Answers to Problems

Chapter 1

1.1 Ionic: a, e, f. **1.6** Linear. **1.7** (a) Expect zero; (b) expect $NF_3 > NH_3$. **1.8** a, e, f. **1.9** (a) $CH_3OH > CH_3NH_2$; (b) $CH_3SH > CH_3OH$; (c) $H_3O^+ > NH_4^+$. **1.10** (a) H_3O^+; (b) NH_4^+; (c) H_2S; (d) H_2O. **1.11** (a) $CH_3^- > NH_2^- > OH^- > F^-$; (b) $NH_3 > H_2O > HF$; (c) $SH^- > Cl^-$; (d) $F^- > Cl^- > Br^- > I^-$; (e) $OH^- > SH^- > SeH^-$. **1.12** $CH_3NH_2 > CH_3OH > CH_3F$. **1.13** (a) $OH^- > H_2O > H_3O^+$; (b) $NH_2^- > NH_3$; (c) $S^= > HS^- > H_2S$. **1.14** $NH_3 > NF_3$.

1. Ionic: a, d, e, g. **4.** Octahedral. **10.** (a) H_3O^+; (b) HCl; (c) HCl in benzene.

Chapter 2

2.1 (a) −8 kcal; (b) +13 kcal; (c) −102 kcal. **2.2** (a) +46, +16, −24 kcal; (b) +36, +33, −20 kcal; (c) +38, −32, −70 kcal. **2.5** (a) (%C + %H) < 100%; (b) 34.8%. **2.6** (a) 69.6% Cl; (b) 70.4% Cl; (c) 24.85 mg; (d) 26.49 mg; (e) 27.44 mg. **2.7** (a) CH_3; (b) $C_3H_6Cl_2$. **2.8** (a) 79.8; (b) C_6H_6; (c) 78. **2.9** $C_4H_8O_2$.

1. A, 93.9% C, 6.3% H; B, 64.0% C, 4.5% H, 31.4% Cl; C, 62.0% C, 10.3% H, 27.7% O. **2.** (a) 45.9% C, 8.9% H, 45.2% Cl; (b) 52.1% C, 13.1% H, 34.8% O; (c) 54.5% C, 9.1% H, 36.3% O; (d) 41.8% C, 4.7% H, 18.6% O, 16.3% N, 18.6% S; (e) 20.0% C, 6.7% H, 26.6% O, 46.7% N; (f) 55.6% C, 6.2% H, 10.8% O, 27.4% Cl. **3.** (a) CH_2; (b) CH; (c) CH_2O; (d) C_2H_5OCl; (e) $C_3H_{10}N_2$; (f) $C_3H_4O_2Cl_2$. **4.** $C_{20}H_{21}O_4N$. **5.** $C_{14}H_{14}O_3N_3SNa$. **6.** (a) 85.8% C, 14.3% H; (b) CH_2; (c) C_6H_{12}. **7.** $C_2H_4O_2$. **8.** CH_2O. **9.** $C_{16}H_{10}O_2N_2$. **10.** (a) 942; (b) 6. **11.** (a) −130; (b) −44; (c) −26; (d) −2; (e) −13; (f) −8; (h) 1st step +46; 2nd steps +10, −3, 0; 3rd steps −23, −5, −1. **12.** +58, +20, −45; (b) E_{act} of a chain-carrying step ≥20 kcal. **13.** (b) Highly improbable, since E_{act} for reaction with Cl_2 is much smaller.

Chapter 3

3.2 No. **3.3** Van der Waals repulsion between "large" methyls. **3.9** (a) and (b) C_3H_8; (c) $CH_3CH_2CH_2D$ and CH_3CHDCH_3. **3.10** (a) 3; (b) 4; (c) 2; (d) 1. **3.14** (a)

44% 1-Cl, 56% 2-Cl; (b) 64% 1°, 36% 3°; (c) 55% 1°, 45% 3°; (d) 21% 1-Cl, 53% 2-Cl, 26% 3-Cl; (e) 28% 1-Cl-2-Me, 23% 2-Cl-2-Me, 35% 3-Cl-2-Me, 14% 1-Cl-3-Me; (f) 45% 1-Cl-2,2,3-triMe, 25% 3-Cl-2,2,3-triMe, 30% 1-Cl-2,3,3-tri-Me; (g) 33% 1-Cl-2,2,4-triMe, 28% 3-Cl-2,2,4-triMe, 18% 4-Cl-2,2,4-triMe, 22% 1-Cl-2,4,4-triMe. **3.15** (a) 4% 1-Br, 96% 2-Br; (b) 0.6% 1°, 99.4% 3°; (c) 0.3% 1°, 99.7% 3°; (d) 1% 1-Br, 66% 2-Br, 33% 3-Br; (e) 0.3% 1-Br-2-Me, 90% 2-Br-2-Me, 9% 3-Br-2-Me, 0.2% 1-Br-3-Me; (f) 0.6% 1-Br-2,2,3-triMe, 99% 3-Br-2,2,3-triMe, 0.4% 1-Br-2,3,3-triMe; (g) 0.5% 1-Br-2,2,4-triMe, 9% 3-Br-2,2,4-triMe, 90% 4-Br-2,2,4-triMe, 0.3% 1-Br-2,4,4-triMe. **3.16** 40:1. **3.17** 1.15:1. **3.22** 2,2-Dimethylhexane.

5. (e) 6. **6.** One monochloro, three dichloro, four trichloro. **7.** c, b, e, a, d. **10.** (a) 1-, 2-, and 3-chlorohexane; (b) 1-, 2-, 3-, and 4-chloro-2-methylpentane, and 1-chloro-4-methylpentane; (c) 1-, 3- and 4-chloro-2,2,4-trimethylpentane, and 1-chloro-2,4,4-trimethylpentane; (d) 1- and 3-chloro-2,2-dimethylbutane, and 1-chloro-3,3-dimethylbutane. **11.** Order of isomers as in Problem 10: (a) 16, 42, 42%; (b) 21, 17, 26, 26, 10%; (c) 33, 28, 18, 22%; (d) 46, 39, 15%. **16.** (a) 2650 g; (b) 8710 kcal; (c) 170 g. **17.** Carius: mono, 45.3% Cl; di, 62.8% Cl. Mol.wt.: mono, 78.5; di, 113. **19.** (a) Methane gas; 1.49 mg CH_3OH; (b) 59, *n*-propyl or isopropyl alcohol; (c) 3; $CH_2OHCHOHCH_2OH$.

Chapter 4

4.1 2 (mirror images). **4.2** (a) 3; (b) 2; (c) 3 (2 are mirror images); (d) 1. **4.3** (a) −39.0°; (b) −2.4°; (c) −0.6°. **4.4** Use a shorter or longer tube, measure rotation. **4.5** Chiral; b, d, f, g, h. **4.6** (b) 3 of 5 are chiral. **4.7** (d) Mirror images: a, b. **4.9** 3°, 2°, 1°, Me. **4.15** (b) Neither active: one is achiral, other is a racemic modification.

3. Equal but opposite specific rotations; opposite R/S specifications: all other properties the same. **4.** (a) Screw, scissors, spool of thread; (b) glove, shoe, coat sweater, tied scarf; (c) helix, double helix; (d) football (laced), golf club, rifle barrel; (e) hand, foot, ear, nose, yourself. **5.** (a) Sawing; (b) opening milk bottle; (c) throwing a ball. **7.** (a) and (b) 3-Methylhexane and 2,3-dimethylpentane. **8.** a, b, e, k, 2 pairs enantiomers; c, d, h, 1 pair enantiomers + 1 *meso*; f, 4 pairs enantiomers; g, 1 pair enantiomers + 2 *meso*; i, 2 diastereomers; j, 1 pair enantiomers. **11.** Attractive dipole–dipole interaction. **12.** 12% *gauche* (as non-resolvable racemic modification), 88% *anti*.

Chapter 5

5.5 (g) None. **5.7** (g) None. **5.9** (a) $(CH_3)_2C{=}CHCH_3$; (b) $(CH_3)_2C{=}CHCH_3$; (c) $(CH_3)_2C{=}C(CH_3)_2$.

3. b, d, g, h, i, k (3 isomers). **4.** (b) 4 show geometric isomerism. **5.** Differ in all except (h); (1) dipole moment would tell. **11.** Both solutions contain isopropyl cation. **12.** (a) $(CH_3)_2C{=}CHCH_3$ (major product) and $CH_2{=}C(CH_3)C_2H_5$.

Chapter 6

6.1 (c) 1-Butene 649.8, *cis*-2-butene 648.1, *trans*-2-butene 647.1. (d) 1-Pentene 806.9, *cis*-2-pentene 805.3, *trans*-2-pentene 804.3. **6.2** (a) H_3O^+; HBr; (b) HBr; (c) HBr. **6.10** Orlon, $CH_2{=}CH{-}CN$; Saran, $CH_2{=}CCl_2$; Teflon, $CF_2{=}CF_2$. **6.12** React with HCl (minimum E_{act} 26 kcal) or HBr (minimum E_{act} 10 kcal). **6.20** A, alkane; B, 2° alcohol; C, alkyl halide; D, alkene; E, 3° alcohol.

6. 3° radical more stable than 2° radical, forms faster. **10.** (d) Steps (2) and (4) are too difficult with HCl. **16.** 3-Hexene.

Chapter 7

7.2 (a) 4; (c) none. **7.4** c, d, e, g. **7.6** −0.89°. **7.7** (f) R,R:*meso* = 29:71. **7.8** (a) 5 fractions, two inactive, others active; (b) 5, all inactive; (c) 6, all inactive; (d) 2,

both active. **7.9** Rapidly inverting pyramid. **7.11** (a) Racemic; *meso*; (b) *syn*; (c) *anti*. **7.12** Racemic modification, a, c, d; *meso*, b.

1. (a) 3; (b) 5; (c) 7 (5 active); (d) 7 (6 active); (e) 1; (f) 3; (g) 2 (1 active); (h) 2. **3.** A, (S,S); B, (R,S); C, (S,S); D, (S,S); E, (2R,3S)-4-bromo-1,2,3-butanetriol; F, (R,R); G, (R,S). **5.** *Anti*; intermediate chloronium ion.

Chapter 8

8.4 (a) Propane. **8.5** Calcium acetylide. **8.6** H goes to terminal C. **8.7** 1,3-Hexadiene. **8.8** (a) 56–60 kcal. **8.11** (c) Position of equilibrium. **8.15** Head-to-tail polymer of isoprene.

7. No reaction: g through n. **8.** No reaction: g through n. **14.** (a) −42.2 kcal. **15.** (a) Two CH_2 planes perpendicular to each other. **19.** Geometric isomers. **23.** Cyclohexene. **24.** 1,3,5-Hexatriene. **25.** (b) Myrcene, $(CH_3)_2C{=}CHCH_2CH_2C(=CH_2)CH{=}CH_2$. **26.** (a) Dihydromyrcene, $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCH_3$; (b) 1,4-addition. **27.** (c) 2 farnesyl units, head-to-head, form squalene skeleton.

Chapter 9

9.4 *Trans* is resolvable. **9.7** (a) 0 kcal; (b) 2.7 kcal; (c) 1.8 kcal + undetnd. methyl–methyl interaction; (d) 0 kcal; (e) 0 kcal; (f) 3.6 kcal. **9.8** (b) 3.6 kcal. **9.9** (a) *cis* > *trans*; (b) *trans* > *cis*; (c) 1.8 kcal/mole in each case. **9.10** More than: (a) 3.2 kcal; (b) 6.8 kcal; (c) 2.3 kcal. **9.11** Resolvable: b, d. *Meso*: c (e and f do not contain chiral centers). **9.12** (a) e; (b) a; (c) c, f; (d) d; (e) b; (f) none. **9.13** Pairs of enantiomers: a, b, c, d. No *meso* compounds. None are non-resolvable racemic modifications. **9.17** (e) For the same degree of unsaturation, there are two fewer hydrogens for each ring. **9.18** All are C_6H_{12}; no information about ring size. **9.19** 2, 2, 1, none.

4. (a) 4; (b) 6; (c) 7; (d) 9; (e) 5; (f) 2; (g) all-equatorial, **5.** A, *cis*-dimethyl; B, *trans*-dimethyl. **7.** (d) In the *trans*-isomer, both large substituents (the other ring) are equatorial; (e) high energy barrier (E_{act}) between decalins since bond must be broken. **11.** (a), (b), (c) 2 (1 active); (d) 2. **14.** (a) 2; (b) 4; (c) 1; (d) 3; (e) 4. **15.** (a) 1; (b) 2; (c) 1; (d) 3; (e) 3; (f) 5; (g) 4.

16. (b)

17. (c) 

Limonene

p-Menthane

18. (b) 

α-Terpinene

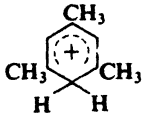
Chapter 10

10.1 (a) +5.6 kcal; (b) −26.8 kcal. **10.2** (a) 824.1 kcal; (b) 35.0 kcal greater. **10.8** *Ortho*, +6°; *meta*, −7°; *para*, +87°. **10.10** 26.0%. **10.11** 22.8%. **10.12** 18.5%. **10.13** 25.9%, 22.9%, 18.6%.

2. (a) 3; (b) 3; (c) 3; (d) 6; (e) 10; (f) 6. **3.** (a) 2, 3, 3, 1, 2; (b) 5, 5, 5, 2, 4 (neglecting stereoisomers; (c) none. **4.** (a) 2; (b) 3; (c) 1; (d) 4; (e) 4; (f) 2; (g) 4; (h) 4; (i) 2; (j) 1; (k) 3; (l) 2. **5.** (a) 1; (b) 1; (c) 2; (d) 1; (e) 2; (f) 3; (g) 2. **6.** Yes. **7.** (c) No, the *ortho* isomer would be chiral, and enantiomers would be possible. **8.** *Ortho*, 104°; *meta*, 63°; *para*, 142°. **9.** (a) For n = 3, 5, 7, 9; n = 5 has poor geometry; (b) $C_9H_9^-$. **11.** (a) $C_6H_6Cl_6$.

Chapter 11

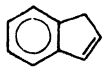
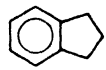
11.3 (d) Carbonium ion mechanism. **11.6** Large size of complex. **11.8** (a) $RC{\equiv}O^+$; (b) ArN_2^+; (c) NO^+. **11.9** (b) D^+. **11.10** (a) 2.05; (b) 1.02 moles HCl:1 mole DCl.

11.11  BF_4^- **11.12** (a) 6.77; (b) yes; (c) no; (d) yes. **11.13** (a) CH_3-$CHCl^+$; (b) $CH_3CH_2^+$; (c) $CH_3CH_2^+$; (e) $^+CH_2CH_2Cl$; (f) CH_3CHCl^+; (h) inductive; (i) resonance.

Chapter 12

12.9 (a) Similar to Fig. 2.3, with E_{act} = 19 kcal, and ΔH = +11 kcal; (b) 8 kcal; (c) steric hindrance to combination.

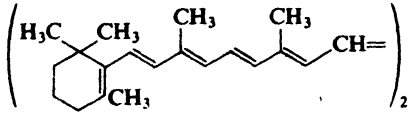
6. $\sim CH_2C_6H_4CH_2C_6H_4CH_2C_6H_4\sim$. **17.** 2-, 3-, 4-, 5-, and 6-phenyldodecane.

26.  Indene  Indane

27. X and Y, racemic and *meso*-$C_6H_5CH(CH_3)$-$CH(CH_3)C_6H_5$; Z, $[C_6H_5C(CH_3)_2]_2$.

Chapter 13

13.1 (a) $(CH_3)_3C^+$; $CH_2{=}CH{-}CH_2^+$; $CH_3CH_2^+$; $CH_2{=}CH^+$.

13.2  β-Carotene **13.3** (a) A, 1,4-pentadiene; B and C, *cis*- and *trans*-1,3-pentadiene. **13.4** (a) 2, 1; (b) 1, 2, 3, 4(1,2-dibromopropane); (c) 3, 2; (d) 2, 4, 3; (e) 3, 1; (f) 2, 4, 3, 5; (g) 2, 4; (h) 3, 1, 5. **13.6** 1 signal. **13.7** Electron release by methyl groups. **13.9** (a) Neopentylbenzene; (b) isobutylene bromide, $(CH_3)_2CBr$-CH_2Br; (c) benzyl alcohol, $C_6H_5CH_2OH$. **13.12** (a) Ethylbenzene; (b) 1,3-dibromopropane; (c) *n*-propyl bromide. **13.16** (a) $CH_3{\cdot}$; (b) $CH_3\dot{C}HCH_3$, $CH_3CH_2\dot{C}HCH_3$; (c) $Ph_3C{\cdot}$. **13.17** Cyclohexane.

1. (a) $CH_2ClCHClCCl_3$; (b) $CH_2ClCCl_2CH_3$; (c) $(CH_3)_2CHCH_2Cl$; (d) $C_6H_5C(CH_3)_3$; (e) $C_6H_5CH_2CH(CH_3)_2$; (f) indane (see answer to Prob. 26, Ch. 12); (g) $C_6H_5CH_2CCl(CH_3)_2$; (h) 1-phenyl-1-methylcyclopropane; (i) $C_6H_5CH_2CH_2CH_2Br$; (j) $CH_2ClCF_2CH_3$. **2.** X, *trans*-1,3-dibromo-*trans*-1,3-dimethylcyclobutane; Y, the *cis,cis*-isomer. **3.** See answer to Prob. 11.11. **4.** 1,2-Dimethylcyclopropene. **5.** See Sec. 29.6. **6.** B,  C, 

7. (a) eeeeee, eecaaa; (b) eeeeea; (c) eeeeaa, eeaeea; (d) eeeeee, no change; eeeaaa, split into two peaks of equal area. **8.** (a) H on C-1; (b) equatorial H downfield from axial H. **9.** 82% equatorial —Br (axial H on C-1). **10.** (a) Isopropylbenzene; (b) isobutylene; (c) phenylacetylene. **11.** (a) Isobutylbenzene; (b) *tert*-butylbenzene; (c) *p*-cymene (*p*-isopropyltoluene). **12.** (a) α-Phenylethyl bromide, $C_6H_5CHBrCH_3$; (b) *tert*-pentylbenzene; (c) *sec*-butyl bromide. **13.** D, α-Methylstyrene, $C_6H_5C(CH_3){=}CH_2$.

Chapter 14

14.4 (a) 1.9%; (b) 16.4%; (c) 66.2%; (d) 95.1%; (e) 99.0%. **14.5** (a) Optical purity: bromide, 60%; alcohol, 40%. (b) 33% racemization, 67% inversion; (c) 17% front-side attack, 83% back-side attack. **14.7** Me, 300; Et 24; *i*-Pr, 1; *t*-Bu 1410. **14.13** *Anti*. **14.14** All —Cl atoms equatorial.

16. A, (1R,2S;1S,2R)-1,2-dichloro-1-phenylpropane; B, (1R,2R;1S,2S)-1,2-dichloro-1-phenylpropane. **20.** 1,1-Dimethylcyclopropane; 1,1-dimethylcyclopropane-2-d. **21.** (b) $(CH_3)_3C^+$, $(CH_3)_2CH^+$. **22.** (a) 1-Methylcyclopropene; (b) cyclopropene.

23. C, 

Chapter 15

15.1 Intramolecular H-bond in *cis*-isomer (see Sec. 24.2). **15.5** (a) Leucine → isopentyl alcohol; isoleucine → active amyl alcohol. **15.8** $C_6H_5CH(OCH_3)CH_3$. **15.10** *syn*-Addition, retention; or *anti*-addition, inversion. **15.12** *syn*-Addition, retention.

7. Intramolecular H-bond between —OH and —G. **8.** Coprostane-3β,6β-diol, by *cis*-hydration at more hindered "top" face of molecule. (b) *cis*-Hydration from beneath gives *alpha* —OH at C–11. **9.** (b) e,e; (c) a,a. **10.** Twist-boat. **12.** *anti*-Elimination.

Chapter 16

16.2 Free radical chlorination of neopentane. **16.9** With 100% inversion. **16.11** $1HIO_4$, a, b, c, e; $4HIO_4$, f, g; no reaction, d. **16.12** A, $(CH_3)_2C(OH)CH_2OH$; B, 1,2-cyclohexanediol; C, 2-hydroxycyclohexanone; D, HOOCCHOHCHOHCOOH; E, $HOCH_2CHOHCHOHCH_2OH$; F, $HOCH_2CHOHCOCHO$; G, $HOCH_2(CHOH)_4CHO$. **16.13** Change concentration. **16.14** (a) 1°, triplet; 2°, doublet; 3°, singlet.

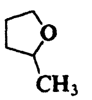
1. (a) Two give iodoform; (c) one gives negative test. **11.** (a) *anti*-Elimination. **13.** B, $HOCH_2CH_2OH$; D, $HOCH_2COOH$; E, OHC(CHOH)CHO; F, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$; J, $CH_2{=}CHCOOH$; M, $HOCH_2C{\equiv}CH$; O, CH_3COCH_3; S, CH_3COONa; U, diacetate of *cis*-1,2-cyclohexanediol; W, triacetate of glycerol; AA, 3-methylbiphenyl, *m*-$CH_3C_6H_4C_6H_5$; GG, active 2,4,6,8-tetramethylnonane; HH, *meso*-2,4,6,8-tetramethylnonane. **15.** (a) Protonated alcohols; (b) and (c) *tert*-butyl cation. **16.** (a) R_3C^+, stabilized by overlap of empty *p* orbital with π clouds of rings. (b) Methyls located unsymmetrically; plane of methyls and trigonal carbon perpendicular to and bisecting ring. **20.** NN, $C_6H_5CH_2CHOHCH_3$; OO, $C_6H_5CH(CH_3)CH_2OH$. **21.** PP, 1,2,2-triphenylethanol; QQ, 1,1,2-triphenylethanol. **22.** (a) *sec*-Butyl alcohol; (b) isobutyl alcohol; (c) ethyl ether. **23.** (a) α-Phenylethyl alcohol; (b) β-phenylethyl alcohol; (c) benzyl methyl ether. **24.** RR, 2-methyl-2-propen-1-ol; SS, isobutyl alcohol. **25.** TT, 3,3-dimethyl-2-butanol. **26.** Geraniol, $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCH_2OH$. **27.** (a) Same as Prob. 26; (b) geometric isomers; (c) in geraniol, —H and $-CH_3$ are *trans*.

Chapter 17

17.7 (a) Configuration of (−)-ether same as (−)-alcohol; (b) maximum rotation is −18.3°. **17.8** (a) Practically complete inversion. **17.10** Trifluoroacetate is weaker base, weaker nucleophile, does not compete with alcohol. **17.18** (f) None. **17.26** 4.

6. Polyisobutylene. **9.** A, 3-bromo-4-methoxytoluene; B, *o*-methoxybenzyl bromide; C, *o*-bromophenetole. **15.** M, $(CH_2{=}CH)_2O$; N, $ClCH_2CHOHCH_2OCH_3$, retention;

O, CH_3OCH_2COOH; P, $CH_3OCH_2CH\text{—}CH_2$ (bridged by O); Q, $CH_2\text{—}CH_2$ / $CH_2\text{—}O$ (ring); R, $C_6H_5CH_2CH_2OH$;

S,  ; T, CH_3CHO; U, racemic *trans*-2-chlorocyclohexanol, inversion;

V, racemic *trans*-methyl-1,2-cyclohexanediol, inversion; W, racemic and *meso*-$HOCH_2CHOHCHOHCH_2OH$; X, racemic 2,3-butanediol; Y, *meso*-2,3-butanediol. **16.** *m*-Methylanisole. **17.** K, anisyl alcohol. **18.** (a) *tert*-Butyl ethyl ether; (b) *n*-propyl ether; (c) isopropyl ether. **19.** L, *p*-methylphenetole; M, benzyl ethyl ether; N, 3-phenyl-1-propanol.

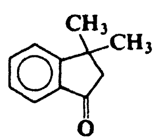
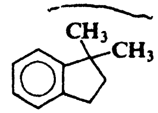
Chapter 18

18.1 91 at 110°, 71 at 156°; association occurs even in vapor phase, decreasing as temperature increases. **18.2** (b) 2-Methyldecanoic acid; (c) 2,2-dimethyldodecanoic acid; (d) ethyl *n*-octylmalonate, *n*-$C_8H_{17}CH(COOEt)_2$. **18.3** (b) 2-Methylbutanoic acid. **18.4** (a) *p*-Bromobenzoic acid; (b) *p*-bromophenylacetic acid. **18.7** (a) F > Cl > Br > I; (b) electron-withdrawing. **18.19** *o*-Chlorobenzoic acid. **18.20** (a) 103; (b) ethoxyacetic acid. **18.21** (a) Two, 83; (b) N.E. = mol.wt./number acidic H per molecule; (c) 70, 57. **18.22** Sodium carbonate.

19. A and B, racemic and *meso*-2,3-dibromobutanoic acid; C, *meso*-HOOCCHOH-CHOHCOOH; F, *cis*-$HOOCCH_2CH\text{—}CHCH_2COOH$ (bridged by CH_2). **20.** G, $HC{\equiv}CMgBr$; J, $OHCCH_2COOH$. **26.** N.E. 165; *o*-nitrobenzoic acid. **27.** Q, *m*-ethylbenzoic acid; U, 3,5-dimethylbenzoic acid. **28.** Tropic acid, $C_6H_5CH(CH_2OH)COOH$; atropic acid, $C_6H_5C({=}CH_2)COOH$; hydratropic acid, $C_6H_5CH(CH_3)COOH$. **29.** (a) $CH_3CHClCOOH$; (b) $ClCH_2COOCH_3$; (c) $BrCH_2COOCH_2CH_3$; (d) $CH_3CH_2CHBrCOOH$; (e) $CH_3CH_2OCH_2COOH$. **30.** (a) Crotonic acid; (b) mandelic acid; (c) *p*-nitrobenzoic acid.

Chapter 19

19.1 $RCH(OH)_2$. **19.4** (a) Acetic, propionic, and *n*-butyric acids; (b) adipic acid. **19.5** (a) 1; (b) 1; (c) 1; (d) 2 (both active); (e) 2; (f) no change. **19.9** (a) Williamson synthesis of ethers; (b) acetals (cyclic). **19.17** Internal "crossed" Cannizzaro reaction.

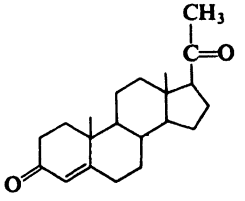
10. B,  C,  D, $PhCH_2CH_2C(OH)(CH_3)_2$.

11. Hemiacetal is oxidized by mechanism of Sec. 19.9. **12.** See Fig. 34.6, Sec. 34.14. **13.** (a) Cyclic ketal. **18.** Hydride transfer from Ph_2CHO^- to excess PhCHO. **20.** Protonated aldehyde is electrophile, double bond is nucleophile. **21.** Chair: in E, all —CCl_3 equatorial; in F, two equatorial, one axial. **23.** (b) *trans*-Isomer: intramolecular H-bonding between —OH and ring oxygen. **26.** $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCHO$, citral *a* (H and CH_3 *trans*), citral *b* (H and CH_3 *cis*); dehydrocitral, $(CH_3)_2C{=}CHCH{=}CHC(CH_3){=}CHCHO$. **27.** Carvotanacetone, 5-isopropyl-2-methyl-2-cyclohexene-1-one. **28.** (a) 2-Butanone; (b) isobutyraldehyde; (c) 2-buten-1-ol. **29.** (a) 2-Pentanone; (b) methyl isopropyl ketone; (c) methyl ethyl ketone. **30.** P, *p*-anisaldehyde; Q, *p*-methoxyacetophenone; R, isobutyrophenone.

Chapter 20

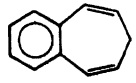
20.3 Maleic acid is *cis* and fumaric acid is *trans*-butenedioic acid, HOOCCH=CHCOOH. **20.4** G, naphthalene. See Fig. 30.2, p. 987. **20.5** Final product is 1-phenylnaphthalene. **20.6** 9,10-Anthraquinone. See Sec. 30.18. **20.7** *o*-(*p*-Toluyl)benzoic acid (p. 993). **20.8** (a) *cis*-Acid: the only one that can form a cyclic anhydride. **20.16** Basicity of leaving group: $Cl^- < RCOO^- < OR^- < NH_2^-$. **20.17** Structure II in Sec. 20.17. **20.21** (a) Formic acid. **20.22** 1-Octadecanol and 1-butanol. **20.27** (b) Nucleophilic addition. **20.28** (a) RCOCl; (b) $RCOO^-NH_4^+$, $RCONH_2$, RCN, amides of low mol.wt. amines; (c) $RCOO^-NH_4^+$; (d) $(RCO)_2O$; (e) RCOOR′. **20.29** (a) 102; (c) 4; (d) no. **20.30** (a) Two, 97; (b) S.E. = mol.wt./number ester groups per molecule; (c) 297.

10. (a) $HOCH_2CH_2CH_2CONH_2$; (b) $HOCH_2CH_2CH_2CH_2OH$; (c) $HOCH_2CH_2CH_2COOEt$. **11.** Second step is S_N2 attack by benzoate anion. **17.** A *meso*; B, racemic. **18.** C, $CO_3^=$; D, $C_2H_5OCONH_2$; M, indene (see Chapter 12, Problem 26); O, *trans*-2-methylcyclohexanol. **19.** Progesterone.



20. AA, 1,3-propanediol; BB, 1,2-propanediol; CC, 2-methoxyethanol; DD, dimethoxymethanol (dimethylacetal of formaldehyde); EE, α-hydroxypropionaldehyde; FF, hydroxyacetone; GG, β-hydroxypropionaldehyde; HH, propionic acid; II, ethyl formate; JJ, methyl acetate; KK, *cis*-1,2-cyclopropanediol; LL,  MM,  **21.** (a) Methyls are *trans* in NN, PP; *cis* in OO, QQ, RR; (b) NN is resolvable. **22.** See p. 1087. **23.** (a) Ethyl acetate; (b) methacrylic acid; (c) phenylacetamide. **24.** (a) *n*-Propyl formate; (b) methyl propionate; (c) ethyl acetate. **25.** SS, benzyl acetate; TT, methyl phenylacetate; UU, hydrocinnamic acid, $PhCH_2CH_2COOH$. **26.** Ethyl anisate. **27.** VV, vinyl acetate. **28.** (a) Ethyl adipate; (b) ethyl ethylphenylmalonate; ethyl acetamidomalonate.

Chapter 21

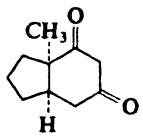
21.1 III, in which the negative charge resides on oxygen, the atom that can best accommodate it. **21.3** Order of decreasing delocalization of the negative charge of the anion. **21.6** (b) Hard to generate *second* negative charge. **21.7** Expect rate of racemization to be twice as fast as exchange. **21.8** (a) Both reactions go through the same slow step (2), formation of the enol. **21.9** (a) HSO_4^-; (b) D_2O. **21.11** Gives a mixture of aldol products. **21.12** Electrophile is protonated aldehyde; nucleophile is enol. **21.14** *Retro* (reverse) aldol condensation. **21.20** (a) γ-Hydrogen will be acidic. **21.23** Elimination → 1- and 2-butene. **21.26** A, $Ph_3P{=}CHOPh$; B, $C_2H_5(CH_3){=}CHOPh$; C, $C_2H_5CH(CH_3)CHO$; a general route to aldehydes. **21.27** D, 1-phenylcyclopentene; E, $Ph_3P{=}CHCH_2CH{=}PPh_3$; F,  **21.30** (a) Intramolecular Claisen condensation leading to cyclization; (b) 2-carbethoxycyclohexanone; (d) ethyl 2,5-dioxocyclohexane-1,4-dicarboxylate. **21.32** (b) 2,4-Hexanedione; (c) 1,3-diphenyl-1,3-propanedione (dibenzoylmethane); (d) 2-(EtOOCCO)cyclohexanone. **21.33** (a) PhCOOEt

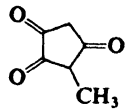
and $PhCH_2COOEt$; (b) EtOOCCOOEt and ethyl glutarate; (c) ethyl phthalate and CH_3COOEt. **21.36** C, citric acid, $(HOOCCH_2)_2C(OH)COOH$.

1. (e) Allylbenzene. **2.** (e) Methylenecyclohexane. **3.** (a) No reaction; (m) $PhCH{=}CHCH{=}CH_2$; (n) $PhCH{=}CHOPh$; (o) $PhCH_2CHO$. **13.** (b) Iodoform test. **15.** Triple aldol cond., followed by crossed Cannizzaro reaction. **18.** Dehydrocitral, $(CH_3)_2C{=}CHCH{=}CHC(CH_3){=}CHCHO$, formed by aldol cond. on γ-carbon of α,β-unsaturated aldehyde.

20. $CH_3COCH_2COOEt + CH_3MgI \rightarrow CH_4\uparrow + (CH_3COCHCOOEt)^-Mg^{++}I^-$.

21. (b) C=C conjugated with second C=O; (c) intramolecular H-bonding.

22. A, 

B,  , a triketone. **23.** (a) *a*, enol $-CH_3$; *b*, keto $-CH_3$; *c*, keto $-CH_2-$; *d*, enol $-CH{=}$; *e*, enol $-OH$. Ratios $a{:}b$ and $2d{:}c$ are equal (5.5 and 5.6) and show 85% enol. (b) All enol; conjugation with ring.

Chapter 22

22.4 $R{:}^-$ undergoes rapid inversion.

6. (a) Putrescine, 1,4-diaminobutane; (b) cadaverine, 1-5-diaminopentane. **9.** Pair of enantiomers: a, c, e, f; one inactive compound, b; inactive *cis-trans* pair, d. **11.** C, $CH_3CH_2CH_2NH_2$. Gabriel synthesis gives 1° amines free from 2° and 3°.

Chapter 23

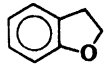
23.2 $(CH_3)_3\overset{+}{N}{:}\overset{-}{B}F_3$. **23.6** 1,3-Pentadiene (from thermal isomerization of 1,4-pentadiene); 2-methyl-1,3-butadiene (isoprene). **23.8** Attack at acyl carbon less hindered than at sulfur; sulfonate better leaving group than carboxylate. **23.9** Free amine is much more reactive. **23.11** (a) *n*-Butyl cation. **23.12** (b) 2-Methyl-2-butene, 2-methyl-1-butene, *tert*-pentyl alcohol. **23.13** Leaving groups $Cl^- > H_2O > OH^-$. **23.18** (a) Electron withdrawal makes diazonium ion more electrophilic. **23.21** (a) 2′-Bromo-4-hydroxy-3,4′-dimethylazobenzene. **23.22** Reduction of azo compound formed by coupling N,N-dimethylaniline with some diazonium salt (usually $^-O_3SC_6H_4N_2^+$ from sulfanilic acid). **23.24** (a) That unknown is 3°; (b) separate, test solubility in acid.

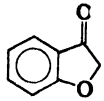
13. See Sec. 32.7. **14.** Poor leaving group (OH^-) converted into a good leaving group (OTs^-). **15.** Reaction of PhN_2^+ is S_N1-like; reaction of p-$O_2NC_6H_4N_2^+$ is S_N2-like. **20.** Choline, $HOCH_2CH_2N(CH_3)_3^+OH^-$; acetylcholine, $CH_3COOCH_2CH_2N(CH_3)_3^+OH^-$. **21.** Novocaine, p-$H_2NC_6H_4COOCH_2CH_2N(C_2H_5)_2$. **22.** I, N-methyl-N-phenyl-*p*-toluamide. **23.** P, 1,3,5,7-cyclooctatetraene. **24.** Pantothenic acid, $HOCH_2C(CH_3)_2CHOHNHCH_2CH_2COOH$. **25.** W, $PhNH_3^+Cl^-$. **26.** (a) *n*-Butylamine; (b) N-methylformamide; (c) *m*-anisidine. **27.** (a) α-Phenylethylamine; (b) β-phenylethylamine; (c) *p*-toluidine. **28.** X, *p*-phenetidine (*p*-ethoxyaniline); Y, N-ethylbenzylamine; Z, Michler's ketone, p,p'-bis(dimethylamino)benzophenone.

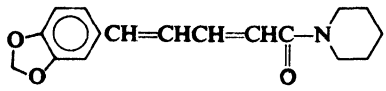
Chapter 24

24.1 Intramolecular H-bond in *o*-isomer unaffected by dilution. **24.4** Benzene, propylene, HF. **24.9** p-Bromophenyl benzoate, p-$BrC_6H_4OOCC_6H_5$. **24.12** (a) The $-SO_3H$ group is displaced by electrophilic reagents, in this case by nitronium ion. **24.17** N.E.

5. No reaction: b, c, f, n. **6.** Reaction only with: c, p, r, s, t, u. **7.** Reaction only

with: c, h, i, j, k, l, n. **13.** (a) Nucleophilic aliphatic substitution; (b) electrophilic aromatic substitution. **16.** Phenacetin, p-$CH_3CONHC_6H_4OC_2H_5$; coumarane, 

3-cumaranone,  carvacrol, 5-isopropyl-2-methylphenol; thymol, 2-isopropyl-5-methylphenol; hexestrol, 3,4-bis(p-hydroxyphenyl)hexane. **17.** Adrenaline, 1-(3,4-dihydroxyphenyl)-2-(N-methylamino)ethanol. **18.** Phellandral, 4-isopropyl-3,4,5,6-tetrahydrobenzaldehyde. **19.** Y, m-cresol. **20.** Z, p-allylanisole; AA, p-propenylanisole. **21.** BB, isopropylsalicylate. **22.** Chavibetol, 2-methoxy-5-allylphenol. **23.** GG, C_6H_5NHOH; HH, p-$HOC_6H_4NH_2$; (d) 2-methyl-4-aminophenol. **23.** Piperine,

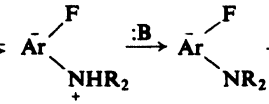
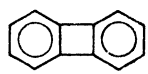


24. Hordinene, p-$HOC_6H_4CH_2CH_2N(CH_3)_2$ or p-$HOC_6H_4CH(CH_3)N(CH_3)_2$ (actually the former). **25.** α-Terpineol, 2-(4-methyl-3-cyclohexenyl)-2-propanol. **26.** Coniferyl alcohol, 3-(4-hydroxy-3-methoxyphenyl)-2-propen-1-ol. **27.** (a) UU, a ketal and lactone. **28.** AAA, piperonal; BBB, vanillin; CCC, eugenol; DDD, thymol; EEE, isoeugenol; FFF, safrole.

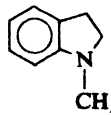
Chapter 25

25.4 (b) Nucleophilic aromatic substitution; (c) electron withdrawal.

1. No reaction: b, c, d, e, f, g, k, l, n, o. **2.** No reaction: h, i, j, k, m, n, o. **5.** (o) $C_6H_6 + HC{\equiv}CMgBr$. Racemic modifications: f, h, k. Optically active: n. **13.** Inductive effect, $o \gg m > p$. **14.** $-N_2^+$ activates molecule toward nucleophilic substitution.

15. $ArF + R_2NH \leftrightharpoons$  $\longrightarrow ArNR_2 + F^-$. **18.** (a) 28, N_2; **44**, CO_2; 76, benzyne, C_6H_4; 152, biphenylene.  (b) Anthranilic acid.

Biphenylene

19. Tetraphenylmethane. **21.**  **23.** $Ar^{\ominus} + Ar'{-}Br \rightleftarrows Ar{-}Br + Ar'^{\ominus}$.

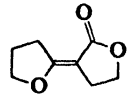
Only carbanions with negative charge *ortho* to halogen are involved.

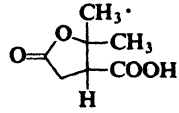
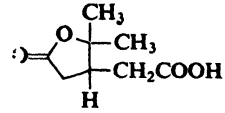
Chapter 26

26.3 Ethyl benzalmalonate, $PhCH{=}C(COOEt)_2$. **26.6** Nucleophilic substitution (S_N2); 1° > 2° ≫ 3° (or none); aryl halides not used. **26.7** (a) $CH_3COCH_2CH_2COOH$, a γ-keto acid; (b) $PhCOCH_2COCH_3$, $CH_3COCH_2CH_2COCH_3$, both diketones. **26.9** A, $EtOOCCOCH(CH_3)COOEt$. **26.11** (a) Charged end loses CO_2. **26.12** Gives relatively stable anion, 2,4,6-$(NO_2)_3C_6H_2{:}^-$ **26.15** Gives relatively stable anion, $PhC{\equiv}C{:}^-$.

26.17, B, ethyl 3-hydroxynonanoate. **26.18** E, Ph  COOEt. **26.22** B, 2-benzalcyclopentanone; F, 3-phenyl-2,2-dimethylpropanal.

3. Cyclopentanone. **4.** C, 1,3-cyclohexanedicarboxylic acid; F, 4,4-cyclohexanedicarboxylic acid; H, succinic acid; J, 1,2-cyclobutanedicarboxylic acid. **5.** K, 1,5-hexadiene; O, 2,5-dimethylcyclopentanecarboxylic acid. **7.** (b) Intramol. aldol cond.; (d) gives 3-methyl-2-cyclohexen-1-one. **11.** (a) *Retro* (reverse) Claisen condensation.

13. S, 1-phenyl-3-nonanone. **16.** V,  ; W, $ClCH_2CH_2CH_2COCH_2CH_2$-CH_2Cl. **17.** Nerolidol, $RCH_2C(CH_3)(OH)CH{=}CH_2$. **18.** Menthone, 2-isopropyl-5-methylcyclohexanone. **19.** Camphoric acid, $HOOCCH_2C(CH_3)(COOH)C(CH_3)_2COOH$.

20. Terebic acid,  Terpenylic acid, 

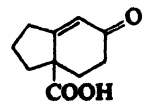
21. Phosphate ion, $H_2PO_4^-$, a better leaving group than OH^-.

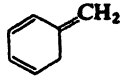
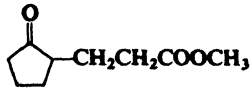
Chapter 27

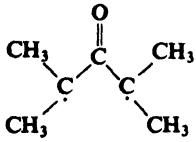
27.2 A, $PhCH_2CH_2CHO$; B, $PhCH_2CH_2CH_2OH$; C, $PhCH{=}CHCH_2OH$. **27.4** (d) ~CH_2CH~ (CN), ~CH_2CH~ (COOMe), ~$CH_2C(CH_3)$~ (COOMe) **27.6** All less stable than I. **27.7** An amide.

Orlon Acryloid Lucite, Plexiglas

27.10 B, $CH_3CH(CH_2COOH)_2$; D, δ-ketocaproic acid; E, $CH_3COCH_2CH_2CH(COOEt)_2$; F, $PhCH(CH_2COPh)_2$; H, $H_2C{=}CHCH(COOH)CH_2CH_2COOH$; I, $EtOOCCH{=}C(COOEt)CH(COOEt)COCH_3$; J, $HOOCCH{=}C(COOH)CH_2COOH$. **27.11** (a) K, $H_2C{=}C(COOEt)_2$; (c) glutaric acid. **27.15** 1,4-Diphenyl-1,3-butadiene + maleic anhydride; 1,3-butadiene + 2-cyclopentenone; 1,3-butadiene (2 moles). **27.16** (a) 3-Ethoxy-1,3-pentadiene + *p*-benzoquinone; (b) 5-methoxy-2-methyl-1,4-benzoquinone + 1,3-butadiene. **27.18** (a) Ease of oxidation; (b) ease of reduction. **27.19** *p*-Nitrosophenol undergoes keto–enol tautomerization to give the mono-oxime.

3. (a) $C_6H_5COCH_2CH(C_6H_5)CH(CN)COOC_2H_5$; (f) $CH_3COCH_2C(CH_3)_2CH(COOEt)COCH_3$; (h) $(EtOOC)_2CHCH_2CH(COOEt)_2$; (j) $O_2NCH_2CH_2CH_2COOMe$; (l) $O_2NC(CH_2CH_2CN)_3$; (m) $Cl_3CCH_2CH_2CN$. **5.** A, $(EtOOC)_2CHCHPhCH_2COCH_2CHPhCH(COOEt)_2$; B, $(EtOOC)_2CHCHPhCH_2COCH{=}CHPh$; C, 4,4-dicarbethoxy-3,5-diphenylcyclohexanone. **6.** (d) 4-Acetylcyclohexene; (g) 5-nitro-4-phenylcyclohexene; (h) 1,4-dihydro-9,10-anthraquinone. **7.** (a) 1,3,5-Hexatriene + maleic anhydride; (b) 1,4-dimethyl-1,3-cyclohexadiene + maleic anhydride; (c) 1,3-butadiene + benzalacetone; (d) 1,3-butadiene + acetylenedicarboxylic acid; (e) 1,3-cyclopentadiene + *p*-benzoquinone; (f) 1,1′-bicyclohexenyl (see Problem 6 (b)) + 1,4-naphthoquinone (see Problem 6 (h)); (g) 1,3-cyclopentadiene + crotonaldehyde; (h) 1,3-cyclohexadiene + methyl vinyl ketone; (i) 1,3-cyclopentadiene (2 moles). **8.** *syn*-Addition. **9.** (a) Racemic modification; (b) *meso*; (c) 2 *meso*; (d) *meso*. **11.** Conjugate addition of OH^-, then *retro*-aldol condensation. **12.** $C_6H_5CH(C_2H_5)CH_2COCH_3$, 4-phenyl-2-hexanone. **14.** N, glyceraldehyde; P, aconitic acid, $HOOCCH{=}C(COOH)CH_2COOH$; R, tricarballylic acid, $HOOCCH(CH_2COOH)_2$; S, "tetracyclone", tetraphenylcyclopentadienone; U, tetraphenylphthalic anhydride; W, pentaphenylbenzene; BB, $(CH_3)_2C(CH_2COOH)_2$; DD, $CH_3CHOHC{\equiv}CCH_3$; EE, $CH_3COC{\equiv}CCH_3$; FF, acetylacetone; GG, $(CH_3)_2C{=}CHCOOH$; JJ, $HOOCCH{=}C(CH_3)CH_2COOH$; MM,  QQ, 

17. IV is correct. **18.** UU,  **19.** 

20. (b)  is intermediate. **21.** Intermediate aryne: dehydrocyclopentadienyl anion.

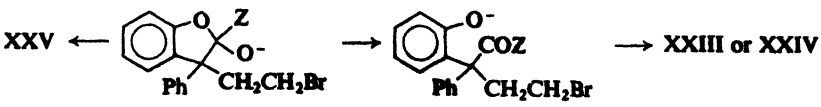
Chapter 28

28.1 (a) Ammonium ion; (b) sulfonium ion; (c) protonated epoxide; (d) epoxide; (e) bromonium ion; (f) benzenonium ion; (g) oxonium ion; (h) ketone (dienone); (i) cyclopropylcarbinyl cation. **28.2** N_2 is leaving group. **28.3** Goes with retention, since only *cis* amino acid can form lactam. **28.4** If reaction (2), Sec. 28.6, occurs, it is not reversible; in view of substituent effect, then, (2) and (3) are concerted. **28.5** (a) *p*-Methoxybenzaldehyde formed by migration of H; *p*-cresol (and formaldehyde), by migration of *p*-tolyl; (b) H migrates somewhat faster than *p*-tolyl. **28.6** H migrates much faster than alkyl. **28.7** Carbonium ion undergoes pinacol-like rearrangement. **28.9** Competition between solvent attack and rearrangement independent of leaving group; hence reaction is S_N1-like, with intermediate carbonium ion. **28.10** Intermediate is carbonium ion, which recombines with water faster than it rearranges. **28.14** Intermediate is an α-lactone. **28.15** Oxygens carry charge by *sharing* electrons. **28.16** Neighboring *trans*-Br and *trans*-I give anchimeric assistance. **28.18** α-Phenylethyl cation, by H-shift.

1. Successive H-shifts occur. **2.** $CH_3COCH_2CH_2CH_2CH_2CH_2OH$, formed by migration of ring carbon. **4.** (a) Analogous to Hofmann rearrangement, with $R'COO^-$ leaving group instead of X^-. **5.** Vinyl migrates predominantly, to give adipaldehyde, most of which undergoes intramolecular aldol to cyclopentene-1-carboxaldehyde. **6.** A, PhCONHPh; B, $PhNH_2$; C, PhCOOH. **8.** (b) *p*-Methoxyphenol and benzophenone; phenol and *p*-chlorobenzophenone. **10.** Two successive H-shifts. **11.** R undergoes 1,2-shift, with retention of configuration, from B to O in intermediate R_3B—OOH, with displacement of OH^-. **13.** Tosylate poorer leaving group than N_2, requires assistance from phenyl. **14.** (a) Neighboring —OH; (b) hydrolyzed. **15.** With *p*-CH_3OPh, nearly all reaction via (symmetrical) bridged ion; with *p*-NO_2Ph, most reaction via open cation; with Ph, about 50:50. **17.** Assistance by π electrons to give following intermediates (in (b), may be nonclassical ion):

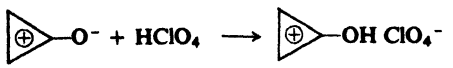
(a) (b) (c)

19. Nucleophilic attack on acyl carbon of XXII by Z to give *tetrahedral intermediate*:



Chapter 29

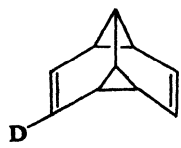
29.1 First, monocation; then aromatic dication with 2 π electrons. **29.2** (a) Aromatic, with 2 π electrons:



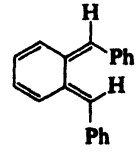
29.3 (a) *Con* closure; I or III → *trans*; II → *cis*; (b) *dis* closure; I or III → *cis*; II → *trans*. **29.4** (a) ψ_1; 2 π electrons; (b) $4n + 2$; *dis* (thermal); (c) $4n$, *con* (thermal); (d) cation, $4n$, *con*; anion, $4n + 2$, *dis*. **29.5** (a) *Dis* opening; (b) *dis* closure; (c) *dis* closure; *con* opening; *dis* closure; (d) *con* opening (4 e); *dis* closure (6 e); (e) *dis* opening of cation (2 e), then combination with water; (f) protonated ketone like a pentadienyl cation, with 4 π electrons; *con* closure. **29.6** Via the cyclobutene, with *con* closures and openings. **29.7** (a) *cis*-3,6-Dimethylcyclohexene; [4 + 2]; (c) Ph's are *cis* to each other (*syn* addition) and *cis* to anhydride bridge (*endo* reaction); (d), (e), (f) all are tetramethylcyclobutanes; in D, one methyl is *trans* to other three. **29.8** (a) Diels-Alder; *retro*-Diels-Alder; (b) *endo* not *exo*. **29.9** (a) [4 + 2], not [6 + 2]; (b) photochemical (intramolecular) *supra,supra* [2 + 2]; (c) *supra,supra* [6 + 4]; (d) *supra,supra* [8 + 2]; (e) *supra,antara* [14 + 2]. **29.10** (a) *supra* [1,5]-H to either face of trigonal carbon; (b) [1,5]-D, not [1,3]-D or [1,7]-D; (c) [1,3]-C (*supra*) with inversion at migrating C.

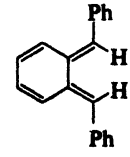
1. (a) Phenols; no; (b) dipolar structure is aromatic with 6 π electrons (compare answer to Problem 29.2); (d) intramolecular H-bond. **2.** (a) *Con* opening (4 e); [1,5]-H *supra*; (b) *con* opening (4 e); *dis* closure (6 e); (c) [1,7]-C *supra* and *dis* closure (4 e); [1,7]-H *supra*; (d) [4 + 4] *supra,supra*; *retro* [4 + 2] *supra,supra* (presumably thermal); (e) allylic cation (2 π electrons) undergoes [4 + 2] cycloaddition, followed by loss of proton; (f) bridge walks around the ring in a series of *supra* [1,5]-C shifts. **3.** (a) A, *trans*-7,8-dialkyl-*cis,cis,cis*-cycloocta-1,3,5-triene; (b) C, $(CH_3)_2C{=}C(CH_3)C(=CH_2)C(CH_3){=}CH_2$; (c) D, 9-methyl-9-ethyl-*trans,cis,cis,cis*-cyclonona-1,3,5,7-tetraene; the *dis* closure takes place with both possible rotations; (d) E, *cis*-bicyclo[5.2.0]nona-8-ene; F, *cis,trans*-cyclonona-1,3-diene; G, *trans*-bicyclo[5.2.0]nona-8-ene. **4.** Symmetry-allowed *con* opening impossible on geometric grounds for bicyclo compound; reaction is probably not concerted. **5.** K, *cis*-bicyclo[4.2.0]octa-2,4-diene; L, Diels-Alder adduct, which undergoes *retro*-Diels-Alder. **6.** (a) [1,2] *supra* sigmatropic shift; π framework is a vinyl radical cation; HOMO is π; predict retention in migrating group; (b) π framework is diene radical cation; HOMO is ψ_2; predict inversion in migrating group.

7. Symmetry-forbidden. **8.**



9. (a) [4 + 2] cycloaddition of benzyne and diene; (b) [2 + 2] thermal cycloaddition symmetry-forbidden; reaction non-concerted, probably via diradicals. **10.**

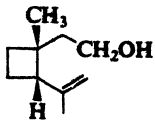




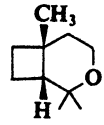
11. (a) *Meso* dibromide gives *cis*-VII (Fig 29.26); racemic dibromide gives *trans*-VII; *cis*-VII contains four non-equivalent olefinic hydrogens; *trans*-VII, two equivalent pairs. **12.** (a) M and N, position isomers, both from *syn exo* addition; O and P, position isomers; (b) *retro*-Diels-Alder. **13.** (a) (Numbering from left to right in Fig. 29.19). Overlap between lobe of C-3 of diene and C-3 of ene, carbons to which bonds are not being formed; (b) lobes

corresponding to those in (a) are of opposite phase.

14. (a)



Y



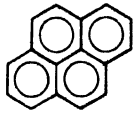
Z

(b) intramolecular solvomercuration possible only for *cis* isomer. **15.** (a) Allowed thermal *con* opening (4 e) would give impossibly strained *cis,cis,trans*-cyclohexa-1,3,5-triene; (b) allowed *antara* [1,3]-H impossible on geometric grounds. **16.** (a) *Con* opening (6 e); [1,7]-H *antara*; (c) *dis* closure. **17.** (a) Via *cis,cis,cis,cis,cis*-cyclodeca-1,3,5,7,9-pentaene; (b) 10 π electrons fits Hückel rule, but evidently not very stable for steric reasons.

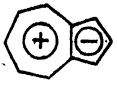
Chapter 30

30.1 2; 10; 14. **30.3** (b) *trans*-Decalin more stable; both large groups (the other ring) on each ring are equatorial; (c) *syn*-addition, rate control; *anti*-addition, equilibrium control. **30.4** Benzylic substitution; elimination of HBr to give conjugated alkenylbenzene; benzylic-allylic substitution; elimination to give aromatic ring. **30.5** (a) Cadalene, 4-isopropyl-1,6-dimethylnaphthalene; (b) cadinene has same carbon skeleton as cadalene, follows isoprene rule. **30.8** (a) Via aryne; (b) direct displacement of —F by amine; (c) both direct displacement and elimination-addition occur. **30.9** 1,2,4-Benzenetricarboxylic acid; 1,2,3-benzenetricarboxylic acid. **30.17** Deactivating acyl group transformed into activating alkyl group. **30.19** Phenanthrene (see Sec. 30.19, and Fig. 30.3, p. 995). **30.20** 23 kcal/mole; 31 kcal/mole. **30.22** (a) Most stable tetrahydro product; (b) reversible sulfonation yields more stable product. **30.24** (a) 1-Nitro-9,10-anthraquinone; (b) 5-nitro-2-methyl-9,10-anthraquinone (with some 8-nitro isomer).

30.29 Pyrene,

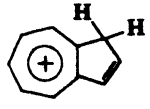


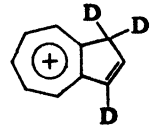
3. 1-, 5-, and 8-nitro-2-methylnaphthalene. **5.** F, phenanthrene. **7.** G, 1,2-benzanthracene; H, chrysene. **8.** α-Naphthol. **9.** (a) Diels-Alder; (c) J, *meso*; K, racemic modification. **10.** (d) β-Tetralone (2-oxo-1,2,3,4-tetrahydronaphthalene). **11.** (a) 1,6-Cyclodecanedione; (b) bicyclic unsaturated ketone, one 7-ring and one 5-ring. **12.** (a)



Azulene

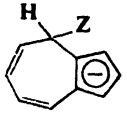
6 π electrons in each ring. (b) From 7-ring toward 5-ring; augmented by C—Cl dipole. **13.** (a)

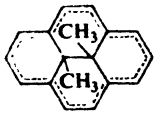




Aromaticity of 7-ring preserved.

(b) Protonation at C-1; azulene upon neutralization. (c) Deuteration via electrophilic substitution at C-1 and C-3, and deuteration again at C-1 comparable to the protonation in (b); expect 1,3-dideuterioazulene upon neutralization; (d) at C-1. **14.** Nucleophilic

substitution in the 7-ring, at C–4;  aromaticity of 5-ring preserved, conjugation in 7-ring. **15.** Eudalene, 7-isopropyl-1-methylnaphthalene. **16.** Y, 2,2′,3,3′,5,5′-hexachloro-6,6′-dihydroxydiphenylmethane; CC, 3,4′-dimethylbiphenyl; FF, compound I, p. 394; HH, tetraphenylmethane; II, 1,3,5-triphenylbenzene. **17.** $—N_2^+$ activates molecule toward nucleophilic aromatic substitution. **18.** (a) JJ, methylene bridge between 9- and 10-positions of phenanthrene; (b) random insertion of methylene into *n*-pentane; (c) three insertion products and one addition product. **19.** KK,  Each ring contains 6 π electrons. **20.** (a) Via an aryne; (b) direct displacement accompanies elimination-addition. Fluoride least reactive toward benzyne formation (p. 838), most reactive toward direct displacement (Sec. 25.12). Piperidine shifts equilibrium (1) toward left, tends to inhibit benzyne formation. **21.** UU is aromatic, with 14 π electrons. Methyl protons are *inside* aromatic ring: see Fig. 13.4, p. 419.

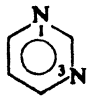


UU

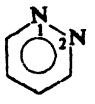
Chapter 31

31.1 B, $[—CH(COOEt)COCH_3]_2$. **31.3** —COOH deactivates ring. **31.4** Two units of starting material linked at the 5-positions through a $—CH_2—$ group. **31.5** Sodium furoate and furfuryl alcohol (Cannizzaro reaction). **31.10** Hygrine, 2-acetonyl-N-methylpyrrolidine; hygrinic acid, N-methyl-2-pyrrolidinecarboxylic acid. **31.11** Orientation ("*para*") controlled by activativg $—NH_2$ group. **31.13** Amine > imine > nitrile. **31.18** Piperidine, a 2° amine, would itself be acylated. **31.23** (a) 8-Nitroquinoline; (b) 8-hydroxyquinoline (8-quinolinol); (c) 4,5-diazaphenanthrene; (d) 1,5-diazaphenanthrene; (e) 6-methylquinoline. **31.28** Electrophilic aromatic substitution or acid-catalyzed nucleophilic carbonyl addition, depending upon viewpoint.

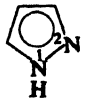
1. No reaction: c, h, i, j. **3.** Pyrroline has double bond between C–3 and C–4. **4.** C, acetonylacetone. **5.** Porphin, with same ring skeleton as in hemin, page 1152. **6.** D, 2–COOH; E, 3–COOH; F, 4–COOH. **7.** (a) 5- or 7-methylquinoline; (b) G, 7-methylquinoline. **9.** (e) Perkin reaction; (g) Reimer-Tiemann reaction. **10.** (See below for parent ring systems.) I, 2,4,6-trihydroxy-1,3-diazine; K, 3,6-dimethyl-1,2-diazine; L, 3,5-dimethyl-1,2-diazole; M, 2,3-dimethyl-1,4-diazanaphthalene; N, 1,3-dioxolan-2-one (ethylene carbonate); P, 3-indolol; R, 2,5-dimethyl-1,4-diazine; S, 1,3-diazolid-2-one (2-imidazolidone, ethyleneurea); T, 4,5-benzo-2-methyl-1,3-diazole (2-methylbenzimidazole); W, 2,4-dihydroxyquinoline; BB, 1,2-diazolid-3-one (3-pyrazolidone); CC, 4,5-diazaphenanthrene; GG, two indole units fused 2,3 to 3′,2′; HH, N-methyl-1,2,3,4-tetrahydroquinoline; II, 2-phenylbenzoxazole; JJ, the benzene ring of II completely hydrogenated.



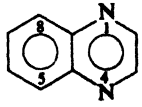
1,3-Diazine (Pyrimidine)



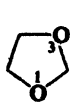
1,2-Diazine (Pyridazine)



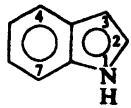
1,2-Diazole (Pyrazole)



1,4-Diazanaphthalene (Quinoxaline)

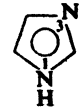


1,3-Dioxolane

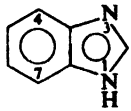


Indole
(Benzopyrrole)

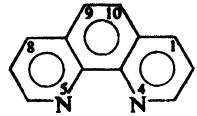
1,4-Diazine
(Pyrazine)



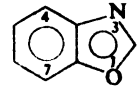
1,3-Diazole
(Imidazole)



Benzo-1,3-diazole
(Benzimidazole)



4,5-Diazaphenanthrene
(4,5-Phenanthroline)



Benzoxazole

11. LL, 3,4-$(CH_3O)_2C_6H_3CH_2CH_2NH_2$; NN, 3,4-$(CH_3O)_2C_6H_3CH_2COCl$; OO, amide; PP, a 1-substituted-7,8-dimethoxy-3,4-dihydroisoquinoline; papaverine, the corresponding substituted isoquinoline. **12.** VV, $(C_2H_5)_2NCH_2CH_2CH_2CHBrCH_3$; XX, 8-amino-6-methoxyquinoline; Plasmochin, 8-amino group of XX alkylated by VV. **13.** Nicotine, 2-(3-pyridyl)-N-methylpyrrolidine. **14.** DDD, *o*-hydroxybenzalacetophenone; (c) oxygen contributes a pair of electrons to complete an aromatic sextet. **15.** Tropinic acid, 2-COOH-5-CH_2COOH-N-methylpyrrolidine. **17.** Pseudotropine has equatorial —OH, is more stable. **18.** (a) Guvacine, 1,2,5,6-tetrahydro-3-pyridinecarboxylic acid; arecaidine, N-methylguvacine; (b) nicotinic acid. **19.** UUU, one enantiomer of ethyl-*n*-propyl-*n*-butyl-*n*-hexylmethane; chirality does not necessarily lead to measurable optical activity (see Sec. 4.13). **20.** Aliphatic NH_2 > "pyridine" N > "pyrrole" NH. **21.** Dipolar ion loses CO_2.

Chapter 32

32.1 (a) Amide; see Sec. 32.7; (b) amide; 6-aminohexanoic acid; (c) ether; ethylene oxide; (d) chloroalkene; 2-chloro-1,3-butadiene; (e) chloroalkane; 1,1-dichloroethene. **32.2** (a) Amide; (b) ester; (c) acetal; (d) acetal. **32.3** 1,2- and 1,4-addition. **32.4** Combination. **32.6** Polymer is transfer agent. **32.9** (a) Chain-transfer.

2. Dehydration, polymerization. **4.** Nucleophilic carbonyl addition. **5.** Hydrolysis gives amine, alcohol, and carbon dioxide. **9.** ~$OCH_2CH_2COOCH_2CH_2COO$~; chain-reaction. **10.** Growing anion abstracts proton from solvent. **11.** *Some* head-to-head polymerization. **12.** (a) ~$NHCH_2(CH_2)_4CO$~; (b) chain-reaction. **13.** Cyclohexanone. **15.** Compounds are ionic, due to stability of benzylic anions. **16.** A, *meso*, resembles isotactic; B, racemic, resembles syndiotactic. **18.** Monomer acts as chain-transfer agent. **19.** Cross-linking by oxygen between allylic positions. **21.** F, syndiotactic; G, isotactic.

Chapter 33

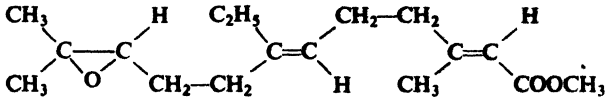
33.1 Decarboxylation. Fatty acids could be precursors of petroleum hydrocarbons. **33.2** (a) Isoprene unit. (b) Likely that petroleum comes from green plants. **33.4** Alkoxide is poor leaving group. **33.5** Preserves semiliquidity of membranes in colder part of body.

1. Nervonic acid, *cis*- or *trans*-$CH_3(CH_2)_7CH{=}CH(CH_2)_{13}COOH$ (actually, *trans*). **2.** Transesterification to more random distribution of acyl groups among glyceride molecules. **3.** Hybrid (allylic) free radical is intermediate. **4.** Spermaceti, *n*-hexadecyl *n*-hexadecanoate. **6.** Cleavage of monoanion as dipolar ion (or with simultaneous trans-

fer of proton) easiest because of (a) protonation of alkoxy group and (b) double negative charge on other oxygens:

$$R-\overset{+}{\underset{H}{O}}-PO_3^{--} \xrightarrow{H_2O} ROH + H_2PO_4^-$$

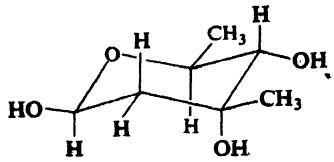
7. Vaccenic acid, *cis*-$CH_3(CH_2)_5CH{=}CH(CH_2)_9COOH$. **8.** Corynomycolenic acid, *cis*-*n*-$C_{13}H_{27}CH_2CH(COOH)CHOH(CH_2)_7CH{=}CHC_6H_{13}$-*n*. **9.** Tuberculostearic acid, 10-methyloctadecanoic acid. **10.** C_{27}-phthienoic acid, $CH_3(CH_2)_7CH(CH_3)CH_2CH(CH_3)CH{=}C(CH_3)COOH$. **11.** CC, octadecanoic acid; DD, 2-methyloctadecanoic acid. **12.** Juvenile hormone,



Chapter 34

34.3 (a) 3; (b) 8. **34.4** Glucose + $5HIO_4 \rightarrow 5HCOOH + HCHO$. **34.5** A, gluconic acid; B, glucitol; C, glucaric acid; D, glucuronic acid. **34.6** Fructose. Aldose → osazone → osone → 2-ketose. **34.7** Identical in configuration at C-3, C-4, and C-5. **34.8** Alditol. **34.9** (a) 2 tetroses; (b) 4 pentoses, 8 hexoses (see Problem 34.2); (c) D; (d) L. **34.11** I, (+)-allose; II, (+)-altrose; VI, (−)-idose; VII, (+)-galactose; VIII, (+)-talose. **34.15** (a) R; (b) R; (c) S; (d) R. **34.16** (S)-(+)-2-butanol. **34.17** (a) S,S-; (b) R,R-; (c) R,S-. **34.18** (b) 1:3; (c) the isomer favored in the L-series will be the mirror image of the isomer favored in the D-series. **34.19** L-(+)-Gulose. **34.20** (a) 36.2% α, 63.8% β. **34.23** (a) CH_3OH, HOOCCHO, and D-glyceric acid. **34.24** HCHO instead of HCOOH. **34.25** (a) Six-membered ring; (b) HCOOH, OHC—CHO, and $HOCH_2CHO$. **34.26** (a) Six-membered ring; (b) enantiomer. **34.27** (a) Five-membered ring; (b) optically active, L-family; (c) enantiomer.

4. E and E′, allitol and galactitol; F, glucitol (or gulitol); H, glucitol (or gulitol); I and I′, allitol and galactitol; N, ribitol; O, arabitol (or lyxitol). **5.** (a) P, glycoside of glucuronic acid; (d) $HOCH_2(CHOH)_3$-COCOOH. **6.** Rate-determining step involves OH^- before reaction with Cu^{++}: probably abstraction of proton leading to formation of enediol. **7.** (a) 5 carbons, five-ring; (b) C-1 and C-4; (c) Q, methyl α-D-arabinofuranoside. **8.** Salicin, *o*-(hydroxymethyl)phenyl β-D-glucopyranoside. **9.** Bio-inonose, the pentahydroxycyclohexanone in which successive —OH groups are *trans* to each other. **11.** (a) T, D-ribose; U, D-arabinose; (b) 3-phosphate. **12.** Z and AA are ketals: Z, furanose with acetone bridging C-1 to C-2 and C-5 to C-6; AA, pyranose, with acetone bridging C-1 to C-2. **14.** S_N1-type, with separation of relatively stable oxonium ion (see Sec. 19.15). **15.** (a) Proton on C-1 most deshielded by two oxygens. (b) JJ, β-anomer; KK, α-anomer; (c) LL, β-anomer; MM, α-anomer; (d) NN, α-mannose; OO, β-mannose; PP, β-glucose; QQ, α-glucose. **16.** L-(−)-Mycarose,



(e) α-glycoside; (f) β-anomer. **17.** (a) Anomeric effect (Sec. 34.20) stabilizes the α-anomer; (b) anomeric effect stabilizes diaxial chlorines. **18.** (a) On steric grounds, neither; anomeric effect would favor axial OAc on C-1. (b) Tells nothing: in either conformation two OAc are equatorial, two are axial. (c) The *e*:*a* peak area ratio would be 2:1 if C-1 OAc were all axial, 1:1 if half axial, 0.5:1 if none axial. Ratio of 1.46:1.00 shows C-1 OAc is axial in 79% of molecules.

Chapter 35

35.4 D-Glucose and D-erythrose; indicates attachment to other ring is at C–4. **35.8** D-Galactose and D-erythrose. **35.10** $C_{12}H_{20}O_{10}$, non-reducing. **35.11** Sucrose is an α-glucoside. **35.13** 1 (0.0025%); 3 (0.0075%); 9 (0.022%). **35.14** (a) A large group in an axial position. **35.15** (a) 3 molecules of HCOOH per molecule of amylose; (b) moles HCOOH/3 = moles amylose; wt. amylose/moles amylose = mol.wt. amylose; mol.wt. amylose/wt. (of 162) per glucose unit = glucose units per molecule of amylose; (c) 474. **35.16** A poly-α-D-glucopyranoside; chain-forming unit, attachment at C–1 and C–6; chain-linking unit, attachment at C–1, C–3, and C–6; chain-terminating unit, attachment at C–1. **35.17** A poly-β-D-xylopyranoside; chain-forming unit, attachment at C–1 and C–4; chain-linking unit, attachment at C–1, C–3, and C–4; chain-terminating unit, attachment at C–1.

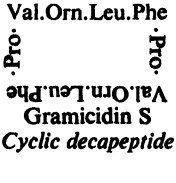
1. Gentiobiose, 6-O-(β-D-glucopyranosyl)-D-glucopyranose. **2.** (a) Trehalose, α-D-glucopyranosyl α-D-glucopyranoside; (b) isotrehalose, α-D-glucopyranosyl β-D-glucopyranoside; neotrehalose, β-D-glucopyranosyl β-D-glucopyranoside. **4.** Raffinose, α-D-galactosyl unit attached at C–6 of glucose unit of sucrose; melibiose, 6-O-(α-D-galactopyranosyl)-D-glucopyranose. **5.** (a) Melezitose, α-D-glucopyranosyl unit attached at C–3 of fructose unit of sucrose; turanose, 3-O-(α-D-glucopyranosyl)-D-fructofuranose. **6.** Panose, α-D-glucopyranosyl unit attached at C–6 of non-reducing moiety of maltose; isomaltose, 6-O-(α-D-glucopyranosyl)-D-glucopyranose. **7.** D-Glucuronic acid; (c) D-xylose. **12.** I, D-$CH_2OHCHOHCHOHCOOH$; J, HOOCCHO. **13.** (a) 3 molecules of HCOOH per molecule of cellulose; (c) 1390 glucose units.

Chapter 36

36.1 $—NH_2 > —COO^-$; proton goes to $—NH_2$ to form $^+H_3NCHRCOO^-$. **36.2** $—COOH > —NH_3^+$; —COOH gives up proton to form $^+H_3NCHRCOO^-$. **36.5** (a) On acid side; (b) on basic side; (c) more acidic and more basic than for glycine. **36.8** 4 isomers. **36.9** CyS–SCy, Hylys, Hypro, Ileu. **36.11** Intermediate for Ala is $CH_3CH(NH_2)CN$. **36.12** A, $(CH_3)_2CHCH(COOEt)COCOOEt$; B, $(CH_3)_2CHCH_2COCOOEt$. **36.15** (a) 22.4 cc; (b) 44.8 cc; (c) no N_2. **36.16** Minimum mol.wt. = 114; could be valine. **36.19** Salmine, $AlaArg_{50}Gly_4IleuPro_6Ser_7Val_3$. **36.20** Same as empirical formula (preceding problem). **36.21** 70300. **36.22** (a) 16700; (b) 4. **36.23** A sulfonamide, which is more resistant to hydrolysis than carboxamides (see Sec. 23.6). **36.24** (a) Phe.Val.Asp.Glu.His; (b) His.Leu.CySH.Gly.Ser.His.Leu; (c) Tyr.Leu.Val.CySH.Gly.Glu.Arg.Gly.Phe.Phe. **36.25** (a) Cbz.Gly.Ala, $SOCl_2$; Phe; H_2, Pd. (b) $PhCH_2OCOCl$, Ala; $SOCl_2$; Gly; H_2, Pd. **36.26** In A, polystyrene has $—CH_2Cl$ groups attached to rings; in B, $—CH_2Br$ groups.

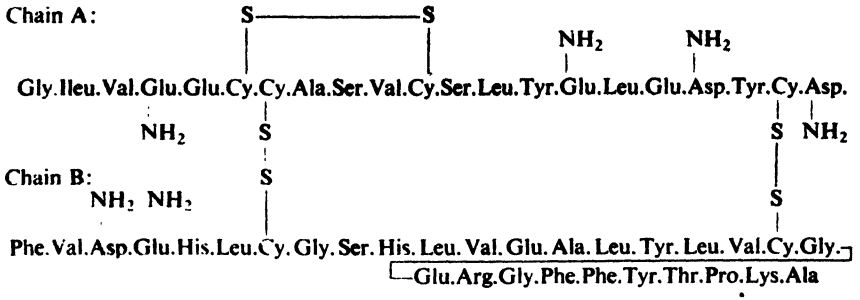
2. D, $HOCH_2CH_2CH_2CH(NH_3^+)COO^-$. **3.** (a) F, $CH_3CONHC(COOC_2H_5)_2CH_2CH_2CHO$; J, $CH_3CONHC(COOC_2H_5)_2CH_2(CH_2)_2CH_2NHCOCH_3$. (b) K, $NCCH_2CH_2CH(COOC_2H_5)_2$; O, $^+H_3NCH_2(CH_2)_2CHClCOO^-$. **4.** (a) Diketopiperazine, cyclic diamide; (b) unsaturated acid; (c) γ-lactam, 5-ring amide; (d) δ-lactam, 6-ring amide. **6.** (a) Betaine, $^+(CH_3)_3NCH_2COO^-$; (b) trigonelline, N-methylpyridinium-3-carboxylate (dipolar ion). **7.** Polarity of solvent lowered; hydrophobic parts of organic molecules come out of their huddle. **9.** Minimum mol.wt. = 13000; minimum of one Fe atom and six S atoms. **10.** (a) Approx. 32 $—CONH_2$ groups; (b) 395–398 peptide links plus $—CONH_2$ groups; (c) 367–370 amino acid residues.

11.



Gramicidin S
Cyclic decapeptide

12. Beef insulin:



(g) $DNP.NH(CH_2)_4CH(NH_3^+)COO^-$ from ϵ-amino group of Lys. If Lys had been terminal, would have gotten a double DNP derivative of it, and no DNP.Phe.

Chapter 37

1. CO_2 becomes the —COOH of malonyl–CoA in reaction (1), Sec. 37.6; this is the carbon lost in reaction 4. **2.** Slow (rate-determining) formation of a tetrahedral intermediate (see Sec. 20.17) followed by fast loss of OR or SR. **3.** (b) Guanine and cytosine, 3 H-bonds per pair; adenine and thymine, only 2. **4.** (a) Aldol-like condensation between ester and keto group of oxaloacetate; (b) aldol-like condensation between ester and keto group of acetoacetyl–CoA; reduction of ester to 1° alcohol by hydride transfer. **5.** A, $C_2H_5OOCCH_2CH_2NHCONH_2$; B, a dihydroxydihydro-1,3-diazine (see p. 1206 for parent diazine ring system); C, a dihydroxydihydro-5-bromo-1,3-diazine; E, 2-chloro-4-amino-1,3-diazine; F, 4-chloro-2-amino-1,3-diazine. **6.** Biological oxidation of fatty acids removes 2 carbons at a time, starting at carboxyl end: "*beta*-oxidation." **7.** *Retro* (reverse) aldol condensation. **8.** (a) Direct transfer of a hydride ion from C–1 of ethanol to C–4 of pyridine ring of NAD^+. There are now two hydrogens on C–4 (see Sec. 36.15) and, if one of them is D, C–4 is chiral center. (Because of chirality of rest of NADD molecule, these are *diastereotopic* hydrogens; see Sec. 13.7.) Of the two hydrogens on C-4, *only* the one originally received from ethanol in part (a) is transferred back to aldehyde, indicating transfer in both directions is stereospecific. (c) Transfer to D-glucose of only the *other* hydrogen on C–4, indicating stereospecificity opposite to that in (b). (d) Chemical reduction is not stereospecific, and gives mixture of diastereomeric NADD molecules. (e) X and Y are the two enantiomers of CH_3CHDOH. Transfer is stereospecific not only with regard to which hydrogen on C–4 is transferred, but with regard to which face of acetaldehyde it becomes attached to. If D becomes attached to that face, X is formed; if H becomes attached, Y is formed.