

Volume 3

Series on Chemistry, Energy and the Environment

Advanced Green Chemistry

Part 1: Greener Organic Reactions and Processes

Edited by István T Horváth • Max Malacria



Series Editors

Karl M. Kadish • Roger Guilard

 World Scientific

สำนักหอสมุดมหาวิทยาลัยเชียงใหม่



Series on Chemistry, Energy and the Environment

Advanced Green Chemistry

Part 1: Greener Organic Reactions and Processes

Edited by

István T Horváth

City University of Hong Kong, Hong Kong

Max Malacria

ICSN, France & Sorbonne Université UPMC, France



Series Editors

Karl M. Kadish

University of Houston, USA

Roger Guilard

Université de Bourgogne, France

 **World Scientific**

NEW JERSEY • LONDON • SINGAPORE • BEIJING • SHANGHAI • HONG KONG • TAIPEI • CHENNAI • TOKYO

Contents

<i>Preface</i>	v
1 Origins and Early History of Green Chemistry	1
<i>Paul T. Anastas</i>	
I. Prehistory of Green Chemistry	1
II. Personal Reflections	8
III. Early Events in Green Chemistry	11
IV. Going Forward	15
V. References	16
2 Conversion of Carbohydrates to Chemicals	19
<i>László T. Mika and Edit Cséfalvay</i>	
I. Introduction	20
II. Renewable Feedstocks	23
A. Composition and Structure of Biomass Resources	23
B. Pretreatment Processes of Biomass Resources	27
III. Platform Chemicals	31
A. Hydrogen and C ₁ Basic Chemicals	31
1. Hydrogen and Carbon Monoxide	31
2. Methanol	34
B. C ₂ and C ₄ Basic Chemicals	34
1. Ethanol	34

2. Lactic Acid	35
3. Glycerol	37
4. Succinic Acid	39
C. C ₅ and C ₆ Basic Chemicals	40
1. Furfural	40
2. Furfuryl Alcohol	42
3. 5-Hydroxymethyl-2-Furfural	45
4. Levulinic Acid	48
5. Gamma-Valerolactone	51
6. 2-Methyltetrahydrofuran	53
7. Isosorbide	54
D. Chitin-Based Chemicals	55
IV. Biomass-Based Solvents	58
A. Lactic Acid and Its Esters	58
B. Glycerol	60
C. Gamma-Valerolactone	62
V. Summary and Future Perspectives	65
VI. References	66
3 Solvation Behavior of Ionic Liquids and Their Role in the Production of Lignocellulosic Biofuels and Sustainable Chemical Feedstocks	77
<i>Coby J. Clarke, Wei-Chien Tu, Lisa Weigand, Agnieszka Brandt and Jason P. Hallett</i>	
List of Abbreviations	78
I. Introduction	81
II. Lignocellulose	83
A. Overview	83
B. Cellulose	83
C. Hemicellulose	84
D. Lignin	84
III. Ionic Liquids	85
IV. Solvent Requirements	87
A. Solvation Behavior of ILs and Biorefining Processes	87
B. IL Solvent Characteristics and Process Economics	87
C. ILs and Biorefining Separations	89

V. Solubility of Lignocellulose in ILs	89
A. IL Solubility	89
1. Cellulose	90
2. Lignin	94
3. Lignocellulose	95
B. Effect of Water	96
VI. Pretreatment and Depolymerization	97
VII. Saccharification	99
VIII. Chemical Modifications and Materials	100
A. Cellulose and Hemicellulose	100
1. Cellulosic Materials	101
2. Platform Chemicals	102
3. HMF Production from Glucose in ILs	103
4. Fructose to HMF	105
5. HMF Production from Cellulose	105
6. Xylose to Furfural	106
7. Levulinic Acid	109
8. Extraction of HMF/Furfural/LA from ILs	111
B. Lignin	113
1. Chemical Production	113
2. Depolymerization	115
3. Materials and Composites	123
IX. Conclusions	126
X. References	127
4 Aliphatic Nitro Compounds as Key Precursors for the Eco-Friendly Synthesis of Fine Chemicals under Solvent-Free Conditions	135
<i>Roberto Ballini and Alessandro Palmieri</i>	
List of Abbreviations	137
I. Introduction	137
II. Reactivity of Aliphatic Nitro Compounds (Nitroalkanes and Nitroalkenes)	138
III. Nitroaldol (Henry) Reaction under SolFC	140
A. Aza-Henry Reaction under SolFC	145

IV. Conjugate Addition of Nitroalkanes to Electron-Poor Alkenes under SolFC	151
A. Chemoselective Conjugate Addition of Nitroalkanes to Electron-Poor Alkenes Possessing Two Electron- Withdrawing Groups in α - and β -Positions, under SolFC	154
V. One-Pot Synthesis of "Fine Chemicals" by the Reaction of Nitroalkanes with Aldehydes or Electrophilic Alkenes, under SolFC	156
A. One-Pot Henry–Michael Reaction	157
B. One-Pot Synthesis of α -Nitro Ketones	157
C. One-Pot Synthesis of Allylrethrone	158
D. One-Pot Synthesis of Cyclohexanol Derivatives	159
E. One-Pot Synthesis of Isoxazoline 2-Oxide Derivatives	160
F. Three-Component Synthesis of Pyrrole Derivatives	162
G. One-Pot Synthesis of Pyrrolidines under SolFC	163
VI. Conjugate Addition of Nucleophiles to β -Nitroacrylates under SolFC	163
A. Solvent-Free, anti-Michael Addition of Methylene Derivatives to β -Nitroacrylates	164
B. Solvent-Free, Friedel–Crafts Reaction of Pyrroles with β -Nitroacrylates under SolFC	164
C. Solvent-Free, Conjugate Addition of Amines to β -Nitroacrylates	165
D. Solvent-Free, One-Pot Process for the Preparation of Highly Substituted Furans from β -Nitroacrylates	167
E. Solvent Free, One-Pot Process for the Preparation of Highly Substituted Pyrroles from β -Nitroacrylates	167
F. Solvent-Free, One-Pot Process for the Preparation of Tetrahydroquinolines and their Conversion into Quinoline-2-Carboxylate Derivatives	170
VII. Conclusions	172
VIII. Acknowledgment	172
IX. References	172

5	Green Reaction Media for Cross-Coupling Reactions: A Recent Overview and Possible Directions	177
	<i>Stefano Santoro, Eleonora Ballerini, Assunta Marrocchi, Oriana Piermatti and Luigi Vaccaro</i>	
	List of Abbreviations	178
	I. Introduction	178
	II. Mizoroki–Heck Reaction	183
	III. Suzuki–Miyaura Reaction	189
	IV. Sonogashira Reaction	195
	V. Other Cross-Coupling Reactions	197
	VI. Conclusions	200
	VII. References	201
6	<i>In Situ</i> Monitoring of the Electrochemical Surface Modification by Thin Organic Layers	205
	<i>Jörg Rappich, Guoguang Sun and Karsten Hinrichs</i>	
	List of Abbreviations	206
	I. Introduction	208
	II. <i>In Situ</i> Methods	212
	A. Cyclic Voltammetry	212
	1. Cathodic Reduction of Diazonium Ions	212
	2. Anodic Oxidation of Heterocycles	213
	B. Electrochemical Quartz Crystal Microbalance	214
	1. Faradaic Efficiency	216
	C. Visible and Near-Infrared Spectroscopic Techniques	219
	1. Photoluminescence Spectroscopy	220
	2. Surface-Enhanced Raman Backscattering Spectroscopy	225
	3. Reflection Anisotropy Spectroscopy	233
	4. <i>In Situ</i> IR Spectroscopic Techniques	236
	5. <i>In Situ</i> Infrared Spectroscopic Ellipsometry	238
	6. IR Microscopy	241
	D. Optical Constants and Anisotropy	242
	III. Vista	245
	IV. Conclusion and Perspectives	248

V. Acknowledgments	248
VI. References	249
7 Continuous Flow Technologies in the Development of "Green" Organic Reactions and Processes <i>Klaus Hellgardt and King Kuok (Mimi) Hii</i>	257
List of Abbreviations	258
I. Introduction	258
II. Development of Flow Chemistry for Organic Synthesis: Myths and Facts	259
A. Myth 1: Enhanced Mixing and Faster Reactions	261
B. Myth 2: More Compact (Small Footprint)	262
C. Myth 3: More Flexible	263
III. Homogeneous Systems	263
A. Minimizing the Inventory of Hazardous Reagents	264
B. Extending the Process Window	265
C. Short-lived Intermediates	267
IV. (Heterogeneous) Catalysis in Flow	268
V. Photochemistry	271
VI. Electrochemistry	273
VII. All Together Now: Telescoped Processes	277
VIII. But Is It Really Green?	278
IX. Conclusions and Future Challenges	281
X. References	282
<i>Index</i>	285