

## Index

### **a**

- acetals and hemiacetals
  - aldehyde hydrates 267
  - chloral hydrate 267
  - cyclohexanone hydrate 267
  - cyclopropanones 267, 268
  - definitions 267
  - formation mechanisms 268, 269
  - protecting group 268, 269
- activation energy 17
- addition reactions, carbenes
  - bicyclic olefins 172–173
  - carbene to alkene, stereospecific addition 170
  - dibromocarbene 168, 169
  - hexafluorobenzene 172, 173
  - pyrroles and indoles 172, 173
  - Simmons–Smith reactions 174, 175
  - Simmons–Smith reagent 173–174
  - singlet carbenes 168, 169
  - stereochemistry 170–171, 172
  - stereoselectivity 173
  - triplet carbenes 168, 169–170
- aldol condensation
  - aldehyde/ketone 78, 79
  - aromatic ketones 78, 79
  - Claisen condensation 78, 80
  - Dieckmann condensation 80
  - esters 78
  - fluoroacetonitrile 78, 79
  - Knoevenagel condensation 81
  - Michael reaction 81
- alkene 30
- alkyl and dialkyl carbenes 185
- allenes (cycloaddition to 1,2-dienes) 176
- allylic hydrogen 228
- amine 29–30

### antiaromatic systems

- benzo-annulation 264
- compounds 262–263
- cyclobutadiene 263
- cyclooctatetraene 264
- cyclopropene 263
- 3-cyclopropenyl anion 263
- dimerization 263–264
- energetically destabilized, conjugation 262, 264
- aryne–metal complexes 227–228
- arynes
  - 1,2-, 1,3-and 1,4-didehydrobenzenes 229–230
  - allylic hydrogen 228
  - 1-aminobenzotriazole, oxidation 235
  - benzenediazonium-2-carboxylate 232, 233–234
  - Bergman cyclization 229
  - coupled cluster (CC) 225
  - cycloaddition reactions 227, 240–243
  - density functional theory (DFT) 225
  - 1,3-dipolar cycloaddition 243–244
  - generation 230
  - and heteroarynes 225
  - isolable zwitterion 234
  - lowest unoccupied molecular orbitals (LUMOs) 227
  - *meta*-benzyne 228, 229
  - nomenclature 226
  - nucleophilic addition 237–238
  - in organic synthesis 245–246
  - *ortho*-, *meta*-and *para*-benzyne 227
  - *ortho*-benzyne 226
  - *para*-benzyne 228, 229
  - reactions 228
  - representative 226

- arynes (*contd.*)  
 – transition metals 227–228  
 – triple bond formation, regiochemistry 239–240
- b**  
 Bamford–Stevens reaction 162, 163, 185  
 Bergman cyclization 229  
 biomedical application 269, 270  
 biradicals 142–146  
 bromination, radicals reactions  
 – allylic 120  
 – benzylic 120, 121  
 – regioselective, 2-methylpropane 125–126  
 – steroid structure, testosterone acetate 120, 122  
 – Wohl–Ziegler reaction 120, 121
- c**  
 camphor tosylhydrazone 162  
 carbanions  
 – C–H bond deprotonation 70  
 – chiral carbanions 90–91  
 – C–X bond reduction 69  
 – enolate reactions, carbonyl groups. *See* enolate reactions, carbonyl groups  
 – homoallylic rearrangements. *See* homoallylic rearrangements  
 – metal reaction, alkene 70–71  
 – negative ion, carbon–carbon double/triple bonds 71  
 – reactions 77–78  
 – stability. *See* stability, carbanions  
 – structure and geometry. *See* structure and geometry, carbanions  
 – and tautomerism 91–95  
 carbene ligands, organometallic chemistry  
 – definition 188–189  
 – Dötz benzannulation 191  
 – Fischer carbenes 189, 190  
 – NHC types, representative 192  
 – Schrock carbenes 189, 190  
 – Tebbe's reagent 190  
 – triazol-5-ylidene carbene 192  
 carbene precursors 160  
 carbenes  
 – addition reactions. *See* addition reactions, carbenes  
 – bent and linear, electronic configurations 155  
 – bond angle and frontier orbitals nature 156  
 – carbenoids 165  
 – characteristics 153–154  
 – chemistry 153  
 – classification 154  
 – cycloaddition to alkynes 177  
 – cycloaddition to 1,2-diene 176  
 – cycloaddition to 1,3-diene 176–177  
 – difluorocarbene 157–158  
 – dimerization 160  
 – dimethoxycarbene, stabilization 158  
 – electron repulsion energy 156–157  
 –  $\alpha$ -elimination 163–164  
 – EPR measurements 156  
 – formation 160  
 – “intersystem crossing” 157  
 – linear 155  
 – methylene 153–160  
 – neutral conditions, formation 165–166  
 – nomenclature 154  
 – nucleophilic, ambiphilic, and electrophilic 158  
 – nucleophilic and electrophilic character 155  
 – persistent carbene 158–159  
 – rearrangement 181–182  
 – singlet carbenes 157  
 – small rings, generation 166–167  
 – substituents 157  
 – triplet methylene 156  
 carbeneoids 165  
 carbocations  
 – alcohol 29  
 – alkene 30  
 – alkyl groups 27  
 – amine 29–30  
 – bonding and solvation 23–24  
 – carbenium ions 23  
 – carbonium ions 22, 23  
 – carbonyl compounds 30  
 – cationic polymerization 50–51  
 – detection 36–37  
 – electronegative atom 28  
 – feature 37  
 – gas phase 26  
 – halide 29  
 – hyperconjugation 27  
 – hypervalent and hypovalent cations 24  
 – hypovalent and hypervalent 25  
 – intermediates 21  
 – methanonium ion 24  
 – methyl cation 26  
 – NMR spectrum 23  
 – nonclassical 51–55  
 – nucleophile 38  
 – PMO description stabilization 28  
 – proton elimination. *See* proton elimination  
 – reaction pathways 38

- rearrangements. *See* rearrangements, carbocations
- solvent effects 30–31
- sp<sup>2</sup>-hybridized model 26
- stability. *See* stability, carbocations
- structure and reactivity 21, 22
- superacids 22
- *tert* butyl cation 25
- trifluoromethoxide anion 28
- triphenylmethanol 22
- tropylum bromide 22
- carbonyl compounds 30
- catalysts 3
- cationic polymerization 50–51
- chemical reaction 3
- chemically induced dynamic nuclear polarization (CIDNP) 107
- chemistry 1–3
- chemoselectivity 7
- chlorination
  - bromination, radical-catalyzed 119
  - cyclohexane 119
  - 2,3-dimethylbutane 129
  - iso-butane and 2-methylbutane 119
- CIDNP. *See* chemically induced dynamic nuclear polarization (CIDNP)
- coupled cluster (CC) 225
- cyclic carbenes 184
- cycloaddition reactions, nitrenes
  - alkenes 209–210
  - alkynes 211–212
  - arenes 212, 213
  - 1,3-dienes 210–211

**d**

- density functional theory (DFT) 225
- diadamantylcarbene 186
- diastereoselective 6
- diazo compounds, photolysis
  - carbene precursors 160
  - diazocarbonyl compounds, decomposition 161
  - diazomethane 160–161
  - and ketene compounds, decomposition 161
- diazocarbonyl compounds, decomposition 161
- diazomethane 160–161
- Dieckmann condensations 80
- Diels–Alder reaction
  - alkenes 242, 243
  - aryne, unexpected formation 241–242
  - benzyne, diradical excited state 242
  - cycloaddition 240

- furan 240–241
- *ortho*-benzyne 240, 241, 243
- taxidione synthesis 242, 243
- difluorocarbene 157–158
- 1,2-diiodobenzene/phthalic anhydride, formation 235–236
- dimerization, carbenes 160
- dimethoxycarbene, stabilization 158
- 1,3-dipolar cycloaddition 243–244
- Dötz benzannulation 191

**e**

- electron paramagnetic resonance (EPR), radicals
  - detection 103
  - energy absorption 104, 105
  - ethyl radical. *See* ethyl radical
  - hyperfine splitting 104
  - and PMR 104
  - principle 104
  - second-derivative spectrum, methyl radical 104, 105
  - spin polarization 104, 105
- electron paramagnetic resonance (EPR) measurements 156

- electron repulsion energy 156–157
- electrophile 4
- enolate reactions, carbonyl groups
  - aldol condensation. *See* aldol condensation
  - enamines 81, 83
  - Robinson ring-forming reaction. *See* Robinson ring-forming reaction
- ethyl radical
  - hyperconjugation model 106
  - location 106

**f**

- Favorskii rearrangement 87, 88
- Fischer carbenes 189, 190
- FMO theory. *See* frontier molecular orbital (FMO) theory
- free radicals. *See* radical(s)
- frontier molecular orbital (FMO) theory 117

**h**

- halide 29
- homoallylic rearrangements
  - allylic and 86–87
  - carbanion 87
  - contraction of rings 88–89
  - Favorskii rearrangement 87, 88
  - Neber rearrangement 89
  - Sommelet–Hauser rearrangement 89
  - Wittig and Stevens rearrangements 87, 88

**i**

- insertion reactions, carbenes
  - alkylcarbenes 178
  - alkylidene carbenes 180
  - C–C bond 179
  - cyclic transition state 177
  - hydrogen abstractions 177
  - intramolecular 180
  - O–H bonds 179–180
  - single bonds 177–178
- insertion reactions, nitrenes
  - aryl nitrenes 214
  - carbamates 212
  - carbazole formation 215
  - cyclization 215
  - functionalization, cyclohexanes 214
  - H abstraction-recombination mechanism 213
  - intramolecular 214–215
  - saturated hydrocarbon 213, 214
  - selectivity 214
  - sulfonylnitrenes 215
  - “intersystem crossing” 157

**k**

- ketene reaction 182, 183
- ketenes and cumulenes
  - acylketenes 249
  - bis-imine, methylketene reaction 252
  - cycloaddition 251–252
  - difluoroketene 248
  - dimerization 251
  - diphenylketene, generation and trapping 247
  - dissociation 248
  - fluoroketene formation 247
  - $\beta$ -lactams formation 253
- ket-enol interconversion mechanism
  - acetone 92
  - acidic solution 91–92
  - benzoyl acetone 94–95
  - bicyclic and alkyl diketones 95
  - carbon–carbon double bond 92–93
  - carbonyl and ester groups 93–94
  - cyclopentane-1,2-dione 95
  - diethyl malonate 94
  - 1,3-diketones 93
  - intramolecular hydrogen bonding 94
  - resonance 94
- Knoevenagel condensation 81

**l**

- laser flash photolysis (LFP) 201
- Lewis acid-catalysis 252

linear carbenes 155

lowest unoccupied molecular orbitals (LUMOs) 227

**m**

- malonic anhydrides, thermal decomposition 250
- meta*-benzyne 228, 229
- methanonium ion 24
- methylene 153, 178, 183
- Michael reaction 81

**n**

- N*-bromosuccinimide (NBS) 120
- NBS. *See N*-bromosuccinimide (NBS)
- Neber rearrangement 89
- neuropeptide S receptors (NPSRs) 258
- N-heterocyclic carbenes (NHCs) 248–249
- nitrenes
  - alkyl and arylcarbonyl 200
  - azides and isocyanates 203
  - azides, formation 203–205
  - azides reaction 197
  - carbenes 198
  - chemical reaction, ground state 199–201
  - common derivatives 197–198
  - cycloaddition reactions. *See* cycloaddition reactions, nitrenes
  - delocalized structure, triplet phenylnitrene 201
  - donor substituents, stabilization 200
  - electronic structures 199
  - electronic/steric effects, aromatic 201–202
  - generation and trapping 198
  - generation methods 203
  - heterocycles 206–207
  - insertion reactions. *See* insertion reactions, nitrenes
  - IR spectroscopy 200
  - isocyanates 205
  - isomerization and hydrogen shifts 197
  - LFP 201
  - molecular entities 197
  - nucleophiles. *See* nucleophiles
  - nucleophilic reagents, aryl 197
  - organic reaction mechanisms 202–203
  - *ortho*-tolyl-nitrene 201
  - oxidation, amines 208
  - phenylnitrene 200
  - photoaffinity labeling, aryl azides 202
  - precursors 204
  - reactive intermediates 197
  - rearrangement. *See* rearrangements, aromatic and heteroaromatic nitrenes

- reduction, nitro and nitroso compounds 207–208
- singlet and triplet states 198–200
- small rings 206
- thermolysis, azides 199
- thermolysis, sulfinylamines 208
- UV and ESR spectra 200
- ylides 205–206
- n**itrogen 17
- N-nitrosoureas, base reaction 161–162
- nonclassical carbocations
  - alkyl chloride 55, 56
  - aryl participation 55, 56
  - bicyclobutonium ions 54
  - C<sub>6</sub>–C<sub>1</sub> bond 52
  - cyclopropylmethyl 53
  - *exo*-and *endo*-norbornyl brosylates 52, 53
  - methoxy group 54, 55
  - neopentyl chloride 55, 56
  - NMR spectroscopy 52
  - 2-norbornyl cation 51–53
  - π bond 54
  - *syn*-isomer 54
  - tetramethylene chlorohydrin 55, 56
  - *trans*-2-hydroxycyclopentyl arene sulfonates 55
- nucleophiles
  - alkene, formaldehyde 38, 40
  - amine formation 218
  - carbenes reactions 187–188
  - definition 4
  - DMSO, stable sulfoximides 218, 219
  - ionization mechanism 38, 39
  - nitrene reactions 218
  - nucleophilicity 4
  - reduction reaction, azido-NBD 219
  - sulfonimidamides 219–220

**o**

- organic structures 15
- ortho*-benzyne
  - aryne–metal complexes 227–228
  - *cine* substitution 232
  - cycloaddition reactions 227
  - Diels–Alder reaction 240, 241, 243
  - 1,2-diiodobenzene/phthalic anhydride, formation 235–236
  - lithiation 231–232
  - nucleophilic addition 237–238
  - *ortho*-dihaloaromatics 230, 231
  - representation 227
  - ring fragmentation reactions 234–235
  - structure 226, 227

- trimethylsilyl, fluoride displacement 232, 233
- ortho*-quinone methides (*o*-QMs)
  - alkenes, reactivity 257
  - charged zwitterions and biradical 254–255
  - *in situ* formation 253
  - forms 253–254
  - intermediate 258, 260
  - intermolecular Michael-type hydroarylation 257, 258
  - metal-catalyzed generation 255
  - neuropeptide S receptors (NPSRs) 258
  - photochemical and thermal generation 255, 256
  - reaction with reagent 259
  - *trans*-2,3-dihydrobenzofurans 256, 257

**p**

- para*-benzyne 228, 229
- persistent carbene 158–159
- perturbational molecular orbital (PMO) 106
- photochemical generation 250–251
- PMO. *See* perturbational molecular orbital (PMO)
- product selectivity
  - chemoselectivity 7
  - diastereoselective 6
  - regioselectivity 6
  - stereoconvergence 6
  - stereoselectivity 6
  - stereospecificity 6–7
- proton elimination
  - alkenes 38, 41
  - carbocation 38, 40
  - sodium hydroxide 27–38, 41

**r**

- radical(s)
  - benzene oxidation, Fenton’s reagent 113
  - biradicals 142–146
  - carbon atoms 101
  - characteristics 103
  - CIDNP 107
  - common 101, 102
  - electrophilic 114
  - EPR spectroscopy. *See* electron paramagnetic resonance (EPR), radicals
  - equilibrium, hexaphenylethane and triphenylmethyl radical 101, 102
  - ferrous ions 113–114
  - formation 111
  - free energy *versus* reaction 101
  - halogens 112
  - heterolysis 111

- radical(s) (*contd.*)
  - homolysis 111
  - intermediate 101
  - metal alkyl decomposition 102
  - methyl 101
  - new carbon-centered 113
  - nitrogen-centered/oxygen-centered 101
  - nomenclature systems 154
  - nucleophilic 114
  - organometallic compounds, homolysis 112
  - paramagnetic 103
  - photolytic generation 112
  - PMO 106
  - reactions. *See* reactions, radicals
  - reactions, advantages 103
  - reactions, disadvantages 103
  - single-electron transfer processes 112
  - stability 114–116
  - structure and bonding. *See* structure and bonding, radicals
  - trapping, nitroso compounds 107
  - triphenylmethyl. *See* triphenylmethyl radicals
- radical cations
  - alkyl groups 58–59
  - analytical tools 57
  - description 55, 57
  - electron ionization 59
  - electron oxidation 57, 58
  - ethene 58
  - hyperconjugation 58
  - organic compounds 57
  - organic radical cations 57
  - reagents 58
  - weak acids 59–60
- reactant/substrate 3
- reaction
  - conditions 3
  - factors 7–640. *See also* reaction, influencing factors
  - intermediates 7
  - mechanism and arrows 4–5
  - product selectivity 6–7
  - properties and characteristics 5–6
  - rates 7
  - reactants and reagents 6
- reaction, influencing factors
  - bonding and steric 8
  - chemical reaction 11
  - collisions 10
  - electron-deficient species 14
  - electronic effects 8
  - endergonic reaction 12
  - energetics 7–8
  - entropy 12–13
  - exergonic reaction 12
  - inductive effect 8
  - intermediates 11
  - kinetic and product-trapping studies 14–15
  - kinetic control 12
  - molecules 9
  - organic reactions 9
  - rate-limiting step 10
  - reactive intermediates 9–10, 14
  - resonance effect 8
  - solvent effects 8–9
  - speeding reactions 10–11
  - spontaneous reaction 13
  - stereoelectronic effects 8
  - steric effects 8
  - thermodynamic control 12
  - thermodynamic product 12
- reactions, radicals
  - addition–elimination 128
  - alcohols 122
  - anti-Markovnikov addition 124, 125
  - bromination. *See* bromination, radicals reactions
  - carboxylic acid chloride 126
  - CCl<sub>4</sub> addition, propylene 124, 125
  - chain reaction steps 117, 118
  - characteristics 117
  - chlorination. *See* chlorination
  - coupling 123, 124
  - coupling, aromatic rings 128, 129
  - cycloalkanes 120–122
  - cyclopropane 122
  - ΔH<sup>0</sup> values 124, 125
  - dimerization 127
  - disproportionation 127, 128
  - FMO theory 117
  - halogens 118
  - Hunsdiecker 129, 130
  - intermediates 116
  - Kolbe synthesis 129, 130
  - methane, photochemical chlorination 129
  - methyl chloroformate, photochemical perchlorination 118–119
  - migrations, chloro group 127
  - NBS 120
  - nucleophilic/electrophilic 117
  - oxidation, 2,6-di-*tert*-butylphenol 123, 124
  - oxidative coupling, 1-naphthol 130–131
  - pinacol 123, 124
  - polymerization 126
  - rearrangement 126–127

- Simonini 130
  - spin trapping 128
  - spin-paired molecule 116–117
  - stereochemistry. *See* stereochemistry, radical reactions
  - stereoselective synthesis 126, 131
  - substitutions 129
  - termination steps 127
  - trapping 122–123
  - trialkyltin hydride with halide 123
  - Ullmann reaction 129
  - reactive intermediates 246–247
  - reagent 3
  - rearrangements, aromatic and heteroaromatic nitrenes
    - conversion, aromatic amides 217–218
    - Curtius 216–217
    - Hofmann 217
    - initiation 216
    - Lossen 218
    - 1,2-shift 216
    - stereochemical configuration 216
    - thermal reaction 216
  - rearrangements, carbocations
    - acetylenic alcohols 49, 50
    - alcohol 43–44
    - alicyclic systems 43, 44
    - alkyl groups 47
    - 2-bromo-2-methylbutane 45
    - carbenium ion formation 46–47
    - carbon–silicon bond 45
    - carboxonium ion 45, 46
    - chloronium ion 49
    - cyclic systems 43
    - dienone 47, 48
    - electrophilic addition 48–49
    - glycols 46
    - hydride 47, 48
    - hydrogen 44
    - isopropyl cation 43
    - methyl group 40, 41
    - migratory aptitude 42
    - *n*-butyl and *sec*-butyl carbenium ion 39–40
    - protons equilibration 42
    - regioselectivity 49, 50
    - *sec*-butyl cation 43
    - shifts 40, 42
    - Wagner–Meerwein shift 43, 45, 46
  - regioselectivity 6
  - Reimer–Tiemann reaction 188
  - Robinson ring-forming reaction
  - $\alpha, \beta$ -unsaturated ketone 81, 82
  - $\beta$ -halocarbonyl compounds 85–86
  - bicyclo[2.2.2]octan-2,6-dione 86
  - carbanion oxidation 85
  - carboxylic acid 82, 84
  - E1cB reactions 85
  - Hofmann elimination 86
  - Kolbe–Schmidt reaction 84
  - nucleophile 82, 84
  - proton donors 82
  - ylide 86
- s**
- Schrock carbenes 189, 190
  - Shapiro reaction 163
  - silyl-substituted ferrocenyl-ketene 249
  - Simmons–Smith reactions 174, 175
  - Simmons–Smith reagent 173–174
  - singlet carbenes 157, 168, 169
  - Sommelet–Hauser rearrangement 89
  - stability, carbanions
    - adjacent heteroatoms 73–74
    - alkyl substitution 72
    - allylic and benzylic anions 73
    - anion 72
    - aromatization 74
    - cyanide and metallocenes 76
    - cyclopentadienyl anion 76
    - enolate 72
    - fluorine atoms alpha 75–76
    - halogens 76
    - kinetic and thermodynamic carbanions 75
    - kinetic anion 75
    - metal alkyls 72–73
    - negative hyperconjugation 74, 75
    - nonadjacent  $\pi$  bond 74
    - nucleophile 72
    - structural features 73
    - sulfur/phosphorus 73
  - stability, carbocations
    - allyl cation 34
    - benzylic cations 34
    - carbenium ions 27, 36
    - classification 32
    - conjugation and aromatization 35
    - hyperconjugation 32
    - “ionizing solvents” 33
    - measurement 31
    - methoxymethyl cation 35
    - organic chemistry 31
    - pi bonds 34
    - planar geometry 36
    - quantitative terms 32–33
    - structural factors 32
  - Stability, radicals 114–116
  - stable aryl(trialkylsilyl) ketene 249

- Stereochemistry, radical reactions
- (*R*)- and (*S*)-enantiomers formations 132
  - acyclic 133–134
  - addition 134, 135
  - bridged radical analogous, bromonium ion 134, 135
  - chemoselective 134, 136
  - cyclization 136–142
  - deuterium bromide 134
  - diastereomers formations 132–133
  - formation, racemic mixture 131–132
  - hydrogen 136
  - non-stereospecific products 135
  - $\pi$ -complex formation, olefin and HBr 134
  - regioselective substitution, chlorine 134, 135
  - stereoselectivity 131–132
- stereoconvergence 6
- stereoselectivity 6
- stereospecificity 6–7
- strained bridgehead alkene 186, 187
- structure and bonding, radicals
- 1-adamantyl and 7-norbornyl formation 110, 111
  - captodative 108
  - carbenium carbon atom, bridgeheads 110
  - cyclic 108
  - geometries calculation, fluoromethyl radicals 109
  - loss of optical activity 108–109
  - methyl radical 109
  - nonplanar nature 109
  - planar and pyramidal 107, 108
  - $\pi$ -radicals 108
  - pyramidalization, ethyl 110
  - vinylic and aromatic 108
- structure and geometry, carbanions
- alkyls 68
  - carbon–metal bonds 68
  - cyano-2,2-diphenylcyclopropane 68–69
  - cyclopropyl carbanion 68
  - electron delocalization 66, 67
  - enols 69
  - inversion of carbanions 66
  - *n*-butyllithium 67
  - $\alpha$ -nitrile carbanions 69
  - rate of inversion 66
  - reactions 65
  - sp<sup>3</sup>-hybridized methanide anion 65, 66
  - tetrahedron 65
  - VSEPR 66
- t**
- tautomerism
- keto-enol interconversion mechanism. *See* keto-enol interconversion mechanism
  - ketone and an enol 91
- Tebb's reagent 190
- tetrahedral intermediates
- carbinol formation 267
  - carbonyl compounds, nucleophilic substitution 265
  - definition 264–265
  - nucleophilic attack 266
  - products formation 265, 266
  - X-ray crystal structures 266–267
- tosylhydrazone
- Bamford–Stevens reaction 162, 163
  - base-catalyzed elimination 162
  - camphor 162
  - Shapiro reaction 163
- trans*-2,3-dihydrobenzofurans 256, 257
- trans*-selective [2+2] cycloaddition 251
- triazol-5-ylidene carbene 192
- trimethylsilyl, fluoride displacement 232, 233
- triphenylmethyl radicals
- reactions 102, 103
  - structure 102
- triple bond formation, regiochemistry 239–240
- triplet carbenes 168, 169–170
- triplet methylene 156
- tropylium bromide 22
- v**
- valence shell electron pair repulsion (VSEPR) 66
- VSEPR. *See* Valence shell electron pair repulsion (VSEPR)
- w**
- Weinreb amides 269
- Wittig and Stevens rearrangements 87, 88
- Wolff rearrangement
- alkyl and dialkyl carbenes 185
  - Bamford–Stevens reaction 185
  - cyclic carbenes 184
  - cyclohexene 184
  - diadamantylcarbene 186
  - dichlorocarbene 184
  - ketene reaction 182, 183
  - mechanism 182, 183
  - ring contraction 183, 184
  - singlet carbene to alkene 185
  - strained bridgehead alkene 186, 187

**z**

ZrO<sub>2</sub>-promoted Ni catalysis 249–250  
zwitterions and dipoles  
– crystalline amino acids 260  
– definition 258  
– dipolar compound 261

– dipolar species 261–262  
– electrostatic interaction 260  
– furan derivatives formation 262  
– glycine 261  
– naturally occurring amino acids 260–261

