

Index

a

absorption 33, 201–203, 205, 484–487, 489
 acetaldehyde 437
 acetyl-CoA 448–452
 2-acetyloxycyclohexyl tosylate 299–301
 acidity 20, 53, 81, 259, 260, 331, 350, 355, 360, 417–419, 451
 activation energy
 definition 17, 18
 in alkene additions 98, 99, 101, 114, 117, 122, 127, 195
 in aromatic CH substitution 226, 227, 229, 231
 in cycloadditions 145, 157, 162, 163, 186, 188, 192
 in eliminations 327, 337–342, 344, 346, 357
 in enzymatic reactions 43, 44
 in green chemistry methodology 48
 in isotope labeling 40
 in nucleophilic aromatic substitution 243, 244
 in radical halogenations 63, 65, 67, 69, 75
 in reactions of carbonyl groups 394, 401, 405–407
 in rearrangement 458, 481, 483
 in relation to Bell–Evans–Polanyi Principle 19, 20
 in relation to kinetic isotope effect 40
 in S_N1 and S_N2 reactions 263, 271, 278, 280, 281, 283, 287

activation enthalpy 18
 activation entropy 145
 agostic interaction 76, 79
 aldehyde 37, 295, 296, 367, 370, 371, 373–376, 379–382, 384, 386, 410, 421, 426, 428, 429, 431, 432, 434, 437–439, 443, 447, 482
 aldolase 384
 aldol reaction 428, 429, 431–433, 435–439, 442, 447, 449–451
 alkane 42, 53, 54, 59, 62–66, 68–71, 73, 76–78, 80–82, 84, 85, 88, 89, 91, 93, 106, 113, 131, 283, 318–320, 322, 334, 336, 338, 342, 348, 350, 352, 356, 417
 alkene 32, 36, 95–101, 103, 105–113, 116, 118, 120, 122–127, 129–131, 133–135, 137, 138, 143–146, 148, 150, 152, 153, 155, 160, 162, 168–174, 176–178, 180, 216, 217, 223, 293, 296, 309, 319–321, 325, 326, 332–342, 344, 345, 348–350, 352, 356–358, 361, 376, 439, 461, 462, 477, 483–485
 alkyne 113, 131, 161, 171, 178–180, 239, 293, 326, 376
 α-D-glucopyranose 377, 378
 6-α-glycosylallyl vinyl ether 482
 anti-addition 85, 96, 107, 117, 128, 129, 133–135, 138
 anti-elimination 317–319, 325, 326, 348, 350, 351

- arene 201–206, 209, 212, 214, 219, 223, 226, 238, 239
 arenium 22, 199, 200, 202–206, 209, 211, 219, 225–227, 229–231, 233, 243, 464
 aromatic nitration 42, 84, 199–203, 205
 aryne 239, 241, 243, 245
 autoxidation 74, 75, 475
 auto redox 208–210, 217–219
 azide 171, 172, 263, 264
 azobisisobutyronitrile (AIBN) 73, 74, 148
- b**
 basicity 37, 259–263, 332, 335, 467
 Baeyer–Villiger oxidation 458, 468, 471, 475
 Baeyer–Villiger rearrangement 471, 473, 475
 Beckmann rearrangement 468–470
 Bell–Evans–Polanyi Principle 19, 98, 281, 318, 339, 341
 benzenium 205, 224–226
 benzoin 412
 benzoquinone 162, 164
 benzyne 239–241, 326
 β -D-glucopyranose 377, 378
 6- β -glycosylallyl vinyl ether 482
 biochemistry 43, 143, 387
 bisphenol A 222, 223, 367
 Boc 437–439
 bond dissociation energy (BDE) 54–58, 63–67, 74, 75, 77, 91, 95, 127, 143, 258, 259, 283, 343, 344
 9-borabicyclo[3.3.1]nonane (9-BBN) 122–125
 bromination 32, 42, 53, 62–67, 69, 70, 73, 74, 92, 135, 137, 229
 busulfan 303–305
 1,3-butadiene 5, 28, 29, 33, 114, 154–157, 160, 162–165, 169, 184
 2-butene (*cis* or *trans*) 101, 122, 126, 130, 145, 146, 148, 152–155, 174, 176–178, 339, 342, 350, 461
- c**
 carbanion 243, 262, 347, 355, 357–360, 412, 413
 carbene 148, 318, 353, 356, 476–478
 carbocation
 in alkene addition 36, 96–106, 108–116
 in alkyne addition 113
 in E1 reaction 317, 336–342, 344, 345, 361
 in electrophilic aromatic substitution 199, 214, 215, 219, 221–223
 produced in superacid 37, 81, 82, 84, 97
 in rearrangement 458–466, 475
 in S_N1 reaction 3, 22, 36, 258, 266, 278–281, 283, 284, 286–288, 292, 297, 298, 301, 303, 309
 structure of 34–36
 carbocation rearrangement 361, 458, 460, 462
 carbon electrophile 39, 222, 259, 367
 carbon nucleophile 258, 291, 293, 295, 419, 421, 426
 carbonic anhydrase 45–47
 carboxylic acid 16, 109, 113, 130, 144, 145, 150, 236, 280, 306, 345, 386, 390–396, 398, 400, 407, 409, 410, 417, 463, 471, 473, 480
 cascade rearrangement 459, 464, 465
 chain reaction 112, 113
 charge transfer 88, 199, 201–205
 charge-transfer nitration 204
 chlorination 53, 59, 61–70, 233, 234, 348, 349, 391
m-chloroperbenzoic acid 144–146
 chorismate 481
 citrate synthase 449, 450
 Claisen rearrangement 49, 458, 479–483
 conjugate diene 160, 165, 184
 conjugation effect 20, 21, 35, 36, 55, 56, 64, 67, 68, 72, 100, 103, 113, 148, 229, 248, 272, 321, 368, 421, 435, 463
 Cope rearrangement 182, 183, 479

- crossed aldol reaction 429, 431
 cyclization 144, 181, 184, 361, 464, 465,
 477
 cycloaddition of 1,3-butadiene 154, 157
 cycloaddition of NS_2^+ 180
 1,3-cyclopentadiene 160–162, 164, 186,
 187
 cyclopropyl methyl ketone 431
 cytochrome P-450 88, 89
- d**
- dichlorocarbene 146–148, 150, 353, 355
 defunctionalization 148, 231, 232, 235
 dehydration 318, 337, 338, 340–342, 344,
 358, 360, 397, 429, 430, 433, 435,
 460, 461, 463
 dehydration of alcohols 338, 340, 342,
 344
 deuterium 40–42, 63, 76, 89, 183, 239,
 326, 356, 477
 diaryl sulfide 208, 209, 247
 diaryl sulfoxide 209, 250
 diazene 185
 diazomethane 171, 172
 dichlorocarbene 146–148, 150, 353, 355
 Diels–Alder reaction 5, 154, 158–166,
 169, 173, 180, 186, 190, 191
 diene 5, 28, 33, 100, 114, 115, 122, 131,
 153–165, 167, 169, 181–187,
 191–193, 430, 431, 479
 dienophile 154, 156–160, 162, 165, 186
 dimethylazodicarboxylate 190, 191
 1,3-dipolar 167, 169, 173, 174, 179, 188,
 189
 1,3-dipolar cycloaddition 167, 173
 1,3-dipolar-like molecule 169
 diradical 148, 484, 485
 dithionitronium 173–175, 204–206, 486
- e**
- E1 reaction 317, 318, 336, 337, 339,
 342–345, 361, 458
 E1cb reaction 318, 357, 358, 360, 433,
 435, 443
 E2 reaction 317–321, 323–337, 342, 343
 early transition state 17–19, 61, 75, 264,
 266, 284
 electrocyclic reaction 181
 electrophile
 in alkane CH functionalization 83
 in alkene addition 98
 in aromatic CH substitution 199, 200,
 204, 212, 222, 226, 229, 231, 235,
 236, 238, 239
 in cycloadditions 144
 definition 33
 examples 33–35, 37–39
 in reactions of carbonyl groups 367,
 422, 423, 428, 429
 in $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions 257–259,
 269, 292, 301
 electrophilic addition 36, 39, 95, 97–102,
 105, 108–110, 113–115, 133, 215,
 286, 384, 458, 459, 461, 462
 electrophilic aromatic substitution (EAS)
 reaction 22, 111, 122, 199, 200,
 205, 208–210, 212–217, 219,
 221–227, 229, 231, 233, 234, 238,
 250
 electrophilicity 38, 77, 84, 103, 106, 111,
 208, 218, 269, 270, 277, 371, 388,
 393, 399, 400, 451
 elimination reaction 260, 317, 318, 321,
 331, 332, 336, 337, 344, 349, 350,
 356–358, 360
 enantiomer 120, 125, 135, 138, 249, 265,
 284–286, 288, 289, 297, 435–438,
 447
 enantiomeric excess 435, 437
 enolate 31, 295, 359, 360, 417–429,
 431–434, 437–452, 480, 481
 (*E*)-enolate 432, 439, 440
 enone 443, 479, 480
 enzyme 43–46, 88, 89, 306, 308, 310, 311,
 318, 358, 360, 361, 384, 386–389,
 403, 405–409, 449–452, 464, 481
 epoxidation 144–146
 ester enolate 359, 360, 438, 441, 444,
 446, 447

- esterification 16, 109, 280, 391–396, 399–404
- f**
- fat 133, 358–361, 401–404, 407–409, 448, 449, 451
- fatty acid 132, 133, 359, 360, 401–404, 407–409, 448, 449, 451
- free energy 1–4, 13–18, 43–45, 126, 331
- Friedel–Crafts reaction 111, 212, 213, 219–221
- frontier molecular orbitals (FMO) 32, 33, 143, 150–156, 168, 169, 180, 186–191, 205, 275, 276, 327, 329
- g**
- Gabriel synthesis 295, 296
- D-glucopyranose 377
- D-glucose 304, 305, 376, 377, 379, 448, 451
- β-glucosidase 307
- glycoside 304–306, 308
- glycosidic bond 304, 306, 308
- good leaving group 104, 150, 224, 225, 257–261, 263, 265, 269, 270, 272, 273, 277, 290, 293, 297, 299, 303, 306, 308, 309, 333, 338, 342, 344, 368, 391, 398, 458, 467, 468, 470, 471, 475, 490
- green chemistry 46, 47, 49, 52, 186, 187, 191, 301, 391, 394, 396, 480
- Grignard reagent 39, 236, 291, 292, 350, 367, 400, 440
- h**
- haloalkane 36, 37, 53, 64, 105, 106, 113, 133, 266, 268, 270–273, 275, 280, 282, 284, 285, 288, 291, 293–298, 310, 311, 317, 326–329, 331, 338, 342–344, 348, 350, 356, 423, 426, 427, 445
- Hammett equation 20–23
- Hammond postulate 18
- hemiacetal 373, 374, 376, 379
- hemiketal 373, 374, 376, 377
- heteroatom 258, 297, 458, 468
- heterocycle 173, 178, 486
- heterogeneous 47, 48, 81, 82, 127, 128
- 1,5-hexadiene 182, 183
- 2,4-hexadiene 165, 184–186
- hexamethylbenzene 201, 203, 205, 206, 210, 211
- 1,3,5-hexatriene 181, 182
- Hg(II) 77–80, 106, 217
- highest occupied molecular orbital (HOMO) 32, 143, 201, 275, 355, 422
- involved in α-elimination 352
- in charge-transfer complexes 201, 204, 205
- in fundamental molecules 29, 32, 33
- involved in reactions of carbonyl groups 422, 442
- involved in rearrangement 483–485
- in relation to cycloadditions 143, 144, 150–159, 161–163, 165, 169, 171, 173, 174, 176, 179–192
- involved in S_N2 reactions 275
- H-mont
- catalysis on nucleophilic substitution 301, 302
- as a solid Bronsted acid 301
- Hofmann reaction 320, 324
- homogeneous 46, 48, 49, 127
- hemolytic 54, 56, 59–62, 71, 76, 86, 87, 89, 112
- Hückel's rule 164, 181, 184
- hydration 103–108, 113, 118, 370–373, 379
- hydrazine 244, 296, 382, 383, 477
- hydrazone 382, 423, 425–427
- hydride donor 384, 386, 409
- hydroboration 103, 106, 117–126
- hydrocarbon 53, 67, 70, 74, 77, 95, 126, 199, 238, 394, 395, 402
- hydrogenated fat 132, 133
- hydrogenation 126, 127, 129–132, 293, 376

hydrogen bond(ing) 43, 44, 47, 48, 86, 189, 191, 193, 245, 271, 272, 280, 306, 308, 384, 388, 403, 405–407, 409, 437, 451, 464, 481
 hydrogen rearrangement 219, 341, 465
 hydrolase 43, 304, 306, 308, 403
 hydrolysis
 acetals/ketals 163, 293, 376
 carboxylic anhydride 435
 esters 266, 311, 400
 halo and other functionalized alkanes 282, 289, 291, 299, 310
 imines 382, 427, 437
 isotope-labeled ester 39–41, 369, 370, 393
 β -ketoester 445, 447
 thioester 449, 451
 triflic/sulfuric acid ester 78, 79, 81
 hydrophobic interface 47–49
 hyperconjugation 35, 36, 55, 56, 64, 103, 144, 229, 231, 357, 368, 417, 418, 421

i

ibuprofen 249, 251
 imine 381, 382, 384, 385, 410, 437–439
 intramolecular reaction 376, 377
 ion-pair 284–286, 288
 ion-radical pair 199, 201–204
 ipso-substitution 231, 233–235
 irradiation 87, 185, 202, 485, 487
 isobutyraldehyde 437
 isotope effect 40, 42, 63, 76, 85, 89
 isotope labeling 39, 40, 326, 477
 isomerization 43, 132, 231–233, 235, 420, 460, 464, 467, 483–485

k

ketal 293, 373–377
 ketene 212, 213
 ketone enolate 432
 kinetic control 64, 115, 162, 320
 kinetic isotope effect 40, 42, 89
 kinetics 2, 6, 20, 39, 68, 180, 263, 278, 410

l

lactone 393, 473, 475
 lanosterol 464, 465
 late transition state 17–19, 40, 61, 266, 268, 283, 344
 LCAO 24, 26, 28, 32
 leaving group
 in acyl substitution reactions 368, 391, 398, 401
 in alkene addition 104
 in cycloaddition 150
 in elimination reactions 333, 338, 342, 344, 356, 358
 in rearrangements 458, 467, 468, 470, 471, 475, 490
 in S_N1 and S_N2 reactions 224, 225, 257–261, 263, 265, 266, 269, 270, 272, 273, 276, 277, 280, 283, 287, 290, 293, 297, 299, 301, 303, 306, 308, 309
 Lewis acid 33, 37, 38, 80, 81, 110, 212, 223, 261, 348, 459, 466, 468
 Lewis base 33, 459
 ligand 76, 77, 106, 273, 274, 277, 278, 353, 354, 420
 linear combinations of atomic orbitals 24
 lipase 407–409
 lithium aluminum hydride 384, 409, 410
 lithium diisopropyl amide (LDA) 243, 419, 420, 431, 432, 447
 lowest unoccupied molecular orbital (LUMO) 32, 143, 275, 355, 422
 in charge-transfer complexes 201, 204, 205
 involved in α -elimination 354–356
 in fundamental molecules 29, 32, 33
 involved in reactions of carbonyl compounds 422
 involved in rearrangement 484, 485
 in relation to cycloadditions 143, 144, 150–159, 161–163, 165, 168, 169, 171–176, 179, 180, 184, 186–192
 involved in S_N2 reactions 274–277

m

magic acid 81
 Markovnikov addition 96, 101, 108, 112, 114, 116, 117
 Markovnikov's rule 97, 100, 101, 103, 108, 109, 111, 116, 216, 459
 non-Markovnikov addition 116, 117
 Meisenheimer complex 243–245, 248
 mercury(II) 77–80, 106, 107, 118, 134, 135, 138
 mesitylene 211, 236, 237
 1-methylcyclopentene 120, 121, 169
 molecular orbital (MO) 25–29, 35, 36, 55, 56, 129, 205, 273–278, 318, 354, 355, 422, 489
 molecular orbital diagram(s) 28, 151, 169, 274, 355
 monosubstitution 59
 molecularity 4, 6

n

neighboring group assisted 297–301, 308
 nitration 42, 84–86, 94, 199, 205, 231
 4-nitrobenzaldehyde 436
 nitronium 84–86, 199–201, 203–206
 NMR 37, 79–81, 203, 205, 246, 459
 norbornene 174, 176
 nucleophile
 in alkene additions 97, 98, 100, 101, 103
 in elimination reactions 326, 332–335
 examples 33, 34, 36–39
 in nucleophilic aromatic substitutions 235, 239–243, 245, 248
 in reactions of carbonyl groups 367–370, 379–381, 400, 419, 421, 422, 426–429, 440, 448
 in S_N1 and S_N2 reactions 257–266, 269–272, 275–278, 280, 283–293, 295, 296, 303, 310
 nucleophilic addition
 of aldehydes and ketones 367, 368, 370, 373–382, 384–387, 389
 involved in aldol reactions 428, 429, 433, 435, 437, 443–445

of carbonyl compounds 37, 39, 40, 46
 involved in nucleophilic aromatic substitution 239

in rearrangements 466, 471, 473
 involved in Wittig reaction 296

nucleophilic aromatic substitution (NAS) reaction 22, 200, 239–241, 243–245, 247, 248, 257

nucleophilicity 37–39, 95, 193, 248, 261–263, 272, 306, 308, 332, 333, 335, 350, 370, 399, 405–407, 417, 419, 421

nucleophilic substitution

on aromatic rings 239–243, 246–248
 on carbonyl groups 368, 390, 398, 400, 401
 involved in rearrangement 461, 462
 on sp³-hybridized carbons 224, 257, 258, 260, 261, 286–288, 290–292, 295, 297–303, 306–310, 318, 445

o

organic functionalization 73
 5-organo-1,3,2,4-dithiadiazolyl 486–489
 organometallic 76, 77, 79
 organoselenium 350, 351
 ortho-metallation directing group 237
 oxidative addition 76, 80
 oxidative functionalization 77, 79, 80, 88–91
 oxime 468–470
 oxygen-exchange (in acetone) 373
 ozone 167–171

p

palladium (Pd) 127, 130
 Pauli repulsion 61, 62
 photochemical(ly) 4, 33, 53, 59, 74, 86, 88, 144, 152, 154, 155, 157, 164, 171, 184, 185, 192, 204, 349, 356, 477, 479, 483–485, 487–489
 photochemically allowed 144, 157, 164, 184, 349, 356
 photochemically symmetry allowed 152, 185, 192, 488, 489

- pinacol 463, 464
 α -pinene 122, 123, 126, 462
 platinum (Pt) 76, 77, 79, 80, 127, 129–131
 polarizability 84
 polycyclic aromatic hydrocarbon 238
 polyhalogenated alkane 348
 polypeptide 45, 192, 195, 384, 388, 403, 407
 poor leaving group 224, 258–260, 265, 301, 338, 344, 358
 primary carbocation 35, 84, 98, 266, 287, 297, 341, 342, 459, 462
 product development 134, 278, 284, 285
 proton tunneling 89, 91
 pyrolysis 345, 346
- q**
 quadricyclane 190, 191
 quinone 229. *Also see “benzoquinone”*
- r**
 radical addition 70, 71, 74, 116, 148
 radical bromination 42, 63, 70, 73
 radical chlorination 60, 66–68
 radical halogenations 42, 59, 63, 64, 67–71, 74
 radical initiator 73, 74, 96, 116
 radical substitution 68
 rate law 6, 7, 9, 12, 42, 69, 71, 202, 225, 263, 269, 278, 280, 289, 290, 298, 319, 335–337, 345, 358, 411, 413
 1,2-rearrangement 356, 357, 464, 465, 468, 470, 475–479
 redox 167, 207–210, 217–219, 386
 regiochemistry 96, 98, 101–103, 111, 113, 116, 118, 121, 123, 138, 141, 159, 160, 226, 317, 318, 320, 324, 338, 340, 342–344, 358, 420, 427, 473
 regioselective 70, 97, 103, 124, 138, 160, 165, 216, 238, 320, 420, 473, 475
 regioselectivity 63–66, 68, 70, 72, 74, 98, 100, 106, 107, 120, 123, 124, 136, 160, 166, 173, 217, 292, 293, 420, 427, 473, 474
 resonance stabilization 30, 31, 56, 57, 59, 103, 105, 208, 209, 214, 221, 261, 262, 299, 417, 419, 421, 442, 463, 464, 466
 retinol 485
 reversibility 14, 15, 185, 370, 371, 393, 418
 ring closure 4, 112, 181, 182, 184, 223, 377–379, 396
 ring contraction 467, 470
 ring expansion 458, 461–464, 467, 469, 473
 ring-opening 4, 181, 182, 192, 193, 212, 213, 377–379
 Robinson annulations 443
- s**
 SbF_5 initiated rearrangement 459
 secondary carbocation 36, 82, 98, 103, 106, 110, 215, 219, 284, 288, 297, 298, 339, 341, 359, 461–464
 semipinacol rearrangement 464
 serine-type hydrolase 403
 S_N1 mechanism 258, 266, 278, 279, 287, 288, 290
 S_N1 reaction 3, 36, 101, 224, 258, 266, 278, 280–290, 297–299, 301, 309, 310, 342, 458
 S_N2 mechanism 219, 224, 258, 259, 261, 264, 265, 272, 273, 277, 286–290, 296, 304, 423
 S_N2 reaction 3, 18, 19, 37, 224, 225, 258, 261, 263–273, 275–278, 280, 283, 284, 286–290, 292–297, 301, 303, 310, 311, 319, 323, 332–336, 424, 427, 445, 446
 steady-state 9–13, 69, 71, 79, 279, 337, 411
 stereospecific 44, 116, 122, 124, 125, 135, 136, 138, 153, 165, 173, 219, 263, 292, 325, 346, 348, 350, 387, 429, 432, 436–438, 447, 451, 465, 466

- stereospecificity 438, 466
 steric effect 124, 125, 209, 262, 287
 steric hindrance 21, 82, 85, 102, 109, 118,
 122–124, 177, 178, 221, 227, 234,
 243, 266–268, 280, 287, 319–321,
 324, 332, 335, 347, 381, 420
 stereochemical control 137
 stereochemistry
 in aldol reactions 432
 in alkene additions 96, 98, 101, 102,
 113, 118, 120, 121, 123, 124, 127,
 129, 133, 135, 138
 in cycloadditions 145–147, 149, 150,
 152, 154, 155, 165, 177
 in eliminations 317–319, 325, 338,
 340, 342
 in rearrangement 477
 in S_N1 and S_N2 reactions 263–265,
 286, 300
 stilbene 247
 styrene 101–103, 188, 189, 216, 217
 substituent effect 158, 225
 sulfide 39, 82, 169, 206, 208, 209, 247,
 248, 265, 332, 451, 452
 sulfoxide 87, 206, 208, 209, 248–250,
 272, 391
 sulfur nucleophile 379, 380
 super good leaving group 225, 259, 261,
 263, 270
 superacid 54, 80–82, 84, 96, 97, 259
 symmetry allow 152, 153, 157, 160, 165,
 169, 171, 175, 176, 179, 185, 191,
 192, 479, 486, 488, 489
 symmetry forbidden 152, 489
syn-addition 95, 96, 117–120, 126,
 128–131, 134, 135, 346
syn-elimination 317, 318, 327, 345–348
- t**
- tertiary carbocation 36, 37, 81, 98, 109,
 111, 112, 221–223, 266, 287, 338,
 341, 344, 345, 361, 459–466
 tetrahedral intermediate 368–371, 385,
 389, 391, 399, 407, 409, 410, 412,
 451, 452, 471, 473, 475
- thermodynamic control 115, 163, 164,
 341, 342
 thiolase 451, 452
 thionyl chloride 206, 207, 390, 391
 three-center, four-electron π bond 168,
 171, 173, 174, 176, 178, 188, 419,
 421, 422
 three-center, two-electron bond 82, 85,
 117
 tosylate 259, 265, 266, 289, 299–301, 322,
 323, 332, 342, 467, 468
 transesterification 401–404
 transition state
 in acyl nucleophilic substitution 369,
 393, 396
 in aldol reactions 432, 439
 in alkene additions 96, 104, 110, 111,
 113, 118, 134
 in C–H bond activation and cleavage
 40, 76, 77, 79, 80, 82, 84
 in Claisen condensations 447, 448
 in cycloaddition reactions 143, 145,
 157, 162–165, 168, 170–172, 174,
 181, 182, 184–186, 188–195
 definition 2, 4, 5, 17–19
 in E1 and E2 reactions 319, 331, 334
 in E1cb reactions 358
 in α -eliminations 356
 in enzymatic reactions 43–46, 389,
 407
 general description 4, 22
 in hydrophobic interface 48
 in nucleophilic addition to carbonyl
 376, 377
 in radical halogenations 42, 59, 61, 62,
 65, 66, 75
 in rearrangement 458, 479–481
 in S_N1 and S_N2 reactions 3, 258, 263,
 264, 266, 268–273, 280, 283, 284,
 306–308
 in unimolecular eliminations 318,
 345–349, 353
 triflic acid 77, 80, 82, 83, 259
 triflate 77, 225, 259
 trypsin 403, 405–407

thermal(ly) 4, 5, 53, 59, 68, 71, 73–75, 80, 86–88, 143, 144, 152, 153, 156, 157, 164, 165, 168, 170–172, 175, 176, 178, 179, 181, 182, 184, 188, 191, 202, 204, 243, 345, 349, 479, 483, 489

thermally allowed 157, 164, 168, 176, 178, 181, 182, 188

thermally forbidden 144, 157, 164, 184

u

unimolecular eliminations 318, 345–349, 353

unimolecular reaction 4, 6, 347

unsaturated aldehyde 429

unsaturated ketone 130, 293, 376,

429–431, 433–435, 442

uranyl 86

v

vinyl 36, 56, 67, 68, 87, 113, 114, 183, 272, 287, 326, 441, 442, 479–482

vitamin 192, 193, 352

W

Wagner–Meerwein rearrangement 458

Williamson ether synthesis 270, 332

Wittig reaction 296, 297

X

xylene 73, 74, 216, 217, 233

Z

(*Z*)-enolate 432, 438, 440, 447, 448

zinc 45, 46, 148, 150, 350–352. *Also see* Zn.

zwitterion 110, 296

zwitterionic adduct 206–209, 213, 217

Zn 45, 46, 148, 150, 350–352. *Also see* zinc.

