

Subject Index

a

absence of stereocontrol 201
acylnitrene 257
Ad-mix α 211
Ad-mix β 45, 50
(\pm)-akuammicine 126, 127, 130
aldol condensation 206
alkyne-dicobalt cluster 160
allylic 1,3-strain 42, 44, 206
anti aldol adduct 206
aza-Cope-Mannich
– reaction 129
– rearrangement 126, 127, 129, 131
– substrates 129

b

Barton-McCombie radical
 desoxygenation 201, 204
benzeneseleninic anhydride 177
Bergman cyclization 68
biomimetic
– grounds 211
– rearrangement 150, 151, 153, 154
– synthetic approach 76
– total synthesis 76
Birch reduction 15, 16, 18, 146, 151
blocking group 99
brevetoxin B 3
Breynin A 179
breynolide 186–190

c

calphostins 200
calphostin A 200–202
(+)-camphorsulfonyl oxaziridine 188

cationic ring closure 236
CeCl₃ 233
CH₂N₂ 28
change
– in reactivity 111
– in strategy 30, 314, 232
chaparrinone 125
(–)-chaparrinone 118, 122, 123
chirality transfer 209
Claisen rearrangement 228, 229, 231
Co₂(CO)₈ 160
compromising
– oxidation step 11
– reduction 59
– synthetic manipulation 35
– stereochemically linear synthetic approach 179
Corey-Fuchs homologation 65, 243, 247, 249, 254
Cp₂TiCl₂ 237
Cp₂TiMe₂ 237
critical epoxidation 11
cross-coupling 17
CSA (chlorosulfonic acid) 127, 243
CuBr · SMe₂ 53
Curtius rearrangement 57
cyclization processes 219
cyclogoniodenin 208
cyclophanic structure 255
cyclopropanation 15
(*p*-cymene)RuCl₂ 256
cytovaricin 205, 107

d

- (+)-damavaricin D 55, 59, 60
- Danheiser cyclization 264, 268
- Dauben's protocol 15, 18
- Davis
 - oxaziridine 90
 - oxidation 192
 - phenyl oxaziridine 160, 184
- DBU (1,7-diazabicyclo[5,4,0]-undecane) 163, 196, 259
- DDQ (dichloro dicyano p-bezoquinone) 90, 93, 239, 245
- dead-end 25, 135, 153, 162
- dehydrosecodine 77, 78
- dehydrotubifoline 131
- (±)-dehydrotubifoline 127
- deoxychaparrinone 122, 125
- (+)-1,3-deoxytedanolide 8, 9, 11
- desired stereochemistry 34, 202
- Dess-Martin periodinane 56, 68, 82, 85, 87, 90, 94, 154
- detour 150, 185
- diastereofacial preference 206
- DIBALH (diisobutyl aluminium hydride) 15, 23, 59, 121, 183, 184, 226, 249, 263
- Diels-Alder cycloaddition 63, 107–109, 114, 116–120, 168, 169, 233, 236
 - adduct 233
 - aza- 76, 77
 - intermolecular 110
 - intramolecular 107, 116, 108, 115
 - retro- 76, 77
 - strategy 109
- DIPT (diisopropyl tartrate) 210
- discorhabdin A 226
- discorhabdin C 220, 222–226
- distal substituent 125
- divinylcyclopropane rearrangement 143, 149
- 1,3-dimethylhexahydro-2-oxo-1,3,5-triazine group 129
- Dowd-Beckwith
 - rearrangement 102, 106, 107
 - ring expansion 100–102, 104

- drawback 189, 225, 247, 265
- dynemicin A 63, 67–70
- dysidiolide 150, 153, 154

e

- Eleutherobin 39
- endo*-transition states 119
- ent-rubifolide 252, 260
- epoxydictymene 164
- (+)-epoxydictymene 156, 157, 165, 166
- Eschenmoser-Claisen rearrangement 45, 49
- especially interesting reagents
 - Ad-mixβ [K₂OsO₂(OH)₄/K₃Fe(CN)₆/(DHDQ)₂-PHAl] 50
 - Lawesson's reagent 51
 - Dess-Martin periodinane 87
 - Ley oxidation reagent (Ley-Griffith reagent) [(Pr₄NRuO₄/NMO/4Å molecular sieve] 138
 - Grieco's alcohol dehydrating protocol 167
 - benzeneseleninyl chloride 191
 - Tebbe's reagent [Cp₂TiCl₂/(CH₃)₃Al] 237
 - Petasis's reagent [Cp₂TiMe₂] 237
- Evans-Tishchenko reduction 10

f

- facial selectivity 115
- failed imine formation 222
- failure
 - of a simple process 86
 - of a transformation 80
 - of a well-tested reaction 227
 - of cycloaddition 108
 - of the conjugated addition 33
 - of the synthesis 223
 - to cyclize 48
- Favorskii
 - rearrangement 166
 - ring contraction 158
- FeCl₃ 201
- Felkin adduct 27

Felkin-Anh model 206
figianolide B 238
Fleming-Terret cuprate 263
Friedel-Crafts ring closure 233, 236
frondosin B 28, 231, 233–236

g

goniocin 208, 210, 211
Grieco's alcohol dehydrating protocol
163
Grieco elimination 45

h

hamigerans 193, 195, 197
– hamigeran A 193, 194
– hamigeran B 193, 197
Heck
– coupling 145
– cyclization 22, 143, 145
– intramolecular 22, 142
– reaction 230
– ring closure 24
– tandem cyclization-carbonylation
22
high-risk
– epoxidation 8
– strategy 4
– work 4
Horner-(Wadsworth)-Emmons
– approach 242
– conditions 242
– cyclization 247
– olefination 59
– reaction 245, 250
– ring closure 241
Huang Minlon reduction 34, 38

i

inadequate protecting group 18
inert group 25, 80, 105
inertia of an intermediate 33
innocent remote substituent 125
Ireland reductive decarboxylation 45, 50

j

Jones oxidation 230
Julia
– coupling 132, 241
– olefination 238

k

Keck macrolactonization 135
key synthetic reactions
– aza-Cope-Mannich rearrangement
131
– Barton-McCombie radical
desoxygenation 204
– Birch reduction 18
– Corey-Fuchs protocol 254
– Dauben's protocol 18
– Davis oxidation 192
– Dowd-Beckwith rearrangement 106
– divinylcyclopropyl rearrangement
149
– Eschenmoser-Claisen rearrangement
49
– Favorskii rearrangement 166
– Heck coupling 25
– Huang-Minlon reduction 38
– Ireland reductive decarbonylation
50
– Luche reduction 49
– Nazaki-Takai-Hiyama-Kishi
coupling 87
– Nicholas reaction 167
– Pauson-Khand reaction 167
– Stille coupling 72
– Swern oxidation 62
– Wolff-Kishner reduction 138
– Yamaguchi macrolactonization 12
KHMDS (potassium
hexamethyldisilazide) 44
klaianone 125
K-Selectride 252

l

laulimalide 237–239
 Lawesson's reagent 3, 47, 51
 LDA (lithium diisopropylamide) 122, 151, 181
 lepadiformine 168, 170, 172
 (+)-lepicidin 30
 lepicidin A 26
 (+)-lepicidin A aglycon 26
 Lewis acid 20, 27
 Ley oxidation reagent 138
 LHMDS (lithium hexamethyldisilazide) 70
 Li(*t*-BuO)₃AlH 14
 Lindlar's catalyst 82
 linear strategy 150
 low-yielding
 – sequence 70
 – step 36
 L-Selectride 187, 206
 lubiminol 100
 (±)-lubiminol 105
 Luche reduction 43, 45, 49, 110

m

main predictable problem 53
 major
 – detours 97
 – strategic change 30, 136
 – tactical change 36, 103
 – tactical detour 117
 MCPBA (*m*-chloroperoxybenzoic acid) 68, 122, 135, 145, 151
 MeLi–LiClO₄ 37
 MeLi–Me₂CuLi 37
 metal ammonia reduction 121
 MeTi(O*i*Pr)₃ 36, 37
 (+)-milbemycin D 132, 135, 136
 MK10 226
 model 41, 63, 99
 – compound 108
 – poor 59, 61
 – simple 41
 – studies 108
 – system 48

molecular mechanics analysis 48
 Mukaiyama salt macrolactamization 59
 myrocin C 116
 (±)-myrocin C 107, 118

n

NaCNBH₃ 229
 NaHB(OAc)₃ 163
 NBS (*N*-bromo succinimide) 181, 197, 201, 256
 NCS (*N*-chloro succinimide) 182
 Ni(II)/Cr(II) protocol 82
 Nicholas
 – cyclization 160
 – reaction 157, 159–161, 167
 NiCl₂/CrCl₂ 85
 NMO 161
 nocardione A 177
 (–)-nocardione A 176
 (–)-nocardione B 176
 Nozaki reagent 116
 Nozaki-Takai-Hiyama-Kishi coupling 87

o

octalactins 82, 85
 – octalactin A 81, 82, 85
 – octalactin B 81, 82, 85
 Oppenauer oxidation 10
o-quinodimethane cycloaddition 193, 198, 199
 OsO₄ 45, 188, 194
 OsO₄ · py 124
 oxidative decarboxylation 197
 oxy-Cope rearrangement 30, 33

p

Paal-Knorr pyrrole synthesis 259
 papuamine 261, 266
 (–)-papuamine 265–268
 Parikh-Doering oxidation 10, 27
 Pr₄NRuO₄ *see* TPAP
 Pauson-Khand reaction 157, 161, 167
 – cyclization 161
 – cyclocarbonylation 160

- PCC (pyridinium chlorochromate) 143
 Pd(0)catalysts 252
 Pd(OAc)₂ 101, 145
 Pd(PPh₃)₄ 17, 60
 Pd(PPh₃)₄/CuI 67
 Pd₂(dba)₃ CHCl₃ 43
 PDC (pyridinium dichromate) 197
 Pearlman's catalyst 169
 Pentafluorophenyl diphenylphosphinate 47
 Petasis' methylenation reagent 237
 PhI(OAc)₂ 42
 photocyclization 193
 [2+2] photocycloaddition 100
 PhSe(O)Cl 187, 191
 phyllanthocin 180
 PIFA (phenyliodonium-bis-trifluoroacetate) 221, 225–227
 (+)-piperazinomycin 51–54
 (–)-polycavernoside A 95, 96
 PPTS 154
 predictable problem 96, 223
 problematic moiety 30
 PtCl₂ 256
 pyrrole
 – nucleus 257
 – ring 255, 258
- r**
 racemization 53, 54
 radical fragmentation 100–102, 104
 Raney nickel 47
 Rathke protocol 68
 reaction conditions
 – optimization 7
 – tune up 7
 reductive cyclization 23
 Reissert reaction 64
 remote functional group 99
 remote inert substituents 99
 retro-aldol fragmentation 234
 ring formation 219
 ring-closing metathesis 239
 – enyne metathesis 255
 – metathesis ring closure 238, 255
 ring closure metathesis 256
 risky assumption 32
 roseophilin 255, 257–260
 rubifolide 247, 251, 253
 RuCl₂(PPh₃)₃ 34
 RuO₄ 36, 148
- s**
 Sc(OTf)₃ 177
 Schlosser's base 158
 scopadulcic acid B 142
 (±) scopadulcic acid 150
 (±) scopadulcic acid B 146, 148
 scopadulin 30–32, 34–36
 Sharpless
 – asymmetric 209
 – dihydroxylation 152
 – epoxidation 245
 sigmatropic rearrangement
 – [2,3]- 135, 136
 – [3,3]- 149
 SmI₂
 SO₃ · py 194
 Sonogashira coupling
 (–)-stenine 42, 45, 47–49
 stereochemically linear synthetic approach 179
 Stille
 – coupling 68, 71, 72, 95, 113
 – cross-coupling 67, 68
 – type reactions 230, 231
 Still's (Z)-selective olefination 56
 strategic
 – change 7, 25, 33, 48, 80, 116, 141, 198, 235, 252, 268
 – major change 30, 136
 – modifications 175
 strychnine 19, 23, 24
 Swern oxidation 56, 62, 65, 143, 186, 250
syn aldol adduct 206
 synthetic drawbacks 96

t

- tactical
– change 7, 12, 19, 25, 33, 48, 91, 97, 112, 183, 190
– detour 153, 199
– major change 36, 103
Takai reagent 94
taxane diterpenes 13
(+)-taxusin 13, 17
TBAF (tetrabutylammonium fluoride) 16, 57, 111
TBHP/VO(acac)₂ 85
TEOC group (trimethylsilyloxy-carbonyl) 221, 223
TESOTf (triethylsilyltriflate) 28
TPAP (Pr₄NRuO₄, tetrapropylammonium perruthenate) 44, 133, 136, 138, 259
TMSCH₂MgCl (trimethylsilylmethyl magnesiumchloride) 17
TMSCl (trimethylsilyl chloride) 158
TMSOTf (trimethylsilyl triflate) 259
transannular bridging 3
triflic anhydride 230
troublesome
– carbon 36
– cyclization step 47
– group 34
– key transformations 76
– scenario 36
– selectivity 203
TsOH 213

u

- Ullmann
– conditions 54
– cyclization 52, 53
– macrocyclization 53
– reaction 52, 53

undesired

- adduct 32
– stereochemistry 162
– transformations 25
unexpected reactivity 18
unfruitful approach 211
unpredictable result 30

v

- Vilsmeier formylation 232
Vilsmeier-Haack conditions 128
VO(acac)₂ 249

w

- Weinreb amide 206
Wieland-Gumlich aldehyde 19, 23
Wilkinson's catalyst 152
Wittig 132, 133
– coupling 211
– methylenylide 143
– olefination 132, 133
– reaction 214
– sequence 165
Wolff-Kishner reduction 38, 148
wrong configuration 201, 202
wrong stereochemistry 28, 30, 120, 175, 194

y

- Yamaguchi
– conditions 91
– macrocyclization 242
– macrolactonization 11, 12, 27, 243
– protocol 242
Yb(OTf)₃ 170

z

- Zn dust 23