

C-1 Building Blocks in Organic Synthesis 1

Additions to Alkenes, Alkynes, and Carbonyl Compounds

Preface	V
Volume Editor's Preface	VII
Abstracts	XI
Table of Contents	XXI
Introduction	
P. W. N. M. van Leeuwen	1
1.1 Addition to Alkenes	23
1.1.1 Hydroformylation of Alkenes	
R. P. J. Bronger, P. C. J. Kamer, and D. Vogt	23
1.1.2 Asymmetric Hydroformylation of Alkenes	
C. Godard, B. F. Perandones, and C. Claver	63
1.1.3 Tandem Hydroformylation of Alkenes	
I. Fleischer and E. Mejía	107
1.1.4 Nonconventional Reaction Media: Hydroformylation, Carbonylation, and Hydroxycarbonylation of Alkenes	
A. Mortreux, M. Sauthier, E. Monflier, and S. Tilloy	165
1.1.5 Hydroformylation of Alkenes: Industrial Applications	
J. G. de Vries	193
1.1.6 Carbonylation of Alkenes	
M. L. Clarke and J. A. Fuentes	229
1.1.7 Cyclopropanation of Alkenes with C-1	
T. R. Belderrain and M. C. Nicasio	259
1.1.8 Addition of Carbon Dioxide to Alkenes and Other Unsaturated Hydrocarbons	
J. Takaya and N. Iwasawa	281
1.1.9 Hydrocyanation of Alkenes	
M. E. Tauchert	309
1.1.10 Stereoselective Conjugate Addition of Methyl and Cyanide	
B. Goldfuss	341

1.1.11	Enantioselective Conjugate Addition of Nitromethane R. Ballini and M. Petrini	381
1.2	Addition to Alkynes	399
1.2.1	Carbonylation of Alkynes M. L. Clarke and J. A. Fuentes	399
1.3	Addition to Carbonyl Compounds and Derivatives	415
1.3.1	Stereoselective (Nucleophilic) Methylation of Ketones and Aldehydes B. Goldfuss	415
1.3.2	Cyanation of Ketones, Aldehydes, and Imines L. L. Lin, X. H. Liu, and X. M. Feng	445
1.3.3	Stereoselective Addition of Nitromethane R. Ballini and M. Petrini	507
	Keyword Index	525
	Author Index	555
	Abbreviations	573

Table of Contents

Introduction

P. W. N. M. van Leeuwen

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

1.1 Addition to Alkenes

1.1.1 Hydroformylation of Alkenes

R. P. J. Bronger, P. C. J. Kamer, and D. Vogt

1.1.1 Hydroformylation of Alkenes	23
1.1.1.1 Hydroformylation of Linear Terminal Alkenes	26
1.1.1.2 Hydroformylation of Branched Terminal Alkenes	32
1.1.1.3 Hydroformylation of Vinylarenes	33
1.1.1.4 Hydroformylation of Terminal Alkene Substrates with Remote Functionality ..	36
1.1.1.5 Hydroformylation of Functionalized Allylic Substrates	37
1.1.1.6 Hydroformylation of Monosubstituted Substrates with the Vinyl Unit Attached to a Functional Group	38
1.1.1.7 Hydroformylation of Internal Alkenes	40
1.1.1.7.1 Cobalt Catalysts	41
1.1.1.7.2 Platinum Catalysts	43
1.1.1.7.3 Palladium Catalysts	46
1.1.1.7.4 Rhodium Catalysts	46
1.1.1.7.4.1 Phosphine Ligands	47
1.1.1.7.4.2 Phosphite Ligands	52
1.1.1.8 Other Substrates	56
1.1.1.8.1 Hydroformylation of Conjugated Dienes	56
1.1.1.8.2 Hydroformylation of Alkynes	56

1.1.2 Asymmetric Hydroformylation of Alkenes

C. Godard, B. F. Perandones, and C. Claver

1.1.2 Asymmetric Hydroformylation of Alkenes	63
1.1.2.1 General Methods for the Determination of Enantiomeric Excess in Asymmetric Hydroformylation	65
1.1.2.2 Asymmetric Hydroformylation of Monosubstituted Alkenes	66

1.1.2.2.1	Asymmetric Hydroformylation of Substrates Containing a Vinyl Unit Attached to an Aromatic Ring	68
1.1.2.2.1.1	Asymmetric Hydroformylation of Vinylarenes	68
1.1.2.2.1.2	Asymmetric Hydroformylation of Vinylhetarenes	72
1.1.2.2.1.2.1	Asymmetric Hydroformylation of Vinylfurans	72
1.1.2.2.1.2.2	Asymmetric Hydroformylation of Vinylthiophenes	73
1.1.2.2.2	Asymmetric Hydroformylation of Alkenes with a Heteroatom Bonded to the Vinyl Group	76
1.1.2.2.2.1	Asymmetric Hydroformylation of Vinyl Acetate	76
1.1.2.2.2.2	Asymmetric Hydroformylation of <i>N</i> -Vinylamines	78
1.1.2.2.2.3	Asymmetric Hydroformylation of Vinyl Sulfides	79
1.1.2.2.3	Asymmetric Hydroformylation of Monosubstituted Substrates with the Vinyl Unit Attached to a CH ₂ R ¹ Group	80
1.1.2.2.3.1	Asymmetric Hydroformylation of Unfunctionalized Allylic Systems	80
1.1.2.2.3.2	Asymmetric Hydroformylation of Allyl Cyanide	82
1.1.2.2.3.3	Asymmetric Hydroformylation of Allyl Ethers	83
1.1.2.2.3.4	Asymmetric Hydroformylation of Allyl Sulfides and Allyl Sulfones	84
1.1.2.2.3.5	Asymmetric Hydroformylation of 4-Vinyl- β -lactams	85
1.1.2.2.4	Asymmetric Hydroformylation of Other Substrates	87
1.1.2.2.4.1	Asymmetric Hydroformylation of Conjugated Dienes	87
1.1.2.2.4.2	Asymmetric Hydroformylation of α,β -Unsaturated Amides	88
1.1.2.3	Asymmetric Hydroformylation of Disubstituted Alkenes	90
1.1.2.3.1	Asymmetric Hydroformylation of 1,2-Disubstituted Alkenes	91
1.1.2.3.1.1	Asymmetric Hydroformylation of Linear 1,2-Disubstituted Alkenes	91
1.1.2.3.1.2	Synthesis of (+)-Patulolide C via Asymmetric Hydroformylation/Macrocyclization Cascade	93
1.1.2.3.1.3	Asymmetric Hydroformylation of Monocyclic 1,2-Disubstituted Alkenes	94
1.1.2.3.1.3.1	Asymmetric Hydroformylation of Dihydrofurans	94
1.1.2.3.1.3.2	Asymmetric Hydroformylation of Dihydropyrroles	97
1.1.2.3.1.3.3	Asymmetric Hydroformylation of Dioxepins	98
1.1.2.3.1.3.4	Synthesis of Garner's Aldehyde by Asymmetric Hydroformylation	98
1.1.2.3.1.4	Asymmetric Hydroformylation of Bicyclic 1,2-Disubstituted Alkenes	99
1.1.2.3.1.4.1	Asymmetric Hydroformylation of 1 <i>H</i> -Indene and 1,2-Dihydronaphthalene	99
1.1.2.3.1.4.2	Asymmetric Hydroformylation of Norbornene Derivatives	101
1.1.2.3.1.5	Asymmetric Hydroformylation of 1,1-Disubstituted Alkenes	102
1.1.2.4	Conclusions	103

1.1.3 Tandem Hydroformylation of Alkenes

I. Fleischer and E. Mejía

1.1.3	Tandem Hydroformylation of Alkenes	107
1.1.3.1	Hydroformylation/Reduction	108
1.1.3.1.1	Hydroformylation/Reduction of Alkenes Catalyzed by a Multifunctional Rhodium Catalyst	109
1.1.3.2	Hydroformylation/Reaction with Oxygen Nucleophiles	111
1.1.3.2.1	Hydroformylation/Intermolecular Formation of <i>O,O</i> -Acetals	111
1.1.3.2.1.1	Intermolecular Acetalization with Ortho Esters	112
1.1.3.2.1.2	Intermolecular Acetalization with Alcohols	113
1.1.3.2.2	Hydroformylation/Intramolecular Hemiacetal Formation	114
1.1.3.2.2.1	Hydroformylation/Intramolecular Hemiacetal Formation and Oxidation	115
1.1.3.2.3	Hydroformylation/Intramolecular Acetal Formation	120
1.1.3.3	Hydroformylation/Reaction with Nitrogen Nucleophiles	121
1.1.3.3.1	Synthesis of <i>O,N</i> -Acetals	122
1.1.3.3.1.1	Synthesis of Pyrrolidine Derivatives	122
1.1.3.3.1.2	Synthesis of Piperidine Derivatives	124
1.1.3.3.1.2.1	Synthesis of 1,2,3,4-Tetrahydropyridines	124
1.1.3.3.1.2.2	Synthesis of Oxazolidinones and Oxazolidines	125
1.1.3.3.2	Synthesis of <i>N,N</i> -Acetals	127
1.1.3.3.3	Synthesis of Imines and Enamines	129
1.1.3.3.4	Synthesis of Indoles	132
1.1.3.3.5	Synthesis of Amines via Hydroaminomethylation	133
1.1.3.3.5.1	Synthesis of Primary Amines	133
1.1.3.3.5.2	Synthesis of Secondary and Tertiary Amines	135
1.1.3.3.5.3	Synthesis of Amines by Hydroaminomethylation of Dialkenes	138
1.1.3.3.5.3.1	Hydroaminomethylation of Conjugated and Nonconjugated Dienes	139
1.1.3.3.5.3.2	Synthesis of α,ω -Diamines by Hydroaminomethylation of α,ω -Dialkenes	140
1.1.3.4	Hydroformylation/ <i>C</i> — <i>C</i> Bond Formation	142
1.1.3.4.1	Hydroformylation/Aldol and Aldol-like Reactions	142
1.1.3.4.1.1	Hydroformylation/Homo-aldol Reaction	142
1.1.3.4.1.2	Hydroformylation/Intermolecular Cross-Aldol Reaction	143
1.1.3.4.1.2.1	Hydroformylation/Intermolecular Cross-Aldol Reaction with Aldehydes	143
1.1.3.4.1.2.2	Hydroformylation/Intermolecular Cross-Aldol Reaction with Ketones	145
1.1.3.4.1.3	Hydroformylation/Intermolecular Knoevenagel Reaction/Reduction	146
1.1.3.4.1.4	Hydroformylation/Intramolecular Aldol Reaction	149

1.1.3.4.1.4.1	Hydroformylation/Intramolecular Aldol Reaction of Alkenyl-Substituted Carbonyl Compounds and Enol Ethers	149
1.1.3.4.2	Hydroformylation/Ene Reaction	151
1.1.3.4.3	Hydroformylation/Wittig Reaction	152
1.1.3.4.4	Hydroformylation/Allylation	155
1.1.3.4.4.1	Hydroformylation/Allylboration/Hydroformylation	155
1.1.3.4.4.2	Silylformylation/Allylsilylation	156
1.1.3.4.5	Hydroformylation/Aromatic Substitution	158
1.1.3.4.6	Hydroformylation/S _N 1 Substitution	160
1.1.4	Nonconventional Reaction Media: Hydroformylation, Carbonylation, and Hydroxycarbonylation of Alkenes A. Mortreux, M. Sauthier, E. Monflier, and S. Tilloy	
1.1.4	Nonconventional Reaction Media: Hydroformylation, Carbonylation, and Hydroxycarbonylation of Alkenes	165
1.1.4.1	Hydroformylation of Alkenes	165
1.1.4.1.1	Hydroformylation of Alkenes in Water	165
1.1.4.1.2	Hydroformylation of Alkenes in Ionic Liquids	169
1.1.4.1.2.1	Hydroformylation of Alkenes in Room-Temperature Classical Ionic Liquids ...	170
1.1.4.1.2.2	Hydroformylation in Ionic Liquids Using an Imidazolium-Modified Phosphorus Ligand	171
1.1.4.1.2.3	Hydroformylation of Alkenes in Ionic Liquids Using Cobalt Catalysts	173
1.1.4.1.2.4	Hydroformylation of Alkenes under Continuous Flow Using Ionic Liquids and Supercritical Carbon Dioxide	173
1.1.4.1.3	Hydroformylation of Alkenes Using Propylene Carbonate as a Cosolvent with Platinum-Based Catalysts	174
1.1.4.1.4	Hydroformylation of Alkenes in Supercritical Carbon Dioxide	176
1.1.4.1.5	Hydroformylation of Alkenes in Fluorous Phases	176
1.1.4.1.6	Hydroformylation of Alkenes Using Thermoregulated Phase-Transfer Catalysts	178
1.1.4.1.7	Hydroformylation of Alkenes in Thermomorphic Multicomponent Solvents ..	180
1.1.4.2	Carbonylation of Alkenes	181
1.1.4.2.1	Hydroesterification (Alkoxy-carbonylation) of Alkenes in Ionic Liquids	181
1.1.4.2.2	Hydroaminomethylation of Alkenes in Water	183
1.1.4.2.3	Carbon Monoxide/Alkene Copolymerization	184
1.1.4.2.3.1	Carbon Monoxide/Alkene Copolymerization in Water	184
1.1.4.2.3.2	Carbon Monoxide/Alkene Copolymerization in Ionic Liquids	186
1.1.4.3	Carboxylation of Alkenes	187

1.1.4.3.1	Hydroxycarbonylation of Alkenes in Water	187
1.1.4.3.2	Hydroxycarbonylation of Alkenes in Supercritical Carbon Dioxide	188
1.1.5	Hydroformylation of Alkenes: Industrial Applications J. G. de Vries	
1.1.5	Hydroformylation of Alkenes: Industrial Applications	193
1.1.5.1	Cobalt-Catalyzed Processes	195
1.1.5.1.1	Unmodified Cobalt Catalysts	195
1.1.5.1.1.1	Hydroformylation of Propene and Dibutene	195
1.1.5.1.1.2	Hydroformylation of Oxirane	197
1.1.5.1.2	Modified Cobalt Catalysts	198
1.1.5.2	Rhodium-Catalyzed Processes	201
1.1.5.2.1	Phosphine-Modified Rhodium Catalysts	201
1.1.5.2.1.1	Hydroformylation of Propene	201
1.1.5.2.1.2	Hydroformylation of Hept-1-ene	206
1.1.5.2.1.3	Hydroformylation of Allyl Alcohol	207
1.1.5.2.1.4	Hydroformylation of Oct-7-enal	209
1.1.5.2.2	Triphenylphosphine Oxide Modified Rhodium Catalysts	211
1.1.5.2.3	Phosphite-Modified Rhodium Catalysts	212
1.1.5.2.3.1	Hydroformylation of Propene	212
1.1.5.2.3.2	Hydroformylation of Butenes	218
1.1.5.2.3.3	Hydroformylation of 3-Methylbut-3-en-1-ol	225
1.1.6	Carbonylation of Alkenes M. L. Clarke and J. A. Fuentes	
1.1.6	Carbonylation of Alkenes	229
1.1.6.1	Mechanism of the Palladium-Catalyzed Carbonylation of Alkenes	231
1.1.6.2	Hydroxycarbonylation of Alkenes	232
1.1.6.2.1	Hydroxycarbonylation of Vinylarenes	232
1.1.6.2.2	Hydroxycarbonylation of Vinylsilanes	235
1.1.6.2.3	Hydroxycarbonylation of Methylenecycloalkanes	235
1.1.6.3	Alkoxy carbonylation of Alkenes	236
1.1.6.3.1	Alkoxy carbonylation of Vinylarenes	236
1.1.6.3.2	Alkoxy carbonylation of Vinylsilanes	238
1.1.6.3.3	Alkoxy carbonylation of Terminal and Internal Linear Alkenes	238
1.1.6.3.4	Alkoxy carbonylation of Naturally Occurring Alkenes	239

1.1.6.3.5	Alkoxy carbonylation of Unsaturated Alcohols: Cyclocarbonylation Reaction ..	240
1.1.6.3.6	Alkoxy carbonylation of Unsaturated Alcohols: Tetrahydrofuran and Tetrahydropyran Synthesis	243
1.1.6.3.7	Amidoesterification of Unsaturated Amines	244
1.1.6.3.8	Intramolecular Amidoesterification of Unsaturated Amino Alcohols	245
1.1.6.3.9	Hetaryl Esterifications	246
1.1.6.3.10	Multiple Carbonylation of Terminal Alkenes	246
1.1.6.4	Asymmetric Carbonylation of Alkenes	247
1.1.6.4.1	Asymmetric Hydroxycarbonylation of Alkenes	247
1.1.6.4.1.1	Asymmetric Hydroxycarbonylation of Vinylarenes	248
1.1.6.4.1.2	Asymmetric Hydroxycarbonylation of Cyclic Alkenes	249
1.1.6.4.2	Asymmetric Alkoxy carbonylation of Alkenes	250
1.1.6.4.2.1	Asymmetric Alkoxy carbonylation of Vinylarenes	250
1.1.6.4.2.2	Asymmetric Alkoxy carbonylation of Cyclic Alkenes	252
1.1.6.4.2.3	Asymmetric Intramolecular Alkoxy carbonylation of Allylic Alcohols	253
1.1.6.4.2.4	Asymmetric Alkoxy carbonylation of <i>N</i> -Vinylphthalimide	254
1.1.6.4.2.5	Asymmetric Multiple Carbonylation of Terminal Alkenes	254
1.1.6.4.2.6	Asymmetric Amidoesterification of Unsaturated Amines	256
1.1.6.5	Conclusions	256
1.1.7	Cyclopropanation of Alkenes with C-1 T. R. Belderrain and M. C. Nicasio	
1.1.7	Cyclopropanation of Alkenes with C-1	259
1.1.7.1	Cyclopropanation of Alkenes with Diazomethane	259
1.1.7.1.1	Uncatalyzed Cyclopropanation Reactions	259
1.1.7.1.2	Transition-Metal-Catalyzed Cyclopropanation Reactions	263
1.1.7.2	(Halomethyl)zinc-Mediated Cyclopropanation Reactions	269
1.1.7.3	Ylide-Mediated Cyclopropanation Reactions	272
1.1.8	Addition of Carbon Dioxide to Alkenes and Other Unsaturated Hydrocarbons J. Takaya and N. Iwasawa	
1.1.8	Addition of Carbon Dioxide to Alkenes and Other Unsaturated Hydrocarbons	281
1.1.8.1	Transition-Metal-Catalyzed Cyclization Reactions of Carbon Dioxide with 1,3-Dienes and Alkynes	282

1.1.8.1.1	δ -Lactone Synthesis by Palladium(0)-Catalyzed Coupling of Carbon Dioxide with 1,3-Dienes	282
1.1.8.1.2	Pyrone Synthesis by Nickel(0)-Catalyzed Cycloaddition of Carbon Dioxide with Diynes	283
1.1.8.2	Nickel-Mediated Carboxylic Acid Synthesis via Oxidative Coupling	285
1.1.8.2.1	Reaction of Ethene with Carbon Dioxide: Acrylic Acid Synthesis	285
1.1.8.2.2	Reaction of Alkynes	286
1.1.8.2.3	Reaction of 1,3-Dienes and Allenes	289
1.1.8.2.4	Carboxylative Cyclization	293
1.1.8.3	Catalytic Carboxylation Reactions via Hydrometalation of Unsaturated Hydrocarbons and Related Reactions	295
1.1.8.3.1	Nickel- or Palladium-Catalyzed Hydrocarboxylation of Alkenes, Dienes, and Alkynes	295
1.1.8.3.2	Copper-Catalyzed Hydro-, Bora-, and Silacarboxylation of Alkynes	302
1.1.9	Hydrocyanation of Alkenes M. E. Tauchert	
1.1.9	Hydrocyanation of Alkenes	309
1.1.9.1	Mechanistic Aspects of Nickel-Catalyzed Hydrocyanation	311
1.1.9.1.1	Hydrocyanation of Alkenes	311
1.1.9.1.1.1	Hydrocyanation of Ethene	311
1.1.9.1.1.2	Hydrocyanation of Terminal Monoenes and Vinylarenes	312
1.1.9.1.1.3	Catalyst Decomposition by Hydrogen Cyanide Poisoning and Reactor Types ..	312
1.1.9.1.1.4	Lewis Acids as Promoters in Alkene Hydrocyanation	313
1.1.9.1.1.5	Ligand Effects	316
1.1.9.1.2	Hydrocyanation of 1,3-Dienes	318
1.1.9.2	Preparation of Hydrogen Cyanide	320
1.1.9.3	Hydrocyanation of Dienes	322
1.1.9.3.1	Hydrocyanation of Buta-1,3-diene	322
1.1.9.3.2	Hydrocyanation of Substituted 1,3-Dienes	324
1.1.9.3.3	Hydrocyanation of α,ω -Dienes	326
1.1.9.4	Hydrocyanation of Vinylarenes	328
1.1.9.4.1	Racemic Hydrocyanation of Vinylarenes	328
1.1.9.4.2	Enantioselective Hydrocyanation of Vinylarenes	330
1.1.9.5	Hydrocyanation of Simple Alkenes	332
1.1.9.5.1	Linear-Selective Hydrocyanation of Alkenes	332
1.1.9.5.2	Hydrocyanation of Alkenes To Form Branched Nitriles	334
1.1.9.5.3	Asymmetric Hydrocyanation of Alkenes	336

1.1.10	Stereoselective Conjugate Addition of Methyl and Cyanide B. Goldfuss	
<hr/>		
1.1.10	Stereoselective Conjugate Addition of Methyl and Cyanide	341
1.1.10.1	Methylation	341
1.1.10.1.1	Methylcuprate Reagents for Enantioselective 1,4-Additions	341
1.1.10.1.2	Catalytic 1,4-Methylations	345
1.1.10.1.2.1	Methylmagnesium Reagents	345
1.1.10.1.2.2	Methylzinc Reagents	348
1.1.10.1.2.3	Methylaluminum Reagents	355
1.1.10.2	Cyanation	365
1.1.10.2.1	Cyanation Using Silyl Cyanides	367
1.1.10.2.2	Cyanation Using Acetone Cyanohydrin	375
1.1.11	Enantioselective Conjugate Addition of Nitromethane R. Ballini and M. Petrini	
<hr/>		
1.1.11	Enantioselective Conjugate Addition of Nitromethane	381
1.1.11.1	Catalysts for Conjugate Addition	381
1.1.11.2	Addition to α,β -Unsaturated Aldehydes	381
1.1.11.3	Addition to α,β -Unsaturated Ketones	386
1.1.11.3.1	Addition to Linear Ketones	386
1.1.11.3.2	Addition to Cyclic Ketones	394
1.1.11.4	Addition to α,β -Unsaturated Carboxylic Acid Derivatives	395
1.2	Addition to Alkynes	
<hr/>		
1.2.1	Carbonylation of Alkynes M. L. Clarke and J. A. Fuentes	
<hr/>		
1.2.1	Carbonylation of Alkynes	399
1.2.1.1	Intermolecular Hydroxycarbonylation of Alkynes	400
1.2.1.2	Intermolecular Alkoxy carbonylation of Alkynes	401
1.2.1.3	Intramolecular Alkoxy carbonylation of Alkynes	404
1.2.1.4	Intermolecular Aminocarbonylation of Alkynes	405
1.2.1.5	Sulfanylcarbonylation of Alkynes	406
1.2.1.6	Oxidative Carbonylation of Alkynes	408
1.2.1.6.1	Alkoxyesterification of Alkynes	408

1.2.1.6.2	Aminoesterification of Alkynes	410
1.2.1.6.3	Alkynoate and Alkynamide Synthesis	411
1.2.1.6.4	Oxidative Double Carbonylation	412
1.2.1.7	Summary	412

1.3 Addition to Carbonyl Compounds and Derivatives

1.3.1 Stereoselective (Nucleophilic) Methylation of Ketones and Aldehydes B. Goldfuss

1.3.1	Stereoselective (Nucleophilic) Methylation of Ketones and Aldehydes ...	415
1.3.1.1	Methyl lithium	416
1.3.1.2	Methyl Grignard Reagents	419
1.3.1.3	Methylzinc Systems	420
1.3.1.4	Methyltitanium Systems	428
1.3.1.4.1	Methylating Titanium Systems Generated from Methylzinc or Methyl Grignard Reagents	429
1.3.1.4.2	Methylaluminum Reagents in Cooperation with Titanium Catalysts	435
1.3.1.5	Methylnickel Systems	438
1.3.1.6	Methylrhodium Systems	440
1.3.1.7	Methylchromium and Methyliron Systems	441
1.3.1.8	Conclusions	441

1.3.2 Cyanation of Ketones, Aldehydes, and Imines L. L. Lin, X. H. Liu, and X. M. Feng

1.3.2	Cyanation of Ketones, Aldehydes, and Imines	445
1.3.2.1	Cyanation Using Hydrogen Cyanide	446
1.3.2.1.1	Cyanation Using Enzymes as Catalysts	446
1.3.2.1.2	Cyanation Using Chiral Ruthenium Complexes as Catalysts	447
1.3.2.1.3	Cyanation Using Chiral Zirconium Complexes as Catalysts	450
1.3.2.1.4	Cyanation Using Chiral Ureas as Catalysts	451
1.3.2.2	Cyanation Using Trimethylsilyl Cyanide	452
1.3.2.2.1	Cyanation without Stereocontrol	453
1.3.2.2.1.1	Cyanation Using Potassium Carbonate as a Catalyst	453
1.3.2.2.2	Asymmetric Cyanation	454
1.3.2.2.2.1	Cyanation of Imines with Chiral Sulfinamides as Auxiliaries	454
1.3.2.2.2.2	Cyanation Using Chiral Titanium Complexes as Catalysts	456

1.3.2.2.2.3	Cyanation Using Chiral Vanadium-Based Catalysts	460
1.3.2.2.2.4	Cyanation Using Chiral Aluminum Complexes as Catalysts	461
1.3.2.2.2.5	Cyanation Using Chiral Ruthenium Complexes as Catalysts	464
1.3.2.2.2.6	Cyanation Using Chiral Lanthanide Complexes as Catalysts	465
1.3.2.2.2.7	Cyanation Using Chiral Gadolinium Complexes as Catalysts	466
1.3.2.2.2.8	Cyanation Using Chiral Boron-Based Catalysts	468
1.3.2.2.2.9	Cyanation Using Chiral Organic Acid Sodium Salts as Catalysts	469
1.3.2.2.2.10	Cyanation Using Chiral Phosphoric Acid Catalysts	471
1.3.2.2.2.11	Cyanation Using Chiral Thioureas as Catalysts	472
1.3.2.2.2.12	Cyanation Using Chiral Bases as Catalysts	475
1.3.2.2.2.13	Cyanation Using <i>N,N'</i> -Dioxides as Catalysts	477
1.3.2.3	Cyanation Using Ethyl Cyanofornate	479
1.3.2.3.1	Cyanation without Stereocontrol	479
1.3.2.3.1.1	Cyanation Using 4-(Dimethylamino)pyridine as a Catalyst	479
1.3.2.3.2	Asymmetric Cyanation	480
1.3.2.3.2.1	Cyanation Using Chiral Titanium Complexes as Catalysts	480
1.3.2.3.2.2	Cyanation Using Chiral Aluminum Complexes as Catalysts	483
1.3.2.3.2.3	Cyanation Using Chiral Vanadium Complexes as Catalysts	485
1.3.2.3.2.4	Cyanation Using Chiral Yttrium Complexes as Catalysts	487
1.3.2.4	Cyanation Using Acetyl Cyanide	488
1.3.2.4.1	Cyanation without Stereocontrol	488
1.3.2.4.1.1	Cyanation Using <i>N,N</i> -Dimethylcyclohexylamine as a Catalyst	488
1.3.2.4.2	Asymmetric Cyanation	489
1.3.2.4.2.1	Cyanation Using Chiral Titanium Complexes as Catalysts	489
1.3.2.4.2.2	Cyanation Using Chiral Thioureas as Catalysts	490
1.3.2.5	Cyanation Using Acetone Cyanohydrin	491
1.3.2.5.1	Cyanation without Stereocontrol	491
1.3.2.5.1.1	Cyanation Using Zirconium(IV) <i>tert</i> -Butoxide as a Catalyst	491
1.3.2.5.2	Asymmetric Cyanation	492
1.3.2.5.2.1	Cyanation Using Chiral Vanadium Complexes as Catalysts	492
1.3.2.5.2.2	Cyanation Using Chiral Phase-Transfer Catalysts	493
1.3.2.6	Cyanation Using Potassium Cyanide	494
1.3.2.6.1	Cyanation without Stereocontrol	495
1.3.2.6.1.1	Cyanation without a Catalyst	495
1.3.2.6.2	Asymmetric Cyanation	496
1.3.2.6.2.1	Cyanation Using Chiral Thioureas as Catalysts	496
1.3.2.6.2.2	Cyanation Using Chiral Quaternary Ammonium Salts as Catalysts	498

1.3.2.7	Cyanation Using Diethylaluminum Cyanide	499
1.3.2.7.1	Cyanation of Imines Using Chiral 1,2-Diamines as Auxiliaries	499
1.3.2.7.2	Cyanation Using Chiral Aluminum Complexes	500
1.3.2.8	Cyanation Using Diethyl Cyanophosphonate	501
1.3.2.8.1	Cyanation Using Chiral Aluminum Complexes as Catalysts	501
1.3.2.8.2	Cyanation Using Chiral Yttrium Complexes as Catalysts	503
1.3.3	Stereoselective Addition of Nitromethane R. Ballini and M. Petrini	
<hr/>		
1.3.3	Stereoselective Addition of Nitromethane	507
1.3.3.1	Stereoselective Addition to Aldehydes	507
1.3.3.1.1	Enantioselective Addition to Aldehydes	507
1.3.3.1.2	Diastereoselective Addition to Aldehydes	514
1.3.3.2	Enantioselective Addition to Ketones	515
1.3.3.3	Stereoselective Addition to Imino Derivatives	517
1.3.3.3.1	Enantioselective Addition to Imino Derivatives	517
1.3.3.3.1.1	Enantioselective Addition to <i>N</i> -Acylimines	517
1.3.3.3.1.2	Enantioselective Addition to <i>N</i> -Tosylimines	521
1.3.3.3.2	Diastereoselective Addition to Imino Derivatives	522
	Keyword Index	525
	Author Index	555
	Abbreviations	573