

## Contents

**Preface** *xi*

### **Part I Carbonyl Molecules as Reactants** 1

<b>1</b>	<b>Carbon Monoxide</b>	<b>3</b>
1.1	Hydroformylation of Alkenes and Alkynes	3
1.1.1	Co Catalysts	4
1.1.2	Rh Catalysts	5
1.1.3	Au Catalysts	7
1.1.4	Ligand-Modified Heterogeneous Catalysts	7
1.1.5	Single-Atom Catalysts	10
1.2	Hydroxy-, Alkoxy-, and Aminocarbonylation of Alkenes and Alkynes	11
1.2.1	Hydroxycarbonylation of Alkenes	11
1.2.2	Hydroxycarbonylation of Alkynes	13
1.2.3	Alkoxy carbonylation of Alkenes	14
1.2.4	Alkoxy carbonylation of Alkynes	16
1.2.5	Aminocarbonylation of Alkenes	17
1.2.6	Aminocarbonylation of Alkynes	19
1.3	The Pauson–Khand Reaction	20
1.3.1	The Catalytic Pauson–Khand Reaction	21
1.3.2	Stereoselective Pauson–Khand Reactions	23
1.3.3	Pauson–Khand Transfer Carbonylation Reactions	25
1.4	Synthesis of Acetic Acid	26
1.4.1	Process Considerations	26
1.4.2	Rhodium-Catalyzed Carbonylation	27
1.4.3	Iridium-Catalyzed Carbonylation	28
1.5	Carbonylation of C–X Bonds	30
1.5.1	Hydroxy-, Alkoxy-, and Aminocarbonylations of C–X Bonds	30
1.5.2	Reductive Carbonylations	34

1.5.3	Carbonylative Coupling Reactions with Organometallic Reagents	36
1.5.4	Carbonylative Sonogashira Reactions	41
1.5.5	Carbonylative C–H Activation Reactions	44
1.5.6	Carbonylative Heck Reactions	46
1.6	Carbonylation of Epoxides	48
1.6.1	Ring-expansion Carbonylation of Epoxides	48
1.6.2	Hydroformylation and Silylformylation of Epoxides	50
1.6.3	Alternating Copolymerization of Epoxides	50
1.6.4	Alkoxy carbonylation and Aminocarbonylation of Epoxides	51
1.7	Carbonylation of Aldehydes	52
1.7.1	Amidocarbonylations of Aldehydes	52
1.7.2	Hydroformylation and Silylformylation of Aldehydes	54
1.7.3	Hetero Pauson–Khand Reactions of Aldehydes	55
1.7.4	Reactions of Aldehydes with Acyl anions	55
1.7.5	Miscellaneous of Aldehydes	56
1.8	Oxidative Carbonylation Reaction	57
1.8.1	Oxidative Carbonylation of Alkenes	57
1.8.2	Oxidative Carbonylation of Alkynes	59
1.8.3	Oxidative Carbonylation of Organometallic Reagents	63
1.8.4	Oxidative Carbonylation of Arenes	65
1.8.5	Oxidative Carbonylation of Amines	67
1.9	Other Reactions	69
1.9.1	Reactions of Diazoalkanes with Carbon Monoxide	70
1.9.2	Reaction of C–NO <sub>2</sub> with CO	73
<b>2</b>	<b>Carbon Dioxide</b>	<b>75</b>
2.1	Synthesis of Urea Derivatives	75
2.1.1	Metal-free Catalyst Systems	75
2.1.2	Ph <sub>3</sub> SbO as Catalyst	75
2.1.3	Pd Catalyst Systems	76
2.1.4	Ionic Liquids as Catalyst	76
2.1.5	CeO <sub>2</sub> as Catalyst	77
2.2	Synthesis of Carbamate Derivatives	78
2.2.1	Ru Catalyst Systems	78
2.2.2	Sn or Ni Catalyst Systems	79
2.2.3	Zeolite as Catalyst	79
2.2.4	Other Catalyst Systems	81
2.3	Synthesis of Carboxyl Acid Derivatives	82
2.4	Cycloaddition of Epoxide with CO <sub>2</sub>	88
2.4.1	Oxides Catalysts	93
2.4.2	Zeolite Catalysts	94
2.4.3	Supported Nanoparticle and Lewis Acid Catalysts	95
2.4.4	Carbon Catalysts	98
2.4.5	Salen, Porphyrins, and Phthalocyanines Catalysts	98

- 2.4.6 Ionic Liquid Catalysts 101
- 2.4.7 Metal–Organic Framework (MOF) Catalysts 106
- 2.4.8 Bifunctional Catalysts 109
- 2.4.9 Other Catalysts 117
- 2.5 Reaction of Polyalcohols/Olefins with CO<sub>2</sub> 119
- 2.6 Formylation of Amines with CO<sub>2</sub> 121
- 2.7 Reactions of Propargyl Alcohols/Propargyl Amines with CO<sub>2</sub> 125
- 2.8 Other Reactions 127
- 2.8.1 Reactions of Aromatic Halides with CO<sub>2</sub> 127
- 2.8.2 Reactions of 2-Aminobenzonitriles with CO<sub>2</sub> 130
  
- 3 Other C<sub>1</sub> Carbonyl Molecules 133**
  - 3.1 Formaldehyde (HCHO) 133
    - 3.1.1 Carbonylation of Halides with HCHO 134
    - 3.1.2 Carbonylation of Olefins with HCHO 136
    - 3.1.3 Carbonylation of Alkynes with HCHO 142
  - 3.2 Formic Acid (HCOOH) 144
    - 3.2.1 Hydroxycarbonylation of Arenes with Formic Acid 144
    - 3.2.2 Carbonylation of Alkenes with Formic Acid 144
    - 3.2.3 Carbonylation of Alkynes with Formic Acid 148
    - 3.2.4 N-Formylation Reactions with Formic Acid 150
      - 3.2.4.1 Metal Oxides Catalysts 150
      - 3.2.4.2 Brønsted Acidic as Catalyst 151
      - 3.2.4.3 Amberlite IR-120 Resins as Catalysts 152
      - 3.2.4.4 Magnetic Catalysts 152
      - 3.2.4.5 Zeolite as Catalyst 153
      - 3.2.4.6 Ionic Liquids (ILs) as Catalyst 154
      - 3.2.4.7 Other Catalysts 156
    - 3.2.5 Carbonylation of C–X with Formic Acid 157
    - 3.2.6 Other Reactions 161
  
- 4 CO Surrogates 163**
  - 4.1 Carbonyl Metal 163
  - 4.2 Formates 165
  - 4.3 Formamides 168
  - 4.4 Formic Anhydride 169
  - 4.5 Silacarboxylic Acid 170
  - 4.6 N-Formylsaccharin 172
  - 4.7 Acyl Chloride 172
  - 4.8 In Situ Generated Carbonyl Source 174
    - 4.8.1 Methanol 174
    - 4.8.2 Glycerol 176
    - 4.8.3 Aldoses 178
    - 4.8.4 Epoxide 179
    - 4.8.5 Chloroform 181

- 4.8.5.1 Pd-catalyzed Carbonylation Reactions 182
- 4.8.5.2 Fe-Catalyzed Carbonylation Reactions 185
- 4.8.5.3 Zn-Catalyzed Carbonylation Reactions 186

## Part I References 187

## Part II Carbonyl Compounds as Catalysts 217

- 5 Acid-Catalyzed Reactions with  $-\text{CO}_2\text{H}$  219**
  - 5.1 Carboxylic Acid Molecules Catalyzed Reactions 219
    - 5.1.1 Hydrolysis/Aminolysis/Ethanolysis Reactions 219
    - 5.1.2 Mutarotation of 2,3,4,6-Tetramethyl-d-glucose (TM-G) 221
    - 5.1.3 Depolymerization of Polyoxymethylenes 221
    - 5.1.4 Elimination Reactions 221
    - 5.1.5 Hydrogen–Deuterium Exchange Reactions 222
    - 5.1.6 Reduction Reactions 222
    - 5.1.7 Decomposition of Diazodiphenylmethane 222
    - 5.1.8 Amino–Imino Tautomerism Reactions 222
    - 5.1.9 Aldol Reaction 224
    - 5.1.10 Friedel–Crafts Reaction 224
    - 5.1.11 Hydrogen Shifts Reaction 225
    - 5.1.12 Cyclization Reaction 226
    - 5.1.13 Hydroboration Reaction 229
    - 5.1.14 Trifluoromethylation Reaction 229
  - 5.2 Carbon Material–Catalyzed Reactions 230
    - 5.2.1 Reduction of Nitric Oxide 230
    - 5.2.2 Oxidative Coupling of Amines to Imines 233
    - 5.2.3 Depolymerization of Cellulose and Lignocellulose 233
    - 5.2.4 Nitrobenzene Reduction Reaction and Beckmann Rearrangement Reaction 236
    - 5.2.5 Ring-Opening Reaction of Styrene Oxide 236
- 6 Reactions via Carbonyl and Hydroxyl Groups Recycling 239**
  - 6.1 Carbon-Catalyzed Selective Oxidation Reactions 239
    - 6.1.1 Oxidative Dehydrogenation of Ethylbenzene 239
    - 6.1.2 Oxidative Dehydrogenation of *n*-Butane 242
    - 6.1.3 Oxidative Dehydrogenation of Isobutane 243
    - 6.1.4 Oxidative Dehydrogenation of Propane 245
  - 6.2 Polymer-Catalyzed Selective Oxidation Reactions 245
    - 6.2.1 Oxidative Dehydrogenation of Ethylbenzene 245
    - 6.2.2 Oxidative Dehydrogenation of Heterocyclic Compounds 246
  - 6.3 Aldehyde/Ketone-Catalyzed Borrowing-Hydrogen Reactions 247
    - 6.3.1 Dehydrative  $\beta$ -C-Alkylation Reaction of Methyl Carbinols with Alcohols 247

6.3.2	Dehydrative $\alpha$ -Alkylation Reactions of Ketones with Alcohols	248
6.3.3	Dehydrative Alkylation Reactions of Fluorenes with Alcohols	248
6.3.4	Dehydrative N-Alkylation Reactions of Amines with Alcohols	249
6.4	Carbon-Catalyzed Borrowing-Hydrogen Reactions	250

## Part II References 251

## Part III The Synthetic Applications of Carbonyl Compounds 255

<b>7</b>	<b>Synthesis of Functional Molecules</b>	<b>257</b>
7.1	Reduction of Carbonyl Compounds	257
7.1.1	Aldehydes and Ketones to Alcohol	257
7.1.2	Acids to the Alcohols and Aldehydes	259
7.1.2.1	To Alcohols	259
7.1.2.2	To Aldehydes	261
7.1.3	Ester to Alcohols and Ethers	263
7.1.3.1	To Alcohols	263
7.1.3.2	To Ethers	264
7.1.4	Amides to Amines	264
7.1.5	Clemmensen Reduction	267
7.1.6	Wolff-Kishner Reduction	268
7.2	Nucleophilic Addition Reactions of Aldehydes and Ketones	270
7.2.1	Carbon Nucleophiles	270
7.2.1.1	Grignard Reagent and Other Organometallic Reagents	270
7.2.1.2	Reformatsky Reaction	271
7.2.1.3	Benzoin Condensation	272
7.2.1.4	CN Group	272
7.2.1.5	Aromatic and Aliphatic C-H Bond	273
7.2.2	Nitrogen Nucleophiles	275
7.2.3	Oxygen Nucleophiles	277
7.2.3.1	H <sub>2</sub> O as a Nucleophile	277
7.2.3.2	ROH as a Nucleophile	277
7.3	Addition Elimination Reactions of Aldehydes and Ketones	278
7.3.1	Aldol Reaction	278
7.3.2	Perkin Reaction	278
7.3.3	Knoevenagel Condensation	280
7.4	Oxidation of Aldehydes and Ketones	281
7.4.1	Baeyer-Villiger Oxidation	281
7.4.2	To Acid	282
7.5	Wittig Reaction	285
7.6	Reductive Amination Reaction	286
7.6.1	Homogeneous Catalyst System	287
7.6.2	Heterogeneous Catalyst System	290

7.7	Hydroboration/Hydrophosponylation/Hydrosilylation/Hydroacylation of Aldehydes and Ketones	293
7.7.1	Hydroboration	293
7.7.2	Hydrophosponylation	296
7.7.3	Hydrosilylation Reactions	297
7.7.4	Hydroacylation Reactions	300
7.8	Oxidative Cross-Coupling Reaction of Aldehydes	302
7.8.1	Homogeneous Catalyst System	302
7.8.2	Heterogeneous Catalyst System	304
7.9	Reductive Coupling Reactions of Aldehydes	306
7.10	Reaction of Acids as Starting Materials	310
7.10.1	Esterification Reactions	310
7.10.2	Amidation Reactions	310
7.10.3	Decarboxylation Coupling Reactions	311
7.11	Reaction of Esters as Starting Materials	317
7.11.1	Hydrolysis Reaction	317
7.11.2	Transesterification Reaction	318
7.11.3	Aminolysis Reaction	319
7.12	Reaction of Amides as Starting Materials	320
7.12.1	Hydrolysis Reaction	320
7.12.2	Alcoholysis Reaction	320
<b>8</b>	<b>Synthesis of Functional Materials</b>	<b>323</b>
8.1	Polyamides	323
8.1.1	Aliphatic Polyamides	324
8.1.2	Aromatic Polyamides	325
8.1.3	Long-Chain Semiaromatic Polyamides	326
8.2	Phenol Formaldehyde Resins	329
8.2.1	Novolac Resins	329
8.2.2	Resole Resins	330
8.3	Polyurethanes	332
8.4	Polyesters	335
	<b>Part III References</b>	<b>339</b>
<b>9</b>	<b>Conclusion and Perspectives</b>	<b>351</b>
9.1	Conclusion	351
9.2	Perspectives	352
	<b>Index</b>	<b>355</b>