Contents

| | Preface ix |
|-------|--|
| | Acknowledgments xv |
| | Abbreviations xvii |
| 1 | Dimerization of Alkynes and Alkenes 1 |
| 1.1 | Markovnikov Dimerization of Terminal Alkynes 1 |
| 1.2 | Anti-Markovnikov (Head-to-Head) Dimerization of Terminal Alkynes 7 |
| 1.3 | Dimerization and Cross-dimerization of Terminal Alkenes 14 |
| 1.4 | Cross-dimerization of Different Alkynes or Alkynes with Alkenes 18 |
| | References 26 |
| 2 | Addition of C(sp)—H Bonds to Unsaturated Compounds 33 |
| 2.1 | Addition of Terminal Alkynes to Carbonyl Compounds 33 |
| 2.2 | Addition of Terminal Alkynes to Alkenes 36 |
| 2.3 | Addition of Terminal Alkynes to Imines 38 |
| 2.4 | Addition of Terminal Alkynes to Other Compounds 40 |
| | References 42 |
| 3 | Functionalized Alkenes from Hydrofunctionalization |
| | of Alkynes 47 |
| 3.1 | Hydroborations of Alkynes 47 |
| 3.2 | Hydrosilylation of Alkynes 52 |
| 3.3 | Hydrostannation of Alkynes 57 |
| 3.4 | Hydroamination of Alkynes 61 |
| 3.4.1 | Hydroamination of Alkynes with Primary Amines 61 |
| 3.4.2 | Hydroamination of Alkynes with Secondary Amines 63 |
| 3.4.3 | Cyclohydroamination of Alkynes 65 |
| 3.4.4 | Aminocarbonylation of Alkynes 67 |
| 3.5 | Hydrophosphination of Alkynes and Related H—P(O) Addition 69 |
| 3.5.1 | Hydrophosphination of Alkynes 70 |
| 3.5.2 | Addition of P ^V (O)—H Bond to Alkynes 72 |
| 3.6 | Hydrothiolation of Alkynes 76 |
| 3.6.1 | Markovnikov Hydrothiolation of Alkynes 77 |

| vi | Contents | |
|----|----------|--|
| | 3.6.2 | Anti-Markovnikov Hydrothiolation of Alkynes 78 |
| | 3.7 | Addition of <i>O</i> -nucleophiles to Alkynes 81 |
| | 3.7.1 | Addition of Alcohols and Phenols to Alkynes 81 |
| | 3.7.2 | Addition of Acids to Alkynes 84 |
| | | References 86 |
| | | |
| | 4 | Hydrofunctionalization of Carbon-Carbon Double Bonds 103 |
| | 4.1 | Hydroboration of Alkenes 103 |
| | 4.1.1 | Markovnikov Hydroboration of Alkenes 104 |
| | 4.1.2 | Anti-Markovnikov Hydroboration of Alkenes 104 |
| | 4.1.3 | Hydroboration of Allenes and 1,3-dienes 105 |
| | 4.1.4 | Asymmetric Hydroboration of Alkenes 106 |
| | 4.2 | Hydrosilylation of Carbon–Carbon Double Bonds 107 |
| | 4.2.1 | Markovnikov and <i>Anti</i> -Markovnikov Hydrosilylation of Alkenes 107 |
| | 4.2.2 | Hydrosilylation of Allenes 109 |
| | 4.2.3 | Hydrosilylation of 1,3-dienes 110 |
| | 4.2.4 | Asymmetric Hydrosilylation of Alkenes 110 |
| | 4.3 | Hydrostannation of Carbon–Carbon Double Bonds 111 |
| | 4.4 | Hydroamination of Carbon–Carbon Double Bonds 113 |
| | 4.4.1 | Markovnikov Hydroamination of Alkenes 113 |
| | 4.4.2 | Anti-Markovnikov Hydroamination of Alkenes 115 |
| | 4.4.3 | Hydroamination of Allenes and 1,3-dienes 116 |
| | 4.4.4 | Asymmetric Hydroamination of Alkenes 118 |
| | 4.4.5 | Nitrogen Heterocycles from Intramolecular Hydroamination of |
| | 4.5 | Alkenes 119 |
| | 4.5 | Hydrophosphination of Alkenes and Related P ^V (O)—H Addition 121 |
| | 4.6 | Hydrothiolation of Carbon–Carbon Double Bonds 125 |
| | 4.7 | Addition of <i>O</i> -nucleophiles to Alkenes 128 References 130 |
| | | References 150 |
| | 5 | Double Functionalization of Alkynes and Alkenes by Addition of Element–Element Bonds 147 |
| | 5.1 | Addition Reaction of Group 13 Element–Element Bonds 147 |
| | 5.1.1 | cis-Addition Reactions to Alkynes 147 |
| | 5.1.2 | trans-Addition Reactions to Alkynes 149 |
| | 5.1.3 | Addition Reactions to Alkenes 150 |
| | 5.1.4 | Synthesis of 1,1-diborylalkanes/Alkenes via Addition of B—B Bond 157 |
| | 5.2 | Addition Reaction of Group 14 Element–Element Bonds 153 |
| | 5.3 | Addition Reaction of Group 15 Element–Element Bond 156 |
| | 5.4 | Addition Reactions of Group 16 Element–Element Bond 159 |
| | 5.4.1 | cis-Addition Reactions to Alkynes 160 |
| | 5.4.2 | trans-Addition Reactions to Alkynes 161 |
| | 5.4.3 | Different Heteroatom Bond Addition Reactions to Alkynes 163 |
| | 5.4.4 | Addition Reactions to Alkenes 163 |

| 5.5 | Addition Reactions of Element–Element Bonds from Different Group Heteroatoms 164 |
|-------|---|
| 5.5.1 | cis-Addition Reactions to Alkynes 165 |
| 5.5.2 | trans-Addition Reactions to Alkynes 169 |
| 5.5.3 | Addition Reactions to Alkenes 172 |
| 0.0.0 | References 174 |
| | References 1/4 |
| 6 | Double Functionalization of Alkynes by Addition of |
| | Carbon–Element Bonds 183 |
| 6.1 | Addition Reactions of Carbon–Group 13 Bonds 183 |
| 6.2 | Addition Reactions of Carbon–Group 14 Bonds 185 |
| 6.2.1 | Addition Reactions of Carbon–Silicon Bonds 185 |
| 6.2.2 | Addition Reactions of Carbon–Germanium Bonds 188 |
| 6.2.3 | Addition Reactions of Carbon–Tin Bonds 189 |
| 6.3 | Addition Reactions of Carbon–Group 15 Bonds 191 |
| 6.4 | Addition Reactions of Carbon–Group 16 Bonds 195 |
| 6.4.1 | Addition Reactions of Carbon–Oxygen Bonds 195 |
| 6.4.2 | Addition Reaction of Carbon–Sulfur Bonds 198 |
| 6.4.3 | Addition Reactions of Carbon–Selenium Bonds 202 |
| 6.5 | Addition Reactions of Carbon–Halogen Bonds to Alkynes 204 |
| 6.5.1 | C(sp ³)—X Activation and Its Addition Reactions 205 |
| 6.5.2 | $C(sp^2)$ —X Activation and Its Addition Reactions 208 |
| 6.5.3 | C(sp)—X Activation and Its Addition Reactions 213 |
| 6.6 | Addition Reactions of Carbon–Carbon Single Bonds 216 |
| 6.6.1 | Addition Reactions of Strained C—C Bonds 216 |
| 6.6.2 | Addition Reactions of C—CN Bonds 218 |
| 6.6.3 | Other Carbon–Carbon Bond Cleavage and Their Addition |
| 0.0.2 | Reactions 222 |
| | References 224 |
| | |
| 7 | Carbocycles from Annulation of Alkynes and Alkenes 235 |
| 7.1 | Four-Membered Carbocycles 235 |
| 7.1.1 | Construction of Cyclobutenes 235 |
| 7.1.2 | Construction of Cyclobutanes 240 |
| 7.2 | Five-Membered Carbocycles 242 |
| 7.2.1 | Five-Membered Carbocycles by $[2+2+1]$ Cycloaddition 242 |
| 7.2.2 | Five-Membered Carbocycles by [3+2] Cycloaddition 243 |
| 7.2.3 | Intramolecular Cycloaddition of Active sp ³ C—H to Carbon–Carbon |
| | Unsaturated Bonds 248 |
| 7.2.4 | Five-Membered Carbocycles from Intramolecular Cycloaddition of |
| | Unsaturated Bonds 250 |
| 7.3 | Six-Membered Carbocycles 251 |
| 7.3.1 | Benzene Ring Formation 251 |
| 7.3.2 | Naphthalene and Polyaromatic Hydrocarbons (PAHs) Ring |
| | Formation 258 |

| viii | Contents | |
|------|----------|--|
| - | 7.3.3 | 1,3-Cyclohexadiene Ring Formation Via Cycloaddition of Alkynes 263 |
| | 7.4 | Seven-Membered Carbocycles 266 |
| | 7.5 | Eight-Membered and Larger Carbocycles 268 |
| | | References 272 |
| | 8 | Heterocycles from Cycloaddition of Alkynes 285 |
| | 8.1 | Four-membered Heterocycles 285 |
| | 8.2 | Five-membered Heterocycles 286 |
| | 8.2.1 | Pyrroles, Furans, and Thiophenes Synthesis 287 |
| | 8.2.2 | Indoles, Benzo[b]Furans, Benzo[b]Thiophenes, and |
| | 0.2.2 | Benzo[b]Selenophenes 300 |
| | 8.2.3 | Five-membered Rings with Two Heteroatoms 308 |
| | 8.3 | Six-membered Heterocycles 319 |
| | 8.3.1 | Pyridine Derivatives via Cycloaddition of Alkynes with Nitriles 320 |
| | 8.3.2 | Benzopyridine Derivatives (Quinolines and Isoquinolines) 326 |
| | 8.3.3 | 2-Pyridone Derivatives and Their Benzo-derivatives (Quinolinones and |
| | | Isoquinolonones) 330 |
| | 8.3.4 | Six-membered <i>N</i> -heterocycles Having Two Nitrogen Atoms 334 |
| | 8.3.5 | 2-Pyrone, Coumarin, Isocoumarin, and Chromone Derivatives 336 |
| | 8.4 | Other Heterocycles 341 |
| | | References 346 |
| | 9 | Carbonyl Compounds from Alkynes and Alkenes 365 |
| | 9.1 | Hydration of Alkynes 365 |
| | 9.2 | Hydroformylation of Alkynes and Alkenes 369 |
| | 9.2.1 | Hydroformylation of Alkynes 369 |
| | 9.2.2 | Hydroformylation of Alkenes 370 |
| | 9.3 | Hydroacylation of Alkynes and Alkenes 372 |
| | 9.4 | Hydroamidation of Alkynes and Alkenes 376 |
| | 9.5 | Hydrocarboxylation of Alkynes and Alkenes 378 |
| | 9.6 | Hydroesterification of Alkynes and Alkenes 379 |
| | 9.7 | Carbonylation of Alkynes and Alkenes 380 |
| | 9.7.1 | Carbonylation of Alkynes 381 |
| | 9.7.2 | Carbonylation of Alkenes 384 |
| | 9.7.3 | Cyclocarbonylation of Alkynes and/or Alkenes 384 |
| | | References 393 |
| | 10 | Natural Product Synthesis via Alkyne Transformation 407 |
| | 10.1 | Hydrofunctionalization of Alkynes in Natural Product Synthesis 407 |
| | 10.2 | Double Functionalization of Alkynes in Natural Product Synthesis 408 |
| | 10.3 | Cycloaddition of Alkynes in Natural Product Synthesis 408 |
| | 10.4 | Carbonylation of Alkynes in Natural Product Synthesis 411 |
| | | References 412 |