

Index

- A-strain (1,3-allylic strain) 1429–30
A₂X systems, in NMR spectroscopy 841
A₂X systems, in NMR spectroscopy 841
AB systems, in NMR spectroscopy 270–4, 838–9
abietic acid 1449
absolute stereochemistry, definition 392
ABX systems, in NMR spectroscopy 840–1
Ac 280
acceptance of electrons by electrophiles 116
acceptor synthons 791
ACE inhibitors 10
acetaldehyde (ethanal) 40, 689, 694, 1452
acetaldehyde, by oxidation of ethanol 31
acetaldehyde, reaction with ammonia to form pyridine 1186
acetaldehyde, use in Claisen ester condensation 723
acetals 35, 342–7
acyclic, conformation of 1133
stereoelectronic effects in 1133
cyclic 346; *see also* spiroketals
conformation of 855, 861
coupling in NMR 826–7
deprotection 1270, 1370
in sugars 1361–2
synthesis of 1138, 1303
thermodynamic control of ring size 1137–8
use as protecting group 347, 632, 1269, 1366, 1370–1
formation, comparison with imine formation 352
from carbonyl compounds and alcohols 342–7
from furan 1160
from orthoesters plus aldehydes or ketones 345
use of trimethylsilyl triflate 1289
hydrolysis 346, 632
compared with S_N1 419
specific/general acid catalysis of 1108
stereoelectronic effects in 1128–9
precursors for Claisen–Cope rearrangement 945
reaction with hydrazine 1206
retrosynthetic analysis of 794
acetanilides, synthesis of 559
acetate thioester, of coenzyme A 744
acetate, as general base catalyst 1105–6
acetate, as leaving group 282
acetate, neighbouring group participation by 970–1, 975
acetic acid 40
by oxidation of ethanol 31
protonation of by hydrochloric acid 183
acetic anhydride
as a dehydrating agent 697
esterification with 280–1, 599, 1105–6
general base catalysis of reactions of 1105–6
in aldol reaction 705
in amide synthesis 616
in Pummerer rearrangement 1263
reaction with pyridine-N-oxides 1155
reaction with water 287
use in formation of anhydride from diacids 751–2, 863
acetic formic anhydride 284
acetoacetate, use in synthesis 677–8, 787, 789
acetoacetic acid 677
acetoacetyl CoA, biosynthesis of 1437
acetone 40
aldol condensation of 690
keto and enol forms 525
use in protection of diols 1138, 1366
acetone, protecting group 1138, 1362, 1366
acetonitrile, as ligand for Pd(II) 1312
acetonitrile, orbitals of 110
acetophenone 141
acetyl chloride 35
reaction with alcohols 280–4
reaction with water 287
use in enol ester formation 725
acetyl CoA 1346, 1389
in biosynthesis of alkaloids 1417–158
in citric acid biosynthesis 1390, 1392–3
in fatty acid and polyketide biosynthesis 1425–36
in mevalonic acid biosynthesis 1437
acetyl coenzyme A, *see* acetyl CoA
acetyl group 280
acetyl, as protecting group 1365–6
acetylation, general base catalysis of 1105–6
acetylation, of cellulose 1471
acetylene, deprotonation of 190
acetylene, orbitals of 107
acetylide, sodium 213
achiral compounds, definition 382
acid and base, catalysis by 1102–9
acid and base, effect on equilibria 311–12
acid anhydrides, *see* anhydrides
acid catalysis
of acetal formation and hydrolysis 343–7, 1371
of aldol reaction 691–2
of amide hydrolysis 293
of conjugate addition 233
of dehydration 692, 709, 714
of enolization 526
of epoxide opening 513–14
of ester formation and hydrolysis 288–9, 311–12, 324
of glycoside hydrolysis 1368
of halogenation of ketones 538
of hemiacetal and hydrate formation and decomposition 146–7, 342–4
of imine and enamine formation and hydrolysis 349–51, 353, 672
specific and general 1102–9
acid chloride, kinetics of reaction with alcohol 319–21
acid chlorides, *see* acyl chlorides
enolates of 529
halogenation of 536
ketenes from 529
acid derivatives, *see* carboxylic acid derivatives
¹³C NMR summary 362–4
distinction by infra red 364–5
distinction from aldehydes and ketones 361–4
acid strength 191–7; *see also* pK_a
acid, defined by Brønsted 182
acid-catalysed aldol reaction 691–2, 715
acidic protons, exchange in ¹H NMR 257–8
acidity 182–97; *see also* pK_a
of hydrochloric acid 182
acids, *see also* carboxylic
as preservatives 185, 187
carboxylic, IR spectra 68–70
Lewis and protic 120
acifran, synthesis 731
ACP (acyl carrier protein) 1427
Acquired Immune Deficiency Syndrome, *see* AIDS
acridine, nitration of N-oxide 1174
acrolein, molecular orbitals of 228, 230
acrolein, in quinoline synthesis 1210
acrylates, polymerization of 1460–1
acrylic acid 228, 1460
acrylonitrile 1460
nucleophilic conjugate addition to 582–3
polymerization of 1461
activating effects of aromatic substituents 568
activating groups in electrophilic aromatic substitution 555–64, 570
activation energy 113, 316, 319, 560, 1136
acyclovir (Zovirax), anti-herpes drug 1351
acyl anion equivalents 1128, 1254–6
acyl carrier protein (ACP) 1427
acyl chlorides 35
¹³C NMR spectra 363
conversion to ketones with Grignard reagents 299
reaction with alcohols 280–1
reaction with ammonia and amines 284, 1122
reaction with aziridine 1125
reaction with carboxylate salts 284
reaction with diazomethane 1056–7
reaction with enamines 1010
reaction with pyridine 282, 1149
reactivity towards nucleophiles 287–8
ynthesis from carboxylic acids 294–6
α,β-unsaturated, reaction with nucleophiles 236
acyl enamine 739
acyl polymalonate pathway 1425–36
acylation
at carbon (of enolates) 736–9
by thioesters 1375–6
Friedel–Crafts, advantages over alkylation 574
of alcohols catalysed by DMAP 1153
of anilines 559
of aromatic rings (Friedel Crafts) 553–4
of enamines 739–40
of enolates 724–8, 736–9
of enols, under acidic conditions 740
of Grignard reagents by acyl chlorides 299
of indole nitrogen 1208
of phosphorus ylids 743
of pyrrole nitrogen 1164
of saturated nitrogen heterocycles 1123–6
of sulfones 743
acylium ion, as electrophile 1299
acylium ion, compared with CO 410
acylium ion, formation of 554, 573
acylium ion, in acylation of enols 740
acylium ion, in Friedel–Crafts acylation 554
acylium ion, in mass spectra and reactions 410
acylium ion, stability of 574
acyloin reaction 1032–3
AD reaction, *see* asymmetric dihydroxylation
Adam's catalyst 626
adamantane 1489
addition
1,2- vs. 1,4- 234
1,4-, *see* conjugate addition
of Grignard reagents and organolithiums to carbonyl compounds 209, 214, 218–24
of nucleophiles to carbonyl compounds 135–49
addition–elimination mechanism 589–97, 1473
adenine 1347
in synthesis of aristeromycin 1333
adenosine monophosphate – AMP 1347, 1364–6, 1381
adenosine triphosphate – ATP 1347, 1391, 1402, 1438
adenosine 1347
adipic acid 1453
adipic acid, diethyl ester 727
adrenaline (epinephrine) 393, 473, 645, 1413, 1420
adriamycin 217–18, 519
A-factor 738
aflatoxin 508
aflatoxin, coupling in NMR 833
aggregation pheromone, of boll weevil 380
agonist 204
agrochemicals 10
AIBN, *see* Azobisisobutyronitrile
AIDS, treatment of 1481–7
aklavinone 180, 577
alanine aminotransferase 1391
alanine 1353, 1378
D-, in bacterial cell walls 386
laboratory synthesis of 386
ways to draw 20, 24
alcohols 32
basicity of 204
by reaction of organometallics with carbonyl compounds 142, 219–22, 616, 790
by reduction of carbonyl compounds with borohydride 140–1
by reduction of esters with lithium aluminium hydride 298
compared with thiols 1249
conjugate addition to unsaturated carbonyl compounds 228, 2334
conversion to alkyl bromides 408–9
elimination in acid 483
from alkenes 518–19, 1279
from ozonolysis of alkene 939
IR spectra of 69–70
nucleophilic substitution of 430–4
oxidation of 638–40, 1240, 1271–2
pK_a of 193–4, 196
protecting groups for 633, 710, 1223, 1290–1
reaction with carbonyl compounds 145–6, 340–2
reaction with carboxylic acids under acid catalysis 289
reaction with diazomethane 1054–5
reaction with epoxides 781

- reaction with PBr_3 408, 411
 reaction with thionyl chloride 789, 796
 aldehyde, reaction with Grignard and organolithium reagents 142, 219–22, 789–90
 aldehydes and ketones, distinguishing from carboxylic acid derivatives 361–4
 aldehydes, *see also* carbonyl compounds
 ^1H NMR spectrum of 255–6
 alkylation of 671–6
 aromatic, synthesis by formylation of arenes 574–5
 as sugars 1360
 Baylis–Hilman reaction with α,β -unsaturated carbonyl compounds 1124
 by oxidation of alcohols 638–9, 1240, 1272
 by ozonolysis of alkene 939
 by reduction of esters and amides 620
 comparison of reactivity with ketones 138–9
 conversion to alkenes by the Wittig reaction 357
 conversion to amino acids by the Strecker reaction 356
 conversion to enamines 353, 1123
 distinguishing from ketones by ^1H NMR 362–3
 enolization of 526–7
 from alkynes 1282
 from carboxylic acids 1225
 functional group and compound class 34
 hydration of 143–5, 307–8
 pK_a of 193, 197
 protection as acetals 347
 reaction with alcohols 145–6, 340–7
 reaction with amines 348–56
 reaction with bisulfite 148
 reaction with diamines 1138
 reaction with orthoesters to form acetals 345
 reduction to alcohols 140–1, 617
 synthesis using OXO process 1318–19
 α,β -unsaturated, reaction with nucleophiles 228–40
 Alder ene reaction 924–7
 with carbonyl enophile, *see* Carbonyl ene reaction
 Alder, Kurt 905
 aldol condensation 691–2, 709
 aldol condensation, *see also* aldol reactions
 geometry of alkene from 807
 in biosynthesis 1401–2, 1434, 1436–7
 aldol product, from *trans* ester enolates 901
 aldol products, comparison with [3+2] cycloadducts 935
 aldol reactions 689–722
 controlling the elimination step 691
 diastereoselective 898–902
 directed 720
 intramolecular 715–18, 761
 of a lactone 693
 of highly enolizable compounds 719
 of lithium enolates 698
 of silyl enol ethers 699–700, 757
 of unsymmetrical ketones 692–3
 thermodynamic control of 718–91
 transition state for 900
 aldolase 1388
 aldose 394, 1360
 aldrin, synthesis using Diels–Alder 909
 aliphatic 255
 alkaline hydrolysis, of glycerides 1375
 alkaloids 2, 635, 1338–9, 1414–25
 indole 1169
 use in AD reaction 1241–3
 alkanes
 compound class 31
 from alcohols via reduction of tosylate 806
 heats of combustion 455
 names of 26
 pK_a of 193
 radical bromination of 1038
 radical chlorination of 1035–9
 alkene geometry, control of 803–20
 alkene geometry
 control using fragmentation 1090–10
 effect on properties of compounds 803–4
 elucidation using NOE 845–6
 in rings 805–6
 inversion and equilibration of 153, 306–7, 317, 326–31, 807–9, 965
 alkenes
 [2+2] cycloadditions of 927–31
 1,3-dipolar cycloaddition to 932–40
 addition of carbenes 1063–8
 allylic bromination of 1039–40
 as nucleophiles or electrophiles 229, 503–504
 bromination 503–5, 512–15, 1015
 by addition to butadiene 819–20
 by elimination 481–93, 803–6
 by insertion reactions of carbenes 1070
 by Julia olefination 810–12
 by McMurry reaction 1031–2
 by Peterson reaction 812–14
 by pyrolysis of formate 1014
 by reduction of alkynes 818–20
 by stereoselective elimination 809–10
 by stereospecific elimination 812–14, 1301–3
 by Wittig reaction 357, 814–18
 chiral, conformation of 895–6
 chiral, diastereoselective addition to 895–7
cis and *trans* coupling in ^1H NMR 267, 273
 cyclic, NMR couplings in 830
 cyclopropanation of 1067–9
 dihydroxylation of 937–8
E and *Z* nomenclature 487
 effect of conjugation on ^{13}C NMR and IR 229–30
 effect of substituents on stability 489
 electrophilic addition to 503–20
 epoxidation of 505–8, 855–6
 functional group and compound class 31
 geometrical isomerism 153
 hydration of 518–19
 hydrogenation as measure of stability 173, 307
 in radical chain reactions 1042–50
 metathesis of 1074–5
 neighbouring group participation by 973
 NMR comparison with benzene 251
 orbitals of 109
 oxidation of 638, 1239–43
 ozonolysis of 938–9
 polymerization of 1459–68
 protonation by acid 510
 radical addition of hydrogen bromide 1020, 1023, 1034
 reaction with hydrogen halides 509–10
 reaction with mercury acetate 1048, 1280
 reaction with mercury(II) ions 518–19
 reaction with NBS in water 1015
 regioselectivity of electrophilic attack on 509–10
 stereoselective synthesis of (summary) 820
 stereoselective synthesis of 803–20, 1295–6
 stereospecific reactions of 514–17
 alkoxides, as leaving groups 281, 285
 alkoxides, conjugate addition of 233
 alkoxy group 32
 alkyd resins 1467, 1469–71
 alkyl bromides, by reaction of hydrogen bromide with alkenes 509
 alkyl bromides, reaction with sodium cyanide 795
 alkyl chlorides, by reaction of hydrogen chloride with alkenes 510
 alkyl chlorides, rates of solvolysis 418
 alkyl groups, migrations of 978–82, 1397
 alkyl groups, names of 26
 alkyl halides, functional group and compound class 33
 alkyl iodides
 as electrophiles in $\text{S}_{\text{N}}2$ reactions 442
 by reaction of hydrogen iodide with alkenes 510
 by substitution of tosylate by iodide 442, 1132
 reaction with aza-enolate 1132
 alkyl nitrites, in diazonium salt formation 597, 602
 alkylation
 by α -halo carbonyl compound 1189
 of aldehydes 671–6
 of alkynes 785
 of allyl sulfide 1257, 1268
 of allylic alcohols using sulfenate rearrangement 1268
 of amines 437–8, 714, 778
 of arenes (Friedel–Crafts) 553–4
 of carboxylic acids 670–1
 of chiral enolates 864, 866–7, 884–5, 897–8, 1230, 1485
 of dithiane 1254
 of enolates, table of methods 663–88, 687 (table)
 of esters 669
 of imidazole 1167
 of ketones 669, 674
 of Mannich base 714
 of nitriles 436
 of pyrazole 1197
 of sulfoxides 1254
 of thiolacetate 439–40
 of thiols 438–9
 of β -dicarbonyl compounds 676
 of β -lactone 853
 using chiral auxiliaries 1230–2
 with tosylates 433–4
 alkylmercury halides, reduction and homolysis of 1021
 alkynes and small rings, comparison of NMR spectra 366–7
 alkynes
 1,3-dipolar cycloadditions to 934–5
 ^1H and ^{13}C NMR spectra 366–7
 alkylation of 785
 as dienophiles 910, 1163
 bromination of 1085
 by elimination 493
 functional group and compound class 32
 hydration of 362, 519
 hydroboration of 1282, 1328
 hydrogenation using Lindlar catalyst 818
 hydrostannylation of 1305–6
 in Sonogashira coupling 1330
 in synthesis 649, 784–6
 in the synthesis of aldehydes 1282
 IR spectra 70
 lithium and magnesium derivatives 213, 785, 1291
 protection as silane 1291–2
 reaction with azide 1203
 reaction with nitrile oxides 1201
 reduction with lithium aluminium hydride 819
 reduction with sodium/ammonia 819
 shape and orbitals of 107
 alkynyl lithium 1291
 alkynyl lithiums as nucleophiles 434
 allenes
 [2+2] cycloadditions of 964
 chirality of 398
 epoxidation of 1112
 shape and orbitals 157
 allopurinol, synthesis 1186
 allyl anion, structure and orbitals 161–3
 allyl borane, reaction with aldehydes 1284–6
 allyl bromide, substitution reactions of 604–5, 936, 1230, 1485
 allyl cation, from electrocyclic ring-opening 963
 allyl cation, in $\text{S}_{\text{N}}1$ reaction 416–17
 allyl cation, structure and orbitals 158–60
 allyl Grignard reagents 224–5
 allyl group 40–1, 158–63
 allyl halides, in $\text{S}_{\text{N}}2$ reactions 424
 allyl iodide, alkylation with 1232
 allyl isothiocyanate, synthesis of 1368
 allyl radical, structure and orbitals 161, 1465
 allyl silanes 1287, 1296–300
 allyl sulfide 1256–7, 1263, 1268
 allyl sulfoxides, in garlic 1272
 allyl sulfoxides, rearrangement of 1267–8
 allylic alcohols
 asymmetric hydrogenation 1236
 diastereoselective epoxidation of 877–8, 897, 1239–41
 oxidation by manganese dioxide 875
 rearrangement during oxidation of 951
 synthesis of 607–8, 789, 1267, 1270
 allylic bromination 1039, 1040
 allylic chlorides, synthesis of 608–9
 allylic compounds, nucleophilic attack on 604
 allylic coupling, in NMR of cyclic alkenes 830
 allylic rearrangement 1285
 allylic: 1,3-allylic strain (A strain) 896, 1429–30
 alpha
 α -effect 588, 1173
 α -elimination 1058–9, 1070
 α,β,γ (names of positions on chain) 228
 α,β -unsaturated, *see* unsaturated
 alphaprodine, synthesis 857
 alternariol 1433
 alumina, catalyst for decomposition of oxalyl chloride 329
 aluminium amalgam, in sulfoxide reduction 1253, 1266–7
 aluminium chloride, catalyst for halogenation of ketones 535–6
 aluminium chloride, in Friedel–Crafts alkylation 569
 aluminium chloride, use as Lewis acid 549, 1298
 amefolide, synthesis 772
 amide group, structure and conjugation in 164–6, 1130
 amide, conjugate base of amine or carboxylic acid derivative 197
 amide, sodium 213
 amides
 ^{13}C NMR spectra 363
 basicity of 201, 204
 by Beckmann rearrangement 997–1000
 difficulty of formation from carboxylic acids and amines 288
 formation using DCC 1172

- from amines and acyl chlorides 284–5
 from amines and esters 285
 from carboxylic acids 1198
 functional group and compound class 34
 hydrolysis 292–4, 325–6
 of aziridine 1125
 p*K*_a of 197
 protonation of 166, 201, 293
 reaction with Grignard reagents or organolithiums to form ketones 300–1
 reaction with Lawesson's reagent 1200
 reactivity of 287–8
 reduction of 355–6, 618–20, 779
 retrosynthetic analysis of 772–3
 slow rotation about C–N bond 247, 305–6, 317
 a,b-unsaturated, reaction with nucleophiles 236
- amidines, basicity of 202, 482, 588
 amidines, in synthesis of pyrimidine 1188, 1198
- aminal 1138, 1417, 1467
- amines
 alkylation of 437, 778
 aromatic, synthesis by Chichibabin reaction 602–4
 as leaving groups 293
 as nucleophiles in S_N2 reactions 437
 basicity of 199–200
 by Curtius or Hofmann rearrangement 1073
 by hydrolysis of amides 292–4
 by reduction of amides 355–6, 779
 by reduction of imines 354
 by reduction of nitro groups 564, 1151
 by reduction of oxime 780
 by reductive amination 354–6, 779–80
 conjugate addition to unsaturated carbonyl compounds 228, 231–2
 cyclic, synthesis of 1338, 1142
 from azide 1242
 from boranes 1282–3
 functional group and compound class 33
 neighbouring group participation by 976–8
 protection of 637, 647, 653
 reaction with acyl chlorides 236, 284
 reaction with BF₃ 117
 reaction with carbonyl compounds to form enamines 353
 reaction with carbonyl compounds to form imines 348–56
 reaction with chloroformates 1151
 reaction with epichlorohydrin 782
 reaction with epoxides 435
 reaction with esters 284
 reactions with substituted pyridines 1151
 retrosynthetic analysis of 776–80
 tertiary, synthesis of 661
- amino acid ammonia lyases 1404
- amino acids
¹H NMR of 248–9, 257, 839–40
 as acids and bases 183
 biosynthesis of aromatic 1400–5
 by the Strecker reaction 356
 chirality 386, 1220
 conjugate addition of 759
 coupling of 1172
 how to draw 20, 24
 in primary metabolism 1346
 resolution of 401
 structures 1353–9
- amino alcohols 794–5
 by reduction of cyanohydrins 149
 reaction with CDI 1166
- amino groups 20, 33
- IR spectra 68
- amino sugars 1372–4
- aminohexanoic
 6-aminohexanoic acid 1454
- aminotransferases 1385, 1387, 1391
- amlodipine 1193
- ammonia
 acidity and basicity 197–8
 conjugate addition to unsaturated carbonyl compounds 228, 232
 reaction with acetaldehyde to form pyridine 1186
 reaction with acyl chlorides 284
 reaction with aldehydes to form imines 350
 shape of 83, 108
- ammonium ion, acidity of 198
- ammonium ion, shape of 107
- ammonium ylid 1394
- amoxycillin 10
- AMP, *see* adenosine monophosphate
- amphetamine 33, 393
- amphoteric 183
- anatabine 1448
- anchimeric assistance, *see* Neighbouring group participation
- angle of attack, by nucleophiles on carbonyl compounds 139
- angles
 bond, in propane 452
 bond, in rings 454
 dihedral or torsion 451
- anhydrides
¹³C NMR spectra 363
 acylium ion from 573
 cyclic, from diicarboxylic acid 751–2, 863
 Friedel–Crafts acylation by 573–4
 from carboxylate and acyl chloride 284
 reaction with alcohols 280–1, 321–2
 reactivity of towards nucleophiles 287–8
- anilides, synthesis of 559
- aniline
 acetylation by acetic anhydride 189
 basicity of 200–1
 bromination of 558
 from bromobenzene 601
 in electrophilic substitution reactions 558–61
 reaction with 1,3-dicarbonyls 1210
 reaction with α,β-unsaturated carbonyl 1210
- anion stabilization, by nitrile 582
- anion stabilization, by sulfur 1252
- anionic polymerization 1461–2
- anions, aromatic 172–3
- anions, non-nucleophilic 410
- anisole 557–9
- annelation, Robinson 761–4, 872
- annulenes, 10 and 18 176–7, 252
- anomeric effect 1129–33, 1361
- anomeric position 1361
- anomers 1361
- anorectic (appetite-suppressant) 1220
- antagonist 204
- antarafacial migration, in sigmatropic hydrogen shifts 955
- antarafacial, definition of 922
- anthocyanidin 1367, 1436
- anthracene, Diels–Alder reaction with benzyne 923
- anthracyclines 519
- anthranilic acid 639
- anthraquinone, structure and use in synthesis 566
- anti*-aldol reaction 898–901
- antibiotic X-206 1232
- antibonding orbitals 96, 120
- anti-cancer drugs, conjugate addition and 238
- anticlinal 453
- antimony pentafluoride 551, 562
- anti-periplanar 453
- anti-periplanarity and E2 490–1
- antipyrene 1147
- antiseptic, phenol in surgery 2
- antisymmetric stretch, in IR 69
- anti-ulcer drugs 204–6, 586–8
- AO *see* atomic orbital
- aprotic solvent 142
- Ar, 'wild card' aryl group 28
- arabinose 395
- arachidonic acid 157, 1426–31
- araldite 1457
- arginine 1355
- arildone 786
- aristeromycin 1333
- Arnold–Eistert homologation 1072
- aromas, good and bad 4, 9
- aromatic aldehydes, by formylation of arenes 574–5
- aromatic amine, by Chichibabin reaction 602
- aromatic heterocycles, *see* heterocycles, aromatic
- aromatic rings, ¹H NMR and electron distribution 252–4
- aromatic sulfonic acids, synthesis of 553
- aromaticity
 effect on p*K*_a 196
 in benzene 549
 of heterocycles 1148
 of porphyrin 1178
 orbitals and 171–8
- aromatisation, of cyclic enone 766
- Arrhenius equation 316
- arrows
 curly 123
 atom-specific 124–5
 fish hook, for radical reactions 126
 how to draw 123–31
 in reaction mechanisms 120–1
 summary 127
 types of (table) 334–5
- arsenic pentaoxide, as oxidant in Skraup quinoline synthesis 1211
- artemisia ketone 1449
- aryl anion, formation and stability of 600–4
- aryl cation 598–600
- aryl diazonium salt 598–600
- aryl groups, coupling of 1329
- aryl groups, neighbouring group participation by 973
- aryl halides, synthesis 599–600
- aryl ketones, by Friedel–Crafts acylation 554
- ascorbic acid 6, 533, 1384
¹H NMR 249
- asparagine 1356
¹³C NMR 364
- aspartame 9, 34, 654–5, 1356
 synthesis 1222
- aspartic acid 654, 1356
 in aspartame synthesis 1222
- aspirin 27, 645
¹³C NMR 364
 mode of action 1432
 solubility of sodium salt 185
 synthesis 558
- asymmetric Diels–Alder reaction 1226–9, 1232
- asymmetric dihydroxylation (AD) reaction 1241–3
- asymmetric epoxidation, Jacobsen 1488
- asymmetric epoxidation, Sharpless 1239–41
- asymmetric hydrogenation 1234
- asymmetric oxidation 1265–6
- asymmetric reducing agent 1234
- asymmetric synthesis of sulfoxides 1265–6
- asymmetric synthesis 1219–43, 1484
- asymmetric synthesis 1484
- atactic polymers 1460
- atomic emission spectra 83–5
- atomic orbitals 87–95
- atoms, number in known universe 316
- ATP, *see* adenosine triphosphate
- atropine mimic 784
- atropine 1416
- atropisomers 398
- attraction between molecules
 charges and dipoles 114
 filled and empty orbitals 114–15, 118–22
 summary 118
- Aufbau principle 93
- avitriptan 1343
- AX NMR spectrum 259–63
- AX₂ NMR spectrum 263–4
- axial attack
 on 6-membered enamine or enolate 858–9
 on cyclic 6-membered enone 858–60, 875
 on cyclohexene oxides 468–70
- axial chirality 398–9, 1235
- axial protons, couplings in NMR 825–8
- axial substituents 459, 462–5
 reactivity of 467–8
- azaenolates
 acylation of 739
 alkylation with benzyl chloride 675, 1132
 as specific enol equivalents 674–6, 697, 708–9
 from butyllithium with hydrazone 1132
- azeotrope 347
- azetidine 1124
- azide, as nucleophile 437, 594
- azides
 cycloadditions of 1202–3
 reduction to amine 438, 1242
 safety of 438
- azidothymidine (AZT) 1351
- azimuthal quantum number 86
- aziridine
 basicity of 1126
 by ring-closing reaction 1134
 electrocyclic ring-opening of 964
 inversion at nitrogen 1126
 reaction with acyl chloride 1125
 ring opening of 1125
 ring strain in 1124
- aziridinium ion 976–8
- azo compounds 431, 1056
- azo dyes, synthesis 572
- azobenzene 431
- azobisisobutyronitrile, in polymerization reactions 1478
- azobisisobutyronitrile, in radical reactions 1021, 1041, 1045–6
- azomethine ylid 964
- AZT 1181, 1351, 1481
- azulene 3
- backbiting, in polymerization 1460, 1471
- back-bonding 1315
- Baeyer–Villiger oxidation 992–5, 1229
 comparison with hydroboration 1280, 1283–4
- Bakelite 1455–6
- bakers' yeast, in ketone reduction 1234
- Baldwin's rules 1140–4
- Balmer series 84
- Balmer, Johann 84
- Bamford–Stevens reaction 1057–8
- Barbier 224

- barium hydroxide, catalyst of aldol reaction 691
- barium sulfate, as support in catalytic hydrogenation 623
- barrier, activation 319
- barrier, to bond rotation 317, 449–50
- Barton, Sir Derek 466
- base and acid, effect on equilibria 311–12
- base catalysis
 general and specific 1102–7
 of aldol reactions 689–722
 of amide hydrolysis 293
 of bromination and iodination of enolates 537–8
 of conjugate addition 233
 of enolization 526, 689–722
 of epoxide opening 513–14
 of ester hydrolysis 291–2, 323–4
 of hemiacetal and hydrate formation and decomposition 146–7, 342
- base, defined by Brønsted 182
- base-pair, in DNA 1349
- basicity 197–206; *see also* pK_a
 of histidine 1390
 of tertiary amines 1397
 of amino acids with second amino group 1355
 of aziridine 1126
 of cyclic amines 1123
 of DABCO 1123
 of dialkylamines 1123
 of piperidine 703
 of pyrazine 1173
 of pyridazine 1173
 of pyridine 1124
 of pyridine 703, 1124, 1149
 of pyrimidine 1173
 of quinuclidine 1123
 of triethylamine 1123
 effect of electronegativity on 198–9
 of nitrogen bases 199–202
 of nucleophile, effect on substitution vs. elimination 479
 of oxygen bases 203–4
- Baylis–Hillman reaction 1124
- BBN: 9-BBN 1281
- Beckmann fragmentation
 mechanism 1114–16
 of bicyclic oxime 999, 1003
- Beckmann rearrangement 997–1000
 in nylon and caprolactam synthesis 997, 1454
- bee alarm pheromone
 ^{13}C NMR spectrum 62
 ^1H NMR spectrum 268, 370
 IR spectrum 71
 mass spectrum 51
- Beechams 205
- beef tallow 292
- belfosil 787
- benomyl 11
- benzaldehyde 141
 in aldol reactions 704
 in protection of diol as benzylidene acetal 1138
 in reductive amination 796
 industrial preparation 574
- benzene rings, synthesis via Diels–Alder reaction 1164
- benzene
 carcinogenicity of 508
 conjugation and aromaticity 154–5, 172, 174–5
 nitration of 552, 572
 NMR of 251
 reaction with carbenes 1068
 reaction with electrophiles 548–55
 structure of 27, 40, 154–5
 benzenesulfonic acid, synthesis 552
- benzilic acid rearrangement 989–90, 992
- benzocaine 644
 ^{13}C NMR spectrum 363
- benzoic acid 187
- benzonitrile, reaction with base 530
- benzophenone 694
 as indicator in THF distillation 1030
- benzoquinone: 1,4-benzoquinone, as oxidant 1337–9
- benzothiazole-2-thiol 1470
- benzoylpropanoic: 3-benzoylpropanoic acid, synthesis 574
- benzyl acrylate, in Diels–Alder reaction 1226–7
- benzyl alcohol, in esterification 1226–8
- benzyl anion 1461
- benzyl bromide, in ether formation 1234
- benzyl cation 410, 416–18, 1455
- benzyl chloride, Friedel–Crafts alkylation with 569
- benzyl chloride, rate of reaction of 425
- benzyl chloroformate 653, 1484
- benzyl cyanide, reaction with base 530
- benzyl ether, use as protecting group 635, 1132
- benzyl, contrasted with phenyl 40–1
- benzyl halides in substitution reactions 424–6
- benzylisoquinoline alkaloids 1418–25
- benzyltriethylammonium chloride 665
- benzyne
 dimer of 602
 formation 600–4
 trapping of by Diels–Alder 923, 1110
- bergamotene, synthesis 636, 987
- Bergman cyclisation 1330
 carotene: β -carotene 29, 32, 157, 170
 dicarbonyl: β -dicarbonyl compounds, alkylation of 676
- BHT 30
 ^{13}C NMR spectrum of 62
 IR spectrum of 69
 mass spectrum of 55
 synthesis 570
- biaryls, chirality of 398
- bicycles 715, 862–3, 871
 diastereoselective reactions of 862–3
 fused 864–70
 reactions of 874–5
spiro, *see* Spirocycle
 synthesis 715, 750, 872
- bimolecular kinetics 319–23
- BIOPOL 1472
- biopterin 1409
- biotin 1399
 synthesis 936
- biperidin 225
- bipy 1156
- Bipyridyl: 2,2'-bipyridyl 1156
- Birch reduction 628–9, 683, 806, 1253
- bis(chloromethyl)ether, a carcinogen 575
- bis(tributyltin) oxide 1305
- bisabolene: α -, β and γ -bisabolene, biosynthesis of 1441
- Bismarck brown 2, 431
- bisphenol A 1454, 1457, 1478
- bisulfite, addition to carbonyl compounds 148
- bitrex 5
- block co-polymer 1462
- blocker: β -blocker drug, retrosynthetic analysis 1259
- Bn 40
- boat conformation 456, 458, 1445
- Boc, protecting group 317, 654–6, 1163, 1165, 1476–7, 1484
- bold bonds 25
- boldine 1424
- bombykol 818
- bond angles, in propane 452
- bond length, comparison of C–X, Si–X and Sn–X 1287, 1305
- bond length, in benzene 549
- bond polarization 210
- bond rotation 447, 449–50
- bond strength
 and leaving group in S_N2 430
 and reactivity 288
 C–O and C=O bonds 280
 comparison of C–X and Si–X 1287
 comparison of P=O with S=O 1259
 force constant and IR frequency 65
 in enols 525
- bond vibration, and IR spectra 65
- bonding orbital 96
- bonding, in transition metal complexes 1312–5
- bonds, hashed, bold, dashed or wiggly 381, 385
- bongkrekic acid 221
- borane
 dimethyl sulfide complex 738, 1228, 1278
 reactions of 618, 738, 1278–87
 shape of 107
- boric acid 1279
- borohydride
 HOMO of 140
 reaction with carbonyl compounds 140–1
 shape of 107
- boron enolate 741, 901
- boron heterocycle, in CBS reagent 1233
- boron trifluoride, as Lewis acid 610, 741, 1254–5, 1298, 1303, 1462
- boron trifluoride, etherate 1126–7
- boron, in synthesis 1278–87
- boron, nuclear spin of ^{11}B 57
- boronic acids 1328
- Bouveault–Blanc reduction 1029
- bowsprit position 458
- brace device, use in drawing structures 701
- Brackets, Owen 699
- branched chains, of carbon atoms 21
- branched polymer 1456, 1468
- Bredt's rule 484
- brefeldin A, in biosynthesis problem 1435, 1449
- brevetoxin 33, 1414
- bridged rings 508, 740
- bridgehead alkenes 484, 717
- bromide, conjugate addition to unsaturated carbonyl compounds 228
- bromide, epoxide opening by 470
- bromides, alkyl, synthesis 431
- bromination
 allylic 1039–40
 of alkanes via radicals 1038
 of alkenes 503–5, 513, 515, 1155 1408
 of alkyne 1085
 of aniline 558–9
 of aromatic compounds, comparison of rate 559, 561
 of furan 1160
 of ketones 535–6, 1015
 of nitrobenzene 565
 of phenol 555, 571
 of pyrrole 1157
- of stilbene with pyridinium tribromide 1155
- of toluene 561
 using catalytic pyridine 1155
- bromine
 isotopes in mass spectrum 52–3
 oxidation of dihydropyridazolone 1196
 reaction with alkenes 503–5, 512–13, 515
 reaction with dienes 511
- bromo-*n*-bromo phenol 571
- bromoalkanes 33
- bromobenzene
 action of *Pseudomonas putida* on 1220
 by bromination of benzene 1155
 from aryl silanes 1293
 in benzyne synthesis 600–2
 nitration of 567–8
- bromoesters, synthesis 536
- bromohydrins 513, 1015
- bromolactonisation 517–518
- bromonium ions 504–5
 regioselectivity of nucleophilic attack on 512
- bromoxynil 569
- Brook rearrangement 1303–4
- broperamole 1203
- propiramine 797
- Brown, Herbert C. 1285
- brufen, *see* ibuprofen
- Bu 26
- Buckminster Fuller, Richard 28
- buckminsterfullerene 28, 82
- BuLi, *see* butyllithium
- bullatenone 277, 747
- Bürgi–Dunitz angle (or trajectory) 139
- burimamide 205
- buta-1,3-diyne, reaction with methanol 367
- butadiene, in radical co-polymerization 1465
- butadiene, orbitals of 166–8
- butadiyne, nucleophilic addition 819, 820
- butanal, in aldol condensation 709
- butane, structure and conformation 38, 452
- butanols, identification by ^{13}C NMR 64
- butanone, in aldol reactions 709
- butenolides, conjugate addition to 854
- butenolides, synthesis of 496, 1328
- butenyl cation, in S_N1 reactions 417
- butyl group 26
- butylated hydroxy toluene, *see* BHT
- butyllithium 212
 addition to carbonyl groups 142, 540
 as base 540, 667, 707, 743, 1248, 1263–4, 1291
 conjugate addition to unsaturated amide 236
 in polymerization of styrene 1461
 lithiation of cyclopropyl ring 1263–4
 reaction with heterocycles 1161–2
- C terminus, in proteins 1358
- C
 ^{13}C isotopic labelling 1426, 1434, 1439
 ^{13}C NMR
 in analysis of reaction intermediates 562, 592
 of bee alarm pheromone 62
 of BHT 62
 of enones 230
 of hexanedioic acid 62
 of lactic acid 61
 of paracetamol 62
 regions of spectrum 61
 ^{13}C satellites, in ^1H NMR spectrum 370
 ^{14}C isotopic labelling 697, 1416, 1419
 C=O bond, polarity of 114
 C_2 symmetry 1363–4

- C-acylation, of enols and enolates 736–9
caesium, origin of name 83
caffeic acid 1400
caffeine 1175, 1347
Cahn–Ingold–Prelog rules 387
calcium carbonate, as support in catalytic hydrogenation 623
calicheamicin 32
callistephin 180, 577
calor gas 2
cAMP 1352
camphene 1449
camphor 473, 1437
 biosynthesis 1440
 diastereoselective reactions of 862–3
camphoric acid, from camphor 863
camphoric anhydride 863
canadensolide 833
Cannabis sativa 1449
Cannizzaro reaction, determination of mechanism 1081–4
Cannizzaro reaction, in synthesis of pentaerythritol 713
caprolactam, synthesis and polymerization of 1453–4
capsaicin 815
captan 906
captodative radicals 1028
captopril 10, 1359
carbamates, from reaction of amine with chloroformate 1151
carbamates, retrosynthetic analysis of 782
carbanions
 acylation of 742
 silyl-stabilized 1302–3
 sulfur-stabilized 1252
carbene, singlet, *see* singlet carbene
carbene, triplet, *see* triplet carbene
carbenes, reactions of 1053–76
carbenes, synthesis of 1056–9
carbenium ions 409
carbenoid
 lithium, from dibromoalkane 1059
 rhodium, from diazo carbonyl 1057
 zinc, by zinc insertion into diiodomethane 1059, 1067–9
carbenoids, comparison with sulfonium ylids 1259
carbocations
 allylic, in S_N1 reactions 416–17
 as intermediates in alkene isomerization 332
 benzylic, in S_N1 reactions 416–18
 by protonation of alkenes 510
 formation in superacid solution 410
 heteroatom-stabilized, in S_N1 419–20
 in Friedel–Crafts alkylation 553–4
 planarity of 415–16
 stability of 408–11, 415–16
 tertiary 415–16, 1439
carbocycles, saturated, rate of formation by ring closing reaction 1135
carbohydrate 1359
carbometallation 1318–23
carbon acids, strength of 193–94
carbon atoms, when to miss out from structures 23–5
carbon chains, names for 21, 26–7
carbon dioxide, as reagent in biosynthesis 1399–400
carbon dioxide, reaction with organometallics 218–19, 1010
carbon disulfide
 as solvent in bromination reactions 557–9
 in dithioester synthesis 1264
 in manufacture of rayon 1472
carbon monoxide
 in Gatterman–Koch reaction 574
 in Pauson–Khand reaction 1311
carbon skeleton, *see* hydrocarbon framework
carbon suboxide, C_3O_2 372
carbon tetrachloride 1453
carbon, abundance of ^{13}C 243
carbon, isotopes of in mass spectrum 54
carbonate linkage 1455
carbon–carbon bond cleavage, in trihaloketones 537
carbonium and carbenium ions 409
carbon–metal bond 210
carbonyl compounds, *see* aldehydes, ketones, carbonyl group, carboxylic acid derivatives
 addition of Grignard reagents and organolithiums to, 142, 209, 214, 218–24
 asymmetric reduction of 1266–7
 basicity of 203
 functional group and compound class 34
 IR spectroscopy, effect of conjugation on 229
 LUMO of 136–7
 orbitals of $C=O$ 109
 pK_a of 193, 197, 203
 reaction with alcohols to form hemiacetals 145–6
 reaction with bisulfite 148
 reaction with cyanide 135
 reaction with sodium borohydride 140–1
 reaction with water 143–5
 reactions under acid catalysis 147
 reactions under base catalysis 147
 substitution ^{16}O for ^{18}O 339–40
 substitution of the carbonyl oxygen atom 339–40
 carbonyl diimidazole 744, 1166
 carbonyl ene reaction 926–7
 carbonyl group *see* carbonyl compounds, aldehydes, ketones, carboxylic acid derivatives
 angle of attack by nucleophiles 139
 $C=O$ bond strength 280
 in ^{13}C NMR spectrum 61, 361–4
 in IR spectrum 71, 364–8
 molecular orbitals of 136
 nucleophilic addition to 135–49
 nucleophilic addition to, writing a mechanism for 135, 139
 protection for 632
 reaction with tosyl azide 1056–7
 reactivity of with nucleophiles 136
 reduction of (summary table) 617, 622
 removal of 627
 substitution of O 340–58
 substitution reactions at 279–301, 319–26
 carbonyl groups, order of reaction at 616
 carbonyl insertion, *see* carbonylation
 carbonylation 1317–19, 1327–8, 1339–41
 carbopalladation 1320, 1323, 1338
 carbobotanation 1463
 carboxybenzyl protecting group, *see* Cbz
 carboxybiotin 1399
 carboxyl group 34
 carboxylate anion, conjugation in 163
 carboxylate salts, reaction with organolithiums to form ketones 299–300
 carboxylate, neighbouring group participation by 971
 carboxylate, reaction with acyl chlorides 284
 carboxylic acid derivatives 280
 interconversion of, summary 296
 IR spectra 288
 reactivity of 286–8
 carboxylic acids
 ^{13}C NMR spectra of 363
 alkylation of 670–1
 by amide hydrolysis 292–294
 by ester hydrolysis 291
 by reaction of Grignard reagent with carbon dioxide 218–19, 1010
 conversion to acyl chlorides 295–6
 formation by oxidation of a methyl group 564
 from alcohols 640
 from ozonolysis of alkene 939
 functional group and compound class 20–1, 34
 homologation to ester 1072
 pK_a of 193–4, 196, 197
 protecting groups for 647, 653
 reaction with alcohols under acid catalysis 289
 reaction with diazomethane 1053, 1054
 reduction of 618
 synthesis 218–19
 tautomerism 525
 unreactivity towards nucleophiles 288
 carcinogens 508, 575, 584
 carnation perfume intermediate, synthesis of 785
 carotene precursor, retrosynthetic analysis and synthesis of 787, 792
 carvone
 (*R*) and (*S*) 1219–20
 ^{13}C NMR spectrum 363
 in synthesis 1011, 1261
 caryophyllene: α -caryophyllene alcohol 983
 caryophyllene 1009, 1449
 cassava 138
 catalysis
 acid 288–9
 general acid, *see* general acid catalysis
 general base, *see* general base catalysis
 in carbonyl substitution reactions 323–6
 nucleophilic 282, 442–3, 1352
 of acetal formation and hydrolysis by acid 342–4
 of hemiacetal and hydrate formation by acid or base 146–7, 342
 of keto–enol tautomerism 526–7
 specific acid, *see* specific acid catalysis
 specific and general 1102–9
 specific base, *see* specific bases catalysis
 using enzymes 1382–8
 catalyst
 for asymmetric dihydroxylation 1241–3
 stabilization of transition state by 327
 STM picture of surface 82
 catalysts, chiral 1233–43
 catalytic cycle
 Heck reaction 1321
 nucleophilic displacement reactions 1331
 the OXO process 1319
 catalytic hydrogenation 598, 600, 621, 623, 1484
 in AMP synthesis 1366
 in deprotection of benzyl ethers 635
 of nitro group 659, 661
 catechol 1420
 catecholamines 1420
 catecholborane, in Suzuki coupling 1328
 catenane, X-ray crystal structure 82
 cationic polymerization 1462–3, 1479
 cations, aromatic 172–3
 cations, in mass spectrometry 50–1
 cats, sleep-inducing substance of 5
 CBS reagent 1233
 Cbz protecting group 652–4, 1484
 NMR of 248
 CDI, *see* carbonyl diimidazole
 CE (condensing enzyme) 1426–8
 Cecropia juvenile hormone 210, 220, 804
 cedrol 484
 cell membrane 1377
 cellophane, manufacture of 1472
 cellulose triacetate 1471
 cellulose xanthate, use in rayon manufacture 1472
 cellulose 347, 1372, 1471
 acetylation of 1471
 use in 'Formica' manufacture 1468
 centre, chiral 385
 centre, stereogenic 385
 cerium chloride 626, 894
 cerium, organometallic derivatives of 217–18
 cerulenin, synthesis 831
 cetaben ethyl ester, synthesis 776
 CFCs 35
 CH groups, 1H and ^{13}C shifts, tables 377
 CH_2 groups, and CH_3 , 1H NMR shifts 248–9
 CH_2 groups, 1H and ^{13}C shifts, tables 376
 CH_3 groups, 1H and ^{13}C shifts, tables 375
 chain propagation, example of 1462
 chain reaction, of radicals, *see* radical chain reactions
 chains, of carbon atoms, *see* carbon chains
 chair conformation 456, 458–61, 1445
 chair transition state
 in aldol reaction 900
 in progesterone synthesis 1447
 in [3,3]-sigmatropic rearrangement 1403
 Chanel No 5 34
 charge, attraction between molecules 114, 120
 charge, conservation of in mechanisms 123–4
 charges, drawing 24
 chelation control, in Felkin–Anh additions 892–4
 cheletropic reaction 1063–6
 chemical ionization mass spectrometry 52
 chemical shift in NMR 59, 245–58
 chemoselectivity 615–41
 in aldol reaction 694, 696
 in peptide synthesis 654
 in reactions of dianions 631
 in reduction of carbonyl group 622
 in retrosynthetic analysis 776
 kinetic control of 630
 thermodynamic control of 630
 chiral auxiliaries 1226–32
 chiral centre 385
 chiral dienophile, use in asymmetric synthesis 1229
 chiral drugs 403
 chiral enolates 1230
 chiral pool 1222–5, 1227
 chiral reagents and catalysts 1233–43
 chiral reducing agents 1233–4
 chiral shift reagents 1231
 chiral stationary phase 403
 chiral sulfoxides, use in synthesis 1266–70
 chiral 382
 chirality 382–4
 in nature 400, 1219–20
 of sulfoxides 1251, 1265–7
 chitin 1372
 chloral hydrate, IR spectrum of 144
 chloral, cycloaddition with ketene 1113–14
 chloramine 503, 1282
 chloramphenicol, synthesis 1242
 chlorbenside, synthesis 775
 chloride
 as leaving group from tetrahedral intermediate 281
 as leaving group in substitution of pyridines 1151

- chloride (*cont.*)
 as nucleophile 470
 conjugate addition to unsaturated carbonyl compounds 228
- chlorides, alkyl, synthesis 430; *see also* alkyl chlorides
- chlorination
 at sulfur 1262
 of alcohols by thionyl chloride 660
 of alkanes via radicals 1035–9
- chlorination, of conjugated enamine 765
- chlorination, of phenoxyacetic acid 557–8
- chlorine, isotopes of, in mass spectrum 53–4
- chlorine, S_N2 at 423
- chloroacetic acid, in synthesis 557
- chloroacids, acidity of, and entropy 313–14
- chloroalkanes 33; *see also* alkyl chlorides, alkyl halides
 α -elimination of 1058,1070
- chlorobenzene
 nitration of 567
 reactivity of 567
- chlorocardolide A 824
- chloroethanol: 2-chloroethanol 660
- chloroform, α -elimination of 1058
- chloroformates, reaction with amines 1151
- chloromethylation 575, 1474
- chlorophyll, structure and conjugation 157
- chloroplatinic acid (H_2PtCl_6) 1294
- chloropyridines, from pyridones 1152
- chlorostyrene: 4-chlorostyrene, in polymerization 1462
- chlorosulfonation, of toluene (mechanism) 563
- chlorosulfonic acid 653, 645
- chlorosulfonium ion, in Swern oxidation 1262, 1272
- chlorotrimethylsilane, *see* trimethylsilyl chloride
- chlorphedianol, synthesis 790
- cholesterol 466
- cholesterol 1374, 1413–14, 1441–2
 biosynthesis from lanosterol 1445
- choline 1377
- chorismic acid, biosynthesis of 1403
- chromatography, chiral 402–4
- chromatography, separation of diastereoisomers 1222
- chromium trioxide, as oxidising agent, *see* chromium(VI)
- chromium(VI)
 as oxidising agent 222, 650, 951, 1303
 rearrangement during oxidation of allylic alcohols by 951
- chrysanthemac acid 29, 1449
- chrysanthemac acid, 1H NMR spectrum 266, 831
- chuangxinmycin, synthesis and NMR 828, 1209
- cigarette beetle, sex pheromone of 4
- cimetidine 204–6, 586–7
- cinchona tree, source of quinine 2
- cinflumide, synthesis 793
- cinnamic acid 705
- cinnamyl bromide 672
- CIP rules 387
- circles, around charges 24
- cis* 390
- cis*-decalin, drawing conformation of 466, 869–72
- cis*-enolates, effect on diastereoselectivity of aldol 899–902
- cis*-fused bicycles, stereoselective reactions of 864–70
- cis*-jasnone 717
- citral, synthesis by two pericyclic reactions 949
- citrate synthase 1390
- citric acid cycle 1390, 1392–3
- citric acid 34, 1346, 1390
- citronella
 (*R*) and (*S*), synthesis 1238
 in menthol synthesis 1237
 synthesis 1234–6
- Claisen condensation 669–70, 723–5, 730
 1,3-dicarbonyls from 1194
 disconnection for 796
 in biosynthesis 743–4, 1437
 intramolecular 734–6, 764–5, 875–6
- Claisen condensation, of acetyl CoA 1417
- of thioesters 744
- Claisen rearrangement 943–7, 949; *see also* Sigmatropic rearrangements
- Claisen–Cope rearrangement, *see* Claisen rearrangement
- Claisen–Schmidt reaction 724
- clathryimine A, structure of 824
- clavulanic acid, structure and NMR 843, 1122
- Clemmensen reduction 627
- clobutinol, retrosynthetic analysis and synthesis of 795–6
- clopirac, structure and synthesis 1158, 1188
- coal, source of organic compounds 2, 21
- CoASH 1389, 1392–3, 1395
- cobalt
 in Pauson–Khand reaction 1311, 1339–40
 in synthesis 1339–41
 in Vollhardt co-trimerization 1339–41
- cocaine 5, 862, 1122
- coconut oil 292
- codeine 186, 1423
- codon (triplet) 1350, 1353
- coenzyme A 744, 1389
- colchicine 180, 577
- collagen 1359
- collision, of molecules 113
- colour
 conjugation and 151, 170–1, 180
 use of in book 16–17
 wavelengths of absorption (table) 170
- combustion, heats of, for alkanes 455
- complementary strand 1349–51
- concentrated nitric acid, in nitration of benzene 552
- concentrated sulfuric acid, in nitration of benzene 552
- concentration, of water in water (55.5 mol dm^{-3}) 308
- concentration, proportionality of rate to 318
- condensation, aldol, *see* aldol condensation
- condensing enzyme (CE) 1426–8
- configuration 385, 448–9
 determination by NMR 825–8
- configurational stability, of organolithiums 1308
- conformation 385, 448–9
 importance in elimination reactions 492–3, 494
 of butane 452
 of chiral alkenes (Houk model) 895
 of chiral carbonyl compounds 888
 of chiral enolates 898
 of cyclohexanes 462–4
 of cyclohexanones 471
 of cyclohexenes 471
 of ethane 450–2
 of propane 452
 of saturated heterocycles 1128–33
 of sugars 1129
 stereoelectronic effects on 1128
- conformations, names for 453
- conformations, of 6-membered rings, names for 458, 461
- conformer 454
- coniine 1121, 1413
- coniochaetone A and B, structure and NMR 835
- conjugate acid, definition 183
- conjugate addition 227–40, 581–9
 and anti-cancer drugs 238
 axial attack in 860, 875
 catalysis by acid or base 233–4, 752–3
 effect of charge on 237–8
 effect of copper(I) salts 239–40
 effect of structure of α, β -unsaturated component 237, 750
 effect of temperature on regioselectivity 235
- equilibration of alkenes geometry via 807
- factors controlling regioselectivity 234–40
- frontier orbitals in 230, 750, 919
- hardness/softness and 238
- in Robinson annelation 761
- kinetic and thermodynamic control 235, 749–50
- of anion of allylic sulfone 1257
- of cyanide as 1,4-disconnection 800
- of enamines 754
- of enolate and enolate equivalents 749–68
- of enols 753–4
- of Grignard reagents and organolithium compounds 239–40, 607–8
- of hydrogen cyanide 237–8, 328
- of hydroperoxide anion 588–9
- of hydroxylamine to enones 371
- of lithium enolates 752
- of nitroalkanes 766–7
- of radicals 1042–8
- of silyl enol ethers 755, 757
- of sulfoxonium ylids 1260
- of tetrazole 1203
- of thiols 228, 237–8, 876, 936
- in drug manufacture 727
- to α, β -unsaturated sulfone 1164
- phase transfer catalysis of 753
- to butenolides 854
- to nitroalkenes 583
- to pulegone 860
- to unsaturated carbonyl compounds 227–40, 684, 735, 749–68, 859–60, 1396–7
- to unsaturated nitrile 582–3, 759, 768
- to vinyl epoxide 1332
- to α, β -unsaturated nitro 760
- vs. direct addition (1,4 vs. 1,2) 234
- conjugate additions, as 1,3-disconnections 783, 784
- conjugate additions, as 1,5-disconnections 798
- conjugate base, definition 183
- conjugate reduction, in polyketide biosynthesis 744
- conjugate substitution 585–8
- conjugated carbonyl compounds, formation by E1cb 496
- conjugated enol 547
- conjugation and delocalization, defined 155
- conjugation in enones 229
- conjugation 151–80; *see also* delocalisation and 1H NMR of alkenes 254–5 and 1H NMR shifts of aromatic rings 253–4
 effect on product stability 586
 effect on reactivity of alkenes 229–31
 effect on reactivity of carbonyl group 286–8, 728–9
 linear and cross 1159
 representation by curly arrows 159
 requirements for 157
 σ or hyper 562
- conrotatory 959–60
- constant, equilibrium 306–7
- constitutional isomers 384
- constructing orbital diagrams 167–8
- contraceptive, oral 214
- control, kinetic and thermodynamic 328
- convergent synthesis 749
- coordinatively saturated and unsaturated 1316
- Cope rearrangement 947–9
 in synthesis of citral 949
 of ectocarpene 949
 of periplanone B 965
- Cope rearrangements, effect of oxyanions 948, 965
- co-polymer 1464, 1489
- co-polymerization 1046, 1464–7, 1473
- copper, *see* cuprates
- copper(I) cyanide, in synthesis of nitriles 607
- copper(I) salts
 as co-catalysts 574, 1330
 effect on conjugate addition of Grignard reagents 239–40
 in nucleophilic aromatic substitutions 599–600
- copper, in acylation of Grignard reagents 299
- copper, phthalocyanine complex of 1179
- coprostanol 466
- Cordura 302
- Corey, E. J. 434
- Corey, enantioselective prostaglandin synthesis by 1229
- cortisone 1441
- corylone, structure and synthesis 9, 727, 747
- COT, *see* cyclooctatetraene
- coumarin 178, 1404
- Couper, Archibald 27
- coupling constants, in 1H NMR, factors affecting size of 268–70, 274 (*summary*)
- coupling
 2J (geminal) 273–4, 834–43
 2J , effect of π -contributions 844
 2J , in 6-membered rings 841–2
 2J , in A_2 systems 841
 2J , in A_2X systems 841
 2J , in AB systems 838–9
 2J , in ABX systems 840–1
 2J , in small rings 843
 2J , size of 838, 844 (*summary*)
 3J , and *cis* and *trans* ring junctions 829
 3J , axial/equatorial couplings 825–8
 3J , effect of dihedral angle on 824
 3J , in 6-membered rings 825–8, 861
 3J , in cyclic alkenes 830
 3J , in epoxides 831
 3J , in small rings 831–3
 3J , karplus relationship 825
 3J , orbital effects on 824–8
 4J , in cyclic alkenes 830
 between 1H and ^{13}C 369–71
 geminal 273–4, 834–43
 heteronuclear 368–71
 in 1H NMR 258–74
 in 1H NMR of furans 833
 in heteronuclear NMR 368–71
 to ^{31}P in NMR 368–9
- covalent bond, molecular orbitals of 102
- Cram, D. 974
- Cram's rule 889
- Crixivan (indinavir) 1116, 1482–7
- cross-condensation reactions 694–715
- cross-coupling reactions 1324–30
- crossed aldols 694–5, 700, 702, 707
- crossed ester condensations 728–32

- cross-linked polymers 1466–8
cross-linking of pre-formed polymers 1469–71
crotyl boranes 1284–6
crotyl bromide 607
crotyl silanes 1300
crotyl stannanes 1306–7
crown ethers, synthesis 1456, 1478
crown: 18-crown-6 1456, 1478
crude oil 21
crystallization, separation of diastereoisomers by 1266
CTP (cytidine triphosphate) 1376
cubane, structure and synthesis 373, 747, 991
cuparenone: α -cuparenone 1071
cuprate, reaction with epoxides 1132
cuprates, in synthesis 240, 1269
curly arrows
double headed 298
passing through an atom 140
tips on drawing 335
Curtius rearrangement 1073
cyanamide 1467
cyanide
as nucleophile 135, 434
conjugate addition as 1,4 disconnection 800
effect of temperature on conjugate addition to unsaturated carbonyl compounds 235
HOMO of 137
in conjugate addition reactions 227–8, 583
reaction with imines to form aminonitriles 356
cyano group 35
cyanoborohydride, *see* sodium cyanoborohydride
cyanoethylation 582–3, 759
cyanohydrins
decomposition in base 138
cyanohydrins 148, 235
hydrolysis of 149
in synthesis 138, 149
reaction with lithium aluminium hydride 149
cyanoimine, in conjugate substitution 587
cyclamate 29
cyclazine, structure and synthesis 1175
cyclic acetal, synthesis and stability 346, 1303
cyclic AMP (cAMP) 1352
cyclic esters, lactones 620
cyclic hemiacetals 341
cyclic nucleosides 1351–2
cyclic oligomers, in crown ether synthesis 1456
cyclic phosphates 1352
cyclic sulfonium salt 1250
cyclic thioacetals, *see* dithianes
cyclic transition state, for aldol reaction 698
cyclic transition state, for crotylation reaction 1306–7
cyclitols 1369–70
cyclization reactions, classification of by Baldwin's rules 1140–4
cyclization
by intramolecular Claisen ester condensation 764–5
of 1,5-dicarbonyl compound 760
of unsaturated radicals 1049–50
cyclizine, synthesis 1123
cyclo-, as prefix 28
cycloaddition 905–40
[2+1], of singlet carbene and alkene 1063–6
[2+2], in synthesis of periplanone B 964
[2+2], of ketene with chloral 1113–14
[2+2], photochemical 927–9
[2+2], thermal 929–32
[4+2], *see* Diels–Alder reaction
[4+3], of furan and oxallyl cation 1016
[8+2], of indolizine and alkyne 1175
[3+2] and 1,3-dipolar 932–9, 964, 1201–3
1,3-dipolar, of osmium tetroxide to alkene, *see* dihydroxylation
1,3-dipolar, of ozone, *see* ozonolysis
reverse 1269
using palladium catalysts 1334–5
cycloadditions
entropy of activation 1101
frontier orbital description 914–15
number of p-electrons 916
thermally allowed 924
cycloalkancarboxylic acids, synthesis of 679
cycloalkanes, ring strain in 455–6
cyclobutadiene, tetra-*t*-butyl, NMR and structure 373
cyclobutane, structure and conformation 29, 38, 457
cyclobutane, synthesis by [2+2]-cycloaddition 931
cyclobutanol 1444
cyclobutanone, effect of ring strain on reactivity 144–5
cyclobutenyllithium, in synthesis 1306
cyclobutyl bromide, synthesis 1443
cyclobutyl cation 1443–4
cyclodecane 38
cycloheptane 38
cycloheptatriene 196
cyclohexadiene 592
cyclohexane
barrier to ring-flipping 461
structure and conformation 29, 38, 456, 457–70
cyclohexanes
how to draw 459–60
substituted, conformation of 462–4
substituted, reactions of 466–70
cyclohexanone 672, 696
cyclohexanones, conformation of 471
cyclohexanones, direction of nucleophilic attack on 472–3
cyclohexene, reaction with electrophiles 549
cyclohexenes, conformation of 471
cyclohexenyl cation 416
cyclohexylamine, in imine formation 708
cyclononane 38
cycloocta-1,5-diene, hydroboration of 1281
cyclooctane 38
cyclooctatetraene
as σ and π complex (η^1 , η^3 and η^5) 1313
dianion and dication 172–3
heat of hydrogenation 173
cyclooxigenase 1431–2
cyclopentadiene
[1,5]-sigmatropic shifts in 953–4
dimerization 315
in Diels–Alder reaction 908, 1226–9
in synthesis 739
p*K*_a of 195–6
polymerization 1451
stable anion from 177
cyclopentadienyl, as σ , π complex (η^1 , η^3) 1313
cyclopentane, structure and conformation 38, 457
cyclopentanone 674, 691
in enamine formation 739
in prostaglandins 1268
cyclopentenediol, precursor for prostaglandin synthesis 1268
cyclopentenyl chloride 677
cyclophanes, ¹H NMR spectra 252
cyclopropanation *see* Simmons–Smith reaction
by biological reaction 1443
use of π -allyl intermediates 1333
using an allylic sulfide 1257
using sulfonium ylids 1260
using sulfoxonium ylids 1261
cyclopropane, conformation of 456–7
cyclopropanes 29, 37, 1066
from alkyl carbene insertion 1070
from carbene reaction with alkene 1063–6, 1068
synthesis of 666; *see also* cyclopropanation, Simmons–Smith reaction
cyclopropanone, effect of ring strain on reactivity 144–5
cyclopropyl cations, electrocyclic reactions of 963
cyclopropyl methanol 1443–4
cyclopropylbenzaldehyde-4-cyclopropylbenzaldehyde 1259
cyclopropyllithium 1263–4
cypermethrin 138
cysteine 1355
in fatty acid biosynthesis 1428
cytidine triphosphate (CTP) 1376
cytosine 1347
¹H NMR 259
d block 89
d orbitals 87
D, L nomenclature 389–90
D: 2,4-D, *see* 2,4-dichlorophenoxyacetic acid
d¹ reagent, dithiane 1256
d¹ reagent, dithioesters 1264
d¹ synthon 1396
d¹ synthon, nature's acyl anion equivalent 1392
d² synthon 791
D₂O shake 548
D₂O, as NMR solvent 257–8
d³ reagent, homoenolate 1303
DABCO, basicity and reactions of 1123–4
DABCO, in the Baylis–Hilman reaction 1124
dacron 291
damascenone, smell of roses 4
daminozide, synthesis 773
dapsone 149, 1247
darvon alcohol 1233
darvon 403
dashed bonds 381, 385
dative covalent bond 116
daunomycin 519, 1433
daunorubicin 217–8
dba, *see* dibenzylidene acetone
DBE (double bond equivalent) 74–5
DBN as base for elimination reactions 202, 482
DBU as base for elimination reactions 202, 482, 485–6
DCC (dicyclohexylcarbodiimide) 1172, 1476–7
DDQ 3, 1192, 1210
stable anion from 54
deactivating groups, in electrophilic aromatic substitution 564–8
DEAD (diethyl azodicarboxylate) 42, 431, 911–2
Dean–Stark head 347
decalin, *see cis*-decalin, *trans*-decalin
synthesis of derivatives 1324
decalins, conformation of 465–6
decalins, ring expansion of 1007, 1009
decamethrin, insecticide 10, 1066
decane 38
decarbonylation 1319
decarboxylase enzymes 1387–8
decarboxylation
in Knoevenagel reaction 703
in ofloxacin synthesis 742
in resveratrol biosynthesis 1436
of acetoacetate and malonate derivatives 678, 736, 751
of amino acids by reaction with pyridoxal 1417
of DOPA 1420
of histidine 1387
of pyrrole 1159
using decarboxylase enzymes 1387–8
decyl group 26
decyne: 1-decyne 649
degeneracy, in atomic orbitals 87
dehydration
enzymatic 1427
in aldol reaction 691–718
in polyketide synthesis 744
in resveratrol biosynthesis 1436
of oximes 569–70
using enolase 1391
dehydrogenase, in shikimate pathway 1402
dehydrogenation
of guaioil with sulfur 830
of heterocycles 1175, 1212
with FAD 1407
dehydroquinic acid 1402
delocalization and conjugation defined 155
delocalization 151–80; *see also* conjugation
effect on reactivity of C=O 287
effects on product stability 586
in carbocation intermediates 562
in enolate chemistry 703
in nucleophilic aromatic substitution 591
in thioesters 744
of enolate anion 527
of lone pair in pyrrole 1157
deoxy: 2-deoxy-D-ribose, in synthesis of (*R*)-sulcatol 1223
deoxycytidine 1351, 1482
deoxyguanosine 1351
deoxyribonucleic acid (DNA) 81, 1348–51
deoxythymidine 1351, 1481
deprotection 632–7, 657
of dioxalanes 1269, 1371
of silyl ethers 738
deprotonation, irreversible 724
deprotonation, of terminal alkyne 1291
deshielding of nuclei in NMR 59–61
Dess–Martin periodinane 639
DET, *see* diethyl tartrate
detoxification of carcinogens 584
deuteration, detection by mass spectrum 525
deuterium
in kinetic isotope effect 486–7
isotopic labelling with 525, 1383, 1409–11, 1426
nuclear spin of 57
deuteriochloroform (CDCl₃) as NMR solvent 59, 245
Dewar benzene 154
dexfenfluramine 1220
dextrorotatory 389
DHQ (dihydroquinine), use as chiral ligand 1241–3
DHQ₂PHAL 1242–3
DHQD (dihydroquinidine), use as chiral ligand 1241–3
DHQD₂PHAL 1242–3
diagrams, energy profile 306–34

- dianions, alkylation of 631, 683
diastereoisomers 390–5
drawing acyclic 887
from aldol reaction 699
diastereomers, *see* diastereoisomers
diastereoselective addition to chiral alkenes 895–7
diastereoselective addition, to acyclic carbonyl compounds 887–96
diastereoselective addition, to bicyclic carbonyl compounds 861–8
diastereoselective addition, to cyclic carbonyl compounds 851–8
diastereoselective aldol reaction 898–902
diastereoselective alkylation of chiral enolates 853–6, 864, 867, 897–8
diastereoselective attack on unsaturated 6-membered rings 858–60
diastereoselective conjugate addition 854
diastereoselective epoxidation of chiral alkenes 855–6
diastereoselective hydrogenation 864–5
diastereoselective reactions 851–902, 1225–30
diastereoselective tandem addition to cyclic enone 855
diastereotopic faces 885–6
diastereotopic 836, 837
diatomics, electronic structure of 96–104
diaxial interactions 462
diazabicyclooctane, *see* DABCO
diazo coupling 572
diazo group, in dyestuffs 566
diazo transfer agent, tosyl azide 1057
diazocarbonyl compounds
carbenes from 1056–7, 1068, 1072
in cyclopropanation reaction 1068
synthesis 1056–7
diazomethane 3, 1054, 1400
formation of 1054
in homologation of acid 1072
in ring expansion of cyclic ketone 988
insertion into ketene 1112
photolysis of 1055
reaction with acid 1053–4
reaction with acyl chloride 1056–7
reaction with alcohols and phenols 1054
diazonium salts
semipinacol rearrangement of, *see* Tiffeneau–Demjanov rearrangement
stability and decomposition of 125, 130, 331
synthesis of 572, 597–600
diazotization 572, 597–600, 647
of amino acids 1223
DIBAL, reduction with 42, 620, 650, 697, 1266–7, 1308, 1451
dibenzoyl ornithine 1416
dibenzoyl peroxide, homolysis of 1021, 1023
dibenzoyl peroxide, in radical polymerization 1459
dibenzylidene acetone 807, 1320
diborane, *see* borane
dibromoalkane, α -elimination of 1059
dibromo: α, α' -dibromoketone, reaction with zinc 924
dibromophenol: 2,4-dibromophenol 556
dicarbonyl
1,3-dicarbonyl compounds, by Claisen condensation 1194
enols of 532–3
reaction with acetamide to form pyridones 1194
reaction with anilines 1210
reaction with hydroxylamine 1201
retrosynthetic analysis of 786
1,4-dicarbonyl compounds, from succinic anhydride 801
in cyclopentenone synthesis 1187
in synthesis of 5-membered heterocycles 1186–7
retrosynthetic analysis of 800
1,5-dicarbonyl compounds, cyclization of 760
1,5-dicarbonyl, from conjugate addition of enolates 749
dichloroalkane, α -elimination of 1058
dichlorocarbene
by decarboxylation of sodium trichloroacetate 1059
by α -elimination of chloroform 1058
reaction with phenol 1069
dichlorodicyanoquinone, *see* DDCQ
dichloroketene, synthesis of 930
dichloromethane, unreactivity of 1133
dichlorophenoxyacetic: 2,4-dichlorophenoxyacetic acid, synthesis 774, 775
dictyoptere 1066
dicyclohexylcarbodiimide, *see* DCC
dicyclohexylurea, by-product in peptide synthesis 1477
Dieckmann condensation 727, 730
dieldrin, by Diels–Alder reaction 909
Diels, Otto 905
Diels–Alder reaction 905–24
dimerisation of dienes by 915–16
endo rule for 912, 916–17
entropy effects on 917
frontier orbital description 906, 914–15, 919–21
in asymmetric synthesis 1226–9, 1232
in synthesis of steroids 876
intramolecular 917–19, 921
of aromatic heterocycles 1163–4
of benzynes 923, 1110
of masked ketenes 931
regioselectivity 919–21
solvent effects 917
stereochemistry 909–13
Woodward–Hoffmann rules and 922–3
dienes
electrophilic addition to 510–11
in the Diels–Alder reaction, *see* Diels–Alder reaction
synthesis 481, 1328
dienone–phenol rearrangement 988–9, 996, 1103, 1424–5
dienophile, chiral, in asymmetric synthesis 1229
dienophile, in the Diels–Alder reaction, *see* Diels–Alder reaction
diethyl azodicarboxylate, *see* DEAD
diethyl carbonate, in Claisen condensations 36, 728, 730–1
diethyl ether 32, 40
diethyl fumarate, conjugate addition to 751
diethyl hexanedioate, *see* adipic acid
diethyl malonate 677, 702
diethyl malonate, conjugate addition of 751, 764
diethyl malonate, magnesium derivative 742
diethyl malonate, reaction with orthoformate 1211
diethyl oxalate, in Claisen condensation 728–9, 731
diethyl oxalate, in Reissert indole synthesis 1208
diethyl phenylmalonate, synthesis 730
diethyl phthalate, in synthesis of pival 732
diethyl tartrate, in asymmetric synthesis 1265–6
diethyl tartrate, L-(+)- and D(-)-, in asymmetric epoxidation 1239–41
diethylaluminium chloride 1227
diethylamine, as thiophile 1268
diethylene glycol 1457
diethylenetriamine 1457
dihedral angle 451
dihedral angle, effect on coupling in NMR 824
dihydropyran 543
reaction with *meta*-chloroperbenzoic acid 828
dihydropyridazolone 1196
dihydropyridine 1383
synthesis and reactions 1191–3
dihydropyridines, as drugs 1192–3
dihydroquinidine (DHQD), use as chiral ligand 1241–3
dihydroquinine (DHQ), use as chiral ligand 1241–3
dihydroquinoline, by reaction of unsaturated carbonyl compound with aniline 1210
dihydroxyacetone-3-phosphate 1360, 1388
dihydroxyketone, reaction to form spiroketal 1131
dihydroxylation
asymmetric, *see* asymmetric dihydroxylation
of alkene by osmium tetroxide 937–8
of enol ether 938
of enone 878, 938
of vinyl silane 1304
dihydroxyphenyl: 3,4-dihydroxyphenylalanine, *see* DOPA
dihydroxyphenylpyruvate 1419–20
di-isobutylaluminium hydride, *see* DIBAL
diisopropylamine 668
diketene, structure and spectra of 372
diketone
1,2-diketone, rearrangement of under basic conditions, *see* benzilic acid rearrangement
synthesis by nitrosation 539
1,3-diketone, by aza-enolate chemistry 740
by crossed Claisen condensation 732
in synthesis of pyrazole 1188, 1196–7
in synthesis of pyrimidine 1188, 1198
retrosynthetic analysis of 796
synthesis of 699, 741, 764–5
1,4-diketone, by conjugate addition of nitroalkane 767–8
by hydrolysis of furan 1161
cyclisation of, to cyclopentenone 1162
in synthesis of pyridazine 1188, 1195
in synthesis of pyrrole 1188
1,5-diketone, in synthesis of pyridine 1187, 1193
diketopiperazine 651
dilute nitric acid, in nitration of phenol 568
dimeone 523–4, 532, 764
dimerization reactions 689–93
dimerization, effect of temperature on equilibrium 315
dimethoxyethane, use as solvent 602, 744
dimethyl dioxirane, in oxidation of furan 1161
dimethyl disulfide, reaction with lithium enolate 1269
dimethyl ether 1258
dimethyl fumarate, as dienophile 910
dimethyl maleate, as dienophile 909
dimethyl sulfate 420, 541, 1197
dimethyl sulfide, alkylation of 1258–9
dimethyl sulfide, cleavage of ozonide 939
dimethyl sulfoxide, *see* DMSO
dimethylallyl pyrophosphate 1439
dimethylaminopyridine, *see* DMAP
dimethylformamide, *see* DMF
dimethylhydrazones, of ketones, reaction with acid chlorides 739
dimethylphenol
2,6-dimethylphenyl esters, in *anti*-aldol reactions 901
dimethylsilyl dichloride 1457
diniconazole, structure and geometrical isomers 804
dinitration of chlorobenzene 591
dinitrophenylhydrazine:
2,4-dinitrophenylhydrazine 612
diol: 1,3-diol, determination of configuration using acetal 861
diols
from epoxidation 938
formation in nature 1220
from pinacol reaction, *see* pinacol reaction
oxidative cleavage with lead tetraacetate 878
reaction with carbonyl compounds to form acetals 346–7
rearrangement of, *see* pinacol rearrangement
retrosynthetic analysis of 799
syn, by dihydroxylation of alkene 937–8
1,1-diols, by reaction of water with carbonyl compounds 143–5
1,3-diones, reaction with methylamine 765
diosgenin 1447
dioxane 1122
dioxolanes 346–7, 505, 1138, 1253, 1269–70; *see also* acetals
DIPAMP 1236
diphenylketone (benzophenone) 694
diphenylmethane, synthesis of 569
dipolar cycloaddition: 1,3-dipolar cycloaddition, *see* cycloaddition, 1,3-dipolar
dipole, caused by electronegativity 114
dipole, reason for attraction between molecules 114
direct addition vs. conjugate addition 234
directed aldol reactions (summary and table) 720
directing effects of aromatic substituents (summary table) 568
disaccharide 1372
disconnection
1,2-C–C 786–90
1,2-diX 780–4
1,3-diCO 796–7
1,3-diO 791–7
1,4-diCO 800
1,5-diCO 798
between C and X 772–84
definition of 772–3
guidelines for 775–87
of 1,4-related groups 800
of allylic alcohols 789
of carbon–carbon bonds 784–801
of ketones 790
1,2-disconnections 781–3
1,3-disconnections 783–4
disiamylborane, structure and synthesis 1281–2
disparlure, pheromone of gypsy moth 4, 1240
dispersol dyes 8
disrotatory 959–60
dissociation, of acids 184–5
dissolving metal reduction 628, 683–4, 1318
disulfide 1249–50
cross linking 1354–5

- in vulcanization of rubber 1469
diterpenes 1439
dithianes, as acyl anion equivalent 1127–8, 1254–6
dithioacetals 1362–3; *see also* dithianes
dithioesters, synthesis of 1264
divinylbenzene: 1,4-divinylbenzene, use in cross-linked polymers 1466
Djerassi, C 989
D-line 389
DMAP, as nucleophilic catalys 1153, 1165, 1484
DMAP, pK_a of 1165
DMDO, *see* dimethyl dioxirane
DMF (dimethylformamide)
as a catalyst of acyl chloride formation with oxalyl chloride 296
as electrophilic source of formyl group 301
as solvent 422, 429, 666, 677
in Vilsmeier reaction 1158
structure and NMR of 42, 165, 363
DMP-266, reverse transcriptase inhibitor 1483
DMSO (dimethyl sulfoxide) 42
as solvent 601, 666
in sulfoxonium ylid synthesis 1261
in swern oxidation 639, 1271–2
DNA (deoxyribonucleic acid) 81, 1348–51
DNA polymerase 584
dnnp 1237
dofetilide (tikosyn), synthesis 658–61
donation of electrons by nucleophiles 116
donor synthons, definition of 791
DOPA, (3,4-dihydroxyphenylalanine) 993, 1220, 1236, 1419–20, 1448
double bond equivalents (DBEs) 74–5
double bond isomers, *see* geometrical isomers
double bond region of IR 70
double bonds, orbitals of C=O, C=N, C=C 108–9
double doublet, in 1H NMR 267
double-headed curly arrows 298
doublet, in 1H NMR 259–63
Dowex resin 234, 1371
doxazolin (Cordura) 444
doxazosin 302
doxipromine, synthesis 794
drawing bonds in transition metal complexes 1313
drawing molecules 21–5
drawing proteins, N and C terminus 1358
driving equilibria in desired direction 310–12
drugs, chirality and 403
Duff reaction 1489
dyestuffs 2, 7–8, 566
E, Z isomers, *see* geometrical isomers
E, Z-dienes, [1,5]-sigmatropic hydrogen shifts in 955
E1 and S_N1 compared 478, 483–7
E1 elimination 477–87
energy profiles 488–90
in polymer termination 1462
of acetals 542
of tertiary alcohol 692
selectivity in 487–90
E1cb elimination 495–500, 1392
in aldol condensation 691–4, 714
rate equation 497
under biological conditions 1402, 1404–5, 1427
E-1-nitropentadec-1-ene 697
E2 elimination 477–87, 490–5, 1401
E-alkenes 487
by Julia olefination 810–12
by lithium aluminium hydride reduction of alkyne 819
by Peterson reaction 812–14
by sodium/ammonia reduction of alkyne 819
by Wittig reaction 817
E-alkenoic acid 703
earth, age of 317
E-cinnamic acid, biosynthesis of 1404
eclanamine, synthesis 435
eclipsed conformation 450–1
E-crotyl boronate 1286
ectocarpene, by Cope rearrangement 949
EDTA, 1H NMR spectrum 257–8
ee (enantiomeric excess), measurement of 1230–43
E-enal, synthesis using selenium dioxide 1271
eicosanoid, arachidonic acid 1431
eighteen: 18-electron rule 1312
elaïdic acid, monosaturated fatty acid 743
elastane polymer 1448, 1463
elastomer, definition of 1458
eldanotide, synthesis via conjugate addition 854
electrocyclic reaction, in synthesis of periplanone B 965
electrocyclic reactions 956–64
conrotatory and disrotatory 959–60
effect of ring strain 957
in superacid media 963
in vitamin D biosynthesis 961
of anions 963
of aziridine 964
of cations in Nazarov cyclization 962
of cyclopropyl cations 963
photochemical 961–2
rules for 960
Woodward–Hoffmann rules for 957–9
electromagnetic radiation, interaction with molecules 47
electron flow, in mechanisms 130
electron impact (EI) mass spectrometry 50
electron paramagnetic resonance (EPR), *see* electron spin resonance
electron spin resonance 87, 1024–5
observation of carbene by 1056
electron: 18-electron rule 1312
electron-donating groups, effect on pK_a 196, 200
electron-donating substituents 561–4
electronegativity
and ^{13}C NMR shifts 63
and 1H NMR shifts 246
carbon and silicon compared 1287
effect on bond polarisation and dipoles 103, 114
effect on coupling in NMR 269, 273
of metals 210
relationship to orbital energy 101
summary 121
electronic effects in electrophilic aromatic substitution 555–76
electronic structure, of atoms 83–95
electronic transitions, $n-\pi^*$ and $\pi-\pi^*$ 171
electrons
aromaticity and number of 173–7
eight, the limit for B, C, N, O, F 128
occupation of orbitals 93–5
electron-withdrawing groups 564–6
effect on pK_a 193, 200
effect on reactivity of carbonyl group 144–5
electron-withdrawing substituents 564–6
electrophile
choice for alkylation (table) 667
definition and examples 115, 119–20
in Heck reaction 1325
electrophiles (one carbon), summary 575
electrophiles, hard and soft 238
electrophiles, reaction with allyl silane 1298
electrophilic addition to alkenes,
stereospecificity of 882
electrophilic addition to alkenes,
stereoselectivity of 514–17
electrophilic alkenes 581–613
electrophilic aromatic substitution of benzene, table of reactions 555
electrophilic aromatic substitution of toluene 562
electrophilic aromatic substitution on aniline 558–9
electrophilic aromatic substitution 547–79
conjugation and stability of intermediates 1159 (ch 43)
intramolecular 1420 (ch 51)
mechanism of 550, 554 (ch 22)
of CO_2 576 (ch 22)
of furan 1160 (ch 43)
of indoles 1170 (ch 43)
of isoquinoline 1174 (ch 43)
of phenols 555–8 (ch 22)
of pyridines 1150–2 (ch 43)
of pyrroles 1157–9 (ch 43)
of quinoline 1174 (ch 43)
of thiophene 1160 (ch 43)
polymerization by 1455 (ch 52)
trapping of intermediate 1109–10 (ch 41)
using michael acceptors 584–5 (ch 23)
 π -complex in 1110 (ch 41)
electrophilic silicon 707 (ch 27)
electrophilic substitution with allylic rearrangement 1298–9 (ch 47)
electrophilicity, of carboxylic acid derivatives 286–8, 704, 728–9 (ch 27)
electrostatic attraction between molecules 114 (ch 1–10)
elimination: α -elimination 1058–9, 1070
elimination mechanisms; E1 477–87 (ch 19)
E1, E2, and E1cb, compared 499–501 (ch 19)
E1cb 495–500 (ch 19)
E2 477–87 (ch 19)
elimination of sulfoxides 1269–70
elimination reactions 444, 477–502
elimination
and conformation 492–3, 494
and steric hindrance 480
anti-periplanar 490–1
comparison with substitution 477–80
compounds that cannot undergo 483–4
formation of alkynes by 493–4
Hofmann and Saytsev 495
in aldol reaction 697
in enamine formation 479
in ester hydrolysis 479
leading to substitution 498
leaving group and 484–7
regioselectivity of 489–90, 495
stereoselective 487–9, 809–11, 884
stereospecific 490–2, 812–13, 882
syn-periplanar, in Peterson reaction 813
to form alkenes 803–6
elimination–addition mechanism 601, 603
empty orbitals, reason for attraction between molecules 114
emulsifier, industrial, identification of 73–4
emulsion paints 1467
enals 228, 692, 699, 708
infra red spectrum of 365
enamine, cyclic 6-membered, axial attack on 858
enamine, in pyridine ring 1385
enamines 353, 671–5, 697, 708–9, 1123
 1H NMR shifts 254–5
acylation of 739–40
as enol equivalents for conjugate additions 754
from 1,3-diones 765
in Robinson annelation 762–3
reaction with acyl chloride 1010
stability of 1123
tautomerism with imines 530
enantiomeric excess (ee), improvement of by recrystallisation 1237
enantiomeric excess (ee), measurement of 1230–2
enantiomerically enriched 1230
enantiomerically pure 386
enantiomers
definition 382
identical nmr spectra 363
in nature 1219–21
enantioselective allylation 1285–6
enantioselective Heck reaction 1324
enantioselective hydrogenation 1235–9, 1484
enantioselective hydrolysis 1438
enantioselective reduction, of pyruvic acid 1382–3
enantioselective synthesis, *see* asymmetric synthesis
enantioselective synthesis, of prostaglandins 1229
enantioselectivity 1233–43
in AD reaction 1241–3
in allylic alkylation 1334
in Sharpless asymmetric epoxidation 1239–41
enantiotopic faces 885, 1383
enantiotopic 835–6, 1374, 1439
endiandric acid, biosynthesis by pericyclic reactions 960, 961
endo face, in bicyclic structure 862, 1254
endo product, from Diels–Alder reaction 1226–8
endo rule, *see* Diels–Alder reaction
enediol 529, 1360
enediolate, from acyloin reaction, *see* acyloin reaction
ene-dynes, synthesis of 1330
energy barrier for reaction 113
energy gap between orbitals in reactions 121–2
energy level diagram
for sodium fluoride 101
of electrons in atomic orbitals 93–95
of hydrogen molecule 96
of other diatomic molecules 100
of π bond 103
energy levels
nuclear, and nmr 57
of electrons in hydrogen atoms 85, 93
of electrons in non-hydrogen atoms 94–5
energy profile diagrams 306–34, 488–90, 554, 560
energy
activation (E_a or ΔG^\ddagger) 316–23
Gibbs free, ΔG° 307–15
of intermediates and transition states 320–3
enol and keto- tautomerism 523–45
enol ester 725
enol ether
ozonolysis of 806, 939
synthesis 541–2, 1303
enol ethers
 1H NMR shifts 254–5
halogenation 543–4

- enol ethers (*cont.*)
 hydrolysis 542–3
¹H NMR coupling constants 269, 273
- enolase 1391
- enolate equivalents, stable 540–1
- enolate formation, order of reactivity of acid derivatives 704
- enolate
 of diethyl malonate 702
 of malonic acid 703
 of Meldrum's acid 1332
- enolates 526–31, 689–722
 addition to α,β -unsaturated nitriles 759
 alkylation 528, 663–87
 boron 901
 chiral 1230
 chiral, conformation of 898
 chiral, diastereoselective alkylation of 897–8
 condensation with ethyl formate 1198
 conjugate addition of 749–68
 cyclic, 6-membered, axial attack on 859
 elimination of β oxygen substituent 852
 for aldol reactions, (table) 712
 geometry of 899–902
 halogenation of 537–8
 in Ireland–Claisen rearrangement 948
o-acylation 528
 of amides 704
 of anhydrides 705
 of esters 705–6
 of free carboxylic acids 706–7
 of thiol esters 744
 reversible addition of 750
 types of, summary 528–31
- enolization 524–5
 acid and base catalysis 526–8
 consequences of 534–5
 in thiol esters 1389–90
 of carboxylic acid derivatives 704
 requirements for 531
 substituents preventing (table) 695
- enols and enolates 523–45, 689–722
- enols
 acidity of 527
 conjugate additions of 753, 754
E and *Z* isomers 525
 evidence for 525–6
 halogenation of 535–6
 kinetically stable 531
 nitrosation of 538–9
 NMR spectra of 531
 of anhydrides 704–5
 of esters 705–6
 of free carboxylic acids 529–30, 706–7
 proportion in equilibrium with ketone 525
 stability 525, 531–3
 types of, summary 528–31
- enones 227–8
 [2+2] cycloaddition with allene 964
 conjugation in 229
 cyclic, aromatisation of 766
 cyclic, axial attack of cuprate on 860, 875
 cyclic, from 1,5-dicarbonyl 760
 cyclic, from diketone 805
 cyclic, tandem addition to 860
 effect of Cu(I) on reaction with Grignard reagents 227
 epoxidation of 804, 809
 formation by elimination 495–9, 692, 693, 694
 geometrical isomerisation of 808, 809
 IR and ¹³C spectroscopy 230
 reaction with amines 231
 reaction with cyanide
- enthalpy and equilibria, ΔH^\ddagger 312–15
 enthalpy of activation, ΔH^\ddagger 319
- entropy and equilibria, ΔS° 312–15, 602
 entropy of activation 319, 1101–2, 1136, 1139
 entropy, as a factor in the formation of hemiacetals and acetals 341, 345, 347
- envelope conformation, of 5-membered rings 457
- enzyme (alliinase), in onions and garlic 1272
- enzyme
 aldolase 1388
 amino acid ammonia lyase 1404
 catalysis of rearrangement by 1398
 citrate synthase 1390
 cyclooxygenase 1431
 DNA polymerase 584
 enolase 1391
 HMG-CoA reductase 1438
 lipoygenase 1432–3
 liver alcohol dehydrogenase 1382–3
 phenylalanine hydroxylase 1409
 ribonuclease 1358
- enzymes
 aminotransferases 1385, 1387, 1391
 epoxidation by 1444
 in biosynthesis 1426–44
 in nature 1358
 in reduction, nitroalkene to nitroalkane 697
 synthesis using a polymer support 1477
- ephedrine 393
- epibatidine 1163
- epichlorohydrin 782, 1457
 mechanism of substitution 1113
 reaction with 1,2,5-thiadiazole 1213
 reaction with amine 782
- epimerization 860
- epinephrine (adrenaline) 393, 1413
- episulfonium ion 1258, 1263–4
- epoxidation 505–8; *see also* epoxides
 by hydrogen peroxide 1408
 diastereoselective 886, 896–7
 enzymatic 1444
 in polymerization 1457
 Jacobsen 1488
 of 5-membered cyclic alkene 855–6
 of allene 1112
 of allylic alcohol by vanadyl (acac)₂ 878
 of allylic alcohol 877
 of aromatic rings 1408–9
 of cyclic compounds 863, 866, 877–8
 of enones 804, 809
 of *homo*-allylic alcohol 877–8
 of vinyl silane 1301
 stereoselectivity of 884
 stereospecificity of 507, 883
- epoxides
 by ring-opening of iodolactonisation products 873
 by S_N2 displacement 1015, 1132, 1134
 coupling in ¹H NMR 831
 formation from alkenes 505–508; *see also* epoxidation
 formation from bromohydrins in base 513
 from sulfur ylids 1168, 1259
 fused to six-membered rings, regioselectivity of reactions 468–70
 in 1,2-disconnections 781, 782
 nucleophilic attack on, *see* opening of, and individual reactions
 opening of 435, 437–8, 513–14, 631–2, 1132, 1241–2, 1301
 opening of, entropy of activation 1101
 opening, by halides 470
 rate of formation by ring-closing reaction 1138
- reaction with alcohols 781
 reaction with hydrazine 782
 reaction with imidazole 1167
 reaction with triazole 1168
 reaction with trimethylaluminium 892
 rearrangement of 985, 1015
 regioselective opening 513–14
 ring strain in 435
 specific base catalysis in opening of 1104
 stereospecific opening 435, 437–8, 514, 883, 1301
- epoxidising agents 505–8, 589, 1484
- epoxy alcohol, Payne rearrangement of 977
- epoxyketones, in Eschenmoser fragmentation 1008
- EPSP, 5-enolpyruvylshikimate 3-phosphate 1403
- equatorial protons, coupling in ¹H NMR 825–8
- equatorial substituents 459, 462–5
 reactivity of 467–8
- equilibria 306–15
 effect of acid and base 311–12
- equilibrium constant
 and composition 306–9
 between acids and bases 185
K, definition 307
 variation with temperature 314–15
 variation with ΔG° 308
- equilibrium control, in aldol reactions 718–19
- equilibrium
 between acetal and carbonyl compound plus alcohol 345
 between axial and equatorial substituents 462–4
 between hemiacetal and aldehyde plus alcohol 341
 between keto- and enol forms 524–7
 control, by removal of product 289
- ergosterol 1441
- erucic acid 649
- erythritol, synthesis of 1363
- erythronolide A, 213–14
- erythrose 1361
- erythrose-4-phosphate 1401
- Eschenmoser fragmentation 1008
- Eschenmoser, A. 1008
- Eschenmoser's salt 714
- esr, *see* electron spin resonance
- essential oils 2, 1437
- ester enolates, equivalents for 706
- ester exchange, mechanism of 322–3
- esterification 289, 644–5, 1454
 nucleophilic catalyst for 1149
 use of acetic anhydride 599
 use of tosyl chloride 655–6
- esters
¹³C NMR spectra 363
 alkylation of 669
 basicity of 203
 conformation of 1133
 decarboxylation of 678–9, 1159
 enols and enolates of 529
 formation, acid catalysis of 310–11
 formation, stereochemistry of 433
 from alcohols and acyl chlorides 280–1
 from alcohols and anhydrides 280–1
 from alcohols, summary 290
 from carbene homologation of acid 1072
 from carboxylic acid and alcohol 289
 from diazomethane reaction with acid 1053, 1054
 from Favorskii rearrangement of α -halo ketone 990–992
 functional group and compound class 34
 geometry of enolates of 901
- hydrolysis, effect of pH on rate 350
 hydrolysis, Hammett relationship in 1090–4
 hydrolysis, mechanism and acid and base catalysis 290, 323–5, 1103–4
 in acyloin reaction, *see* acyloin reaction
 in conjugate addition reactions 751
 orbitals of 1133
 p*K*_a of 197
 reaction with amines 285
 reaction with Grignard reagents or organolithiums to form tertiary alcohols 297–8, 790
 reactivity of towards nucleophiles 287–8
 reduction of 298, 618, 620, 1242, 1253
 retrosynthetic analysis of 772
 reversibility of formation 289–90, 309–11
 stability of 1133
t-butyl, hydrolysis by S_N1 436
 α,β -unsaturated, reaction with nucleophiles 228–32, 236, 240
- estradiol, *see* oestradiol
- Et 26
- eta: η , hapto number 1312–13
- eta: η^3 allyl complex, in Ziegler–Natta polymerization 1464
- eta: η^4 diene complex, in Ziegler–Natta polymerization 1464
- ethanal, *see* acetaldehyde
- ethane, lack of functional groups 31
- ethane, structure and conformation of 37, 450–2
- ethane-1,2-diol (ethylene glycol) 1454
- ethanediamine, use in polyurethane synthesis 1458
- ethanol 31
- ethene, *see* ethylene
- ethenol 531
- ether (diethyl ether) 32, 40
- ethers
 basicity of 204
 by reaction of diazomethane with alcohols or phenols 1054–5
 cleavage 434
 cyclic, synthesis of 1337
 from alkyl halides 420–1, 1234
 functional group and compound class 32
 neighbouring group participation by 972, 973
 retrosynthetic analysis of 774, 796
- ethoxide, as base in Claisen ester condensation 726
- ethyl 3-oxobutanoate, *see* ethyl acetoacetate
- ethyl acetate 40
- ethyl acetate, in Claisen ester condensation 724
- ethyl acetoacetate 677, 702, 724
- ethyl acrylate 228, 584
- ethyl benzoate, in crossed ester condensation 728
- ethyl formate, in crossed ester condensation 728, 1198
- ethyl group 26
- ethyl lactate
 (*S*)-ethyl lactate 1223–4
- ethyl magnesium bromide 1266
- ethyl magnesium bromide, use in aza enolate formation 675
- ethyl phenylacetate, use in crossed ester condensation 730
- ethylene (ethene), orbitals of 106, 152
- ethylene glycol (ethane-1,2-diol) 346, 1454, 1457
- ethylene oxide 505
- ethylene oxide, in polymerization 1457
- ethyne, *see* acetylene
- ethynloestradiol 214

- eukaryotes 1377
 Evans' oxazolidinone chiral auxiliaries 1228–9, 1232, 1485
E-vinyl boranes 1282
E-vinyl boronic acids, synthesis of 1328
 exact masses, of isotopes for mass spectrometry 56
 exaltone, synthesis *via* ring expansion 1008
 exchange, of acidic protons in ¹H NMR 257–8
 excited state, of an atom 84
exo face, in bicyclic structure 862, 1254
 exocyclic double bond 1253
exo-methylene group 714, 1335
exo-methylene lactone, as Michael acceptors 584, 757–9
 extent of reaction 307
 extraction, acid–base 186
 Eyring equation 319
- fblock 89
 f orbitals 87
 FAD (flavin adenine dinucleotide) 1384, 1394–5, 1407–10
 FADH₂ 1395, 1407–8
 farnesol 213–14, 1440
 farnesyl pyrophosphate, in biosynthesis 1439, 1442
 fast green FCF 7
 fats 34
 fats, hydrolysis of 292
 fatty acids 21, 292
 biosynthesis of 743, 1425–33
 saturated and unsaturated 5, 173, 1374
 table of types 1426
 Favorskii rearrangement 990–2
 by-product of oxyallyl cation cycloaddition 1016
 mechanism of 1111–12
 Feist's acid 397
 Feldene (piroxicam), arthritis drug 1247
 Feldene, stable enol 533
 Felkin–Anh model, of nucleophilic addition to carbonyl groups 888–91; *see also* chelation control
 felodipine, synthesis 1193
 fenarimol 216
 fenfluramine, synthesis 780, 1220
 fenpiprane, synthesis 790
 fentiazac, synthesis 1200
 ferrocene 1314
 FGI, *see* functional group interconversion
 fialuridine 11
 field, high and low, in NMR 61
 fingerprint region, of IR spectra 72
 first order reactions 321
 Fischer carbenes 1057
 Fischer esterification 289
 Fischer indole synthesis 950, 1204–9
 Fischer projections 395
 fission, heterolytic and homolytic 126
 five-membered rings, conformation of 457
 flagstaff position 458
 flavin adenine dinucleotide (FAD) 1384, 1394–5, 1407–10
 flavin mononucleotide (FMN) 1407
 flavones, biosynthesis of 1436
 flavours 9, 34
 flexibilene 1032
 flipping, of six-membered rings 460–1
 fluconazole, synthesis 1168
 fluoradene, p*K*_a of 195
 fluorene, p*K*_a of 195
 fluoride
 as a nucleophile 1288–9
 as leaving group in nucleophilic aromatic substitution 593–4
 for removal of silyl protecting groups 1290–1
 fluorine, orbital overlap in aromatic compounds 567
 fluorine: ¹⁹F coupling in nmr 368–9
 fluorine: ¹⁹F nmr, use in determination of enantiomeric excess 1231–2
 fluoroaldehydes, hydration of 144
 fluoroalkanes 33
 fluorobenzene, ¹³C NMR spectrum 369
 fluorobenzene, nitration of 567
 fluoroketones, hydration of 144
 fluoropyruvate, ¹H NMR 379
 fluvalinate 138
 fluxional structure 1409
 FMN (flavin mononucleotide) 1407
 Fmoc protecting group 195, 497, 656, 1478
 folic acid, structure and biological synthesis 1179
 force constant, and IR frequency 65
 formaldehyde
 ¹³C NMR spectrum, in water 143
 addition of organometallics to 219
 bisulfite addition compound from 149
 from cracking of paraformaldehyde, 219, 1489
 hydrate of 143, 1452
 in Mannich reaction 712
 in Bakelite synthesis 1455–6
 formaldehyde, orbitals of 136
 formaldehyde, use in chloromethylation 575
 formalin 713, 1452
 formate esters, ¹H NMR spectra 255
 formate esters, pyrolysis of 1014
 formate ion 713
 formic acid 40
 p*K*_a of 197
 formica 1468, 1478
 foscarnet 12
 four membered rings, conformation of 457
 four membered rings, formation using benzyne 604, 679, 1264
 fragmentation
 Beckmann, *see* Beckmann fragmentation
 Eschenmoser, *see* Eschenmoser fragmentation
 solvent effect on 332–4
 fragmentations 1003–17
 entropy of activation 1101
 of saturated heterocycles 1128
 fragments, in mass spectrometry 50
 fredericamycin 215
 Friedel–Crafts acylation 553–4, 573–4, 645
 Friedel–Crafts acylation, of heterocycles 1160
 Friedel–Crafts alkylation, rearrangement during 573, 984
 Friedel–Crafts alkylation 553, 569, 572–3
 Fries rearrangement 645
 frontalin, structure and NMR 838–9
 frontier orbitals
 and Alder ene reaction 925
 and conjugate addition reactions 919, 750
 and cycloadditions 914–16, 919–21
 in radical chain reactions 1044–5
 of α,β -unsaturated carbonyl compounds 230
 fructose 1361
 fructose-1,6-diphosphate 1388
 fruity peony perfume, synthesis 788
 frustulosin 380
 fucose 1373–4
 fumaric acid 153, 390
 fuming nitric acid 565
 fuming sulfuric acid, use in sulfonation 571
 functional group interconversion, in retrosynthetic analysis 777–80
 functional group interconversions, of alkynes 785
 functional groups 20–1, 31–5
 and IR spectra 65
 drawing 23–4
 effects on ¹H and ¹³C NMR, tables 375–8
 removal of 627
 fungicides 11
 furan 1159, 1360
 as dienophile 912
 reactions of 1160–2
 by reduction of lactone 1189
 cycloaddition to oxyallyl cation 1016
 in Diels–Alder reaction with benzyne 1110
 NMR of 833
 synthesis, from 1,4-dicarbonyl 1186
 furanone: 2H-furanone (butenolide), synthesis of 1328
 furanoside 1360
 furonol, meat flavour 9
 fused rings 508
- galactose 1373–4
 galanthamine 635
 gas chromatography, use in determination of enantiomeric excess 1231
 gas constant, *R* 307
 gas phase rates 317
 gastrin 654
 Gatterman reaction 575
 Gatterman, Ludwig 574
 Gatterman–Koch reaction 574–5
 gauche conformation 453, 491
 gauche effects, *see* stereoelectronic effects
 geminal coupling, *see* coupling, ²*J*
 general acid catalysis 1105–9, 1390
 general base catalysis 324–5, 1105–8
 geodesic dome 28
 geometrical isomers 385, 390; *see also* alkenes, geometry of imines and oximes 350
 geraniol 1440
 asymmetric hydrogenation of 1236
 geranyl pyrophosphate 1439, 1449
 Gibbs free energy 307–15, 1019–20
 Gilman reagents 610
 gingerol, synthesis 710–11, 792
 glucose 146, 347, 1346, 1360–1
 in synthesis of vitamin C 1369
 use by nature as a protecting group 1367
 glucose-6-phosphate 1369
 glucuronic acid, synthesis of 1369
 glutamic acid derivatives, p*K*_a of 208
 glutamic acid, (*R*) and (*S*) 1225, 1356
 glutamic acid, from α -keto-glutaric acid 1386
 glutamine 1356
 glutathione 584, 1247, 1356
 glyceraldehyde 1360
 glyceraldehyde-3-phosphate 1388
 glycerol 21, 292, 1374
 in Skraup quinoline synthesis 1210
 glycerol-3-phosphate 1374–5
 glycine 651, 1353, 1359
 ways to draw 20, 24
 glycolysis pathway 1388, 1392–3
 glycoproteins 1373, 1377
 glycosides 1367–8
 gout, cause of 1176
 grandisol 29, 380, 1447
 synthesis of 649, 1072
 grapefruit, flavour of 5
 graphite, model 82
 Greek letters, to label atoms 534
 Grignard reagents 209–24
 addition to chiral ketones 863, 887, 893
 addition to enones 227
 detailed structure 1316
 disconnections using 788–90
 effect of Cu(I) on regioselectivity of attack on enones 239
 formation of 143, 211
 in deprotonation of terminal alkynes 1291
 in synthesis 632–3
 reaction with acyl chlorides to form ketones 299
 reaction with amides or nitriles to form ketones 300–1, 351
 reaction with carbon dioxide 1010
 reaction with carbonyl compounds 142, 209–24, 789–90
 reaction with dithioesters 1264
 reaction with esters to form tertiary alcohols 297–8, 790
 Grignard, Victor 142
 ground state, of an atom 84
 Grubbs' catalyst, in alkene metathesis, *see* alkene metathesis
 guaiazulene, synthesis and NMR 830
 guaioil, dehydrogenation of 830
 guanidine, basicity of 202, 587
 guanidine, reaction with 1,3-dicarbonyl 1198
 guanine 1347
 gulonic acid, synthesis of 1369
 gypsy moth, pheromone of 4 (ch 1-h: haem 1406, 1431
 haemoglobin 1406, 1178
 half-chair conformation 461
 half-life and rate 316
 halide, conjugate addition to unsaturated carbonyl compounds 228
 haloalkanes 33; *see also* chloroalkanes, alkyl chlorides *etc.*
 halo
 α -halocarbonyl compounds, as reagents for 1,4-disconnections 800
 α -halocarbonyl compounds, Favorskii rearrangement of, *see* Favorskii rearrangement
 α -halocarbonyl compounds, in 1,2-disconnections 782
 α -halocarbonyl compounds, substitution of 424–5, 646, 972, 1189
 halogen, radical substitution of 1040–1
 halogenation of carbonyl compounds 535–8
 halogen–metal exchange 216–17, 225
 halogens
 compounds containing 11
 deactivating effect on electrophilic substitution 566–8
 homolysis by light 1020
 halomon 11
 Hammett relationship, in determination of mechanism 1090–100, 1308
 Hammond postulate 554, 560, 1038
 Hantzsch pyridine synthesis 1191–2, 1212
 hapto number *h* 1312–13
 hard and soft 237, 441, 479, 528, 536
 hashed bonds 25, 381, 385
 heat of combustion, of alkanes 455
 Heck reaction 1311, 1321–3, 1339
 Heisenberg uncertainty principle 90
 helenalin 238
 helium, lack of bonding in He₂ 98
 hemiacetals 145–6, 1452
 anomeric effects in 1129
 formation from alcohols and aldehydes 340–2
 in sugars 1129, 1360
 stable cyclic 341
 hemithioacetal 1363

- heptan-2-one, *see* bee alarm pheromone
 heptane 38
 heptyl group 26
 herbicides, bromoxynil and ioxynil 569
 Hertz, units for coupling in nmr 262
 heteroatom couplings (aryl or vinyl to N, S or P) 1335
 heterocycles
 synthesis, summary 1214–16
 aromatic, examples of natural products containing 1147
 aromatic, in Diels–Alder reaction 1163–4
 aromatic, reactions of 1147–81
 aromatic, suggested learning table 1180
 aromatic, synthesis of 1185–1216
 aromaticity 177–9
 definition of 1121
 saturated 1121–44
 saturated, anomeric effects in 1129
 saturated, NMR of 1129–30
 saturated, nomenclature 1125
 saturated, reactions of 1122–8
 saturated, sulfur containing 1127–8
 saturated, synthesis via ring-closing reactions 1134–44
 synthesis by ionic cyclizations 1214–15
 synthesis by pericyclic reactions 1215
 synthesis by ring modification 1216
 heterolysis 126, 1019
 heteronuclear coupling, in nmr 368–71
 heteronuclear diatomics, electronic structure of 100–4
 hexachloroacetone, in Mitsunobu reaction 608–9
 hexachloroethane, bond rotation in 452
 hexafluoroacetone, hydration of 144
 hexamethyldisilazane 669
 hexamethyldisiloxane, silicon analogue of water 543, 1289, 1300
 hexamethylditin, reductive cleavage of 1305
 hexamethylenetetramine 1489
 hexamethylphosphoramide (HMPA) 667
 hexamethylphosphorous triamide (HMPT) 667
 hexane 31, 38
 hexane-1,6-diamine 1453
 hexanedioic acid
 ¹³C NMR spectrum of 62
 IR spectrum of 71
 shape and X-ray crystal structure 48
 hexatriene, shape and NMR 155–6
 hexyl group 26
 hinalchene, synthesis 706
 hindrance, in S_N1 and S_N2 reactions 427; *see also* steric hindrance
 hirsutene 1041
 histamine 204, 586
 role in gastric secretion 586, 1387
 histidine decarboxylase 1387
 histidine 1180, 1355
 HIV, inhibitors of proteases 1351, 1481–2
 HMG-CoA reductase 1438
 HMG-CoA, biosynthesis of 1438
 HMPA, hexamethylphosphoramide 667
 HMPT, hexamethylphosphorous triamide 667
 HOBt, *see* 1-hydroxybenzotriazole
 Hoesch reaction 575
 Hofmann and Saytsev elimination 495
 Hofmann rearrangement 1073
 HOMO (highest occupied molecular orbital) 122
 of allyl cation and anion 159–61
 of benzyl anion 556
 of borohydride 140
 of cyanide 137
 of enolate 528
 of methyl lithium 142
 of α,β-unsaturated carbonyl compounds 230
 homoallylic alcohol, epoxidation by vanadyl (acac)₂ 877–8
 homoallylic alcohol, from allyl silane 1299
 homoallylic ether, synthesis of 1300
 homoenolate, d³ reagent 1303
 homogeneous catalysis 1319–21
 homogentisic acid 1409–10
 HOMO–LUMO gap, and uv spectrum 169
 HOMO–LUMO interaction, in S_N2 reaction 440–1
 homolysis 126, 1019–21
 homonuclear diatomic, electronic structure of 95–100
 homotopic 835–6, 885
 Hooke's law, and frequency of IR stretch 65
 Horner–Wadsworth–Emmons reaction 817
 horse liver alcohol dehydrogenase, *see* liver alcohol dehydrogenase
 Houk model, for reactions of chiral alkenes 886, 895–7, 1282
 HPLC, in determination of enantiomeric excess 1231
 Hückel's rule 176–7
 Hughes, E. D. 411
 Human Immunodeficiency Virus, *see* HIV
 humulene 1437, 1449
 Hund's rule 94, 176
 hybrid molecular orbitals 106
 hybridization
 effect on pK_a 194, 200
 of carbon atoms 105–7
 of non-carbon atoms 107–8
 hydrochloric acid, as catalyst in Mannich reaction 714
 hydroperoxide, epoxidation by 588–9
 hydrates, in Cannizzaro reaction 713
 hydrates, of aldehydes and ketones 143–5
 hydration, of terminal alkene 1337
 hydrazine
 by reduction of diazonium salt 1206
 in nucleophilic aromatic substitution 591
 in synthesis of pyridazine and pyrazole 1188, 1195–6
 reaction with acetal 1206
 reaction with epoxide 782
 hydrazones 351, 739, 1132
 intermediates in Fischer indole synthesis 1204
 hydride migration 980, 1015
 hydride, as a base and a nucleophile 139–40
 hydride: 1,2-hydride shift, in steroid backbone rearrangement 1444
 hydrogen fluoride, use in polymer-bound peptide cleavage 1477
 hydroalumination 1293–4
 hydroboration
 followed by amination 1282–3
 followed by oxidation 1279–80
 of alkynes 1328
 or alkene 868, 1278–82, 1285
 hydrocarbon framework 20–1
 represented as zig-zag 22–3
 hydrocarbons, pK_a of 193–4
 hydrochloric acid, ionization of 182
 hydroformylation, of alkenes 1318–19
 hydrogen atoms
 ionisation of 83–5
 when to miss out from structures 23–5
 hydrogen bonding
 in IR spectra 69
 in *ortho*-nitrophenol 568
 hydrogen bromide
 reaction with alcohols 431
 reaction with alkenes 509
 reaction with dienes 511
 hydrogen chloride
 addition to alkenes 510
 dissociation energy of 1019
 hydrogen chloride
 radicals from homolytic cleavage of 1019
 reaction with alcohols 430
 hydrogen cyanide
 conjugate vs. direct addition 328
 use in Gatterman reaction 575
 hydrogen iodide
 addition to alkenes 510
 use in deprotection of methyl ethers 648
 hydrogen molecule, orbitals of 96
 hydrogen peroxide
 as nucleophile and oxidising agent 588–9, 1265, 1279, 1288, 1408
 in Baeyer–Villiger oxidation, *see* Baeyer–Villiger oxidation
 in cleavage of ozonide 939
 hydrogen sulfide, addition to alkenes 510
 hydrogen, abundance of ¹H 243
 hydrogenated vegetable oil 625
 hydrogenation
 asymmetric 1234–9, 1484
 heat of as measure of stability 173–4
 of alkenes 173, 624, 1164, 1484
 of aromatic nitro 1198
 of imines to amines 355
 of nitrile oxide cycloaddition products 935
 of unsaturated acetal 826
 of unsaturated carbonyl compounds 864–5, 869
 of alkynyl silanes 1293
 hydrogenolysis of benzyl group 646, 1370–1
 hydrogenolysis, mechanism of 622
 hydrogenolysis, of C–S bond with raney nickel 1256, 1262–3
 hydrolysis
 and decarboxylation, of b-keto-ester 728
 enantioselective 1438
 in work-up 699
 of acetals 346, 632
 of acetals, stereoelectronic effects on 1129
 of amides 292–4, 599
 of aromatic ester 576
 of *cis*-fused bicyclic diester 867
 of dithianes 1255–6
 of esters 290–2, 597, 616, 736
 of esters, effect of pH on rate 350
 of esters, Hammett relationship for 1090–4
 of fats and glycerides 292, 1375
 of hydrazones 1132
 of imines 350, 708, 1385–7
 of nitriles 294
 of thiol esters 1418
 of trialkylborate 1280
 of b-halo amine with rearrangement 976–8
 hydrometallation 1318–19
 hydronium ion (H₃O⁺), shape of 108
 hydronium ion 182, 184
 hydropalladation 1323
 hydroperoxide 1408
 hydrophobic region, in enzyme 1387
 hydrosilylation 1294
 hydrostannylation, of an alkyne 1305–6
 hydroxide
 as leaving group 589
 formation by dissociation of water 184
 in Cannizzaro reaction 713
 hydroxy: 4-hydroxy-3-methylbutan-2-one, ¹³C NMR spectrum 370
 hydroxy: 4-hydroxy-4-methylpentan-2-one 691
 hydroxyacids, by hydrolysis of cyanohydrins 149
 hydroxyacyl: 3-hydroxyacyl-ACP dehydratase 1427–9
 hydroxybenzoic: 2-hydroxybenzoic acid (salicylic acid), synthesis of 558
 hydroxybenzotriazole (HOBt), structure, synthesis and use of 1171–2
 hydroxybutyric: 3-hydroxybutyric acid, use in P(3-HB) manufacture 1472
 hydroxyketone, oxidative cleavage of 902
 hydroxyl group 31–2
 hydroxylamine 348
 conjugate addition of 232, 371
 in oxime synthesis 569–70
 reaction with 1,3-dicarbonyls 1201
 hydroxylation
 benzylic 1420
 of aromatic rings 1408–9
 of ester enolates 1229
 of phenylalanine 1409
 hydroxyproline (Hyp) 1359
 hydroxypyridines, tautomerism in 1152
 hydroxystannane, synthesis of 1307
 hydroxyvaleric: 3-hydroxyvaleric acid, use in 'biopol' synthesis 1472
 hygrine 1416
 hypoglycin 1066
i-, as prefix 29
 I⁺ source 1486
i-Bu 30
 ibuprofen 30, 402, 535
 ¹³C NMR spectrum 363
 identification of unknown compounds 64, 72–8
 imidazole 1149
 imidazole, as catalyst in silyl ether formation 633, 1166, 1290
 imidazole, basicity 202–3, 1165
 imidazole, delocalisation in 1165
 imidazole, in Claisen thiol ester condensation 744
 imidazole, reaction with electrophiles 1167
 imidazole, tautomerism 525, 1167
 imidazoline, basicity of 202
 imides, pK_a of 197
 imine salt 714, 1417–18, 1420, 1467
 imine, as intermediate in Gatterman reaction 575
 imines
 basicity of 200
 comparison (and interconversion) with enamines 353, 530, 1405
 formation 348–56, 621, 675, 708, 1384–5
 hydrolysis 350–1, 708
 in aldol reactions 708
 in synthesis of b-lactam via cycloaddition 931
 orbitals of C=N 109
 reaction with cyanide 356
 reduction of 171, 354–5, 622
 stereoisomers of 350
 iminium ions 352–3, 672–3
 indigo 8, 171
 indinavir, *see* Crixivan
 indole alkaloids 1169
 indole 1169
 reaction at nitrogen 1207–8
 reactions of 1170–1
 synthesis 1338–9
 indoles, synthesis, Fischer indole 1204–9
 indoles, synthesis, Reissert 1208
 indolizine, [8+2]-cycloaddition with alkyne 1175
 indomethacin, structure and synthesis 1169, 1203, 1207

- inductive effect 561
and aromatic ^1H NMR shifts 253–4
of halogens 594, 596
of oxygen 603
on electrophilic aromatic substitution 561–4, 566–8
on ester electrophilicity 728–9
industrial emulsifier, identification 73–4
infra-red absorptions, of functional groups 66–72
infra-red absorptions, position, strength, and width 71
infra-red spectra, and force constant 65
infra-red spectra, and reduced mass 65
infra-red spectrometer 66
infra-red spectroscopy 65–72
infra-red spectrum of carbonyl groups 364–8
effect of conjugation 230
of the carbonyl group 364–8
of enones 229–30
regions of 67
infra-red stretching frequency, of C=O, relationship to reactivity 288
Ingold, Sir Christopher 411
inositol 396, 1369–71
insect pheromones, mass spectrum of 51
insecticides 10
insertion reactions, of carbenes 1069–71
insertion, oxidative, of metal into alkyl halide 211
integration of proton nmr spectra 244
intermediate, variation of concentration with time 329
intermediates, compared with transition state 321
intermediates, detected by spectroscopy 371–2
intermolecular and intramolecular reactions 145
intramolecular acylation (Dieckmann reaction) 705, 727, 730, 734
intramolecular aldol reaction 715–18
intramolecular alkylation 666, 1333
intramolecular Friedel–Crafts acylation 572–4
iodide
alkyl, from alkyl chloride 789
as a nucleophile for epoxide opening 470
as leaving group in semipinacol rearrangement 987
as nucleophilic catalyst 442–3
in radical chain reaction 1043–5
iodination of benzene ring 647
iodine, equilibration of alkene geometry using 808
iodo-5'-iodo-thymidine 1352
iodoalkanes 33
iodobenzene, nitration of 567
iodobenzoic: 2-iodobenzoic acid 639
iodoform reaction 537–8
iodolactonisation 517–18, 872–4, 878
stereospecificity of 882
in prostaglandin synthesis 1229
iodomethylstannane, use as alkylating agent 676
iodonium ion, in Crixivan synthesis 1486
iodosobenzene, oxidising agent 1489
ion-exchange resin 1473–4
ionic bond, molecular orbitals of 102
ionic polymerization 1467–8
ionization
of hydrochloric acid 182
of hydrogen 83
of water 184
ions, one-electron, orbitals of 87
ioxynil, synthesis of 569
i-Pr 29
iproniazid 29
iposenol, (S)-(-)-, synthesis of 1222–3
ipso position 548
ipso substitution 1292
IR, *see* infra-red
Ireland–Claisen rearrangement 948
iridium, in Vaska's complex 1316
iron powder, use in bromination of nitro benzene 565
iron(II), complex of porphyrin 1178
iron(III) chloride, reaction with 2,2'-bipyridyl 1156
isoboldine, a benzyl isoquinoline alkaloid 1422
isobutene, polymerization 1462
isobutene, reaction with hydrogen bromide 509
isobutyl group 30
isobutyraldehyde, hydration of 307–10
isobutyraldehyde, in crossed aldol reactions 707
isocyanates
by Curtius and Hofmann rearrangement 1073
in polymerization 1458
in thermal [2+2] cycloaddition 929–2
isoelectronic molecules 108, 552, 575
isoindole, structure of 1179
isoleucine 1353, 1397–8
isomenthol 464
isomerization, of alkenes in acid 510
isomers
constitutional 384
definition of 29
of alkenes, *see* alkene, geometry
stereo- 384
isooctane, 2,3,5-trimethylpentane, in petrol 3, 31
isooctane, combustion energy 315
isoprene (2-methylbuta-1,3-diene) 511, 1437
isoprene, polymerization of 1464
isoprene, reaction with hydrogen bromide 131
isopropanol 29
isopropylbenzene, synthesis of 573
isopropyl group 29
isopropyl iodide, use as alkylating agent 1254
isopropylamine, in epoxide opening 1241
isoquinoline 1174, 1419
isoquinolines, naming 1209
isoquinolines, synthesis, via intramolecular Vilsmeier 1212
isotactic polymers 1460, 1463
isothiazole 1176
isothiocyanate 1368
isotope effects, kinetic 486–7, 1100
isotopes separated by mass spectrometry 52–6
isotopic labelling 282, 291–2, 339, 340, 1086–8, 1416–17, 1432
and Cannizzaro reaction 1082
in aldol reaction 696–7
of carbonyl compounds with ^{18}O 339–40
use in biosynthetic studies 1438
use in steroid biosynthesis analysis 1442
isoxazoles
from 1,3-dicarbonyl and hydroxylamine 1201
by 1,3-dipolar cycloaddition 934–5, 1201
reduction of 1176
Jacobsen asymmetric epoxidation 1488–90
Japanese beetle pheromone (japonilure) 4, 1221
jasmone, *cis* 2, 9
jawsamycin, structure of 1066
jeans, blue, colour of 8
Jones oxidation 638
Julia olefination 810–12, 1248
junionone, structure and synthesis 701
juvenile hormone 210, 220
synthesis *via* fragmentation reactions 1009, 1010
Karplus relationship 825
Katsuki manganese-salen complex 1489
Kekulé, Auguste 27
Kekulé structure of benzene, naphthalene, phenol 154, 549
Kelvin, temperature scale 307
ketene acetals, formation 482, 707
ketene dimer, structure and spectra of 372
ketene
carbene insertion into 1112
dichloro, *see* dichloroketene
formation by E1cb elimination from enolate 529
in cycloaddition with chloral 1113–14
in thermal [2+2] cycloaddition 929–31
intermediate in acylation 500
masked, reaction in Diels–Alder 931
structure and spectra of 372
keto: 5-keto-glucose 1371
keto-alkynes, from Eschenmoser fragmentation 1008
keto-enol tautomerism 523–45, 585
keto
 α -keto-acid, from amino acids 1385–6
 β -ketoacyl-ACP reductase 1427–9
 β -keto-esters, formation of (summary) 733
keto-esters, in Robinson annelation 762
ketones and aldehydes, distinguishing from acid derivatives 361–4
ketones, *see* carbonyl compounds
alkylation of 669, 680
aromatic, synthesis of 575
Baeyer–Villiger oxidation of, *see* Baeyer–Villiger oxidation
by hydration of alkynes 519
by oxidation of alcohols, 222
by rearrangement of epoxides 1015
comparison of reactivity with aldehydes 138–9
conversion to alkenes by the Wittig reaction 357
cyclic, 6-membered, nucleophilic addition to 472, 857, 861
disconnections of 790
distinguishing from aldehydes by ^1H NMR 362–3
from acyl chlorides and Grignard reagents 299
from carboxylate salts with organolithiums 299–300, 648–9
from *N*-acyl aziridines 1125
from nitriles and Grignard reagents 301, 351
from nitroalkanes 767–7, 931
from Weinreb amides 300
functional group and compound class 34
halogenation of 535–8
in McMurry reaction, *see* McMurry reaction
IR spectroscopy, effect of conjugation on 229
methyl, synthesis of 519, 648–9, 1305, 1337
 pK_a of 197
reaction with alcohols to form acetals 342–7
reaction with alcohols to form hemiacetals 145–6
reaction with amines to form imines 348–56
reaction with bisulfite 148
reaction with cyanide 135
reaction with NBS 1015
reaction with organolithiums and Grignard reagents 142, 209–24, 790
reaction with orthoesters to form acetals 345
reaction with secondary amines to form enamines 353
reaction with sulfur ylids 1168
reduction of 140–1, 646
removal of 649
reversible reaction with water 144–5
unsaturated 227; *see also* enones
ketorolac 1162
ketose 394
ketyl radical anion, as indicator in thf distillation 1023, 1030; *see also* pinacol reaction
KHMS, potassium hexamethyl disilazane 669
kinetic control 235, 328–31, 630, 681–2
vs. thermodynamic control 1260
kinetic enolate, formation of 682, 709
kinetic isotope effect 486–7, 1100, 1412
kinetics 316–27
of E2 reaction 478
of $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ 411–14
knock-out drops 144
Knoevenagel reaction 703
Knorr pyrrole synthesis 1191
Kolb–Schmidt reaction 575
Krapcho decarboxylation 679
K-selectride 685
labelling reactions, of indole 1170
labelling studies, of neighbouring group participation 975–6
labelling, isotopic, *see* isotopic labelling
lachrymator, in raw onion 1273
lactam
 β -lactam, antibiotics 10
 β -lactam, infra red spectrum of C=O 366
 β -lactam, NMR couplings in 832
 β -lactam, synthesis by [2+2] cycloaddition 931
lactic acid 290, 387–8, 1382–3
 ^{13}C NMR of 61
as member of chiral pool 1224–5
as metabolic by-product 31
lactol 146
lactone 693
by iodolactonisation, *see* iodolactonisation
laetrile 35
laevorotatory 389
LAH, *see* lithium aluminium hydride
lamivudine (3-TC), anti-AIDS drug 1351
lanosterol, biosynthesis from squalene 1442–5
large rings, definition of 456
lauric acid 1426
Lawesson's reagent 1187, 1200, 1264–5
LCAO 95
LDA 29, 42, 668, 698–709, 1124
in acylation of sulfones 743
in aldol reactions 698–709
in alkylation of sulfoxides 1269
in directed *c*-acylation 737
in elimination reactions 493–4
in formation of enol esters 725
in formation of kinetic enolates 682
in formation of lithium aza-enolates 676
reaction with tributyltin hydride 1307
to form lithium enolates 540, 1230

- Le Chatelier's principle 315
lead tetraacetate, oxidative cleavage of diol 878
lead, use as fuel additive 1021
leaving group ability, relationship of pK_a to 283, 285
leaving group ability, role of acid catalysts 289
leaving group
 hydroxide as 589
 in nucleophilic aromatic substitution 593–4
 in S_N1 and S_N2 412, 429–31
 mesylate as 587
 tosylate as 563
leaving groups 126, 279–80, 283, 285
 axial and equatorial 467–8
 compared with nucleophiles 441–3
 in elimination reactions 484–7
leucine 651, 1353
 (S)-, in pheromone synthesis 1222–3
 ways to draw 20, 23–5
leukotriene LTA₄, biosynthesis of 1431–3
leukotrienes, synthesis of 434, 883–4
Lewis acid catalysis
 in acylation of enols 741
 in Alder ene reaction 926
 in aldol reactions 699
 in cationic polymerization 1462
 in Diels–Alder reactions 921, 1229
 in formation of acylium ion 554
 in Friedel–Crafts alkylation 553
 in reactions of silyl enol ethers 755–7
 of electrophilic substitution reactions 1298–300
Lewis acid catalysts
 aluminium chloride 549
 boron trifluoride 1127, 1254–5
 diethylaluminium chloride 1227
 sulfur *s*-elective 1255
 tin tetrachloride 1263
 titanium isopropoxide 756
 titanium tetrachloride 755–6
 trimethylsilyl triflate 1289
 trityl perchlorate 757
 zinc chloride 575, 1299
Lewis acids, definition 120
Lewis acid catalysis, of decomposition of *t*-alkyl chloride 569
lifetime, of ion in mass spectrometer 51
ligand migration 1318
ligands (table of) 1314
ligands, phosphine 1311
light, and rotation of π -bonds 153
light, as reagent, symbol *h* ν 373
lignin fragment, structure of 1401
LiHMDS, lithium hexamethyldisilazide 668–9
lilac perfume, synthesis 788
limit of electrons and bonds for B, C, N, O, F 128
limonene, (*R*)-(+)- and (*S*)-(–)- 31, 1219–20
limonene, biosynthesis of 1440
linalool, synthesis 789
Lindlar catalyst, composition of 623, 625, 818
Lindlar catalyst, in *cis*-selective reduction 649, 818, 1221, 1224, 1293
linear carbon atoms 107
linearmycin 26
linoleic acid 22, 171, 1426
linoleic acid, ways to draw and not to draw 21–3
linolenic acid 171, 1426
lipid bilayers 1377
lipids 1345, 1374–7
lipoic (thioctic) acid, ¹³C NMR spectrum 363
lipoic acid 1384, 1392
lipoxygenase 1432–3
lithiation, of furan 1161–2
lithiation, of thiophene 1161
lithium 2,2,6,6-tetramethylpiperidine 1124
lithium acetylide 616
lithium aluminium hydride 616, 646
 comparison with sodium borohydride 141
 reaction with water 141
 reduction of alkynes 819
 reduction of amides to amines 355–6
 reduction of esters 298, 646, 1234, 1253
 reduction of ketones 853, 862, 871
 reduction of nitrile oxide cycloaddition adducts 935–6
 reduction of tosylate 806
 reductive removal of chiral auxiliary 1232
lithium carboxylates, reaction with organolithiums 299–300
lithium cuprates, use as nucleophile 240, 1269, 1301
lithium diethylamide 675, 1238
lithium diisopropylamide, *see* LDA
lithium enolates 540–1; *see also* enolates
 alkylation of 668–71
 in aldol reactions 697–9
 in conjugate addition reaction 752
 in synthesis 738
 of esters 705–6
 tetrahedral structure 698
lithium hexamethyldisilazide 668–9, 711
lithium hydride, use in alkylation of *b*-dicarbonyl compounds 679
lithium isopropylcyclohexylamide 668, 670
lithium tetramethylpiperidide (LTMP) 668
lithium thiolates, coupling with vinyl triflate 1335
lithium triethylborohydride 627
lithium tri-*sec*-butylborohydride, *see* *L*-selectride
lithium
 alkyl derivatives 209–22
 reaction with alkyl halides to form organolithiums 212
 use in Birch reduction 628–9
liver alcohol dehydrogenase 1382–3
locking groups 465
lone pairs 100
lone pairs, drawing 25
long range coupling, in ¹H NMR 269–70, 274
long range coupling, with alkyne protons (⁴*J* and ³*J*) 367
longifolene, synthesis 739, 1007, 1010
Loschmidt, Josef 27
low temperatures, to slow reactions 331–2
LSD, *see* lysergic acid diethylamide
L-selectride 472, 685, 854
LTMP, *see* lithium tetramethylpiperidide
Lumière–Barbier method 188
LUMO (lowest unoccupied molecular orbital) 122
LUMO
 of 1,2 dicarbonyl 728
 of allyl cation and anion 159–61
 of carbonyl group 136–7
 of α,β -unsaturated carbonyl compounds 230
lyase enzyme 1404
lycopene, red plant pigment 116, 170
Lycorea sex pheromone 374
Lyman series 84
Lyman, Theodore 84
lyophilization 1371
lysergic acid diethylamide 178, 1169
lysine imine, in aminotransferase 1385
lysine 1355
 in biosynthesis 1385–92, 1418, 1448
 ways to draw 20, 24, 27
lysis 1404
lyxose 395
m-, as prefix 39
macrocyclisation 1326–7
magnesium bromide, in epoxide rearrangements 985
magnesium enolates 736
magnesium oxide, as base in Cannizzaro reaction 713
magnesium, alkyl derivatives 209–24
magnesium, reaction with alkyl halides to form Grignard reagents 143, 211
magnetic field, nucleus in 57
magnetic quantum number 86, 92
malate, oxidation of 1384
maleic acid 153, 390
 from chloral and ketene 1113–14
maleic anhydride, ¹³C NMR spectrum 363
maleic anhydride, as dienophile 912
maleic diadehyde, from furan 1160, 1161
maleic diadehyde, in Wittig reaction 1161
maleic hydrazide, reaction with phosphoryl chloride 1173
maleic hydrazide, tautomerism in 1173
malic acid 34
malonate esters, as reagents for *d*² synthons 787
malonate half-thioester, in biosynthesis 744
malonate radical, reactivity of 1046
malonate, diethyl, enol form 532
malonic acid 677, 703
malonic anhydride, spectra of 372
malonyl CoA, in biosynthesis 1425–6
maltol, flavouring 9
maltose 347
mandelic acid 294, 389
manganese dioxide, oxidation of allylic alcohols 875
manganese, in asymmetric epoxidation 1488–9
manicone, synthesis 700
Mannich base, formation of 714
Mannich reaction 712–15, 758–9
in alkaloid biosynthesis 1420–1
in synthesis of 3-amino alcohols 795
of indole 1171
of pyrroles 1158
mannitol 1363
mannose 1363, 1373
margarine manufacture 173
Markovnikov's rule 510
mass spectrometry 50–56
mass spectrum
 base peak in 51
 molecular ion in 50–1
 of 2-phenylethylamine 52
 of bee alarm pheromone 51
 of BHT (butylated hydroxy toluene) 55
 of DDT 54
maytansine 765
maytansinoids 576
McMurry reaction 1031–2
m-CPBA
 epoxidation by 506, 589, 650
 in Baeyer–Villiger oxidation, *see* Baeyer–Villiger oxidation
 oxidation of pyridine to *N*-oxide 1153
 oxidation of sulfides and selenides 1265, 1269–71
 reaction with dihydropyran 828
 stereoselective epoxidation by 856, 863, 866–9, 874
Me 26
mechanism
 equilibria, and rates 305–37
 for ester aldol reaction 706
 how to draw 127–32
 in biological chemistry 1381–410
 short cuts in drawing 335
 summary 334–5
 two-step 129
 use of curly arrows to depict 120–32
mechanistic determination 1079–117
medium rings, definition of 456
medium rings, transannular interactions in 1137
Meerwein's salt 541, 1258
melamine, synthesis 1467
Meldrum's acid 1332
menthofuran, structure and synthesis 1188
menthol 2, 9
 L-, synthesis of 926–7, 1237
menthol, use in asymmetric sulfoxide synthesis 1266
mercaptan 1255; *see also* thiol
mercuration 1339
mercury(II) acetate, reaction with alkene 518–19; *see also* oxymercuration
mercury(II) bromide, reaction with Grignard reagent 1048
mercury(II) chloride, in hydrolysis of dithiane 1128, 1255
mercury(II), as oxidising agent 1418
mercury(II), in hydration of alkyne 362
mercury, amalgam with sodium amalgam 810
Merrifield peptide synthesis 657, 1476–7
mesityl oxide, reaction with ethyl malonate 764
meso compounds 395
mesylate, as leaving group 485–6, 496, 587
mesylation
 in biotin synthesis 1253
 in hydroxyl group removal 1223
 in propranolol synthesis 1241
 mechanism 485–6
meta coupling, in ¹H NMR 270
meta directing groups 564–6
meta position 39, 548
meta, as prefix 39
meta-bromonitrobenzene, synthesis of 565
meta-chloroperbenzoic acid, *see* *m*-CPBA
meta-cyclophane, synthesis of 1255
meta-dinitrobenzene, synthesis of 565
metal carbonyls 1315
metaldehyde 1452
metal–halogen exchange 216–17, 225
metal–ligand interaction 1311
metallocarbenes 1057
metals, electronegativity of 210
methanal, *see* formaldehyde
methane
 in chemical ionization mass spectrometry 52
 protonation of 52
 tetrahedral arrangement of H atoms 37, 82–3, 107
methanesulfonamide 1241–3
methanesulfonyl chloride 485, 659, 608, 659, 661
methicillin 219
methionine 655, 1348, 1353, 1355
 ways to draw 20, 24, 27
methoxatin, co-enzyme 48, 180, 243, 577
methoxide, as base in Claisen ester condensation 733
methoxybenzene, *see* anisole
methoxymethyl cation, in S_N1 reactions 419
methyl: 1,2 methyl shift, in steroid backbone rearrangement 1444

- methyl 2-cyanoacrylate, in 'superglue' 1461
 methyl: 6-methyl salicylic acid (6-MSA) 1409, 1434
 methyl acetoacetate, ¹H NMR 251
 methyl acrylate 1460
 methyl anion, shape of 108
 methylbenzene, *see* toluene
 methyl ether, use as protecting group 635, 647–8
 methyl glycoside 1362, 1365
 methyl group, ¹H NMR shifts as guide to chemistry 247
 methyl group 26
 methyl groups, ¹H and ¹³C NMR shifts, tables of 375
 methyl iodide
 reaction rate with tertiary amines 1123
 carcinogenicity 33
 use in alkylation 714–15
 methyl ketones, synthesis of 519, 648–9, 1305, 1337
 methyl lactate, ¹H NMR 249
 methyl lithium
 structure 1452
 reaction with silyl enol ethers 541
 use in methyl ketone synthesis 648–9
 methyl methacrylate, ¹³C NMR spectrum 363
 methyl methacrylate 1460
 methyl mycaminoside, synthesis 1224–5
 methyl orange, synthesis 572
 methyl *trans*-chrysanthemate 1257
 methyl vinyl ketone 228, 1260
 methylation
 by SAM 1417, 1420–1
 in hydrolysis of dithiane 1256
 in living things 1347–8
 of amines by reductive amination with formaldehyde 354–355
 of indole nitrogen 1207
 of carbonyl compounds by the Wittig reaction 357
 methyl lithium
 HOMO of 142
 reaction with water 142
 methylphenol: 4-methylphenol (*p*-cresol), in synthesis 570
 metiamide 206
 mevalonic acid, biosynthesis of 1437–9
 mevalonic acid, in biosynthesis 1425, 1442
 mevalonic acid, in rubber synthesis 1463
 mevalonolactone, biosynthesis of 1437
 micelles 1375
 Michael acceptors 584, 696, 758
 exomethylene lactones 584, 757
 in electrophilic aromatic substitution 584–5
 Michael addition, *see* conjugate addition 29)
 Mickey Finn 144
 microscopic reversibility 1105
 in Baldwin's rules 1143
 migration of silicon, from carbon to oxygen 1303–4
 migration origin, definition of 977
 migration terminus, definition of 977
 migration
 in lanosterol biosynthesis 1445
 of alkyl groups 978–82
 of hydride 980, 1015
 1,2-migration, of hydrogen in carbene 1070
 migratory insertion 1317
 mirror images 381–2
 Mitsunobu reaction 431–3, 608–9
 Mitsunobu, Oyo 431
 MO, *see* molecular orbital
 models, molecular 381, 448
 models, space-filling 452
 Mogadon 33
 molecular formula, by high resolution mass spectrometry 56
 molecular ion, in mass spectrometry 50, 52
 molecular models 381, 448
 molecular orbitals, in 1,3 dipolar cycloadditions 1202–3
 molecular orbital theory 95–105
 molecular orbitals
 and conjugate addition 230
 of butadiene 230
 of unsaturated carbonyl compounds 230
 in Diels–Alder reaction 915
 in [2+2] cycloadditions 927–30
 generation of by combination of atomic orbitals 95–105
 of methane and other molecules with >2 atoms 104–5
 of radicals 1025–76
 molecular sieves 345
 molecular weights, odd and even 56
 monastral dyes 8
 monodisperse polymer, definition of 1462
 mono-unsaturated fatty acid 743, 1426
 monoterpene, definition of 1439
 morphine alkaloids, from reticuline 1422–4
 morphine 1416
 morpholine 672, 739, 1122
 Mosher's esters, use in analysis of enantiomeric excess 1231
 movement of molecules 113
 moxnidazole, synthesis 782
 Mozingo reaction 627
 MSA: 6-MSA, *see* 6-methyl salicylic acid
 Mukaiyama, Teruaki 711
 multicolanic acid, synthesis 729–30
 muscalure, synthesis 648–9
 muscone 28, 1008
 mustard gas 973, 1258
 myoglobin 1406
 myo-inositol, synthesis of 1369–70
 myrcene, achiral terpene 1238
 myristic acid 292
 myrtenal, ¹H NMR spectrum 248, 255, 273
 N terminus, in proteins 1358
 n-, as prefix 29
 N,N-dimethylaniline, in azo dye synthesis 572
 N,N-dimethylaniline, rate of bromination compared to benzene 559
 N-acetyl-galactosamine 1372–3
 N-acetyl-glucosamine 1372–3
 NADH and NAD⁺ 1381–4, 1386, 1392, 1395, 1418
 NADPH and NADP⁺ 1382, 1397–8, 1402
 NADPH, stereo and chemoselective reduction 1409, 1427
 NADPH, in biosynthesis 1438, 1442–3
 nafimidone, synthesis 782, 783
 naming compounds 37–45
 naphthalene 177, 207
 Kekulé representation 549
 naphthol, β- or 2- 332, 1422
 naphthol, α- or 1-, in propranolol synthesis 1241
 naproxen 402, 1234–5
 naringenin and naringin 1436
 natural gas, methane 2
 natural products 1413–47
 Nazarov cyclisation 962, 1309
 N-bromosuccinimide, *see* NBS
 NBS
 in allylic radical bromination 1039–40
 reaction with alkenes 856, 1015
 reaction with ketones 1015
 n-butyllithium, *see* butyllithium
 N-chlorosuccinimide (NCS) 765, 1262
 Nef reaction 767
 neighbouring group participation 969–1000
 by sulfur 1258, 1263–4
 neopentyl group 978
 nerol 1440
 neryl pyrophosphate 1439–40
 Newman projection 450–1, 1309
 N-glycoside 1367
 NH, protons in NMR 256–8
 nickel, in catalytic hydrogenation 623
 Nicolaou, K.C. 961
 nicotinamide adenine dinucleotide, *see* NADH
 nicotine, ¹H NMR spectrum 249
 nicotine, structure of 1121, 1416
 nicotinic acid 1154, 1448
 niflumic acid, synthesis 1154
 ninhydrin, hydration of 150
 N-iodosuccinimide (NIS) 1486
 nisoxetine, synthesis 796
 nitration
 in synthesis 591
 of acridine N-oxide 1174
 of activated pyridine 1153
 of aryl halides 567, 591, 600, 660
 of benzene 552
 of furan 1160
 of imidazole 1167
 of isoquinoline 1174
 of methyl benzoate 566
 of *para*-xylene 1208
 of phenol 576, 660
 of furan 1160
 of imidazole 1167
 of isoquinoline 1174
 of methyl benzoate 566
 of *para*-xylene 1208
 of phenol 576, 660
 of phenyltrimethylammonium ion 564
 of pyridine-N-oxide 1153
 of quinoline 1174
 of substituted pyrazole 1198
 of toluene 644
 of trifluoromethylbenzene 564, 578
 trapping of intermediates in 1109, 1110
 nitrazepam 33
 nitrene 1073
 nitric acid
 as oxidant 863, 1212
 concentrated, in nitration of benzene 552
 dilute, in nitration of phenol 568
 fuming, in nitration of benzene 565
 nitric oxide (NO) 1414
 nitrile oxides, synthesis and 1,3-dipolar cycloadditions of 934–6, 1201
 nitrile, unsaturated, conjugate addition to 759, 768
 nitriles 35
 alkylation of 664–6
 anions from 530
 as nucleophiles 436
 basicity of 200
 by substitution with cyanide 607, 795, 1202
 hydrolysis of 294
 in nucleophilic aromatic substitution 595
 reaction with azide 1202
 reaction with Grignard reagents 301, 351
 reduction of using rhodium catalyst 768, 795
 removal of 650
 substitution of cyanide 1206
 nitrite, in diazonium salt formation 597–600
 nitro compounds 33
 unsaturated, *see* nitroalkenes
 nitro group
 in nucleophilic aromatic substitution 590–5
 introduction of 552
 IR spectra 71
 reduction of 569, 626
 stabilization of benzylic anion 1208
 structure and conjugation 33, 164
 nitroaldol 697
 nitroalkanes alkylation of 666–7
 nitroalkanes
 conjugate additions of 766–7
 conversion to carbonyl compounds 767, 931
 pK_a and deprotonation of 193, 530, 1208
 nitroalkenes
¹H NMR of 254–6
 as dienophiles 907
 conjugate addition to 760, 936
 termite defence compounds 696–7
 nitrobenzene, as solvent in Friedel–Crafts acylation 574
 nitrobenzene, in Skraup quinoline synthesis 1210
 nitrobenzenes, in nucleophilic substitution reactions 593
 nitrogen acids 197
 nitrogen bases 199–203
 nitrogen heterocycles 1147–56, 1162–216
 nitrogen molecule, electronic structure 100
 Nitrogen: ¹⁵N, isotopic labelling with 1416
 nitromethane 696
 nitronates 696
 nitron, synthesis and 1,3-dipolar cycloadditions 932–4
 nitronium ion, in electrophilic aromatic substitution 552
 nitrosation, of enols 538–9, 599
 nitroso group 538–40, 598–9
 nitroso: 9-nitrosojulolidine 3
 nitrous acid, in diazonium salt formation 572, 597
 NMO, N-methylmorpholine-N-oxide, oxidant 639, 934
 NMR spectra, chemical shift scale 59
 NMR spectra, shielding of nuclei by electrons 59
 NMR spectrometer
 advantage of high field 268
 picture 57
 rating in MHz 60, 262
 NMR
¹H and ¹³C compared 243
¹H 243–78
¹H, chemical shifts 245–58
¹H, coupling 258–74
¹H, exchange of OH, SH, and NH 256–8
¹H, integration 244–5
¹H, long range coupling 269–70, 274
¹H, regions and scale 243
 abbreviations used 267
 aldehyde region 255–6
 alkene and benzene region 251–5
 alkynes and small rings 365–7
 benzene ring current 251
 coupling in, *see* coupling
 determination of configuration by 825–8, 861, 1129–30
 effects of electronegativity, table 375
 how it works 57–8
 observation of carbocation rearrangement by 979, 980
 of axial/equatorial substituents 834
 of carbonyl compounds, summary 361–5
 of CH, CH₂, and CH₃ groups 244–5
 of cyclohexane 460
 of keto- and enol forms 524
 of methyl group, table 247, 375
 nodal plane 91
 nodal surface 90
 node, in benzylic anion 556
 nodes, in orbitals 90, 556
 NOE, *see* nuclear Overhauser effect
 nomenclature 37–9

- of saturated heterocycles 1125
 nonane 38
 non-bonding electrons 100
 non-steroidal anti-inflammatory drug (NSAID) 402
 nonyl group 26
 nootkatone, synthesis *via* fragmentation 1010–14
 nor-, as prefix 473
 noradrenaline (norepinephrine) 473, 1420
 norbornadiene, as dieneophile 909
 norbornane 473
 norbornanone, diastereoselective reactions of 862–3
 norephedrine, use in synthesis of chiral auxiliary 1228
 norlaudanosine 1421, 1424
 norlaudanosoline 1421
 norreticuline 1421–2
 Norvir, HIV protease inhibitor 1482
 novrad 403
N-oxide, of pyridine, *see* pyridine-*N*-oxide
n-propanol, structure 29
n-propylbenzene 573
N-propylglucosamine, as a resolving agent 402
 NSAID 402
 nuciferal, synthesis 1257, 1268
 nuclear energy levels and NMR spectra 243, 260–5
 nuclear magnetic resonance, *see* NMR
 nuclear Overhauser effect 844–7, 917
 nuclear spin, and NMR 57
 nucleic acids 1345–51
 nucleophile, definition 115
 nucleophile, S_N1 mechanism and 436–7
 nucleophile, S_N2 mechanism and 412–13
 nucleophiles
 anionic and neutral compared 119, 125, 286
 compared with leaving group 441–3
 examples 118–19
 hard and soft 237–8, 441
 in conjugate addition and substitution reactions 228, 581–9
 thiols as 1249
 π -bonds as 119, 124
 σ -bonds as 119, 126
 nucleophilic addition
 Cram model for 889
 diastereoselective 884, 887–95
 Felkin–Anh model for 888–91
 in asymmetric synthesis 1225–6
 of ylids 1259
 to carbonyl groups 135–7
 to styrene 1461
 to vinyl epoxide 1332
 nucleophilic aromatic substitution 576, 589–97, 659
 on heterocycles 1149–50, 1162, 1212–13
 nucleophilic attack
 on alkenes coordinated to Pd 1336
 on electrophilic alkenes (summary) 611
 on epoxide 659, 1224–5, 1241–2
 nucleophilic catalysis 282, 1149, 1153, 1155, 1166, 1173
 nucleophilic epoxidation 588
 nucleophilic substitution
 at saturated carbon 407–45; *see also* S_N1 , S_N2
 at silicon 1288–9
 effect of adjacent carbonyl 890
 of cyanide by amine 1206
 on six-membered rings 466–8
 stereospecificity of 882
 to allylic carbonates 1333
 nucleophilic sulfur 1248
 nucleophilicity towards C=O, relationship to pKa 286
 nucleosides 1347
 analogues of 1204
 cyclic 1351–2
 nucleotide, synthesis 1365–7
 nucleotides 1346–7, 1381
 numbering, in nomenclature 38
 Nurofen, *see* ibuprofen
 Nutrasweet, *see* aspartame
 nylon 997, 1453
 o-, as prefix 39
 obesity drug, synthesis 771–2, 776–7
 Oblivon 616
 ocfentanil, synthesis 779, 780
 octane, structure 38
 octyl group 26
 oestradiol 28, 1441
 oestrone 214
 ofloxacin, synthesis 595–7, 742, 1211
 ofornine, synthesis 777, 778
O-glycoside 1367
 OH protons, in NMR 256–8
 oil, crude, as source of organic compounds 2, 21
 Olah, George 410, 408, 592
 olefin metathesis, *see* alkenes, metathesis
 olefination, Julia, *see* Julia olefination
 olefins, *see* alkenes
 oleic acid 171, 1374, 1426
 oleum 553, 566
 oligomers, definition of 1452–3
 olive fly, sex pheromone of 5
 olivetol 1448
 olyphosphoric acid, in synthesis of spirocycles 870
 omeprazole 178
 ondansetron, synthesis 1206–7
 opium poppies 1418
 optical activity 388
 optical purity 1231
 orb weaver spider 356
 orbital angular momentum quantum number 86
 orbital descriptions 954–5, 980, 1006
 orbital diagram, for S_N2 440
 orbital diagram, showing conjugation 154, 161, 167–8
 orbital
 1s, density plot 90
 2p, density plot 91
 2s, density plot 90
 orbitals
 and NMR couplings 824–8
 atomic 87–95
 energy, a and b notation for 152
 how to draw 91
 hybrid 105–10
 in hydrogen atoms 86–8
 interaction in reactions 117
 of butadiene 230
 of C–Li bond 210
 of conjugated cyclic hydrocarbons 175–7
 of enolate and allyl anions 528
 of α,β -unsaturated carbonyl compounds 230
 organic compounds, types of 1–6
 organic elements 27, 45 (*table*)
 organoboron chemistry 1277–87
 organocerium reagents 217–18
 organocopper reagents 239–240, 299, 685–6
 organolithiums 209–22, 236, 1307
 decomposition of solvents 1127
 reaction with carbonyl compounds 142
 reaction with esters to form tertiary alcohols 297–298
 reaction with water 142
 organometallics 209–24, 1311–41
 as bases 212
 reaction with carbonyl compounds 142, 209–24
 organosulfur chemistry 1247–73
 organotin chemistry 1304–8
 organozincs 217
 orientaline 1448
 orientation, of molecules for successful reaction 116–17
 ornithine 1416–18
 orotidylic acid, synthesis 1365
 orsellinic acid, synthesis and biosynthesis 744, 1433–4
ortho-, as prefix 39, 556
ortho-, *para*-directing groups 556, 566, 571, 602–3
 Orthoester, general base catalysed hydrolysis of 1108
 orthoesters 345, 974
 orthoformate, reaction with diethyl malonate 1211
 ortholithiation 214–17, 219, 301, 331
ortho-toluenesulfonyl chloride 645
 osmium tetroxide (OsO_4) 1241–3, 1304; *see also* dihydroxylation
 Owen Brackets 699
 oxaloacetate 1384, 1390
 oxalyl chloride
 decomposition of 329
 in Swern oxidation 1271–2
 reaction with carboxylic acids to form acyl chlorides 296
 oxanamide intermediate, synthesis 792
 oxaphosphetane 357, 814
 oxazine, synthesis by Ritter reaction 1115–16
 oxazole 1176
 oxazolidinone, as chiral auxiliary 1228
 oxepin 1409
 oxetane 505, 1126
 1H NMR spectrum 265
 ring-opening and closing 1127, 1134, 1138
 oxidation level, of carbon atoms and functional groups 35–6
 oxidation of alcohols 222
 oxidation
 Baeyer–Villiger, *see* Baeyer–Villiger oxidation
 of alkenes to epoxides 505–8; *see also* epoxidation
 of allylic alcohol to enone 875
 of aromatic methyl groups 564
 of dihydropyridazolone 1196
 of dihydropyridine 1191–2
 of dihydroquinoline with DDQ 1210
 of furan with DMDO 1161
 of quinoline 1174
 of thiophene 1164
 oxidative addition 211, 1315–25, 1328–30
 oxidative cleavage, of hydroxy ketone 902
 oxidative coupling 1423
 oxidative insertion 211
 oxidising agents 564, 637–640, 1488
 oximes 348, 351
 fragmentation and rearrangement of in, *see* Beckmann fragmentation, Beckmann rearrangement
 hydrolysis of 351, 539
 in pyrrole synthesis 1190
 reaction to form nitrile oxide 1201
 reduction of 780
 stereoisomers of 350
 synthesis of 569–70
 oxine, *see* 8-quinolinol,
 oxirane 505, 1126
 OXO process 1318–19
 oxobutanoic: 3-oxobutanoic acid 677
 oxonium ion 343, 352, 1299–1300
 as intermediate 1367–8
 comparison with bromonium ion 504
 from vinyl ether 1462–3
 oxonium salt 1258
 oxopropanoic: 2-oxopropanoic acid (pyruvic acid) 1390–1
 oxyallyl cation 924, 1111–12
 cycloadditions of 924, 1016
 in Favorski reaction 991, 1016
 oxygen bases (*table*) 203–4
 oxygen, transport by haemoglobin 1178
 oxygen: ^{18}O , isotopic labelling with 282, 291–2, 339, 1410, 1432
 oxyhaemoglobin 1406
 oxymercuration 1048, 1280
 oxypalladation 1336–7, 1469
 oxytocin 652
 ozone 938; *see also* zonolysis
 ozone, in oxidation of quinoline 1174
 ozonide 938–9
 ozonolysis 372, 767–8, 806, 938–9, 1447
 p block 89
 p character, in small rings 366
 p orbitals 87, 91
 P(3-HB), poly(hydroxybutyrate) 1472
 P(3-HV), poly(hydroxyvalerate) 1472
p-, as prefix 39
 palladium(0), catalysis by 1311–39
 palladium(II), catalysis by 1311, 1314, 1321–2, 1324, 1336–7, 1339
 palladium
 as catalyst for dehydrogenation 1175
 as catalyst for hydrogenation 623–7, 1164, 1198
 tetrakis(triphenyl)phosphine 12
 π allyl-complex of 1331–3
 pallescensin A, synthesis 736
 palm oil 292
 palmitic acid 292, 743, 1426
 palytoxin 19
 PAM spacer unit 1476
 pantothenic acid 1389
 papaverine 1181, 1418–21
para-, as prefix 39, 556
para-acetaminophen, *see* paracetamol
 paracetamol 27–8, 34, 616
 ^{13}C NMR spectrum 62
 effects of an overdose 1357
 IR spectrum 69
 retrosynthetic analysis of 773
 synthesis 568–9, 773
 paraformaldehyde 144, 219–20, 713, 1452
para-hydroxyphenylpyruvate hydroxylase 1409
 paraldehyde, *see* paraformaldehyde
para-nitrophenol 568, 660
 parasitic equilibrium 693
para-toluenesulf-, *see* toluene-*p*-sulf-
para-xylene, nitration of 1208
 Parkinson's disease 1220, 1236
 Parr hydrogenator 623
 partial bond, in transition state 318
 participation, *see* neighbouring group participation
 Pascal's triangle, and splitting in NMR 265
 Pauli exclusion principle 88
 Pauling, Linus 121
 Pauson–Khand reaction 1311, 1339–40
 Payne rearrangement, of epoxy alcohol 977
 PCC 638
 PCC, *see* pyridinium chlorochromate
 PDC, *see* pyridinium dichromate

- pea moth pheromone, synthesis 448, 785–6
 pederin 841–2
 pelargonidin 1436
 pelletierine, synthesis 1448
 penaresidin A, synthesis 891–2
 penicillin G 1414
 penicillin V 499
 penicillin 10, 1247
 mode of action 1378
 penicillins, NMR coupling in 832
 pentaerythritol, synthesis and use 713, 1467
 pentanolactone 1071
 pentan-2-one, condensation 709, 827
 pentanal, in aldol reaction 710–11
 pentane 31, 38
 pentyl group 26
 PEP (phosphoenolpyruvate) 1391, 1401–2
 peptide bond 1356
 peptides 165–6, 1356
 synthesis 651, 1474, 1477–8
 peracids, *see* peroxyacids
 perfloracin 1209
 perfume 2, 9
 pericyclic reactions 905–65, 1267
 summary of 956
 Woodward–Hoffmann rules for 922–3
 periodate, in oxidative cleavage of hydroxy ketone 902
 periodic table 11, 88–89
 Periplanone B, synthesis 964–65
 Perkin reaction 704
 peroxyacids, comparison to other carbenoids 505–8, 1069; *see also* *m*-CPBA
 peroxyimide acid 1484
 persistent radicals 1024, 1028
 perspective, use in representing bonds 25
 Peterson reaction 812–814, 1296–7, 1300–3
 petrol 3
 PGE₁ 1268
 pH 183–5
 Ph 27, 40
 pH, effect on rates 324, 350
 pH, relationship to pK_a 187
 phase transfer catalysis 606, 665, 753
 phase, of an orbital 91–2
 phenaglycodol, synthesis 302, 799
 phenol formaldehyde resins 1455, 1468
 phenol 40
 ¹H NMR spectrum 548
 as enol 533, 547–9
 basicity of 203
 reaction with bromine 555–7
 reaction with diazomethane 1054
 reaction with dichlorocarbene 1069
 phenolic proton 548
 phenols
 by rearrangement of dienones, *see* dienone-phenol rearrangement
 protecting groups for 635
 synthesis by diazotization 598
 phenonium ion 973–5
 phenoxide ion, in electrophilic substitution reaction 558
 phenoxyacetic acid, synthesis and chlorination 557–8
 phenyl group 27
 phenyl, contrasted with benzyl 40–1
 phenylalanine 655, 1354–6
 ¹H NMR spectrum 248–9
 biological chemistry of 1404, 1409
 biosynthesis of 1400
 in synthesis of aspartame 1222
 ways to draw 20, 24, 27
 phenylethylamine: 2-phenylethylamine, mass spectrum of 52
 phenylfluorene: 9-phenylfluorene, pK_a of 195
 phenylhydrazine 351, 1204
 phenyllithium 142, 1225
 phenylmagnesium bromide 632
 phenylmenthol: 8-phenylmenthol, as chiral auxiliary 1229
 phenylsulfenic acid 1269–70
 phenylsulfenyl chloride, in sulfoxide synthesis 1268–9
 phenyramidol, synthesis 781
 pheromone
 aggregation, of boll weevil 380
 insect, mass spectrum of 51
 of *Lycore* 374
 of pea moth 448
 pheromones 648
 synthesis of 1221–4
 phosgene 1454
 phosphate ester, cyclic 1352
 phosphate ester, in nucleotides 1347
 phosphate, in primary metabolism 1346
 phosphatidyl choline 1377
 phosphatidyl ethanolamine 1376
 phosphine oxide 357
 of BINAP 1235
 phosphines, as ligand 1311
 phosphines, shape of 108
 phosphites, structure by NMR 368
 phosphoenolpyruvate (PEP) 1391, 1401–2
 phosphoglycerate: 2-phosphoglycerate 1391
 phospholipids 1375–7
 phosphonate, stabilization of enolates by 701
 phosphonium intermediate, in Mitsunobu reaction 609
 phosphonium salt 700
 in the Wittig reaction 357, 1474
 NMR spectrum 369
 synthesis 442–3
 phosphonium ylid, comparison with sulfonium ylid 1259
 phosphonium ylid, in the Wittig reaction 357, 1302
 phosphonium ylids, acylation of 743
 phosphorane 700, 814
 phosphoric acid, in eliminations 483, 494
 phosphorous acid, structure by NMR 368
 phosphorus pentachloride, in synthesis of acyl chlorides 295
 phosphorus pentachloride, in synthesis of thioamides 1264
 phosphorus pentoxide, in dehydration of oximes 569–70
 phosphorus tribromide, reaction with alcohols 431
 phosphorus ylid, *see* phosphonium ylid
 phosphorus, S_N2 at 423, 431–2
 phosphorus–oxygen double bond, strength of 358
 phosphoryl chloride
 in Vilsmeier reaction 1158
 reaction with maleic hydrazide 1173
 reaction with pyridazolonone 1196
 reaction with pyridone 1152
 reaction with quinolones 1212
 phosphorylation, chemoselective 1402
 photochemical [2+2] cycloaddition, *see* cycloaddition, [2+2]
 photochemical chlorination, of tetramethylsilane 1301
 photochemical electrocyclic reactions, *see* electrocyclic reactions, photochemical
 photochemical rotation of π-bonds 153
 photochemical sigmatropic hydrogen shifts 955–6
 photography, colour, pigments in 8
 phthalazine ligands, use in AD reaction 1242–3
 phthalimide 1179
 pK_a of 197
 phthalocyanine dyestuffs 8, 1179
 physical organic chemistry 305–37, 1079–117
 phytol 1437
 pi
 π-orbital 98
 π-complex, in electrophilic aromatic substitution 1110
 π bond, in C=C and C=O, energy level diagram 103
 π complex 1313
 π orbital 98
 π stacking 1232
 picric acid, acidity of 193
 pigment red 254 8
 pinacol reaction 1029–31
 pinacol rearrangement 984–8; *see also* semipinacol rearrangement
 pinacol rearrangement, enzyme catalysed 1398–9
 pinacol-like rearrangements 1397–8
 pinene
 α-pinene 31, 862, 1437
 α-pinene, biosynthesis of 1440
 β-pinene 925, 1238
 piperazine 1122, 1484
 piperidine 595, 672, 703, 714, 1122
 pirimicarb 178
 Pirkle, William 1221
 piroxicam (Feldene) 1247
 pival 732
 pK_a values, table 188
 pK_a 181–206; *see also* acidity, basicity and equilibria 311–12
 and leaving group ability 283
 and nucleophilicity towards C=O 286
 calculations with 185–9
 definition 185
 effect of aromaticity of base 196
 effect of bond strength to H 191
 effect of delocalisation 191–2
 effect of electronegativity 191
 effect of electron-withdrawing groups 193
 effect of hybridisation 194
 in aldol reaction 702
 in Claisen ester condensation 724
 of alkanes 213, 216, 1252
 of alkynes 213, 1291
 of benzenes 216
 of carbon acids, table 193
 of C–H bonds, and elimination 496–7
 of common organic acids 192
 of dimethylaminopyridine 1165
 of hydrogen peroxide 588
 of nitromethane 666
 of nucleophiles and leaving groups compared 442
 of phenol 548, 558
 of pyrrole 1164
 of sulfone, sulfoxide and sulfide 1252
 of tetrazole 1168
 of thioacetal 1254
 of triazole 1168
 relationship to pH 187
 role of solvation 196
 use in aldol chemoselectivity 696
 pK_{aH} 198; *see also* basicity
 pK_B, definition 198; *see also* basicity
 plane of symmetry 383, 391
 plane-polarized light, rotation of 388
 plasticizers 1465
 platinum, in catalytic hydrogenation 623–4, 627
 plus: +, – nomenclature 389
 podophyllotoxin 179, 1404
 polarimetry 388
 polarization, effect on bond cleavage 1004
 polarized light 388
 poly(1,1-dichloroethene) 1465
 poly(4-bromostyrene) 1473
 poly(acrylonitrile) 1461
 poly(dimethylsiloxane) 1457, 1469
 poly(ethylene), *see* polythene
 poly(hydroxybutyrate), P(3-HB) 1472
 poly(hydroxyvalerate), P(3-HV) 1472
 poly(isoprene) 1464
 poly(propylene) 1463
 poly(vinyl chloride), PVC 33, 41, 315, 1459, 1465
 poly(vinylalcohol) (PVA) 1468–9
 poly(vinylidene dichloride) 1465
 polyacrylamide gel, in peptide synthesis 1477–8
 polyamide 1453–4
 polycarbonates 1454–5
 polyenes 155, 157
 polyester 291, 1454
 polyethers 1456–7
 polyketides 1425–36
 polymerization, of alkenes 1459–68
 polymerization 1451–78
 and entropy 315
 anionic 1461–2
 cationic 1462–3
 of acrylates 1460–1
 of acrylonitrile 1461
 of epoxides 1457
 of pyrrole in acid 1157
 Ziegler–Natta 1463–4
 polymers 6, 1451–78
 polymer-supported reagents 657–8, 1466–7, 1473–8
 polyoxymethylene 1452
 polyphosphoric acid
 (PPA), in acylation of enols 740
 in Fischer indole synthesis 1206
 polyphosphoric acid, in intramolecular Friedel–Crafts acylation 574
 polysaccharides 347, 1346
 polystyrene 29, 1459, 1466, 1475–6
 polythene 26, 1459
 polyunsaturated fats 34, 1426
 polyzonimine, in problem 1447
 porphyrin
 aromaticity of 1178
 from pyrrole 1178
 in haemoglobin 1406
 potassium amide, use as base 669
 potassium carbonate
 as base 605, 667, 713
 in AD reaction 1241–2
 in Heck reaction 1321–2
 removal of TMS by 1291
 potassium hexamethyl disilazide 669
 potassium permanganate, as oxidising agent 564, 640, 644–5, 1174, 1265
 Potassium *tert*-butoxide, as base for kinetic conjugate addition 294, 752, 1329
 PPA, *see* polyphosphoric acid
 Pr 26, 29
 precocene 277
 prenyl bromide 417, 511, 605
 prephenic acid, biosynthesis of 1403
 presqualene pyrophosphate, biosynthesis of 1443
 primary alcohols, oxidation of 638
 primary carbon atoms 30
 primary kinetic isotope effect, *see* kinetic isotope effect
 primary metabolism 1345–6, 1414

- principal quantum number 85–6
 priority rules 387
 prismane, isomer of benzene 154
 prochiral and prochirality 837, 838, 884–6, 1233
 procyclidine *problem 10225*
 pro-drug 1247
 product of reaction, identification of unknown 76–8
 products, kinetic and thermodynamic 328–31
 progesterone, synthesis 1446–7
 projection, Newman 450–1
 prokaryotes 1377
 proline, (S)- 452, 1354, 1359
 in synthesis of CBS catalyst 1233
 ways to draw 20, 24
 propane, structure and conformation 37, 452
 propane-1,2,3-triol, *see* glycerol
 propanedioic acid 677
 propanedithiol: 1,3-propanedithiol 1254–5
 propanone, *see* acetone
 proparacaine, synthesis 578
 propiconazole 11
 propranolol, heart drug 49
 propranolol, structure and synthesis 49, 781–2, 1113, 1241
 propyl bromide 665
 propyl group 26
 propylene oxide, (R)- and (S)-, synthesis using 1224
 propylene, polymerization of 1463
 propynyllithium 214
 prostaglandins, biosynthesis of 1431–2
 prostaglandins, synthesis 686, 1229, 1268
 protecting group
 acetal 632, 1138, 1253, 1269, 1366, 1370–1
 acetyl 1365–6
 for alcohols 633, 738, 1132
 for aldehydes and ketones 347
 for diols 1138
 for phenol 635
 for pyrrole 1163
 for sugars 1138, 1365
 in chemical synthesis of peptides 1475
 silyl ether 710, 738, 1290–1
 silyl ethers 1290–1
 table 657
t-butyl ester 1254
 use in AMP synthesis 1365
 use of glucose in nature 1367
 protecting groups 632–7, 651–8
 proteins 1345–6
 proteins, synthesis 1353–9
 protodesilylation 1296
 proton coupled ¹³C NMR spectra 370–1
 proton decoupled ¹³C NMR spectra 370–1
 proton exchange, in NMR 258
 proton NMR, *see* ¹H NMR
 proton, solvation by water 182
 protonation, of sulfuric acid 553
 protonation, of water in the gas phase 317
 pseudoaxial 469, 853
 pseudoephedrine 393
 pseudoequatorial 469, 853
Pseudomonas putida 1220
 PTFE (Teflon) 1460
p-toluenesulf-, *see* toluene-*p*-sulf-
 pulegone, (S)-, conjugate addition to 860
 pulegone, (S)-, in synthesis 1229
 Pummerer rearrangement 1262–3
 purine bases 1175, 1347
 purple benzene, oxidising agent 1456
 push and pull mechanisms 130
 putrescine 33, 1416
 PVA, *see* poly(vinyl alcohol)
 PVC, *see* poly(vinyl chloride)
 pyran 543, 1360
 pyranoside 1360
 pyrazine, basicity of 1173
 pyrazine, structure of 9, 1148
 pyrazole 1149
 alkylation of 1197
 nitration of 1198
 synthesis 1188, 1196–7
 pyrethrin, insecticides 10, 1066
 pyridazine 1148
 basicity of 1173
 reactivity of 1173
 synthesis of 1188, 1195–6
 pyridazolone 1196
 pyridine 40, 703, 1148–9
 as a nucleophilic catalyst 485, 1149
 as catalyst of bromination 1155
 as solvent 281–2, 418
 basicity of 202–3, 616, 1149
 electrophilic aromatic substitution of 1150–2
 nitration of 1150, 1153
 NMR spectra and conjugation 256, 259
 NMR spectrum of 1148
 nucleophilic aromatic substitution of 1150
 orbitals of 1148
 pyridine-*N*-oxide
 2-methyl, reaction with acetic anhydride 1155
 by oxidation of pyridine 1153
 reactions of 1153–5
 pyridines, reactions of 1148–56
 pyridines, synthesis of 1186–7, 1191–5, 1212
 pyridinium chlorochromate (PCC) 42, 638
 pyridinium dichromate 639, 1156, 1240
 pyridinium tribromide 1155
 pyridone
 from acetamide and 1,3-dicarbonyl 1194
 from hydroxypyridines 1152
 reaction with phosphoryl chloride 1152
 structure of 1152, 1209
 pyridoxal phosphate 1384–8, 1403, 1417–18
 pyridoxal transaminase 1419
 pyridoxal transamination 1403–4, 1409
 pyridoxal 355
 pyridoxamine phosphate 1384–6
 pyridoxamine 355, 1384–6
 pyridyl: 2-pyridyl allyl sulfide 1257
 pyrilium 1157, 1367
 pyrimidine bases 1347
 pyrimidine
 basicity of 1173
 from amidine and 1,3-diketone 1188, 1198
 structure of 1148
 pyrolysis, of formate esters 1014
 pyrones 1156, 1164
 pyrophosphate 1376, 1381–2
 pyrophosphorylation 1364, 1438
 pyrrole
 decarboxylation 1159
 delocalisation of lone pair in 1157
 ack of basicity 203
 NMR spectrum of 374, 1148
 orbitals and structure 1148–9, 1157
 p*K*_a of 1164
 polymerisation 1157
 porphyrins from 1178
 protection of 1163, 1165
 reactions of 1157–9, 1162–5
 pyrroles, synthesis 1186–91
 pyrrolidine alkaloids 1416–18
 pyrrolidine 672, 714, 1122, 1416
 p*K*_a of 1164
 synthesis via azomethine ylid
 cycloaddition 964
 pyrrolidines, rate of formation by ring-closing reaction 1138
 pyruvate 1383, 1391–5; *see also* pyruvic acid
 pyruvic acid 348, 1346, 1390–2
 by oxidation of lactic acid 31
 conversion to alanine by reductive amination 355
 reduction of 1382–3
 quanta, of energy 83–4
 quantum mechanics 83–4
 quantum numbers 85–7
 quartet, in proton NMR 265–6
 quaternary ammonium salts 673
 quaternary ammonium salts, elimination 484–5
 queen bee substance, synthesis of 1269–70
 quench, of reaction 219
 quinic acid 1400, 1402
 quinine 2, 1147
 quinoline yellow, dyestuff 7
 quinoline
 electrophilic substitution of 1174
 in Lindlar reduction 623, 1174
 numbering of 1209
 quinoline-*N*-oxide 1175
 quinolines, synthesis of 1209–11
 quinolines, nucleophilic aromatic substitution of 1175, 1212
 quinolinol: 8-quinolinol, synthesis and metal complexes 1211
 quinolone antibiotics 742, 1211–12
 quinolone, synthesis 1211
 quinolone: 2-quinolone, structure of 1209
 quinolones, reaction with phosphoryl chloride 1212
 quinone, as dienophile 907
 quintet, in proton NMR 265–6
 quinuclidine, basicity and nucleophilicity of 1123
 R, as 'wild card' alkyl group 27, 32
 R, gas constant 307
 R, S nomenclature 386
 racemic mixture 385–6, 1225
 racemization
 in S_N1 422–3
 of amino acids 534, 1386
 of ibuprofen 535
 of sulfoxides 1267
 via enolization 534
 radial node 90
 radical chain reaction 1033–50
 allylic bromination by 1039–40
 carbon–carbon bond formation using 1042–6
 frontier orbital effects in 1044–5
 in copolymerisation 1046
 in polymerization 1459–61, 1468
 intramolecular 1049–50
 of alkanes 1035–9
 of alkenes 1020, 1034, 1042–50
 of alkyl halides 1040–5
 reactivity of radicals in 1043–6
 summary of steps in 1035
 synthesis by 1041
 tributyltin hydride in 1046
 radical co-polymerization 1465
 radical coupling 1029–33, 1421–5
 radical reactions 1019–50
 radical
 addition to alkene 1023
 allyl, orbitals for 161
 captodative 1028
 electron spin resonance of 1024–5
 formation 1019–23, 1057–60
 hard/soft description of 1047
 in acyloin reaction 1032–3
 in mass spectrometry 50–1
 molecular orbitals of 1025–77, 1045
 persistent, *see* Persistent radicals
 reaction of Vitamin E with 1024
 stability of 1026–8
 triphenylmethyl 1022, 1028
 umpolung reactivity of 1048
 writing mechanisms involving 1022
 radio waves and NMR 47, 57–9
 Raney nickel 626
 for hydrogenation of C–S bond 744, 876, 1161, 1256, 1262–3
 for hydrogenation reactions 826, 1223
 reduction of nitro group with 1151
 ranitidine (Zantac) 10, 587–8
 rapamycin, synthesis using Stille coupling 1326–7
 raspberry ketone 34, 626
¹³C NMR spectrum 363
 rate constant 318
 rate equation 318–23
 concentration effects 690
 for aldol reaction 690
 for S_N1 and S_N2 411–14, 421
 rate expression, *see* rate equation
 rate
 and collision frequency 318
 and half-life 317
 and spectroscopy 461
 of epoxidation of different enone geometries 804
 of multistep reactions 350
 of nitration of halobenzenes 567
 of nucleophilic aromatic substitution 593, 595
 of ring formation 1135, 1136
 of S_N1 and S_N2 compared 427–8
 rate-determining step
 in aldol reaction 690
 in electrophilic aromatic substitution 551
 in eliminations 481, 496
 in ester hydrolysis 1389
 in nucleophilic aromatic substitution 594–5
 in S_N1 and S_N2 411
 rates of reaction 315–35
 rayon, manufacture of 1472
 reaction rate, *see* rate
 rearrangement in biosynthesis 1397–9
 rearrangement reactions 443, 984, 976–1000
 rearrangement
 during Friedel–Crafts reaction 573, 984
 enzyme catalysed 1398
 of carbene 1071–3
 of epoxide to ketone 1015
 of nitrene 1073
 recrystallization, use in improving ee 1237
 recrystallization, use in purification 568, 1232
 RedAl 1293
 reduced mass 65
 reducing agents 616–29
 reduction
 catalytic asymmetric 1484
 chelation control in 893–4
 diastereoselective 887
 in polyketide synthesis 744
 of alkenes 623–6, 1164
 of alkynes 819
 of amide 779
 of aromatic rings 623
 of carbonyl compounds with sodium, *see* Bouveault–Blanc reduction
 of C–S bonds 876, 1161
 of dihaloketone by zinc 930, 1111–12
 of isoxazole 1176

- of nitrile 768, 795
of nitro group 564, 569, 572, 576, 598, 626, 1151, 1198
of nitroalkene 583
of *N*-oxides 1153
of oximes 780
of tosylate to alkane 627, 806
of unsaturated carbonyl compounds 607–8
 using borane 618–20, 738
 using Red Al 1293
reductive amination 354–6, 621, 640, 779–80, 796, 1384
 in nature 1384–8
reductive elimination 1316–30, 1336
Redux (slimming pill) 1220
Reformatsky reaction 706, 792
regioselectivity
 and S_N1 on allylic cations 417
 azide attack on epoxide 1242
 in aromatic substitution reaction 555–7, 563
 in chlorosulfonation of toluene 563
 in Claisen condensations (using ketones) 731
 in Diels–Alder reaction 919–21
 in electrophilic aromatic substitution (review) 571–7
 in electrophilic attack on alkenes 509–10
 in hydroboration of alkyne 1279–82, 1328
 in nucleophilic attack on benzyne 603–4
 in steroid backbone rearrangement 1444–5
 in synthesis of substituted alkenes 1295–6
 of conjugate addition 235
 of E1 487–90
 of E2 494–5
 of enol(ate) formation 528–40
 of enolate reactions 528, 539, 541, 544, 680
 of epoxide opening 513
 of intramolecular Diels–Alder 921
 of sulfonium ylid reactions 1260
regiospecific, definition of 607
Reimer–Tiemann reaction 575, 1069
Reissert indole synthesis 1208
relative stereochemistry 392
repulsion between molecules 118
resolution 399–404, 738, 1235, 1485
resonance 154–5
resveratrol 6, 1436
reticuline 1421–4
retinal, 11-*cis* 1
retinal, all *trans*, ^{13}C NMR spectrum 363
retro-aldol reaction, in enolate conjugate addition 750
retrosynthetic analysis 771–801
 chemoselectivity problems in 776
 of 1,3-related groups 791–7
 of 1,4-related groups 800
 of 1,5-related groups 798
 of acetals 794
 of alkynes 784–6
 of amides 772
 of amines 776, 778–80
 of diols 799
 of esters 772
 of ethers 774, 796
 of sulfides 775
 of α,β -unsaturated compounds 792–3
 of β -hydroxy ketones 791
 using aldol reaction 791
 using umpolung 798–801
retrosynthetic arrow, definition of 772
retrosynthetic retrosynthetic analysis, of 1,2-related groups 799
reverse cycloaddition 1269
reversibility, and thermodynamic control 328–9
rhodium acetate, reaction with diazo carbonyl 1057
rhodium, as catalyst for asymmetric hydrogenation 1234–9
rhodium, as catalyst in nitrile reduction 795
riboflavin, vitamin B₂ 1407
ribo-furanoside 1360
ribonuclease 1358
ribonucleic acid (RNA) 1350
ribonucleotide 1360
ribo-pyranoside 1360
ribose 5-phosphate, synthesis of 1364
ribose 146, 394–5, 1346, 1360
ring closing reactions 1136–44
ring contraction 868
ring expansion 982–3, 988, 1007–9
ring flipping 460–1
ring inversion 460–1
ring junction, NMR coupling across 829
ring opening reactions, of saturated heterocycles 1124–8
ring strain 144–5, 454–6, 957, 1124–6, 1136
rings
 3-membered, conformation of 456–7
 NMR coupling in 831
 4-membered, conformation of 457
 NMR coupling in 832
 5-membered, conformation of 457, 853
 NMR couplings in 833
 6-membered, axial attack on 858–60
 conformation of 456, 457–74
 how to draw 459–60
 NMR couplings in 834
 bond angles in 454
 geometry of alkenes in 805–6
 of carbon atoms 21, 27–9
 small, medium and large, definitions 456
 stereoselectivity of reactions on 851–79
Ritter reaction 436–7
 and Beckmann fragmentation 999, 1000
 determination of mechanism 1114–16
 in synthesis of Crixivan 1115–16, 1484–5
RNA (ribonucleic acid) 1350
Robinson annelation 761–4
 stereochemistry of ring formation 872
Robinson tropinone synthesis 1418
Robinson, Sir Robert 761
rogletimide 786, 798
roofing, in NMR spectra 272
Rosenmund reaction 623
roses, smell of 4
rosoxacin, structure and synthesis 1212
rotation of bonds 247, 447
rotation, barriers to 449–50
rubber 1463, 1471
rubidium 83
ruthenium, as catalyst for catalytic hydrogenation 623–4
Rydberg constant 85

s block 89
s orbitals 87, 90
SAC, *see* specific acid catalysis
saccharides 1372–4
saccharin, synthesis of 564, 644
S-adenosyl methionine, *see* SAM
salbutamol 636, 645–6
salen ligand 1488–9
salicylic acid 558, 645
 ^{13}C NMR spectrum 363
SAM (*S*-adenosyl methionine) 1348, 1417, 1420–1
saponification 292
saturated carbon atoms 32
saturated fat 34, 292, 625, 743, 1426
Saytsev elimination 495
SBC, *see* specific base catalysis

s-Bu 30
s-butyl group 30
s-butyllithium 215, 1302
scalemic, definition of 1230
scanning tunneling microscopy 82
Schiff base 335, 1385
Schlosser's base 1058
Schotten, Carl 285
Schotten–Baumann method 285
Schreiber, Stuart 964
Schrödinger equation 86
s-cis 1228–9
scurvy 1359
sec-butanol, inversion by S_N2 422–3
sec-butyl group 30
second order kinetics 319–23
secondary alcohols, oxidation of 638
secondary carbocations 573
secondary carbon atoms 30
secondary metabolism 1414–15
Selectride 472
selenium dioxide 1270–1
self-condensation reactions 689–93
semicarbazide 351
semicarbazone 351
semipinacol rearrangement 986–8; *see also* Tiffeneau–Demjanov rearrangement
separating acids and bases 186
serine 1354, 1404–5
serotonin 1, 1181, 1205, 1220, 1447
serriicornin 4
sesquifenchene 1252–3
sesquiterpenes 1439
seven membered ring formation 715, 1339
sex pheromones 4–5, 374
S-glycoside 1367
SH protons in NMR 256–8
shading, of orbitals to show phase 92
shapes of molecules, representing in two dimension 25
Shapiro reaction 1294
Sharpless asymmetric dihydroxylation 1485, 1490
Sharpless asymmetric epoxidation 1239–43, 1265–6, 1484
Sharpless, K. Barry 1239
shaving gel, constituents of 6–7
Sheppard approach, to peptide synthesis 657
shielding, in NMR 59–61
shikimate dehydrogenase 1402
shikimic acid pathway 1400–5
shikimic acid 363, 1400–5, 1447
shorthand mechanisms 285, 298
sialic acid 1373
sialyl Lewis X 1373–4
sight 1
sigma orbital 98–9
sigma
 σ complex 1313
 σ conjugation 416, 562, 728
 σ orbital 98–9
sigmatropic hydrogen shifts 953–5
sigmatropic rearrangements 943–56
 [2,3] 951–3
 [3,3] 943–51, 1273, 1403; *see also* Claisen–Cope rearrangement, Ireland–Claisen rearrangement, Cope rearrangement
 [3,3], in chromium oxidations 951
 [3,3], in Fischer indole synthesis 950, 1204
 in selenium dioxide oxidation 1271
 of sulfoxides 1267–9
sila-Pummerer rearrangement 1304
sildenafil, *see* Viagra
silica 402

silicon Baeyer–Villiger rearrangement 1288, 1293
silicon putty 1469
silicon
 comparison with carbon 1287–9
 in Robinson annelation 763
 S_N2 at 423
 stabilization of carbanions by 1302–3
 stabilization of carbocation by 1292
 silver acetate 1352
 silver nitrite 978
 silver oxide 971
 silyl enol ether 671, 674, 681, 697, 699
 formation of 540–1, 1289–90, 1304
 in aldol reactions 699–712, 757
 in Ireland–Claisen rearrangement 948
 of an ester 705–6
 silyl enol ethers
 ^1H NMR of 254–5
 alkylation of 674
 halogenation of 543–4
 hydrolysis of 543
 in conjugate additions 240, 755
 sulfenylation of 544
 silyl ether protecting group 710, 738, 1290–2
 silyl ketene acetal 707, 755–7
 silyl: β -silyl cation 1291–300
 Simmons–Smith reaction 1067–9
 single bond, barrier to rotation about 317
 singlet carbene
 bond angles of 1060
 electronic structure of 1061
 reaction with alkene 1063–6
 singlet, in proton NMR 259
 Singly occupied molecular orbital, of radicals 1026, 1045
sinigrin 1367
sirenin 1068, 1271
six-membered rings 456–74
 how to draw 459–60
 reactions of 466–73
Skraup quinoline synthesis 1210–1
skunk, thiols in smell of 3
skytalone 1447–8
small rings, definition of 456
small rings, infra red and NMR spectra 366–7
Smith, Kline and French 205
SmithKline Beecham 205
 S_N1 and S_N2 mechanisms 411–43
 choice between 414–15, 426
 introduced 408
 S_N1 mechanism, in nucleophilic aromatic substitution 597–600
 S_N1 , comparison with E1 478
 S_N2 mechanism, at Si, Sn, P, and Cl 423, 540–4, 1288–90, 1305
 S_N2 reaction
 at α -halo ketones 646
 effect of nucleophiles, (tables) 439–41
 in polymerization 1456–7
 intramolecular 737
 orbitals and 440
 rate and structure, tables 425, 441
 stabilization of transition state by silicon 1300–2
 stereochemistry of 422–3
 transition state for 421–2, 604–5
 unimportance of charge 440
 S_N2 reactions 420–5
 S_N2' mechanism 604–6
 S_N2' reaction, stereochemistry of 610–11
soap 292, 1375
sodium amide, as base for deprotonation of acetylene 190, 669
sodium amide, in benzyne formation 600–4
sodium azide 1242
sodium benzenesulfonate 553

- sodium bisulfite, reaction with carbonyl compounds 148
- sodium borohydride 140–1, 616–17, 626, 1382–3
- cleavage of ozonide by 939
- in asymmetric reduction 1370
- in oxymercuration-reduction of alkenes 1280
- in radical chain reactions 1044
- reaction with epoxides 1132
- reaction with unsaturated carbonyl compounds 236, 607–8
- reduction of carbonyl compounds 140–1
- reduction of ester 1242
- reduction of nitro-alkene 583
- sodium cyanide 795, 1202
- sodium cyanoborohydride 354, 1384
- sodium dichromate 638
- sodium ethoxide 729–30
- sodium hexamethyldisilazide 669
- sodium hydride, as base in Claisen condensation 730, 736
- sodium hypochlorite, oxidising agent 1488
- sodium iodide, substitution by 789, 1132
- sodium lamp 83
- sodium nitrite 597–600
- sodium perborate 1281–2
- sodium periodate 1229, 1253–5, 1269
- oxidative cleavage of diols by 939
- sodium phenoxide 558
- sodium salicylate, synthesis 558
- sodium sulfide 1253
- sodium triacetoxyborohydride 354
- sodium trichloroacetate, in dichlorocarbene synthesis 1059
- sodium, in Birch reduction 628–9, 819
- sodium, reduction of carbonyls by 861, 1023; *see also* Bouveault–Blanc reduction
- sodium–amalgam reduction 1253
- soft and hard nucleophiles 237, 441
- solanaceae alkaloids 1416
- solanine 1416
- solid phase synthesis 656–8
- solubility, of acids and bases 185–6
- solvation, effect on pK_{aH} 196
- of hydronium ions 182
- of salts by water 333
- solvent effects, in Diels–Alder reaction 917
- solvent effects, in S_N1 and S_N2 428–9
- solvent isotope effect, in specific acid and base catalysis 1103–4
- solvents for organolithium reagents 212
- solvents
- effect on rates and products 332–4
- for Grignard reagents 211
- polar aprotic 333, 429
- protic 333
- solvolysis, *see* Neighbouring group
- SOMO, *see* singly occupied molecular orbital
- Sonogashira coupling 1330
- sp orbitals 107
- sp² orbitals 106–107
- sp³ orbitals 105–107
- space-filling models 452
- spacer unit, in polymer 1474–6
- specific acid catalysis 1102–4
- in acetal hydrolysis 1108
- specific base catalysis 1104–5
- specific enol equivalent, for aldehydes 707
- for esters 705–6
- for ketones 709–12
- specific enol equivalents 671, 697–712
- specific enolate equivalent, for carboxylic acid derivatives 704
- specific rotation 388–9
- spectroscopy 47–79
- and rates 461
- elucidating structure using 823–48
- NMR, *see* NMR spectroscopy
- sphingosine, synthesis of 811, 819
- spin angular momentum quantum number 87
- spin, nuclear, and NMR 57
- spiro rings 508, 685
- spiroketals, conformation of 1131–2
- squalene, from farnesyl pyrophosphate 1442–3
- stability of molecules, meaning 305–15
- stabilization, of transition state 604
- staggered conformation 450–1
- standard Gibbs energy, DG° 307–15
- stannanes 1304–8
- starting materials, available 222, 789
- stearic acid 171, 292, 1426
- stephanine, in problem 1447–8
- stereochemistry
- and fragmentation 1005–7, 1009
- of epoxide opening 435, 438
- of Mitsunobu reaction 433
- of S_N1 and S_N2 422–3
- of the S_N2' reaction 610–11
- representing in two dimensions 25
- stereoelectronic effects
- definition of 1122; *see also* anomeric effect, Baldwin's rules
- in acyclic acetals 1133
- in esters 1134
- in fragmentation reactions 1128
- in saturated heterocycles 1128–33
- stereogenic centre 384
- stereogenic centres, multiple 392–6
- stereoisomers 384, 448
- of imines and oximes 350
- stereoselective alkylation of sulfoxide 1269
- stereoselective and stereospecific, definition 492
- stereoselective reduction using NADPH 1427
- stereoselective synthesis
- of substituted alkenes 803–820, 1295–6
- use of crotyl silanes 1300
- using crotyl stannanes 1306–7
- stereoselective, definition of 881
- stereoselective, elimination reactions 809, 810
- stereoselectivity
- of alkylation reactions 884
- of amination reaction 1138
- of elimination reaction 487–90, 882–4
- of epoxidation reactions 589, 884, 863, 866
- of Julia olefination 811
- of Peterson reaction 813
- of reactions on cyclic compounds 851–79
- of Wittig reaction 815
- of [2,3]-sigmatropic rearrangement 1271
- stereospecific cross-coupling reactions 1324
- stereospecific, definition of 881
- stereospecificity
- of bromination reactions 515–17
- of Diels–Alder reaction 909–13
- of dihydroxylation of alkene 937, 38
- of electrophilic addition reactions 882
- of elimination reactions 491–3, 812–13, 1301–3
- of epoxidation reactions 589, 883
- of epoxide opening 883, 1301
- of iodolactonisation reactions 882
- of nucleophilic substitution reactions 882
- of [2,3]-sigmatropic rearrangement 1269
- steric acceleration 427
- steric effects, definition 139
- steric hindrance
- and enol stability 531
- definition 139
- effect on conjugate additions 237
- effect on nucleophilic attack on benzyne 603
- effect on reactivity of carbonyl group 138–9, 143–4
- in aromatic substitution 559–60
- in elimination reactions 480–1, 494
- in S_N1 , S_N2 and S_N2' reactions 427, 605
- steroid backbone rearrangement 1444
- steroid nucleus, synthesis and numbering of 761, 874, 876, 999, 1341, 1441
- steroid, biosynthesis of 1441–7
- steroids 28, 214
- conformation of 466
- Stetter reagent 1396
- stilbene 1155
- Stille coupling 1325–8
- STM, *see* scanning tunneling microscopy
- strain, effect on IR spectrum of carbonyl group 366
- strain, in rings 454–6
- Strecker reaction 356, 401
- street lamps, colour of 83
- strength, of acids and bases 184–91; *see also* basicity, pK_a
- Streptomyces griseus* 738
- streptomycin, (an antibiotic) 738
- stretching of bonds, in IR spectra 67–72
- structure determination, by spectroscopy, outline 49–50, 371–4, 823–48
- structures, guidelines for drawing 21–5
- strychnine 28, 41
- styrene, in polymers 1465–6, 1473
- styrene, reaction with hydrogen bromide 509
- substitution and elimination compared 477, 498
- substitution at C=O, factors controlling 286
- substitution at saturated carbon and C=O compared 440–1
- substitution reactions, of acyl chlorides 280–1, 284, 299
- substitution reactions, of anhydrides 280–1
- substitution
- at the carbonyl group 279–301, 339–58
- electrophilic aromatic 547–77
- nucleophilic aromatic 589–600
- nucleophilic, at saturated carbon 407–45; *see also* S_N1 , S_N2
- nucleophilic, on six-membered rings 466–8
- succinic anhydride, Friedel–Crafts acylation with 574, 801
- sucrose 3, 32, 1361
- Sudafed 393
- sugars 1345–7, 1359–74
- anomeric effects in 1129
- as examples of stable hemiacetals and acetals 341, 347
- protection strategies of 1137–8
- stereoisomers of 394–5
- sulcatol, synthesis of 1223–4
- sulfa drugs 571, 1180
- sulfanilamides, first antibiotics 571
- sulfanilic acid, synthesis 571
- sulfapyridine, structure and synthesis 571, 1147
- sulfenate ester, in [2,3]-sigmatropic rearrangement 952, 1267
- sulfene, intermediate in mesylation 485, 500
- sulfenic acid 1272
- sulfenyl chlorides 544, 1249–51
- sulfide group 20
- sulfide 1248, 1251
- neighbouring group participation of 972
- oxidation of 1253–4, 1268
- pK_a of 1252
- retrosynthetic analysis of 775
- synthesis by S_N2 438–9
- sulfinate anion
- as a nucleophile 1250
- as leaving group 1257
- sulfinate ester, in asymmetric synthesis of sulfoxide 1266
- sulfonamides 564, 644, 658–9, 1206
- sulfonate esters 1206, 1248, 1484
- sulfonate salts 1248
- sulfonating agent 553
- sulfonation
- in synthesis of polymer supported reagents 1473
- of amines 571
- of anthraquinone 566
- of benzene 552–3
- of bromobenzene 568
- of toluene 563
- reversibility of 571
- reversibility of 571
- sulfone 1248, 1251
- acylation of 743
- alkylation of 952
- in nucleophilic aromatic substitution 595
- pK_a of 1252
- sulfonic acid 552–3, 1251
- sulfonic acids, pK_a of 433
- sulfonium salt 1250–1, 1257–9
- sulfonium ylid 1069, 1258–61
- sulfonyl chloride 1251, 1265
- sulforaphane, synthesis of 1368
- sulfoxide 1248, 1251, 1265–70
- alkylation of 1253
- chirality of 1265–7
- elimination of 1269–70
- oxidation of 1265
- pK_a of 1252
- sulfoxonium ylids 1261
- sulfur (S_8), structure of 1452
- sulfur chemistry 1247–73
- sulfur compounds, bad smell of 4
- sulfur nucleophiles, in S_N2 436–7
- sulfur radical 1470
- sulfur trioxide 563, 571
- sulfur ylid 1168
- sulfur
- as electrophile 1249–51
- functional groups containing (table of) 1251
- in dehydrogenation of guaial by 830
- oxidation states of 1248–9
- stabilisation of a-anions by 1127
- use in vulcanization of rubber 1469
- sulfuric acid (concentrated)
- in nitration of benzene 552
- as dehydrating reagent 716
- in eliminations 483
- in sulfonation 563
- reaction with benzene 552
- sulfur-stabilized anions 1251–7
- sulfur-stabilized cations 1261–4
- sulfuryl chloride 1249–50
- sulph-, *see* sulf-
- Sumatriptan, structure and synthesis 1181, 1205–6
- super protons 1293
- superacids 410, 562, 963
- superglue 8, 1461
- suprafacial 922, 955, 1269
- Suzuki coupling 1325, 1328–9
- sweeteners 9
- Swern oxidation 639, 699, 1271–2, 1370
- symmetric stretch in IR 69
- symmetry, and ¹³C NMR 64

- symmetry, plane of 383, 391
syn-aldol product 898–9, 901–2
 synclinal 453
 syndiotactic, definition of 1460
syn-periplanar 453
 synthesis problems 661–2
 synthon, definition of 773
 synthons, donor and acceptor 791
 systematic nomenclature 37–9
- tables, of ^1H and ^{13}C NMR shifts 375–7
 Tagamet 206, 586–7, 1147
 tamoxifen 488–9
 tar, coal, source of organic compounds 2
 target molecule 771
 tartaric acid 34, 395, 1363
 tautomerism of imines and enamines 530, 1405
 tautomerism 205, 524–5, 585, 702
 in biosynthesis 1405
 in heterocycles 1152, 1167–8, 1172–3
 tautomers 205, 702
 Taxol, geminal coupling in 823, 844, 847, 1031
 tazadolene 796
 TBAF, *see* tetrabutylammonium fluoride
 TBDMS 1232, 1290
 TBDPS 1290–1
t-Boc protecting group, *see* Boc
t-Bu 30
t-butanol
 reaction with HBr 408
 use as solvent 1241
t-butoxide, as base 480–2
t-butyl cation 553, 570
t-butyl chlorides, reaction with aluminium trichloride (AlCl_3) 570
t-butyl ester
 as blocking group in pyrrole synthesis 1190
 as protecting group 652–3, 1254
 hydrolysis by $\text{S}_{\text{N}}1$ 436
t-butyl group 30
 effect on conformation of cyclohexanes 465, 737
 use in drug stability 645
t-butyl hydroperoxide, use as oxidant 1239–41, 1265–6, 1271
t-butyl thiol, smell of gas 4
t-butyldimethylsilyl chloride 1232
t-butyldiphenylsilyl protecting group 1290–1
t-butyllithium 215, 217
t-butyloxycarbonyl, *see* Boc
 TC: 3-TC (lamivudine), anti-AIDS drug 1351, 1482
 TCP 28
 Teflon, synthesis of 1460
 temperature
 convenience of -78°C 331
 effect on equilibrium constants 314–15
 effect on rates 315–19, 328–32
 TEMPO, *see* Tetramethylpiperidine *N*-oxide
 ten membered ring
 conformational of 715
 formation using Stille coupling 1326
 terephthalic acid 291, 1454
 termination, in cationic polymerization 1462
 termination, in radical chain reactions 1034–5
 termite defence compound 228
 termolecular kinetics 325–6, 690
 terodilin 780
 terpenes 1437–47
tert-butyl group 30
 tertiary amines, rate of methylation 1123
 tertiary carbocations, in cationic polymerization 1462
 tertiary carbocations, stability 415–16, 1439
 tertiary carbon atoms 30
 terylene 291, 1454
 testosterone 28, 1441
 tetraalkyl ammonium salts, in phase transfer catalysis 606, 665
 tetrabutylammonium fluoride 753, 1288, 1291
 tetrabutyltin, as by-product 1306–8
 tetracycline antibiotic 577
 tetraethyllead 27
 tetrafluoroborate 1258
 tetrafluoroethylene, polymerization of 1460
 tetrahedral angle 22
 tetrahedral C atoms 107
 tetrahedral intermediate 281, 321–3
 evidence for 282
 stability of 282–3, 299–301
 tetrahedrane 373
 tetra-*t*-butyl, NMR and structure 373
 tetrahedron, shape adopted by C, N or O 82–3
 tetrahydrocannabinol 1449
 tetrahydrofuran
 complexation with lithium enolates 698
 decomposition by organometallics 332, 1127
 structure 32, 42, 1126
 tetrahydropyran, coupling in ^1H NMR coupling 1129–30
 tetrahydropyranyl, as protecting group 543, 634, 650, 1132
 tetrahydropyrans, by ring-closing reaction 1134
 tetrakis(triphenylphosphine) palladium(0) 1314, 1320
 tetramer, methyl lithium 1452
 tetramethylene glycol 1457
 tetramethylpiperidine *N*-oxide 1024, 1028
 tetramethylsilane, in NMR 60, 244
 tetramethylsilane, photochemical chlorination of 1301
 tetramethyltin 1305
 tetra-*n*-propylammonium perruthenate, TPAP 639
 tetrazole 1168
 in drugs 1169
 pK_{a} of 1168
 synthesis, from nitrile and azide 1202
 tautomerism in 1168
 tetrodotoxin, structure of 1122
 treose 1361
 TFAE, 2,2,2-trifluoro-1-(9-anthryl)ethanol 1232
 theobromine 1347
 thermodynamic and kinetic products 328–31, 630
 thermodynamic control 235
 in 6-membered cyclic ketone 860
 in acetal formation 1361
 in conjugate addition 583, 749–50
 in enolate formation 680–1, 682
 in intramolecular aldol reaction 716–18
 in ring-closing reactions 1137
 thermodynamic enolate, formation of 711
 thermodynamic product 235
 thermosetting polymers 1456
 thexyl borane 1281–2
 THF, *see* tetrahydrofuran
 thiaburimamide 205
 thiadiazole: 1,2,5-Thiadiazole 1177, 1213
 thiamine pyrophosphate 1392, 1395–7
 thiazole 1176, 1200, 1392
 thiazolium salt 1392, 1396
 thiazolium ylid 1394–8
 thienamycin, structure and NMR of 832
 thiiranium ion, *see* episulfonium ion
 thioacetal 627, 1254–6; *see also* dithianes
 thioaldehyde 1272–3
 thioamide, from amide 1200, 1264–5
 thiocarbonyl compounds 1264–5
 thioctic (lipoic) acid, ^{13}C NMR spectrum 363
 thioether, *see* sulfide
 thiol ester 439, 1389–90, 1392, 1438
 conjugation in 744
 hydrolysis of 1418
 in biosynthesis 744
 thiol group, in glutathione 584
 thiol 1249, 1251
 as nucleophile 439
 by addition of hydrogen sulfide to alkenes 510
 comparison with alcohol 1249
 conjugate addition of 228, 237–8, 876
 in skunk smell 3
 in vulcanization of rubber 1469
 oxidation to disulfides 1355–7
 synthesis 439
 thiolacetate, as nucleophile 439
 thiolate anion 1151, 1248–50
 thionyl chloride, reaction with alcohols 789, 796
 thionyl chloride, reaction with carboxylic acids to form acyl chlorides 295
 thiophene sulfone 1164
 thiophene sulfoxide 1164
 thiophene, from 1,4-dicarbonyl compounds 1187
 thiophene, reactions of 1159–4
 thiophenol 237
 thiophile 1267–8
 thiosulfinate ester, from allylic sulfoxide 1272
 Thorpe–Ingold effect 1138–40
 THP, *see* tetrahydropyranyl
 three membered rings, conformation of 456–7
 three membered rings, formation of 1257
 three-dimensional structures, representing 25
 threitol 1363
 threonine 1354
 threose 1361, 1363
 thromboxane 1413–14, 31
 thujone 1413
 thymine 1347
 thymoxamine, synthesis of 598–9
 thyroxine 577, 646
 Tiffeneau–Demjanov rearrangement 987–8, 96
 timolol 1177, 1213
 tin tetrachloride, as Lewis acid 755–6, 674, 699, 708, 711, 921, 1263, 1299–1300, 1487
 tin(II) chloride, reduction of diazonium salt by 1206
 tin–lithium exchange 1306–8
 TIPS 1290–1
 titanium tetraisopropoxide 756, 1239–41
 titanium, in McMurry reaction, *see* McMurry reaction
 TMS, use as protecting group 1290–1
 TNT 33
 Todd, Alexander 1365–6
 tolmetin 1158
 toluene 40
 bromination of 561
 chlorosulfonation of 563
 electrophilic aromatic substitutions of 562
 nitration of 644
 sulfonation of 563
 toluene-*p*-sulfinyl chloride 1266
 toluene-*p*-sulfonate, *see* tosylate
 toluene-*p*-sulfonic acid (PTSA, TsOH) 345, 563, 700
 toluene-*p*-sulfonyl chloride (TsCl), *see* tosyl chloride, tosylation
 Toray process 1038
 torsion angle 451
 tosic acid 345, 563, 700
 tosyl azide 1056–7
 tosyl chloride (TsCl) 422, 433–4, 563, 645, 1132, 1250, 1484; *see also* tosylation
 in esterification 655–6
 in synthesis 631, 646–7
 tosylate, as leaving group 422, 433–4, 485, 986–7, 1132, 1223, 1248, 1484
 tosylate, reduction of 806
 tosylation 485, 646–7, 1223–4, 1234, 1242
 tosylhydrazine, in Eschenmoser fragmentation 1008
 tosylhydrazones 1057–8
 TPAP 639
trans 390
 transamination 1386–8, 1399, 1403–4
 transannular interactions, in medium rings 1137
trans-decalin 466
 conformation of 863–4
trans-diaxial opening, of bicyclic lactone epoxide 874
 transesterification 290, 1383
trans-fused bicycles 863–4
 transition metal complexes 1312
 transition state
 compared with intermediate 321
 definition 318
 E1 488–90
 E2 490–1
 for [3,3]-sigmatropic rearrangement 1403
 $\text{S}_{\text{N}}2$ 421–5
 transmetalation 217, 1324–8
 tri(*o*-tolyl)phosphine 1322, 1335
 triacylborate 619
 trialkyl borate, in hydroboration 1280
 trialkylsilyl, use as protecting group 633, 1290
 triazine: 1,3,5-triazine, anomeric effects in 1133
 triazole 11, 1149, 1167–8
 pK_{a} of 1168
 synthesis 1203
 tribromo
 2,4,6-tribromoaniline 558
 2,4,6-tribromophenol 555–6
 tribromoketones, cleavage in base 537
 tribromomethane, pK_{a} of 537
 tributylstannyl 1305
 tributyltin hydride 1040–1, 1046
 reaction with LDA 1307
 trichloroacetaldehyde hydrate, IR spectrum of 144
 trichlorophenol: 2,4,6-trichlorophenol 28, 656
 triethylamine
 as base in Heck reaction 1321–2
 basicity of 1123
 reaction rate with methyl iodide 1123
 triethylene glycol 1457
 trifluoro: 2,2,2-trifluoro-1-(9-anthryl)ethanol (TFAE) 1232
 trifluoroacetic acid 658
 ^{13}C NMR spectrum 369
 trifluoroethanol, as solvent 1016
 trifluoromethyl group, in nucleophilic aromatic substitutions 595
 triflyl group 1321, 1326

- triglyceride 1374–5
 trigonal carbon atoms 107
 triketide, biosynthesis of 1438
 trimethoprim 1198
 trimethyl aluminium, in epoxide opening 892
 trimethylenemethane 1334–5
 trimethylxonium fluoroborate 1258; *see also* Meerwein's salt
 trimethylxonium fluroborate (Me₃O⁺BF₄⁻) 1258
 trimethylphosphite 1267–9
 trimethylsilyl chloride 540, 699, 707–8
 in acyloin reaction, *see* acyloin reaction
 in conjugate additions of cuprates 240
 trimethylsilyl triflate, as a Lewis acid 1289–90, 1300
 trimethylsilyl, as protecting group 1290–1
 trimethylsilylacetylene 1291
 trimetozine, synthesis of 1122
 trioxane
 1,3,5-trioxane 1452
 triphenylmethyl anion 726
 triphenylmethyl radical 1022, 1028
 triphenylmethyl sodium, synthesis and use as base 726
 triphenylmethyl, *see* trityl
 triphenylphosphine oxide (Ph₃P=O), stability of 434
 triphenylphosphine oxide, as by-product of the Wittig reaction 357
 triphenylphosphine
 in Mitsunobu reaction 431
 in S_N2 reactions 442–3
 in Wittig reaction 357, 814
 reaction with α -bromo-esters 536
 reduction of azides by 438, 1242
 use in the Wittig reaction 357
 triplet (codon), set of three nucleotides 1350, 1353
 triplet carbene, reactions 1064–6
 triplet carbene, structure 1060–1
 triplet, in proton NMR 263–6
 trisporol B 1329
 trityl cation in S_N1 418
 trityl perchlorate, as Lewis acid 757
 trityl, as protecting group 1370
 tropinone 1416
 Trost, Barry 1269
 truffles, smell of 4
 tryptophan 1169, 1354
 biosynthesis of 1400
 ways to draw 20, 24
 twist-boat conformation 458, 461
 two group disconnections 783–4, 791–800
 tyrosine 1354, 1448
 biosynthesis of 1400
 in benzyloquinoline alkaloid syntheses 1418–21
 nitration of 646
 ulcer, prevention of 586–8
 umbelliferone, a shikimate product 1404
 umpolung reactivity 798–801, 1048, 1254–6
 unimolecular kinetics 321
 unknown compounds, identification by spectra 72–8
 unsaturated amides, in conjugate addition 757
 unsaturated carbon atoms 32
 unsaturated carbonyl compounds
 as dienophiles 907, 909
 conjugate additions to 228–34, 876, 1011, 1203
 in photochemical [2+2] cycloadditions 928
 reaction with organocopper reagents 240
 regioselectivity of attack by nucleophiles 234–40
 retrosynthetic analysis of 792–3
 unsaturated fat 34, 625
 unsaturated fatty acids 173, 1374, 1430
 unsaturated nitriles, as dienophiles 920
 unsaturated nitriles, conjugate addition to 759, 768)
 unsaturated nitro compounds, *see* nitroalkenes
 unsaturated: γ,δ -unsaturated carbonyl compounds, synthesis by Claisen–Cope 945–6
 uracil 1181, 1347
 urethanes 1458
 uric acid 1175–6
 UV (ultraviolet) and visible spectra 169–71
 UV absorption, use in HPLC 1231
 valence-shell electron pair repulsion theory 83
 valine 1353
 biosynthesis of 1397–8
 use in chiral auxiliary formation 1226–8
 Valium 403
 vanadyl (acac)₂, epoxidation using 877–8
 vancomycin 386, 1378
 vanillin 9
 ¹³C NMR spectrum 363
 Vaska's complex 1316
 venlafaxine 795
 vernolepin 238
 Viagra 10, 65, 179, 1147
 synthesis of 1196–8
 vibrational spectra (infrared) 65
 vicinal coupling, *see* coupling, ³J
 Vilsmeier reaction 1158, 1170
 vinegar 185
 vinyl acetate, radical polymerization of 1468
 vinyl alcohol 531
 vinyl cation, in progesterone synthesis 1446–7
 vinyl group 40–1
 vinyl halides, elimination of 493–4
 vinyl halides, from vinyl silanes 1296
 vinyl phosphine oxide, synthesis of 1302
 vinyl silane 1301–2, 1293–4
 vinyl stannane 1305–6, 1326
 vinyl sulfide 1335
 vinyl triflate 1335
 vinyl
 4-vinyl pyridine, co-polymerization with styrene 1473
 vinylolithium, by halogen–metal exchange 212, 216–17, 225
 vinylogous amides 586
 viprostol 222
 viscose rayon, manufacture of 1472
 visible and UV spectra 169–71
 vitamin B₁₂ 41
 vitamin B₂ 1407
 vitamin C
 ¹H NMR of 249
 as enol 533
 ascorbic acid 6
 reduced and oxidised form 1384
 synthesis of 1368–9
 use in toxin scavenging 584
 use in treatment of scurvy 1359
 Vitamin D, biosynthesis via pericyclic reactions 956, 961
 Vitamin E, as radical trap 1024
 vivalan, structure and synthesis 768
 Vollhardt co-trimerization 1339–41
 VSEPR 83
 vulcanization of rubber 1469–70
 W coupling, in ¹H NMR 270
 Wacker oxidation 1337, 1469
 Wagner–Meerwein rearrangement 980–2
 water
 addition to carbonyl compounds 143
 as an acid and a base 183
 as solvent in Diels–Alder reaction 917
 concentration of 185
 deprotonation by strong bases 189–90
 protonation by strong acids 189–90
 protonation in the gas phase 317
 shape of 83
 wave function 86, 89–90
 wavelength of absorption and colour (table) 170
 wedged bonds 25, 381, 385
 Weinreb amides 300
 Weinreb, S. M. 300
 Wieland–Miescher ketone
 wiggly bonds 385
 Wilkinson's catalyst 1316
 Wittig reaction 357, 650, 701 814–18
 in synthesis 1014, 1223, 1225, 1240, 1253, 1296–7
 stereoselectivity of 815
 using phosphonate esters, *see* Horner–Wadsworth–Emmons reaction
 Wittig reagents, as specific enol equivalents 700
 Wolff rearrangement 1072
 Wolff–Kishner reduction 627, 650
 Woodward–Hoffmann rules 922–3
 in [1,5]-sigmatropic hydrogen shifts 955
 in [2,3]-sigmatropic rearrangements 952
 in [3,3]-sigmatropic rearrangements 946
 in Alder ene reaction 925
 in Diels–Alder reactions 922, 923
 in electrocyclic reactions 957–9
 work-up 142
 xanthate salt 1472
 X-ray structure determination 48–9
 X-rays 47
 xylenes, as solvents 443
 xylitol, synthesis of 1364
 xylose 395, 1364
 yeast, bakers' 1234
 yellow compounds, and UV absorption 171
 ylid 357
 ammomium 1394
 from carbene insertion 1073–4
 in aldol reaction 700
 in Wittig reaction 814
 stabilized and unstabilized 815–17
 sulfonium 1258–61
 thiazolium 1394–8
 yomogi alcohol 1449
 Z-alkenes 487
 by conjugate addition to butadiene 819–20
 by Lindlar reduction of alkyne 818
 from Peterson reaction 812–14
 from Wittig reaction 815–16
 Zantac, synthesis 587–8
 zeolite 345
 Ziegler–Natta polymerization 1463–4, 1317
 zig-zag, drawing structures as 22–3
 Zimmerman–Traxler transition state, for aldol reaction 900
 zinc amalgam, reduction by 574
 zinc chloride, as Lewis acid 575, 1299
 zinc chloride, in asymmetric carbonyl reduction 1266–7
 zinc enolates 706
 zinc
 in cleavage of nitrene cycloaddition adducts 933
 organo- 217
 zinc, reaction with α,α' -dihaloketones 924, 930, 1111–12
 zwiebelane 1273
 zwitterions 183, 602, 1377
 zwitterions, amino acids as 1353