

Index

a

- acetals
 - as electrophiles 13, 111
 - oxidation 151
- acetanilides
 - acylation 91, 94, 99
 - alkylation 184
 - arylation 182, 184
 - conversion to indolines 184
 - cyclization to benzoxazoles 142, 194
 - halogenation 129, 131, 142
 - hydroxylation 182
 - nitration 172, 175
 - olefination 49
- acetic formic anhydride 106, 111
- acetone
 - arylation 27
 - preparation 30
- acetophenones
 - arylation 32
 - ortho alkylation 8
 - ortho olefination 48
 - reaction with XeF_2 132
- acetoxylation 172, 181
- acetylenes, see alkynes
- acetyl nitrate 164, 170
- acid catalysis
 - ether cleavage 89
 - isomerizations 89, 99, 210
 - $\text{S}_\text{N}\text{Ar}$ 211
- acrylates
 - alkylation with 10, 23
 - oxidative arylation 48–53
- acryloyl chloride 87, 100
- active hydrogen compounds, arylation 209, 214, 221, 226, 234, 235
- acylation of
 - acylarenes 89, 93
 - alkenes 88–90
 - alkynes 88–90
 - anilines 90–92
 - arenes 85–111
 - arylketones 89, 93
 - enamines 100
 - indoles 97, 108
 - nitroarenes 92
 - phenols 90–92
 - phthalic anhydride 100
 - pyridines 94
 - thiophenols 90–92
- acyl fluorides 86
- acyl halides
 - decarbonylation 95
 - isomerization 99
- acyl peroxides, as precursors to radicals 67
- alcohols
 - arylation 217, 218, 250
 - as electrophiles 94
 - oxidation 94, 227
 - reaction with diazonium salts 228
 - reduction 259
- aldehydes
 - as electrophiles 13, 94
 - conversion to acyl radicals 110
 - halogenation 151
 - oxidation 94, 151
- alkali fusion of aryl sulfonates 218
- alkanesulfonyl halides, arylation 192
- alkenes
 - acylation 88–90
 - alkylation with 4, 8–10, 14, 16–23
 - arylation 45–54
 - halogenation 148
 - olefination with 22, 45–52
- alkylation of
 - arenes 1–34

- alkylation of (*contd.*)
 - aryl halides 214, 221, 226, 233, 234, 236, 237, 240, 248
- alkyl chloroformates 105
- alkyl esters, as electrophiles 98, 101–103
- alkyl fluorides, as electrophiles 6
- alkyl groups
 - amidation 183
 - arylation 11, 213
 - dehydrogenation 32, 170
 - halogenation 126, 134, 138, 146, 148, 151
 - hydroxylation 164
 - isomerization 89, 99
 - nitration 164
 - oxidation 164, 166, 169, 170
 - substitution 125, 139, 163, 164, 170
- N-alkylpyridinium salts, as electrophiles 1
- alkynes
 - acylation 90
 - arylation 54–56
 - oxidative dimerization (Eglinton reaction) 57
 - reaction with BrCN 107
- allenes
 - arylation 52
 - formation 55
- allylic electrophiles 17, 22, 52, 53
- aluminum anilides 18
- amidation
 - of alkanes 183
 - of arenes 177–184
- amides
 - N-arylation 173, 180, 245
 - N-benzylation 183
 - halogenation 151, 152
 - hydrolysis 127
 - nitration 169
 - oxidation 152
- amination of arenes 175–177
- amines
 - alkylation 4, 14, 17, 18, 258
 - arylation 176, 242–248, 254
 - dealkylation 92, 100, 141, 142, 148, 244, 248
 - dehydrogenation 100, 141
 - displacement 9, 238
 - as electrophiles 1
 - nitration 165, 171
 - nitrosation 142, 166
 - oxidation 100, 148
 - reaction with acyl halides 100
 - reaction with diazonium salts 227
 - reaction with halogens 148
- aminoalcohols
 - arylation 217
 - as electrophiles 33
- ammonia, arylation of 241–243
- anhydrides, mixed carboxylic 110
- anilines
 - acylation 90
 - alkylation 13–18, 258
 - arylation 176, 218, 245, 246
 - conversion to benzimidazoles 181
 - conversion to phenols 207
 - dealkylation 92, 142, 148
 - formation 214, 241–243
 - halogenation 138–143
 - nitration 164, 166, 171
 - nitrosation 142, 166, 174
 - oxidation 138, 140–142, 148
 - sulfonylation 199
 - sulfonation 191
 - trifluoromethylation 16
 - tritylation 16
- anthracenes, halogenation 126
- anti Markovnikov addition 20
- arenesulfonic acids
 - formation 191, 217, 225, 229
 - S_NAr 206, 218
- aromatic nucleophilic substitutions 205–259
 - acid-/base-catalysis 211
 - mechanisms 205
 - regioselectivity 205
 - transition-metal catalysis 211
- arylations with aryl halides 61–69
 - via cationic intermediates 61–63
 - via radicals 63–65
 - by transition-metal catalysis 67–69
 - via transition-metal chelates 65–67
- arylations with diazonium salts 69–73
- arylations with unsubstituted arenes 78
- aryl cations 62, 63
- aryl esters
 - Fries rearrangement 91, 106
 - S_NAr 232
- arylethers
 - dealkylation 88, 89, 103, 206
 - S_NAr 207, 229, 230, 236, 237
- aryl halides
 - arylation 61–69
 - dehalogenation 71, 145, 229, 236, 241, 243, 249, 254, 255, 259
 - formation 121–152, 253, 259
 - homocoupling 71
 - hydrolysis 248, 250
 - isomerization 210
- aryl thioethers
 - cleavage 150, 231, 257

- formation 196–201, 216, 225, 227, 229, 230, 252, 253
- halogenation 149–151
- isomerization 99, 210
- arynes 195, 218, 232, 233, 241
- azide ion, arylation of 247–250
- azides
 - amidations with 181
 - decomposition of 145
 - formation 182, 247–250
 - reduction 145, 249, 250
- aziridines 24
- azoles
 - acylation 93–98
 - alkylation 19
 - halogenation 144–146
 - nitration 167, 173

b

- Bamberger cleavage 94, 96
- Bartoli reaction 238
- benzaldehydes
 - as acylating reagents 94
 - acylation 86
 - as alkylating reagents 10, 13
 - arylation 70
 - formation 106–110, 149
 - halogenation 122, 129, 139, 151
 - nitration 162, 163
 - olefination 49
 - S_NAr 216
 - sulfonylation 191
- benzamides, hydrolysis 127
- benzimidazoles
 - C-alkylation 10, 19
 - N-arylation 217
 - formation 179, 181
- benzofurans
 - from 2-arylphenols 139
 - from 1,2-dihalobenzenes 235
 - dithiocarboxylation 104
- benzoic acid derivatives
 - acylation with 86, 91–96, 101
 - alkylation 7, 8, 11
 - amination 175
 - arylation 69
 - decarboxylation 74, 136, 164
 - formation 101–108
 - halogenation 127, 134–137
 - nitration 163
 - olefination 49, 52, 55
 - preparation 101–108
- benzonitriles
 - amination 175
 - arylation 64
 - formation 107, 108, 178, 219, 224, 226, 230
 - halogenation 137
 - hydrolysis 137, 251
 - nitration 169
 - S_NAr of cyano group 209
- benzophenone
 - as alkylating reagent 10
 - alkylation 7
 - nitration 165
- benzoquinone
 - as oxidant 46, 52, 53, 75, 76
 - preparation 141
- benzoquinones
 - alkylation 11
 - formation 138, 141, 152, 173
 - nitration 174
- benzothiazoles
 - arylation 70
 - formation 230
- benzotriazoles, formation 179
- benzoxazoles
 - acylation 98
 - aminomethylation 4
 - from anilides 142
 - arylation 98
- benzylic
 - acylation 97
 - alkylation 211
 - arylation 16
 - cyanation 211
 - halogenation 126, 134, 138, 141, 146, 151
 - nitration 164, 169
 - substitution vs S_NAr 212, 213
- biaryls, formation 61–79
- binaphthol 78
- bis(chloromethyl)ether, as electrophile 7
- boronic acid esters
 - arylation with 9
 - olefination with 48
- boronic acids
 - arylation with 75
 - halogenation 137, 142
 - nitration 163
- boron trihalides 26, 90, 91
- bromination of
 - arenes with $BrCN$ 107
 - benzaldehyde 150
 - benzyl bromides 148
 - hydroquinones 139
 - indanes 126
 - phenols 6, 139
- 2-bromomalonates, as brominating reagent 6

- N*-bromosuccinimide 123
- tert*-butyl chloride, as electrophile 3, 6
- tert*-butyl groups
 - introduction with pivaloyl chloride 99
 - ipso substitution 89
- tert*-butyl iodide 11
- butyrolactone, as electrophile 101, 102

- c**
- caffeine, arylation 75
- Cannizzaro reaction 9, 216, 217
- carbamates
 - as electrophiles 105, 108, 111, 232, 237
 - as nucleophiles 214
- carbamoyl chlorides 105
- carbazoles
 - bromination 130
 - carboxylation 103
 - dimerization 130, 179
 - formation 179, 184, 239, 246
 - iodination 140
- carbenes
 - aromatic C–H insertion 28
 - dimerization 93, 96
 - reaction with phenolates 107–109
- carbocations
 - hydride abstraction by 6, 89
 - rearrangement 6, 7, 22, 102
- carbodiimides, cyclization to benzimidazoles 179
- carbonate ion, arylation 252
- carbonic acid derivatives, as electrophiles 101–107, 232, 259
- carbon dioxide, as electrophile 104
- carbon disulfide, as electrophile 104
- carbon monoxide
 - acylations with 95, 98
 - carboxylation with 105
 - extrusion from acyl cations 95, 99
 - formylations with 106
- carboxylation 101–105
- carboxylic acids
 - conversion to radicals 73, 74
 - decarboxylation 73, 74, 136, 163, 256
 - as electrophiles 86, 99
 - formation 101–105, 150, 165, 167, 169
 - as leaving group 232
 - as nucleophiles 252
 - O-arylation 252
- carboxylic anhydrides 110, 111
- carboxylic esters
 - as electrophiles 89, 92, 98–103, 232, 236, 250
 - formation 104, 106, 108, 149, 252
- catalysis
 - Friedel–Crafts acylation 85
 - Friedel–Crafts alkylation 2–5
 - halogenation 128, 129
 - nitration 167
 - poisons 50
 - S_NAr 211
- catechols, fluorination 132
- chelate formation 46, 48, 65, 68, 69
- chloramines 175, 178
- chlorination 121–152
- chloroacetic acid 25
- chloroacetic esters 25–27
- chloroacetone, as electrophile 25–27
- chloroacetonitrile 26
- chlorobenzene, conversion to phenol 217
- chloroformates 105, 108, 259
- chloromethylation 7
- N*-chlorosuccinimide 123, 134, 137, 146, 150
- chromanes, formation 14
- chromium carbonyl complexes 218
- cine substitution 207–209
- cinnamic acid anhydride, olefination with 48
- cinnamic acid esters, from acrylates 48, 49
- cumene (isopropylbenzene)
 - conversion to phenol 30
 - as hydride donor 6
- cyanation
 - electrophilic 104, 107, 108
 - nucleophilic 214, 219, 224, 226, 230
- cyanide ion
 - as leaving group 209, 234
 - from DMF 79
 - in S_NAr 214, 219, 224, 226, 230
- cynoacetic esters
 - arylation 214
 - reaction with nitroarenes 226
- cyanogen halides 104, 107, 108
- cyanohydrins, as electrophiles 32
- cyanuric chloride, arylation 61, 62
- cyclohexanes, arylation 11, 213
- cyclohexenones 12, 15
- cyclopropanoyl chlorides, isomerization 99

- d**
- DDT 1
- dealkylation, of
 - amines 92, 100, 142
 - arenes 89, 125, 139, 163, 170
 - ary ethers 88, 89, 206, 207, 230, 236, 250
 - benzylic alcohols 125, 139
 - pyridines 169
- dearomatization 15, 126, 130–132, 138, 139, 169, 205

- decarbonylation, of acyl halides 95, 99
 - decarboxylation 73, 74, 136, 163, 256
 - decyanation 209
 - dediazonation 226–228
 - deformylation 53, 163
 - dehalogenation
 - aryl halides 71, 229, 236, 241, 243, 249, 254, 255, 259
 - imidazoles 144, 145
 - thiazoles 145, 241
 - dehydration, of propanol 30
 - dehydrogenation
 - of alkyl groups 32, 170
 - of amines 100, 141
 - of β -ketoesters 32
 - during nitrations 170
 - with thionyl chloride 198
 - dehydroxylation, phenols 20, 229, 259
 - diacylperoxides, as precursors to radicals 11, 65, 67
 - 1,1-diarylalkanes 17, 28, 30, 31
 - diarylamines
 - arylation 179, 218, 246
 - conversion to carbazoles 179
 - formation 239
 - oxidation 179
 - dialkoalkanes 1
 - diazocarbonyl compounds 26, 28, 171
 - diazomethane 11
 - diazonium salts
 - arylation of (Gomberg–Bachmann) 226
 - conversion to indazoles 69
 - dediazonation of 69, 72–74
 - hydrolysis of 74
 - as precursors to arynes 233
 - reaction with alcohols 227, 228
 - S_NAr reactions of 228
 - 1,3-dicarbonyl compounds, arylation 30, 209, 234, 235
 - dichlorocarbene 107, 108
 - dichloromethane, as electrophile 4
 - Diels–Alder reaction, of furans 54
 - 1,1-dihaloalkenes, as electrophiles 88
 - diketene, arylation 103
 - diketones, arylation 30, 235
 - dimerization, of
 - arenes 32, 62, 66, 122, 128, 130, 178, 179, 240
 - aryl halides 71, 240, 255
 - boronic acids 75
 - diazonium salts 228
 - fluorenes 225
 - furans 53
 - imidazoles 76, 96
 - indoles 97, 173, 194
 - oxazoles 74
 - oxiranes 24
 - phenols 78
 - pyridines 76, 96
 - dimethylformamide (DMF)
 - arylation 216
 - conversion to cyanide ion 79
 - formylations with 108, 130
 - as solvent for Friedel–Crafts acylations 92
 - as source of dimethylamine 243
 - dimethylsulfoxide (DMSO)
 - as solvent 197
 - thiomethylation with 200
 - diols, arylation 253
 - diquat 76, 78
 - disulfides
 - arylation 199–201
 - formation 149
 - dithiocarboxylic acids, preparation 103
 - Dow phenol synthesis 217, 218
 - Duff reaction 107, 108
 - durene (1,2,4,5-tetramethylbenzene)
 - acylation 93
 - alkylation 22
 - nitration 164
- e**
- Eglinton reaction 57
 - enolates, arylation 209, 214, 226
 - epichlorohydrin 24
 - epoxides, arylation 23, 24
 - esters
 - as electrophiles 98, 100–103, 232, 236
 - formation 104, 106, 108, 149, 252
 - reaction with azides 250
 - ethanolamines, as electrophiles 33
 - ethers
 - alkylation with 17
 - cleavage 89, 149, 233
 - halogenation 149
 - nucleophilic displacement 207, 230, 236, 237
 - ethylation, of benzene 3
 - ethylene glycol, as electrophile 33
- f**
- ferrocene, acylation 87
 - fluorene, alkylation 32
 - fluorenones
 - as electrophiles 16, 28
 - formation 74, 77, 105
 - nitration 162

- fluoride ion, arylation 129–132, 258
- fluorination 129–132
 - of acetanilides 131
 - of arylketones 129, 132
 - of benzamides 127
 - of benzylic alcohols 125
 - of catechols 132
 - of indoles 131
 - of nitroarenes 258
 - of phenols 259
 - of pyridines 124
- formaldehyde, reaction with
 - aniline 17, 18
 - terephthalic acid 7
- formamides, arylation 216
- formic acetic anhydride 106, 111
- formic acid, carboxylation with 105
- formylation 106, 130
- formyl fluoride 106
- Friedel–Crafts
 - acylation 85–111
 - alkylation 1–34
 - catalysts 85
 - solvents 87, 92
- Fries rearrangement 91, 106
- furans
 - acylation 104
 - alkylation 3
 - Diels–Alder reaction 54
 - dimerization 53
 - halogenation 123
 - nitration 162
 - olefination 53
 - sulfonylation 123

g

- Gattermann–Koch reaction 106
- glucose, as reducing reagent 71, 216
- glycidyl ethers, as electrophiles 23, 24
- glycolic acid, alkylation of indole 33
- Gomberg–Bachmann reaction 69
- Grignard reagents, S_NAr with 235–237

h

- Hale–Britton process 217, 218
- halide ions, arylation of 253, 258
- Haller–Bauer reaction 9, 217
- N*-haloamides 142, 181
- N*-haloamines 175, 178
- α -haloesters, as electrophiles 6, 24, 25, 27, 101
- haloform reaction 104
- halogenation 121–152
 - regioselectivity 125

- halogen dance 210
- N*-haloimides
 - as halogenating reagents 121–123
 - isomerization 123
- α -haloketones, as electrophiles 25–27
- α -halosulfones, vicarious S_NAr 219
- hard and soft organometallics
 - reaction with lactones 102, 103
 - S_NAr 235–241
- Heck reaction 21, 22, 46, 50, 53
- hexanitrobenzene 161
- Hofmann rearrangement 152
- homodimerization, see dimerization
- Hunsdieker reaction 136
- hydrazines
 - arylation 230, 245
 - conversion to radicals 73
 - vicarious nucleophilic substitution 222
- hydrazones, reaction with nitroarenes 222
- hydride ions, as leaving group in S_NAr 205, 219
- hydrogen fluoride, as solvent 21, 85
- hydrolysis, of aryl halides 248
- hydroperoxides 30, 222
- hydroquinones, halogenation 139
- hydroxamic acids, olefination 50, 52
- hydroxide ion, arylation of 248
- hydroxyalkylation 7, 10, 24, 30
- hydroxylamine, as reducing reagent 216
- hydroxylamines, isomerization 224
- hydroxylation, aromatic 182
- hydroxylation, as side reaction of
 - carboxylation 105
 - halogenation 124, 131, 144, 146
 - nitration 171
- hydroxymethylation 7

i

- imidazoles
 - acylation 95
 - alkylation 10, 19
 - arylation 75, 76
 - cleavage 96
 - dehalogenation 145
 - dimerization 76, 96
 - halogenation 143–145, 209
 - nitration 209
- imides
 - *N*-arylation 183
 - *N*-halo 121–123
- indanes
 - bromination 126
 - formation 22, 90, 100, 102
- indazoles, from arenediazonium salts 69

- indenes, formation 55, 138
 - indoles
 - acylation 97, 98, 148
 - alkylation 19, 24, 31, 33, 206
 - alkynylation 47
 - amidation 181
 - amination 124, 178
 - arylation 70, 208, 217
 - azidation 182
 - conversion to quinolines 109
 - deformylation 53
 - dimerization 97, 173, 194
 - fluorination 131
 - formation 50, 55, 240
 - formylation 108
 - halogenation 124, 131, 143–147, 150, 193
 - nitration 173
 - olefination 53, 54
 - S_NAr 208, 230
 - sulfenylation 200
 - sulfonylation 193, 194
 - trimerization 146
 - interhalogens, halogenation with 122
 - iodide ion, as reducing agent 259
 - iodonium salts
 - arylation with 75, 180, 182, 235, 253, 257
 - formation, during halogenations 125
 - iodination with 181
 - ionic liquids, as solvents for acylations 87
 - ipso substitution, of
 - acyl groups 132, 163, 165
 - alkoxy groups 9, 183, 229, 230
 - amino groups 9
 - benzyl groups 170
 - boron 75, 137, 163, 174
 - carboxyl groups 74, 136, 163
 - diazonium groups 69–73, 226
 - ethyl groups 89
 - halides 53, 61–69, 164, 205–259
 - hydroxyalkyl groups 125, 139, 170
 - hydroxyl groups 20, 132, 229
 - methyl groups 164
 - nitro groups 219
 - silanes 163
 - sulfonyl groups 195
 - *tert*-butyl groups 89, 163
 - isocyanates, as electrophiles 108
 - isomerization of
 - alkylarenes 89
 - cyclopropanoyl halides 99
 - polyhaloarenes 210
 - thioethers 99, 210
 - isopropylbenzene (cumene)
 - conversion to phenol 30
 - as hydride donor 6
 - isothiocyanates, formation by S_NAr 257
- k**
- ketones
 - cleavage 132, 165
 - as electrophiles 10, 25–32
 - fluorination 132
 - as nucleophiles 211, 233
 - Kolbe–Schmitt reaction 103
- l**
- lactams
 - N-arylation 180
 - halogenation 146, 151
 - nitration 169
 - from pyrroles 144, 178
 - lactones
 - arylation 234
 - as electrophiles 89, 101–103
 - formation 7, 170
 - lithiation vs alkylation of haloarenes 235–237
- m**
- malonic esters
 - arylation 209
 - 2-bromo, as brominating reagent 6
 - malononitrile, as source of cyanide 226
 - Markovnikov addition 20
 - Meerwein arylation 227
 - Meisenheimer salts 206
 - mercaptans
 - alkylation 231, 257
 - arylation 252
 - halogenation 149–151
 - mesitylene
 - alkylation 6, 25
 - chlorination 178
 - olefination 47
 - mesylates
 - cleavage 231
 - as electrophiles 25
 - meta-selective reactions 4, 51, 140, 174
 - methoxy groups
 - dealkylation 89, 230, 236
 - displacement 9, 48, 230, 236, 247
 - as nucleophile in S_NAr 220, 254
 - methylation 19, 20
 - Michael addition 21, 23, 29
 - Mitsunobu reaction 11
 - mixed carboxylic anhydrides 110
 - mixed carboxylic carbonic anhydrides 111

n

- naphthalenes
 - nitration 167
 - oxidative degradation 167
 - S_NAr at 206, 214, 216, 222, 223, 225, 229, 230, 237, 248, 256, 258
- nitramines 172
- nitration of arenes 161–175
 - catalysis 167
 - electron-deficient arenes 167
 - mechanisms 161
 - regioselectivity 164
- nitrile oxides 27, 74
- nitriles
 - displacement of cyano group 209
 - formation by S_NAr 212, 214, 219, 220, 223, 224, 226
- nitrite ion, arylation 244
- nitroalkanes
 - as electrophiles 26–29
 - as nucleophiles 221
- nitroalkenes, arylation 21, 29
- nitroarenes
 - amination 176, 222
 - cyanation 220, 223, 224, 226, 230
 - as dipolarophiles 219, 222
 - formation 161–175, 244
 - halogenation 133, 137
 - hydroxylation 222
 - reaction with alcohols 227, 253, 254
 - reaction with C–H acidic compounds 226
 - reaction with halide ions 253, 258
 - reaction with hydrazones 222
 - reaction with Grignard reagents 239, 240
 - reaction with sulfide ion 220
 - reaction with thiols 256
 - reduction 220, 224, 225, 227, 259
 - S_NAr reactions of 219
 - vicarious nucleophilic substitution 107, 219, 221
- nitrobenzene
 - acylation 92
 - arylation 69, 77
 - chloromethylation 7
 - conversion to 3-phenylindole 55
 - as solvent 87, 219
- nitromethane, as solvent 87, 194
- nitrosation 142, 166
- nitrosoarenes, formation 142, 166, 239, 240
- norbornene, reaction with aniline 17
- nucleophilic substitution,
 - aromatic 205–259

o

- olefination with alkynes 54–57, 90
- olefination with leaving-group-substituted
 - olefins 45–48
- olefination with unsubstituted olefins 46–54
- olefins
 - acylation 88–90
 - alkylation with 4, 8–10, 14, 16–23
 - arylation 45–54
 - halogenation 148
 - olefination with 22, 45–52
- organomagnesium compounds, S_NAr with 235–237
- organometallics, hard and soft
 - acylation 94, 97, 102, 103
 - arylation 235–241
 - reaction with lactones 102, 103
- ortho alkylation of acetophenones 8
- ortho-directed halogenation 127–129
- ortho-directing groups 46, 68
- orthoesters, formation 91, 109
- oxalyl chloride 92, 95, 104, 106
- oxazoles
 - acylation 98
- from anilides 142
- arylation 74, 98
- dimerization 74, 77
- oxidation of
 - acetals 151
 - alcohols 94, 139, 227
 - aldehydes 94, 150, 151
 - alkyl groups 164, 166, 169, 170
 - amines 100, 148
 - anilines 18, 138, 141, 148
 - diarylamines 179
 - diarylmethanes 18
 - naphthalenes 167
 - phenols 173
 - sulfoxides 150
 - thioethers 149–151
 - thiols 149–151
 - thiophenes 162
- oxiranes, arylation 23, 24
- ozone, for nitration 161

p

- paraquat 76
- pararosaniline 18
- peroxides
 - as methylating reagents 20
- reaction with nitroarenes 222
- Pfitzner–Moffatt oxidation 195
- phenacyl halides 25
- phenol, synthesis 28, 30, 217

- phenols
 - acylation 90
 - alkylation 9, 11, 20, 26
 - arylation 15, 66, 139, 235, 246
 - carboxylation 103, 105
 - conversion to aryl halides 259
 - deoxygenation 20, 132, 229
 - dimerization 78
 - as electrophiles 15
 - formation 105, 171, 217, 248, 251
 - formylation 106–109
 - halogenation 6, 132, 139, 147
 - methylation 20
 - nitration 164, 173, 174
 - nitrosation 174
 - oxidation 173, 174
 - S_NAr reactions of 206, 229
 - sulfenylation 196, 199
 - phenylacetic acids, halogenation 127
 - phenylalanine, halogenation 127
 - phosgene 90, 96, 104, 106
 - phosphines, arylation 217
 - phthalic acids
 - acylation 100
 - as electrophile 93
 - formation by oxidation of naphthalenes 167
 - Piria reaction 224, 225
 - pivaloyl chloride, decomposition 99
 - polyelectrophiles 22, 23, 100, 110
 - polyhaloarenes, isomerization 210
 - polynitroarenes, preparation 162–173
 - 1-propanol, as electrophile 7
 - propiolactones, as electrophiles 103
 - Pummerer reaction 197
 - purines, S_NAr 206, 213
 - pyridine
 - arylation 66, 71, 75, 76
 - dimerization 76, 96
 - halogenation 124, 133–136
 - nitration 168
 - olefination 56
 - pyridines
 - acylation 94, 110
 - alkylation 11, 12, 234
 - amination 175, 176
 - arylation 65, 66, 68, 70, 71, 76
 - cyanation 214
 - dealkylation 169
 - dimerization 76, 96
 - halogenation 124, 133–136
 - metallation 94
 - nitration 168
 - olefination 47, 49, 53
 - pyridine *N*-oxides
 - alkylation 10, 22
 - arylation 53, 64, 78
 - halogenation 135
 - nitration 168
 - olefination 49, 53
 - pyrroles
 - alkylation 24, 27, 31
 - amidation 180
 - amination 135
 - arylation 66, 75
 - conversion to lactams 144
 - conversion to pyridines 109
 - dimerization 130
 - formation 76
 - halogenation 123, 130, 135, 143, 144
 - imidation 123
 - nitration 162
 - sulfenylation 123, 197
 - sulfinylation 197
- q**
- quaternization of amines, by arylation 244, 248
 - quinolines
 - formation 109, 227
 - formylation 110
 - from tetrahydroquinolines 141
 - S_NAr 215, 240
 - quinones
 - addition of nitrite to 174
 - alkylation 11, 12
 - from anilines 141
 - from benzamides 152
 - from phenols 173, 174
- r**
- racemization, of electrophiles during alkylations 1, 5
 - radicals, arylation 11, 12, 20, 27, 63–67, 72–74, 110
 - rearrangement
 - allylic 21, 22, 52, 53, 55
 - of carbocations 5, 6, 89, 93
 - of cyclopropanes 99
 - of hydrazones 179
 - of polyhaloarenes 138, 210
 - of sulfoxides 197
 - of thioethers 99, 210
 - von Richter 220, 223
 - reduction of
 - aryl halides 71, 145, 229, 236, 241, 243, 249, 254, 255, 259
 - azido groups 145, 249, 250

reduction of (*contd.*)
 – bromomalonates 6
 – nitro groups 220, 225–227, 239, 249, 254
 – sulfoxides 150, 196, 197
 – tertiary alcohols 31
 reductive alkylation 31
 Reimer–Tiemann reaction 107–109
 resveratrol, iodination 147
 rhodanide ion, arylation of 257

S

saccharin, N-benylation 183
 salicylic acid, preparation 103
 Sandmeyer reaction 227
 scavengers, for halogenations 138, 147, 148
 Scholl reaction 7
 Schotten–Baumann procedure 193
 silanes
 – ipso substitution 163
 – nitration 163
 – reaction with benzyl esters 101
 – as reducing agents 31
 S_NAr 205–259
 – vs benzylic substitution 211, 212
 – solvent effects 207, 234, 236
 solvents for Friedel–Crafts acylation 87, 92, 103
 solvents for oxidations 51
 steric crowding, S_NAr 219
 stilbenes
 – formation 27, 48–50, 54, 55, 241
 – halogenation 147
 styrene
 – arylation 16
 – dimerization 90
 styrenes
 – acylation 88, 90
 – formation 45–57
 substitution, aromatic
 nucleophilic 205–259
 succinimides, N-halo 121–123
 sulfenylation 199–201
 sulfide ion, S_NAr 220
 sulfinates
 – arylation with 75
 – conversion to sulfoxides 196, 197
 – formation 193
 sulfinylation 195
 sulfite ion, arylation 225
 sulfolane, as solvent 87, 92
 sulfonamides, N-arylation 180, 181
 sulfonates (sulfonic acid esters)
 – cleavage 231, 243
 – formation 191

sulfones
 – formation 191–194
 – S_NAr 208, 235
 sulfonic acids
 – formation 191, 217, 225, 229
 – S_NAr 206
 sulfonic acid anhydrides, arylation 192
 sulfonic acid esters, see sulfonates
 sulfonium salts, formation 196
 sulfonylation 191
 sulfonyl halides
 – arylations with 194
 – conversion to sulfones 194
 – formation 191, 192
 sulfoxides
 – alkylation with 10
 – as electrophiles 196
 – formation 196, 197
 – isomerization 197
 – reduction 150
 sulfur fluorides 132
 sulfuric acid
 – as solvent 141
 – sulfonylation with 191
 sulfuryl chloride (SO_2Cl_2)
 – chlorination with 140, 195
 – sulfonylation with 195
 Swern oxidation 195

T

tele substitution 207–209
 terephthalic acid
 – hydroxymethylation 7
 – iodination 135
 tertiary amines
 – N-arylation 244, 248
 – dealkylation 92, 100, 142, 148, 166, 248
 – dehydrogenation 100
 – displacement 238
 – nitrosation 142, 166
 tetrahydroquinolines
 – halogenation 141, 147
 – nitration 171
 tetralones
 – arylation 32
 – formation 15, 88, 101, 102
 1,2,4,5-tetramethylbenzene (durene)
 – acylation 93
 – alkylation 22
 – nitration 164
 thiazoles
 – arylation 70, 74, 77
 – dehalogenation 145, 241
 – dimerization 77

- formation 141
- thiocyanates, formation 107, 124
- from anilines 124
- by S_NAr 257
- thioethers
 - cleavage 150, 257
 - conversion to thiocyanates 107
- formation 123, 208, 216, 220, 225, 227, 229, 230, 233, 252
- halogenation 149–151
- isomerization 99, 210
- nucleophilic displacement 13, 88, 229–231
- oxidation 149–151
- thiols
 - arylation 216, 220, 225, 229, 252, 253
 - formation 220, 257
 - halogenation 149–151
- thionyl chloride ($SOCl_2$)
 - chlorinations with 150, 198
 - dehydrogenations with 198
 - reaction with anilines 140
 - reaction with cinnamic acids 198
 - reaction with pyridine 96
 - reaction with sulfoxides 150, 196
 - sulfinylations with 198
- thiophenes
 - acylation 102, 110
 - alkylation 10, 33
 - arylation 63, 64, 78
 - cleavage 227
 - dimerization 76
 - formation 198
 - metallation 10, 102
 - nitration 162, 163
 - olefination 51, 53
- thiophenols
 - acylation 90, 91
 - alkylation 13
 - arylation 230
 - formation 220, 231, 257
- toluene
 - bromination 126
 - reaction with CS_2 103, 104

- toluenesulfonamides, halogenation 127
- tosyl chloride, chlorination with 123, 128
- triarylmethane dyes 18
- triazenes, cyclization to benzotriazoles 179
- 1,3,5-triazines, arylation 62
- triazoles, olefination 53
- (trichloromethyl)arenes, reaction with nucleophiles 209
- triethylamine, dehydrogenation 100
- trifluoromethylation 8, 16
- trihaloalkanes, as electrophiles 88, 209
- trihaloethanols, as electrophiles 32
- trinitrobenzene
 - arylation 71
 - formation 259
- trioxane 7, 110
- triposgene 106
- tritylation of arenes 16
- trityl chloride 1
- Tröger's base 17
- twofold acylation of arenes 93

u

- Ullmann coupling reaction 45, 63
- urotropine 107, 108

v

- valerolactone, as electrophile 101, 102
- vanadates, catalysts for oxidations 18
- vicarious nucleophilic substitution 107, 219, 221
- Vilsmeier reaction 92, 106
- vinyl acetates, as electrophiles 48
- vinyl carbocations 47
- vinylsilanes, alkylation with 9
- von Richter rearrangement 220–223

x

- xenon fluorides 132
- xylene, nitration 164, 171

