

Catalytic Oxidation in Organic Synthesis

	Preface	V
	Volume Editor's Preface	IX
	Abstracts	XI
	Table of Contents	XXV
1	Introduction	
	K. Muñiz	1
2	General Concepts in Catalytic Oxidation	7
2.1	Photocatalytic Oxidation	
	A. G. Griesbeck, S. Sillner, and M. Kleczka	7
2.2	Catalytic Oxidations with Hypervalent Iodine	
	F. V. Singh and T. Wirth	29
2.3	Water as an Oxygen Source for Oxidation Reactions	
	P. Garrido-Barros, I. Funes-Ardoiz, P. Farràs, C. Gimbert-Suriñach, F. Maseras, and A. Llobet	63
2.4	Dehydrogenation	
	Y. Kayaki and T. Ikariya	81
2.5	Biomimetic Oxidation in Organic Synthesis	
	L. Vicens, M. Borrell, and M. Costas	113
3	Metal-Catalyzed Oxidation of Alkanes To Give Esters or Amines	
	A. Caballero, M. M. Díaz-Requejo, and P. J. Pérez	155
4	Allylic, Benzylic, and Propargylic Oxidation	
	P. Chen and G. Liu	191
5	Oxidation of Alkenes	245
5.1	Epoxidation of Alkenes	
	A. Berkessel, H. Engler, and T. M. Leuther	245
5.2	Dioxygenation of Alkenes	
	C. Martínez and K. Muñiz	309
5.3	Aminohydroxylation and Aminooxygenation of Alkenes	
	S. R. Chemler and T. Wdowik	343

5.4	Halogenation and Halocyclization of Alkenes A. Andries-Ulmer and T. Gulder	389
5.5	The Wacker Process N. J. Race, H. H. Patel, and M. S. Sigman	429
6	Sulfinyl- and Sulfonyl-Containing Directing Groups in C–H Oxidation of Arenes R. Gómez-Arrayas and N. Rodríguez	449
7	Gold-Catalyzed Oxidation of Alkynes P. Calleja, R. Dorel, and A. M. Echavarren	479
8	Oxidation of Alcohols	529
8.1	Recent Developments in Catalytic Alcohol Oxidation Using Nitroxyl Radicals L. M. Dornan, N. L. Hughes, and M. J. Muldoon	529
8.2	Enantioselective Oxidation of Alcohols B. M. Stoltz, A. C. Wright, D. C. Ebner, and N. Park	569
9	Catalytic Aerobic Oxidation of Phenols J.-P. Lumb and K. V. N. Esguerra	587
10	α-Oxidation of Carbonyl Compounds M. Uyanik and K. Ishihara	635
11	Oxidation of Amines and N-Hetarenes N. Jiao and Z. Li	671
12	Aerobic Oxidative Intermolecular Cross-Coupling and Heck Reactions F. Bellina and L. A. Perego	721
	Keyword Index	767
	Author Index	797
	Abbreviations	833

Table of Contents

1	Introduction K. Muñiz	
1	Introduction	1
2	General Concepts in Catalytic Oxidation	
2.1	Photocatalytic Oxidation A. G. Griesbeck, S. Sillner, and M. Kleczka	
2.1	Photocatalytic Oxidation	7
2.1.1	Triplet Oxygen Trapping of Photogenerated Radicals	8
2.1.1.1	Trapping of Monoradicals	9
2.1.1.1.1	Radical Addition to Alkenes To Generate Carbon Radicals	9
2.1.1.1.2	Hydrogen Abstraction To Generate Carbon Radicals	10
2.1.1.1.3	Deprotonation of Radical Cations To Generate Carbon Radicals	10
2.1.1.2	Trapping of Radical Cations	11
2.1.1.3	Trapping of Biradicals	12
2.1.2	Photochemical Superoxide Generation and Reactions	13
2.1.2.1	Aromatic Hydroxylation via Arylboronates	13
2.1.2.2	Benzylic Oxidation via Acridinium Photocatalysis	14
2.1.2.3	Benzylic Activation by Electron-Transfer-Initiated C—H Bond Cleavage and Radical Trapping with Superoxide	14
2.1.2.4	Benzylic Activation by Electron-Transfer-Initiated C—C Bond Cleavage and Radical Trapping with Superoxide	15
2.1.2.5	Benzylic Activation by Electron Transfer and Radical Cation Trapping with Superoxide	15
2.1.3	Photochemical Singlet Oxygen Generation and Reaction	17
2.1.3.1	Singlet Oxygen Ene Reactions	18
2.1.3.2	Singlet Oxygen [4 + 2]-Cycloaddition Reactions	20
2.1.3.3	Singlet Oxygen [2 + 2]-Cycloaddition Reactions	22
2.1.3.4	Singlet Oxygen Heteroatom Oxidation	23
2.1.4	Miscellaneous Photooxidation Processes	23

2.2	Catalytic Oxidations with Hypervalent Iodine F. V. Singh and T. Wirth	
2.2	Catalytic Oxidations with Hypervalent Iodine	29
2.2.1	Oxidation Reactions Using Iodoarenes as Precatalysts	29
2.2.1.1	Iodine(III)-Catalyzed Oxidation Reactions	29
2.2.1.1.1	Iodine(III)-Catalyzed Oxidation of Alcohols	29
2.2.1.1.2	Iodine(III)-Catalyzed Oxidation of Phenols	32
2.2.1.1.2.1	Iodine(III)-Catalyzed Oxidation of Phenols without Cyclization	32
2.2.1.1.2.2	Iodine(III)-Catalyzed Oxidation of Phenols with Cyclization	35
2.2.1.1.3	Iodine(III)-Catalyzed Oxidation of Alkylarenes	40
2.2.1.1.4	Iodine(III)-Catalyzed Oxidation of Alkenes and Alkynes	41
2.2.1.2	Iodine(V)-Catalyzed Oxidation Reactions	44
2.2.1.2.1	Iodine(V)-Catalyzed Oxidation of Alcohols	45
2.2.1.2.1.1	1-Hydroxy-1,2-benziodoxol-3(1 <i>H</i>)-one 1-Oxide Catalyzed Oxidation of Alcohols	45
2.2.1.2.1.2	2-Iodylbenzenesulfonic Acid Catalyzed Oxidation of Alcohols	49
2.2.1.2.1.3	Iodylbenzene-Catalyzed Oxidation of Alcohols	50
2.2.1.2.2	Iodine(V)-Catalyzed Oxidation of Phenols	53
2.2.1.2.3	Iodine(V)-Catalyzed Oxidation of Alkylarenes	54
2.2.1.3	Hypervalent Iodine Catalyzed Enantioselective Oxidation Reactions	57
2.3	Water as an Oxygen Source for Oxidation Reactions P. Garrido-Barros, I. Funes-Ardoiz, P. Farràs, C. Gimbert-Suriñach, F. Maseras, and A. Llobet	
2.3	Water as an Oxygen Source for Oxidation Reactions	63
2.3.1	Preliminary Considerations	65
2.3.2	Case Studies on the Use of Water as an Oxygen Source	67
2.3.2.1	Organic Substrate Oxidation Reactions with Water and Light Using a Manganese Porphyrin Complex as Catalyst	67
2.3.2.2	Photocatalytic Oxidation of Sulfides and Benzylic Alcohols Using Water, Oxoruthenium(IV)-Based Catalysts, and Bismuth Vanadate	70
2.3.2.3	Oxidation of Alcohols to Carboxylic Acids Using Water as the Oxygen Source: A One-Pot Process with a Ruthenium Pincer Complex	72
2.3.3	Integral Photoelectrochemical Cells	74
2.3.4	Conclusions	77

2.4	Dehydrogenation Y. Kayaki and T. Ikariya	
2.4	Dehydrogenation	81
2.4.1	Transfer Dehydrogenation of Alcohols	81
2.4.2	Aerobic Dehydrogenation of Alcohols	86
2.4.3	Acceptorless Dehydrogenation of Alcohols and Amines	88
2.4.3.1	Acceptorless Dehydrogenation of Alcohols	88
2.4.3.2	Acceptorless Dehydrogenative Coupling of Alcohols	95
2.4.3.2.1	Synthesis of Esters and Lactones	95
2.4.3.2.2	Acceptorless Dehydrogenation of Alcohols Combined with Dehydrative Condensations	97
2.4.3.3	Acceptorless Dehydrogenative Coupling of Alcohols and Amines	98
2.4.3.3.1	Synthesis of Carboxamides and Imines	98
2.4.3.3.2	Synthesis of Heterocycles	101
2.4.3.4	Acceptorless Dehydrogenation of Amines	102
2.4.4	Dehydrogenation of Alkanes	104
2.4.4.1	Dehydrogenation of Hydrocarbons	104
2.4.4.2	Dehydrogenation of Aldehydes and Ketones as Functionalized Alkanes	106
2.5	Biomimetic Oxidation in Organic Synthesis L. Vicens, M. Borrell, and M. Costas	
2.5	Biomimetic Oxidation in Organic Synthesis	113
2.5.1	P450-like Oxidations and Related Reactions	114
2.5.1.1	Metalloporphyrins as C—H Oxidation Catalysts	114
2.5.1.2	Halide and Pseudohalide Transfer with Metalloporphyrins	119
2.5.2	Non-Heme Iron-Dependent Oxygenases as Models for Oxidation Catalysts ..	125
2.5.2.1	C—H Oxidations with Non-Heme Iron Complexes	125
2.5.2.2	Iron-Catalyzed <i>syn</i> -Dihydroxylation	131
2.5.2.3	Iron-Catalyzed Asymmetric <i>cis</i> -Dihydroxylation	134
2.5.2.4	Iron-Catalyzed Epoxidation	135
2.5.2.5	Iron-Catalyzed Asymmetric Epoxidation	140
2.5.3	Copper-Catalyzed Biomimetic Oxidations	143
2.5.3.1	Selective Aliphatic C—H Oxidation with Dicopper Complexes	144
2.5.3.2	Galactose Oxidase Related Oxidations	145
2.5.3.2.1	Alcohol Oxidation with Copper Compounds and 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO) and Related Radicals	145
2.5.3.3	<i>ortho</i> -Hydroxylation of Phenols with Tyrosinase Models	148

3	Metal-Catalyzed Oxidation of Alkanes To Give Esters or Amines A. Caballero, M. M. Díaz-Requejo, and P. J. Pérez	
3	Metal-Catalyzed Oxidation of Alkanes To Give Esters or Amines	155
3.1	Metal-Catalyzed Oxidation of Alkanes to Esters Using Diazo Compounds	156
3.1.1	Seminal Studies in Carbene Transfer to C—H Bonds of Alkanes	160
3.1.2	Rhodium-Based Catalysts	160
3.1.3	Coinage-Metal-Based Catalysts	163
3.1.4	Catalysts Based on Other Metals	166
3.1.5	Methane and Gaseous Alkanes as Substrates	166
3.1.6	Asymmetric Carbene Insertion from Diazo Compounds	169
3.2	Metal-Catalyzed Oxidation of Alkanes to Amines	169
3.2.1	Alkane Conversion into Amines by Nitrene Insertion	170
3.2.1.1	Cycloalkanes as Substrates	170
3.2.1.1.1	Using Isolated Hypervalent Iodine(III) Sources	171
3.2.1.1.2	Using In Situ Generated Hypervalent Iodine(III) Sources	173
3.2.1.1.3	Using Organic Azides	175
3.2.1.2	Linear and Branched Alkanes as Substrates	178
3.2.2	Alkane Amination Reactions Involving Substitution of a Hydrogen Atom	180
3.2.2.1	Isocyanates as the Nitrogen Source	180
3.2.2.2	Azoles and Derivatives as the Nitrogen Source	181
3.2.2.3	Amines or Amides as the Nitrogen Source	182
3.3	Summary and Outlook	185
4	Allylic, Benzylic, and Propargylic Oxidation P. Chen and G. Liu	
4	Allylic, Benzylic, and Propargylic Oxidation	191
4.1	Allylic Oxidation	191
4.1.1	Allylic Oxygenation	191
4.1.1.1	Allylic Oxygenation via a Hydrogen-Atom Abstraction Process	192
4.1.1.2	Allylic Oxygenation via a Concerted Metalation–Deprotonation Process	194
4.1.1.3	Allylic Oxygenation via Other Processes	196
4.1.2	Allylic Amination	197
4.1.2.1	Allylic Amination via a Hydrogen-Atom Abstraction Process	197
4.1.2.2	Allylic Amination via a Concerted Metalation–Deprotonation Process	197
4.1.2.3	Allylic Amination Involving Nitrene Insertion	198

4.1.3	Allylic Alkylation and Arylation	198
4.1.3.1	Allylic Alkylation and Arylation via a Hydrogen-Atom Abstraction Process	198
4.1.3.2	Allylic Alkylation and Arylation via a Concerted Metalation–Deprotonation Process	199
4.1.4	Allylic Fluorination	202
4.1.4.1	Allylic Fluorination via a Hydrogen-Atom Abstraction Process	202
4.1.4.2	Allylic Fluorination via a Concerted Metalation–Deprotonation Process	203
4.1.5	Allylic Silylation	203
4.2	Benzylic Oxidation	203
4.2.1	Benzylic Oxygenation	203
4.2.1.1	Benzylic Oxygenation via a Hydrogen-Atom Abstraction Process	204
4.2.1.2	Benzylic Oxygenation via a Concerted Metalation–Deprotonation Process ...	211
4.2.1.3	Benzylic Oxygenation via an Imine–Enamine Tautomerization Process	213
4.2.2	Benzylic Amination	214
4.2.2.1	Benzylic Amination via a Hydrogen-Atom Abstraction Process	214
4.2.2.2	Benzylic Amination via a Concerted Metalation–Deprotonation Process	218
4.2.2.3	Benzylic Amination via Nitrene Insertion	220
4.2.3	Benzylic Arylation and Alkylation	225
4.2.3.1	Benzylic Arylation and Alkylation via a Hydrogen-Atom Abstraction Process .	225
4.2.3.2	Benzylic Arylation via a Concerted Metalation–Deprotonation Process	228
4.2.3.3	Benzylic Alkylation via Carbene Insertion	229
4.2.4	Benzylic Fluorination	230
4.2.4.1	Benzylic Fluorination via a Hydrogen-Atom Abstraction Process	231
4.2.4.2	Benzylic Fluorination Involving Concerted Metalation–Deprotonation C–H Activation	234
4.2.5	Benzylic Silylation	235
4.2.6	Benzylic Borylation	237
4.3	Propargylic Oxidation	239
5	Oxidation of Alkenes	
5.1	Epoxidation of Alkenes A. Berkessel, H. Engler, and T. M. Leuther	
5.1	Epoxidation of Alkenes	245
5.1.1	Epoxidation of Nonfunctionalized Alkenes	245
5.1.1.1	Enantioselective Epoxidation with Titanium-Based Catalysts	245

5.1.1.1.1	Using <i>trans</i> -Cyclohexanediamine-Derived Titanium–Salan Complexes	245
5.1.1.1.2	Using <i>cis</i> - and <i>trans</i> -Cyclohexanediamine-Derived Titanium–Salalen Complexes	248
5.1.1.2	Enantioselective Epoxidation with Iron-Based Catalysts	251
5.1.1.2.1	Using Iron–Porphyrin Complexes	251
5.1.1.2.2	Using Non-Porphyrin Iron Complexes	252
5.1.1.3	Enantioselective Epoxidation with Manganese-Based Catalysts	255
5.1.1.3.1	Using Manganese–Salen Catalysts	255
5.1.1.3.2	Using Manganese–Tetraamine (N4) Complexes	259
5.1.1.4	Enantioselective Epoxidation with Ruthenium-Based Catalysts	264
5.1.1.5	Enantioselective Epoxidation with Organocatalysts	265
5.1.1.5.1	Chiral Ketone Catalyzed Enantioselective Epoxidation	265
5.1.1.5.2	Chiral Iminium Salt Catalyzed Enantioselective Epoxidation	266
5.1.1.6	Enantioselective Epoxidation by Enzymatic Methods	267
5.1.2	Epoxidation of Allylic and Homoallylic Alcohols	273
5.1.2.1	Enantioselective Epoxidation with Titanium-Based Catalysts	273
5.1.2.2	Enantioselective Epoxidation with Zirconium- and Hafnium-Based Catalysts ..	274
5.1.2.3	Enantioselective Epoxidation with Vanadium-Based Catalysts	277
5.1.2.4	Enantioselective Epoxidation with Tungsten-Based Catalysts	278
5.1.3	Epoxidation of Acceptor-Substituted Alkenes	280
5.1.3.1	Enantioselective Epoxidation with Manganese-Based Catalysts	280
5.1.3.2	Enantioselective Epoxidation with Iron-Based Catalysts	283
5.1.3.3	Enantioselective Epoxidation with Other Metal Catalysts	288
5.1.3.4	Enantioselective Epoxidation with Polyamino Acid Catalysts	291
5.1.3.5	Enantioselective Epoxidation with Organocatalysts	292
5.1.3.5.1	Using α,α -Diaryl-L-prolinols and Related Catalysts	292
5.1.3.5.2	Using Cinchona Alkaloid Catalysts	296
5.1.3.5.3	Phase-Transfer Catalysis	300
 5.2	 Dioxygenation of Alkenes C. Martínez and K. Muñoz	
5.2	Dioxygenation of Alkenes	309
5.2.1	The Sharpless Dihydroxylation	309
5.2.1.1	Second Cycle Catalysis	322
5.2.2	Dihydroxylation of Alkenes Catalyzed by Ruthenium Oxidants	325

5.2.3	Metal-Free Dihydroxylation of Alkenes	328
5.2.3.1	Metal-Free Enantioselective Dioxygenation Mediated by Hypervalent Iodine(III)	329
5.2.4	Conclusions	339
5.3	Aminohydroxylation and Aminooxygenation of Alkenes S. R. Chemler and T. Wdowik	
5.3	Aminohydroxylation and Aminooxygenation of Alkenes	343
5.3.1	Intermolecular Aminooxygenation and Aminohydroxylation	343
5.3.1.1	Osmium-Catalyzed Intermolecular Aminohydroxylation	344
5.3.1.1.1	Osmium-Catalyzed Aminohydroxylation of Arylalkenes	345
5.3.1.1.2	Osmium-Catalyzed Aminohydroxylation of α,β -Unsaturated Esters	350
5.3.1.1.3	Osmium-Catalyzed Aminohydroxylation of Unactivated Alkenes	351
5.3.1.2	Copper-Catalyzed Intermolecular Aminooxygenation	352
5.3.1.3	Iron-Catalyzed Intermolecular Aminooxygenation	354
5.3.1.4	Rhodium-Catalyzed Intermolecular Aminooxygenation	359
5.3.1.5	Palladium-Catalyzed Intermolecular Aminoacetoxylation	361
5.3.1.6	Manganese-Catalyzed Intermolecular Hydroxyazidation	362
5.3.1.7	(Acetylamino)oxygenation of Glucals	364
5.3.2	Intramolecular Aminohydroxylation and Aminooxygenation To Form Nitrogen Heterocycles	365
5.3.2.1	Osmium-Catalyzed Intramolecular Aminohydroxylation	366
5.3.2.2	Copper-Catalyzed Intramolecular Aminooxygenation	368
5.3.2.3	Iron-Catalyzed Intramolecular Aminooxygenation	371
5.3.2.4	Rhodium-Catalyzed Intramolecular Aminooxygenation	373
5.3.2.5	Palladium-Catalyzed Intramolecular Aminooxygenation	374
5.3.2.6	Hypervalent-Iodine-Mediated Intramolecular Aminooxygenation	376
5.3.3	Intramolecular Aminooxygenation and Oxyazidation Reactions To Form Oxygen Heterocycles	381
5.3.3.1	Palladium-Catalyzed Intramolecular Aminooxygenation	381
5.3.3.2	Copper-Promoted or -Catalyzed Intramolecular Aminooxygenation and Oxyazidation	382
5.3.3.3	Metal-Free Intramolecular Aminooxygenation of Unsaturated Hydroxamic Acids	385

5.4 Halogenation and Halocyclization of Alkenes

A. Andries-Ulmer and T. Gulder

5.4	Halogenation and Halocyclization of Alkenes	389
5.4.1	Chemoselective Halofunctionalization	390
5.4.1.1	Bromocarbocyclization Catalyzed by Hypervalent Iodanes	390
5.4.1.2	Rearrangement Catalyzed by Hypervalent Iodanes	392
5.4.1.3	Organocatalytic Dihalogenation	394
5.4.2	Diastereoselective <i>syn</i> Halofunctionalization	398
5.4.2.1	<i>syn</i> Dichlorination Catalyzed by Selenium	398
5.4.3	Asymmetric Halofunctionalization	400
5.4.3.1	Chiral Ion-Pairing Catalysis	402
5.4.3.1.1	Haloetherification Catalyzed by 1,1'-Bi-2-naphthol-Derived Phosphoric Acid Derivatives	402
5.4.3.1.2	Halolactonization Catalyzed by Bifunctional 1,1'-Binaphthyl-Derived Amidines	404
5.4.3.1.3	Intermolecular Bromoamidation Catalyzed by 1,1'-Bi-2-naphthol-Derived Phosphoric Acid Derivatives	405
5.4.3.1.4	Intramolecular Halocyclization by Chiral Anion Phase-Transfer Catalysis	405
5.4.3.1.5	Bromolactonization Catalyzed by C ₃ -Symmetric Trisimidazolines	407
5.4.3.1.6	Halocyclization Catalyzed by Chiral Amino Ureas	409
5.4.3.2	Chiral Lewis Base Catalysis	412
5.4.3.2.1	Bromoaminocyclization Catalyzed by Selenium Lewis Bases	412
5.4.3.2.2	Bromoetherification of Prochiral Diols Catalyzed by Sulfur Lewis Bases	413
5.4.3.2.3	Bromooxycyclization Catalyzed by Phosphorus Lewis Bases	414
5.4.3.3	Chiral Hydrogen-Bonding Catalysis	415
5.4.3.3.1	Bromolactamization Catalyzed by Quinidine-Derived Carbamates	415
5.4.3.3.2	Desymmetrization via Bromoetherification Catalyzed by <i>O</i> -Alkyl Thiocarbamates	416
5.4.3.3.3	Bromolactonization Catalyzed by Proline-Derived <i>S</i> -Alkyl and <i>O</i> -Alkyl Thiocarbamates	417
5.4.3.3.4	Bromine-Induced Semipinacol Rearrangement Catalyzed by Dimeric Cinchona Alkaloids	418
5.4.3.3.5	Dihalogenation Catalyzed by Dimeric Alkaloids	419
5.4.3.4	Chiral Lewis Acid Catalysis	420
5.4.3.4.1	Iodocarbocyclization of Malonates Catalyzed by Titanium(IV) Lewis Acids	420
5.4.3.4.2	Dibromination of Cinnamyl Alcohols Catalyzed by Titanium(IV) Lewis Acids ..	422
5.4.3.4.3	Iodoetherification Catalyzed by Cobalt(II) Lewis Acids	423
5.4.3.4.4	Intermolecular Chloroamination Catalyzed by Scandium(III) Lewis Acids	424

5.5	The Wacker Process N. J. Race, H. H. Patel, and M. S. Sigman	
5.5	The Wacker Process	429
5.5.1	Ketone-Selective Wacker Oxidations	430
5.5.1.1	Direct Molecular Oxygen Coupled Conditions	430
5.5.1.2	Peroxide-Based Wacker Oxidations	432
5.5.1.3	Wacker Oxidation of Protected Allylic Amines	435
5.5.1.4	Wacker Oxidation of Homoallylic Alcohols	436
5.5.2	Aldehyde-Selective Wacker Oxidations	437
5.5.2.1	Wacker Oxidation of Terminal Alkenes: Unbiased Substrates	437
5.5.2.2	Wacker Oxidation of Phthalimide-Protected Allylic Amines	439
5.5.2.3	Wacker Oxidation of Allylic Esters	440
5.5.2.4	Wacker Oxidation of Styrene Derivatives	440
5.5.2.5	Wacker Oxidation of Allylic Fluorides	441
5.5.2.6	Wacker Oxidation of Sterically Hindered Terminal Alkenes	443
5.5.3	Wacker Oxidation of Internal Alkenes	445
5.5.3.1	Inductive Effects in the Wacker Oxidation of Internal Alkenes	447
6	Sulfinyl- and Sulfonyl-Containing Directing Groups in C—H Oxidation of Arenes R. Gómez-Arrayas and N. Rodríguez	
6	Sulfinyl- and Sulfonyl-Containing Directing Groups in C—H Oxidation of Arenes	449
6.1	Sulfinyl-Based Directing Groups	451
6.1.1	Aryl Sulfoxide Based Directing Groups	451
6.1.1.1	Oxidative C—H Bond Arylation of Arenes	451
6.1.1.2	Redox-Neutral C—H Bond Arylation of Arenes	453
6.1.1.3	Directed C—H Bond Alkenylation of Arenes	453
6.1.2	Removable 2-Pyridylsulfinyl Group Assisted C—H Bond Activation	456
6.1.2.1	Direct C—H Bond Alkenylation of Arenes	456
6.1.2.2	Direct C—H Bond Arylation of Arenes	457
6.1.2.2.1	Suzuki–Miyaura-Type Coupling	457
6.1.2.2.2	Dehydrogenative Arylation	458
6.1.2.3	Direct C—H Bond Alkylation of Arenes	458
6.1.2.4	C—H Acetoxylation	459

6.1.3	Sulfoxides as Chiral Directing Groups	459
6.1.3.1	Direct C—H Bond Alkenylation of Arenes	460
6.1.3.2	Other Sulfoxide-Directed Asymmetric Mild C—H Functionalization Processes ·	461
6.2	Sulfonamide-Based Directing Groups	462
6.2.1	<i>N</i> -Sulfonylaniline and <i>N</i> -Sulfonyl(arylalkyl)amine Derivatives	462
6.2.2	Arene- and Arylalkanesulfonamide Derivatives	469
6.3	Sulfone-Based Directing Groups	473
6.4	Summary and Outlook	476
 7	 Gold-Catalyzed Oxidation of Alkynes P. Calleja, R. Dorel, and A. M. Echavarren	
7	Gold-Catalyzed Oxidation of Alkynes	479
7.1	Mechanism	479
7.2	Oxidative Reactions of Alkynes	480
7.2.1	Intramolecular Oxidation of Alkynes	480
7.2.2	Intermolecular Oxidation of Alkynes	489
7.2.2.1	Intramolecular Trapping of α -Oxo Gold Carbenes	490
7.2.2.2	Intermolecular Trapping of α -Oxo Gold Carbenes	497
7.3	Oxidative Reactions of Enynes	508
7.4	Applications in Total Synthesis	520
 8	 Oxidation of Alcohols	
8.1	Recent Developments in Catalytic Alcohol Oxidation Using Nitroxyl Radicals L. M. Dornan, N. L. Hughes, and M. J. Muldoon	
8.1	Recent Developments in Catalytic Alcohol Oxidation Using Nitroxyl Radicals	529
8.1.1	Mechanistic Understanding	530
8.1.2	Oxidation of Alcohols to Aldehydes and Ketones	533
8.1.2.1	Hypochlorite and Hypervalent Iodine Based Oxidations	533
8.1.2.2	Nitroxyl Radical/ NO_x Based Systems	537
8.1.2.2.1	Anaerobic Oxidations	537
8.1.2.2.2	Aerobic Nitroxyl Radical/ NO_x Systems	539

8.1.2.3	Nitroxyl Radical/Copper Salt Systems	541
8.1.2.3.1	Copper/TEMPO Oxidation of Primary Alcohols	541
8.1.2.3.2	Copper/Nitroxyl Radical Oxidation of Secondary Alcohols	542
8.1.2.3.3	Copper/Nitroxyl Radical Oxidation of Amino Alcohols into Amino Carbonyl Compounds	544
8.1.2.3.4	Copper/Nitroxyl Radical Systems for the Selective Oxidation of Diols	546
8.1.3	Synthesis of Nitriles via Alcohol Oxidation	549
8.1.4	Oxidation of Alcohols and Amines to Imines	550
8.1.5	Oxidation of Alcohols and Amines to Amides	551
8.1.6	Oxidation of Alcohols to Carboxylic Acids	553
8.1.6.1	1-Me-AZADO Oxoammonium Salts and Sodium Chlorite	553
8.1.6.2	Oxidation of Alcohols to Carboxylic Acids Using Hypervalent Iodine as the Terminal Oxidant	556
8.1.6.3	Oxidative Cleavage of Terminal Diols to Dehomologated Carboxylic Acids ...	557
8.1.6.4	Oxidation of 1,2-Diols to α -Hydroxy Acids and Further Oxidation to α -Oxo Acids	559
8.1.7	Safety and Scalability	563
8.2	Enantioselective Oxidation of Alcohols B. M. Stoltz, A. C. Wright, D. C. Ebner, and N. Park	
8.2	Enantioselective Oxidation of Alcohols	569
8.2.1	Kinetic Resolution via Transfer Hydrogenation	570
8.2.2	Kinetic Resolution/Desymmetrization Using Molecular Oxygen as Terminal Oxidant	571
8.2.2.1	Palladium-Catalyzed Oxidative Kinetic Resolution of Secondary Alcohols	571
8.2.2.2	Ruthenium-Catalyzed Oxidative Kinetic Resolution of Secondary Alcohols ...	574
8.2.2.3	Iridium-Catalyzed Oxidative Kinetic Resolution and Desymmetrization of Alcohols	575
8.2.2.4	Iron-Catalyzed Oxidative Kinetic Resolution of Secondary Alcohols	576
8.2.2.5	Oxidative Kinetic Resolution of Hydroxy Esters and Ketones	577
8.2.3	Kinetic Resolution of Secondary Alcohols Using Nitroxyl Radical Based Systems	578
8.2.4	Kinetic Resolution of Secondary Alcohols Using Manganese–Salen Complexes	580
8.2.5	Biocatalytic Kinetic Resolution of Secondary Alcohols	582
8.2.5.1	Bacterial Kinetic Resolutions	582

9	Catalytic Aerobic Oxidation of Phenols J.-P. Lumb and K. V. N. Esguerra	
9	Catalytic Aerobic Oxidation of Phenols	587
9.1	Oxidative Dimerization of Phenols	589
9.1.1	Oxidative C—C Dimerization of Phenols to Biphenols	590
9.1.1.1	Oxidative Dimerization Using Homogeneous Catalysts	590
9.1.1.2	Oxidative Dimerization Using Heterogeneous Catalysts	594
9.1.1.3	Regioselective Cross Coupling	594
9.1.1.4	Stereoselective Cross Coupling	595
9.1.2	Oxidative C—C Dimerization and Oxidation of Phenols to Pummerer's Ketone	596
9.1.3	Oxidative C—C Dimerization and Ring Expansion	598
9.2	Oxidative Polymerization of Phenols	602
9.3	Aerobic Intramolecular Arene–Phenol Coupling	606
9.4	Oxygenation of Phenols to Quinones	609
9.4.1	Oxidation of Phenols to Benzo-1,4-quinones	610
9.4.2	Oxidation of Phenols to Benzo-1,2-quinones	618
9.5	Aerobic Nitration and Amination of Phenols	623
9.6	Catalytic Aerobic Halogenation of Phenols	626
10	α-Oxidation of Carbonyl Compounds M. Uyanik and K. Ishihara	
10	α-Oxidation of Carbonyl Compounds	635
10.1	Metal Catalysis	635
10.1.1	α -Hydroxylation	635
10.1.2	Oxidative α -C—O Coupling	639
10.1.3	Oxidative α -C—N Coupling	641
10.2	Enantioselective Organocatalysis	643
10.2.1	Phase-Transfer Catalysis	643
10.2.2	Organobase Catalysis	646
10.2.3	Chiral Ketone Catalyzed Epoxidation of Enol Esters	647
10.3	Iodine-Based Catalysis	649
10.3.1	Organoiodine(III) Catalysis	650
10.3.1.1	α -Acyloxylation	650
10.3.1.2	α -Tosyloxylation	651

10.3.2	Inorganic Iodine Catalysis	654
10.3.2.1	α -Acyloxylation	654
10.3.2.2	Oxidative Coupling of Carbonyl Compounds with Phenols	658
10.3.2.3	α -Hydroxylation	659
10.3.2.4	Oxidative α -C—N Coupling	661
10.3.2.5	Enantioselective α -Oxidative Coupling	666
11	Oxidation of Amines and N-Hetarenes N. Jiao and Z. Li	
11	Oxidation of Amines and N-Hetarenes	671
11.1	Catalytic Oxidation of Amines	671
11.1.1	Direct Oxidation of Secondary Amines to Imines	671
11.1.2	Oxidation of Primary Amines to Imines	674
11.1.3	Oxidation of Amines to Nitriles	676
11.1.4	Oxidation of Amines to Oximes	678
11.1.5	Oxidation of Amines to Nitroso Compounds	680
11.1.6	Oxidation of Amines to Nitro Compounds	680
11.1.7	Oxidation of Amines to <i>N</i> -Oxides	682
11.1.7.1	Oxidation of Tertiary Amines to <i>N</i> -Oxides	682
11.1.7.2	Oxidation of Secondary Amines to Nitrones	685
11.1.7.3	Other Oxidations on the Nitrogen Atom	687
11.1.8	Oxidation of Amines to Amides	689
11.1.8.1	Oxidation of Methylamines to Formamides	689
11.1.8.2	Oxidation of Benzylic Amines to Benzamides	689
11.1.8.3	Oxidation of Cyclic Amines to Lactams	690
11.1.8.4	Oxidation of Common Aliphatic Amines to Amides	691
11.1.9	Oxidation of Amines to Diazenes and Derivatives	692
11.1.9.1	Oxidation of Amines to Diazene Oxides or Dioxides by Hydrogen Peroxide ...	692
11.1.9.2	Aerobic Oxidation of Amines to Diazenes	693
11.1.9.3	Oxidation of Amines to Diazenes by Other Oxidants	694
11.1.10	Photocatalyzed Oxidation of Amines to Imines and Nitriles	695
11.1.11	Biochemical and Biomimetic Catalysis in Amine Oxidation	697
11.1.11.1	Biochemical Oxidation of Amines by Enzymes	697
11.1.11.2	Biomimetic Oxidation of Amines by Flavin Derivatives	698
11.1.11.3	Biomimetic Oxidation of Amines by Quinone Derivatives	701

11.2	Catalytic Oxidation of Hetarenes	702
11.2.1	Oxidation of Six-Membered Hetarenes To Give <i>N</i> -Oxides	703
11.2.2	Oxidation of Six-Membered Hetarenes To Give Pyridinones	705
11.2.3	Oxidation of Azoles	706
11.2.4	Oxidation of Pyrroles	708
11.2.5	Oxidation of Indoles	710
11.2.6	Oxidation of Purines	712
11.2.6.1	Oxidation on the Imidazole Ring of Guanines	712
11.2.6.2	Oxidation on the Pyrimidine Ring of Adenines	715
12	Aerobic Oxidative Intermolecular Cross-Coupling and Heck Reactions F. Bellina and L. A. Perego	
12	Aerobic Oxidative Intermolecular Cross-Coupling and Heck Reactions ...	721
12.1	General Mechanistic Considerations of Aerobic Oxidative Couplings	722
12.1.1	C–H Activation of Arenes and Hetarenes by Palladium(II) Complexes	723
12.1.2	Regeneration of the Palladium Catalyst by Oxidation with Molecular Oxygen	724
12.2	Aerobic Oxidative Heck Alkenylation of Arenes and Hetarenes	725
12.2.1	Aerobic Oxidative Heck Coupling in the Presence of a Co-oxidant	725
12.2.1.1	Heteropolyoxometalates of Molybdenum and Vanadium as Co-oxidant	725
12.2.1.2	Manganese(III) Salts as Co-oxidant	727
12.2.1.3	Ammonium Persulfate as Co-oxidant	728
12.2.2	Aerobic Oxidative Heck Coupling Using Transition-Metal Ligands	729
12.2.2.1	Benzoic Acid as a Ligand	729
12.2.2.2	Monoprotected Amino Acids as Ligands	730
12.2.2.3	Pyridines and Other Nitrogen Ligands	732
12.2.2.4	Thioethers as Ligands	735
12.2.3	Directing Groups for the Aerobic Oxidative Heck Alkenylation of Arenes and Hetarenes	736
12.2.3.1	Aerobic Heck Alkenylation of Arenes	736
12.2.3.2	Aerobic Heck Alkenylation of Hetarenes	739
12.3	Aerobic Oxidative Cross Coupling of Two Arenes	740
12.3.1	Aerobic Aryl–Aryl Oxidative Cross Coupling	741
12.3.1.1	Oxidative Coupling of <i>N</i> -Arylamides with Simple Arenes	741
12.3.1.2	Oxidative Coupling of Polyfluorinated Arenes with Simple Arenes	742
12.3.2	Aerobic Hetaryl–Aryl Oxidative Cross Coupling	743
12.3.2.1	Oxidative Coupling of Hetarenes with Simple Arenes	743
12.3.2.2	Oxidative Coupling of Hetarenes with Polyfluoroarenes	747

12.3.3	Aerobic Hetaryl–Hetaryl Oxidative Cross Coupling	749
12.4	Aerobic Oxidative Alkynylation of Arenes and Hetarenes	754
12.4.1	Copper-Promoted Aerobic Oxidative Alkynylation of Arenes and Hetarenes ..	754
12.4.1.1	Alkynylation of Perfluoroarenes	754
12.4.1.2	Alkynylation of Hetarenes	755
12.4.1.3	Copper-Promoted Alkynylation of Arenes and Hetarenes Using Directing Groups	757
12.4.2	Palladium-Catalyzed Aerobic Oxidative Alkynylation of Hetarenes	759
12.4.2.1	Alkynylation of Azoles	760
	Keyword Index	767
	Author Index	797
	Abbreviations	833