

**Volume 26:  
Ketones**

	<b>Preface</b> .....	V
	<b>Volume Editor's Preface</b> .....	VII
	<b>Table of Contents</b> .....	XI
	<b>Introduction</b>	
	J. Cossy .....	1
<b>26.1</b>	<b>Product Class 1: Aliphatic and Alicyclic Ketones (Excluding Cyclobutanones and Cyclopropanones)</b>	
	P. Vogel .....	13
<b>26.1.1</b>	<b>Synthesis by Oxidation of Heterosubstituted Alkanes</b>	
	S. von Angerer .....	39
<b>26.1.2</b>	<b>Synthesis by Oxidation of Alkenes and Alkanes (Excluding Allylic or Benzylic Derivatives)</b>	
	T. S. Balaban .....	127
<b>26.1.3</b>	<b>Synthesis by Reduction of 1,2-Diketones and <math>\alpha</math>-Diazo Ketones, <math>\alpha,\alpha</math>-Dihetero- and <math>\alpha</math>-Heterosubstituted Ketones, Enones, and Yrones</b>	
	M. Yus and C. Nájera .....	153
<b>26.1.4</b>	<b>Synthesis from Carboxylic Acids and Derivatives by Substitution with a Carbon Nucleophile</b>	
	B. Figadère and X. Franck .....	243
<b>26.1.5</b>	<b>Synthesis from Aldehydes by Substitution of the Aldehyde Hydrogen</b>	
	B. Figadère and X. Franck .....	293
<b>26.1.6</b>	<b>Synthesis from Thioketones, Acetals, Cyanohydrins, Enol Ethers, Enamines, Other Ene Derivatives, and Related Compounds</b>	
	D. Desmaële .....	301
<b>26.1.7</b>	<b>Synthesis by Addition</b>	
	B. Figadère and X. Franck .....	401
<b>26.1.8</b>	<b>Synthesis by Fragmentation and Rearrangement</b>	
	T. Constantieux and J. Rodriguez .....	413
<b>26.1.9</b>	<b>Synthesis from Other Ketones</b>	
	J.-C. Plaquevent, D. Cahard, and F. Guillen .....	463
<b>26.1.10</b>	<b>Synthesis from Enones by Formation of C—C Bonds</b>	
	J.-C. Plaquevent, D. Cahard, and F. Guillen .....	513

26.2	<b>Product Class 2: Cyclobutanones and Their Precursors</b> J. Salaün .....	557
26.3	<b>Product Class 3: Cyclopropanones and Their Precursors</b> J. Salaün .....	607
26.4	<b>Product Class 4: 1,2-Diketones and Related Compounds</b> Y. Landais and J. M. Vincent .....	647
26.5	<b>Product Class 5: <math>\alpha,\alpha</math>-Diheterosubstituted Ketones</b> J.-L. Parrain and J. Thibonnet .....	745
26.6	<b>Product Class 6: <math>\alpha</math>-Heterosubstituted Ketones</b> J. Suffert .....	869
26.7	<b>Product Class 7: Yrones</b> A. Nelson .....	971
26.8	<b>Product Class 8: Aryl Ketones</b> J. M. Campagne and Y. Six .....	989
26.9	<b>Product Class 9: Enones</b> S. P. Marsden .....	1045
26.10	<b>Product Class 10: Saturated or Unsaturated Ketones with an Additional Carbonyl, Nitrile, or Carboxy Substituent or Equivalent at a <math>\beta</math> or More Remote Position: Synthesis of the Ketone Functionality</b> I. Chataigner, A. Harrison-Marchand, and J. Maddaluno .....	1123
26.11	<b>Product Class 11: Saturated and Unsaturated Ketones Containing a <math>\beta</math>- or More Remote Heteroatom Substituent</b> A. Harrison-Marchand, I. Chataigner, and J. Maddaluno .....	1225
	<b>Keyword Index</b> .....	1287
	<b>Author Index</b> .....	1341
	<b>Abbreviations</b> .....	1417

## Table of Contents

### Introduction

J. Cossy

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

### 26.1 Product Class 1: Aliphatic and Alicyclic Ketones (Excluding Cyclobutanones and Cyclopropanones)

P. Vogel

<b>26.1 Product Class 1: Aliphatic and Alicyclic Ketones (Excluding Cyclobutanones and Cyclopropanones)</b> .....	13
---	----

### 26.1.1 Synthesis by Oxidation of Heterosubstituted Alkanes

S. von Angerer

<b>26.1.1 Synthesis by Oxidation of Heterosubstituted Alkanes</b> .....	39
<b>26.1.1.1 Oxidation of Halides</b> .....	40
<b>26.1.1.1.1 Method 1: With Sodium Dichromate or Sodium Periodate</b> .....	40
<b>26.1.1.1.2 Method 2: With Dimethyl Sulfoxide</b> .....	40
<b>26.1.1.1.3 Method 3: With Nitrogen–Oxygen Compounds</b> .....	41
<b>26.1.1.2 Oxidation of Secondary Alcohols</b> .....	42
<b>26.1.1.2.1 Method 1: By Hydrogen Elimination</b> .....	42
<b>26.1.1.2.2 Method 2: With Chromium(VI) Compounds</b> .....	43
<b>26.1.1.2.2.1 Variation 1: With Chromic Acid in Aqueous Solution</b> .....	44
<b>26.1.1.2.2.2 Variation 2: With Chromic Acid in Acetic Acid</b> .....	44
<b>26.1.1.2.2.3 Variation 3: With Chromic Acid in Acetone</b> .....	46
<b>26.1.1.2.2.4 Variation 4: With Chromic Acid in a Two-Phase System</b> .....	47
<b>26.1.1.2.2.5 Variation 5: With Chromium(VI) Oxide in Pyridine</b> .....	49
<b>26.1.1.2.2.6 Variation 6: With Halochromates</b> .....	51
<b>26.1.1.2.3 Method 3: With Manganese Compounds</b> .....	53
<b>26.1.1.2.3.1 Variation 1: With Permanganate</b> .....	53
<b>26.1.1.2.3.2 Variation 2: With Manganese(IV) Oxide</b> .....	55
<b>26.1.1.2.4 Method 4: With Other Metal Compounds</b> .....	58
<b>26.1.1.2.4.1 Variation 1: With Iron Compounds</b> .....	58
<b>26.1.1.2.4.2 Variation 2: With Ruthenium(VIII) Oxide</b> .....	59
<b>26.1.1.2.4.3 Variation 3: With Copper(II) Salts</b> .....	60
<b>26.1.1.2.5 Method 5: Oxidation of Secondary Alcohols with Halogen Compounds</b> ..	60
<b>26.1.1.2.5.1 Variation 1: With Hypofluorous Acid</b> .....	60
<b>26.1.1.2.5.2 Variation 2: With Hypochlorite and Related Oxidants</b> .....	61
<b>26.1.1.2.5.3 Variation 3: With <i>N</i>-<i>tert</i>-Butylbenzenesulfinimidoyl Chloride</b> .....	64
<b>26.1.1.2.5.4 Variation 4: With Bromo Compounds</b> .....	65
<b>26.1.1.2.5.5 Variation 5: With Periodate</b> .....	67
<b>26.1.1.2.5.6 Variation 6: With Organic Iodine(V) Compounds</b> .....	68
<b>26.1.1.2.5.7 Variation 7: With Organic Iodine(III) Compounds</b> .....	71

26.1.1.2.6	Method 6:	Oxidation by Molecular Oxygen	74
26.1.1.2.6.1	Variation 1:	With Ruthenium-Based Catalysts	74
26.1.1.2.6.2	Variation 2:	With Cobalt-Based Catalysts	75
26.1.1.2.6.3	Variation 3:	With Vanadium-Based Catalysts	76
26.1.1.2.6.4	Variation 4:	With Copper-Based Catalysts	78
26.1.1.2.6.5	Variation 5:	With Palladium-Based Catalysts	79
26.1.1.2.6.6	Variation 6:	With Other Reagents	82
26.1.1.2.7	Method 7:	Oxidation with Hydrogen Peroxide	83
26.1.1.2.8	Method 8:	Oxidation with Hydroperoxides and Peracids	84
26.1.1.2.8.1	Variation 1:	With <i>tert</i> -Butyl Hydroperoxide	85
26.1.1.2.8.2	Variation 2:	With Peracids	86
26.1.1.2.9	Method 9:	Oxidation with Dioxiranes	88
26.1.1.2.10	Method 10:	Oxidation with Dimethyl Sulfoxide	89
26.1.1.2.11	Method 11:	Oxidation with Peroxomonosulfate	95
26.1.1.2.12	Method 12:	Oxidation with Nitrogen Compounds	96
26.1.1.2.12.1	Variation 1:	With Organic Oxoammonium Salts	96
26.1.1.2.12.2	Variation 2:	With <i>N</i> -Oxides	98
26.1.1.2.12.3	Variation 3:	With Other Nitrogen-Based Oxidants	98
26.1.1.2.13	Method 13:	Oppenauer Oxidation	99
26.1.1.2.14	Method 14:	Dehydrogenation with Alkenes and Alkynes	102
26.1.1.2.14.1	Variation 1:	With Alkenes	103
26.1.1.2.14.2	Variation 2:	By Isomerization of Allyl Alcohols	103
26.1.1.2.14.3	Variation 3:	By Isomerization of $\alpha$ -Hydroxyalkynes	104
26.1.1.2.15	Method 15:	Other Methods	105
26.1.1.3		Oxidation of Secondary Alcohol Derivatives	108
26.1.1.3.1	Method 1:	Oxidation of Ethers	108
26.1.1.3.2	Method 2:	Oxidative Deprotection of Silyl Ethers	111
26.1.1.4		Oxidation of Nitrogen Compounds	113
26.1.1.4.1	Method 1:	From Nitroalkanes (The Nef Reaction)	113
26.1.1.4.2	Method 2:	From Amines	115
26.1.2		<b>Synthesis by Oxidation of Alkenes and Alkanes (Excluding Allylic or Benzylic Derivatives)</b> T. S. Balaban	
26.1.2		<b>Synthesis by Oxidation of Alkenes and Alkanes (Excluding Allylic or Benzylic Derivatives)</b>	127
26.1.2.1	Method 1:	Oxidation of Alkenes without Cleavage of the Skeleton	127
26.1.2.1.1	Variation 1:	Using Mercury Salts	127
26.1.2.1.2	Variation 2:	Using Palladium Salts with Oxygen and a Copper Cocatalyst or Other Oxidant Systems	128
26.1.2.1.3	Variation 3:	Using Rhodium Salts with Oxygen	131
26.1.2.1.4	Variation 4:	By Oxidation of Intermediate Boron Adducts	131
26.1.2.2	Method 2:	Oxidation of Alkenes with Cleavage of a C=C Bond	133
26.1.2.2.1	Variation 1:	Using Transition Metal Compounds	134
26.1.2.2.2	Variation 2:	Using Permanganate and Periodate Reagents	134

26.1.2.2.3	Variation 3: By Ozonolysis .....	135
26.1.2.2.4	Variation 4: By Other Methods .....	136
26.1.2.3	Method 3: Transition-Metal-Catalyzed Oxidation of Alkanes .....	137
26.1.2.3.1	Variation 1: Using Oxygen .....	137
26.1.2.3.2	Variation 2: Using Ozone .....	140
26.1.2.3.3	Variation 3: Using Hydrogen Peroxide and Organic Peroxides .....	140
26.1.2.3.4	Variation 4: Using Sodium Periodate .....	144
26.1.2.3.5	Variation 5: Using Iodosylbenzene .....	145
26.1.2.3.6	Variation 6: Under Irradiation .....	146
26.1.2.4	Method 4: Oxidation of Alkanes by Other Methods .....	146
26.1.2.4.1	Variation 1: Using Chromates and Permanganates under Lewis Acid Catalysis .....	146
26.1.2.4.2	Variation 2: Using Dioxiranes .....	147
26.1.2.4.3	Variation 3: Using Ozone .....	148
26.1.2.4.4	Variation 4: Electrochemical Oxidation .....	148
26.1.3	<b>Synthesis by Reduction of 1,2-Diketones and <math>\alpha</math>-Diazo Ketones, <math>\alpha,\alpha</math>-Dihetero- and <math>\alpha</math>-Heterosubstituted Ketones, Enones, and Yrones</b> M. Yus and C. Nájera	
<hr/>		
26.1.3	<b>Synthesis by Reduction of 1,2-Diketones and <math>\alpha</math>-Diazo Ketones, <math>\alpha,\alpha</math>-Dihetero- and <math>\alpha</math>-Heterosubstituted Ketones, Enones, and Yrones</b> ...	153
26.1.3.1	Reduction of 1,2-Diketones and $\alpha$ -Diazo Ketones .....	153
26.1.3.1.1	Method 1: Reduction of 1,2-Diketones .....	153
26.1.3.1.2	Method 2: Reduction of $\alpha$ -Diazo Ketones .....	155
26.1.3.2	Reduction of $\alpha,\alpha$ -Diheterosubstituted Ketones .....	157
26.1.3.2.1	Method 1: Reduction of $\alpha,\alpha$ -Dihalo Ketones .....	157
26.1.3.2.2	Method 2: Reduction of $\alpha$ -Oxo Thioacetals .....	158
26.1.3.3	Reduction of $\alpha$ -Heterosubstituted Ketones .....	160
26.1.3.3.1	Reduction of $\alpha$ -Silylated Ketones .....	160
26.1.3.3.1.1	Method 1: Acidic Conditions .....	161
26.1.3.3.1.2	Method 2: Basic Conditions .....	162
26.1.3.3.2	Reduction of $\alpha$ -Halo Ketones .....	163
26.1.3.3.2.1	Method 1: Reduction of $\alpha$ -Fluoro Ketones .....	165
26.1.3.3.2.2	Method 2: Reduction of $\alpha$ -Chloro Ketones .....	166
26.1.3.3.2.2.1	Variation 1: Active Metals and Salts .....	166
26.1.3.3.2.2.2	Variation 2: Nucleophilic Reagents .....	167
26.1.3.3.2.2.3	Variation 3: Hydrides .....	169
26.1.3.3.2.3	Method 3: Reduction of $\alpha$ -Bromo Ketones .....	170
26.1.3.3.2.3.1	Variation 1: Active Metals or Salts and Electrolysis .....	170
26.1.3.3.2.3.2	Variation 2: Nucleophilic Reagents .....	172
26.1.3.3.2.3.3	Variation 3: Hydrides .....	173
26.1.3.3.2.4	Method 4: Reduction of $\alpha$ -Iodo Ketones .....	175
26.1.3.3.3	Reduction of $\alpha$ -Oxygenated Ketones .....	176

26.1.3.3.3.1	Method 1:	Reduction of $\alpha$ -Hydroxy Ketones	177
26.1.3.3.3.1.1	Variation 1:	Active Metals and Salts	177
26.1.3.3.3.1.2	Variation 2:	Nucleophilic Reagents	178
26.1.3.3.3.2	Method 2:	Reduction of $\alpha$ -Alkoxy, $\alpha$ -Acyloxy, and $\alpha$ -Sulfonyloxy Ketones	180
26.1.3.3.3.2.1	Variation 1:	Active Metals and Salts	180
26.1.3.3.3.2.2	Variation 2:	Nucleophilic Reagents and Hydrides	182
26.1.3.3.3.3	Method 3:	Reduction of $\alpha,\beta$ -Epoxy Ketones	184
26.1.3.3.3.3.1	Variation 1:	Active Metals and Salts	184
26.1.3.3.3.3.2	Variation 2:	Nucleophilic Reagents	186
26.1.3.3.4		Reduction of $\alpha$ -Sulfurated Ketones	187
26.1.3.3.4.1	Method 1:	Reduction of $\alpha$ -Sulfanyl Ketones	188
26.1.3.3.4.2	Method 2:	Reduction of $\alpha$ -Sulfinyl Ketones	190
26.1.3.3.4.3	Method 3:	Reduction of $\alpha$ -Sulfonyl Ketones	191
26.1.3.3.4.3.1	Variation 1:	Active Metals and Salts	191
26.1.3.3.4.3.2	Variation 2:	Radicals and Nucleophilic Reagents	195
26.1.3.3.5		Reduction of $\alpha$ -Selenyl Ketones	195
26.1.3.3.6		Reduction of $\alpha$ -Nitrogenated Ketones	198
26.1.3.4		Reduction of Enones	199
26.1.3.4.1	Method 1:	Catalytic Hydrogenation	199
26.1.3.4.1.1	Variation 1:	Hydrogenation under Heterogeneous Conditions	199
26.1.3.4.1.2	Variation 2:	Hydrogenation under Homogeneous Conditions	202
26.1.3.4.1.3	Variation 3:	Transfer Hydrogenation	204
26.1.3.4.2	Method 2:	Reduction with Hydrides	206
26.1.3.4.2.1	Variation 1:	Boron Hydrides	206
26.1.3.4.2.2	Variation 2:	Aluminum Hydrides	208
26.1.3.4.2.3	Variation 3:	Silicon Hydrides	210
26.1.3.4.2.4	Variation 4:	Tin Hydrides and Metal Hydroselenides/Hydrotellurides	212
26.1.3.4.2.5	Variation 5:	Transition Metal Hydrides	214
26.1.3.4.3	Method 3:	Reduction with Dissolving Metals	216
26.1.3.4.3.1	Variation 1:	Main Group Metals	216
26.1.3.4.3.2	Variation 2:	Transition Metals and Salts	220
26.1.3.4.4	Methods 4:	Other Methodologies	221
26.1.3.5		Reduction of Ynones	224
26.1.3.5.1	Method 1:	Partial and Full Reduction Methodologies	224
26.1.4		<b>Synthesis from Carboxylic Acids and Derivatives by Substitution with a Carbon Nucleophile</b>	
		B. Figadère and X. Franck	
26.1.4		<b>Synthesis from Carboxylic Acids and Derivatives by Substitution with a Carbon Nucleophile</b>	243
26.1.4.1	Method 1:	Synthesis from Acyl Halides	243
26.1.4.1.1	Variation 1:	With Organotin Reagents	244
26.1.4.1.2	Variation 2:	With Organoboron Reagents	244
26.1.4.1.3	Variation 3:	With Organoaluminum Reagents	245

26.1.4.1.4	Variation 4:	With Organozinc Reagents	247
26.1.4.1.5	Variation 5:	With Organocadmium Reagents	248
26.1.4.1.6	Variation 6:	With Organomercury Reagents	248
26.1.4.1.7	Variation 7:	With Organocopper Reagents	249
26.1.4.1.8	Variation 8:	With Organocobalt, Organorhodium, or Organoiron Reagents	252
26.1.4.1.9	Variation 9:	With Organomanganese Reagents	253
26.1.4.1.10	Variation 10:	With Organotitanium or Organozirconium Reagents	254
26.1.4.1.11	Variation 11:	With Grignard Reagents	255
26.1.4.1.12	Variation 12:	With Organolithium Reagents	257
26.1.4.1.13	Variation 13:	With Miscellaneous Organometallic Reagents	258
26.1.4.2	Method 2:	Synthesis from Carboxylic Acids	258
26.1.4.2.1	Variation 1:	With Grignard Reagents	259
26.1.4.2.2	Variation 2:	With Organolithium Reagents	260
26.1.4.3	Method 3:	Synthesis from Carboxylic Esters	261
26.1.4.3.1	Variation 1:	With Grignard Reagents	261
26.1.4.3.2	Variation 2:	With Organolithium or Organosodium Reagents	263
26.1.4.4	Method 4:	Synthesis from Carboxylic Anhydrides	264
26.1.4.4.1	Variation 1:	With Organosilicon Reagents	264
26.1.4.4.2	Variation 2:	With Organotin Reagents	265
26.1.4.4.3	Variation 3:	With Organoboron Reagents	266
26.1.4.4.4	Variation 4:	With Organoaluminum Reagents	266
26.1.4.4.5	Variation 5:	With Organozinc Reagents	267
26.1.4.4.6	Variation 6:	With Organocadmium Reagents	268
26.1.4.4.7	Variation 7:	With Organocopper Reagents	268
26.1.4.4.8	Variation 8:	With Organomanganese Reagents	269
26.1.4.4.9	Variation 9:	With Grignard Reagents	270
26.1.4.4.10	Variation 10:	With Organolithium or Organosodium Reagents	271
26.1.4.5	Method 5:	Synthesis from <i>S</i> -Alkyl or <i>S</i> -Aryl Thioesters	272
26.1.4.5.1	Variation 1:	With Organosilicon or Organoboron Reagents	272
26.1.4.5.2	Variation 2:	With Organozinc Reagents	273
26.1.4.5.3	Variation 3:	With Organocopper Reagents	274
26.1.4.5.4	Variation 4:	With Grignard Reagents	274
26.1.4.6	Method 6:	Synthesis from Amides	275
26.1.4.6.1	Variation 1:	With Grignard Reagents	275
26.1.4.6.2	Variation 2:	With Organolithium Reagents	276
26.1.4.7	Method 7:	Synthesis from Nitriles	277
26.1.4.7.1	Variation 1:	With Organozinc Reagents	277
26.1.4.7.2	Variation 2:	With Organotitanium and Organozirconium Reagents	278
26.1.4.7.3	Variation 3:	With Grignard Reagents	278
26.1.4.7.4	Variation 4:	With Organolithium Reagents	279
26.1.4.7.5	Variation 5:	With Alkylidenephosphorane Reagents	279
26.1.4.8	Method 8:	Synthesis from Dihydroimidazoles	280
26.1.4.8.1	Variation 1:	With Grignard Reagents	280
26.1.4.8.2	Variation 2:	With Organolithium Reagents	281
26.1.4.9	Method 9:	Synthesis from Miscellaneous Acylating Reagents	281
26.1.4.9.1	Variation 1:	From Carbon Dioxide and Its Derivatives	281
26.1.4.9.2	Variation 2:	From 5,6-Dihydro-1,3-oxazines	282
26.1.4.9.3	Variation 3:	From 1,3-Benzoxathiol-1-ium Salts and Related Compounds	283

26.1.4.9.4	Variation 4: From Ortho Esters .....	283
26.1.4.9.5	Variation 5: From Acyl Cyanides .....	284
26.1.4.9.6	Variation 6: From Acylsilanes .....	284
26.1.5	<b>Synthesis from Aldehydes by Substitution of the Aldehyde Hydrogen</b> B. Figadère and X. Franck	
<hr/>		
26.1.5	<b>Synthesis from Aldehydes by Substitution of the Aldehyde Hydrogen</b> ...	293
26.1.5.1	Method 1: Radical Reaction of Aldehydes with Alkenes .....	293
26.1.5.2	Method 2: Addition of Diazoalkanes to Aldehydes .....	294
26.1.5.3	Method 3: Hydroacylation of Aldehydes .....	295
26.1.5.3.1	Variation 1: With Ruthenium Complexes .....	296
26.1.5.3.2	Variation 2: With Cobalt Complexes .....	296
26.1.5.3.3	Variation 3: With Rhodium Complexes .....	297
26.1.6	<b>Synthesis from Thioketones, Acetals, Cyanohydrins, Enol Ethers, Enamines, Other Ene Derivatives, and Related Compounds</b> D. Desmaële	
<hr/>		
26.1.6	<b>Synthesis from Thioketones, Acetals, Cyanohydrins, Enol Ethers, Enamines, Other Ene Derivatives, and Related Compounds</b> .....	301
26.1.6.1	Synthesis from Thioketones .....	301
26.1.6.1.1	Method 1: Hydrolysis of Thioketones .....	301
26.1.6.1.2	Method 2: Oxidative Cleavage of Thioketones .....	302
26.1.6.1.3	Method 3: Nitrosative Cleavage of Thioketones .....	304
26.1.6.2	Synthesis from Iminium Ions, Ketimines, and Derivatives .....	304
26.1.6.2.1	Method 1: Hydrolysis of Iminium Salts and Imines .....	304
26.1.6.3	Synthesis from <i>N</i> -Sulfanyl- and <i>N</i> -Sulfonylimines .....	307
26.1.6.3.1	Method 1: Hydrolysis of <i>N</i> -Sulfanyl- and <i>N</i> -Sulfonylimines .....	307
26.1.6.4	Synthesis from Oximes and Derivatives .....	307
26.1.6.4.1	Method 1: Hydrolysis of Oximes and Derivatives .....	307
26.1.6.4.1.1	Variation 1: Sodium Hydrogen Sulfite Assisted Hydrolysis of Oximes and Derivatives .....	308
26.1.6.4.1.2	Variation 2: Metal Salt Assisted Hydrolysis of Oximes and Derivatives ....	309
26.1.6.4.2	Method 2: Cleavage of Oximes and Derivatives by the Exchange Method	310
26.1.6.4.3	Method 3: Oxidative Cleavage of Oximes and Derivatives .....	311
26.1.6.4.3.1	Variation 1: Aerobic Oxidation and Ozonolysis of Oximes and Derivatives	311
26.1.6.4.3.2	Variation 2: Oxidative Cleavage of Oximes and Derivatives with Peroxidic Compounds .....	312
26.1.6.4.3.3	Variation 3: Oxidative Cleavage of Oximes and Derivatives with High-Valency Metals .....	313
26.1.6.4.3.4	Variation 4: Other Oxidative Cleavages of Oximes and Derivatives .....	316
26.1.6.4.4	Method 4: Nitrosative Cleavage of Oximes and Derivatives .....	317
26.1.6.4.5	Method 5: Reductive Cleavage of Oximes and Derivatives .....	318

26.1.6.4.5.1	Variation 1:	Metal-Catalyzed Reductive Cleavage of Oximes and Derivatives .....	318
26.1.6.4.5.2	Variation 2:	Other Reductive Cleavages of Oximes and Derivatives .....	320
26.1.6.5		Synthesis from Hydrazone Derivatives .....	320
26.1.6.5.1	Method 1:	Hydrolysis of Hydrazone Derivatives .....	320
26.1.6.5.1.1	Variation 1:	Acidic Hydrolysis of Hydrazones and Derivatives .....	321
26.1.6.5.1.2	Variation 2:	Metal Salt Assisted Hydrolysis of Hydrazone Derivatives .....	321
26.1.6.5.2	Method 2:	Cleavage of Hydrazone Derivatives by the Exchange Method .....	323
26.1.6.5.3	Method 3:	Oxidative Cleavage of Hydrazone Derivatives .....	324
26.1.6.5.3.1	Variation 1:	Aerobic Oxidation and Ozonolysis of Hydrazone Derivatives .....	324
26.1.6.5.3.2	Variation 2:	Oxidative Cleavage of Hydrazone Derivatives with Peroxidic Compounds .....	325
26.1.6.5.3.3	Variation 3:	Oxidative Cleavage of Hydrazone Derivatives with High-Valency Metals .....	327
26.1.6.5.3.4	Variation 4:	Other Oxidative Cleavages of Hydrazone Derivatives .....	329
26.1.6.5.4	Method 4:	Nitrosative Cleavage of Hydrazone Derivatives .....	331
26.1.6.5.5	Method 5:	Reductive Cleavage of Hydrazone Derivatives .....	332
26.1.6.5.6	Method 6:	Enzymatic Cleavage of Hydrazone Derivatives .....	332
26.1.6.6		Synthesis from <i>O,O</i> -Acetals .....	333
26.1.6.6.1	Method 1:	Hydrolysis of <i>O,O</i> -Acetals .....	333
26.1.6.6.2	Method 2:	Hydrolysis of <i>O,O</i> -Acetals by Exchange with Another Carbonyl Compound .....	335
26.1.6.6.3	Method 3:	Metal-Induced Cleavage of <i>O,O</i> -Acetals .....	336
26.1.6.6.4	Method 4:	Electrophilic Cleavage of <i>O,O</i> -Acetals .....	338
26.1.6.6.5	Method 5:	Oxidative Cleavage of <i>O,O</i> -Acetals .....	339
26.1.6.6.6	Method 6:	Reductive Cleavage of <i>O,O</i> -Acetals .....	340
26.1.6.6.7	Method 7:	Nucleophilic Cleavage of <i>O,O</i> -Acetals .....	341
26.1.6.6.8	Method 8:	Photolysis of <i>O,O</i> -Acetals .....	342
26.1.6.7		Synthesis from <i>O,S</i> -Acetals .....	343
26.1.6.7.1	Method 1:	Hydrolysis of <i>O,S</i> -Acetals .....	343
26.1.6.7.2	Method 2:	Cleavage of <i>O,S</i> -Acetals by Exchange with Another Carbonyl Compound .....	344
26.1.6.7.3	Method 3:	Metal-Induced Cleavage of <i>O,S</i> -Acetals .....	344
26.1.6.7.4	Method 4:	Oxidative Cleavage of <i>O,S</i> -Acetals .....	345
26.1.6.7.5	Method 5:	Nitrosative Cleavage of <i>O,S</i> -Acetals .....	346
26.1.6.8		Synthesis from $\alpha$ -Hydroxylated Sulfones .....	347
26.1.6.8.1	Method 1:	Cleavage of $\alpha$ -Alkoxyalkylated Sulfones .....	347
26.1.6.9		Synthesis from <i>O,N</i> -Acetals .....	348
26.1.6.9.1	Method 1:	Hydrolysis of <i>O,N</i> -Acetals .....	348
26.1.6.9.2	Method 2:	Reductive Cleavage of <i>O,N</i> -Acetals .....	349
26.1.6.10		Synthesis from $\alpha$ -Hydroxy and $\alpha$ -Trimethylsiloxy Alkylphosphonates .....	350
26.1.6.10.1	Method 1:	Deprotection of $\alpha$ -Hydroxy Alkylphosphonates .....	350
26.1.6.11		Synthesis from <i>S,S</i> -Acetals .....	351
26.1.6.11.1	Method 1:	Hydrolysis of <i>S,S</i> -Acetals .....	352

26.1.6.11.2	Method 2:	Metal-Induced Cleavage of <i>S,S</i> -Acetals	352
26.1.6.11.3	Method 3:	Alkylative and Electrophilic Cleavage of <i>S,S</i> -Acetals	354
26.1.6.11.4	Method 4:	Oxidative Cleavage of <i>S,S</i> -Acetals	355
26.1.6.11.5	Method 5:	Nitrosative Cleavage of <i>S,S</i> -Acetals	358
26.1.6.11.6	Method 6:	Photolysis of <i>S,S</i> -Acetals	359
26.1.6.12		Synthesis from Dithioketal Monosulfoxides and Dithioketal Disulfoxides	359
26.1.6.12.1	Method 1:	Hydrolysis of Dithioketal Monosulfoxides and Dithioketal Disulfoxides	359
26.1.6.12.2	Method 2:	Metal-Catalyzed Cleavage of Dithioketal Monosulfoxides and Dithioketal Disulfoxides	360
26.1.6.13		Synthesis from <i>S</i> - or <i>N</i> - $\alpha$ -Substituted Sulfones	361
26.1.6.13.1	Method 1:	Acidic Hydrolysis of <i>S</i> - or <i>N</i> - $\alpha$ -Substituted Sulfones	361
26.1.6.13.2	Method 2:	Metal-Induced Hydrolyses of $\alpha$ -(Methylsulfanyl)methyl Sulfones	362
26.1.6.14		Synthesis from 1-[(Methylsulfanyl)methyl]-1 <i>H</i> -1,2,3-benzotriazoles, Dihydrobenzothiazoles, or Nitromethyl Sulfides	363
26.1.6.14.1	Method 1:	Acidic Hydrolysis of 1-[(Methylsulfanyl)methyl]-1 <i>H</i> -benzotriazoles	363
26.1.6.14.2	Method 2:	Metal-Induced Hydrolysis of Dihydrobenzothiazoles	363
26.1.6.14.3	Method 3:	Reductive Cleavage of Nitromethyl Sulfides	364
26.1.6.15		Synthesis from Diselenoacetals	365
26.1.6.15.1	Method 1:	Metal-Induced Cleavage of Diselenoacetals	365
26.1.6.15.2	Method 2:	Oxidative and Nitrosative Cleavage of Diselenoacetals	365
26.1.6.16		Synthesis from <i>N,N</i> -Acetals	366
26.1.6.16.1	Method 1:	Hydrolysis of <i>N,N</i> -Acetals	366
26.1.6.17		Synthesis from $\alpha$ -Heterosubstituted Nitriles	367
26.1.6.17.1	Method 1:	Hydrolysis of $\alpha$ -Halogenated Nitriles	367
26.1.6.17.2	Method 2:	Hydrolysis of Cyanohydrins and Derivatives	368
26.1.6.17.2.1	Variation 1:	Cleavage of <i>O</i> -Silylated Cyanohydrins	369
26.1.6.17.2.2	Variation 2:	Hydrolysis of <i>O</i> -Acylation Cyanohydrins	370
26.1.6.17.3	Method 3:	Hydrolysis of $\alpha$ -Cyanodithiocarbamates	371
26.1.6.17.4	Method 4:	Hydrolytic Cleavage of $\alpha$ -(Dialkylamino)nitriles	372
26.1.6.18		Synthesis from Haloalkenes	372
26.1.6.18.1	Method 1:	Acidic Hydrolysis of Haloalkenes	372
26.1.6.18.2	Method 2:	Metal-Assisted Hydrolysis of Haloalkenes	374
26.1.6.19		Synthesis from Enol Derivatives	374
26.1.6.19.1	Method 1:	Synthesis from Enol Ethers	374
26.1.6.19.2	Method 2:	Hydrolysis of Enol Esters	375
26.1.6.19.3	Method 3:	Synthesis from Silylated Enol Ethers	376
26.1.6.19.3.1	Variation 1:	Miscellaneous Cleavages of Silylated Enol Ethers	377
26.1.6.19.3.2	Variation 2:	Alkylation of Silylated Enol Ethers	378
26.1.6.19.4	Method 4:	Alkylation of Stannylated Enols	379

26.1.6.19.5	Method 5: Hydrolysis of Enol Trifluoromethanesulfonates and Enol Phosphates .....	380
26.1.6.20	Synthesis from Vinyl Sulfides and Vinyl Selenides .....	381
26.1.6.20.1	Method 1: Hydrolysis of Vinyl Sulfides and Vinyl Selenides .....	382
26.1.6.20.2	Method 2: Metal-Catalyzed Hydrolysis of Vinyl Sulfides and Vinyl Selenides .....	382
26.1.6.21	Synthesis from Enamines and Derivatives .....	383
26.1.6.21.1	Method 1: Hydrolysis of Enamines and Derivatives .....	383
26.1.6.21.2	Method 2: Hydrolysis of Enamides .....	385
26.1.6.22	Synthesis from Nitroalkenes .....	386
26.1.6.22.1	Method 1: Reduction of Nitroalkenes .....	386
26.1.6.22.2	Method 2: Reductive Alkylation of Nitroalkenes .....	387
26.1.7	<b>Synthesis by Addition</b> B. Figadère and X. Franck	
26.1.7	<b>Synthesis by Addition</b> .....	401
26.1.7.1	Method 1: Synthesis from Alkynes .....	401
26.1.7.1.1	Variation 1: By Mercury-Catalyzed Hydration .....	401
26.1.7.1.2	Variation 2: By Gold-Catalyzed Hydration .....	402
26.1.7.1.3	Variation 3: By Palladium-Catalyzed Hydration .....	403
26.1.7.1.4	Variation 4: By Platinum-Catalyzed Hydration .....	403
26.1.7.1.5	Variation 5: By Iron-Catalyzed Hydration .....	404
26.1.7.1.6	Variation 6: By Ruthenium-Catalyzed Hydration .....	404
26.1.7.1.7	Variation 7: By a Hydroboration–Oxidation Sequence .....	405
26.1.7.2	Method 2: Synthesis from Allenes .....	406
26.1.7.2.1	Variation 1: By Mercury-Catalyzed Hydration .....	406
26.1.7.2.2	Variation 2: By a Hydroboration–Oxidation Sequence .....	407
26.1.7.3	Method 3: Synthesis from Ketenes .....	407
26.1.7.3.1	Variation 1: With Organozinc Reagents .....	408
26.1.7.3.2	Variation 2: With Grignard Reagents .....	408
26.1.7.3.3	Variation 3: With Organolithium Reagents .....	409
26.1.8	<b>Synthesis by Fragmentation and Rearrangement</b> T. Constantieux and J. Rodriguez	
26.1.8	<b>Synthesis by Fragmentation and Rearrangement</b> .....	413
26.1.8.1	Method 1: Fragmentation of Alkenes .....	413
26.1.8.2	Method 2: Fragmentation of 1,2-Diols .....	414
26.1.8.2.1	Variation 1: Fragmentation of 1,2-Diols with Periodates .....	414
26.1.8.2.2	Variation 2: Fragmentation of 1,2-Diols with Lead(IV) Acetate .....	415
26.1.8.2.3	Variation 3: Fragmentation of 1,2-Diols with <i>N</i> -Halosuccinimide .....	417
26.1.8.2.4	Variation 4: Miscellaneous Fragmentation Reactions of 1,2-Diols .....	418
26.1.8.3	Method 3: Fragmentation of 1,3-Diheterofunctionalized Compounds (Grob Fragmentation) .....	419

26.1.8.3.1	Variation 1:	Fragmentation of 1,3-Amino Halides, 1,3-Amino Sulfonates, and 1,3-Hydroxy Halides	420
26.1.8.3.2	Variation 2:	Fragmentation of 1,3-Amino Alcohols	420
26.1.8.3.3	Variation 3:	Fragmentation of Acyclic 1,3-Diols and Derivatives	421
26.1.8.3.4	Variation 4:	Fragmentation of Cyclic 1,3-Diol Monosulfonates and Derivatives (Wharton Fragmentation)	422
26.1.8.4	Method 4:	Fragmentation of $\alpha,\beta$ -Unsaturated Ketones (Eschenmoser Fragmentation)	425
26.1.8.5	Method 5:	Fragmentation of Ketones (Norrish Type II Fragmentation)	428
26.1.8.6	Method 6:	Electrocyclic Rearrangements	430
26.1.8.6.1	Variation 1:	Claisen-Type Rearrangements	431
26.1.8.6.2	Variation 2:	Oxy-Cope Rearrangement	433
26.1.8.7	Method 7:	Isomerization of Allylic Alcohols	434
26.1.8.7.1	Variation 1:	Metal-Promoted Isomerization	435
26.1.8.7.2	Variation 2:	Tandem Isomerization–Aldol Reaction	437
26.1.8.7.3	Variation 3:	Enantioselective Isomerization	438
26.1.8.7.4	Variation 4:	Isomerization with Ring Expansion	439
26.1.8.8	Method 8:	Rearrangement of 1,2-Diheterofunctionalized Compounds	440
26.1.8.8.1	Variation 1:	1,2-Diols and Derivatives	441
26.1.8.8.2	Variation 2:	2-Sulfanyl and 2-Selenyl Alcohol Derivatives	443
26.1.8.8.3	Variation 3:	2-Aza Alcohol Derivatives	444
26.1.8.8.4	Variation 4:	2-Halo Alcohols and Derivatives	445
26.1.8.8.5	Variation 5:	2-Hydroxy Ketones and Derivatives	448
26.1.8.8.6	Variation 6:	2-Epoxy Alcohols	449
26.1.8.9	Method 9:	Rearrangement of Epoxides	451
26.1.8.9.1	Variation 1:	Alkyl- and/or Aryl-Substituted Epoxides	451
26.1.8.9.2	Variation 2:	$\alpha,\beta$ -Epoxy Ketones	454
26.1.8.9.3	Variation 3:	Epoxy silanes	455

## 26.1.9

**Synthesis from Other Ketones**

J.-C. Plaquevent, D. Cahard, and F. Guillen

26.1.9	<b>Synthesis from Other Ketones</b>	463	
26.1.9.1	Method 1:	Monoalkylation of Lithium Enolates	464
26.1.9.1.1	Variation 1:	Enantioselective Alkylation via Chiral Lithium Amide Deprotonation	470
26.1.9.2	Method 2:	Monoalkylation of Sodium Enolates	471
26.1.9.3	Method 3:	Monoalkylation of Potassium Enolates	473
26.1.9.4	Method 4:	Palladium-Catalyzed Asymmetric Alkylations and Arylations of Alkali Ketone Enolates	475
26.1.9.5	Method 5:	Monoalkylation of Magnesium Enolates	481
26.1.9.6	Method 6:	Monoalkylation of Manganese Enolates	482
26.1.9.7	Method 7:	Monoalkylation Using Sodium Triethylgermanate(II)	484
26.1.9.8	Method 8:	Miscellaneous Metal-Mediated Alkylations of Enolates	485
26.1.9.9	Method 9:	Alkylation by Phase-Transfer Catalysis	487
26.1.9.10	Method 10:	Free Radical Alkylation	489
26.1.9.11	Method 11:	Polyalkylation of Enols and Enolates	493
26.1.9.12	Method 12:	Isomerization by Carbonyl Transposition	497

26.1.9.13	Method 13:	Epimerization via Enols and Enolates	498
26.1.9.14	Method 14:	Deracemization by Enantioselective Protonation of Enolates	502
26.1.9.14.1	Variation 1:	With a Chiral Proton Source	502
26.1.9.14.2	Variation 2:	With an Achiral Proton Source under the Influence of a Chiral Ligand	505
26.1.9.14.3	Variation 3:	Fungal Deracemization	506
26.1.9.15	Method 15:	Norrish Type II Fragmentation	507
26.1.9.16	Method 16:	Ring Expansion of Alicyclic Ketones	507

## 26.1.10 Synthesis from Enones by Formation of C—C Bonds

J.-C. Plaquevent, D. Cahard, and F. Guillen

26.1.10	<b>Synthesis from Enones by Formation of C—C Bonds</b>	513	
26.1.10.1	Method 1:	By Addition of Organosilicon Reagents	513
26.1.10.2	Method 2:	By Addition of Organostannane Reagents	515
26.1.10.3	Method 3:	By Addition of Organoboron Reagents	516
26.1.10.4	Method 4:	By Addition of Organoaluminum Reagents	519
26.1.10.5	Method 5:	By Addition of Organozinc Reagents	520
26.1.10.6	Method 6:	By Addition of Organocopper Reagents	525
26.1.10.7	Method 7:	By Addition of Grignard Reagents	532
26.1.10.8	Method 8:	By Michael and Michael-Type Addition Reactions	533
26.1.10.8.1	Variation 1:	Organometallic Catalysis	533
26.1.10.8.2	Variation 2:	Heterobimetallic Catalysis	537
26.1.10.8.3	Variation 3:	Organocatalysis	541
26.1.10.8.4	Variation 4:	Phase-Transfer Catalysis	544
26.1.10.8.5	Variation 5:	Mukaiyama–Michael Reaction	547
26.1.10.9	Method 9:	By the Sakurai–Hosomi Reaction	549

## 26.2 Product Class 2: Cyclobutanones and Their Precursors

J. Salaün

26.2	<b>Product Class 2: Cyclobutanones and Their Precursors</b>	557	
26.2.1	Synthesis of Product Class 2	557	
26.2.1.1	Method 1:	Ring Formation by Cyclodialkylation of Protected Carbonyl Groups by 1,3-Dihalopropanes	557
26.2.1.1.1	Variation 1:	From 1,3-Dithiane	557
26.2.1.1.2	Variation 2:	From Methyl (Methylsulfanyl)methyl Sulfoxide	558
26.2.1.1.3	Variation 3:	From Tosylmethyl Isocyanide	558
26.2.1.2	Method 2:	Ring Formation by Cyclodialkylation of Ketones by 1,3-Dimetalated Propan-2-iminium Salts	559
26.2.1.3	Method 3:	Cyclization by Intramolecular Substitution	559
26.2.1.3.1	Variation 1:	Of a $\delta$ -Halo Cyanohydrin	559
26.2.1.3.2	Variation 2:	Of O-Protected Alk-3-en-1-ols or Alk-3-yn-1-ols	559
26.2.1.4	Method 4:	Ring Formation by Carbonylation	560
26.2.1.4.1	Variation 1:	Of Titanacyclobutanones	561
26.2.1.4.2	Variation 2:	Of (Alkoxyalkylidene)chromium Complexes	561
26.2.1.4.3	Variation 3:	Of a Cobaltacyclopentan-2-one	562

26.2.1.5	Method 5:	Reduction .....	562
26.2.1.5.1	Variation 1:	Of 2-Acetoxycyclobutanones .....	562
26.2.1.5.2	Variation 2:	Of 2,2-Dichlorocyclobutanones .....	563
26.2.1.6	Method 6:	Oxidation .....	564
26.2.1.6.1	Variation 1:	Of Cyclobutanols .....	564
26.2.1.6.2	Variation 2:	Of Methylene cyclobutane .....	564
26.2.1.7	Method 7:	Ring Formation by [2 + 2] Cycloaddition .....	564
26.2.1.7.1	Variation 1:	Of Ketenes and Alkenes .....	565
26.2.1.7.2	Variation 2:	Of Mono- or Dichloroketenes and Alkenes .....	567
26.2.1.7.3	Variation 3:	Of Keteniminium Salts and Alkenes .....	568
26.2.1.7.4	Variation 4:	Of Ketene Acetals and Acrylic or Maleic Acid Derivatives .....	570
26.2.1.7.5	Variation 5:	Of Ketene Thioacetals and Alkenes .....	571
26.2.1.7.6	Variation 6:	Of Ketene Silyl Acetals and Alkenes .....	572
26.2.1.7.7	Variation 7:	Of <i>N,N</i> -Diethylprop-1-yn-1-amine and Alkenes .....	573
26.2.1.8	Method 8:	Ring Enlargement of Cyclopropanones Formed by Addition of Diazomethane to Ketenes .....	574
26.2.1.9	Method 9:	Ring Enlargement of the Cyclopropane Intermediate Formed by a Simmons–Smith Cyclopropanation Reaction .....	575
26.2.1.10	Method 10:	Rearrangement of Spiro[2.2]pentanes .....	576
26.2.1.10.1	Variation 1:	Of 1-Oxaspiro[2.2]pentanes .....	576
26.2.1.10.2	Variation 2:	Of 1-Azaspiro[2.2]pentanes .....	579
26.2.1.11	Method 11:	Rearrangement of (1-Hydroxyalkyl)cyclopropanes .....	580
26.2.1.11.1	Variation 1:	Of 1-Alkoxy-1-(1-hydroxyalkyl)cyclopropanes .....	580
26.2.1.11.2	Variation 2:	Of 1-(Arylsulfonyl)-1-(1-hydroxyalkyl)cyclopropanes .....	581
26.2.1.11.3	Variation 3:	Of 1-(1-Hydroxyalkyl)-1-selanyl cyclopropanes .....	583
26.2.1.11.4	Variation 4:	Of 1-(1-Hydroxyalkyl)-1-(trimethylsilyl)cyclopropanes .....	584
26.2.1.11.5	Variation 5:	Of (1-Formylamino)-1-(1-hydroxyalkyl)cyclopropanes .....	584
26.2.1.12	Method 12:	Rearrangement of Cyclopropanol Derivatives .....	585
26.2.1.12.1	Variation 1:	Of 1-Vinylcyclopropanols .....	585
26.2.1.12.2	Variation 2:	Of 1-(1-Hydroxyalkyl)- or 1-Formylcyclopropanols .....	587
26.2.1.12.3	Variation 3:	Of 1-(Aminomethyl)cyclopropanols .....	593
26.2.1.12.4	Variation 4:	Of a Bicyclo[4.1.0]heptan-2-one Tosylhydrazone .....	594
26.2.1.13	Method 13:	Rearrangement of (1-Bromoalkylidene)cyclopropanes .....	594
26.2.1.14	Method 14:	Ring Contraction .....	595
26.2.1.14.1	Variation 1:	Of $\gamma$ -Lactone Tosylhydrazones .....	595
26.2.1.14.2	Variation 2:	Of Cyclohex-2-enones .....	595
26.2.1.14.3	Variation 3:	Of Cyclohex-3-enones .....	596
26.2.1.14.4	Variation 4:	Of Cycloocta-2,4,6-trienones .....	596
26.2.1.15	Method 15:	Preparation from Preformed Four-Membered Rings .....	597
26.2.1.15.1	Variation 1:	From Cyclobutanones .....	597
26.2.1.15.2	Variation 2:	From Cyclobutenones .....	600
26.2.1.15.3	Variation 3:	From 1,2-Bis(trimethylsiloxy)cyclobutene .....	601

<b>26.3</b>	<b>Product Class 3: Cyclopropanones and Their Precursors</b> J. Salaün	
<b>26.3</b>	<b>Product Class 3: Cyclopropanones and Their Precursors</b> .....	607
<b>26.3.1</b>	<b>Product Subclass 1: Cyclopropanones</b> .....	607
<b>26.3.1.1</b>	Synthesis of Product Subclass 1 .....	607
<b>26.3.1.1.1</b>	Method 1: Photolysis of Strained Rings .....	607
<b>26.3.1.1.1.1</b>	Variation 1: Photodecarbonylation of Cyclobutanediones .....	607
<b>26.3.1.1.1.2</b>	Variation 2: Photodenitrogenation of Dihydropyrazolones .....	608
<b>26.3.1.1.2</b>	Method 2: Ring-Closing Dehalogenation of $\alpha$ -Halo and $\alpha,\alpha'$ -Dihalo Ketones .....	608
<b>26.3.1.1.2.1</b>	Variation 1: With Sterically Hindered Bases .....	608
<b>26.3.1.1.2.2</b>	Variation 2: Electrochemical Dehalogenation .....	609
<b>26.3.1.1.2.3</b>	Variation 3: Sodium Iodide Induced Dehalogenation .....	609
<b>26.3.1.1.2.4</b>	Variation 4: Carbonylmetalate-Induced Dehalogenation .....	610
<b>26.3.1.1.3</b>	Method 3: Addition of Diazoalkanes to Ketenes .....	610
<b>26.3.1.1.4</b>	Method 4: Isomerization of Allene Oxides .....	611
<b>26.3.1.1.4.1</b>	Variation 1: Thermal Isomerization .....	612
<b>26.3.2</b>	<b>Product Subclass 2: Cyclopropanone Hemiacetals</b> .....	612
<b>26.3.2.1</b>	Synthesis of Product Subclass 2 .....	612
<b>26.3.2.1.1</b>	Method 1: Photodecarbonylation of Cyclobutanediones .....	612
<b>26.3.2.1.2</b>	Method 2: Ring-Closing Dehalogenation .....	613
<b>26.3.2.1.2.1</b>	Variation 1: Electroreduction of $\alpha,\alpha'$ -Dihalo Ketones .....	613
<b>26.3.2.1.2.2</b>	Variation 2: Base-Induced Dehydrohalogenation of $\alpha$ -Halo Ketones .....	613
<b>26.3.2.1.2.3</b>	Variation 3: Sodium-Mediated Ring Closure of $\beta$ -Halo Esters .....	614
<b>26.3.2.1.2.4</b>	Variation 4: Sodium-Mediated Ring Closure of $\beta$ -Haloamides .....	614
<b>26.3.2.1.3</b>	Method 3: Addition Reactions of Ketenes .....	615
<b>26.3.2.1.3.1</b>	Variation 1: Cyclopropanation of Silylketene Acetals .....	615
<b>26.3.2.1.3.2</b>	Variation 2: Cyclopropanation of 1-Alkoxyvinyl Esters .....	615
<b>26.3.2.1.3.3</b>	Variation 3: Addition of Glacial Acetic Acid to Cyclopropanones .....	616
<b>26.3.3</b>	<b>Product Subclass 3: Cyclopropanone Hemiaminals</b> .....	616
<b>26.3.3.1</b>	Synthesis of Product Subclass 3 .....	616
<b>26.3.3.1.1</b>	Method 1: Addition of Amines to Cyclopropanone .....	616
<b>26.3.4</b>	<b>Product Subclass 4: Cyclopropanone Acetals</b> .....	617
<b>26.3.4.1</b>	Synthesis of Product Subclass 4 .....	617
<b>26.3.4.1.1</b>	Method 1: Alcoholysis of 1'-Substituted Cyclopropyl Ethers .....	617
<b>26.3.4.1.1.1</b>	Variation 1: From 1,1-Dihalocyclopropanes .....	618
<b>26.3.4.1.2</b>	Method 2: Reductive Cyclization of $\alpha,\alpha'$ -Dihalopropanone Acetals .....	618
<b>26.3.4.1.3</b>	Method 3: Addition of Carbenes or Carbenoids to Ketene Acetals .....	619
<b>26.3.4.1.3.1</b>	Variation 1: Addition of Dialkoxycarbenes to Ketones .....	620
<b>26.3.4.1.4</b>	Method 4: Addition to Cyclopropenone Acetals .....	621
<b>26.3.4.1.5</b>	Method 5: Ring Closure of ( $\gamma,\gamma$ -Dialkoxyallyl)zirconocenes .....	622
<b>26.3.4.1.6</b>	Method 6: Photoisomerization of Dienedione Monoacetals .....	622

<b>26.3.5</b>	<b>Product Subclass 5: Cyclopropane-1,1-diamines</b> .....	623
<b>26.3.5.1</b>	Synthesis of Product Subclass 5 .....	623
<b>26.3.5.1.1</b>	Method 1: Secondary Amine Induced Ring Closure of $\alpha$ -Halo Ketones ...	623
<b>26.3.5.1.2</b>	Method 2: Amine Addition to Cyclopropanone .....	623
<b>26.3.6</b>	<b>Product Subclass 6: Cyclopropane Thioacetals</b> .....	624
<b>26.3.6.1</b>	Synthesis of Product Subclass 6 .....	624
<b>26.3.6.1.1</b>	Method 1: Substitution of Cyclopropanone Derivatives .....	624
<b>26.3.6.1.1.1</b>	Variation 1: Using Basic Conditions .....	624
<b>26.3.6.1.1.2</b>	Variation 2: By Metalation .....	625
<b>26.3.6.1.2</b>	Method 2: Ring Closure of 1,1,3-Tris(phenylsulfanyl)alkanes .....	625
<b>26.3.6.1.3</b>	Method 3: Addition of Thiols to Cyclopropanones .....	626
<b>26.3.7</b>	<b>Product Subclass 7: 1,1-Bis(seleno)cyclopropanes</b> .....	626
<b>26.3.7.1</b>	Synthesis of Product Subclass 7 .....	626
<b>26.3.7.1.1</b>	Method 1: Substitution of Cyclopropanone Derivatives .....	626
<b>26.3.7.1.2</b>	Method 2: Ring Closure of Seleno Derivatives .....	627
<b>26.3.8</b>	<b>Product Subclass 8: Cyclopropenones</b> .....	628
<b>26.3.8.1</b>	Synthesis of Product Subclass 8 .....	628
<b>26.3.8.1.1</b>	Method 1: Hydrolysis .....	628
<b>26.3.8.1.1.1</b>	Variation 1: Of Cyclopropenone Acetals .....	628
<b>26.3.8.1.1.2</b>	Variation 2: Of Dichlorocyclopropenes .....	630
<b>26.3.8.1.1.3</b>	Variation 3: Of Cyclopropenylium Salts .....	630
<b>26.3.8.1.2</b>	Method 2: Oxidation of Cyclopropenes .....	631
<b>26.3.8.1.3</b>	Method 3: Photodecarbonylation of Cyclobutenediones .....	632
<b>26.3.8.1.4</b>	Method 4: Dehydrohalogenation of $\alpha, \alpha'$ -Dihalo Ketones .....	632
<b>26.3.9</b>	<b>Product Subclass 9: Cyclopropyl Ketones and Cyclopropanecarbaldehydes</b> .....	633
<b>26.3.9.1</b>	Synthesis of Product Subclass 9 .....	633
<b>26.3.9.1.1</b>	Method 1: Ring-Closure Reactions .....	633
<b>26.3.9.1.1.1</b>	Variation 1: Of $\gamma$ -Chloro Ketones .....	633
<b>26.3.9.1.1.2</b>	Variation 2: Of 4-Oxopentyl Phosphate Carbanions .....	634
<b>26.3.9.1.1.3</b>	Variation 3: Of Methyl 2,3-Dihalopropanoates .....	634
<b>26.3.9.1.1.4</b>	Variation 4: Of Oxoenolates .....	635
<b>26.3.9.1.2</b>	Method 2: Cyclization of Oxo Esters and Ketones with 1,2-Dibromoethane .....	635
<b>26.3.9.1.3</b>	Method 3: Addition Reactions .....	636
<b>26.3.9.1.3.1</b>	Variation 1: Of Carbenes to Undec-2-en-5-yn-1-ol .....	636
<b>26.3.9.1.3.2</b>	Variation 2: Of Diphenylsulfonium Isopropylide to Chiral Lactams .....	636
<b>26.3.9.1.3.3</b>	Variation 3: Of Diazocyclopropane to Aldehydes .....	638
<b>26.3.9.1.4</b>	Method 4: Oxidation Reactions .....	638
<b>26.3.9.1.4.1</b>	Variation 1: Swern Oxidation of Cyclopropylcarbinols .....	638
<b>26.3.9.1.4.2</b>	Variation 2: Oxidative Ring Opening .....	639
<b>26.3.9.1.5</b>	Method 5: Addition of Methylolithium to Cyclopropane Carboxylic Acids	640
<b>26.3.9.1.6</b>	Method 6: Rearrangement of Allene Oxides .....	640
<b>26.3.9.1.7</b>	Method 7: Photolysis of $\beta, \gamma$ -Unsaturated Ketones .....	641

**26.4 Product Class 4: 1,2-Diketones and Related Compounds**

Y. Landais and J. M. Vincent

<b>26.4</b>	<b>Product Class 4: 1,2-Diketones and Related Compounds</b>	647
<b>26.4.1</b>	<b>Product Subclass 1: 1,2-Diketones</b>	649
<b>26.4.1.1</b>	Synthesis of Product Subclass 1	649
<b>26.4.1.1.1</b>	Method 1: Coupling Reactions	649
<b>26.4.1.1.1.1</b>	Variation 1: Coupling of Aldehydes	650
<b>26.4.1.1.1.2</b>	Variation 2: Coupling of Carboxylic Acid Derivatives	651
<b>26.4.1.1.1.3</b>	Variation 3: Coupling of $\alpha$ -Oxonitriles	656
<b>26.4.1.1.1.4</b>	Variation 4: Carbonylative Coupling of Alkyl Halides with Organometallic Reagents	658
<b>26.4.1.1.1.5</b>	Variation 5: Nucleophilic Acylation of Carboxylic Acid Derivatives by Acyllithium Reagents	660
<b>26.4.1.1.1.6</b>	Variation 6: Addition of Organometallic Reagents to 1,2-Diacyl Derivatives	662
<b>26.4.1.1.1.7</b>	Variation 7: Friedel–Crafts Acylation	665
<b>26.4.1.1.2</b>	Method 2: Substitution of Heteroatoms	667
<b>26.4.1.1.2.1</b>	Variation 1: Hydrolysis of $\alpha$ -Oxo Ketals	667
<b>26.4.1.1.2.2</b>	Variation 2: Hydrolysis of $\alpha$ -Oxo Thioketals	668
<b>26.4.1.1.2.3</b>	Variation 3: Hydrolysis of $\alpha$ -Oxo Imines	670
<b>26.4.1.1.2.4</b>	Variation 4: Hydrolysis of $\alpha,\alpha$ -Dihalo Ketones	671
<b>26.4.1.1.2.5</b>	Variation 5: From $\alpha$ -Diazo Ketones	672
<b>26.4.1.1.3</b>	Method 3: Oxidation	673
<b>26.4.1.1.3.1</b>	Variation 1: Of Ketones	673
<b>26.4.1.1.3.2</b>	Variation 2: Of Enones by Ozonolysis	675
<b>26.4.1.1.3.3</b>	Variation 3: Of $\alpha$ -Hydroxy Ketones	676
<b>26.4.1.1.3.4</b>	Variation 4: Of 1,2-Diols	677
<b>26.4.1.1.3.5</b>	Variation 5: Of Alkenes	679
<b>26.4.1.1.3.6</b>	Variation 6: Of Alkynes	681
<b>26.4.1.1.3.7</b>	Variation 7: Of Arenes, Phenols, and Catechols	682
<b>26.4.1.1.3.8</b>	Variation 8: Of $\alpha$ -Oxo Phosphorus Ylides	684
<b>26.4.1.1.3.9</b>	Variation 9: Of $\alpha$ -Bromo Ketones	686
<b>26.4.1.1.4</b>	Method 4: Addition of Bromine to 1,2-Bis(siloxy)alkenes	687
<b>26.4.1.1.5</b>	Method 5: Rearrangements of $\alpha,\beta$ -Epoxy Ketones	688
<b>26.4.1.1.6</b>	Methods 6: Additional Methods	689
<b>26.4.1.2</b>	Applications of Product Subclass 1 in Organic Synthesis	691
<b>26.4.1.2.1</b>	Method 1: Oxidation of 1,2-Diketones to Carboxylic Acids	691
<b>26.4.1.2.2</b>	Method 2: Addition Reactions with 1,2-Diketones	692
<b>26.4.1.2.2.1</b>	Variation 1: Addition of Hydrogen	692
<b>26.4.1.2.2.2</b>	Variation 2: Addition of Organometallic Reagents	693
<b>26.4.1.2.2.3</b>	Variation 3: Addition of Carbon Functionalities	694
<b>26.4.1.2.2.4</b>	Variation 4: Addition of Heteroatoms	696
<b>26.4.1.2.2.5</b>	Variation 5: Cycloadditions of 1,2-Diketones	698
<b>26.4.1.2.3</b>	Method 3: Ring Contraction of Cyclic 1,2-Diketones	698

<b>26.4.2</b>	<b>Product Subclass 2: <math>\alpha</math>-Thioxo Ketones</b> .....	699
<b>26.4.2.1</b>	Synthesis of Product Subclass 2 .....	699
<b>26.4.2.1.1</b>	Method 1: Substitution of Heteroatoms .....	699
<b>26.4.2.1.1.1</b>	Variation 1: In 1,2-Diketones .....	699
<b>26.4.2.1.1.2</b>	Variation 2: In $\alpha$ -Diazo Ketones .....	700
<b>26.4.2.1.2</b>	Method 2: Oxidation of Active Methylene Compounds .....	701
<b>26.4.2.1.2.1</b>	Variation 1: Of Ketones .....	701
<b>26.4.2.1.2.2</b>	Variation 2: Of $\alpha$ -Sulfanyl Ketones .....	702
<b>26.4.2.1.3</b>	Method 3: Addition .....	704
<b>26.4.2.1.3.1</b>	Variation 1: Of Thionyl Chloride to Silyl Enol Ethers .....	704
<b>26.4.2.1.3.2</b>	Variation 2: Of Sulfur Ylides to Carboxylic Acid Derivatives .....	704
<b>26.4.2.1.4</b>	Method 4: Rearrangements .....	705
<b>26.4.2.1.4.1</b>	Variation 1: Retro-Diels–Alder Reactions .....	705
<b>26.4.2.1.4.2</b>	Variation 2: Rearrangement of Thiirene or Thiirane S-Oxides .....	706
<b>26.4.2.2</b>	Applications of Product Subclass 2 in Organic Synthesis .....	707
<b>26.4.3</b>	<b>Product Subclass 3: <math>\alpha</math>-Selenoxo Ketones</b> .....	708
<b>26.4.3.1</b>	Synthesis of Product Subclass 3 .....	708
<b>26.4.3.1.1</b>	Method 1: Substitution of Heteroatoms .....	708
<b>26.4.3.1.1.1</b>	Variation 1: In $\alpha$ -Diazo Ketones .....	708
<b>26.4.3.1.1.2</b>	Variation 2: From $\alpha$ -Oxo Sulfonium Ylides .....	709
<b>26.4.3.1.2</b>	Method 2: Oxidation of Active Methylene Compounds .....	710
<b>26.4.3.1.3</b>	Method 3: Addition of Selenoxides to Activated Alkynes .....	711
<b>26.4.3.1.4</b>	Methods 4: Additional Methods .....	712
<b>26.4.3.2</b>	Applications of Product Subclass 3 in Organic Synthesis .....	712
<b>26.4.4</b>	<b>Product Subclass 4: <math>\alpha</math>-Imino, <math>\alpha</math>-Hydroxyimino, and <math>\alpha</math>-Hydrazone Ketones</b> .....	713
<b>26.4.4.1</b>	Synthesis of Product Subclass 4 .....	714
<b>26.4.4.1.1</b>	Method 1: Coupling Reactions between Carboxylic Acid Derivatives and Imine Derivatives .....	714
<b>26.4.4.1.2</b>	Method 2: Substitution of Heteroatoms in 1,2-Diketones .....	717
<b>26.4.4.1.3</b>	Method 3: Oxidation .....	718
<b>26.4.4.1.3.1</b>	Variation 1: Nitrosation of Ketones .....	718
<b>26.4.4.1.3.2</b>	Variation 2: Nitrosation of Enones .....	719
<b>26.4.4.1.3.3</b>	Variation 3: Nitrosation of Phenols .....	720
<b>26.4.4.1.4</b>	Method 4: From $\alpha$ -Hydroxyimino Ketones .....	721
<b>26.4.4.1.5</b>	Methods 5: Additional Methods .....	722
<b>26.4.4.2</b>	Applications of Product Subclass 4 in Organic Synthesis .....	723
<b>26.4.5</b>	<b>Product Subclass 5: <math>\alpha</math>-Diazo Ketones</b> .....	724
<b>26.4.5.1</b>	Synthesis of Product Subclass 5 .....	724
<b>26.4.5.1.1</b>	Method 1: Substitution .....	724
<b>26.4.5.1.1.1</b>	Variation 1: Of Acyl Halides .....	724
<b>26.4.5.1.1.2</b>	Variation 2: Of Hydrazones .....	725
<b>26.4.5.1.2</b>	Method 2: Oxidation .....	726
<b>26.4.5.1.2.1</b>	Variation 1: Diazo-Transfer Reactions with Active Methylene Compounds .....	726
<b>26.4.5.1.2.2</b>	Variation 2: Diazotization of Amines .....	728

26.4.5.1.3	Method 3: From $\alpha$ -Diazo Carbonyl Compounds .....	729
26.4.5.2	Applications of Product Subclass 5 in Organic Synthesis .....	730
26.5	<b>Product Class 5: <math>\alpha,\alpha</math>-Diheterosubstituted Ketones</b> J.-L. Parrain and J. Thibonnet	
26.5	<b>Product Class 5: <math>\alpha,\alpha</math>-Diheterosubstituted Ketones</b> .....	745
26.5.1	<b>Product Subclass 1: <math>\alpha,\alpha</math>-Difluoro Ketones</b> .....	745
26.5.1.1	Synthesis of Product Subclass 1 .....	745
26.5.1.1.1	Method 1: Direct Fluorination of Ketones .....	745
26.5.1.1.2	Method 2: Oxidation of $\alpha,\alpha$ -Difluoro Alcohols .....	746
26.5.1.1.3	Method 3: Synthesis from Difluoro Enoxysilanes .....	747
26.5.1.1.4	Method 4: Synthesis via Reformatsky-Type Aldol Reactions .....	749
26.5.1.1.5	Method 5: Synthesis from Lewis Acid Mediated Aldol-Type Reactions ...	750
26.5.1.1.6	Method 6: Synthesis from Anhydrides, Esters, or Amides and Organometallic Reagents .....	750
26.5.1.1.7	Method 7: Addition of Difluoroiodomethyl Ketones to Alkenes .....	752
26.5.1.1.8	Method 8: Synthesis from Alkynes .....	753
26.5.1.1.9	Method 9: Conversion of Arylperfluoroalkanes into Aryl Perfluoroalkyl Ketones .....	754
26.5.1.1.10	Method 10: Synthesis by Rearrangement .....	755
26.5.2	<b>Product Subclass 2: <math>\alpha,\alpha</math>-Dichloro Ketones</b> .....	756
26.5.2.1	Synthesis of Product Subclass 2 .....	757
26.5.2.1.1	Method 1: Synthesis by Direct Chlorination of Ketones .....	757
26.5.2.1.2	Method 2: Via Acylation Reactions .....	759
26.5.2.1.3	Method 3: By Addition of Organometallic Reagents .....	761
26.5.2.1.4	Method 4: Chlorination of Terminal Alkynes .....	761
26.5.2.1.5	Method 5: [2 + 2]-Cycloaddition Reactions of Dichloroketenes .....	762
26.5.2.1.6	Method 6: Intramolecular Insertion of Trichloromethyl Ketones into Alkenes, Catalyzed by Ruthenium Complexes .....	763
26.5.3	<b>Product Subclass 3: <math>\alpha,\alpha</math>-Dibromo Ketones and <math>\alpha,\alpha</math>-Diiodo Ketones</b> .....	764
26.5.3.1	Synthesis of Product Subclass 3 .....	764
26.5.3.1.1	Method 1: Synthesis of Dibromo Ketones by Direct Bromination of Ketones .....	764
26.5.3.1.2	Method 2: Synthesis of Diiodo Ketones by Direct Iodination of Ketones .	767
26.5.3.1.3	Method 3: Synthesis from $\alpha$ -Diazo Ketones .....	768
26.5.3.1.4	Method 4: Synthesis via $\alpha,\alpha$ -Dibromo Anions .....	769
26.5.3.1.5	Method 5: Synthesis from Alkynes .....	770
26.5.4	<b>Product Subclass 4: <math>\alpha</math>-Alkoxy-<math>\alpha</math>-halo Ketones</b> .....	771
26.5.4.1	Synthesis of Product Subclass 4 .....	772
26.5.4.1.1	Method 1: Fluorination of $\alpha$ -Alkoxy Ketones .....	772
26.5.4.1.2	Method 2: Chlorination of $\alpha$ -Alkoxy Ketones .....	772
26.5.4.1.3	Method 3: Bromination of $\alpha$ -Alkoxy Ketones .....	773
26.5.4.1.4	Method 4: From $\alpha$ -Alkoxy- or $\alpha$ -Halo- $\alpha,\beta$ -unsaturated Ketones .....	775

26.5.4.1.5	Method 5:	From $\alpha$ -Diazo Ketones	776
26.5.4.1.6	Method 6:	By Addition of an Organometallic Group	776
26.5.4.1.7	Method 7:	By Addition of Bromine to 1,2-Dialkoxyalkenes	777
26.5.5	<b>Product Subclass 5: <math>\alpha</math>-Halo-<math>\alpha</math>-sulfanyl and <math>\alpha</math>-Halo-<math>\alpha</math>-sulfinyl Ketones</b>		778
26.5.5.1	Synthesis of Product Subclass 5		778
26.5.5.1.1	Method 1:	Substitution of Hydrogen with Sulfur Reagents	778
26.5.5.1.2	Method 2:	Halogenation of $\alpha$ -Sulfanyl Ketones	779
26.5.5.1.3	Method 3:	Oxidation of $\alpha$ -Chloro- $\alpha$ -sulfinyl Alcohols	781
26.5.6	<b>Product Subclass 6: <math>\alpha</math>-Amino-<math>\alpha</math>-halo and <math>\alpha</math>-Halo-<math>\alpha</math>-nitro Ketones</b>		781
26.5.6.1	Synthesis of Product Subclass 6		782
26.5.6.1.1	Method 1:	Synthesis of $\alpha$ -Fluoro- $\alpha$ -nitro Ketones Using Perchloryl Fluoride	782
26.5.6.1.2	Method 2:	Chlorination of $\alpha$ -Amino Ketones	782
26.5.6.1.3	Method 3:	Oxidation of $\alpha$ -Chloro- $\alpha$ -nitro Alcohols	783
26.5.6.1.4	Method 4:	Synthesis from Trichloronitromethane	784
26.5.7	<b>Product Subclass 7: <math>\alpha,\alpha</math>-Dialkoxy Ketones</b>		784
26.5.7.1	Synthesis of Product Subclass 7		785
26.5.7.1.1	Method 1:	Synthesis of $\alpha,\alpha$ -Dialkoxy Ketones from Ketones	785
26.5.7.1.2	Method 2:	Synthesis of $\alpha,\alpha$ -Dialkoxy Ketones from $\alpha$ -Sulfinyl Ketones	786
26.5.7.1.3	Method 3:	Oxidation of $\alpha$ -Hydroxy Acetals	786
26.5.7.1.3.1	Variation 1:	Oxidation by Dess–Martin Periodinane	787
26.5.7.1.3.2	Variation 2:	Swern Oxidation	787
26.5.7.1.3.3	Variation 3:	Oxidation by Chromium(VI) Oxide	788
26.5.7.1.3.4	Variation 4:	Oxidation by Ruthenium(IV) Oxide	789
26.5.7.1.4	Method 4:	Oxidation of 2-Alkoxyphenols	789
26.5.7.1.5	Method 5:	Synthesis from Anhydrides, Esters, or Amides and an Organometallic Reagent	790
26.5.7.1.5.1	Variation 1:	Synthesis from Functional Anhydrides, Esters, Nitriles, or Amides	790
26.5.7.1.5.2	Variation 2:	Synthesis from Dialkoxyethylithium Reagents	791
26.5.7.1.6	Method 6:	Synthesis from $\alpha$ -Diazo Ketones	792
26.5.7.1.7	Method 7:	Synthesis of Dialkoxy-cyclobutanones via [2 + 2]-Cycloaddition Reactions	793
26.5.7.1.8	Method 8:	Synthesis by Insertion of a Dialkoxy-carbene into Strained Cyclic Ketones	793
26.5.7.1.9	Method 9:	Synthesis by Acetalization of 1,2-Diketones or 1,2-Oxoaldehydes	794
26.5.7.1.10	Method 10:	Synthesis by Rearrangement of $\alpha,\alpha'$ -Dialkoxy Ketones	795
26.5.7.1.11	Method 11:	Synthesis from Reagents Derived from $\alpha,\alpha$ -Dialkoxy Ketones	795
26.5.7.1.11.1	Variation 1:	Reactions of Enolates Derived from Dialkoxy Ketones	795
26.5.7.1.11.2	Variation 2:	By Wittig Reaction	796
26.5.7.2	Applications of Product Subclass 7 in Organic Synthesis		797
26.5.7.2.1	Method 1:	Stereoselective Applications	797

<b>26.5.8</b>	<b>Product Subclass 8: <math>\alpha</math>-Oxy-<math>\alpha</math>-sulfanyl Ketones</b> .....	798
<b>26.5.8.1</b>	Synthesis of Product Subclass 8 .....	799
<b>26.5.8.1.1</b>	Method 1: By Oxidation of $\beta$ -Oxo Sulfides .....	799
<b>26.5.8.1.2</b>	Method 2: From $\alpha$ -Oxo Sulfoxides: Pummerer Reaction .....	800
<b>26.5.8.1.2.1</b>	Variation 1: Synthesis of $\alpha$ -Acetoxy- $\beta$ -oxo Sulfides .....	801
<b>26.5.8.1.2.2</b>	Variation 2: Synthesis of $\alpha$ -Siloxy- $\beta$ -oxo Sulfides .....	802
<b>26.5.8.1.3</b>	Method 3: By Oxidation of Functional Secondary Alcohols .....	802
<b>26.5.8.1.3.1</b>	Variation 1: By Swern Oxidation .....	803
<b>26.5.8.1.3.2</b>	Variation 2: Using Pyridinium Dichromate or Pyridinium Chlorochromate ·	803
<b>26.5.8.1.4</b>	Method 4: Synthesis from $\alpha$ -Halo- $\alpha$ -sulfanyl- or $\alpha$ -Halo- $\alpha$ -oxo Ketones ·	804
<b>26.5.8.1.5</b>	Method 5: Synthesis from $\alpha$ -Diazo- $\beta$ -oxo Sulfones .....	805
<b>26.5.8.1.6</b>	Method 6: Synthesis from Anhydrides, Esters, or Amides and an Organometallic Reagent .....	806
<b>26.5.8.1.7</b>	Method 7: Synthesis from $\alpha$ -Oxoaldehydes or 1,2-Diketones .....	809
<b>26.5.8.1.8</b>	Method 8: Epoxidation of $\alpha$ -Sulfanyl- $\alpha,\beta$ -unsaturated Ketones .....	810
<b>26.5.8.1.9</b>	Method 9: Synthesis by Rearrangement .....	812
<b>26.5.8.2</b>	Applications of Product Subclass 8 in Organic Synthesis .....	812
<b>26.5.9</b>	<b>Product Subclass 9: <math>\alpha</math>-Alkoxy-<math>\alpha</math>-seleno Ketones</b> .....	813
<b>26.5.9.1</b>	Synthesis of Product Subclass 9 .....	814
<b>26.5.9.1.1</b>	Method 1: Synthesis from $\alpha$ -Seleno Ketones .....	814
<b>26.5.9.1.2</b>	Method 2: Synthesis from $\alpha$ -Diazo Ketones .....	815
<b>26.5.10</b>	<b>Product Subclass 10: <math>\alpha</math>-Alkoxy-<math>\alpha</math>-amino and <math>\alpha</math>-Amino-<math>\alpha</math>-hydroxy Ketones</b>	816
<b>26.5.10.1</b>	Synthesis of Product Subclass 10 .....	817
<b>26.5.10.1.1</b>	Method 1: By Oxidation of $\alpha$ -Amino Ketones .....	817
<b>26.5.10.1.2</b>	Method 2: By Oxidation of $\alpha$ -Hydroxy <i>N,O</i> -Acetals .....	818
<b>26.5.10.1.3</b>	Method 3: By Substitution of Heteroatoms .....	820
<b>26.5.10.1.3.1</b>	Variation 1: From $\alpha,\alpha$ -Dihydroxy Ketones .....	820
<b>26.5.10.1.3.2</b>	Variation 2: From $\alpha$ -Alkoxy- $\alpha$ -halo Ketones .....	821
<b>26.5.10.1.3.3</b>	Variation 3: From $\alpha$ -Amino- $\alpha$ -halo Ketones .....	822
<b>26.5.10.1.4</b>	Method 4: From $\alpha$ -Diazo Ketones .....	823
<b>26.5.10.1.5</b>	Method 5: By Addition of Organometallic Reagents .....	824
<b>26.5.10.1.5.1</b>	Variation 1: From Functionalized Esters, Nitriles, or Amides .....	824
<b>26.5.10.1.5.2</b>	Variation 2: From $\alpha$ -Lithio <i>N,O</i> -Acetal Reagents .....	825
<b>26.5.10.1.6</b>	Method 6: [3 + 2] Cycloaddition to Cyclopropenone .....	826
<b>26.5.10.1.7</b>	Method 7: Epoxidation of $\alpha,\beta$ -Unsaturated $\beta$ -Amino Ketones .....	826
<b>26.5.10.1.8</b>	Method 8: By Addition of Alcohols or Amines .....	827
<b>26.5.10.1.8.1</b>	Variation 1: Addition of Alcohols to 1,2-Oxoimines or 1,2-Oxoenamines ·	827
<b>26.5.10.1.8.2</b>	Variation 2: Addition of Amines to 1,2-Diketones .....	828
<b>26.5.10.1.9</b>	Method 9: By Cycloaddition .....	829
<b>26.5.11</b>	<b>Product Subclass 11: <math>\alpha,\alpha</math>-Disulfanyl Ketones</b> .....	830
<b>26.5.11.1</b>	Synthesis of Product Subclass 11 .....	831
<b>26.5.11.1.1</b>	Method 1: Substitution of Hydrogen with Sulfur Reagents .....	831
<b>26.5.11.1.2</b>	Method 2: From $\alpha$ -Oxo Sulfoxides .....	833
<b>26.5.11.1.3</b>	Method 3: Oxidation of $\alpha$ -Hydroxy-1,3-dithianes .....	833

26.5.11.1.4	Method 4:	By Addition of Organometallic Reagents	834
26.5.11.1.5	Method 5:	[2 + 2]-Cycloaddition Reactions of Disulfanyl Ketenes	836
26.5.11.1.6	Method 6:	[3 + 2]-Cycloaddition Reactions from $\alpha$ -Oxo Dithioesters	836
26.5.11.1.7	Method 7:	By Addition of Dithiols to 1,2-Diketones	837
26.5.11.1.8	Method 8:	By Rearrangement	838
26.5.11.1.9	Method 9:	Synthesis with Retention of the Functional Group	839
26.5.11.1.9.1	Variation 1:	Oxidation of $\alpha$ -Oxo Dithianes	839
26.5.11.1.9.2	Variation 2:	Alkylation of Enolates Bearing $\alpha$ -Dithianes	840
26.5.11.1.9.3	Variation 3:	Enolates Bearing $\alpha$ -Dithiane Sulfoxides	841
26.5.12	<b>Product Subclass 12: <math>\alpha</math>-Amino-<math>\alpha</math>-sulfanyl Ketones</b>		842
26.5.12.1	Synthesis of Product Subclass 12		842
26.5.12.1.1	Method 1:	Via Pummerer Reaction from $\alpha$ -Sulfoxy Ketones	842
26.5.12.1.2	Method 2:	By Sulfanylation of $\alpha$ -Amino Ketones	843
26.5.12.1.3	Method 3:	From $\alpha$ -Alkylsulfanyl Ketones	844
26.5.12.1.4	Method 4:	By Substitution of Heteroatoms	844
26.5.12.1.4.1	Variation 1:	From $\alpha$ -Amino- $\alpha$ -halo Ketones or Dihydroxy Ketones	844
26.5.12.1.4.2	Variation 2:	From $\alpha,\alpha$ -Diamino Ketones	845
26.5.12.1.4.3	Variation 3:	From $\alpha$ -Diazo Ketones	846
26.5.12.1.5	Method 5:	Using $\alpha$ -Amino- $\alpha$ -(sulfonylmethyl)lithium Reagents	846
26.5.12.1.6	Method 6:	From 1,2-Diketones or 1,2-Oxoaldehydes	847
26.5.13	<b>Product Subclass 13: <math>\alpha,\alpha</math>-Diselanyl Ketones</b>		848
26.5.13.1	Synthesis of Product Subclass 13		849
26.5.13.1.1	Method 1:	By Addition of Metal Enolates to Elemental Selenium	849
26.5.13.1.2	Method 2:	From $\alpha$ -Selanyl Ketones	850
26.5.13.1.3	Method 3:	From $\alpha$ -Diazo Ketones	850
26.5.14	<b>Product Subclass 14: <math>\alpha,\alpha</math>-Diamino Ketones</b>		851
26.5.14.1	Synthesis of Product Subclass 14		851
26.5.14.1.1	Method 1:	By Substitution of Halogen	851
26.5.14.1.2	Method 2:	Via Cycloaddition	852
26.5.14.1.3	Method 3:	By Addition of Diaminoalkylmetal Reagents	853
26.5.14.1.4	Method 4:	From 1,2-Diketones or $\alpha$ -Oxoaldehydes	854
26.6	<b>Product Class 6: <math>\alpha</math>-Heterosubstituted Ketones</b>		
	J. Suffert		
26.6	<b>Product Class 6: <math>\alpha</math>-Heterosubstituted Ketones</b>		869
26.6.1	<b>Product Subclass 1: <math>\alpha</math>-Fluoro Ketones</b>		869
26.6.1.1	Synthesis of Product Subclass 1		870
26.6.1.1.1	Method 1:	Substitution of a Hydrogen Atom from an Alkanone	870
26.6.1.1.1.1	Variation 1:	Direct Fluorination of Ketones without a Base	870
26.6.1.1.1.2	Variation 2:	Deprotonation with an External Base	871
26.6.1.1.1.3	Variation 3:	From an Alkanone via a Preformed Acetate Enol Ether	872
26.6.1.1.1.4	Variation 4:	From Alkanones through Preformed Enol Silyl Ethers	873
26.6.1.1.1.5	Variation 5:	Via a Preformed Enamine or Enamide	874

26.6.1.1.2	Method 2: Synthesis from Trifluoromethyl Ketones via Fluorinated Silyl Enol Ethers .....	876
26.6.2	<b>Product Subclass 2: <math>\alpha</math>-Chloro Ketones</b> .....	877
26.6.2.1	Synthesis of Product Subclass 2 .....	878
26.6.2.1.1	Method 1: Substitution of a Hydrogen Atom from an Alkanone .....	878
26.6.2.1.1.1	Variation 1: Direct Chlorination with Chlorine .....	878
26.6.2.1.1.2	Variation 2: Direct Chlorination with Sulfuryl Chloride .....	881
26.6.2.1.1.3	Variation 3: Direct Chlorination with Selenium Oxychloride .....	883
26.6.2.1.1.4	Variation 4: Direct Chlorination with Sodium Chlorite/Manganese(III) Acetylacetonate .....	884
26.6.2.1.1.5	Variation 5: Direct Chlorination with Manganese(IV) Chloride .....	884
26.6.2.1.1.6	Variation 6: Direct Chlorination with Chlorotrimethylsilane/Dimethyl Sulfoxide .....	885
26.6.2.1.1.7	Variation 7: Direct Chlorination with Copper(II) Chloride/Lithium Chloride .....	886
26.6.2.1.1.8	Variation 8: Direct Chlorination with Trichloroisocyanuric Acid .....	888
26.6.2.1.1.9	Variation 9: Direct Chlorination with Hydrogen Chloride and Potassium Permanganate .....	888
26.6.2.1.1.10	Variation 10: Deprotonation with a Base Prior to Chlorination .....	889
26.6.2.1.1.11	Variation 11: Via a Preformed Enamine .....	890
26.6.2.1.1.12	Variation 12: Via a Preformed Silyl Enol Ether .....	892
26.6.2.1.1.13	Variation 13: Via a Preformed Enol Ether or Enol Ester .....	894
26.6.2.1.2	Method 2: Synthesis from $\alpha, \alpha$ -Dichloro Ketones by Reduction .....	895
26.6.2.1.3	Method 3: Synthesis by Oxidative Addition to an Alkene .....	898
26.6.2.1.3.1	Variation 1: Oxidation of an Alkene with Nitrosyl Chloride .....	898
26.6.2.1.3.2	Variation 2: Oxidation of an Alkene with Chromyl Chloride .....	900
26.6.2.1.3.3	Variation 3: Oxidation of an Alkene with 2-Cyanopyridinium Chlorochromate .....	901
26.6.2.1.3.4	Variation 4: Oxidation of an Alkene with Chromium(VI) Oxide and Chlorotrimethylsilane .....	901
26.6.2.1.3.5	Variation 5: Oxidation of an Alkene with Iron(III) Chloride .....	902
26.6.2.1.4	Method 4: Synthesis via the Opening of an Epoxide .....	903
26.6.2.1.4.1	Variation 1: Ring Opening of Epoxides with Chloro(dimethyl)sulfonium Chloride .....	904
26.6.2.1.4.2	Variation 2: Opening of an $\alpha, \beta$ -Epoxy Ketone with Benzoyl Chloride .....	904
26.6.3	<b>Product Subclass 3: <math>\alpha</math>-Bromo Ketones</b> .....	905
26.6.3.1	Synthesis of Product Subclass 3 .....	906
26.6.3.1.1	Method 1: Substitution of Hydrogen by Bromine .....	906
26.6.3.1.1.1	Variation 1: Direct Bromination with Bromine in Acetic Acid/Water or in the Presence of Urea .....	906
26.6.3.1.1.2	Variation 2: Direct Bromination with Bromine in Concentrated Sulfuric Acid .....	908
26.6.3.1.1.3	Variation 3: Direct Bromination with Bromine in Methanol or Carbon Tetrachloride .....	908
26.6.3.1.1.4	Variation 4: Direct Bromination with Bromine in the Presence of Potassium Chlorate or Sodium Chlorate in Water .....	910
26.6.3.1.1.5	Variation 5: Bromination of an Enolate with Bromine .....	911

26.6.3.1.1.6	Variation 6:	Bromination with Perbromide Salts	911
26.6.3.1.1.7	Variation 7:	Bromination with Copper Bromide	913
26.6.3.1.1.8	Variation 8:	Bromination with Bromine Donors in Dimethyl Sulfoxide	913
26.6.3.1.1.9	Variation 9:	Bromination with Bromine Donors: Perfluoroalkanesulfonyl Bromides or Benzeneselenenyl Bromide	915
26.6.3.1.1.10	Variation 10:	Bromination with Bromine Donors: Hexabromocyclopentadiene and Bromomalonic Derivatives	916
26.6.3.1.1.11	Variation 11:	Bromination with Bromine Donors: <i>N</i> -Bromosuccinimide in the Presence of Ammonium Acetate	917
26.6.3.1.1.12	Variation 12:	Bromination in the Presence of an Oxidant	918
26.6.3.1.2	Method 2:	Synthesis from an Enol Ether	919
26.6.3.1.3	Method 3:	Synthesis from an $\alpha,\beta$ -Unsaturated Ketone by Reductive Bromination	920
26.6.3.1.4	Method 4:	Synthesis via the Ring Opening of an Epoxide	921
26.6.3.1.4.1	Variation 1:	Photocatalytic Bromination of an Epoxide	921
26.6.3.1.4.2	Variation 2:	Opening of an Epoxide with Bromo(dimethyl)sulfonium Bromide	922
26.6.3.1.5	Methods 5:	Additional Methods	922
26.6.4	<b>Product Subclass 4: <math>\alpha</math>-Iodo Ketones</b>		923
26.6.4.1	Synthesis of Product Subclass 4		923
26.6.4.1.1	Method 1:	Substitution of Hydrogen by Iodine	923
26.6.4.1.1.1	Variation 1:	Direct Iodination under Acidic Conditions	924
26.6.4.1.1.2	Variation 2:	Iodination of Enolates	925
26.6.4.1.2	Method 2:	Synthesis by Conjugate Addition to $\alpha$ -Iodocycloalkenones	927
26.6.4.1.3	Method 3:	Synthesis from an Enol Ether by Enol Acetate	927
26.6.4.1.3.1	Variation 1:	Via an Iodonium Ion Transfer Reagent and an Enol Acetate	927
26.6.4.1.3.2	Variation 2:	Via an Iodonium Ion Transfer from the Reagent to a Silyl Enol Ether	929
26.6.4.1.4	Method 4:	Synthesis via the Ring Opening of an Epoxide	930
26.6.4.1.4.1	Variation 1:	Using Iodotrimethylsilane	930
26.6.4.1.4.2	Variation 2:	Via the Ring Opening of an $\alpha$ -Nitro Epoxide	931
26.6.4.1.5	Method 5:	Synthesis via Oxidative Addition to an Alkene	931
26.6.4.1.5.1	Variation 1:	Using Silver Chromate and Iodine	932
26.6.4.1.5.2	Variation 2:	Using Pyridinium Dichromate and Iodine	932
26.6.4.1.5.3	Variation 3:	Using Bis(2,4,6-trimethylpyridine)iodonium(I) Tetrafluoroborate/Dimethyl Sulfoxide	933
26.6.5	<b>Product Subclass 5: <math>\alpha</math>-Hydroxy and <math>\alpha</math>-Oxo Ketones</b>		934
26.6.5.1	Synthesis of Product Subclass 5		934
26.6.5.1.1	Method 1:	Substitution of an $\alpha$ -Hydrogen Atom	934
26.6.5.1.1.1	Variation 1:	From Alkanones by Deprotonation/Oxidation	934
26.6.5.1.1.2	Variation 2:	By Oxidation with Dimethyldioxirane or an Oxaziridine	935
26.6.5.1.1.3	Variation 3:	By Oxidation of a Titanium Enolate	936
26.6.5.1.1.4	Variation 4:	By Reaction of a Tin Enolate with Nitrosobenzene	937
26.6.5.1.1.5	Variation 5:	By Oxidation with a Molybdenum Complex	938
26.6.5.1.1.6	Variation 6:	By Oxidation with Thallium(III) Salts	939
26.6.5.1.1.7	Variation 7:	By Oxidation with Hydroxy(mesyloxy)iodobenzene	939

26.6.5.1.1.8	Variation 8:	By Treatment with Oxygen and Triethyl Phosphite	940
26.6.5.1.2	Method 2:	Synthesis via a Silyl Enol Ether	941
26.6.5.1.2.1	Variation 1:	Oxidation with 3-Chloroperoxybenzoic Acid	941
26.6.5.1.2.2	Variation 2:	Oxidation with Osmium(VIII) Oxide/4-Methylmorpholine N-Oxide	942
26.6.5.1.3	Method 3:	Synthesis via Oxidative Addition to an Alkene	942
26.6.5.1.3.1	Variation 1:	By Oxidation with Permanganate Salts	942
26.6.5.1.3.2	Variation 2:	By Oxidation with Ruthenium(III) Chloride and Peracetic Acid	943
26.6.6	<b>Product Subclass 6: <math>\alpha</math>-Sulfanyl Ketones</b>		944
26.6.6.1	Synthesis of Product Subclass 6		945
26.6.6.1.1	Method 1:	Substitution of a Hydrogen Atom	945
26.6.6.1.2	Method 2:	$\alpha$ -Sulfanylation of Silyl Enol Ethers or Enamines	946
26.6.6.1.3	Method 3:	Regioselective $\alpha$ -Sulfanylation of Boryl Enol Ethers	946
26.6.7	<b>Product Subclass 7: <math>\alpha</math>-Selanyl Ketones</b>		947
26.6.7.1	Synthesis of Product Subclass 7		947
26.6.7.1.1	Method 1:	Substitution of a Hydrogen Atom	947
26.6.7.1.1.1	Variation 1:	Selanylation under Neutral Conditions	947
26.6.7.1.1.2	Variation 2:	Selanylation under Basic Conditions	949
26.6.7.1.1.3	Variation 3:	Selanylation under Acidic Conditions	950
26.6.7.1.2	Method 2:	Regioselective $\alpha$ -Selanylation of O-Silylated Enols or Boryl Enol Ethers	952
26.6.7.1.3	Method 3:	Synthesis by Homologation from Phenylselenoacetaldehyde	952
26.6.8	<b>Product Subclass 8: <math>\alpha</math>-Amino Ketones</b>		953
26.6.8.1	Synthesis of Product Subclass 8		954
26.6.8.1.1	Method 1:	Neber Rearrangement	954
26.6.8.1.2	Method 2:	Synthesis from Silyl Enol Ethers by Aminohydroxylation	955
26.6.8.1.3	Method 3:	Synthesis from $\alpha$ -Bromo Ketones by Substitution	956
26.6.8.1.4	Method 4:	Synthesis from Aldehydes and Iminium Salts	957
26.6.8.1.5	Method 5:	Synthesis from $\alpha$ -Amino Acids via an Oxazolidin-5-one	958
26.6.8.1.6	Method 6:	Synthesis via the Cyclization of an $\alpha$ -Amino Ester	958
26.6.8.1.7	Method 7:	Synthesis via the Electroreductive Coupling of Aliphatic Amides	959
26.6.8.1.8	Method 8:	Synthesis via the Selective Reduction of Acyl Cyanides	959
26.6.8.1.9	Method 9:	Synthesis from Amines	960
26.6.9	<b>Product Subclass 9: <math>\alpha</math>-Phosphino and <math>\alpha</math>-Phosphoryl Ketones</b>		961
26.6.9.1	Synthesis of Product Subclass 9		961
26.6.9.1.1	Method 1:	2-(Diphenylphosphoryl)cycloalkanones by Base-Mediated Phosphinylation/Oxidation of Cycloalkanones	961
26.6.9.1.2	Method 2:	$\alpha$ -(Dialkoxyphosphoryl) Ketones by Rearrangement of a Vinyl Phosphate	962
26.6.9.1.3	Method 3:	Diethyl (2-Oxoethyl)phosphonates from $\alpha$ -Bromo Ketones and Diethyl Chlorophosphate	963
26.6.9.1.4	Method 4:	$\alpha$ -Phosphorylated Ketones from $\alpha$ -Chloro Ketones	964

<b>26.7</b>	<b>Product Class 7: Yrones</b>	
	A. Nelson	
<hr/>		
<b>26.7</b>	<b>Product Class 7: Yrones</b>	971
<b>26.7.1</b>	<b>Product Subclass 1: Propargyl Ketones</b>	971
<b>26.7.1.1</b>	Synthesis of Product Subclass 1	971
<b>26.7.1.1.1</b>	Method 1: Acylation of Organometallic Reagents	971
<b>26.7.1.1.1.1</b>	Variation 1: Acylation of Lithiated Alkynes with Carbonyl Compounds	972
<b>26.7.1.1.1.2</b>	Variation 2: Copper(I)-Catalyzed Coupling of Terminal Alkynes and Acid Chlorides	973
<b>26.7.1.1.1.3</b>	Variation 3: Coupling of Terminal Alkynes and Acid Chlorides under Bimetallic Copper(I)/Palladium Conditions	973
<b>26.7.1.1.1.4</b>	Variation 4: Palladium(0)-Catalyzed Coupling of Trialkynylindiums with Acid Chlorides	974
<b>26.7.1.1.1.5</b>	Variation 5: By Acylation of an Organometallic Reagent with a Propargylic Ester	975
<b>26.7.1.1.2</b>	Method 2: Oxidation of Propargyl Alcohols	975
<b>26.7.1.1.2.1</b>	Variation 1: By Propargylic Oxidation of Alkynes	976
<b>26.7.1.1.3</b>	Method 3: Three-Component Couplings Involving Carbon Monoxide	977
<b>26.7.1.1.4</b>	Method 4: By Elimination of Aminoalkenones	977
<b>26.7.1.1.5</b>	Method 5: By Oxy-Cope Rearrangement	978
<b>26.7.1.1.6</b>	Method 6: By Elimination of $\alpha,\gamma$ -Dioxo Phosphonium Ylides	978
<b>26.7.2</b>	<b>Product Subclass 2: <math>\beta,\gamma</math>-Alkynyl Ketones</b>	979
<b>26.7.2.1</b>	Synthesis of Product Subclass 2	979
<b>26.7.2.1.1</b>	Method 1: By Alkynylation of Enolates	979
<b>26.7.2.1.2</b>	Method 2: By Rearrangement of 3-Furyllithium	980
<b>26.7.2.1.3</b>	Method 3: By 1,2-Shift of an Alkynyl Group	980
<b>26.7.3</b>	<b>Product Subclass 3: <math>\gamma,\delta</math>-Alkynyl Ketones</b>	981
<b>26.7.3.1</b>	Synthesis of Product Subclass 3	982
<b>26.7.3.1.1</b>	Method 1: By Conjugate Addition to $\alpha,\beta$ -Unsaturated Ketones	982
<b>26.7.3.1.1.1</b>	Variation 1: Addition of Alkynylaluminum Reagents	982
<b>26.7.3.1.1.2</b>	Variation 2: Addition of Alkynylboronates	982
<b>26.7.3.1.1.3</b>	Variation 3: Transition-Metal-Catalyzed Addition of Terminal Alkynes	983
<b>26.7.3.1.2</b>	Method 2: By Propargylation of Enolates	984
<b>26.7.3.1.3</b>	Method 3: By Fragmentation	984
<b>26.7.4</b>	<b>Product Subclass 4: Other Alkynyl Ketones</b>	985
<b>26.7.4.1</b>	Synthesis of Product Subclass 4	985
<b>26.7.4.1.1</b>	Method 1: By Eschenmoser Fragmentation	985

<b>26.8</b>	<b>Product Class 8: Aryl Ketones</b> J. M. Campagne and Y. Six	
<b>26.8</b>	<b>Product Class 8: Aryl Ketones</b> .....	989
<b>26.8.1</b>	<b>Product Subclass 1: Nonsubstituted and Carbon-Substituted Aryl Ketones</b> .....	989
<b>26.8.1.1</b>	Synthesis of Product Subclass 1 .....	989
<b>26.8.1.1.1</b>	Method 1: Friedel–Crafts Acylation .....	989
<b>26.8.1.1.2</b>	Method 2: Oxidation .....	991
<b>26.8.1.1.2.1</b>	Variation 1: Oxidation of Benzylic Halides .....	991
<b>26.8.1.1.2.2</b>	Variation 2: Oxidation of Benzylic Alcohols and Ethers .....	992
<b>26.8.1.1.2.3</b>	Variation 3: Oxidation of Benzylic Sulfur Compounds .....	993
<b>26.8.1.1.2.4</b>	Variation 4: Oxidation of Benzylic Nitrogen Compounds .....	994
<b>26.8.1.1.2.5</b>	Variation 5: Oxidative Decyanation .....	994
<b>26.8.1.1.2.6</b>	Variation 6: Benzylic Oxidation .....	995
<b>26.8.1.1.2.7</b>	Variation 7: Wacker Oxidation .....	997
<b>26.8.1.1.3</b>	Method 3: Acylation of Organometallic Reagents .....	997
<b>26.8.1.1.3.1</b>	Variation 1: Arylstannyl Reagents .....	998
<b>26.8.1.1.3.2</b>	Variation 2: Arylboryl Reagents .....	998
<b>26.8.1.1.3.3</b>	Variation 3: Aryl Grignard Reagents .....	999
<b>26.8.1.1.3.4</b>	Variation 4: Aryllithium Reagents .....	1000
<b>26.8.1.1.3.5</b>	Variation 5: Miscellaneous Aryl Organometallic Reagents .....	1001
<b>26.8.1.1.4</b>	Method 4: Transition-Metal-Catalyzed Carbonylation of Aryl Halides and Pseudohalides .....	1002
<b>26.8.1.1.5</b>	Method 5: Hydration of Arylalkynes .....	1003
<b>26.8.1.1.6</b>	Method 6: Oxidation of Arylalkynes to 1,2-Diketones .....	1004
<b>26.8.1.1.7</b>	Method 7: Oxidative Cleavage of <i>gem</i> -Disubstituted Arylalkenes .....	1004
<b>26.8.1.1.8</b>	Method 8: Synthesis by Aromatic Ring Formation .....	1004
<b>26.8.1.1.8.1</b>	Variation 1: Ionic [2 + 2 + 2] Benzannulation .....	1004
<b>26.8.1.1.8.2</b>	Variation 2: Transition-Metal-Catalyzed [2 + 2 + 2] Benzannulation .....	1005
<b>26.8.1.1.9</b>	Method 9: Aryl Ketones by Aromatization of Diels–Alder Adducts .....	1005
<b>26.8.1.1.10</b>	Method 10: Aryl Ketones by Electrocyclization and Aromatization .....	1006
<b>26.8.1.1.11</b>	Method 11: Transition-Metal-Catalyzed <i>ortho</i> Alkylation of Aryl Ketones ·	1006
<b>26.8.1.1.12</b>	Method 12: Transition-Metal-Catalyzed <i>ortho</i> Vinylation of Aryl Ketones ·	1007
<b>26.8.1.1.13</b>	Method 13: Transition-Metal-Catalyzed <i>ortho</i> Arylation of Aryl Ketones ·	1007
<b>26.8.1.2</b>	Applications of Product Subclass 1 in Organic Synthesis .....	1008
<b>26.8.1.2.1</b>	Method 1: Asymmetric Reduction .....	1008
<b>26.8.1.2.2</b>	Method 2: Photochemistry .....	1008
<b>26.8.1.2.3</b>	Method 3: Willgerodt Reaction .....	1009
<b>26.8.1.2.4</b>	Method 4: 1,2-Aryl Shift .....	1010
<b>26.8.1.2.5</b>	Method 5: Haller–Bauer Reaction .....	1011
<b>26.8.2</b>	<b>Product Subclass 2: Heteroatom-Substituted Aryl Ketones</b> .....	1012
<b>26.8.2.1</b>	Synthesis of Product Subclass 2 .....	1012
<b>26.8.2.1.1</b>	Method 1: Friedel–Crafts Acylation .....	1012
<b>26.8.2.1.1.1</b>	Variation 1: Halogen-Substituted Aryl Ketones .....	1012

26.8.2.1.1.2	Variation 2:	Oxygen-Substituted Aryl Ketones	1013
26.8.2.1.1.3	Variation 3:	Sulfur-Substituted Aryl Ketones	1014
26.8.2.1.1.4	Variation 4:	Nitrogen-Substituted Aryl Ketones	1014
26.8.2.1.2	Method 2:	Houben–Hoesch Reaction	1015
26.8.2.1.3	Method 3:	Fries Rearrangement	1015
26.8.2.1.3.1	Variation 1:	Hydroxy-Substituted Aryl Ketones	1015
26.8.2.1.3.2	Variation 2:	Amino-Substituted Aryl Ketones	1016
26.8.2.1.4	Method 4:	Hydroxy-Substituted Diaryl Ketones by Acyl Radical <i>ipso</i> Substitution	1017
26.8.2.1.5	Method 5:	Aryl Ring Formation	1017
26.8.2.1.5.1	Variation 1:	Amino-Substituted Aryl Ketones by Ionic [2 + 2 + 2] Aromatic Ring Formation	1017
26.8.2.1.5.2	Variation 2:	Hydroxy-Substituted Aryl Ketones by [3 + 3] Aromatic Ring Formation	1018
26.8.2.1.5.3	Variation 3:	Heteroatom-Substituted Aryl Ketones by [4 + 2] Aromatic Ring Formation: Aromatization of Cycloadducts Derived from Cyanophthalides	1019
26.8.2.1.5.4	Variation 4:	Heteroatom-Substituted Aryl Ketones by [4 + 2] Aromatic Ring Formation: Aromatization of Adducts Derived from Activated Cyanomethylene Compounds	1019
26.8.2.1.5.5	Variation 5:	Beirut Reaction	1019
26.8.2.1.5.6	Variation 6:	Aromatization of Diels–Alder Adducts	1020
26.8.2.1.6	Method 6:	Heteroatom-Substituted Aryl Ketones by Intramolecular Cyclization and Aromatization	1021
26.8.2.1.6.1	Variation 1:	Intramolecular Anionic Condensation	1021
26.8.2.1.6.2	Variation 2:	Radical Oxidative Cyclization	1021
26.8.2.2	Applications of Product Subclass 2 in Organic Synthesis		1022
26.8.2.2.1	Method 1:	Friedländer Quinoline Synthesis	1022
26.8.3	<b>Product Subclass 3: Aryl Ketones with the Carbonyl in a Ring</b>		1023
26.8.3.1	Synthesis of Product Subclass 3		1023
26.8.3.1.1	Method 1:	Intramolecular Acylation by Electrophilic Aromatic Substitution	1023
26.8.3.1.2	Method 2:	Intramolecular Alkylation by Electrophilic Aromatic Substitution	1024
26.8.3.1.3	Method 3:	Free Radical Cyclization onto Aromatic Rings	1026
26.8.3.1.4	Method 4:	Intramolecular Alkylation of Aromatic Carboxylic Acid Derivatives	1027
26.8.3.1.5	Method 5:	Cyclization of Aroyl Radicals	1027
26.8.3.1.6	Method 6:	Benzocyclobutanones from Heteroatom-Substituted Benzoyl Compounds	1028
26.8.3.1.7	Method 7:	[2 + 2] Cycloaddition to Benzyne Species Generated from Aromatic Halides	1028
26.8.3.1.8	Method 8:	Acylation and Carbonylation of Aryl Metallic Species Generated from Aromatic Halides	1030
26.8.3.1.9	Method 9:	By Ring Formation	1031

26.8.3.1.9.1	Variation 1: By Transition-Metal-Catalyzed [2 + 2 + 2] Aromatic Ring Formation .....	1031
26.8.3.1.9.2	Variation 2: By [3 + 3] Aromatic Ring Formation .....	1031
26.8.3.1.9.3	Variation 3: By [4 + 2] Aromatic Ring Formation .....	1031
26.8.3.1.9.4	Variation 4: By Electrocyclization and Aromatization .....	1033
<b>26.9</b>	<b>Product Class 9: Enones</b>	
	S. P. Marsden	
<b>26.9</b>	<b>Product Class 9: Enones</b> .....	1045
<b>26.9.1</b>	<b>Product Subclass 1: <math>\alpha,\beta</math>-Unsaturated Ketones</b> .....	1045
<b>26.9.1.1</b>	Synthesis of Product Subclass 1 .....	1045
<b>26.9.1.1.1</b>	Method 1: Oxidation Adjacent to Alkenes .....	1045
<b>26.9.1.1.1.1</b>	Variation 1: Allylic Oxidation with Stoichiometric Chromium Reagents ..	1045
<b>26.9.1.1.1.2</b>	Variation 2: Allylic Oxidation with Peroxides and Catalytic Metal Salts ...	1046
<b>26.9.1.1.1.3</b>	Variation 3: Allylic Oxidation with Selenium Reagents .....	1047
<b>26.9.1.1.2</b>	Method 2: Oxidation of Allylic Alcohols .....	1048
<b>26.9.1.1.3</b>	Method 3: Acylation of Organometallic Reagents .....	1050
<b>26.9.1.1.3.1</b>	Variation 1: Addition of Alkenylmetals to Carboxylic Acids .....	1050
<b>26.9.1.1.3.2</b>	Variation 2: Addition of Alkenylmetals to Carboxylic Esters and Derivatives .....	1051
<b>26.9.1.1.3.3</b>	Variation 3: Addition of Alkenylmetals to Carboxylic Amides and Derivatives .....	1052
<b>26.9.1.1.3.4</b>	Variation 4: Direct Addition of Alkenylmetals to Carboxylic Acid Halides and Anhydrides .....	1053
<b>26.9.1.1.3.5</b>	Variation 5: Lewis Acid Catalyzed Addition of Alkenylmetals to Carboxylic Acid Halides and Anhydrides .....	1055
<b>26.9.1.1.3.6</b>	Variation 6: Transition-Metal-Catalyzed Coupling of Alkenylmetals with Carboxylic Acid Halides and Anhydrides .....	1056
<b>26.9.1.1.3.7</b>	Variation 7: Transition-Metal-Catalyzed Coupling of Alkenylmetals with Organic Halides and Carbon Monoxide .....	1057
<b>26.9.1.1.3.8</b>	Variation 8: Addition of Alkenylmetals to Nitriles .....	1058
<b>26.9.1.1.3.9</b>	Variation 9: Addition of Organometallics to $\alpha,\beta$ -Unsaturated Carboxylic Acids .....	1059
<b>26.9.1.1.3.10</b>	Variation 10: Addition of Organometallics to $\alpha,\beta$ -Unsaturated Carboxylic Amides .....	1059
<b>26.9.1.1.3.11</b>	Variation 11: Transition-Metal-Catalyzed Coupling of Organometallics with Alkenyl Acid Halides .....	1060
<b>26.9.1.1.3.12</b>	Variation 12: Transition-Metal-Mediated Coupling of Organometallics with Alkenyl Halides and Carbon Monoxide .....	1062
<b>26.9.1.1.3.13</b>	Variation 13: Addition of Organometallics to $\alpha,\beta$ -Unsaturated Nitriles ...	1063
<b>26.9.1.1.4</b>	Method 4: Substitution of Alkenes .....	1063
<b>26.9.1.1.4.1</b>	Variation 1: Lewis Acid Catalyzed Substitution with Acid Halides .....	1063
<b>26.9.1.1.4.2</b>	Variation 2: Transition-Metal-Catalyzed Substitution with Acid Halides ..	1064
<b>26.9.1.1.5</b>	Method 5: Elimination Reactions .....	1065
<b>26.9.1.1.5.1</b>	Variation 1: Oxidative Elimination of Metal Hydride from Enol Derivatives	1065
<b>26.9.1.1.5.2</b>	Variation 2: Elimination of a Hydrogen Halide from $\alpha$ -Halo Ketones .....	1066

26.9.1.1.5.3	Variation 3:	Elimination from $\beta$ -Heterosubstituted Ketones . . . . .	1067
26.9.1.1.5.4	Variation 4:	Pericyclic Elimination of $\alpha$ -Sulfinyl and $\alpha$ -Seleninyl Ketones . . . . .	1069
26.9.1.1.5.5	Variation 5:	Pericyclic Elimination of $\beta$ -Acetoxy, $\beta$ -Sulfinyl, and $\beta$ -Seleninyl Ketones . . . . .	1070
26.9.1.1.6	Method 6:	Reduction of Propargylic Ketones . . . . .	1071
26.9.1.1.7	Method 7:	Organometallic Addition to $\beta$ -Heterosubstituted $\alpha,\beta$ -Unsaturated Ketones . . . . .	1072
26.9.1.1.7.1	Variation 1:	Direct Substitution . . . . .	1072
26.9.1.1.7.2	Variation 2:	Substitution by Addition/Rearrangement . . . . .	1073
26.9.1.1.8	Method 8:	Aldol Condensation . . . . .	1074
26.9.1.1.8.1	Variation 1:	Intermolecular Aldol Reaction of Ketones . . . . .	1074
26.9.1.1.8.2	Variation 2:	Intermolecular Aldol Reaction of Enamines and Enol Ethers . . . . .	1075
26.9.1.1.8.3	Variation 3:	Intramolecular Aldol Condensation . . . . .	1077
26.9.1.1.8.4	Variation 4:	Tandem Michael Addition/Intramolecular Aldol Reaction (Robinson Annulation) . . . . .	1078
26.9.1.1.9	Method 9:	Wittig-Type Alkenations . . . . .	1080
26.9.1.1.9.1	Variation 1:	Wittig Reaction of Oxophosphanes . . . . .	1080
26.9.1.1.9.2	Variation 2:	Horner–Wittig Reaction of Oxophosphine Oxides . . . . .	1082
26.9.1.1.9.3	Variation 3:	Horner–Wadsworth–Emmons Reaction . . . . .	1082
26.9.1.1.9.4	Variation 4:	Peterson Reaction of $\alpha$ -Silyl Ketones . . . . .	1084
26.9.1.1.9.5	Variation 5:	Wittig Alkenation of 1,2-Dicarbonyls . . . . .	1085
26.9.1.1.10	Method 10:	Cyclocondensation of Danishefsky-Type Dienes with Alkenes . . . . .	1086
26.9.1.1.11	Method 11:	Union of Alkynes, Alkenes, and Carbon Monoxide . . . . .	1087
26.9.1.1.11.1	Variation 1:	Using Hexacarbonyldicobalt–Alkyne Complexes (Pauson–Khand Reaction) . . . . .	1087
26.9.1.1.11.2	Variation 2:	By Direct Transition-Metal-Promoted Coupling . . . . .	1089
26.9.1.1.12	Method 12:	Transition-Metal-Catalyzed Addition of Aryl Halides and Carbon Monoxide to Allenes . . . . .	1090
26.9.1.1.13	Method 13:	Addition of Nucleophiles to Propargylic Ketones . . . . .	1091
26.9.1.1.14	Method 14:	$\alpha$ -Alkylation of Preformed $\alpha,\beta$ -Unsaturated Ketones . . . . .	1093
26.9.1.1.14.1	Variation 1:	By Base-Mediated Dienolate Formation . . . . .	1093
26.9.1.1.14.2	Variation 2:	By Catalyzed Nucleophilic Addition/Alkylation/Elimination . . . . .	1094
26.9.1.1.15	Method 15:	$\alpha'$ -Alkylation of Preformed $\alpha,\beta$ -Unsaturated Ketones . . . . .	1095
26.9.1.1.16	Method 16:	$\gamma$ -Alkylation of Preformed $\alpha,\beta$ -Unsaturated Enones . . . . .	1096
26.9.1.1.16.1	Variation 1:	By Direct $\gamma$ -Alkylation . . . . .	1096
26.9.1.1.16.2	Variation 2:	By $\alpha'$ -Alkylation of Vinylogous Esters with Rearrangement . . . . .	1097
26.9.1.1.17	Method 17:	Alkylation of Umpoled Enal Anion Equivalents . . . . .	1098
26.9.1.1.18	Method 18:	Hydroacylation of Alkynes . . . . .	1099
26.9.1.1.19	Method 19:	Oxidative Ring Opening of Furans . . . . .	1100
26.9.1.1.20	Method 20:	Retro-Diels–Alder Reaction . . . . .	1101
26.9.1.1.21	Method 21:	Nazarov Cyclization of Dienones . . . . .	1102
26.9.1.1.22	Method 22:	Isomerization of Propargylic Alcohols . . . . .	1103
26.9.1.1.23	Method 23:	Alkene Metathesis . . . . .	1104
26.9.2	<b>Product Subclass 2: <math>\beta,\gamma</math>-Unsaturated Ketones</b> . . . . .		1105
26.9.2.1	Synthesis of Product Subclass 2 . . . . .		1105
26.9.2.1.1	Method 1:	Acylation of Allyl Organometallics . . . . .	1105
26.9.2.1.1.1	Variation 1:	Addition of Allylmetals to Carboxylic Acids . . . . .	1106

26.9.2.1.1.2	Variation 2:	Addition of Allylmetals to Carboxylic Amides	1106
26.9.2.1.1.3	Variation 3:	Addition of Allylmetals to Reactive Carboxylic Acid Derivatives	1107
26.9.2.1.1.4	Variation 4:	Addition of Allylmetals to Nitriles	1109
26.9.2.1.2	Method 2:	Deconjugative Alkylation of $\alpha,\beta$ -Unsaturated Ketones	1109
26.9.2.1.3	Method 3:	Transition-Metal-Catalyzed Vinylation of Enolates	1110
26.9.3	<b>Product Subclass 3: <math>\gamma,\delta</math>-Unsaturated Ketones</b>		1111
26.9.3.1	Synthesis of Product Subclass 3		1111
26.9.3.1.1	Method 1:	Coupling of Enolates with Transition-Metal-Allyl Complexes	1111
26.9.3.1.2	Method 2:	Claisen Rearrangement	1115
26.9.4	<b>Product Subclass 4: <math>\delta,\epsilon</math>-Unsaturated Ketones</b>		1115
26.10	<b>Product Class 10: Saturated and Unsaturated Ketones with an Additional Carbonyl, Nitrile, or Carboxy Substituent or Equivalent at a <math>\beta</math>- or More Remote Position: Synthesis of the Ketone Functionality</b> I. Chataigner, A. Harrison-Marchand, and J. Maddaluno		
26.10	<b>Product Class 10: Saturated and Unsaturated Ketones with an Additional Carbonyl, Nitrile, or Carboxy Substituent or Equivalent at a <math>\beta</math>- or More Remote Position: Synthesis of the Ketone Functionality</b> . . . . . 1123		
26.10.1	<b>Product Subclass 1: Oxonitriles</b>		1123
26.10.1.1	Synthesis of Product Subclass 1		1124
26.10.1.1.1	Method 1:	Oxidation	1124
26.10.1.1.1.1	Variation 1:	Of Hydroxynitriles	1124
26.10.1.1.1.2	Variation 2:	Of Nitronitriles	1124
26.10.1.1.1.3	Variation 3:	Of Unsaturated Nitriles	1125
26.10.1.1.2	Method 2:	Electrophilic Acylation of Nitriles	1126
26.10.1.1.2.1	Variation 1:	With Acyl Halides	1126
26.10.1.1.2.2	Variation 2:	With Carboxylic Acids, Esters, or Anhydrides	1127
26.10.1.1.2.3	Variation 3:	With Amides and Nitriles	1128
26.10.1.1.3	Method 3:	Nucleophilic Acylation of Cyano Derivatives	1129
26.10.1.1.3.1	Variation 1:	With Aldehydes and Derivatives (Cyanohydrins)	1129
26.10.1.1.3.2	Variation 2:	With Metal-Carbonyl Complexes	1130
26.10.1.1.3.3	Variation 3:	With Miscellaneous Nucleophiles	1131
26.10.1.1.4	Method 4:	Radical Acylation of Cyano Derivatives	1131
26.10.1.1.4.1	Variation 1:	With Anhydrides or Aldehydes	1132
26.10.1.1.4.2	Variation 2:	With Selenoesters	1132
26.10.1.1.4.3	Variation 3:	With Transition-Metal Complexes	1133
26.10.1.1.4.4	Variation 4:	With $\beta$ -Acyl Radicals	1134
26.10.1.1.5	Method 5:	Carbonylation of Cyano Compounds	1134
26.10.1.1.5.1	Variation 1:	Free-Radical Carbonylation Reactions	1134
26.10.1.1.5.2	Variation 2:	With Transition-Metal Complexes	1136
26.10.1.1.6	Method 6:	Ring-Opening and Ring-Expansion Reactions	1136
26.10.1.1.7	Method 7:	Cyclizations and Cycloadditions	1138
26.10.1.1.7.1	Variation 1:	Thorpe-Ziegler and Related Cyclizations	1138
26.10.1.1.7.2	Variation 2:	Cycloaddition Reactions	1139

26.10.1.1.7.3	Variation 3:	Other Concerted Reactions	1140
26.10.1.1.8	Method 8:	Hydrolysis	1141
26.10.1.1.9	Methods 9:	Miscellaneous Methods	1142
26.10.2	<b>Product Subclass 2: Oxo Esters and Oxo Amides</b>		1142
26.10.2.1	Synthesis of Product Subclass 2		1143
26.10.2.1.1	Method 1:	Oxidation	1143
26.10.2.1.1.1	Variation 1:	From Oxygen-Containing Carbonyl Compounds	1143
26.10.2.1.1.2	Variation 2:	From Nitrogen-Containing Carbonyl Compounds	1145
26.10.2.1.1.3	Variation 3:	From Unsaturated Carbonyl Compounds	1146
26.10.2.1.2	Method 2:	Electrophilic Acylation	1149
26.10.2.1.2.1	Variation 1:	With Acyl Halides and Acyl Cyanides	1149
26.10.2.1.2.2	Variation 2:	With Carboxylic Acids, Anhydrides, or Esters	1151
26.10.2.1.2.3	Variation 3:	With Amides or Nitriles	1153
26.10.2.1.2.4	Variation 4:	With Miscellaneous Electrophiles	1155
26.10.2.1.3	Method 3:	Nucleophilic Acylation	1156
26.10.2.1.3.1	Variation 1:	With Aldehydes (via Cyanohydrins and Related Compounds)	1156
26.10.2.1.3.2	Variation 2:	With Metal–Carbonyl Reagents	1157
26.10.2.1.3.3	Variation 3:	With Miscellaneous Nucleophiles	1158
26.10.2.1.4	Method 4:	Radical Acylation of Unsaturated Carbonyl Compounds	1160
26.10.2.1.4.1	Variation 1:	With Aldehydes	1160
26.10.2.1.4.2	Variation 2:	With Anhydrides	1161
26.10.2.1.4.3	Variation 3:	With Selenoesters	1162
26.10.2.1.4.4	Variation 4:	With Cyclopropanols	1164
26.10.2.1.5	Method 5:	Carbonylation	1164
26.10.2.1.5.1	Variation 1:	The Pauson–Khand Reaction	1165
26.10.2.1.5.2	Variation 2:	Free-Radical Carbonylation	1167
26.10.2.1.5.3	Variation 3:	With Organometallic Complexes	1169
26.10.2.1.6	Method 6:	By Rearrangement	1170
26.10.2.1.6.1	Variation 1:	Ring Expansions by Radical Methods	1170
26.10.2.1.6.2	Variation 2:	Ring Expansion by Nonradical Methods	1172
26.10.2.1.6.3	Variation 3:	Electrocyclic Rearrangements	1174
26.10.2.1.6.4	Variation 4:	Miscellaneous Rearrangements	1176
26.10.2.1.7	Method 7:	Cyclization and Cycloaddition	1178
26.10.2.1.7.1	Variation 1:	Dieckmann Condensation	1178
26.10.2.1.7.2	Variation 2:	Cycloadditions and Miscellaneous Cyclizations	1180
26.10.2.1.8	Methods 8:	Miscellaneous Methods	1182
26.10.2.1.8.1	Variation 1:	Solvolyses	1182
26.10.2.1.8.2	Variation 2:	Hydration of Alkynes	1184
26.10.2.1.8.3	Variation 3:	Arylation of Baylis–Hillman Adducts	1184
26.10.3	<b>Product Subclass 3: Diketones and Oxo Imines</b>		1185
26.10.3.1	Synthesis of Product Subclass 3		1186
26.10.3.1.1	Method 1:	Oxidation	1186
26.10.3.1.1.1	Variation 1:	Of Hydroxy Ketones and Diols	1186
26.10.3.1.1.2	Variation 2:	Of Nitro Ketones	1188
26.10.3.1.1.3	Variation 3:	Of Alkanones and Alkenones	1189
26.10.3.1.1.4	Variation 4:	Of Sulfur-Containing Compounds	1190

26.10.3.1.2	Method 2:	Electrophilic Acylation	1191
26.10.3.1.2.1	Variation 1:	With Acyl Halides and Acyl Cyanides	1191
26.10.3.1.2.2	Variation 2:	With Anhydrides, Carboxylic Acids, and Esters	1193
26.10.3.1.2.3	Variation 3:	Of Amides	1195
26.10.3.1.3	Method 3:	Nucleophilic Acylation	1195
26.10.3.1.3.1	Variation 1:	By Aldehydes (via Cyanohydrins and Related Compounds)	1195
26.10.3.1.3.2	Variation 2:	By Metal–Carbonyl Reagents	1196
26.10.3.1.4	Method 4:	By Radical Acylation of $\alpha,\beta$ -Unsaturated Ketones	1198
26.10.3.1.4.1	Variation 1:	By Acyl Radicals	1198
26.10.3.1.4.2	Variation 2:	By Carbon Monoxide Gas	1199
26.10.3.1.5	Method 5:	Carbonylation of Functionalized Ketones	1200
26.10.3.1.5.1	Variation 1:	By the Pauson–Khand Reaction	1200
26.10.3.1.5.2	Variation 2:	With Organorhodium and Organopalladium Compounds	1201
26.10.3.1.6	Method 6:	Rearrangement	1202
26.10.3.1.6.1	Variation 1:	Ring Opening of Oxygenated Heterocycles	1202
26.10.3.1.6.2	Variation 2:	Ring Opening of Cycloalkanes	1203
26.10.3.1.6.3	Variation 3:	Ring Expansion	1205
26.10.3.1.6.4	Variation 4:	Sigmatropic Rearrangement	1205
26.10.3.1.7	Method 7:	Hydration/Hydrolysis	1206
26.10.3.1.7.1	Variation 1:	From Alkynones	1206
26.10.3.1.7.2	Variation 2:	From Ene Halides	1207
26.10.3.1.7.3	Variation 3:	From Nonoxygenated Acetals or Other Functions	1208

**26.11 Product Class 11: Saturated and Unsaturated Ketones with a  $\beta$ - or More Remote Heteroatom Substituent**

A. Harrison-Marchand, I. Chataigner, and J. Maddaluno

26.11	<b>Product Class 11: Saturated and Unsaturated Ketones with a <math>\beta</math>- or More Remote Heteroatom Substituent</b>	1225
26.11.1	<b>Product Subclass 1: Halo Ketones</b>	1225
26.11.1.1	Synthesis of Product Subclass 1	1225
26.11.1.1.1	Method 1: Oxidation of Halo Alcohols	1225
26.11.1.1.2	Method 2: Electrophilic Acylation of Acid Chlorides and Anhydrides	1226
26.11.1.1.3	Method 3: Nucleophilic Acylation of $\alpha$ -Chloro Ketones	1227
26.11.1.1.4	Method 4: Carbonylation of Aliphatic Dihalides	1227
26.11.1.1.5	Method 5: Rearrangement	1228
26.11.1.1.5.1	Variation 1: Ring Opening of Cyclopropyl Silyl Ethers	1228
26.11.1.1.5.2	Variation 2: Decomposition of Tertiary Alkyl Hypochlorites	1228
26.11.1.1.6	Method 6: Hydrolysis of Hydrazones	1229
26.11.1.1.7	Methods 7: Miscellaneous Reactions	1229
26.11.2	<b>Product Subclass 2: Hydroxy and Sulfanyl Ketones and Derivatives</b>	1230
26.11.2.1	Synthesis of Product Subclass 2	1230
26.11.2.1.1	Method 1: Oxidation	1230
26.11.2.1.1.1	Variation 1: From Monoprotected Diols and Hydroxy Sulfides	1230
26.11.2.1.1.2	Variation 2: From Unprotected Diols	1232
26.11.2.1.1.3	Variation 3: From Nitro Compounds	1233

26.11.2.1.1.4	Variation 4:	From Alkanes and Alkenes	1234
26.11.2.1.2	Method 2:	Electrophilic Acylation	1236
26.11.2.1.2.1	Variation 1:	From Acyl Halides	1236
26.11.2.1.2.2	Variation 2:	From Hydroxy- and Sulfanyl-Substituted Carboxylic Acids, Esters, and Thioesters	1237
26.11.2.1.2.3	Variation 3:	From Hydroxy- and Sulfur-Substituted Amides and Nitriles	1239
26.11.2.1.3	Method 3:	Hetero-Michael Additions	1240
26.11.2.1.3.1	Variation 1:	Addition of Alcohols	1240
26.11.2.1.3.2	Variation 2:	Addition of Thiols	1241
26.11.2.1.4	Method 4:	Nucleophilic Acylation	1242
26.11.2.1.4.1	Variation 1:	From Cyanohydrins	1242
26.11.2.1.4.2	Variation 2:	From Isocyanides	1243
26.11.2.1.4.3	Variation 3:	From $\alpha$ -Sulfanyl Sulfones	1243
26.11.2.1.5	Method 5:	Radical Acylation	1244
26.11.2.1.6	Method 6:	Carbonylation	1245
26.11.2.1.7	Method 7:	Rearrangement	1247
26.11.2.1.7.1	Variation 1:	Ferrier and Petasis Rearrangement	1247
26.11.2.1.7.2	Variation 2:	Pinacol and Related Rearrangements	1248
26.11.2.1.7.3	Variation 3:	Ring Opening	1249
26.11.2.1.7.4	Variation 4:	Ring Expansion	1250
26.11.2.1.7.5	Variation 5:	Electrocyclic Rearrangements	1251
26.11.2.1.8	Method 8:	Cyclization and Cycloaddition	1252
26.11.2.1.9	Method 9:	Hydrolysis and Hydration Reactions	1253
26.11.2.1.10	Methods 10:	Miscellaneous Reactions	1254
26.11.3	<b>Product Subclass 3: Amino and Phosphono Ketones and Derivatives</b>		1254
26.11.3.1	Synthesis of Product Subclass 3		1255
26.11.3.1.1	Method 1:	Oxidation	1255
26.11.3.1.1.1	Variation 1:	From Amino Alcohol Derivatives	1255
26.11.3.1.1.2	Variation 2:	From Amino Nitrogenated and Related Compounds	1255
26.11.3.1.1.3	Variation 3:	From Alkyl-, Alkenyl-, and Alkynylamines	1256
26.11.3.1.2	Method 2:	Electrophilic Acylations	1258
26.11.3.1.2.1	Variation 1:	From Acyl Halides	1258
26.11.3.1.2.2	Variation 2:	From Carboxylic Acids, Esters, Lactones, and Anhydrides	1260
26.11.3.1.2.3	Variation 3:	From Amino Amides, Lactams, and Aminonitriles	1261
26.11.3.1.2.4	Variation 4:	Conjugate Additions to $\alpha,\beta$ -Unsaturated Ketones	1263
26.11.3.1.3	Method 3:	By Carbonylation	1264
26.11.3.1.3.1	Variation 1:	Via the Pauson–Khand Reaction	1264
26.11.3.1.3.2	Variation 2:	By Other Carbonylative Methods	1266
26.11.3.1.4	Method 4:	By Rearrangements, Cycloadditions, and Cyclizations	1267
26.11.3.1.4.1	Variation 1:	Pinacol-Type Rearrangements	1267
26.11.3.1.4.2	Variation 2:	Ring Openings	1267
26.11.3.1.4.3	Variation 3:	Ring Expansions	1268
26.11.3.1.4.4	Variation 4:	Electrocyclic Rearrangements	1270
26.11.3.1.4.5	Variation 5:	Cycloadditions and Cyclizations	1270
26.11.3.1.4.6	Variation 6:	Miscellaneous Rearrangements	1272
26.11.3.1.5	Method 5:	By Hydration/Hydrolysis	1273
26.11.3.1.5.1	Variation 1:	Hydrolysis	1273

---

<b>26.11.3.1.5.2</b>	Variation 2: Hydrations .....	1274
	<b>Keyword Index</b> .....	1287
	<b>Author Index</b> .....	1341
	<b>Abbreviations</b> .....	1417

