

Volume 48: Alkanes

	Preface	V
	Table of Contents	IX
	Introduction	
	H. Hiemstra	1
48.1	Product Class 1: Acyclic Alkanes	
48.1.1	Synthesis by Metal Substitution with Retention of the Carbon Framework E. A. B. Kantchev and M. G. Organ	9
48.1.2	Synthesis by Metal Substitution with Extension of the Carbon Framework E. A. B. Kantchev and M. G. Organ	29
48.1.3	Synthesis by Reduction without C–C Bond Cleavage	
48.1.3.1	Reduction of Carbonic or Carboxylic Acids, Aldehydes, Ketones, or Derivatives J. Wicha	97
48.1.3.2	Reduction of Haloalkanes P. Margaretha	149
48.1.3.3	Reduction of Alkanols and Derivatives J. Wicha	163
48.1.3.4	Reduction of Other Heterofunctionalities J. Drabowicz, D. Krasowska, and J. Wicha	245
48.1.3.5	Reduction of Alkynes N. Chessum, S. Couty, and K. Jones	265
48.1.3.6	Reduction of Alkenes	
48.1.3.6.1	Reduction by Heterogeneous Catalysis N. Chessum, S. Couty, and K. Jones	275
48.1.3.6.2	Reduction by Homogeneous Catalysis or Biocatalysis M. Tsukamoto and M. Kitamura	341
48.1.3.6.3	Reduction by Noncatalytic Methods M. Zaidlewicz, M. P. Krzemiński, and A. Dzieleńdziak	359

48.1.4	Synthesis by Reduction of Alkenes via Intermolecular C—C Bond Formation	
	P. Eilbracht	393
48.1.5	Synthesis by Reduction with C—C Bond Cleavage	
	P. Margaretha	439
48.1.6	Synthesis from Other Alkanes	
48.1.6.1	Bond Cleavage Reactions	
	Á. Molnár and P. Margaretha	459
48.1.6.2	Dehydrodimerization Reactions	
	Á. Molnár	469
48.1.6.3	Isomerization Reactions	
	Á. Molnár	473
48.2	Product Class 2: Cyclopropanes	
	A. de Meijere and S. I. Kozhushkov	477
48.3	Product Class 3: Cyclobutanes	
	R. Kostikov and M. S. Baird	615
48.4	Product Class 4: Five-Membered and Larger-Ring Cycloalkanes	
	M. J. Palframan and A. F. Parsons	647
48.5	Product Class 5: Hydrocarbon Polymers	
	W. Kaminsky	695
	Keyword Index	739
	Author Index	783
	Abbreviations	825

Table of Contents

	Introduction H. Hiemstra	
	Introduction	1
48.1	Product Class 1: Acyclic Alkanes	
48.1.1	Synthesis by Metal Substitution with Retention of the Carbon Framework E. A. B. Kantchev and M. G. Organ	
48.1.1	Synthesis by Metal Substitution with Retention of the Carbon Framework	9
48.1.1.1	Method 1: Synthesis by Protonation of Carbon–Metal Bonds	9
48.1.1.1.1	Variation 1: Acidolysis of Alkyl Derivatives of Metals from Groups 14 and 15 (Including Boron)	10
48.1.1.1.2	Variation 2: Protonolysis of Alkyl Derivatives of Metals from Groups 5–11	14
48.1.1.1.3	Variation 3: Protonolysis of Alkyl Derivatives of Metals from Groups 3, 4, 12, and 13 (Including Lanthanides and Actinides, Excluding Boron)	15
48.1.1.1.4	Variation 4: Protonolysis of Alkyl Derivatives of Metals from Groups 1 and 2	18
48.1.1.2	Method 2: Synthesis by Hydrogenolysis of Carbon–Metal Bonds	23
48.1.1.2.1	Variation 1: Hydrogenolysis and Reductive Cleavage of Carbon–Metal Bonds	23
48.1.1.2.2	Variation 2: Reductive Elimination from Alkyl–Transition Metal Hyrido Complexes	25
48.1.2	Synthesis by Metal Substitution with Extension of the Carbon Framework E. A. B. Kantchev and M. G. Organ	
48.1.2	Synthesis by Metal Substitution with Extension of the Carbon Framework	29
48.1.2.1	Method 1: Noncatalyzed Coupling Reactions of Nonactivated Alkyl Electrophiles with Organometallic Reagents	30
48.1.2.1.1	Variation 1: Using Main-Group Organometallic Reagents	30
48.1.2.1.2	Variation 2: Using Transition-Metal Organometallic Reagents	32
48.1.2.2	Method 2: Catalyzed Coupling Reactions of Nonactivated Alkyl Electrophiles with Organometallic Reagents	36
48.1.2.2.1	Variation 1: Couplings of Alkyl Grignard Reagents (Kumada–Tamao–Corriu Reaction) Mediated by Copper, Silver, Nickel, Palladium, Iron, and Cobalt	38
48.1.2.2.2	Variation 2: Couplings of Alkylzinc Reagents (Negishi Reaction) Mediated by Nickel and Palladium	51

48.1.2.2.3	Variation 3:	Couplings of Alkyl Boron Compounds (Suzuki–Miyaura Reaction) Mediated by Palladium and Nickel	63
48.1.2.2.4	Variation 4:	Couplings of Other Alkyl Organometallic Compounds	76
48.1.2.3	Method 3:	Oxidative Coupling of Alkyl Organometallic Reagents	77
48.1.2.3.1	Variation 1:	Reductive Elimination from Dialkyl Transition-Metal Complexes	83
48.1.2.3.2	Variation 2:	Kolbe Electrolysis	85
48.1.2.4	Method 4:	Reductive Coupling of Alkyl Halides	87

48.1.3 **Synthesis by Reduction without C–C Bond Cleavage**

48.1.3.1 **Reduction of Carbonic or Carboxylic Acids, Aldehydes, Ketones, or Derivatives**

J. Wicha

48.1.3.1	Reduction of Carbonic or Carboxylic Acids, Aldehydes, Ketones, or Derivatives	97
48.1.3.1.1	Method 1: The Clemmensen Reduction (Deoxygenation of Aldehydes or Ketones Using Zinc and Hydrochloric Acid)	99
48.1.3.1.1.1	Variation 1: Reduction with Zinc–Hydrochloric Acid in an Aqueous Solution	100
48.1.3.1.1.2	Variation 2: Reduction with Zinc–Hydrochloric Acid in the Presence of Water-Miscible Solvents	101
48.1.3.1.1.3	Variation 3: Reduction with Zinc–Hydrochloric Acid in the Presence of Water-Immiscible Solvents	102
48.1.3.1.1.4	Variation 4: Reduction with Zinc in Organic Solvents Saturated with Hydrogen Chloride	102
48.1.3.1.1.5	Variation 5: Ultrasound-Assisted Zinc–Protic Acid Reduction	104
48.1.3.1.1.6	Variation 6: Miscellaneous Methods	104
48.1.3.1.2	Method 2: Other Direct Deoxygenation Methods	105
48.1.3.1.2.1	Variation 1: Deoxygenation of Aromatic Ketones with Hydrogen Iodide	105
48.1.3.1.2.2	Variation 2: Deoxygenation of Carbonyl Compounds by Catalytic Hydrogenation	105
48.1.3.1.2.3	Variation 3: Deoxygenation of Aromatic Acids, Aldehydes, and Ketones Using the Trichlorosilane–Tripropylamine Couple	106
48.1.3.1.2.4	Variation 4: Deoxygenation of Ketones Using the Triethylsilane–Trifluoroacetic Acid Couple	107
48.1.3.1.2.5	Variation 5: Deoxygenation of Carboxylic Acids, Esters, Aldehydes, and Ketones Using Silanes in the Presence of Lewis Acids	108
48.1.3.1.2.6	Variation 6: Deoxygenation of Aromatic and α,β -Unsaturated Ketones Using the Sodium Borohydride–Trifluoroacetic Acid Couple	110
48.1.3.1.2.7	Variation 7: Miscellaneous Methods	111
48.1.3.1.3	Method 3: The Wolff–Kishner Reduction (Reduction of Aldehydes and Ketones via Hydrazones)	111
48.1.3.1.3.1	Variation 1: The Huang–Minlon Modification	114
48.1.3.1.3.2	Variation 2: The Barton Modification	117
48.1.3.1.3.3	Variation 3: The Cram and the Henbest Modifications	119

48.1.3.1.3.4	Variation 4:	The Nagata–Itazaki Modification	121
48.1.3.1.3.5	Variation 5:	The Furrow–Myers Modification	123
48.1.3.1.3.6	Variation 6:	Microwave-Assisted Wolff–Kishner Reductions	125
48.1.3.1.3.7	Variation 7:	Miscellaneous Reactions	125
48.1.3.1.4	Method 4:	Reduction of Aldehydes and Ketones via Tosylhydrazones ...	126
48.1.3.1.4.1	Variation 1:	Reduction of Tosylhydrazones with Lithium Aluminum Hydride	127
48.1.3.1.4.2	Variation 2:	Reduction of Tosylhydrazones with Sodium Borohydride ...	128
48.1.3.1.4.3	Variation 3:	Reduction of Tosylhydrazones with Sodium Cyanoborohydride–Protic Acid	129
48.1.3.1.4.4	Variation 4:	Reduction of Tosylhydrazones with Catecholborane	131
48.1.3.1.4.5	Variation 5:	Miscellaneous Methods	133
48.1.3.1.5	Method 5:	Deoxygenation of Aldehydes and Ketones via Dithioacetals and Other Sulfur-Containing Derivatives	134
48.1.3.1.5.1	Variation 1:	Reduction of Dithioacetals Using Raney Nickel	135
48.1.3.1.5.2	Variation 2:	Reduction of Dithioacetals Using Dissolving Metals	138
48.1.3.1.5.3	Variation 3:	Reduction of Dithioacetals Using Tributyltin Hydride	138
48.1.3.1.5.4	Variation 4:	Reduction of Dithioacetals with Hydrazine	140
48.1.3.1.5.5	Variation 5:	Miscellaneous Methods	140
48.1.3.2	Reduction of Haloalkanes P. Margaretha		
48.1.3.2	Reduction of Haloalkanes		149
48.1.3.2.1	Method 1:	Alkanes from Fluoroalkanes	149
48.1.3.2.1.1	Variation 1:	Reduction of Fluoroalkanes with Alkali Metals	150
48.1.3.2.1.2	Variation 2:	Reduction of Fluoroalkanes with Hydrides	151
48.1.3.2.2	Method 2:	Alkanes from Chloroalkanes	151
48.1.3.2.2.1	Variation 1:	Reductive Cleavage of Chloroalkanes	151
48.1.3.2.2.2	Variation 2:	Reductive Cleavage of Bromochloroalkanes	153
48.1.3.2.3	Method 3:	Alkanes from Bromoalkanes	154
48.1.3.2.3.1	Variation 1:	Reductive Cleavage of Bromoalkanes	155
48.1.3.2.4	Method 4:	Alkanes from Iodoalkanes	157
48.1.3.3	Reduction of Alkanols and Derivatives J. Wicha		
48.1.3.3	Reduction of Alkanols and Derivatives		163
48.1.3.3.1	Method 1:	Direct Replacement of C–OH Bonds by C–H Bonds in Benzylic, Allylic, or Other Activated Alcohols	165
48.1.3.3.1.1	Variation 1:	Acid-Promoted Catalytic Hydrogenolysis of Alcohols	165
48.1.3.3.1.2	Variation 2:	Dissolving-Metal Reduction of Benzylic Alcohols	166
48.1.3.3.1.3	Variation 3:	Reduction of Alcohols by Mixed Metal Hydrides in the Presence of Lewis or Protic Acids	166
48.1.3.3.1.4	Variation 4:	Reduction of Alcohols with the Triethylsilane/Trifluoro- acetic Acid System or Other Silane/Acid Combinations	167

48.1.3.3.1.5	Variation 5:	Deoxygenation of Alcohols with Diiododimethylsilane or Iodotrimethylsilane	168
48.1.3.3.1.6	Variation 6:	Microwave-Promoted Deoxygenation of Benzylic Alcohols with Lawesson's Reagent and Hexacarbonylmolybdenum(0) Catalyst	169
48.1.3.3.1.7	Variation 7:	Deoxygenation of Alcohols by Electrolysis in the Presence of a Trialkyl- or Triarylphosphine	169
48.1.3.3.1.8	Variation 8:	Deoxygenation of α -Hydroxy Ketones or α -Hydroxyaldehydes	170
48.1.3.3.1.9	Variation 9:	Deoxygenation of Alcohols via Diazenes	170
48.1.3.3.2	Method 2:	Deoxygenation of Alcohols via Carboxylic Esters	175
48.1.3.3.2.1	Variation 1:	Photolysis of Carboxylic Esters	175
48.1.3.3.2.2	Variation 2:	Deoxygenation of Alcohols through Electrochemical Reduction of Their Esters	177
48.1.3.3.2.3	Variation 3:	Dissolving-Metal Deoxygenation of Alcohols via Their Carboxylic Esters	177
48.1.3.3.2.4	Variation 4:	Deoxygenation of Alcohols via Their <i>N,N'</i> -Dicyclohexylcarbamimidate Esters	179
48.1.3.3.3	Method 3:	Deoxygenation of Alcohols via Their Sulfonyl Derivatives	179
48.1.3.3.3.1	Variation 1:	Reduction of Sulfonate Esters with Lithium Aluminum Hydride and Lithium Triethylborohydride	181
48.1.3.3.3.2	Variation 2:	Deoxygenation of Sulfonate Esters with Sodium Borohydride, Sodium Cyanoborohydride, or Lithium (Diisopropylamino)-borohydride	185
48.1.3.3.3.3	Variation 3:	Deoxygenation of Sulfonate Esters with Complex Copper Hydrides	186
48.1.3.3.3.4	Variation 4:	Miscellaneous Reactions	186
48.1.3.3.4	Method 4:	Deoxygenation of Alcohols via Phosphoryl Derivatives	187
48.1.3.3.4.1	Variation 1:	Reduction of Phosphoramidate Derivative of Alcohols with Lithium in Ethylamine or with Lithium Naphthalenide	187
48.1.3.3.4.2	Variation 2:	Reduction of Phosphate Esters of Alcohols with Lithium in Ethylamine or with Lithium Naphthalenide	190
48.1.3.3.4.3	Variation 3:	Reduction of Alkoxyphosphonium Salts with Lithium Triethylborohydride	190
48.1.3.3.5	Method 5:	The Barton–McCombie Deoxygenation Reaction Using Tributyltin Hydride or Other Metal Hydrides as the Hydrogen-Atom Source	190
48.1.3.3.5.1	Variation 1:	Deoxygenation of Alcohols via <i>S</i> -Methyl Xanthates	195
48.1.3.3.5.2	Variation 2:	Deoxygenation of Alcohols via Their 1 <i>H</i> -Imidazol-1-ylcarbonothioyl Derivatives	202
48.1.3.3.5.3	Variation 3:	Deoxygenation of Alcohols via <i>O</i> -Alkyl <i>O</i> -Phenyl Carbonothioates or <i>O</i> -Alkyl <i>O</i> -(Halophenyl) Carbonothioates	207
48.1.3.3.5.4	Variation 4:	Deoxygenation of Alcohols via Benzenecarbonothioates	214
48.1.3.3.5.5	Variation 5:	Deoxygenation of Alcohols via Acylcarbamothioates	215
48.1.3.3.5.6	Variation 6:	Deoxygenation of Alcohols via Thioformates	216
48.1.3.3.5.7	Variation 7:	Deoxygenation of One Hydroxy Group in a Diol via a Cyclic Carbonothioate	217
48.1.3.3.5.8	Variation 8:	Deoxygenation of Alcohols via Methyl Oxalates	219
48.1.3.3.5.9	Variation 9:	Deoxygenation of Alcohols via Other Radicophilic Derivatives	222

48.1.3.3.5.10	Variation 10:	Deoxygenation of Alcohols Using Polymer-Bound Stannanes	222
48.1.3.3.5.11	Variation 11:	Deoxygenation of Alcohols Using Modified Stannanes	224
48.1.3.3.5.12	Variation 12:	Deoxygenation of Alcohols Using Other Metal Hydrides	225
48.1.3.3.5.13	Variation 13:	Deoxygenation of Alcohols Using Bis(tributyltin) Oxide–Poly(methylhydrosiloxane)	225
48.1.3.3.6	Method 6:	The Barton–McCombie Deoxygenation of Alcohols Using Silanes as the Hydrogen-Atom Source	226
48.1.3.3.6.1	Variation 1:	Using Triethylsilane	227
48.1.3.3.6.2	Variation 2:	Using Diphenylsilane	227
48.1.3.3.6.3	Variation 3:	Using 5,10-Dimethyl-5,10-dihydrosilaanthracene Derivatives	228
48.1.3.3.6.4	Variation 4:	Using Tetraphenyldisilane	229
48.1.3.3.6.5	Variation 5:	Using Tris(trimethylsilyl)silane	229
48.1.3.3.6.6	Variation 6:	Using Silylated Dienes	231
48.1.3.3.6.7	Variation 7:	Using a Silane–Thiol System	231
48.1.3.3.6.8	Variation 8:	Reduction of Trifluoroacetates by Diphenylsilane	232
48.1.3.3.7	Method 7:	The Barton–McCombie Deoxygenation of Alcohols Using Phosphorus Compounds and Miscellaneous Hydrogen-Atom Donors	232
48.1.3.3.7.1	Variation 1:	Using Phosphinic Acid and Its Salts	233
48.1.3.3.7.2	Variation 2:	Using Dialkyl Phosphites	234
48.1.3.3.7.3	Variation 3:	Using Other Phosphorus Compounds	235
48.1.3.3.7.4	Variation 4:	Using Propan-2-ol	235
48.1.3.3.7.5	Variation 5:	Using Formate Anion	236
48.1.3.3.7.6	Variation 6:	Using Water	237

48.1.3.4 Reduction of Other Heterofunctionalities

J. Drabowicz, D. Krasowska, and J. Wicha

48.1.3.4	Reduction of Other Heterofunctionalities	245	
48.1.3.4.1	Method 1:	Desulfurization of Thiols and Sulfides	245
48.1.3.4.1.1	Variation 1:	Using Raney Nickel	245
48.1.3.4.1.2	Variation 2:	Using Dissolving Metals and Amalgams	248
48.1.3.4.1.3	Variation 3:	Using Nickel, Cobalt, Iron, or Copper Compounds and Metal Hydrides	248
48.1.3.4.1.4	Variation 4:	Using Free-Radical Reagents	249
48.1.3.4.2	Method 2:	Reduction of Sulfoxides and Sulfones	251
48.1.3.4.2.1	Variation 1:	Using Raney Nickel	251
48.1.3.4.2.2	Variation 2:	Using Dissolving Metals and Amalgams	251
48.1.3.4.2.3	Variation 3:	Miscellaneous Reactions	252
48.1.3.4.3	Method 3:	Reduction of Selenium Compounds	252
48.1.3.4.3.1	Variation 1:	Using Raney Nickel or Nickel Boride	252
48.1.3.4.3.2	Variation 2:	Using Dissolving Metals	253
48.1.3.4.3.3	Variation 3:	Using Tributyltin Hydride and Related Reagents	253
48.1.3.4.3.4	Variation 4:	Miscellaneous Reactions	253
48.1.3.4.4	Method 4:	Replacement of an Amino Group by Hydrogen (Deamination)	254
48.1.3.4.4.1	Variation 1:	Deamination of Amines via Arylsulfonyl Derivatives	254
48.1.3.4.4.2	Variation 2:	Deamination via Diazo Derivatives	256

48.1.3.4.4.3	Variation 3:	Deamination via Free-Radical Reactions	257
48.1.3.4.4.4	Variation 4:	Miscellaneous Reactions	257
48.1.3.4.5	Method 5:	Replacement of a Nitro Group by Hydrogen (Denitration)	258
48.1.3.4.5.1	Variation 1:	Free-Radical Denitration Reactions	258
48.1.3.4.5.2	Variation 2:	Miscellaneous Reactions	259
48.1.3.4.6	Method 6:	Reduction of a Cyano Group	260
48.1.3.4.6.1	Variation 1:	Catalytic Hydrogenation	260
48.1.3.4.6.2	Variation 2:	Miscellaneous Reactions	261
48.1.3.4.7	Method 7:	Replacement of an Isocyano Group by Hydrogen	261
48.1.3.5	Reduction of Alkynes		
	N. Chessum, S. Couty, and K. Jones		
<hr/>			
48.1.3.5	Reduction of Alkynes		265
48.1.3.5.1	Method 1:	Reduction Using Heterogeneous Catalysis	265
48.1.3.5.1.1	Variation 1:	Using Classical Conditions	265
48.1.3.5.1.2	Variation 2:	Using Microwave Irradiation	266
48.1.3.5.1.3	Variation 3:	Using Hydrogen-Transfer Conditions	267
48.1.3.5.2	Method 2:	Reduction Using Homogeneous Catalysis	268
48.1.3.5.3	Method 3:	Miscellaneous Reduction Methods	269
48.1.3.5.3.1	Variation 1:	Ionic Hydrogenation	269
48.1.3.5.3.2	Variation 2:	Hydrogenation Using a Nickel–Lithium System	270
48.1.3.5.4	Method 4:	Hydrogenation in the Presence of Other Reducible Groups	271
48.1.3.5.5	Method 5:	Reduction of Polyynes	273
48.1.3.6	Reduction of Alkenes		
<hr/>			
48.1.3.6.1	Reduction by Heterogeneous Catalysis		
	N. Chessum, S. Couty, and K. Jones		
<hr/>			
48.1.3.6.1	Reduction by Heterogeneous Catalysis		275
48.1.3.6.1.1	Reduction of Alkenes (Monoenes)		275
48.1.3.6.1.1.1	Effect of Apparatus upon Reduction Using Hydrogen Gas		276
48.1.3.6.1.1.1.1	Method 1:	Synthesis Using Classical Reactors	276
48.1.3.6.1.1.1.1.1	Variation 1:	Under Atmospheric Pressure	277
48.1.3.6.1.1.1.1.2	Variation 2:	With Control of Hydrogen Consumption	277
48.1.3.6.1.1.1.1.3	Variation 3:	Using a Pressure Reactor	278
48.1.3.6.1.1.1.1.4	Variation 4:	Using a Continuous Reactor	278
48.1.3.6.1.1.1.2	Method 2:	Synthesis Using the H-Cube Reactor	280
48.1.3.6.1.1.2	Effect of Reaction Conditions upon Reduction Using Hydrogen Gas		281
48.1.3.6.1.1.2.1	Method 1:	Synthesis under Classical Conditions	285
48.1.3.6.1.1.2.1.1	Variation 1:	More Recent Developments	286
48.1.3.6.1.1.2.2	Method 2:	Synthesis Using Ultrasound	288
48.1.3.6.1.1.3	Effect of Catalyst upon Reduction Using Hydrogen Gas		289

48.1.3.6.1.1.3.1	Method 1:	Synthesis Using Cobalt Catalysts	290
48.1.3.6.1.1.3.2	Method 2:	Synthesis Using Copper Catalysts	291
48.1.3.6.1.1.3.3	Method 3:	Synthesis Using Iron Catalysts	291
48.1.3.6.1.1.3.4	Method 4:	Synthesis Using Nickel Catalysts	292
48.1.3.6.1.1.3.4.1	Variation 1:	Using Reduced Nickel	292
48.1.3.6.1.1.3.4.2	Variation 2:	Using Nickel from Nickel Formate	292
48.1.3.6.1.1.3.4.3	Variation 3:	Using Raney Nickel	293
48.1.3.6.1.1.3.4.4	Variation 4:	Using Urushibara Nickel	296
48.1.3.6.1.1.3.4.5	Variation 5:	Using Nickel Boride	297
48.1.3.6.1.1.3.4.6	Variation 6:	Using Nickel Nanoparticles	299
48.1.3.6.1.1.3.5	Method 5:	Synthesis Using Palladium Catalysts	300
48.1.3.6.1.1.3.6	Method 6:	Synthesis Using Platinum Catalysts	306
48.1.3.6.1.1.3.7	Method 7:	Synthesis Using Miscellaneous Catalysts	309
48.1.3.6.1.1.4		Effect of Substrate Structure upon Reduction Using Hydrogen Gas	311
48.1.3.6.1.1.4.1	Method 1:	Reduction of Monosubstituted Alkenes	312
48.1.3.6.1.1.4.2	Method 2:	Reduction of Disubstituted Alkenes	312
48.1.3.6.1.1.4.3	Method 3:	Reduction of Trisubstituted Alkenes	313
48.1.3.6.1.1.4.4	Method 4:	Reduction of Tetrasubstituted Alkenes	314
48.1.3.6.1.1.4.5	Method 5:	Hydrogenation of Alkenes in the Presence of Other Functional Groups	315
48.1.3.6.1.1.4.5.1	Variation 1:	Selective Hydrogenation in the Presence of Oxygen or Nitrogen Protective Groups	315
48.1.3.6.1.1.4.5.2	Variation 2:	Selective Hydrogenation in the Presence of a Carbonyl Group	318
48.1.3.6.1.1.4.5.3	Variation 3:	Selective Hydrogenation in the Presence of a Halogen	319
48.1.3.6.1.1.4.5.4	Variation 4:	Selective Hydrogenation in the Presence of a Cyclopropyl Group	320
48.1.3.6.1.1.4.5.5	Variation 5:	Selective Hydrogenation in the Presence of an Allylic C—O Bond	321
48.1.3.6.1.1.4.5.6	Variation 6:	Selective Hydrogenation in the Presence of an Aromatic Ring	321
48.1.3.6.1.1.4.5.7	Variation 7:	Selective Hydrogenation in the Presence of a Cyano Group	322
48.1.3.6.1.1.4.6	Method 6:	Stereoselective Synthesis of Alkanes	323
48.1.3.6.1.1.4.6.1	Variation 1:	Hydrogenation of Sterically Hindered Alkenes	325
48.1.3.6.1.1.4.6.2	Variation 2:	Hydrogenation of Alkenes with Polar Groups	326
48.1.3.6.1.1.5		Synthesis Using Hydrogen Transfer	327
48.1.3.6.1.1.5.1	Method 1:	Catalytic Transfer Hydrogenation	328
48.1.3.6.1.1.5.2	Method 2:	Catalytic Transfer Hydrogenation in the Presence of a Lewis Acid	330
48.1.3.6.1.1.5.3	Method 3:	Catalytic Transfer Hydrogenation under Microwave Irradiation	330
48.1.3.6.1.1.5.4	Method 4:	Catalytic Transfer Hydrogenation in an Ionic Liquid	331
48.1.3.6.1.2		Reduction of Dienes and Polyenes	332
48.1.3.6.1.2.1	Method 1:	Reduction of Dienes	332
48.1.3.6.1.2.1.1	Variation 1:	Of Hindered Diene Systems	333
48.1.3.6.1.2.2	Method 2:	Reduction of Polyenes	333

48.1.3.6.2	Reduction by Homogeneous Catalysis or Biocatalysis M. Tsukamoto and M. Kitamura	
<hr/>		
48.1.3.6.2	Reduction by Homogeneous Catalysis or Biocatalysis	341
48.1.3.6.2.1	Method 1: Hydrogenation	342
48.1.3.6.2.1.1	Variation 1: Of Dienes	342
48.1.3.6.2.1.2	Variation 2: Of Aryl-Substituted Alkenes	344
48.1.3.6.2.1.3	Variation 3: Of Alkylated Alkenes	347
48.1.3.6.2.2	Method 2: Transfer Hydrogenation	350
48.1.3.6.2.2.1	Variation 1: Using Formic Acid	350
48.1.3.6.2.2.2	Variation 2: Using an Alcohol	351
48.1.3.6.2.2.3	Variation 3: Using Borane–Dimethylamine Complex	352
48.1.3.6.2.3	Method 3: Reduction of α,β -Unsaturated Carboxylic Acid Derivatives by Biocatalysis	352
48.1.3.6.3	Reduction by Noncatalytic Methods M. Zaidlewicz, M. P. Krzemiński, and A. Dzieleńdziak	
<hr/>		
48.1.3.6.3	Reduction by Noncatalytic Methods	359
48.1.3.6.3.1	Method 1: Reduction of Alkenes or Dienes with Diimide	359
48.1.3.6.3.1.1	Variation 1: Anaerobic/Aerobic Hydrogenation	365
48.1.3.6.3.1.2	Variation 2: On a Solid Support	366
48.1.3.6.3.2	Method 2: Hydrogenation by Metals or Dissolving Metals	368
48.1.3.6.3.2.1	Variation 1: Using Sodium/Hexamethylphosphoric Triamide/ <i>tert</i> -Butyl Alcohol	368
48.1.3.6.3.2.2	Variation 2: Using Alkali Metals in Solvents	369
48.1.3.6.3.3	Method 3: Reduction with Samarium(II) Iodide	371
48.1.3.6.3.4	Method 4: Hydroboration–Protonolysis, and Reduction of Organoboranes	372
48.1.3.6.3.4.1	Variation 1: Hydroboration–Protonolysis	373
48.1.3.6.3.4.2	Variation 2: Reduction of <i>B</i> -Alkyl Catecholboranes	375
48.1.3.6.3.5	Method 5: Hydrozirconation–Protonolysis	377
48.1.3.6.3.5.1	Variation 1: Protonolysis Using Schwartz’s Reagent	377
48.1.3.6.3.5.2	Variation 2: Hydrometalation–Protonolysis	380
48.1.3.6.3.6	Method 6: Ionic Hydrogenation	382
48.1.3.6.3.6.1	Variation 1: Via Carbocations	382
48.1.3.6.3.6.2	Variation 2: Via Cation Radicals	384
48.1.3.6.3.7	Method 7: Hydrogenation with Metal Hydrides–Metal Salts	386
48.1.3.6.3.7.1	Variation 1: Using Lithium Aluminum Hydride–Metal Salts	386
48.1.3.6.3.7.2	Variation 2: Using Sodium Borohydride–Metal Salts	387
48.1.3.6.3.7.3	Variation 3: Using Metal Hydrides–Metal Alkoxides or Metal Salts	388

48.1.4	Synthesis by Reduction of Alkenes via Intermolecular C—C Bond Formation P. Eilbracht	
<hr/>		
48.1.4	Synthesis by Reduction of Alkenes via Intermolecular C—C Bond Formation	393
48.1.4.1	Additions of Carbon Electrophiles	394
48.1.4.1.1	Method 1: Hydroalkylation of Alkenes with Haloalkanes and Similar Electrophilic Alkylating Reagents	394
48.1.4.1.2	Method 2: Hydroalkylation of Alkenes with Alkyl Chloroformates and Ethylaluminum Sesquichloride	400
48.1.4.1.3	Method 3: Hydroalkylation of Alkenes with Alkanes in the Presence of Acids	402
48.1.4.2	Additions of Carbon Nucleophiles	404
48.1.4.2.1	Method 1: Carbolithiation and Hydrolysis	405
48.1.4.2.2	Method 2: Carbomagnesiation and Hydrolysis	409
48.1.4.2.2.1	Variation 1: Uncatalyzed Carbomagnesiation	409
48.1.4.2.2.2	Variation 2: Catalyzed Carbomagnesiation	410
48.1.4.2.2.3	Variation 3: Stereoselective Carbomagnesiation	412
48.1.4.2.3	Method 3: Carbozincation and Hydrolysis	413
48.1.4.2.3.1	Variation 1: Uncatalyzed Carbozincation	414
48.1.4.2.3.2	Variation 2: Catalyzed Carbozincation	415
48.1.4.2.4	Method 4: Carbocupration and Hydrolysis	416
48.1.4.2.5	Method 5: Carboalumination and Hydrolysis	417
48.1.4.2.5.1	Variation 1: Uncatalyzed Carboalumination	417
48.1.4.2.5.2	Variation 2: Catalyzed Carboalumination	418
48.1.4.2.5.3	Variation 3: Enantioselective Carboalumination	421
48.1.4.2.5.4	Variation 4: Enantioselective Carboalumination in Target-Oriented Natural Product Synthesis	425
48.1.4.2.6	Method 6: Carbotitanation and Hydrolysis	428
48.1.4.2.7	Method 7: Carbozirconation and Hydrolysis	429
48.1.4.2.8	Method 8: Other Carbometalation Processes	430
48.1.4.3	Additions of Radicals	433
48.1.4.3.1	Method 1: Additions of Alkanes to Alkenes	433
48.1.5	Synthesis by Reduction with C—C Bond Cleavage P. Margaretha	
<hr/>		
48.1.5	Synthesis by Reduction with C—C Bond Cleavage	439
48.1.5.1	Alkanes by Carbon Monoxide Extrusion from Aldehydes	440
48.1.5.1.1	Method 1: Decarbonylation in the Presence of Rhodium Complexes	440
48.1.5.1.2	Method 2: Decarbonylation in the Presence of Other Group 8–10 Metal Complexes	442
48.1.5.1.3	Method 3: Light-Induced Decarbonylation	443

48.1.5.1.4	Method 4: Functional Decarbonylation via Homolytically Induced Decomposition of Unsaturated Peroxyacetals	444
48.1.5.2	Alkanes by Base-Induced Cleavage of Ketones	445
48.1.5.2.1	Method 1: Synthesis by the Haller–Bauer Reaction	445
48.1.5.3	Alkanes from Carboxylic Acid Derivatives	446
48.1.5.3.1	Method 1: Synthesis from Acid Chlorides	446
48.1.5.3.2	Method 2: Synthesis from Esters	447
48.1.5.3.3	Method 3: Synthesis from Thioesters	447
48.1.5.3.4	Method 4: Synthesis from Selenoesters	448
48.1.5.4	Alkanes from Carboxylic Acid Derivatives by Decarboxylation	450
48.1.5.4.1	Method 1: Synthesis from Peroxy Esters	450
48.1.5.4.2	Method 2: Synthesis from Acyl Derivatives of Hydroxamic Acids	451
48.1.5.4.3	Method 3: Synthesis from Acyl Derivatives of Thiohydroxamic Acids	452
48.1.5.5	Alkanes from Alkanecarbonitriles	454
48.1.5.5.1	Method 1: Reduction with Lithium or Sodium in Ammonia	454
48.1.5.5.2	Method 2: Reduction with Potassium Metal	455
48.1.5.5.3	Method 3: Reductive Decyanation Using Alkylolithium Reagents	456
48.1.6	Synthesis from Other Alkanes	
48.1.6.1	Bond Cleavage Reactions Á. Molnár and P. Margaretha	
48.1.6.1	Bond Cleavage Reactions	459
48.1.6.1.1	Method 1: Ring Opening of Small Carbon Rings	459
48.1.6.1.1.1	Variation 1: Catalytic Hydrogenolysis	459
48.1.6.1.1.2	Variation 2: Reductive Cleavage by Alkali Metals	463
48.1.6.1.2	Method 2: Demethylation of Alkanes	465
48.1.6.2	Dehydrodimerization Reactions Á. Molnár	
48.1.6.2	Dehydrodimerization Reactions	469
48.1.6.2.1	Method 1: Dehydrodimerization of Alkanes	469
48.1.6.3	Isomerization Reactions Á. Molnár	
48.1.6.3	Isomerization Reactions	473
48.1.6.3.1	Method 1: Skeletal Isomerization of Alkanes	473

48.2	Product Class 2: Cyclopropanes	
	A. de Meijere and S. I. Kozhushkov	
<hr/>		
48.2	Product Class 2: Cyclopropanes	477
48.2.1	Synthesis of Product Class 2	479
48.2.1.1	Method 1: Synthesis by Cyclization Reactions	479
48.2.1.1.1	Variation 1: Intramolecular β -C—H Insertion of a Carbene	479
48.2.1.1.2	Variation 2: Radical Insertion into a C—H Bond	481
48.2.1.1.3	Variation 3: Radical Insertion into a C—C Bond	483
48.2.1.1.4	Variation 4: 1,5-Addition and Cycloaddition Reactions of Norbornadiene	484
48.2.1.2	Method 2: Synthesis by Cyclizing Elimination Reactions from a C ₃ Building Block	489
48.2.1.2.1	Variation 1: 1,3-Elimination of Two Heteroatoms	489
48.2.1.2.2	Variation 2: 1,3-Elimination of HX (X = Heteroatom or Heteroatom-Containing Functional Group)	495
48.2.1.2.3	Variation 3: γ -Elimination of Group 14 Elements in a Carbocationic Species	498
48.2.1.3	Method 3: Synthesis by Ring-Contraction Reactions	500
48.2.1.3.1	Variation 1: Ring-Contracting Elimination of Nitrogen from 4,5-Dihydro-3H-pyrazoles	500
48.2.1.3.2	Variation 2: Ring-Contracting Elimination of One or Two C=O Units from Cyclobutanones or Cyclopentanediones	504
48.2.1.4	Method 4: Synthesis by Cycloaddition Reactions	506
48.2.1.4.1	Variation 1: Cyclopropanation with Photochemically or Thermally Generated Carbenes	506
48.2.1.4.2	Variation 2: Cyclopropanation with Catalytically Generated Methylene	509
48.2.1.4.3	Variation 3: Cyclopropanation with Methylenoids (Simmons–Smith Cyclopropanation)	516
48.2.1.4.4	Variation 4: Cyclopropanation with Dihalocarbenes Followed by Reductive Dehalogenation	527
48.2.1.4.5	Variation 5: Cyclopropanation with Arylcarbenes (Arylcarbenoids)	540
48.2.1.4.6	Variation 6: Cycloaddition Reactions of Cyclopropenes	550
48.2.1.4.7	Variation 7: Dimerization and Oligomerization Reactions of Cyclopropenes	558
48.2.1.5	Method 5: Synthesis by Addition to C=C Bonds of Cyclopropenes with Retention of the Cyclopropane Ring	561
48.2.1.5.1	Variation 1: Hydrogenation	561
48.2.1.5.2	Variation 2: Addition of Organometallic Species	564
48.2.1.6	Method 6: Synthesis by Rearrangement of the Carbon Skeleton	565
48.2.1.6.1	Variation 1: Homoallyl or Cyclobutyl Rearrangements to a Cyclopropylmethyl Group	565
48.2.1.6.2	Variation 2: Rearrangements in Oligoene Systems	567
48.2.1.6.3	Variation 3: Miscellaneous Rearrangements	572
48.2.1.7	Method 7: Synthesis by Transformation of Other Cyclopropanes	573
48.2.1.7.1	Variation 1: Reactions without Ring Opening of the Cyclopropane Moieties	573
48.2.1.7.2	Variation 2: Reactions with Ring Opening of the Cyclopropane Moieties	574

48.2.1.8	Methods 8:	Miscellaneous Reactions	576
48.2.1.8.1	Variation 1:	Reductive Cyclopropanation of a Carbonyl Group	576
48.2.1.8.2	Variation 2:	Cycloaddition and Insertion Reactions of Carbenoids	578
48.2.1.8.3	Variation 3:	Oligo- and Polymerization Reactions	584
48.2.1.8.4	Variation 4:	Cyclopropanation with Sulfur Ylides	586
48.2.2		Applications of Product Class 2 in Organic Synthesis	588
48.3	Product Class 3: Cyclobutanes		
	R. Kostikov and M. S. Baird		
48.3	Product Class 3: Cyclobutanes		
48.3.1	Synthesis of Product Class 3		
48.3.1.1	Method 1:	Ring-Opening Reactions	615
48.3.1.1.1	Variation 1:	Opening of the Central Bond in Bicyclo[1.1.0]butanes	615
48.3.1.1.2	Variation 2:	Ring Opening of One Bond in [1.1.n]Propellanes	616
48.3.1.2	Method 2:	1,4-Cycloelimination of Two Heteroatoms from 1,4-Dihalides or Similar Difunctional Compounds	619
48.3.1.3	Method 3:	Ring-Contraction Reactions	620
48.3.1.3.1	Variation 1:	Elimination of Nitrogen from Six-Membered Heterocycles	620
48.3.1.3.2	Variation 2:	Decarbonylation of Cyclopentanones	623
48.3.1.3.3	Variation 3:	Elimination of a Metal Atom from Metallacyclopentanes	624
48.3.1.3.4	Variation 4:	Rearrangement of Bicyclo[4.1.0]hept-2-ene Derivatives	626
48.3.1.4	Method 4:	[2 + 2]-Cycloaddition Reactions	627
48.3.1.4.1	Variation 1:	Cycloaddition Reactions of Cyclopropenes	628
48.3.1.4.2	Variation 2:	Cycloaddition Reactions of Methylene cyclopropanes	628
48.3.1.4.3	Variation 3:	Cycloaddition Reactions of Cyclobutene	630
48.3.1.4.4	Variation 4:	Miscellaneous Intramolecular Cycloadditions	630
48.3.1.5	Method 5:	Synthesis with Retention of the Cyclobutane Ring	631
48.3.1.5.1	Variation 1:	Hydrogenation of Unsaturated Hydrocarbons	631
48.3.1.5.2	Variation 2:	Hydrogenation of 1-(Organosulfonyl)cyclobutenes	634
48.3.1.6	Method 6:	Rearrangement of the Carbon Framework	635
48.3.1.6.1	Variation 1:	Rearrangement of Cyclopropylmethyl and Homoallyl Derivatives	635
48.3.1.6.2	Variation 2:	Rearrangement of Compounds Containing Hexa-1,5-dienyl or Dicyclopropyl Fragments	636
48.3.1.7	Method 7:	Transformation of Other Cyclobutanes	638
48.3.2		Applications of Product Class 3 in Organic Synthesis	640
48.4	Product Class 4: Five-Membered and Larger-Ring Cycloalkanes		
	M. J. Palframan and A. F. Parsons		
48.4	Product Class 4: Five-Membered and Larger-Ring Cycloalkanes		
48.4.1	Synthesis of Product Class 4		
48.4.1.1	Method 1:	Synthesis by Reduction without C—C Bond Cleavage	647
48.4.1.1.1	Variation 1:	Of Cycloalkenes	647

48.4.1.1.2	Variation 2:	Of Cycloienes	650
48.4.1.1.3	Variation 3:	Of Substituted Benzenes	651
48.4.1.2	Method 2:	Synthesis by Radical Cyclization	652
48.4.1.2.1	Variation 1:	Formation of Cyclopentanes and Cyclohexanes	652
48.4.1.2.2	Variation 2:	Formation of Medium-Sized Rings	663
48.4.1.2.3	Variation 3:	Formation of Large-Sized Rings	664
48.4.1.3	Method 3:	Synthesis by Polar Cyclization	665
48.4.1.3.1	Variation 1:	Nucleophilic Substitution	665
48.4.1.3.2	Variation 2:	Nucleophilic Addition	668
48.4.1.4	Method 4:	Synthesis by Metal-Promoted Cyclization	673
48.4.1.4.1	Variation 1:	Of Dienes	673
48.4.1.4.2	Variation 2:	Of Enynes	675
48.4.1.4.3	Variation 3:	Of Diynes	679
48.4.1.4.4	Variation 4:	Of Trimethylenemethanes	681
48.4.1.4.5	Variation 5:	Of Unsaturated Diazo Compounds	683
48.4.1.5	Method 5:	Synthesis by Ring Expansion	685
48.4.1.6	Method 6:	Synthesis by Ring Contraction	687

48.5 Product Class 5: Hydrocarbon Polymers

W. Kaminsky

48.5	Product Class 5: Hydrocarbon Polymers	695
48.5.1	Product Subclass 1: Polyethenes	696
48.5.1.1	Synthesis of Product Subclass 1	696
48.5.1.1.1	Method 1: Synthesis by Decomposition of Diazomethane	696
48.5.1.1.2	Method 2: Synthesis by Radical Polymerization	697
48.5.1.1.3	Method 3: Synthesis by Coordination Catalysis	699
48.5.1.1.3.1	Variation 1: Using Early Ziegler–Natta Catalysts: Titanium Halides–Alkylaluminum Complexes	699
48.5.1.1.3.2	Variation 2: Using Third-Generation Supported Ziegler–Natta Catalysts	701
48.5.1.1.3.3	Variation 3: Using Phillips Catalysts	701
48.5.1.1.3.4	Variation 4: Using Homogeneous (Single-Site) Catalysis with Metallocenes Activated by Methylaluminumoxane	702
48.5.1.1.3.5	Variation 5: Using Homogeneous (Single-Site) Catalysis with Metallocenes Activated by Fluorinated Boranes or Borates	705
48.5.1.1.3.6	Variation 6: Using Homogeneous (Single-Site) Catalysis with Late-Transition-Metal Catalysts	705
48.5.2	Product Subclass 2: Polyethene Copolymers	708
48.5.2.1	Synthesis of Product Subclass 2	708
48.5.2.1.1	Method 1: Copolymerization of Ethene with Alk-1-enes	708
48.5.2.1.1.1	Variation 1: Using Ziegler–Natta Catalysts	709
48.5.2.1.1.2	Variation 2: Of Short- to Medium-Chain Alk-1-enes Using Single-Site Catalysts	709
48.5.2.1.1.3	Variation 3: Of Medium- to Long-Chain Alk-1-enes Using Single-Site Catalysts	711
48.5.2.1.2	Method 2: Synthesis of Ethene–Propene Rubbers	712

48.5.2.1.2.1	Variation 1: Using Vanadium-Based Catalysts	712
48.5.2.1.2.2	Variation 2: Using Metallocene-Based Catalysts	713
48.5.2.1.3	Method 3: Copolymerization of Ethene with Cycloalkenes	713
48.5.2.1.3.1	Variation 1: Using Metallocene-Based Catalysts	714
48.5.2.1.3.2	Variation 2: Using Palladium-Based Catalysts	715
48.5.3	Product Subclass 3: Polypropenes	716
48.5.3.1	Synthesis of Product Subclass 3	718
48.5.3.1.1	Method 1: Synthesis of Isotactic Polypropenes Using Ziegler–Natta Catalysts	718
48.5.3.1.1.1	Variation 1: Using Titanium Chlorides–Alkylaluminum Reagents	718
48.5.3.1.1.2	Variation 2: Using a Supported Titanium Chloride Reagent	720
48.5.3.1.1.3	Variation 3: With Addition of Donors	721
48.5.3.1.2	Method 2: Synthesis Using Homogeneous Catalysts	722
48.5.3.1.2.1	Variation 1: Of Isotactic Polypropenes	722
48.5.3.1.2.2	Variation 2: Of Syndiotactic Polypropenes	725
48.5.3.1.2.3	Variation 3: Of Atactic Polypropenes	726
48.5.4	Product Subclass 4: Other Hydrocarbon Polymers	727
48.5.4.1	Synthesis of Product Subclass 4	728
48.5.4.1.1	Method 1: Synthesis of Polybutenes	728
48.5.4.1.2	Method 2: Synthesis of Poly(isobutenes)	728
48.5.4.1.3	Method 3: Synthesis of Poly(methyl-substituted alk-1-enes)	730
48.5.4.1.4	Method 4: Synthesis of Poly(cycloalkenes)	730
	Keyword Index	739
	Author Index	783
	Abbreviations	825