

Index

• Numerics •

- 1,1,2,2,3,3,4,4-octamethylcyclobutane, 108, 113
- 1,2-addition reactions, 223–228, 236
- 1,2-dimethyl-1-cyclohexanol, 209
- 1,2-hexanediol, 210
- 1,3,5,7-cyclooctatetraene, 139, 157, 247, 256
- 1,3-cyclobutadiene, 246
- 1,3-cyclopentadienyl anion, 246, 255
- 1,3-cyclopentadienyl cation, 246, 255
- 1,4-addition reactions, 223–228, 236, 237
- 1-butylcyclopentane, 104
- 1-chloro-3,3-dimethyl-1-pentyne, 166
- 1-cyclohexanol, 209
- 1-cyclohexene, 138, 155
- 1-cyclopentanol, 209, 218
- 1-cyclopentene, 154
- 1-cyclopropyl-1,3-diethylcyclooctane, 107, 112
- 1H peak, 301
- 1-pentene, 137, 154
- 1-pentyne, 166
- 1s orbitals, 16
- 1-t-butylcyclohexane, 105, 110
- 2,2-dimethyl-3-hexyne, 167, 180
- 2,3-dimethylhexane, 104, 109
- 2,4,6-nonatriene, 156–157
- 2-butanol, 210, 218–219
- 2-chloropropane, 272, 276
- 2E,4E,6E-2,4,6-nonatriene, 156–157
- 2-ethyl-1-pentene, 138, 154
- 2H peak, 301, 303, 317–318
- 2-heptene, 154–155
- 2-hexanone, 268
- 2-hexene, 137
- 2-methyl-1-penten-3-yne, 167, 180
- 2-methylhexane, 265–266
- 2-methylpentane, 267, 274
- 2-octanol, 209, 218
- 2-pentyne, 280
- 2-propanol, 281, 290
- 2R-1,2-hexanediol, 210, 219
- 2-t-butyl-1,1-dimethylcyclohexane, 107
- 3,3-dichloro-1-methyl-1-cyclohexene, 138, 155
- 3,3-dimethyl-1-cyclooctyne, 167, 180
- 3,3-dimethyl-1-cyclopentene, 138, 154
- 3,5-nonadiene, 155–156
- 3,6-dimethyl-5-propylnonane, 105, 111–113
- 3-D models
 - chiral centers, 79–82
 - Fischer projections, 86–88
 - meso compounds, 89–91
 - R and S configurations, 83–85
 - stereoisomers, 89–91
 - substituent priorities, 79–82
- 3-dimethyl-5-propylnonane, 111
- 3H peak, 301, 303
- 3-heptanol, 208
- 3-isopropyl-2,2,4-trimethylhexane, 107, 111
- 3-methylpentane, 267, 274
- 3-t-butyl-2-cyclopropyl-1-cyclopentanol, 209, 218
- 4,5-diethyl-3-methyl-2-octanol, 209, 218
- 4-cyclobutyl-2-pentyne, 166
- 4-ethyl-2-methylheptane, 103
- 4H peak, 301
- 4-isopropyl-3,4-dimethyloctane, 106
- 4-isopropyl-3-heptanol, 208
- 4-isopropyl-3-methylheptane, 109–110
- 4-methyl-5-propyldecane, 105, 110
- 4n + 2 rule, 242–243, 254–255
- 4-sec-butyl-5-cyclopentylnonane, 108, 112–113
- 6H peak, 301
- 9H peak, 301

• A •

- absorbances, 277–278
- acetaldehyde, IR spectrum of, 289, 291
- acetic acid
 - IR spectra, 289, 291
 - pKa value of, 75
- acetone
 - IR spectra, 289, 291
 - mass spectrum, 276
- acetylene
 - in multistep synthesis, 179
 - orbital diagram, 16

- acetylide ions, 175–177, 185
- achiral molecules, 89, 99
- acid-base equilibrium, 69–70, 75–76
- acid-base reactions
 - answer key, 71–76
 - Bronsted-Lowry, 60–61
 - Lewis, 62–63
 - organic molecules, 63–68
 - pKa values, 69–70
- acids
 - Bronsted-Lowry, 59–61
 - comparing, 63–64
 - conjugate, 60
 - and conjugate bases, 63–65, 72
 - defined, 59–60
 - electronegativity effects, 66–67, 73
 - Lewis, 60, 62–63
 - pKa values, 69–70
 - resonance effects, 67–68, 74
 - strength, 64–65
- acylation, 248, 258
- addition reactions
 - alkenes, 143–150
 - alkynes, 168–175
 - conjugated dienes, 223–228, 236–237
 - halogens, 143–146
 - hydrogen, 170–172
 - hydrohalic acids, 170–172, 223–228
 - water, 147–150, 172–175
- alcohols
 - answer key, 218–222
 - defined, 207
 - IR absorption, 278–279, 291
 - nomenclature, 207–210
 - oxidation reactions, 215–217, 221
 - parent chain, 208–209
 - primary, 211–217, 220–221
 - reactions, 215–217, 221–222
 - secondary, 211, 215–217
 - stereochemistry, 208
 - substituents, 208
 - synthesis of, 210–214
 - tertiary, 215–217, 221
- aldehydes
 - formation of, 184, 220–221
 - fragments, 301
 - IR spectrum, 278, 290–291, 303
 - reduction reactions, 210–211
- alkanes
 - answer key, 109–113
 - conformational stability, 119–121
 - cycloalkanes, 103
 - defined, 101
 - drawing structures of, 106–108
 - eclipsed conformation, 117
 - IR absorption, 291
 - Newman projections, 115–118
 - nomenclature, 101–105
 - parent chain, 101–102, 136
 - staggered conformation, 117
 - structures, 106–108
 - substituents, 102
- alkenes
 - addition of water, 147–150
 - answer key, 154–164
 - carbocation rearrangements, 151–153
 - halogenation reactions, 143–146
 - hydroboration reactions, 212
 - hydrogenation reactions, 143–146
 - hydrohalic acids, addition of, 140–143
 - IR absorption, 278, 284–285, 287
 - Markovnikov addition, 140–143, 158–159
 - nomenclature, 135–139, 154–158
 - parent chain, 136
 - rate of reaction, 142, 159
 - stereochemistry, 136
 - substituents, 136
 - trans*, 168–169, 181
- alkoxide, 215–216, 222
- alkyl halides
 - answer key, 201–206
 - elimination reactions, 194–196
 - reaction with magnesium metal, 211–212
 - substitution reactions, 189–193, 201–202
- alkyl shift, 151, 163
- alkyl substituents, 249, 260
- alkylation, 248
- alkynes
 - answer key, 180–186
 - creating, 175–177
 - defined, 165
 - halogenation reactions, 170–172
 - hydrogenation reactions, 168–169
 - hydrohalic acid addition reactions, 170–172
 - internal, 175–177
 - IR spectra, 278, 280

multistep synthesis, 178–179
nomenclature, 165–167
parent chain, 165–166
reduction reactions, 168–169
substituents, 166
terminal, 175–177
water-addition reactions, 172–174
allene, 17, 22
all-trans-2,4,6-nonatriene, 139, 156–157
alpha cleavage, 276
alternating double bonds, 47–48
aluminum trichloride, 71–72
amines, IR spectra of, 278, 290
ammonia, 64, 72
angles, of bonds, 14–15
anions, 72
[10]-annulene, 245, 255
anti conformation, 119
anti-aromatic rings, 242–245, 254–255
anti-Markovnikov addition. *See also*
 Markovnikov addition
 adding water to alkenes, 147–150, 162
 adding water to alkynes, 172–174, 184
 alcohol synthesis, 212–213
 hydroboration reaction, 219
antiperiplanar geometry, 194–195, 203, 205
aprotic solvents, 202, 206
aromatic compounds
 answer key, 254–260
 chemical shifts, 300, 312
 defined, 241
 IR absorption, 278, 287–288, 291
 meta directors, 248–251
 molecular orbital diagram, 245–247
 ortho-para directors, 248–251
 polysubstituted, multistep synthesis of,
 251–254, 258–260
 reactions of, 247–251
 ring aromaticity, 242–245
arrow-pushing
 Bronsted-Lowry acids/bases, 60–61
 deprotonation, 61
 Diels-Alder reaction, 229
 double bonds, 45–46
 halogenation reactions to alkynes, 170–171
 hydrohalic acid addition to alkynes, 170–171
 Lewis acids/bases, 62–63
 lone pairs, 43–44

lone pairs next to double or triple bonds,
 43–44
multiple resonance structures, 49–50
pi electrons onto electronegative atoms,
 45–46
ring systems with alternating double bonds,
 47–48
triple bonds, 45–46
aryl substituents, 248–249
atoms
 connectivity, 7
 electronegativity difference, 10–11
 formal charges, 23–25
 hybridization of, 14–16
 in Lewis structures, 7–9
 lone pairs, 25–26
 octet, 8
 in resonance structures, 39
 sizes and acidity, 63–64
Aufbau principle, 245
axial bonds, 123
axial hydrogens, 123
azide, 179, 190, 204

• B •

backside attack, 144, 160, 204
baking soda, 59
base peak, 265
bases
 acid-base equilibria, 69–70
 Bronsted-Lowry, 59–61
 conjugate, 60, 63–65
 defined, 59–60
 Lewis, 60, 62–63
 resonance effects, 67–68
benzene
 chemical shift, 300, 312
 disubstituted, 247–248
 molecular orbital diagram of, 246
 polysubstitution reactions, 251–253
 resonance structure, 47
bicyclic products, 229–230, 237
bonds. *See also* resonance structures
 angles, 14–15
 covalent, 10
 dipole moments, 12–13
 dipoles, 11–12
 ionic bond, 10
 line-bond structures, 29–32

bonds (*continued*)

- Newman projections, 115–118
 - orbital diagrams, 15–17
 - polar covalent, 10
 - types, 10–11
- borane
- addition to alkanes, 147–150, 162
 - addition to alkynes, 172–173, 179
 - as Lewis acid, 62
- boron
- electronegativity, 18
 - formal charges, 33
 - hydroboration reaction, 149
- bromides, 170–172
- bromination, 182, 248
- bromine
- addition to alkanes, 143–146
 - addition to alkynes, 170–171
 - addition to double bonds, 160–161
 - chiral centers, 83–84
 - electronegativity, 73
 - isotopes, 271, 275
 - Markovnikov addition, 141–142
 - ortho-para director, 259
 - reaction with aromatic compounds, 248, 250
- bromoethane, 272
- bromohydrin, 161
- bromonium ion, 144–145, 160–161, 170–172, 183–184
- Bronsted-Lowry acids, 59–61, 71
- Bronsted-Lowry bases, 59–61, 71
- butane
- highest-energy conformation, 120, 129
 - lowest-energy conformation, 120
 - Newman projections, 118, 127–128
 - substituent name, 102
- 2-butanol, 210, 218–219
- butanone, 283, 290
- butene, 136
- butenone, 283, 290
- butyl substituent, 102, 104
- 2-t-butyl-1,1-dimethylcyclohexane, 107
- 3-t-butyl-2-cyclopropyl-1-cyclopentanol, 209, 218
- cis*-1-t-butyl-4-methylcyclohexane, 126, 134
- 1-t-butylcyclohexane, 105, 110
- 1-butylcyclopentane, 104

• C •

- ¹³C NMR spectrum, 294–296, 299, 311–312
 - C=N double bond, formation of, 44, 54, 57
 - C=O double bond, formation of, 44–45, 54–55
 - C₁₀H₁₄, structure of, 304, 313–314
 - C₃H₇Br, structure of, 308, 316
 - C₄H₁₀O, structure of, 305, 314
 - C₄H₈O₂, structure of, 302–303
 - C₄H₉Cl, structure of, 304, 313
 - C₈H₇OCl, structure of, 306, 314–315
 - C₉H₁₀O, structure of, 307, 316
 - Cahn-Ingold-Prelog rules, 80–81, 156
- carbocations
- defined, 40
 - intermediate, 224
 - Markovnikov addition, 140–143
 - mass spectrum, 264
 - primary, 140–142, 151, 192, 201–202
 - rearrangements, 151–153, 163–164
 - ring expansions, 151–152
 - secondary, 140–142, 151, 201
 - stability of, 141, 151, 153, 159, 163, 192, 201
 - tertiary, 140–142, 151, 201–202
- carbon
- chiral center, 80
 - electronegativity, 19
 - formal charges, 33
 - hybridization, 20–22
 - valence electrons, 8, 18
- carbon dioxide, 12
- carbon NMR, 293–296
- carbonate ion, 7–8
- carbonyl compound
- condensed structures, 27
 - formation of, 173–174, 183–184
 - Grignard reactions, 211–212, 221
 - IR spectrum, 278–279, 281, 284–285, 290, 303
 - mass spectrum, 276
 - meta director, 256
 - rearrangements, 264
- carboxylic acids
- formation of, 215, 221
 - IR spectrum, 278, 286, 290, 291
 - polysubstitution reactions, 252
 - reduction reactions, 211, 213, 220
- catalysts, 161, 168–169, 181

- cations
 defined, 40
 radical, 263
 in resonance structures, 40–42, 49
 secondary, 141
 tertiary, 141
- C-C bond, 13, 19, 41, 43
- C-Cl bond, 13, 19
- central atoms, 7–8, 18–19
- C-H bond
 bond dipoles, 13
 IR absorption, 279
 line-bond structures, 29–32
 orbital diagrams, 16
- CH groups, 301
- CH₂ clusters, 27
- CH₃(CH₂)₆Br, structure of, 28, 35
- CH₃CH₂CH₂Cl, 309, 317
- CH₃NH₂, 71
- CH₃OCH₃, structure of, 28, 35
- chair conformations. *See also* conformations
 of chlorocyclohexane, 124, 130
 for disubstituted cyclohexane, 124, 131
 of methylcyclohexane, 124
 ring flip, 123
 stabilities of, 125–126, 132–134
- charge patterns, 24
- chemical environments, 294
- chemical shift, 296–303
- chiral centers
 defined, 79
 Fischer projections, 86–88, 97–98
 identifying, 79–81
 priorities of attached atoms/groups, 80, 82
 R and S configurations, 80–81, 83–85
- chiral molecules, 89
- chlorination, 248
- chlorine
 and ¹³C NMR spectrum, 312
 addition to alkenes, 143–146
 and chiral centers, 83–84
 electronegativity, 12, 73
 IR absorption, 279
 isotopes, 271, 275, 276
 as substituent, 137, 138, 154–155
 valence electrons, 33
- chlorine substituents, 155, 158, 166
- cis*-1-chloro-1-pentene, 154–155
- cis*-1-chloro-2-heptene, 138, 154–155
- trans*-1-chloro-2-methylcyclohexane, 122, 130
- 1-chloro-3,3-dimethyl-1-pentyne, 166
- (2Z,4E)-2-chloro-5-fluoro-4-methyl-2,4-heptadiene, 139, 157–158
- chlorocyclohexane, 124, 130
- chlorohydrin, 161
- chloronium ion, 144, 160
- 2-chloropropane, 272, 276
- cis* configuration, 121–122
- cis* stereochemistry, 136
- cis*-1,2-dichloroethene, 12–13
- cis*-1,2-diisopropylcyclopropane, 122, 130
- cis*-1,3-dimethylcyclohexane, 122, 126, 133–134
- cis*-1-chloro-1-pentene, 154–155
- cis*-1-chloro-2-heptene, 138, 154–155
- cis*-1-*t*-butyl-4-methylcyclohexane, 126, 134
- cis*-3-hexen-1,5-diyne, 167, 181
- cis*-alkene, 136, 168–169, 181, 186
- class attendance, and success, 324
- clusters, 27
- C-O bond, 12, 281, 290
- cocaine, identification of, 278
- condensed structures, 26–28, 33
- conformations
 answer key, 127–134
 anti, 119
 chair, 123–126
 cis configuration, 121–122
 defined, 115
 eclipsed, 119
 gauche, 119
 Newman projections, 115–118
 stability of, 119–121
 staggered, 117, 119
 totally eclipsed, 119
 trans configuration, 121–122
- conjugate acid, 60–65, 71
- conjugate base, 60–65, 71
- conjugated dienes
 1,2-addition reactions, 223–228
 1,4-addition reactions, 223–228
 answer key, 236–240
 defined, 223
 Diels-Alder reactions, 228–233
 reaction coordination diagram, 225, 228
- coupling, 296, 299–300, 302
- covalent bond, 10–11
- crack cocaine, identification of, 278

cyanide, 179, 190, 204
 cyano substituent, 231, 237, 240
 cycloalkanes, 103, 121–122, 125. *See also*
 alkanes; ring structures
 1,3-cyclobutadiene, orbital diagram of, 246
 cyclobutane, 113
 cyclobutyl substituent, 166
 4-cyclobutyl-2-pentyne, 166
 cyclohexane. *See also* ring structures
 antiperiplanar geometry, 205
 chair conformations, 123–124, 130–131
 chair stabilities, 125–126
 NMR spectrum of, 296, 311
 as parent name, 107, 110
 planes of symmetry, 311
 1-cyclohexanol, 209
 1-cyclohexene, 138, 155
 cyclooctane, 112
 1,3,5,7-cyclooctatetraene, 139, 157, 247, 256
 1,3-cyclopentadienyl anion, 246, 255
 1,3-cyclopentadienyl cation, 246, 255
 1-cyclopentanol, 209, 218
 cyclopentene, 154
 1-cyclopentene, 154
 cyclopentyl group, 113
 cyclopentyl substituent, 113
 cyclopropane, 103
 cyclopropenyl cation, 247, 256
 cyclopropyl group, 112
 cyclopropyl substituent, 103, 112
 1-cyclopropyl-1,3-diethylcyclooctane, 107, 112

• D •

dashed line, in Newman projection, 116
 decane, 102, 110
 decene, 136
 decyl substituent, 102
 degrees of unsaturation, 300
 demurcation, 147–150, 161–162
 deprotonation, 61, 194
 diamagnetic anisotropy, 296, 312
 diastereomers, 89–91, 99
trans-1,2-dibromocyclohexane, 125, 126
 3,3-dichloro-1-methyl-1-cyclohexene, 138, 155
cis-1,2-dichloroethene, 12–13
trans-1,2-dichloroethene, 13, 20
 dichloromethane, 19

Diels-Alder reaction, 228–233
 number of diene and dienophile, 229
 orientation of diene and dienophile, 229
 products, 231–232, 237–238
 reverse engineering, 233–235, 239–240
 stereochemistry, 229
 dienes
 conjugated, 223–228
 Diels-Alder reaction, 228–233
 dienophiles, 228–233
 nomenclature, 139, 155–156
 dienophile, 228–233
 4-5-diethyl-3-methyl-2-octanol, 209, 218
 (3*E*,5*E*)-4,6-diethyl-3-methyl-3,5-nonadiene,
 139, 155–156
 diethylamine, 282, 290
trans-1,4-diethylcyclohexane, 126, 132
 dihalide, 144, 170–172, 182
cis-1,2-diisopropylcyclopropane, 122, 130
 dimethyl sulfoxide (DMSO), 193, 202
 1,2-dimethyl-1-cyclohexanol, 209
 3,3-dimethyl-1-cyclooctyne, 167, 180
 3,3-dimethyl-1-cyclopentene, 138, 154
 2,2-dimethyl-3-hexyne, 167, 180
 3,6-dimethyl-5-propylnonane, 105, 111–113
 dimethylamino groups, 238
cis-1,3-dimethylcyclohexane, 122, 126, 133
trans-1,2-dimethylcyclohexane, 126, 133–134
 dimethylformamide (DMF), 193, 202
 2,3-dimethylhexane, 104, 109
 dipole moments, 12–13
 dipole vector, 11–13
 “disguised anions,” 212
 disiamyl borane, 173–174, 184
 disubstituted benzene, 247–248
 disubstituted cyclohexane, 124
 DNA, 59
 double bonds. *See also* conjugated dienes
 alternating, around a ring, 47–48
 arrow pushing, 45–46
 and chiral centers, 93
 and electronegative atoms, 45–46
 hydrogenation reactions, 143–146
 IR absorption, 278, 290
 and lone pairs, 43–44
 Markovnikov addition, 140–143, 158–159
 multiple resonance structures, 49–50

orbital diagrams, 16
 protonation, 159
 resonance structures, 40–42, 53–54
 double dehydrohalogenation, 175–178
 doublet, 296, 298

● E ●

E stereochemistry, 136, 156–158
 E1 reactions, 194–203
 E2 reactions, 176, 194–206
 easy questions (exam tips), 325
 eclipsed conformation, 117, 119
 electron pairs, 62–63
 electron-donating groups, 229, 239
 electronegative atoms, 45–46
 electronegativity
 and acidity, 63–64, 66–67, 73
 and bond types, 10–11
 boron, 18
 difference in, 10–11
 fluorine, 18, 19
 nearby atoms, effects of, 66–67
 nitrogen, 18–19
 and octets, 51
 partial charges, 12
 and resonance structures, 45–46, 55–56
 electrons
 and bond types, 10
 Bronsted-Lowry acids/bases, 60–61, 71
 and carbocation rearrangements, 151–152
 conjugate bases, 73–74
 double bonds, 140–141
 Lewis acids/bases, 62–63, 71–72
 Lewis structures, 7–9
 in orbital diagrams, 15
 pi electrons, 40–41, 45–46, 242–245, 254–256
 valence, 8, 18, 23–25, 33
 electron-withdrawing groups, 229, 239, 249
 electrophiles, 248
 electrophilic aromatic substitution, 247–251
 elimination reactions, 189, 194–200
 enantiomers, 89–91, 99, 149, 160–161
 endo stereochemistry, 229, 237
 energy hill, 224
 enols, 173–174
 equatorial bonds, 123
 equatorial hydrogens, 123
 esters, 210–213, 220, 278, 291

ethane, 102, 116, 221
 ethanol, 207
 ethene, 136
 ethers, 215–217, 222
 ethoxide, 193, 202
 ethyl substituent, 102–103, 112, 154, 264, 276
 2-ethyl-1-pentene, 138, 154
 4-ethyl-2-methylheptane, 103
 ethyne, 179
 exo stereochemistry, 230

● F ●

falling behind, and success, 323
 fermentation, 207
 Fischer projections, 86–88, 97–98
 fluorine
 and ^{13}C NMR spectrum, 312
 electronegativity, 18, 19, 64
 as substituent, 137
 food products, acids in, 59
 formal charges, 23–25, 39–40
 formaldehyde, 17, 21–22, 211
 4H peak, 301
 four-membered ring, 30, 37
 $4n + 2$ rule, 242–243, 254–255
 fragmentation patterns, 263–264
 Friedel-Crafts acylation, 258
 Friedel-Crafts alkylation, 259
 Frost circles, 245–247, 256
 functional groups
 alcohols, 194–200, 207–222
 alkenes, 135–164
 alkynes, 165–186
 aromatic compounds, 241–260
 conjugated dienes, 223–240
 elimination reactions, 189, 194–200
 IR spectra, 278, 284–289
 substitution reactions, 189–193, 197–200

● G ●

gamma hydrogen, 264, 266
 gauche conformation, 119
 geometries, 14–15
 geometries, of molecules, 14–15
 Grignard reaction, 211–212, 221
 Grignard reagents, 211–212, 221

• H •

^1H NMR spectrum, 294–299, 311–312
 H_2 /Lindlar catalyst, 168–169, 181
 H_2 /Pd catalyst, 168–169
 H_2 /Pd(D) catalyst, 168–169, 181
 H_2 /Pt catalyst, 168–169
halides
 addition to alkynes, 170–172
 addition to conjugated dienes, 223–228
 in condensed structures, 27
 electrophiles, 179
 leaving groups, 195
 in Lewis structures, 8
 in substitution reactions, 190, 204
halogen substituents, 166
halogenation reactions
 alkenes, 143–146
 alkynes, 170–172, 182
halohydrin, 144
halonium ion, 143–144, 159
heptane, 102, 103
3-heptanol, 208
heptene, 136
2-heptene, 154–155
heptyl substituent, 102
heteroatoms, 243
hexachloroethane, 19
hexane, 102, 109, 111
2R-1,2-hexanediol, 210, 219
1,2-hexanediol, 210
2-hexanone, 268
cis-3-hexen-1,5-diyne, 167, 181
hexene, 136
2-hexene, 137
hexyl substituent, 102
higher priority groups, 80–82
Hückel number, 242–243, 254–255
Hund's rule, 245
hybridization, 14–17, 63–64
hydride shift, 151, 203
hydroboration, 173–175, 184, 212–213, 219
hydrocarbons
 alkanes, 101–113
 alkenes, 135–164
 alkynes, 165–186
 fragments, 271
 substituents, 166
hydrogen atoms, 8
hydrogen bromide, 141, 182, 226

hydrogen chloride
 acidity, 64, 72
 IR absorption, 279
 reaction with alkenes, 142–143, 158–159
 reaction with alkynes, 182
hydrogen fluoride, 64, 72
hydrogen iodide, 64, 142, 158
hydrogen peroxide, 147
hydrogen sulfide, 65, 72
hydrogenation reactions, 143–146, 170–172
hydrogens, 38, 297–298, 301
hydrohalic acids, 140–143, 170–172, 182,
 223–228
hydroxyl (OH) group, 147, 207, 279, 286

• I •

infrared (IR) spectroscopy
 absorbances, 277
 answer key, 290–291
 defined, 276
 functional groups, 277–283, 284–289
 spectrum, 280–283, 290, 305, 306, 314–316
 wavenumbers, 277
integration curves, 296–298
internal alkynes, 175–177, 280
International Union of Pure and Applied
 Chemistry (IUPAC), 101
iodide, 158, 195, 198
iodine, 64, 71, 271
ionic bond, 10
ions. *See also* carbocations
 acetylide, 175–177, 185
 anions, 72
 bromonium, 144–145, 160–161, 170–172,
 183–184
 cations, 40–42, 49, 141, 263
 halonium, 143–144, 159
 mercurinium, 147–150
 molecular (M^+ peak), 264
iron tribromide (FeBr_3), 248, 250
isopropyl alcohol, 207
isopropyl benzene, 270, 276
isopropyl group, 106, 111
isopropyl substituent, 109–110
3-isopropyl-2,2,4-trimethylhexane, 107, 111
4-isopropyl-3,4-dimethyloctane, 106
4-isopropyl-3-heptanol, 208
4-isopropyl-3-methylheptane, 109–110
isotopes, 271

• **J** •

Jones' reagent, 215–217, 221

• **K** •

Kekulé structures, 29–31

ketones

formation of, 174

IR absorption, 278

IR spectra, 284–285

mass spectrum, 268, 276

McLafferty rearrangement, 266, 268, 275

reduction reactions, 211, 213, 220

kinetic products, 224–226, 236

K-N bond, electronegativity value of, 11

• **L** •

leaving groups

elimination reactions, 194–196

substitution reactions, 189–193

less-substituted carbon, 140–142, 158

Lewis acids, 60, 62–63, 247

Lewis bases, 60, 62–63

Lewis structures

condensed structures, 26–28

constructing, 7–9

formal charges, 23–25

line-bond structures, 29–31, 36–37

lone pairs, 43–44

octet rule, 8–9

orbital diagrams, 15–17, 21–22

and resonance structures, 39

Lindlar's catalyst, 168–169, 181

line-angle structures. *See* line-bond structures

linear geometry, 14–15

line-bond structures

carbon chain in, 29, 36–37

hydrogens on, 31–32, 38

triple bonds in, 36

lithium aluminum hydride (LiAlH₄), 210–211, 213, 220

lone pairs, 25–26

alternative resonance structures, 57

in atom hybridizations, 14

multiple resonance structures, 49–50

resonance structures, 40, 43–44

lower priority groups, 80–82

• **M** •

M⁺ peak, 264, 269, 271, 276

M+2 peak, 271–273

magnesium, 211–214, 221

Markovnikov addition, 140

hydrohalic acids to alkenes, 140–143, 158

oxymercuration, 213, 220

water to alkenes, 147–150, 162

water to alkynes, 172–174, 184

mass, 264

mass spectrometry

answer key, 274–276

base peak, 265

defined, 263

fragmentation patterns, 265, 267, 268, 270, 272, 275, 316

identifying fragments in, 263–271

M⁺ peak, 264

predicting structures from, 271–273

radical cations, 263

mass-to-charge-ratio (m/z), 264, 265

mauve dye, 241

McLafferty rearrangement, 264, 266, 268, 275

mechanisms, understanding of, and

success, 322

memorization, 322, 327

mercurinium ion, 147–150

mercury acetate, 147, 161, 183–184

mercury sulfate, 173–175, 183–184

meso compounds, 89–91, 99, 160

meta directors, 248, 249, 251–253, 256, 258–259

meta substituents, 251

meta substitution, 247–251

methane, 17, 21, 64, 72, 102

methanol, 12, 71, 207

methine carbons, NMR spectrum of, 294–295, 298

methine proton, 298

methoxy group, 238, 239

methyl acetate, IR spectrum of, 289, 291

methyl alcohol, 195

methyl group

chemical shift, 303

molecular weight, 264–266

naming, 111

NMR spectrum, 294–296

ortho-para directing, 256

substituents, 102–103, 109–113, 154

methyl substrates, 190, 197–200, 204
2-methyl-1-penten-3-yne, 167, 180
trans-5-methyl-2-hexene, 137
4-methyl-5-propyldecane, 105, 110
methylcyclohexane, 124
methylene groups, 271, 276, 301
2-methylhexane, 265–266
2-methylpentane, 267, 274
3-methylpentane, 267, 274
mirror planes, 294
molecular formula, 276, 302–303, 313–316
molecular fragments, 271–273, 301–303
molecular ion (M^+ peak), 264
molecular orbital diagram, 245–247
molecular structures. *See also* resonance structures
 alkanes, 106–108, 111–113
 condensed structures, 26–28
 IR spectrum, 284–289
 Lewis structures, 7–9
 line-bond structures, 29–32
 mass spectrum, 271–273
 spectroscopic analysis of, 300–316
 3-D models, 79–99
molecular symmetry, 89–90, 293–296, 311
molecular weight, 264
molecules. *See also* resonance structures
 3-D shapes, 14–16
 bond dipoles, 11–12
 bond types, 10–11
 chiral, 89
 chiral centers, 80–85
 condensed structures, 26–28
 connectivity of atoms, 7–8
 dipole moments, 12–13
 Fischer projections, 86–88
 fragments, 263–264
 geometries, 14–15
 IR absorption, 277–280
 Lewis structures, 7–9
 line-bond structures, 29–32
 meso compounds, 89–90
 mirror planes, 294
 orbital diagrams, 15–17
 predicting structures of, 271–273
 stereoisomers, 89–90
more-substituted carbon, 140–142, 158
multiple resonance structures, 49–50

multistep synthesis, 165, 178–179, 251–253
multisubstituted aromatics, 258–260

● N ●

$n + 1$ rule, 300, 312
N=O double bond, 57
 NaNH_2 , 175–177, 179, 185–186
 Na/NH_3 , 168–169, 181
naphthalene, 245, 255
negative charges, 24–25, 63–64, 73–74
Newman projections, 115–121
N-H bond, 11
9H peak, 301
nitration, 248
nitriles, IR absorption of, 278
nitro group, 239
nitrogen
 in amines, 290
 in aromatic rings, 243, 254
 electronegativity, 55–56, 72–74
 formal charges, 24, 33
N-K bond, 11
nomenclature
 alcohols, 207–210
 alkanes, 101–105
 alkenes, 135–139, 154–158
 alkynes, 165–167, 180–181
 dienes, 228–233
3,5-nonadiene, 155–156
nonane, 102, 112
nonaromatic rings, 242–245, 254–255
2E,4E,6E-2,4,6-nonatriene, 156–157
2,4,6-nonatriene, 156–157
nonene, 136
nonyl substituent, 102
normal line, in Newman projection, 116
nuclear magnetic resonance (NMR)
 spectroscopy
 answer key, 311–318
 chemical shift, 296
 common fragments, 301
 coupling, 296, 298–300
 defined, 293
 integration curves, 296–298
 molecular symmetry, 293–296
 solving for unknown structures, 300–310
nucleophiles, 189–193, 202

● **O** ●

octamethyl substituent, 113
 1,1,2,2,3,3,4,4-octamethylcyclobutane,
 108, 113, 223–228
 octane, 102
 2-octanol, 209, 218
 octene, 136
 octet rule, 8–9, 18, 47, 51, 62–63
 octyl substituent, 102
 O-H bond, 12
 old exams (exam tips), 326–327
 1H peak, 301
 orbital diagrams, 15–17, 21–22
 organic compounds
 acid-base reactions, 63–68, 74
 alcohols, 207–222
 alkanes, 101–113
 alkenes, 135–164
 alkynes, 165–186
 aromatic compounds, 241–260
 conjugated dienes, 223–233
 stereochemistry, 79–99
 ortho substituents, 251
 ortho substitution, 247–251
 ortho-para directors, 248, 249, 251–253, 256,
 259, 260
 oxidation reactions, 215–217, 221–222
 oxidizing agents, 215, 221
 oxygen
 electronegativity, 19, 45, 55–56, 73
 formal charges, 24, 33
 valence electrons, 8
 oxymercuration, 147–150, 161–162, 172–174,
 184, 213, 220

● **P** ●

palladium catalyst, 168–169, 181
 para substituents, 251
 para substitution, 247–251
 parent chains
 alcohols, 208–209
 alkanes, 101–102
 alkenes, 136
 alkynes, 165
 defined, 101
 partial charges, 12, 19
 Pd/C catalyst, 161
 pentane, 102, 118, 121, 128, 129
 pentavalent bond, 43
 pentene, 136
 1-pentene, 137, 154
 pentyl substituent, 102
 1-pentyne, 166
 2-pentyne, 280
 peripheral atoms, 7–8
 Perkin, William (chemist), 241
 permanganate oxidations, 250, 257
 pi bonds, 16, 22, 45–46, 170
 pi electrons, 242–245
 in benzene rings, 312
 in resonance structures, 40–41, 45–46
 and ring aromaticity, 254–256
 pKa values, 69–70
 planes of symmetry, 294, 311
 “poisoned” palladium catalyst, 168–169
 polar covalent bond, 10
 polysubstituted aromatics, 251–254, 258–260
 positive charges, 24–25, 40–42
 positive outlook and success, 324
 potassium amide, 11
 potassium hydroxide, 192
 potassium permanganate, 252, 259
 potassium tert-butoxide, 196, 203
 primary alcohols, 211–217, 220–221
 primary amide, 288, 291
 primary amine, 282, 290
 primary carbocation, 140–142, 151, 192,
 201–202
 primary carbon, 216
 primary cation, 141
 primary halides, 222
 primary substrates, 190–191, 197–200,
 205–206
 priority, assigning, 80–82
 propane
 lowest-energy conformation, 120, 128
 Newman projections, 117, 118, 127
 as substituent, 102
 2-propanol, 281, 290
 propene, 136
 propionic acid, 281, 290
 propyl group, 264, 274
 propyl substituent, 102, 110, 111
 propylamine, 282, 290
 propylbenzene, 270, 276
 protic solvents, 194–195, 206

proton acceptor, 60
proton donor, 60
proton NMR, 293–296
protonation, 143, 159
pyridinium chlorochromate (PCC),
215–217, 221

• Q •

quartet, 312
quaternary carbons, 257
questions and success, 324

• R •

R configuration, 83–85, 98
R-3-methyl-2-butanol, 210, 218–219
racemic products, 190, 204
radical cations, 263
rate equation, 190, 193, 194–195, 202, 206
reaction coordination diagram, 225–228,
236–237
reactions. *See names of specific types of reactions*
rearrangements, of carbocations, 151–153
reduction reactions, 168–169, 211
relative ratio, 297–298, 303
resonance structures
and acidity, 67–68, 74
answer key, 53–58
arrow-pushing, 40–41
assigning importance to, 51–52, 58
cationic molecules, 40–41
conjugated dienes, 223–228
defined, 39
double bonds, 45–46
and electronegative atoms, 45–46
lone pairs and double or triple bond, 43–44
multiple, 49–50
of ring systems, 56
ring systems with alternating double bonds,
47–48
rules for, 39
triple bonds, 45–46
retrosynthesis, 178, 233–235
ring expansions, 151–152
ring flip, 123, 132–134
ring structures, 36–37
alternating double bonds, 47–48
aromaticity of, 242–245

condensed structures, 27
cycloalkanes, 103, 121–126
molecular orbital diagrams, 245–247
resonance structures, 47–48, 56
three-membered, 256
rubbing alcohol, 207

• S •

S configuration, 83–85, 97
saturated hydrocarbons. *See alkanes*
scanning method, 33
s-cis conformation, 229–230, 238–239
sec-butyl group, 112
4-sec-butyl-5-cyclopentylnonane, 108, 112–113
secondary alcohols, 211, 215–217
secondary amine, 282, 290
secondary carbocation, 140–142, 151, 159,
192, 201–202
secondary cation, 141
secondary substrates, 190–191, 197–200,
204–205
septet, 298
sextet, 312
sigma adduct, 258
single bonds, 16
in aromatic compounds, 242–243
and chiral centers, 80, 93
in Lewis structures, 24, 33
in meso compounds, 89
in orbital diagrams, 16
in resonance structures, 39
singlet, 312
6H peak, 301
sleep (exam tips), 327–328
 S_N1 reactions, 189–193, 197–204
 S_N2 reactions, 175–176, 189–193, 197–204, 216
sodium, 19, 163, 181, 215
sodium borohydride (NaBH_4), 147–150,
210–211, 213, 220
sodium fluoride, 11
sodium hydride, 215
sodium metal, 215
soft drinks, acids in, 59
solid wedge, in Newman projection, 116
solubilities, 12
solvent, 190, 193, 194–195, 202, 206
sp hybridization, 14–15, 20–22
*sp*² hybridization, 14–16, 20–22, 242–245
*sp*³ hybridization, 14–16, 20–22

spectroscopy
infrared, 277–291
mass, 263–276
nuclear magnetic resonance, 293–318
staggered anti conformation, 119
staggered conformation, 117, 119
staggered gauche conformation, 119
stereochemistry
alcohols, 208–209
alkenes, 136
answer key, 92–99
chiral centers, 79–82
of cycloalkanes, 121–122
defined, 79
diastereomers, 89
Diels-Alder reaction, 229–230
exo, 230
Fischer projections, 86–88
meso compounds, 89–91
planes of symmetry, 89–90
R and S configurations, 83–85
stereoisomers, 89–91
substitution reactions, 190
stereoisomers, 79, 89–91
steric strain, 239
s-trans conformation, 238
strong bases, 175–177, 190, 194–195
structures, using (exam tips), 327
study group (exam tips), 326
study time (exam tips), 326
studying and success, 322–323
substituents
alcohols, 208
alkanes, 102
alkenes, 136
alkyl, 249, 260
alkynes, 166
aryl, 248–249
and chiral centers, 79–82
defined, 102
halogen, 166
hydrocarbons, 166
meta, 251
ortho, 251
para, 251
substituted benzenes, 247–248
substitution reactions, 189–193, 197–202,
247–251
substrates, 190, 194–201
sulfonation, 248

sulfonic acid, 250, 256
sulfur, electronegativity of, 55, 72–73
sulfuric acid, 217, 221
symmetry
meso compounds, 89–90, 99
and signals in NMR spectroscopy,
293–296, 311
syn addition, 144, 147
synthesis
alcohols, 210–214, 219–221
aldehydes, 184, 215–216, 220–221
alkenes, 168–169, 181
alkynes, 178–179
aromatic compounds, polysubstituted,
251–254, 258–260
carbonyl compounds, 173–174, 183–184
carboxylic acids, 221
ketones, 174

• T •

tautomerization, 172–174, 183–184
terminal alkynes, 175–177
tert-butoxide, 193, 202, 205
tert-butyl group, 107, 301
tert-butyl substituent, 110
tert-butylcyclohexane, 105, 110
tertiary alcohols, 215–217, 221
tertiary carbocations, 140–142, 151, 159, 192,
201–202
tertiary cation, 141
tertiary halide, 191
tertiary substrates, 191, 197–204
tetrabromide, 179, 186
tetrahalide, 170–172
tetrahedral geometry, 14–15
thermodynamic products, 224, 236
thiols, 179, 190
3-D models, 79–99
Cahn-Ingold-Prelog rules, 80, 86
chiral centers, 79–82
diastereomers, 89
Fischer projections, 86–88
meso compounds, 89–91
planes of symmetry, 89–90
R and S configurations, 83–85
stereoisomers, 89–91
substituent priorities, 79–82
3H peak, 301, 303
tosylate, 195

totally eclipsed conformation, 119
trans alkenes, formation of, 168–169, 181
trans stereochemistry, 121–122
 alkenes, 136–137, 157
 and chair conformations, 124, 134
 and chair stabilities, 125
 cycloalkanes, 121–122
trans-1,2-dibromocyclohexane, 125, 126
trans-1,2-dichloroethene, 13, 20
trans-1,2-dimethylcyclohexane, 126
trans-1,4-diethylcyclohexane, 126, 132
trans-1-chloro-2-methylcyclohexane, 122, 130
trans-5-methyl-2-hexene, 137
trans-dichloride, 159
trigonal planar geometry, 14–15
triple bonds, 16
 arrow pushing, 45–46
 and chiral centers, 93
 and electronegative atoms, 45–46
 IR absorption, 280
 and lone pairs, 43–44
 multiple resonance structures, 49–50
 orbital diagrams, 15–17
 resonance structures, 40, 41, 44, 53–54
 water-addition reactions, 173–174
triplet, 296, 312
2H peak, 301, 303, 317–318

• U •

unsaturated C-H stretch, 284–285
unsaturated hydrocarbons. *See* alkenes;
 alkynes
unsaturation, 300

• V •

valence electrons, 8, 18, 23–25, 33
valence orbitals, 16, 21–22
vector addition, 13
vinyl cations, 171

• W •

water
 acidity of, 65, 72
 addition to alkenes, 147–150, 162
 addition to alkynes, 172–175
 as Bronsted base, 61
 in halogenation reactions, 144
 in hydroboration reactions, 212–213, 219
wavenumbers, 277
weak bases, 179, 190, 202–204
Williamson ether synthesis, 215–217, 222

• Y •

yeast enzymes, 207

• Z •

Z stereochemistry, 136–137, 157–158
Z-1-chloro-1-fluoro-1-pentene, 137