Silylketenes</b> D. M. George and R. L. Danheiser	
<b>23.2</b>	<b>Product Class 2: Silylketenes</b> .....	53
<b>23.2.1</b>	<b>Product Subclass 1: Silyl-Substituted Aldoketenes</b> .....	54
<b>23.2.1.1</b>	Synthesis of Product Subclass 1 .....	54
<b>23.2.1.1.1</b>	Method 1: Dehydrohalogenation of Acyl Halides .....	54
<b>23.2.1.1.2</b>	Method 2: Dehydration of Silylacetic Acids .....	55
<b>23.2.1.1.3</b>	Method 3: Thermolysis of 1-Alkoxy-2-silylacetylenes .....	55
<b>23.2.1.1.4</b>	Method 4: 1,3-Silyl Shift of (Trimethylsiloxy)acetylene .....	57
<b>23.2.1.1.5</b>	Method 5: Thermolysis of Silylacetic Anhydrides .....	57
<b>23.2.1.2</b>	Applications of Product Subclass 1 in Organic Synthesis .....	58
<b>23.2.1.2.1</b>	Method 1: [2 + 2] Cycloadditions Leading to $\beta$ -Lactones .....	58
<b>23.2.1.2.2</b>	Method 2: [2 + 2] Cycloadditions Leading to $\beta$ -Lactams .....	64
<b>23.2.1.2.3</b>	Method 3: [2 + 2] Cycloadditions Leading to Cyclobutanones .....	65
<b>23.2.1.2.4</b>	Method 4: Formation of Allenes via Wittig Reaction with Phosphorus Ylides .....	65
<b>23.2.1.2.5</b>	Method 5: Formation of Ketenimines via Reaction with Iminophosphoranes .....	66
<b>23.2.1.2.6</b>	Method 6: Formation of Cyclopropanones and Cyclobutanones via Reaction with Diazo Compounds .....	67
<b>23.2.1.2.7</b>	Method 7: Formation of $\alpha$ -Silyl Ketones .....	68
<b>23.2.1.2.8</b>	Method 8: Formation of 2 <i>H</i> -1-Benzopyran-2-ones from Phenols .....	70
<b>23.2.1.2.9</b>	Method 9: (Trimethylsilyl)acetylation of Alcohols and Amines .....	71
<b>23.2.2</b>	<b>Product Subclass 2: (Silyl)(trialkylmetal)ketenes</b> .....	72
<b>23.2.2.1</b>	Synthesis of Product Subclass 2 .....	72
<b>23.2.2.1.1</b>	Method 1: Elimination from (Silyl)(trialkylmetal)acetates .....	72
<b>23.2.2.1.2</b>	Method 2: Trapping of Lithium 2-Lithioacetylen-1-olate Generated from 2-Phenyl-2,3-dihydrofurans or 3-Phenylisoxazoles .....	72
<b>23.2.2.1.3</b>	Method 3: Carbonylation and Trapping of Lithiated Diazo(trimethyl- silyl)methane .....	73
<b>23.2.2.1.4</b>	Method 4: Lithiation of (Trialkylsilyl)ketenes and Trapping with Chlorosilanes .....	74
<b>23.2.2.1.5</b>	Method 5: Synthesis of Bis(silyl)ketenes from Other Bis(silyl)ketenes via Potassium 2-Silylacetylen-1-olates .....	74
<b>23.2.3</b>	<b>Product Subclass 3: (Aryl)- and (Alkyl)silylketenes</b> .....	76
<b>23.2.3.1</b>	Synthesis of Product Subclass 3 .....	76
<b>23.2.3.1.1</b>	Method 1: 1,3-Silyl Shift of 1-(Siloxy)alk-1-yne .....	76
<b>23.2.3.1.2</b>	Method 2: Wolff Rearrangement of $\alpha$ -Diazo- $\alpha$ -silyl Ketones .....	77
<b>23.2.3.1.2.1</b>	Variation 1: By Thermolysis .....	77
<b>23.2.3.1.2.2</b>	Variation 2: By Photolysis .....	77
<b>23.2.3.1.2.3</b>	Variation 3: By Metal Catalysis .....	78
<b>23.2.3.2</b>	Applications of Product Subclass 3 in Organic Synthesis .....	79
<b>23.2.3.2.1</b>	Method 1: [2 + 2] Cycloadditions Leading to $\beta$ -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	<b>Product Subclass 4: Silyl(vinyl)ketenes</b> .....	84
23.2.4.1	Synthesis of Product Subclass 4 .....	84
23.2.4.1.1	Method 1: Dehydrohalogenation of $\alpha$ -Silyl- $\alpha,\beta$ -unsaturated Acid Chlorides	84
23.2.4.1.2	Method 2: Wolff Rearrangement of $\alpha$ -Diazo- $\alpha$ -silyl $\alpha',\beta'$ -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	<b>Product Subclass 5: Miscellaneous Silylketenes</b> .....	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	<b>Product Class 3: Halogen-Substituted Ketenes</b> T. T. Tidwell	
23.3	<b>Product Class 3: Halogen-Substituted Ketenes</b> .....	101
23.3.1	<b>Product Subclass 1: Fluoro- and Difluoroketenes</b> .....	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 $\alpha$ -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:	$\beta$ -Lactams by [2 + 2] Cycloaddition of Fluoroketenes with Imines .....	113
23.3.2	<b>Product Class 2: Chloro- and Dichloroketenes</b> .....		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-Chloroacetyl 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-Chloroacetyl 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:	Cyclobutenones by [2 + 2] Cycloaddition of Chloroketenes with Alkynes .....	138
23.3.2.2.4	Method 4:	$\beta$ -Lactams by [2 + 2] Cycloaddition of Chloroketenes with Imines .....	140
23.3.2.2.4.1	Variation 1:	$\beta$ - and $\delta$ -Lactams by [2 + 2]- and [4 + 2]-Cycloaddition Reactions of Chloroketenes with Vinylic Imines .....	141
23.3.2.2.4.2	Variation 2:	$\gamma$ -Lactams and $\gamma$ -Lactones by [3 + 2] Cycloaddition of Dichloroketene with <i>N</i> -Vinylsulfimides .....	143
23.3.2.2.5	Method 5:	$\beta$ -Lactones by [2 + 2] Cycloaddition of Chloroketenes with Carbonyl Compounds .....	146
23.3.2.2.6	Method 6:	$\gamma$ -Lactones from Dichloroketene with Vinyl Sulfoxides .....	148
23.3.2.2.6.1	Variation 1:	$\gamma$ -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:	$\gamma$ -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	<b>Product Subclass 3: Bromo- and Iodoketenes</b>	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: $\beta$ - and $\delta$ -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	<b>Product Class 4: Oxygen-Substituted Ketenes</b> C. Palomo, M. Oiarbide, and J. M. Aizpuru	
23.4	<b>Product Class 4: Oxygen-Substituted Ketenes</b>	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 $\alpha$ -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, $\beta$ -Lactones, and $\beta$ -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	<b>Product Class 5: Sulfur- and Selenium-Substituted Ketenes</b> C. Palomo, J. M. Aizpurua, I. Ganboa, and E. Gómez-Bengoa		
23.5	<b>Product Class 5: Sulfur- and Selenium-Substituted Ketenes</b> .....		
23.5.1	<b>Product Subclass 1: Sulfur-Substituted Ketenes</b> .....		
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 $\beta$ -Lactams .....	212
23.5.1.2.2	Method 2:	Formation of Allenes by Wittig Alkenation .....	214
23.5.2	<b>Product Subclass 2: Selenium-Substituted Ketenes</b> .....		
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 $\beta$ -Lactams .....	217
23.6	<b>Product Class 6: Nitrogen- and Phosphorus-Substituted Ketenes</b> C. Palomo and J. M. Aizpurua		
23.6	<b>Product Class 6: Nitrogen- and Phosphorus-Substituted Ketenes</b> .....		
23.6.1	<b>Product Subclass 1: Nitrogen-Substituted Ketenes</b> .....		
23.6.1.1	Synthesis of Product Subclass 1 .....		

23.6.1.1.1	Method 1: Elimination Reactions of $\alpha$ -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 $\beta$ -Lactams	230
23.6.1.2.4	Method 4: Lewis Acid Catalyzed Bellus–Claisen Rearrangement	233
23.6.2	<b>Product Subclass 2: Phosphorus-Substituted Ketenes</b>	234
23.6.2.1	Synthesis of Product Subclass 2	235
23.6.2.1.1	Method 1: Elimination Reactions of $\alpha$ -Phosphorylcarboxylic Acid Derivatives	235
23.6.2.1.2	Method 2: Wolff Rearrangement of $\alpha$ -Diazo- $\beta$ -oxophosphonates	238
23.6.2.1.3	Method 3: Dehydroalkoxylation of $\alpha$ -Triarylphosphoranylidene Esters	239
23.6.2.1.4	Method 4: Thermolysis of Phosphinoethynyl Ethers	240
23.7	<b>Product Class 7: Alkylideneketenes</b> W. F. Austin, J. J. Kowalczyk, G. B. Dudley, and R. L. Danheiser	
23.7	<b>Product Class 7: Alkylideneketenes</b>	245
23.7.1	<b>Product Subclass 1: Substituted Methyleneketenes</b>	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 $\alpha$ -Alkylidene-Substituted $\beta$ -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	<b>Product Subclass 2: Carbon Suboxide</b>	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

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

<b>23.9.3</b>	<b>Product Subclass 3: <math>\alpha</math>-(Oxomethylene)cycloalkenones</b> .....	291
<b>23.9.3.1</b>	Synthesis of Product Subclass 3 .....	291
<b>23.9.3.1.1</b>	Method 1: Thermolysis Reactions .....	291
<b>23.9.3.1.1.1</b>	Variation 1: Of Salicylic Acid Derivatives .....	291
<b>23.9.3.1.1.2</b>	Variation 2: Of Fused Furan-2,3-diones .....	292
<b>23.9.3.1.1.3</b>	Variation 3: Of 2-Diazo-1 <i>H</i> -indene-1,3(2 <i>H</i> )-dione .....	293
<b>23.9.3.1.2</b>	Method 2: Photolysis Reactions .....	293
<b>23.9.3.1.2.1</b>	Variation 1: Of 2-Phenyl-4 <i>H</i> -1,3-benzodioxin-4-one .....	293
<b>23.9.3.1.2.2</b>	Variation 2: Of 2,3-Benzodioxin-1,4-dione .....	293
<b>23.9.3.1.2.3</b>	Variation 3: Of Fused 2-Diazo-1,3-diketones .....	294
<b>23.9.3.1.3</b>	Method 3: Addition of Alkynes to Carbon Suboxide .....	295
<b>23.9.4</b>	<b>Product Subclass 4: <math>\alpha</math>-(Oxomethylene)heterocycloalkanones</b> .....	296
<b>23.9.4.1</b>	Synthesis of Product Subclass 4 .....	296
<b>23.9.4.1.1</b>	Method 1: Thermolysis of a Furo[3,4- <i>d</i> ]-1,3-dioxinone .....	296
<b>23.9.4.1.2</b>	Method 2: Photolysis Reactions .....	297
<b>23.9.4.1.2.1</b>	Variation 1: Of 5-Diazo-2,2-dimethyl-1,3-dioxane-4,6-dione .....	297
<b>23.9.4.1.2.2</b>	Variation 2: Of 3-Diazo-1-methylquinoline-2,4(1 <i>H</i> ,3 <i>H</i> )-dione .....	298
<b>23.9.5</b>	<b>Product Subclass 5: Dialkanoylketenes</b> .....	299
<b>23.9.5.1</b>	Synthesis of Product Subclass 5 .....	299
<b>23.9.5.1.1</b>	Method 1: Flash-Vacuum Pyrolysis of 5- <i>tert</i> -Butyl-4-pivaloylfuran-2,3-dione .....	299
<b>23.9.5.2</b>	Applications of Product Subclass 5 in Organic Synthesis .....	300
<b>23.9.5.2.1</b>	Method 1: Cycloaddition Reactions .....	300
<b>23.9.5.2.2</b>	Method 2: Addition of Nucleophiles .....	301
<b>23.9.6</b>	<b>Product Subclass 6: Monoaroylketenes</b> .....	302
<b>23.9.6.1</b>	Synthesis of Product Subclass 6 .....	302
<b>23.9.6.1.1</b>	Method 1: Thermolysis Reactions .....	302
<b>23.9.6.1.1.1</b>	Variation 1: Of $\beta$ -Oxo Esters .....	302
<b>23.9.6.1.1.2</b>	Variation 2: Of 4 <i>H</i> -1,3-Dioxin-4-ones and 1,3-Dioxane-4,6-diones .....	302
<b>23.9.6.1.1.3</b>	Variation 3: Of Furan-2,3-diones .....	303
<b>23.9.6.1.1.4</b>	Variation 4: Of 2-Diazo-1,3-diketones .....	305
<b>23.9.6.1.2</b>	Method 2: Photolysis Reactions .....	310
<b>23.9.6.1.2.1</b>	Variation 1: Of 5-Phenylfuran-2,3-dione .....	310
<b>23.9.6.1.2.2</b>	Variation 2: Of 2-Diazo-1,3-diketones .....	310
<b>23.9.6.1.2.3</b>	Variation 3: Of a Mesoionic Compound .....	311
<b>23.9.7</b>	<b>Product Subclass 7: Diaroylketenes</b> .....	311
<b>23.9.7.1</b>	Synthesis of Product Subclass 7 .....	311
<b>23.9.7.1.1</b>	Method 1: Flash-Vacuum Pyrolysis of 4-Benzoyl-5-phenylfuran-2,3-dione .....	311
<b>23.9.7.1.2</b>	Method 2: Thermolysis of 4-Benzoyl-5-phenylfuran-2,3-dione .....	312
<b>23.9.8</b>	<b>Product Subclass 8: Carboxyketenes</b> .....	314
<b>23.9.8.1</b>	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	<b>Product Subclass 9: (Alkoxy carbonyl)ketenes</b>	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- <i>a</i> ]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	<b>Product Subclass 10: Acyl(alkoxy carbonyl)ketenes</b>	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	<b>Product Subclass 11: Bis(alkoxy carbonyl)ketenes</b>	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	<b>Product Subclass 12: (Chloro carbonyl)ketenes</b>	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	<b>Product Subclass 13: Fluorinated Acylketenes</b>	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-trifluoroacetate	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		<b>Product Subclass 14: Acyl(phosphoryl)ketenes and Acyl(trialkylmetal)ketenes</b>	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		<b>Product Class 10: Imidoylketenes</b>	
		G. Kollenz	
23.10		<b>Product Class 10: Imidoylketenes</b>	351
23.10.1		<b>Product Subclass 1: <i>N</i>-Unsubstituted and <i>N</i>-Alkyl-Substituted Imidoylketenes</b>	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		<b>Product Subclass 2: (<i>N</i>-Acylimidoyl)ketenes</b>	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		<b>Product Subclass 3: (<i>N</i>-Arylimidoyl)ketenes</b>	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	<b>Product Subclass 4: <i>N</i>-Hetaryl-Substituted Imidoylketenes</b>		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	<b>Product Subclass 5: Acyl(imidoyl)ketenes</b>		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	<b>Product Subclass 6: <i>N</i>-Unsubstituted 6-(Oxomethylene)cyclohexa-2,4-dien-1-imines</b>		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	<b>Product Subclass 7: <i>N</i>-Substituted 6-(Oxomethylene)cyclohexa-2,4-dien-1-imines</b>		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	<b>Product Class 11: Alk-1-ynylketenes</b>		
	H. W. Moore		
23.11	<b>Product Class 11: Alk-1-ynylketenes</b>		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

<b>23.12</b>	<b>Product Class 12: Aryl- and Hetarylketenes</b>	
	T. T. Tidwell	
<hr/>		
<b>23.12</b>	<b>Product Class 12: Aryl- and Hetarylketenes</b>	391
<b>23.12.1</b>	<b>Product Subclass 1: Monoarylketenes</b>	392
<b>23.12.1.1</b>	Synthesis of Product Subclass 1	393
<b>23.12.1.1.1</b>	Method 1: Monoarylketenes by Dehydration of Arylacetic Acids	393
<b>23.12.1.1.2</b>	Method 2: Monoarylketenes from Arylacetic Anhydrides	393
<b>23.12.1.1.2.1</b>	Variation 1: Arylketene by Decarboxylation of Arylmalonic Acids	394
<b>23.12.1.1.3</b>	Method 3: Monoarylketenes from Arylacetate Esters	394
<b>23.12.1.1.4</b>	Method 4: Monoarylketenes by Dehydrohalogenation of Arylacetyl Chlorides	395
<b>23.12.1.1.4.1</b>	Variation 1: Monoarylketenes by Dehydrochlorination Using a Shuttle Procedure with a Kinetic Base and a Stoichiometric Base	396
<b>23.12.1.1.5</b>	Method 5: Monoarylketenes by Dehalogenation of Arylhaloacetyl Halides	399
<b>23.12.1.1.6</b>	Method 6: Monoarylketenes by Wolff Rearrangement of $\alpha$ -Diazo Ketones	400
<b>23.12.1.1.6.1</b>	Variation 1: Metal-Catalyzed Wolff Rearrangement	401
<b>23.12.1.1.6.2</b>	Variation 2: Monoarylketenes by Microwave and Ultrasound-Enhanced Wolff Rearrangement	403
<b>23.12.1.1.6.3</b>	Variation 3: Monoarylketenes by Photochemical Wolff Rearrangement	404
<b>23.12.1.1.6.4</b>	Variation 4: Phenylketene by Wolff-Type Rearrangement of a Sulfur Ylide	405
<b>23.12.1.1.7</b>	Method 7: Monoarylketenes from Ynols and Ynolates	405
<b>23.12.1.1.8</b>	Method 8: Monoarylketenes by Oxidation of Arylacetylenes	406
<b>23.12.1.1.8.1</b>	Variation 1: Monoarylketenes by Oxidation of Lithium Arylacetylides	407
<b>23.12.1.1.8.2</b>	Variation 2: Monoarylketenes by Ruthenium-Catalyzed Alkyne Oxygenation	408
<b>23.12.1.1.9</b>	Method 9: Monoarylketenes from Metal–Carbene Complexes	409
<b>23.12.1.2</b>	Applications of Product Subclass 1 in Organic Synthesis	410
<b>23.12.1.2.1</b>	Method 1: Esters and Amides by Addition of Nucleophiles to Monoarylketenes	410
<b>23.12.1.2.2</b>	Method 2: Ketones and Vinyl Ethers by Addition of Carbon Electrophiles	410
<b>23.12.1.2.3</b>	Method 3: <i>N</i> -Aroyloxyamines by Aminoxyl Radical Addition to Monoarylketenes	411
<b>23.12.1.2.4</b>	Method 4: Cyclobutanones by [2 + 2] Cycloaddition with Alkenes and Dienes	412
<b>23.12.1.2.5</b>	Method 5: Cyclobutenones by [2 + 2] Cycloaddition of Monoarylketenes with Alkynes	414
<b>23.12.1.2.6</b>	Method 6: $\beta$ -Lactams by [2 + 2] Cycloaddition of Monoarylketenes with Imines	416
<b>23.12.1.2.6.1</b>	Variation 1: Pyrimidinones by [4 + 2] Cycloaddition of Monoarylketenes with 1,3-Diazabuta-1,3-dienes	418
<b>23.12.1.2.7</b>	Method 7: 2-Arylacetate Derivatives by [4 + 2] Cycloaddition of <i>o</i> -Chloranil with Ketene Enolates	419
<b>23.12.1.2.8</b>	Method 8: Carbene Formation by Decarbonylation of Monoarylketenes	419
<b>23.12.2</b>	<b>Product Subclass 2: Alkyl(aryl)- and Aryl(vinyl)ketenes</b>	420
<b>23.12.2.1</b>	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 $\alpha$ -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:	$\beta$ -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	<b>Product Subclass 3: Diarylketenes</b>		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 $\alpha$ -Diazo Ketones	448
23.12.3.1.5.1	Variation 1:	Diarylketenes by Photochemical Wolff Rearrangement of $\alpha$ -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:	$\beta$ -Lactams by [2 + 2] Cycloaddition with Imines	459
23.12.3.2.7.1	Variation 1:	$\delta$ -Lactams by [4 + 2] Cycloaddition with Chiral 2-Vinyl-4,5-dihydrothiazoles	461
23.12.3.2.8	Method 8:	$\beta$ -Lactones by [2 + 2] Cycloaddition with Carbonyl Groups	462
23.12.3.2.8.1	Variation 1:	$\gamma$ -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		<b>Product Subclass 4: Fulvenones</b>	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 $\alpha$ -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		<b>Product Subclass 5: Hetarylketenes</b>	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 $\alpha$ -Diazo Ketones ..	476
23.12.5.1.4.1	Variation 1:	Hetarylketenes by Rhodium-Catalyzed Wolff Rearrangement of $\alpha$ -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	<b>Product Subclass 6: Ferrocenylketenes</b> .....		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 $\alpha$ -Diazo Ketones .....	485
23.13	<b>Product Class 13: Alkenylketenes</b>		
	R. L. Danheiser, G. B. Dudley, and W. F. Austin		
23.13	<b>Product Class 13: Alkenylketenes</b> .....		493
23.13.1	<b>Product Subclass 1: Vinylketenes</b> .....		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 $\alpha'$ -Diazo- $\alpha,\beta$ -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 $\beta$ -Lactams .....	520
23.13.2	<b>Product Subclass 2: 1,3-Dienylketenes and (2-Arylviny)ketenes</b> .....		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 $\alpha'$ -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	<b>Product Subclass 3: Alk-1-en-3-ynylketenes</b>		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	<b>Product Class 14: Alkyl- and Cycloalkylketenes</b>		
	T. T. Tidwell		
23.14	<b>Product Class 14: Alkyl- and Cycloalkylketenes</b>		569
23.14.1	<b>Product Subclass 1: Monoalkylketenes</b>		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:	$\beta$ -Amino Acid Derivatives by the Arndt–Eistert Reaction .....	593
23.14.1.2.2.3	Variation 3:	$\beta$ -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:	$\gamma$ -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- $\beta$ -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:	$\beta$ -Lactams by [2 + 2] Cycloaddition of Monoalkylketenes with Imines .....	608
23.14.1.2.9	Method 9:	$\beta$ -Lactones by [2 + 2] Cycloaddition of Monoalkylketenes with Aldehydes .....	609
23.14.1.2.10	Method 10:	$\gamma$ -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	<b>Product Subclass 2: Dialkylketenes and (Oxomethylene)cycloalkanes</b> .....		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 $\alpha$ -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:	$\beta$ -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:	$\beta$ -Lactones by [2 + 2] Cycloaddition of Dialkylketenes with Aldehydes .....	655
23.14.2.2.7.1	Variation 1:	$\beta$ -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		<b>Product Subclass 3: Cyclopropylketene, (Cycloprop-2-enyl)ketene, and Oxiranylketene</b> .....	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		<b>Product Subclass 4: (Fluoroalkyl)ketenes</b> .....	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		<b>Product Class 15: Bisketenes</b> T. T. Tidwell	
23.15		<b>Product Class 15: Bisketenes</b> .....	679
23.15.1		<b>Product Subclass 1: 1,2-Bisketenes</b> .....	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 $\beta$ -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	<b>Product Subclass 2: 1,3- and Higher Bisketenes</b>		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	<b>Product Subclass 3: Bis(oxomethylene)cyclohexanes and -cyclohexadienes</b>		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	<b>Product Subclass 4: Other Bisketenes</b>		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 Diynediamine	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	<b>Product Class 16: Sulfur, Selenium, and Tellurium Analogues of Ketenes</b> C. Spanka and E. Schaumann		
23.16	<b>Product Class 16: Sulfur, Selenium, and Tellurium Analogues of Ketenes</b>		735
23.16.1	<b>Product Subclass 1: Thioketenes</b>		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 S,X-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 Alkylidenephosphoranes 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	<b>Product Subclass 2: Cumulated Thioketenes and Their Derivatives</b>		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	<b>Product Subclass 3: Thioketene S-Oxides</b>		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	<b>Product Subclass 4: Selenoketenes</b>		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	<b>Product Subclass 5: Telluroketenes</b>		776
23.17	<b>Product Class 17: Ketenimines</b>		
	H. Perst		
23.17	<b>Product Class 17: Ketenimines</b>		781
23.17.1	<b>Product Subclass 1: Monoketenimines</b>		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:	$\beta$ -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 $\alpha$ -Haloimidoyl Halides .....	795
23.17.1.1.1.3.3	Variation 3:	$\beta$ -Elimination from Imidocarboxylic Acid Esters .....	796
23.17.1.1.1.4	Method 4:	$\beta$ -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 Phosphonium 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 $\alpha$ -Cyanoenamines .....	825
23.17.1.1.2.2	Method 2:	Dehydrohalogenation of $\alpha$ -Haloenamines .....	826
23.17.1.1.2.3	Method 3:	Eliminations from Ketene <i>N,S</i> -Acetals .....	828



---

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 <i>N</i> -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 <i>N</i> -Silyl- or <i>N</i> -Stannylketenimines .....	886
23.17.1.2.7.3	Variation 3:	Alk-2-enenitriles from <i>C,C,N</i> -Tris(trimethylsilyl)ketenimine and Aldehydes .....	888
23.17.2	<b>Product Subclass 2: Bisiminopropa-1,2-dienes</b> .....		889
23.17.2.1	Synthesis of Product Subclass 2 .....		889
23.17.2.1.1	Method 1:	Thermolysis of Isoxazonoketene <i>N,S</i> -Acetals .....	889
	<b>Keyword Index</b> .....		899
	<b>Author Index</b> .....		1013
	<b>Abbreviations</b> .....		1049