Contents

Lan Zhao, Man Zhao, Meng-Ge Wei, Hong-Ru Li, and Liang-Nian He
Introduction 1
Alcohols as Green Solvents 6
Hydrogenation/Reduction Reaction 6
Oxidation Reaction 8
Substitution Reaction 10
Addition Reaction 11
Cyclization Reaction 13
Coupling Reaction 18
Condensation/Ring Condensation Reaction 21
Alcohols as Green Solvents and Catalysts 28
Addition Reaction 28
Cyclization Reaction 28
Coupling Reaction 30
Condensation Reaction 30
Metathesis Reaction 35
Alcohols as Green Solvents and Hydrogen Donors 35
Miscellaneous 39
Polyethylene Glycol as a Solvent for CO ₂ Capture and Conversion 39
Polyethylene Glycol Radical-Initiated Oxidation Reactions in
Compressed Carbon Dioxide 41
Ring-Opening Reaction 43
Summary and Concluding Remarks 45
Acknowledgments 46
References 46
Recent Achievements in Organic Reactions in MeCN 51
Tongtong Xing, Guizhi Zhai, Linna Wu, Xiaofen Wang, and Zechao Wang
Introduction 51
MeCN in Transition Metal-catalyzed Reactions Without Radicals
Involved 52



vi	Contents	
	2.2.1	Transition Metal-catalyzed Addition Reactions in MeCN 52
	2.2.2	Transition Metal-catalyzed Oxidation Reactions in MeCN 56
	2.2.3	Transition Metal-catalyzed Reduction Reactions in MeCN 64
	2.2.4	Transition Metal-catalyzed Substitution Reactions in MeCN 66
	2.2.5	Transition Metal-catalyzed Cyclization Reactions in MeCN 74
	2.3	MeCN in Transition Metal-free Catalyzed Reactions Without Radicals
		Involved 80
	2.3.1	Transition Metal-free Catalyzed Cyclization Reactions in MeCN 80
	2.3.2	Transition Metal-free Catalyzed Multicomponent Reactions in
		MeCN 84
	2.3.3	Transition Metal-free Catalyzed C—X Bond Formation in MeCN 87
	2.4	MeCN in C—X Bonds Formation With Radicals Involved 90
	2.4.1	C—C, C—Si Bond Formation in MeCN 90
	2.4.2	C—N, C—P Bond Formation in MeCN 93
	2.4.3	C—O, C—S Bond Formation in MeCN 96
	2.4.4	C-Halogen Bond Formation in MeCN 98
	2.5	Conclusion 102
		References 102
	3	Recent Achievements in Organic Reactions in Bio-based Solvents 107
		Shaomin Chen, Noman Haider Tariq, and Yanlong Gu
	3.1	Introduction 107
	3.2	Glycerol 108
	3.3	Polyethylene Glycols (PEGs) 112
	3.4	2-Methyltetrahydrofuran (2-MeTHF) 114
	3.5	Cyclopentyl Methyl Ether (CPME) 117
	3.6	Organic Carbonates 120
	3.7	γ-Valerolactone (GVL) 125
	3.8	Ethyl Lactate (EL) 128
	3.9	Miscellaneous 130
	3.10	Conclusions and Outlook 131
		References 131
	4	Recent Achievements in Organic Reactions in DMSO 137
		Peng Yuan, Jia-Chen Xiang, and An-Xin Wu
	4.1	Pummerer-type Activation of DMSO 138
	4.2	Selectfluor-enabled Activation of DMSO 148
	4.3	Activation of DMSO Enabled by Single-electron Transformation 151
	4.4	Electrocatalytic Synthesis Enabled Activation of DMSO 163
	4.5	Photocatalytic Reaction Enabled Activation of DMSO 164
	4.6	DMSO Acts as the Metal Ligand 171
	4.7	Some Special Activation or Usage of DMSO 174
	4.8	Summary and Outlook 181
		References 181

5	The Use of DMC as Green Solvent in Organic Synthesis 185
	Xinxin Qi and Xiao-Feng Wu
5.1	Introduction 185
5.2	Organic Reactions in DMC 185
	References 197
6	Applications of Green Deep Eutectic Solvents (DESs) in Synthetic Transformations 199
<i>(</i> 1	Zhuan Zhang and Taoyuan Liang
6.1	Introduction 199
6.2	Cross-coupling Reactions in Deep Eutectic Solvents 201
6.2.1	C—C Bond Couplings 201
6.2.2	C—N Bond Couplings 210
6.2.3	C—O Bond Couplings 211
6.2.4	C—S Bond Couplings 212
6.3	Oxidation Reactions in Deep Eutectic Solvents 213
6.3.1	Metal-catalyzed Oxidation 213
6.3.2	Other Oxidative Processes 214
6.4	Reduction Reactions in Deep Eutectic Solvents 217
6.4.1	Metal-catalyzed Reduction 217
6.4.2	Other Catalytic Reduction 218
6.5	Cyclization Reactions in Deep Eutectic Solvents 219
6.5.1	Synthesis of Five-membered Ring 219
6.5.2	Synthesis of Six-membered Ring 220
6.6	Condensation Reactions in Deep Eutectic Solvents 221
6.6.1	DES as the Catalyst/Solvent System for Condensation 221
6.6.2	Other Catalytic System for Condensation 223
6.7	Multicomponent Reactions in Deep Eutectic Solvents 224
6.7.1	One-pot Three-component Reaction 224
6.7.2	One-pot Four-component Reaction 227
6.8	Other Organic Reactions in Deep Eutectic Solvents 228
6.8.1	Isomerization Reaction 228
6.8.2	Ring-opening Reaction 230
6.8.3	Esterification Reaction 230
6.9	Polymerization in DSEs 231
6.9.1	Anionic Polymerization of Alkenes 231
6.9.2	Glycolysis and Polyesterification 231
6.9.3	Oxidative Polymerization 232
6.9.4	Visible-light-driven RAFT Polymerization 232
6.10	Conclusion 233
	References 233
7	Recent Achievements in Organic Reactions in Ionic
	Liquids 237
	Jianxiao Li and Huanfeng Jiang
7.1	Introduction 237

riii	Contents	
•	7.2	Transition Metal-catalyzed Reactions 238
	7.2.1	Palladium-catalyzed Cascade Cyclization Reaction 239
	7.2.2	Carbonylation Reactions 248
	7.2.3	Sonogashira Coupling Reactions 252
	7.2.4	Suzuki Coupling Reactions 255
	7.2.5	Copper-catalyzed Coupling Reactions 257
	7.3	Outlook 259
		List of Abbreviations 259
		References 260
	8	Recent Achievements in Organic Reactions in Ketones and Esters 263
		Fan-Lin Zeng and Bing Yu
	8.1	Introduction 263
	8.2	Organic Reactions in Ketones 263
	8.2.1	Organic Reactions in Cyrene 263
	8.2.2	Organic Reactions in NBP 266
	8.3	Organic Reactions in Esters 268
	8.3.1	Organic Reactions in Organic Carbonates 268
	8.3.2	Organic Reactions in γ-Valerolactone 270
	8.3.3	Organic Reactions in Ethyl Lactate 273
	8.4	Conclusion 275
		References 275
	9	Recent Achievements in Organic Reactions in Polyethylene
		Glycol 279
		Zhiping Yin
	9.1	Introduction 279
	9.2	PEG in Pd-catalyzed Coupling Reactions 280
	9.2.1	Pd-catalyzed C—C, C—Si Bonds Formation in PEG 280
	9.2.2	Pd-catalyzed C—N, C—P Bond Formation in PEG 290
	9.2.3	Pd-catalyzed C—O Bond Formation in PEG 291
	9.2.4	Pd-catalyzed C—B Bond Formation in PEG 291
	9.3	PEG in Cu-catalyzed Reactions 292
	9.3.1	Cu-catalyzed C—C Bond Formation in PEG 292
	9.3.2	Cu-catalyzed C—N Bond Formation in PEG 293
	9.3.3	Cu-catalyzed C—O, C—S, and C—Se Bond Formation in PEG 296
	9.4	PEG in Ni, Ru, and Pt-catalyzed Reactions 299
	9.5	PEG in Organocatalysis Reactions 302
	9.6	PEG in Multicomponent Reactions 304
	9.7	PEG in Cyclization Reactions 306

Synthesis of Five-membered Ring Systems 306

Conclusion 309

Acknowledgments 310 References 310

Synthesis of Six and Seven-membered Ring Systems 308

9.7.1

9.7.2

9.8

10	Recent Advances in Organic Reactions Using Water as
	Solvent 317
	Chang-Sheng Wang, Qiao Sun, Guowei Wang, Wei He, Zheng Fang,
	and Kai Guo
10.1	Introduction 317
10.2	Cross-Coupling Reactions 318
10.2.1	C–C Cross-Coupling 318
10.2.2	C–N Cross-Coupling 336
10.2.3	C–S Cross-Coupling 342
10.2.4	C–P Cross-Coupling 346
10.3	C–H Functionalization 347
10.3.1	C–C Bond Formation 347
10.3.2	C–N Bond Formation 364
10.3.3	C–O Bond Formation 367
10.3.4	C–X Bond Formation 369
10.3.5	C-H Annulation/Cyclization 370
10.4	C–C Activation 374
10.5	C–O Cleavage Reactions 376
10.6	Oxidative and Reductive Reactions 377
10.6.1	Electrochemical Oxidation 377
10.6.2	Reduction and Related Reactions 379
10.7	Substitution Reactions 381
10.7.1	Nucleophilic Substitution 381
10.7.2	Electrophilic Substitution 383
10.7.3	Radical Substitution 384
10.8	Addition Reactions 386
10.8.1	Nucleophilic Addition 386
10.8.2	Alkene/Alkyne Functionalization via Radical Addition 392
10.8.3	Alkene or Alkyne Functionalization via Radical-Free Addition 396
10.8.4	Cycloaddition Reactions 399
10.9	Cyclization or Annulation Reactions 403
10.9.1	Radical-Free Cyclization/Annulation 403
10.9.2	Radical Cyclization 406
10.10	Multicomponent Reaction (MCR) 410
10.11	Domino/Tandem/Cascade Reactions 417
10.11.1	Chemo-Domino/Tandem/Cascade Reactions 417
10.11.2	Chemoenzymatic Reactions 422
10.12	Rearrangement or Insertion Reactions 425
10.12.1	Rearrangement Reactions 425
10.12.2	Carbene Insertion/Transfer Reactions 429
10.13	Amide Condensation Reactions 431
10.14	Summary and Conclusions 435
	Acknowledgments 435
	References 435