

Free Radicals: Fundamentals and Applications in Organic Synthesis 1

Preface	V
Abstracts	XI
Table of Contents	XXI
Introduction: Radicals, from Gomberg to Planet Mars	
L. Fensterbank and C. Ollivier	1
1.1 Improving Radical Persistence through Confinement: A Survey	
M. P. Bertrand, E. Besson, and S. Gastaldi 	5
1.2 Nitroxides in Organic Synthesis	
G. Casano and O. Ouari 	29
1.3 Modelling Radicals and Their Reactivities	
E. Derat and B. Braïda	91
1.4 Electron Catalysis	
E. Shirakawa 	135
1.5 Photochemistry and Radical Generation: Approaches in Mechanism Elucidation	
S. B. Cahoon and T. P. Yoon	159
1.6 Sulfur-, Selenium-, and Silicon-Centered Radicals	
A. Kaga and H. Yorimitsu	207
1.7 Phosphorus-Centered Radicals	
C. Bellanger, S. Chelli, and S. Lakhdar 	227
1.8 Nitrogen-Centered Radicals	
X.-L. Lu, B. Wang, and S. Chiba 	273
1.9 Oxygen-Centered Radicals	
J. Zhang, D. Liu, and Y. Chen	323

1.10	Boron-Centered Radicals	F.-L. Zhang and Y.-F. Wang	381
1.11	Generation of Radicals from Organoboranes	E. André-Joyaux, L. Gnägi, C. Meléndez, V. Soulard, and P. Renaud 	431
1.12	Intermolecular Radical C–H Functionalization	M. Bietti and F. Dénès 	495
1.13	Intramolecular Hydrogen-Atom Transfer	S. M. Treacy, X. Zhang, and T. Rovis	605
1.14	Palladium(I)-Mediated Reactions	G. Maestri and A. Serafino 	651
 Keyword Index		671	
 Author Index		707	
 Abbreviations		731	

Table of Contents

Introduction: Radicals, from Gomberg to Planet Mars

L. Fensterbank and C. Ollivier

Introduction: Radicals, from Gomberg to Planet Mars	1
---	---

1.1 Improving Radical Persistence through Confinement: A Survey

M. P. Bertrand, E. Besson, and S. Gastaldi 

1.1 Improving Radical Persistence through Confinement: A Survey	5
1.1.1 Nonstructured Systems	6
1.1.1.1 Adsorption onto Metal Oxides	6
1.1.1.2 Grafting onto Bulk Silica	7
1.1.2 Structured Systems	7
1.1.2.1 Porous Systems	7
1.1.2.1.1 Zeolites	7
1.1.2.1.2 Mesoporous Silicas	9
1.1.2.1.2.1 Noncovalently Functionalized Mesoporous Silicas	9
1.1.2.1.2.2 Covalently Functionalized Mesoporous Silicas	10
1.1.2.1.2.3 Periodic Mesoporous Organic Silicas	13
1.1.2.2 Layered Structures	13
1.1.2.2.1 Graphene Oxide	13
1.1.2.2.2 Lamellar Polysilsesquioxanes	14
1.1.3 Organic Supramolecular Assemblies	14
1.1.3.1 Single-Walled Carbon Nanotubes	15
1.1.3.2 Cyclodextrins, Cucurbit[n]urils, and Cyclophanes	15
1.1.3.3 Metal–Organic Frameworks (MOFs)	21
1.1.3.4 Self-Assembled Systems	21
1.1.3.4.1 Conclusion and Perspectives	25

1.2 Nitroxides in Organic Synthesis

G. Casano and O. Ouari 

1.2 Nitroxides in Organic Synthesis	29
1.2.1 The Persistent Radical Effect	34
1.2.2 Transformation of Alcohols, Diols, and Amines	44
1.2.2.1 Oxidation of Alcohols	44

1.2.2.1.1	Oxidation Using Nitroxides in Combination with a Secondary Chemical Oxidant (Metal-Free Approach)	47
1.2.2.1.2	Aerobic Oxidation Using Nitroxides and Metal Ions	59
1.2.3	Transformations of Other Functional Groups Using TEMPO or Derivatives	72
1.2.4	Recovery of Nitroxide Reagents	85
1.2.5	Conclusion	85
 1.3	 Modelling Radicals and Their Reactivities	
	E. Derat and B. Braïda	
<hr/> 1.3	Modelling Radicals and Their Reactivities	91
1.3.1	DFT for Simulating Radical Species	91
1.3.1.1	DFT: Successes and Caveats for Radicals	91
1.3.1.2	Constrained DFT (CDFT) and Radicals	92
1.3.1.3	Predicting Reactivity by Estimating Radical Stability	94
1.3.1.4	Shedding New Light on Baldwin's Rules	95
1.3.2	Valence Bond Methods for Radicals	96
1.3.2.1	Valence Bond Wave Functions	96
1.3.2.2	Valence Bond Methods and Programs	98
1.3.2.3	The Valence Bond Diagram Model	100
1.3.3	Stable Three-Electron Bonded Radicals and Their Potential Role in Reactivity	103
1.3.3.1	The Nature of the Two-Center, Three-Electron 2c-3e Bond	103
1.3.3.2	How to Characterize 2c-3e Bonded Systems from Bare Radicals	105
1.3.3.3	The Catalytic Role of the 2c-3e Bonds in C—H Bond Activation	106
1.3.4	Diradical Reactivity	109
1.3.4.1	Quantifying Diradical Character from a Valence Bond Perspective	109
1.3.4.2	Connection between Diradical Character and Reactivity: 1,3-Dipolar Cycloadditions as a Case Study	112
1.3.5	Modelling Radicals in Enzymes: Horseradish Peroxidase (HRP) as a Case Study	115
1.3.5.1	Function of Peroxidases	115
1.3.5.2	Structure of Horseradish Peroxidase	116
1.3.5.3	Quantum Mechanics Studies	117
1.3.5.4	Quantum Mechanics/Molecular Mechanics Studies	118
1.3.6	Conclusion	130

1.4	Electron Catalysis	
	E. Shirakawa	
<hr/>		
1.4	Electron Catalysis	135
1.4.1	S _{RN} 1 Reaction of Aryl Halides	137
1.4.1.1	Direct Arylation of Arenes	137
1.4.1.2	Arylation of Styrenes	141
1.4.1.3	Arylation of Carbon Monoxide	143
1.4.2	Electron-Catalyzed Cross-Coupling Reactions of Aryl and Alkenyl Halides	145
1.4.2.1	Cross-Coupling Reaction with Aryl Grignard Reagents	145
1.4.2.2	Cross-Coupling Reactions with Organozinc Reagents	150
1.4.2.3	Cross-Coupling Reaction with Other Organometallics	153
1.4.3	Conclusion	156
<hr/>		
1.5	Photochemistry and Radical Generation: Approaches in Mechanism Elucidation	
	S. B. Cahoon and T. P. Yoon	
<hr/>		
1.5	Photochemistry and Radical Generation: Approaches in Mechanism Elucidation	159
1.5.1	Techniques for the Investigation of Photochemical Reaction Mechanisms	160
1.5.1.1	Techniques To Study Photocatalytic Initiation	161
1.5.1.1.1	Photocatalyst Characterization	161
1.5.1.1.1.1	Absorption Spectroscopy	161
1.5.1.1.1.2	Emission Spectroscopy	163
1.5.1.1.1.3	Electrochemistry	164
1.5.1.1.1.4	Calculation of Excited-State Redox Potentials	165
1.5.1.1.2	Determining the Thermodynamics of Electron- and Energy-Transfer Steps	166
1.5.1.1.3	Control Reactions	167
1.5.1.1.4	UV-vis Spectroscopy	168
1.5.1.1.5	Time-Resolved Emission and Absorption Spectroscopy	168
1.5.1.1.6	Steady-State Stern–Volmer Quenching Studies	169
1.5.1.1.7	Alternate Chemical Initiation	170
1.5.1.1.8	Correlations	170
1.5.1.2	Techniques To Study Product Formation	170
1.5.1.2.1	Quantum Yield	170
1.5.1.2.2	Kinetic Tools	173

1.5.2	Case Studies in the Investigation of Photocatalytic Mechanisms	173
1.5.2.1	Characterization of Chains	173
1.5.2.2	Mechanistically Guided Enantioselective Photochemical Methods	177
1.5.2.3	Characterization of Proton-Coupled Electron Transfer (PCET)/ Hydrogen-Atom Transfer (HAT) Processes	181
1.5.2.4	Metallaphotoredox Reactions	194
1.5.2.5	Selected Studies of Electron Donor–Acceptor (EDA) Complexes	197
1.5.2.6	Hydrogen-Bonding Chiral Photocatalysts	199
1.5.3	Conclusion	203

1.6 Sulfur-, Selenium-, and Silicon-Centered Radicals

A. Kaga and H. Yorimitsu

1.6	Sulfur-, Selenium-, and Silicon-Centered Radicals	207
1.6.1	Incorporation of Sulfur, Selenium, and Silicon into Products	207
1.6.1.1	C(sp ³)—E (E = S, Se, Si) Bond Formation	207
1.6.1.1.1	C(sp ³)—Sulfur Bond Formation	208
1.6.1.1.2	C(sp ³)—Selenium Bond Formation	210
1.6.1.1.3	C(sp ³)—Silicon Bond Formation	210
1.6.1.2	C(sp ²)—E (E = S, Se, Si) Bond Formation	213
1.6.1.2.1	C(sp ²)—Sulfur Bond Formation	213
1.6.1.2.2	C(sp ²)—Silicon Bond Formation	214
1.6.2	Sulfur, Selenium, and Silicon Radicals as Catalysts/Reagents	216
1.6.2.1	Polarity-Reversal Catalysis	216
1.6.2.1.1	Polarity-Reversal Catalysis Using Sulfur Radicals	216
1.6.2.1.2	Polarity-Reversal Catalysis Using Selenium Radicals	217
1.6.2.2	Asymmetric Catalysis	218
1.6.2.2.1	Carbohydrate-Derived Chiral Thiols as Polarity-Reversal Catalysts	218
1.6.2.2.2	Chiral Thiol Catalysis Involving an Addition–Elimination Mechanism	218
1.6.2.3	Sulfur, Selenium, and Silicon Radicals as Reducing Agents To Generate Carbon-Centered Radicals	220
1.6.2.3.1	Sulfur Radicals in Reductions	220
1.6.2.3.2	Silicon Radicals in Reductions	220

1.7	Phosphorus-Centered Radicals	
	C. Bellanger, S. Chelli, and S. Lakhdar	
1.7	Phosphorus-Centered Radicals	227
1.7.1	Reactions of Phosphinyl Radicals ($R_2^1P^\bullet$)	227
1.7.1.1	Generation of Phosphinyl Radicals through Hydrogen-Atom Transfer	228
1.7.1.1.1	Photocatalytic Arylation and Alkylation of Phosphines	228
1.7.1.1.1.1	Arylation of Phosphines	228
1.7.1.1.1.2	Alkylation of Phosphines	230
1.7.1.2	Generation of Phosphinyl Radicals from Diphosphines	232
1.7.1.2.1	Preparation of (<i>E</i>)-1,2-Diphosphinoethenes by Addition to Terminal Alkynes	232
1.7.1.2.2	Preparation of P-Perfluoroalkylated Phosphines by Reaction with Perfluoroalkyl Iodides	234
1.7.1.2.3	Preparation of 1,4-Diphosphinobut-2-enes by Addition to Buta-1,3-dienes	235
1.7.2	Reactions of Phosphinoyl Radicals ($R_2^1P=O^\bullet$)	236
1.7.2.1	P—C(sp ³) Formation	236
1.7.2.1.1	Hydrophosphinylation of Alkenes	236
1.7.2.1.2	Preparation of β -Oxo Phosphine Oxides by Hydrophosphinylation of Alkynes or Alkenes	237
1.7.2.1.3	Phosphonocarboxylation of Alkenes	240
1.7.2.1.4	Phosphorylalkylation of Hetarenes	241
1.7.2.1.5	Enantioselective Cyanophosphorylation of Alkenes	245
1.7.2.2	P—C(sp ²) Formation	247
1.7.2.2.1	Phosphorylation of (Het)Arenes	247
1.7.2.2.1.1	Phosphorylation of Thiazoles and Derivatives	247
1.7.2.2.1.2	Phosphonylation of Indoles	249
1.7.2.2.1.3	Phosphorylation of 1-Benzopyran-2-ones and Quinolinones	250
1.7.2.2.1.4	Phosphorylation of Pyridines	251
1.7.2.2.1.5	Preparation of Arylphosphonates, Arylphosphine Oxides, and Arylphosphinates by Dual Catalytic Reaction of P—H Species with Aryl (Pseudo)halides	253
1.7.2.2.1.6	Photocatalyst-Free Synthesis of Arylphosphonates and Arylphosphine Oxides by Reaction of P—H Species with Aryl Halides	256
1.7.2.2.2	Addition to Alkynes	257
1.7.2.2.2.1	Preparation of Z-Alkenylphosphine Oxides	257
1.7.2.2.2.2	Preparation of E-Alkenylphosphine Oxides	258
1.7.2.2.2.3	Preparation of 3-Phosphorylated 2-Aryl-4 <i>H</i> -1-benzothiopyran-4-ones	260
1.7.2.2.2.4	Preparation of Phosphorylated N-Heteroaromatics	261
1.7.3	Reactions of Phosphonium Radicals ($R_3^1P^{++}$)	263

1.7.4	Reactions of Phosphoranyl Radicals ($R^1_4P^\bullet$)	264
1.7.4.1	Radical Addition to Trivalent Phosphorus Compounds	265
1.7.4.1.1	Preparation of Arylphosphonates by Addition of Aryl Bromides to Phosphites	265
1.7.4.1.2	Preparation of Phosphate Esters by Reaction of N-Alkoxyypyridinium Salts with Trialkyl Phosphites	266
1.7.4.2	Nucleophilic Addition to Phosphorus Radical Cations	267
1.7.5	Conclusion	269
 1.8	Nitrogen-Centered Radicals	
	X.-L. Lu, B. Wang, and S. Chiba 	
 1.8	Nitrogen-Centered Radicals	273
1.8.1	Aminyl and Aminium Radicals	274
1.8.1.1	Oxidative Generation	274
1.8.1.1.1	From Secondary and Primary Amines	274
1.8.1.1.2	From Tertiary Amines	277
1.8.1.2	Reductive Generation	278
1.8.1.2.1	From <i>N</i> -Chloroamines	278
1.8.1.2.2	From O-Arylhydroxylamines	279
1.8.1.3	Photoexcitation of Imines	280
1.8.2	Amidyl and Imidyl Radicals	282
1.8.2.1	Oxidative Generation	282
1.8.2.1.1	From Amides and Imides	282
1.8.2.1.1.1	By Proton-Coupled Electron Transfer	282
1.8.2.1.1.2	By Electrochemical Oxidation	287
1.8.2.1.1.3	By Other Oxidative Methods	289
1.8.2.1.2	From α -Amidoxy Acids	292
1.8.2.2	Reductive Generation	295
1.8.2.2.1	From <i>N</i> -Fluorobenzenesulfonimide or <i>N</i> -Fluorosulfonamides	295
1.8.2.2.2	From <i>N</i> -Arylhydroxamates and Their Derivatives	297
1.8.2.2.3	From <i>N</i> -Hydroxyphthalimide and Its Derivatives	300
1.8.2.3	Generation by N—S Bond Homolysis of <i>N</i> -(Allylsulfonyl)amides	304
1.8.2.4	Generation of Phthalimidyl Radicals via N—O Bond Homolysis of <i>N</i> -(Alkenyloxy)phthalimides	305
1.8.3	Iminyl Radicals	306
1.8.3.1	Oxidative Generation	307
1.8.3.1.1	From Oxime Derivatives	307
1.8.3.1.2	From Carboximidates	310

1.8.3.2	Reductive Generation	312
1.8.3.2.1	From Oxime Derivatives	312
1.8.3.2.2	From N-Phenoxyimides	315
1.8.3.3	N—O Bond Homolysis of Oxime Derivatives	317
1.8.4	Conclusion	318
1.9	Oxygen-Centered Radicals	
	J. Zhang, D. Liu, and Y. Chen	
<hr/>		
1.9	Oxygen-Centered Radicals	323
1.9.1	Carboxyl Radicals	324
1.9.1.1	Traditional Carboxyl Radical Generation and Functionalization	324
1.9.1.2	Visible-Light-Induced Carboxyl Radical Generation and Functionalization	325
1.9.1.2.1	Alkyl Carboxyl Radicals	326
1.9.1.2.2	α -Oxo Acids	335
1.9.1.2.3	Aryl Carboxyl Radicals	340
1.9.2	Alkoxy Radicals	344
1.9.2.1	Traditional Alkoxy Radical Generation and Functionalization	344
1.9.2.2	Visible-Light-Induced Alkoxy Radical Generation and Functionalization	345
1.9.2.2.1	Inert C(sp ³)—H Bond Functionalization	346
1.9.2.2.2	Inert C(sp ³)—C(sp ³)/C(sp ³)—X Bond Functionalization	357
1.9.2.2.3	Alkoxy Radical Addition Reactions to Alkenes	365
1.9.3	Other Oxygen-Centered Radicals	366
1.9.3.1	Acyclic Aminoxyl Radicals	366
1.9.3.1.1	Traditional Aminoxyl Radical Generation and Functionalization	366
1.9.3.1.2	Visible-Light-Induced Iminoxyl Radical Generation and Functionalization	367
1.9.3.2	Trifluoromethoxyl and Difluoromethoxyl Radicals	368
1.9.3.2.1	Traditional Trifluoromethoxyl and Difluoromethoxyl Radical Generation	368
1.9.3.2.2	Visible-Light-Induced Trifluoromethoxyl and Difluoromethoxyl Radical Generation and Functionalization	369
1.9.3.3	Phenoxy Radicals	371
1.9.3.3.1	Traditional Phenoxy Radical Generation and Functionalization	371
1.9.3.3.2	Electrochemical Phenoxy Radical Generation and Functionalization	371
1.9.3.3.3	Visible-Light-Induced Phenoxy Radical Generation and Functionalization	373
1.9.3.4	Vinyloxy Radicals	373
1.9.4	Conclusion	376

1.10	Boron-Centered Radicals	
	F.-L. Zhang and Y.-F. Wang	
<hr/>		
1.10	Boron-Centered Radicals	381
1.10.1	Reactions Using Lewis Base–Borane Complexes as Boryl Radical Precursors	381
1.10.1.1	Organoboron Synthesis	381
1.10.1.1.1	Radical (Hydro)borations	381
1.10.1.1.2	Radical Borylative Cyclizations	386
1.10.1.1.3	Radical C–F Borylation	387
1.10.1.1.4	Photoredox Catalysis Enabled Radical Borylation	388
1.10.1.2	Reductive Radical Transformations	392
1.10.1.3	N-Heterocyclic Carbene–Boryl Radical Catalyzed Reactions	395
1.10.2	Reactions Using Lewis Base–Diboron Compounds as Boryl Radical Precursors	398
1.10.2.1	Organoboron Synthesis	398
1.10.2.1.1	Radical Borylation of Organic Halides	398
1.10.2.1.2	Radical Decarboxylative Borylation of Carboxylic Acid Derivatives	402
1.10.2.1.3	Radical Deaminative Borylation	405
1.10.2.1.4	Radical Deoxygenative Borylation	408
1.10.2.1.5	Radical Borylation of In Situ Generated Dithiocarbamates	415
1.10.2.1.6	Radical Borylation of Arylsulfonium Salts	417
1.10.2.1.7	Borylation of Carbon Radicals Derived from Radical Tandem Reactions	417
1.10.2.2	Boryl Radical Enabled C–C Bond Formation	418
1.10.3	Boron-Centered Carboranyl Radicals	425
1.10.4	Conclusion	427
<hr/>		
1.11	Generation of Radicals from Organoboranes	
	E. André-Joyaux, L. Gnägi, C. Meléndez, V. Soulard, and P. Renaud 	
<hr/>		
1.11	Generation of Radicals from Organoboranes	431
1.11.1	Generation of Radicals via Nucleohomolytic Substitution at Boron	431
1.11.1.1	Basic Principles	431
1.11.1.2	Initiation of Radical Reactions	432
1.11.1.3	Chain Reactions Involving Boron-Based Radical Precursors	437
1.11.1.3.1	Chain Reactions with Trialkylboranes	437
1.11.1.3.2	Chain Reactions with <i>B</i> -Alkylcatecholboranes	439
1.11.1.3.3	Chain Reactions with Pinacol Alkylboronic Esters	450
1.11.1.3.4	Chain Reactions with Boronic Acids	452
1.11.1.4	Organoboron Derivatives as Chain-Transfer Reagents	454

1.11.1.4.1	The Concept of Organoborane-Initiated Chain-Transfer Reactions	454
1.11.1.4.2	Oxime Ethers as Radical Traps	454
1.11.1.4.3	Hydrazones as Radical Traps	456
1.11.1.4.4	Imines as Radical Traps	458
1.11.1.4.5	Isocyanates as Radical Traps	459
1.11.1.4.6	Azides as Radical Traps	461
1.11.1.4.7	Aldehydes as Radical Traps	461
1.11.1.4.8	Enones as Radical Traps	464
1.11.1.4.9	Vinyl Epoxides as Radical Traps	466
1.11.1.4.10	Sulfones and Other Sulfonyl Reagents as Radical Traps	468
1.11.1.4.11	Hydrogen-Atom Transfer from Water, Alcohols, and Thiols	469
1.11.1.4.11.1	Deiodination with 4- <i>tert</i> -Butylcatechol	469
1.11.1.4.11.2	Hydroalkylation with 4- <i>tert</i> -Butylcatechol	471
1.11.1.4.11.3	Hydrothiolation in the Presence of Catechol	472
1.11.1.4.11.4	Deoxygenation and Deiodination Mediated by a Trialkylborane–Water Complex	473
1.11.1.4.11.5	Deiodination Catalyzed by Thiols in the Presence of Triethylborane	475
1.11.2	Generation of Radicals via Redox Processes	477
1.11.2.1	Electrochemical Methods	477
1.11.2.2	Oxidation of Arylboronic Acids	477
1.11.2.3	Oxidation of Pinacol Alkylboronic Esters	481
1.11.2.4	Oxidation of Trifluoroborates	483
1.11.2.4.1	Chemical Oxidation	483
1.11.2.4.2	Photoredox Catalysis	484
1.11.2.4.2.1	Iridium Catalysis	484
1.11.2.4.2.2	Ruthenium Catalysis	486
1.11.2.4.2.3	Organic Catalysis	486
1.11.2.4.3	Dual Catalysis	488
1.11.3	Conclusion	490
1.12	Intermolecular Radical C–H Functionalization	
	M. Bietti and F. Dénès 	
1.12	Intermolecular Radical C–H Functionalization	495
1.12.1	Definitions and Mechanistic Considerations: Factors Governing the Selectivity of Hydrogen-Atom Transfer (HAT)	497
1.12.2	C–H Bond Activation α to an Oxygen, Nitrogen, or Sulfur Atom	504
1.12.2.1	Simple Addition onto Alkenes and Alkynes	504

1.12.2.2	The Fragmentation Method	512
1.12.2.3	Addition to Aldehydes	514
1.12.2.4	Arylation	515
1.12.2.5	Oxidative Cross Coupling	519
1.12.2.6	Introduction of a Heteroatom (Chalcogenation and Amination)	520
1.12.2.7	Cross-Coupling Reactions	523
1.12.3	C—H Bond Activation of Aldehydes	530
1.12.3.1	Intra- and Intermolecular Trapping with Alkenes	530
1.12.3.2	Homolytic Aromatic Substitution with Aldehydes	531
1.12.3.3	Copper-Catalyzed Radical Oxidative Cross-Coupling Reactions between Alkenes and Aldehydes	533
1.12.3.4	Trapping with Isocyanides	534
1.12.3.5	Transition-Metal-Catalyzed Cross-Coupling Reactions	535
1.12.4	C—H Bond Activation at Allylic, Propargylic, or Benzylic Positions	537
1.12.4.1	Halogenation	537
1.12.4.2	Oxidation	539
1.12.4.3	Amination	542
1.12.4.4	C—C Bond Forming Reactions	547
1.12.5	C—H Bond Activation α to an Electron-Withdrawing Group (Ester, Nitrile, etc.)	550
1.12.5.1	C—C Bond Forming Reactions	550
1.12.6	C—H Bond Activation of Unactivated Aliphatic Positions	555
1.12.6.1	C—Heteroatom Bond Forming Reactions	555
1.12.6.1.1	Halogenation (Chlorination, Bromination, Fluorination)	555
1.12.6.1.2	Oxidation to Alcohols, Ketones, or Carboxylic Acids	561
1.12.6.1.3	Amination and Related Processes	577
1.12.6.1.4	Sulfochlorination (Reed Process)	583
1.12.6.1.5	Chalcogenation	584
1.12.6.2	C—C Bond Forming Reactions	586
1.12.6.2.1	Giese-Type Reactions	586
1.12.6.2.2	Homolytic Aromatic Substitution	589
1.12.6.2.3	Fragmentation Methods	591
1.12.6.2.4	Carbonylation Reactions	591
1.12.6.2.5	Cross-Coupling Reactions	592
1.12.7	Conclusion	596

1.13	Intramolecular Hydrogen-Atom Transfer	
	S. M. Treacy, X. Zhang, and T. Rovis	
<hr/>		
1.13	Intramolecular Hydrogen-Atom Transfer	605
1.13.1	Intramolecular Hydrogen-Atom Transfer for Molecules Bearing an sp ³ -Hybridized Nitrogen Atom	605
1.13.1.1	Remote Functionalization and Cyclization of Amines	607
1.13.1.2	Remote Functionalization and Cyclization of Amides and Sulfonamides	607
1.13.2	Intramolecular Hydrogen-Atom Transfer for Molecules Bearing an sp ² - or sp-Hybridized Nitrogen Atom	620
1.13.2.1	Remote Functionalization and Cyclization of Imines, Amidines, and Imidates	620
1.13.2.2	Remote Functionalization and Cyclization of Oximes	622
1.13.2.3	Remote Functionalization and Cyclization of Organic Azides	623
1.13.3	Intramolecular Hydrogen-Atom Transfer for Molecules with Oxygen-Containing Functional Groups	627
1.13.3.1	Remote Functionalization of Alcohols	627
1.13.3.2	Remote Functionalization of Carboxylic Acids and Ketones	638
1.13.4	Intramolecular Hydrogen-Atom Transfer via Carbon—Heteroatom Cleavage	642
1.13.4.1	Remote Functionalization of Organic Halides	642
1.13.4.2	Remote Functionalization via Carbon—Nitrogen Bond Cleavage	644
<hr/>		
1.14	Palladium(I)-Mediated Reactions	
	G. Maestri and A. Serafino	
<hr/>		
1.14	Palladium(I)-Mediated Reactions	651
1.14.1	Reactions Promoted by Visible Light	651
1.14.1.1	Dehydrogenation of Aliphatic Amines	651
1.14.1.2	Heck Reactions	653
1.14.1.3	Chelation-Assisted C—H Activation	654
1.14.1.4	Incorporation of Carbon Dioxide	656
1.14.1.5	Decarboxylative Heck-Type Reactions	657
1.14.2	Palladium Precursors with an Odd Formal Oxidation State	658
1.14.2.1	Chalcogenations	658
1.14.2.2	Selective Activation of Polyfunctional Substrates	659

1.14.3	Palladium Precursors with an Even Formal Oxidation State	661
1.14.3.1	Heck-Type Couplings	661
1.14.3.2	Couplings with Boron Species	662
1.14.3.3	Sequences Involving C—H Functionalizations	663
1.14.3.4	Carbonylation Reactions	665
1.14.3.5	Reactions Featuring Formal Halogen-Atom Transfers	666
1.14.3.6	Miscellaneous Reactions	668
 Keyword Index		671
 Author Index		707
 Abbreviations		731