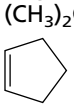
APPENDIX 1

PHYSICAL PROPERTIES

TABLE A Selected Physical Properties of Representative Hydrocarbons

Compound name	Molecular formula	Structural formula	Melting point, °C	Boiling point, °C (1 atm)
Alkanes				
Methane	CH_4	CH_4	−182.5	−160
Ethane	C_2H_6	CH_3CH_3	−183.6	−88.7
Propane	C_3H_8	$CH_3CH_2CH_3$	−187.6	−42.2
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	−139.0	−0.4
2-Methylpropane	C_4H_{10}	$(CH_3)_3CH$	−160.9	−10.2
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	−129.9	36.0
2-Methylbutane	C_5H_{12}	$(CH_3)_2CHCH_2CH_3$	−160.5	27.9
2,2-Dimethylpropane	C_5H_{12}	$(CH_3)_4C$	−16.6	9.6
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	−94.5	68.8
Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	−90.6	98.4
Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	−56.9	125.6
Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$	−53.6	150.7
Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	−29.7	174.0
Dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$	−9.7	216.2
Pentadecane	$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$	10.0	272.7
Icosane	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$	36.7	205 (15 mm)
Hectane	$C_{100}H_{202}$	$CH_3(CH_2)_{98}CH_3$	115.1	
Cycloalkanes				
Cyclopropane	C_3H_6		−127.0	−32.9
Cyclobutane	C_4H_8			13.0
Cyclopentane	C_5H_{10}		−94.0	49.5
Cyclohexane	C_6H_{12}		6.5	80.8
Cycloheptane	C_7H_{14}		−13.0	119.0
Cyclooctane	C_8H_{16}		13.5	149.0
Cyclononane	C_9H_{18}			171
Cyclodecane	$C_{10}H_{20}$		9.6	201
Cyclopentadecane	$C_{15}H_{30}$		60.5	112.5 (1 mm)
Alkenes and cycloalkenes				
Ethene (ethylene)	C_2H_4	$CH_2{=}CH_2$	−169.1	−103.7
Propene	C_3H_6	$CH_3CH{=}CH_2$	−185.0	−47.6
1-Butene	C_4H_8	$CH_3CH_2CH{=}CH_2$	−185	−6.1
2-Methylpropene	C_4H_8	$(CH_3)_2C{=}CH_2$	−140	− 6.6
Cyclopentene	C_5H_8		−98.3	44.1

(Continued)

TABLE A Selected Physical Properties of Representative Hydrocarbons *(Continued)*

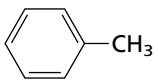
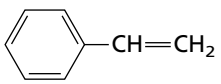
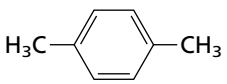
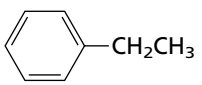
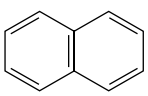
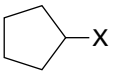
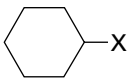
Compound name	Molecular formula	Structural formula	Melting point, °C	Boiling point, °C (1 atm)
1-Pentene	C_5H_{10}	$CH_3CH_2CH_2CH{=}CH_2$	−138.0	30.2
2-Methyl-2-butene	C_5H_{10}	$(CH_3)_2C{=}CHCH_3$	−134.1	38.4
Cyclohexene	C_6H_{10}		−104.0	83.1
1-Hexene	C_6H_{12}	$CH_3CH_2CH_2CH_2CH{=}CH_2$	−138.0	63.5
2,3-Dimethyl-2-butene	C_6H_{12}	$(CH_3)_2C{=}C(CH_3)_2$	−74.6	73.5
1-Heptene	C_7H_{14}	$CH_3(CH_2)_4CH{=}CH_2$	−119.7	94.9
1-Octene	C_8H_{16}	$CH_3(CH_2)_5CH{=}CH_2$	−104	119.2
1-Decene	$C_{10}H_{20}$	$CH_3(CH_2)_7CH{=}CH_2$	−80.0	172.0
Alkynes				
Ethyne (acetylene)	C_2H_2	$HC{\equiv}CH$	−81.8	−84.0
Propyne	C_3H_4	$CH_3C{\equiv}CH$	−101.5	− 23.2
1-Butyne	C_4H_6	$CH_3CH_2C{\equiv}CH$	−125.9	8.1
2-Butyne	C_4H_6	$CH_3C{\equiv}CCH_3$	−32.3	27.0
1-Hexyne	C_6H_{10}	$CH_3(CH_2)_3C{\equiv}CH$	−132.4	71.4
3,3-Dimethyl-1-butyne	C_6H_{10}	$(CH_3)_3CC{\equiv}CH$	−78.2	37.7
1-Octyne	C_8H_{14}	$CH_3(CH_2)_5C{\equiv}CH$	−79.6	126.2
1-Nonyne	C_9H_{16}	$CH_3(CH_2)_6C{\equiv}CH$	−36.0	160.6
1-Decyne	$C_{10}H_{18}$	$CH_3(CH_2)_7C{\equiv}CH$	−40.0	182.2
Arenes				
Benzene	C_6H_6		5.5	80.1
Toluene	C_7H_8		−95	110.6
Styrene	C_8H_8		−33	145
p-Xylene	C_8H_{10}		−13	138
Ethylbenzene	C_8H_{10}		−94	136.2
Naphthalene	$C_{10}H_8$		80.3	218
Diphenylmethane	$C_{13}H_{12}$	$(C_6H_5)_2CH_2$	26	261
Triphenylmethane	$C_{19}H_{16}$	$(C_6H_5)_3CH$	94	

TABLE B Selected Physical Properties of Representative Organic Halogen Compounds

Alkyl Halides

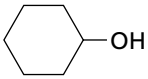
Compound name	Structural formula	Boiling point, °C (1 atm)				Density, g/mL (20°C)		
		Fluoride	Chloride	Bromide	Iodide	Chloride	Bromide	Iodide
Halomethane	CH_3X	−78	−24	3	42			2.279
Haloethane	CH_3CH_2X	−32	12	38	72	0.903	1.460	1.933
1-Halopropane	$CH_3CH_2CH_2X$	−3	47	71	103	0.890	1.353	1.739
2-Halopropane	$(CH_3)_2CHX$	−11	35	59	90	0.859	1.310	1.714
1-Halobutane	$CH_3CH_2CH_2CH_2X$		78	102	130	0.887	1.276	1.615
2-Halobutane	$CH_3CHCH_2CH_3$ (X on CH)		68	91	120	0.873	1.261	1.597
1-Halo-2-methylpropane	$(CH_3)_2CHCH_2X$	16	68	91	121	0.878	1.264	1.603
2-Halo-2-methylpropane	$(CH_3)_3CX$		51	73	99	0.847	1.220	1.570
1-Halopentane	$CH_3(CH_2)_3CH_2X$	65	108	129	157	0.884	1.216	1.516
1-Halohexane	$CH_3(CH_2)_4CH_2X$	92	134	155	180	0.879	1.175	1.439
1-Halooctane	$CH_3(CH_2)_6CH_2X$	143	183	202	226	0.892	1.118	1.336
Halocyclopentane			114	138	166	1.005	1.388	1.694
Halocyclohexane			142	167	192	0.977	1.324	1.626

Aryl Halides

	Halogen substituent (X)*							
	Fluorine		Chlorine		Bromine		Iodine	
Compound	mp	bp	mp	bp	mp	bp	mp	bp
C_6H_5X	−41	85	−45	132	−31	156	−31	188
o-$C_6H_4X_2$	−34	91	−17	180	7	225	27	286
m-$C_6H_4X_2$	−59	83	−25	173	−7	218	35	285
p-$C_6H_4X_2$	−13	89	53	174	87	218	129	285
1,3,5-$C_6H_3X_3$	−5	76	63	208	121	271	184	
C_6X_6	5	80	230	322	327		350	

*All boiling points and melting points cited are in degrees Celsius.

TABLE C Selected Physical Properties of Representative Alcohols, Ethers, and Phenols

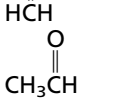
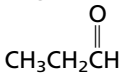
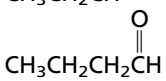
Compound name	Structural formula	Melting point, °C	Boiling point, °C (1 atm)	Solubility, g/100 mL H_2O
Alcohols				
Methanol	CH_3OH	−94	65	∞
Ethanol	CH_3CH_2OH	−117	78	∞
1-Propanol	$CH_3CH_2CH_2OH$	−127	97	∞
2-Propanol	$(CH_3)_2CHOH$	−90	82	∞
1-Butanol	$CH_3CH_2CH_2CH_2OH$	−90	117	9
2-Butanol	$CH_3CHCH_2CH_3$ (OH)	−115	100	26
2-Methyl-1-propanol	$(CH_3)_2CHCH_2OH$	−108	108	10
2-Methyl-2-propanol	$(CH_3)_3COH$	26	83	∞
1-Pentanol	$CH_3(CH_2)_3CH_2OH$	−79	138	
1-Hexanol	$CH_3(CH_2)_4CH_2OH$	−52	157	0.6
1-Dodecanol	$CH_3(CH_2)_{10}CH_2OH$	26	259	Insoluble
Cyclohexanol		25	161	3.6
Ethers				
Dimethyl ether	CH_3OCH_3	−138.5	−24	Very soluble
Diethyl ether	$CH_3CH_2OCH_2CH_3$	−116.3	34.6	7.5
Dipropyl ether	$CH_3CH_2CH_2OCH_2CH_2CH_3$	−122	90.1	Slight
Diisopropyl ether	$(CH_3)_2CHOCH(CH_3)_2$	−60	68.5	0.2
1,2-Dimethoxyethane	$CH_3OCH_2CH_2OCH_3$		83	∞
Diethylene glycol dimethyl ether (diglyme)	$CH_3OCH_2CH_2OCH_2CH_2OCH_3$		161	∞
Ethylene oxide		−111.7	10.7	∞
Tetrahydrofuran		−108.5	65	∞

(Continued)

TABLE C Selected Physical Properties of Representative Alcohols, Ethers, and Phenols *(Continued)*

Compound name	Melting point, °C	Boiling point, °C	Solubility, g/100 mL H_2O
Phenols			
Phenol	43	182	8.2
o-Cresol	31	191	2.5
m-Cresol	12	203	0.5
p-Cresol	35	202	1.8
o-Chlorophenol	7	175	2.8
m-Chlorophenol	32	214	2.6
p-Chlorophenol	42	217	2.7
o-Nitrophenol	45	217	0.2
m-Nitrophenol	96		1.3
p-Nitrophenol	114	279	1.6
1-Naphthol	96	279	Slight
2-Naphthol	122	285	0.1
Pyrocatechol	105	246	45.1
Resorcinol	110	276	147.3
Hydroquinone	170	285	6

TABLE D Selected Physical Properties of Representative Aldehydes and Ketones

Compound name	Structural formula	Melting point, °C	Boiling point, °C (1 atm)	Solubility, g/100 mL H_2O
Aldehydes				
Formaldehyde		−92	−21	Very soluble
Acetaldehyde		−123.5	20.2	∞
Propanal		−81	49.5	20
Butanal		−99	75.7	4
Benzaldehyde		−26	178	0.3

(Continued)

TABLE D Selected Physical Properties of Representative Aldehydes and Ketones *(Continued)*

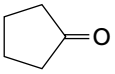
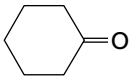
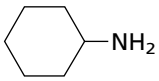
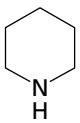
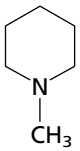
Compound name	Structural formula	Melting point, °C	Boiling point, °C (1 atm)	Solubility, g/100 mL H_2O
Ketones				
Acetone	CH_3CCH_3 (O)	−94.8	56.2	∞
2-Butanone	$CH_3CCH_2CH_3$ (O)	−86.9	79.6	37
2-Pentanone	$CH_3CCH_2CH_2CH_3$ (O)	−77.8	102.4	Slight
3-Pentanone	$CH_3CH_2CCH_2CH_3$ (O)	−39.9	102.0	4.7
Cyclopentanone		−51.3	130.7	43.3
Cyclohexanone		−45	155	
Acetophenone	$C_6H_5CCH_3$ (O)	21	202	Insoluble
Benzophenone	$C_6H_5CC_6H_5$ (O)	48	306	Insoluble

TABLE E Selected Physical Properties of Representative Carboxylic Acids and Dicarboxylic Acids

Compound name	Structural formula	Melting point, °C	Boiling point, °C (1 atm)	Solubility, g/100 mL H_2O
Carboxylic acids				
Formic acid	HCO_2H	8.4	101	∞
Acetic acid	CH_3CO_2H	16.6	118	∞
Propanoic acid	$CH_3CH_2CO_2H$	−20.8	141	∞
Butanoic acid	$CH_3CH_2CH_2CO_2H$	−5.5	164	∞
Pentanoic acid	$CH_3(CH_2)_3CO_2H$	−34.5	186	3.3 (16°C)
Decanoic acid	$CH_3(CH_2)_8CO_2H$	31.4	269	0.003 (15°C)
Benzoic acid	$C_6H_5CO_2H$	122.4	250	0.21 (17°C)
Dicarboxylic acids				
Oxalic acid	HO_2CCO_2H	186	Sublimes	10 (20°C)
Malonic acid	$HO_2CCH_2CO_2H$	130–135	Decomposes	138 (16°C)
Succinic acid	$HO_2CCH_2CH_2CO_2H$	189	235	6.8 (20°C)
Glutaric acid	$HO_2CCH_2CH_2CH_2CO_2H$	97.5		63.9 (20°C)

TABLE F Selected Physical Properties of Representative Amines

Alkylamines

Compound name	Structural formula	Melting point, °C	Boiling point, °C	Solubility, g/100 mL H_2O
Primary amines				
Methylamine	CH_3NH_2	−92.5	−6.7	Very high
Ethylamine	$CH_3CH_2NH_2$	−80.6	16.6	∞
Butylamine	$CH_3CH_2CH_2CH_2NH_2$	−50	77.8	∞
Isobutylamine	$(CH_3)_2CHCH_2NH_2$	−85	68	∞
sec-Butylamine	$CH_3CH_2CHNH_2$ (CH$_3$ branch)	−104	66	∞
tert-Butylamine	$(CH_3)_3CNH_2$	−67.5	45.2	
Hexylamine	$CH_3(CH_2)_5NH_2$	−19	129	Slightly soluble
Cyclohexylamine		−18	134.5	∞
Benzylamine	$C_6H_5CH_2NH_2$	10	184.5	∞
Secondary amines				
Dimethylamine	$(CH_3)_2NH$	−92.2	6.9	Very soluble
Diethylamine	$(CH_3CH_2)_2NH$	−50	55.5	Very soluble
N-Methylpropylamine	$CH_3NHCH_2CH_2CH_3$		62.4	Soluble
Piperidine		−10.5	106.4	∞
Tertiary amines				
Trimethylamine	$(CH_3)_3N$	−117.1	2.9	41
Triethylamine	$(CH_3CH_2)_3N$	−114.7	89.4	∞
N-Methylpiperidine		3	107	

(Continued)

TABLE F Selected Physical Properties of Representative Amines *(Continued)*

Arylamines

Compound name	Melting point, °C	Boiling point, °C
Primary amines		
Aniline	−6.3	184
o-Toluidine	−14.7	200
m-Toluidine	−30.4	203
p-Toluidine	44	200
o-Chloroaniline	−14	209
m-Chloroaniline	−10	230
p-Chloroaniline	72.5	232
o-Nitroaniline	71.5	284
m-Nitroaniline	114	306
p-Nitroaniline	148	332
Secondary amines		
N-Methylaniline	−57	196
N-Ethylaniline	−63	205
Tertiary amines		
N,*N*-Dimethylaniline	2.4	194
Triphenylamine	127	365

APPENDIX 2

ANSWERS TO IN-TEXT PROBLEMS

Problems are of two types: in-text problems that appear within the body of each chapter, and end-of-chapter problems. This appendix gives brief answers to all the in-text problems. More detailed discussions of in-text problems as well as detailed solutions to all the end-of-chapter problems are provided in a separate *Study Guide and Student Solutions Manual.* Answers to part (a) of those in-text problems with multiple parts have been provided in the form of a sample solution within each chapter and are not repeated here.

CHAPTER 1

1.1 4

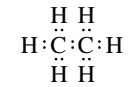
1.2 All the third-row elements have a neon core containing 10 electrons ($1s^2 2s^2 2p^6$). The elements in the third row, their atomic numbers *Z,* and their electron configurations beyond the neon core are Na($Z = 11$)$3s^1$; Mg($Z = 12$)$3s^2$; Al($Z = 13$) $3s^2 3p_x{}^1$; Si($Z = 14$) $3s^2 3p_x{}^1 3p_y{}^1$; P ($Z = 15$) $3s^2 3p_x{}^1 3p_y{}^1 3p_z{}^1$; S ($Z = 16$) $3s^2 3p_x{}^2 3p_y{}^1 3p_z{}^1$; Cl ($Z = 17$) $3s^2 3p_x{}^2 3p_y{}^2 3p_z{}^1$; Ar ($Z = 18$) $3s^2 3p_x{}^2 3p_y{}^2 3p_z{}^2$.

1.3 Those ions that possess a noble gas electron configuration are (a) K^+; (c) H^-; (e) F^-; and (f) Ca^{2+}.

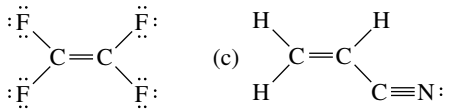
1.4 Electron configuration of C^+ is $1s^2 2s^2 2p^1$; electron configuration of C^- is $1s^2 2s^2 2p^3$. Neither C^+ nor C^- possesses a noble gas electron configuration.

1.5

1.6



1.7 (b) (c)

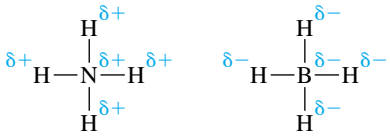


1.8 Carbon bears a partial positive charge in CH_3Cl. It is partially negative in both CH_4 and CH_3Li, but the degree of negative charge is greater in CH_3Li.

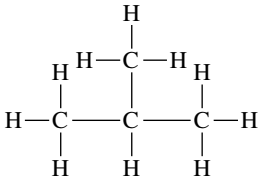
1.9 (b) Sulfur has a formal charge of +2 in the Lewis structure given for sulfuric acid, the two oxygens bonded only to sulfur each have a formal charge of −1, and the oxygens and hydrogens of the two OH groups have no formal charge; (c) none of the atoms have a formal charge in the Lewis structure given for nitrous acid.

1.10 The electron counts of nitrogen in ammonium ion and boron in borohydride ion are both 4 (half of 8 electrons in covalent bonds). Since a neutral nitrogen has 5 electrons in its valence shell, an electron count of 4 gives it a formal charge of +1. A neutral boron has 3 valence electrons, so that an electron count of 4 in borohydride ion corresponds to a formal charge of −1.

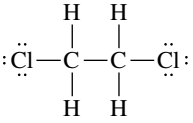
1.11



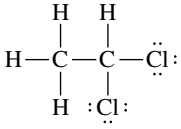
1.12 (b)



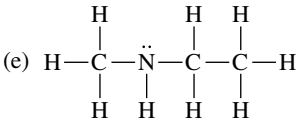
(c)



(d)



(e)



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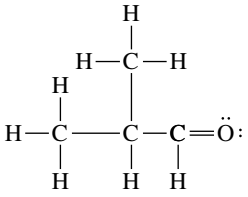
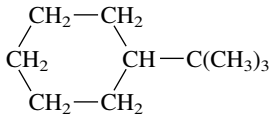
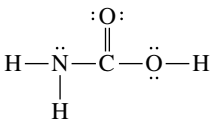


1.13 (b) $(CH_3)_2CHCH(CH_3)_2$ (c) $HOCH_2CHCH(CH_3)_2$ (d)

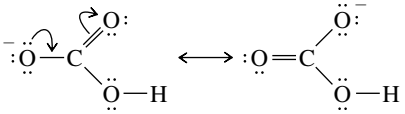


1.14

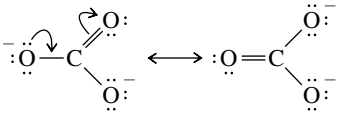


1.15 (b) $CH_3CH_2CH_2OH$, $(CH_3)_2CHOH$, and $CH_3CH_2OCH_3$. (c) There are seven isomers of $C_4H_{10}O$. Four have —OH groups: $CH_3CH_2CH_2CH_2OH$, $(CH_3)_2CHCH_2OH$, $(CH_3)_3COH$, and $CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3$. Three have C—O—C units: $CH_3OCH_2CH_2CH_3$, $CH_3CH_2OCH_2CH_3$, and $(CH_3)_2CHOCH_3$

1.16 (b)



(c)



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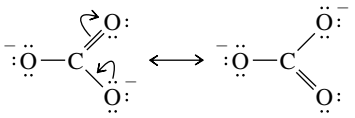
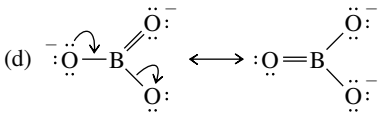


(d) 

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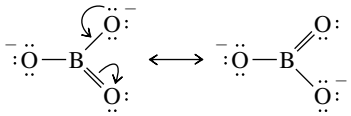
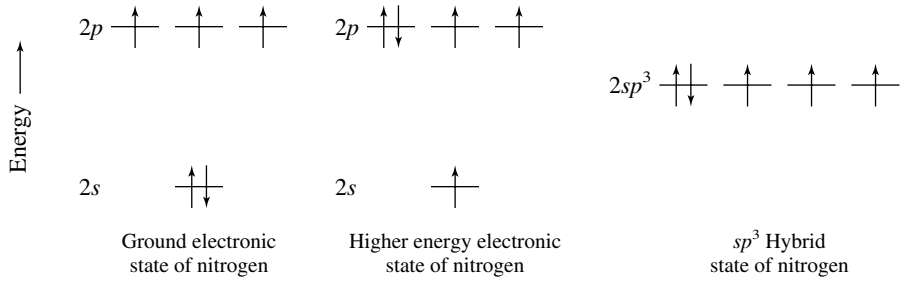


1.17 The H—B—H angles in BH_4^- are 109.5° (tetrahedral).

1.18 (b) Tetrahedral; (c) linear; (d) trigonal planar

1.19 (b) Oxygen is negative end of dipole moment directed along bisector of H—O—H angle; (c) no dipole moment; (d) dipole moment directed along axis of C—Cl bond, with chlorine at negative end, and carbon and hydrogens partially positive; (e) dipole moment directed along bisector of H—C—H angle, with oxygen at negative end; (f) dipole moment aligned with axis of linear molecule, with nitrogen at negative end.

1.20 The sp^3 hybrid state of nitrogen is just like that of carbon except nitrogen has one more electron. Each N—H bond in NH_3 involves overlap of an sp^3 hybrid orbital of N with a 1*s* orbital of hydrogen. The unshared pair of NH_3 occupies an sp^3 orbital.

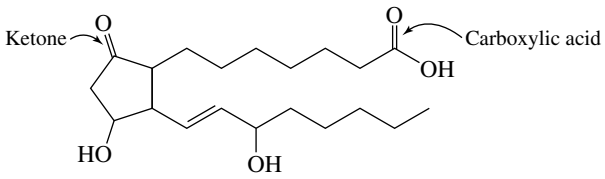


1.21 Carbon and silicon are both sp^3-hybridized. The C—Si bond involves overlap of a half-filled sp^3 orbital of carbon with a half-filled sp^3 hybrid orbital of silicon. The C—H and Si—H bonds involve hydrogen 1*s* orbitals and sp^3 hybrid orbitals of C and Si, respectively. The principal quantum number of the valence orbitals of silicon is 3.

1.22 (b) sp^2; (c) carbon of CH_2 group is sp^2, and carbon of C═O is *sp*; (d) two doubly bonded carbons are each sp^2, while carbon of CH_3 group is sp^3; (e) carbon of C═O is sp^2, and carbons of CH_3 group are sp^3; (f) two doubly bonded carbons are each sp^2, and carbon bonded to nitrogen is *sp*.

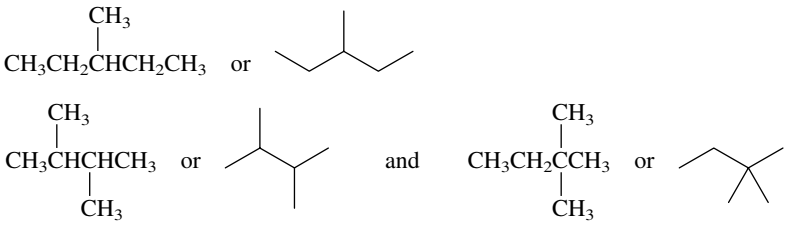
CHAPTER 2

2.1

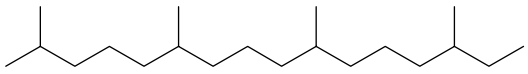


2.2 $CH_3(CH_2)_{26}CH_3$

2.3 The molecular formula is $C_{11}H_{24}$; the condensed structural formula is $CH_3(CH_2)_9CH_3$.

2.4 

2.5 (b) $CH_3(CH_2)_{26}CH_3$; (c) undecane

2.6 

2.7 (b) $CH_3CH_2CH_2CH_2CH_3$ (pentane), $(CH_3)_2CHCH_2CH_3$ (2-methylbutane), $(CH_3)_4C$ (2,2-dimethylpropane); (c) 2,2,4-trimethylpentane; (d) 2,2,3,3-tetramethylbutane

2.8 $CH_3CH_2CH_2CH_2CH_2$— (pentyl, primary); $CH_3CH_2CH_2\underset{|}{C}HCH_3$ (1-methylbutyl, secondary); $CH_3CH_2\underset{|}{C}HCH_2CH_3$ (1-ethylpropyl, secondary); $(CH_3)_2CHCH_2CH_2$— (3-methylbutyl, primary); $CH_3CH_2CH(CH_3)CH_2$— (2-methylbutyl, primary); $(CH_3)_2\underset{|}{C}CH_2CH_3$ (1,1-dimethylpropyl, tertiary); and $(CH_3)_2CH\underset{|}{C}HCH_3$ (1,2-dimethylpropyl, secondary)

2.9 (b) 4-Ethyl-2-methylhexane; (c) 8-ethyl-4-isopropyl-2,6-dimethyldecane

2.10 (b) 4-Isopropyl-1,1-dimethylcyclodecane; (c) cyclohexylcyclohexane

2.11 2,2,3,3-Tetramethylbutane (106°C); 2-methylheptane (116°C); octane (126°C); nonane (151°C)

2.12  $+ \ 9O_2 \longrightarrow 6CO_2 + 6H_2O$

2.13 13,313 kJ/mol

2.14 Hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$) > pentane ($CH_3CH_2CH_2CH_2CH_3$) > isopentane [$(CH_3)_2CHCH_2CH_3$] > neopentane [$(CH_3)_4C$]

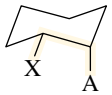
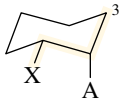
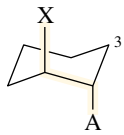
2.15 (b) Oxidation of carbon; (c) reduction of carbon

CHAPTER 3

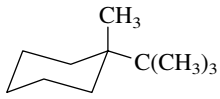
3.1 (b) Butane; (c) 2-methylbutane; (d) 3-methylhexane

3.2 Red circles gauche: 60° and 300°. Red circles anti: 180°. Gauche and anti relationships occur only in staggered conformations; therefore, ignore the eclipsed conformations (0°, 120°, 240°, 360°).

3.3 Shape of potential energy diagram is identical with that for ethane (Figure 3.4). Activation energy for rotation about the C—C bond is higher than that of ethane, lower than that of butane.

3.4 (b)  (c)  (d) 

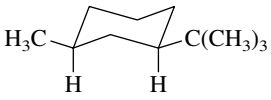
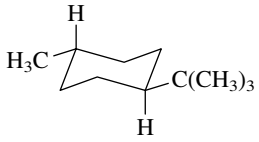
3.5 (b) Less stable; (c) methyl is equatorial and down

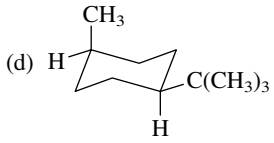
3.6 

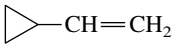
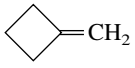
3.7 Ethylcyclopropane: 3384 kJ/mol (808.8 kcal/mol); methylcyclobutane: 3352 kJ/mol (801.2 kcal/mol)

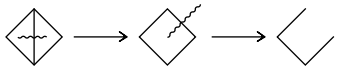
3.8 1,1-Dimethylcyclopropane, ethylcyclopropane, methylcyclobutane, and cyclopentane

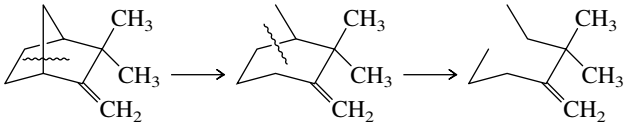
3.9 *cis*-1,3,5-Trimethylcyclohexane is more stable.

3.10 (b)  (c) 

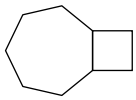
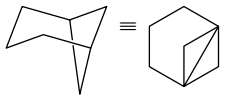
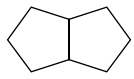
(d) 

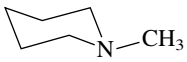
3.11  and 

3.12 



Other pairs of bond cleavages are also possible.

3.13 (b)  (c)  (d) 

3.14 

CHAPTER 4

4.1

	$CH_3CH_2CH_2CH_2Cl$	$CH_3\underset{\displaystyle Cl}{\underset{\vert}{C}}HCH_2CH_3$
Substitutive name:	1-Chlorobutane	2-Chlorobutane
Functional class names:	*n*-Butyl chloride or butyl chloride	*sec*-Butyl chloride or 1-methylpropyl chloride
	$(CH_3)_2CHCH_2Cl$	$(CH_3)_3CCl$
	1-Chloro-2-methylpropane Isobutyl chloride or 2-methylpropyl chloride	2-Chloro-2-methylpropane *tert*-Butyl chloride or 1,1-dimethylethyl chloride

4.2

	$CH_3CH_2CH_2CH_2OH$	$CH_3CHCH_2CH_3$ (OH)
Substitutive name:	1-Butanol	2-Butanol
Functional class names:	*n*-Butyl alcohol or butyl alcohol	*sec*-Butyl alcohol or 1-methylpropyl alcohol

	$(CH_3)_2CHCH_2OH$	$(CH_3)_3COH$
	2-Methyl-1-propanol Isobutyl alcohol or 2-methylpropyl alcohol	2-Methyl-2-propanol *tert*-Butyl alcohol or 1,1-dimethylethyl alcohol

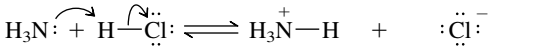
4.3

$CH_3CH_2CH_2CH_2OH$	$CH_3CHCH_2CH_3$ (OH)	$(CH_3)_2CHCH_2OH$	$(CH_3)_3COH$
Primary	Secondary	Primary	Tertiary

4.4 The carbon–bromine bond is longer than the carbon–chlorine bond; therefore, although the charge e in the dipole moment expression $\mu = e \cdot d$ is smaller for the bromine than for the chlorine compound, the distance d is greater.

4.5 Hydrogen bonding in ethanol (CH_3CH_2OH) makes its boiling point higher than that of dimethyl ether (CH_3OCH_3), in which hydrogen bonding is absent.

4.6

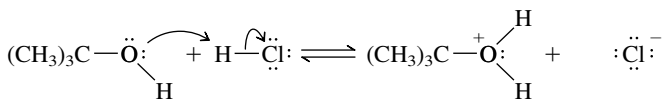


Base	Acid	Conjugate acid	Conjugate base

4.7 $K_a = 8 \times 10^{-10}$; hydrogen cyanide is a weak acid.

4.8 Hydrogen cyanide is a stronger acid than water; its conjugate base (CN^-) is a weaker base than hydroxide (HO^-).

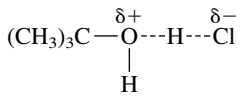
4.9



Base	Acid	Conjugate acid	Conjugate base

4.10 Greater than 1

4.11

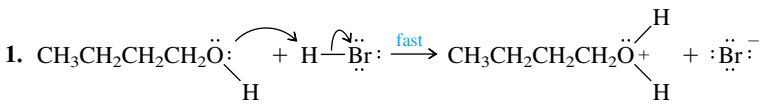


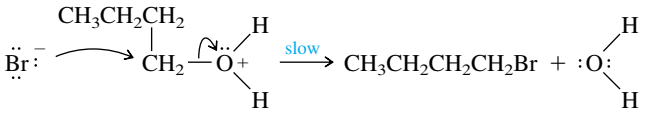
4.12 (b) $(CH_3CH_2)_3COH + HCl \longrightarrow (CH_3CH_2)_3CCl + H_2O$
(c) $CH_3(CH_2)_{12}CH_2OH + HBr \longrightarrow CH_3(CH_2)_{12}CH_2Br + H_2O$

4.13 $(CH_3)_2\overset{+}{C}CH_2CH_3$

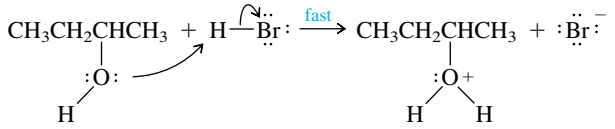
4.14 ***1-Butanol:*** Rate-determining step is bimolecular; therefore, S_N2.

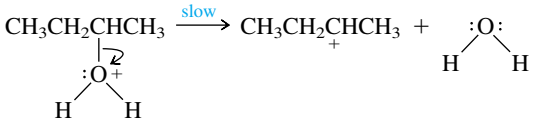
1.

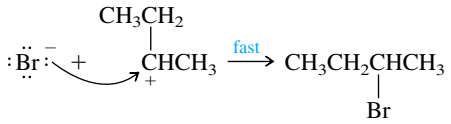


2. 

2-Butanol: Rate-determining step is unimolecular, therefore, S_N1.

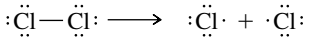
1. 

2. 

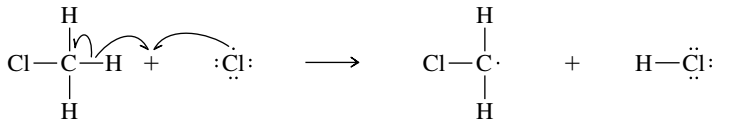
3. 

4.15 $(CH_3)_2\dot{C}CH_2CH_3$

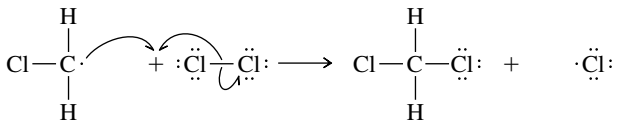
4.16 (b) The carbon–carbon bond dissociation energy is lower for 2-methylpropane because it yields a more stable (secondary) radical; propane yields a primary radical. (c) The carbon–carbon bond dissociation energy is lower for 2,2-dimethylpropane because it yields a still more stable tertiary radical.

4.17 ***Initiation:*** 

Chlorine — 2 Chlorine atoms

Propagation: 

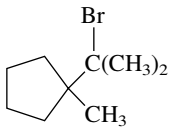
Chloromethane — Chlorine atom — Chloromethyl radical — Hydrogen chloride

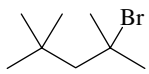


Chloromethyl radical — Chlorine — Dichloromethane — Chlorine atom

4.18 CH_3CHCl_2 and $ClCH_2CH_2Cl$

4.19 1-Chloropropane (43%); 2-chloropropane (57%)

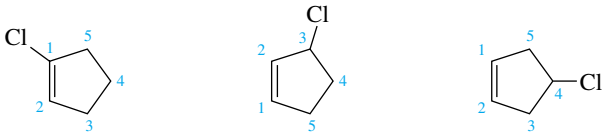
4.20 (b) 

(c) 

CHAPTER 5

5.1 (b) 3,3-Dimethyl-1-butene; (c) 2-methyl-2-hexene; (d) 4-chloro-1-pentene; (e) 4-penten-2-ol

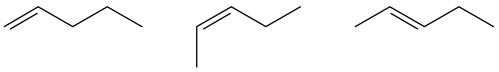
5.2



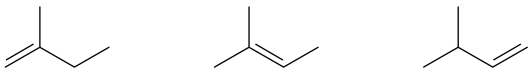
1-Chlorocyclopentene 3-Chlorocyclopentene 4-Chlorocyclopentene

5.3 (b) 3-Ethyl-3-hexene; (c) two carbons are sp^2-hybridized, six are sp^3-hybridized; (d) there are three sp^2–sp^3 σ bonds and three sp^3–sp^3 σ bonds.

5.4

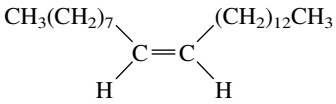


1-Pentene *cis*-2-Pentene *trans*-2-Pentene



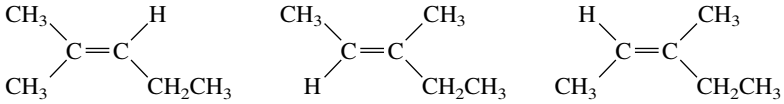
2-Methyl-1-butene 2-Methyl-2-butene 3-Methyl-1-butene

5.5



5.6 (b) *Z;* (c) *E;* (d) *E*

5.7

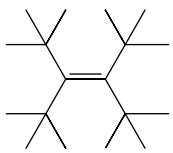


2-Methyl-2-pentene (*E*)-3-Methyl-2-pentene (*Z*)-3-Methyl-2-pentene

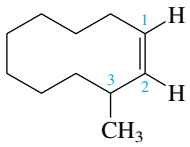
5.8 $(CH_3)_2C{=}C(CH_3)_2$

5.9 2-Methyl-2-butene (most stable) > (*E*)-2-pentene > (*Z*)-2-pentene > 1-pentene (least stable)

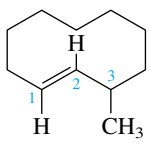
5.10 Bulky *tert*-butyl groups are cis to one another on each side of the double bond and cause the alkene to be highly strained and unstable.

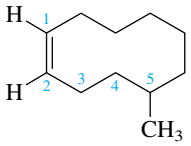


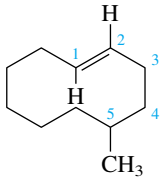
5.11 (c)



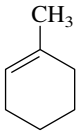
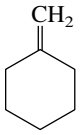
(d)



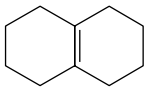
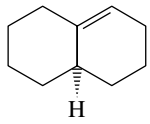
(e) 

(f) 

5.12 (b) Propene; (c) propene; (d) 2,3,3-trimethyl-1-butene

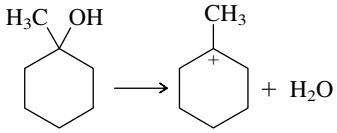
5.13 (b)  and 

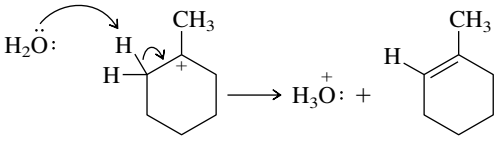
Major Minor

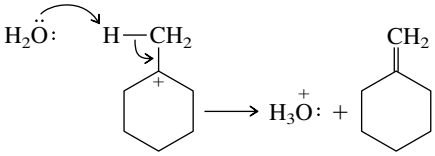
(c)  and 

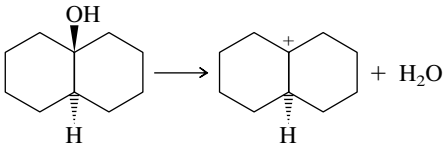
Major Minor

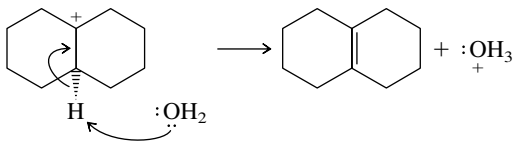
5.14 1-Pentene, *cis*-2-pentene, and *trans*-2-pentene

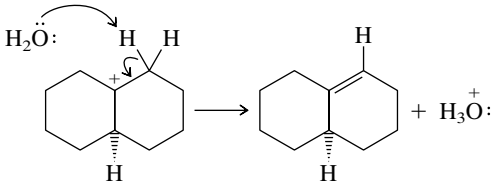
5.15 (b) 



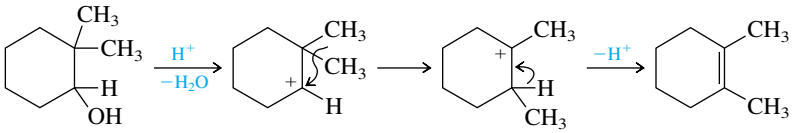
and 

(c) 



and 

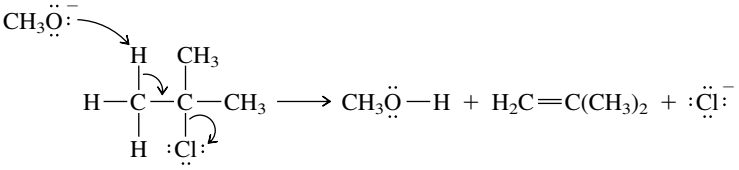
5.16



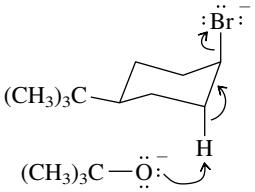
5.17 (b) $(CH_3)_2C{=}CH_2$; (c) $CH_3CH{=}C(CH_2CH_3)_2$; (d) $CH_3CH{=}C(CH_3)_2$ (major) and $CH_2{=}CHCH(CH_3)_2$ (minor); (e) $CH_2{=}CHCH(CH_3)_2$; (f) 1-methylcyclohexene (major) and methylenecyclohexane (minor)

5.18 $CH_2{=}CHCH_2CH_3$, *cis*-$CH_3CH{=}CHCH_3$, and *trans*-$CH_3CH{=}CHCH_3$.

5.19



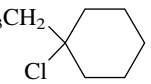
5.20

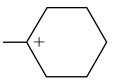


CHAPTER 6

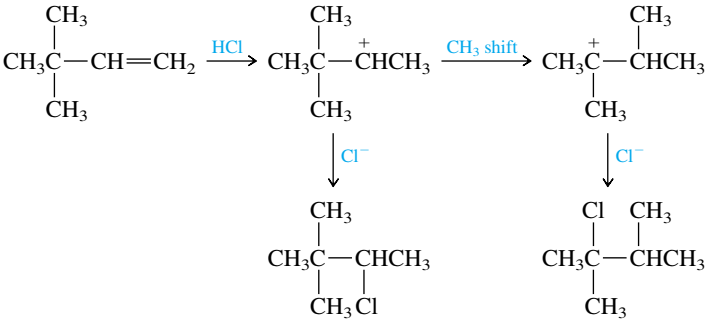
6.1 2-Methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene

6.2 2-Methyl-2-butene (112 kJ/mol, 26.7 kcal/mol), 2-methyl-1-butene (118 kJ/mol, 28.2 kcal/mol), and 3-methyl-1-butene (126 kJ/mol, 30.2 kcal/mol)

6.3 (b) $(CH_3)_2CCH_2CH_3$ (Cl) (c) $CH_3CHCH_2CH_3$ (Cl) (d) 

6.4 (b) $(CH_3)_2\overset{+}{C}CH_2CH_3$ (c) $CH_3\overset{+}{C}HCH_2CH_3$ (d) 

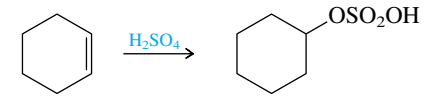
6.5



6.6 Addition in accordance with Markovnikov's rule gives 1,2-dibromopropane. Addition opposite to Markovnikov's rule gives 1,3-dibromopropane.

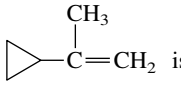
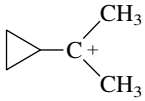
6.7 Absence of peroxides: (b) 2-bromo-2-methylbutane; (c) 2-bromobutane; (d) 1-bromo-1-ethylcyclohexane. Presence of peroxides: (b) 1-bromo-2-methylbutane; (c) 2-bromobutane; (d) (1-bromoethyl)cyclohexane.

6.8

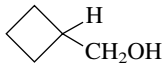
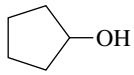


Cyclohexene Cyclohexyl hydrogen sulfate

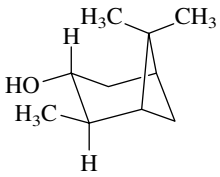
6.9 The concentration of hydroxide ion is too small in acid solution to be chemically significant.

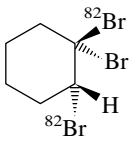
6.10  is more reactive, because it gives a tertiary carbocation  when it is protonated in acid solution.

6.11 E1

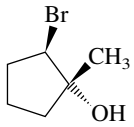
6.12 (b) $CH_3CHCH_2CH_3$ (OH) (c)  (d) 

(e) $CH_3CHCH(CH_2CH_3)_2$ (OH) (f) $HOCH_2CH_2CH(CH_2CH_3)_2$

6.13 

6.14 

6.15 2-Methyl-2-butene (most reactive) > 2-methyl-1-butene > 3-methyl-1-butene (least reactive)

6.16 (b) $(CH_3)_2C(OH)-CH(Br)CH_3$ (c) $BrCH_2CH(OH)CH(CH_3)_2$ (d) 

6.17 *cis*-2-Methyl-7,8-epoxyoctadecane

6.18 *cis*-$(CH_3)_2CHCH_2CH_2CH_2CH_2CH{=}CH(CH_2)_9CH_3$

6.19 2,4,4-Trimethyl-1-pentene

6.20 $(CH_3)_3CBr \xrightarrow[\text{heat}]{NaOCH_2CH_3} (CH_3)_2C{=}CH_2 \xrightarrow[H_2O]{Br_2} (CH_3)_2C(OH)-CH_2Br$

6.21 Hydrogenation over a metal catalyst such as platinum, palladium, or nickel

CHAPTER 7

7.1 (c) C-2 is a stereogenic center; (d) no stereogenic centers.

7.2 (c) C-2 is a stereogenic center; (d) no stereogenic centers.

7.3 (b) (*Z*)-1,2-Dichloroethene is achiral. The plane of the molecule is a plane of symmetry. A second plane of symmetry is perpendicular to the plane of the molecule and bisects the carbon-carbon bond.

(c) *cis*-1,2-Dichlorocyclopropane is achiral. It has a plane of symmetry that bisects the C-1—C-2 bond and passes through C-3.

(d) *trans*-1,2-Dichlorocyclopropane is chiral. It has neither a plane of symmetry nor a center of symmetry.

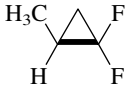
7.4 $[\alpha]_D$ − 39°

7.5 Two-thirds (66.7%)

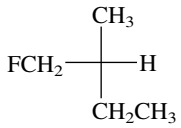
7.6 (+)-2-Butanol

7.7 (b) *R*; (c) *S*; (d) *S*

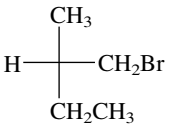
7.8 (b)



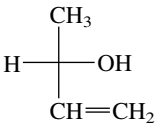
7.9 (b)



(c)

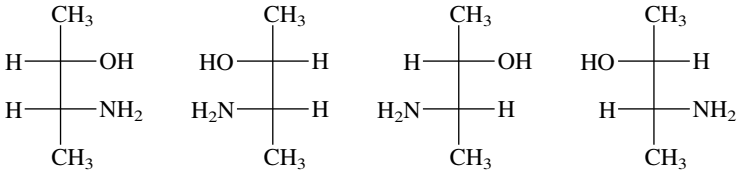


(d)



7.10 *S*

7.11



7.12 2*S*,3*R*

7.13 2,4-Dibromopentane

7.14 *cis*-1,3-Dimethylcyclohexane

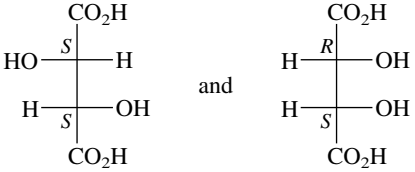
7.15 *RRR RRS RSR SRR SSS SSR SRS RSS*

7.16 Eight

7.17 Epoxidation of *cis*-2-butene gives *meso*-2,3-epoxybutane; *trans*-2-butene gives a racemic mixture of (2*R*,3*R*) and (2*S*,3*S*)-2,3-epoxybutane.

7.18 No. The major product *cis*-1,2-dimethylcyclohexane is less stable than the minor product *trans*-1,2-dimethylcyclohexane.

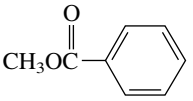
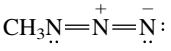
7.19



7.20 No

7.21 (*S*)-1-Phenylethylammonium (*S*)-malate

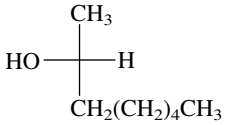
CHAPTER 8

8.1 (b) $CH_3OCH_2CH_3$ (c)  (d) 

(e) $CH_3C{\equiv}N$ (f) CH_3SH (g) CH_3I

8.2 $ClCH_2CH_2CH_2C{\equiv}N$

8.3 No

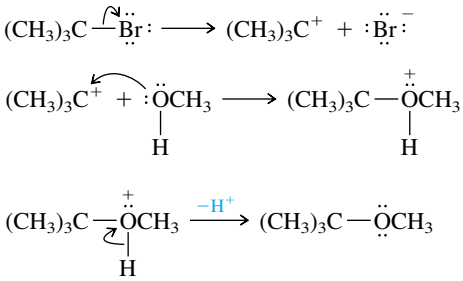
8.4 

8.5 Hydrolysis of (*R*)-(−)-2-bromooctane by the S_N2 mechanism yields optically active (*S*)-(+)-2-octanol. The 2-octanol obtained by hydrolysis of racemic 2-bromooctane is not optically active.

8.6 (b) 1-Bromopentane; (c) 2-chloropentane; (d) 2-bromo-5-methylhexane; (e) 1-bromodecane

8.7 $CH_3CH(CH_2)_5CH_3$ (NO$_2$) and $CH_3CH(CH_2)_5CH_3$ (ONO)

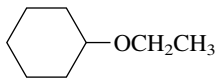
8.8 Product is $(CH_3)_3COCH_3$. The mechanism of solvolysis is S_N1.



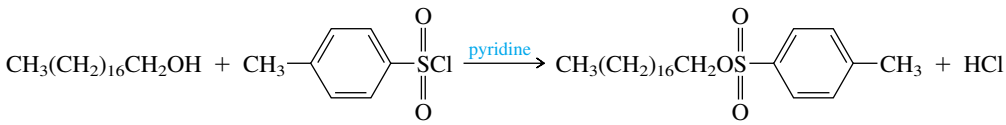
8.9 (b) 1-Methylcyclopentyl iodide; (c) cyclopentyl bromide; (d) *tert*-butyl iodide

8.10 Both *cis*- and *trans*-1,4-dimethylcyclohexanol are formed in the hydrolysis of either *cis*- or *trans*-1,4-dimethylcyclohexyl bromide.

8.11 A hydride shift produces a tertiary carbocation; a methyl shift produces a secondary carbocation.

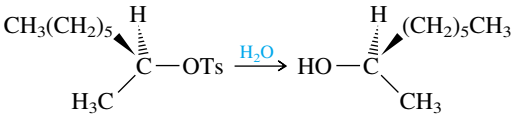
8.12 (b)  (c) $CH_3CHCH_2CH_3$ (OCH$_3$)

(d) *cis*- and *trans*-$CH_3CH{=}CHCH_3$ and $CH_2{=}CHCH_2CH_3$

8.13 

8.14 (b) $CH_3(CH_2)_{16}CH_2I$; (c) $CH_3(CH_2)_{16}CH_2C{\equiv}N$; (d) $CH_3(CH_2)_{16}CH_2SH$;
(e) $CH_3(CH_2)_{16}CH_2SCH_2CH_2CH_2CH_3$

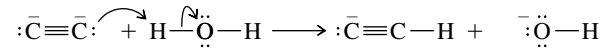
8.15 The product has the *R* configuration and a specific rotation $[\alpha]_D$ of $-9.9°$.



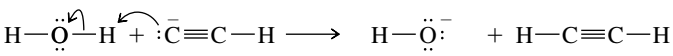
8.16 $CH_3CH_2C(CH_3)_2$ with Cl on the second carbon

CHAPTER 9

9.1



Carbide ion Water Acetylide ion Hydroxide ion

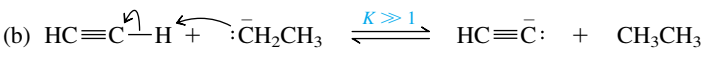


Water Acetylide ion Hydroxide ion Acetylene

9.2 $CH_3CH_2CH_2C{\equiv}CH$ (1-pentyne), $CH_3CH_2C{\equiv}CCH_3$ (2-pentyne), $(CH_3)_2CHC{\equiv}CH$ (3-methyl-1-butyne)

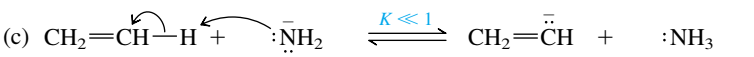
9.3 The bonds become shorter and stronger in the series as the electronegativity increases; N—H longest and weakest, H—F shortest and strongest.

9.4 (b)



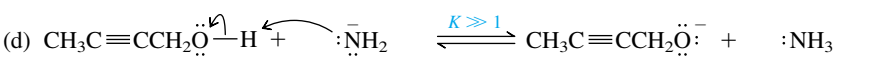
Acetylene (stronger acid) Ethyl anion (stronger base) Acetylide ion (weaker base) Ethane (weaker acid)

(c)



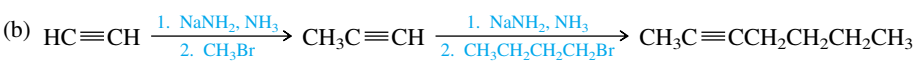
Ethylene (weaker acid) Amide ion (weaker base) Vinyl anion (stronger base) Ammonia (stronger acid)

(d)

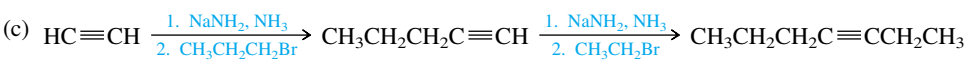


2-Butyn-1-ol (stronger acid) Amide ion (stronger base) 2-Butyn-1-olate anion (weaker base) Ammonia (weaker acid)

9.5 (b)

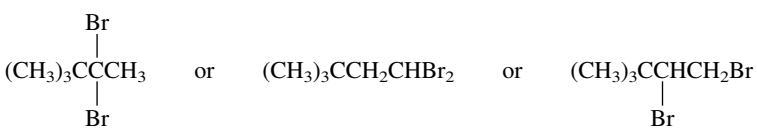


(c)



9.6 Both $CH_3CH_2CH_2C{\equiv}CH$ and $CH_3CH_2C{\equiv}CCH_3$ can be prepared by alkylation of acetylene. The alkyne $(CH_3)_2CHC{\equiv}CH$ cannot be prepared by alkylation of acetylene, because the required alkyl halide, $(CH_3)_2CHBr$, is secondary and will react with the strongly basic acetylide ion by elimination.

9.7



9.8 (b) $CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{H_2SO_4} CH_3CH{=}CH_2 \xrightarrow{Br_2} CH_3\overset{\overset{Br}{|}}{C}HCH_2Br \xrightarrow[2.\ H^+]{1.\ NaNH_2} CH_3C{\equiv}CH$

(c) $(CH_3)_2CHBr \xrightarrow{NaOCH_2CH_3} CH_3CH{=}CH_2$; then proceed as in parts (a) and (b).

(d) $CH_3CHCl_2 \xrightarrow[2.\ H_2O]{1.\ NaNH_2} HC{\equiv}CH \xrightarrow[2.\ CH_3Br]{1.\ NaNH_2} CH_3C{\equiv}CH$

(e) $CH_3CH_2OH \xrightarrow[\text{heat}]{H_2SO_4} CH_2{=}CH_2 \xrightarrow{Br_2} BrCH_2CH_2Br \xrightarrow[2.\ H_2O]{1.\ NaNH_2} HC{\equiv}CH$; then proceed as in part (d).

9.9 $HC{\equiv}CH \xrightarrow[2.\ CH_3CH_2CH_2Br]{1.\ NaNH_2,\ NH_3} CH_3CH_2CH_2C{\equiv}CH \xrightarrow[2.\ CH_3CH_2CH_2Br]{1.\ NaNH_2,\ NH_3}$

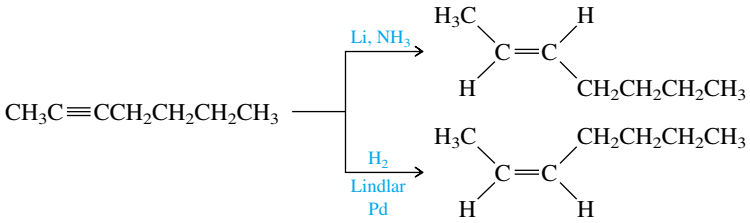
$$CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3 \xrightarrow[Pt]{H_2} CH_3(CH_2)_6CH_3$$

or $HC{\equiv}CH \xrightarrow[2.\ CH_3(CH_2)_5Br]{1.\ NaNH_2,\ NH_3} CH_3(CH_2)_5C{\equiv}CH \xrightarrow[Pt]{H_2} CH_3(CH_2)_6CH_3$

9.10 Oleic acid is *cis*-$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$. Stearic acid is $CH_3(CH_2)_{16}CO_2H$.

9.11 Elaidic acid is *trans*-$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$.

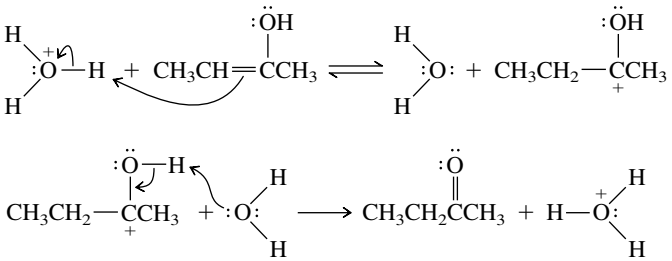
9.12 $CH_3C{\equiv}CH \xrightarrow[2.\ CH_3CH_2CH_2CH_2Br]{1.\ NaNH_2,\ NH_3}$



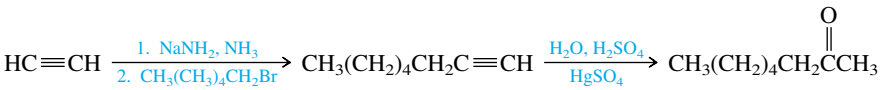
9.13 (b) $CH_2{=}CHCl \xrightarrow{HCl} CH_3CHCl_2$

(c) $CH_3CHBr_2 \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} HC{\equiv}CH \xrightarrow{2HCl} CH_3CHCl_2$

9.14 $CH_3C{\equiv}CCH_3 \xrightarrow[H_2SO_4]{H_2O,\ Hg^{2+}} \left[CH_3C(OH){=}CHCH_3\right] \longrightarrow CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$



9.15 2-Octanone is prepared as shown:

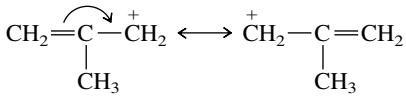


4-Octyne is prepared as described in Problem 9.9 and converted to 4-octanone by hydration with H_2O, H_2SO_4, and $HgSO_4$.

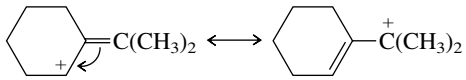
9.16 $CH_3(CH_2)_4C{\equiv}CCH_2CH_2C{\equiv}C(CH_2)_4CH_3$

CHAPTER 10

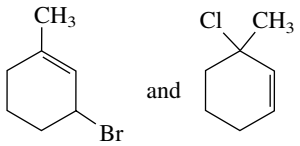
10.1 (b)



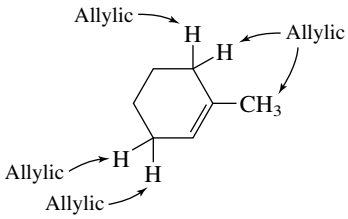
(c)



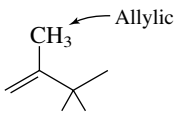
10.2



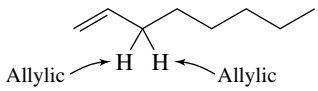
10.3 (b)



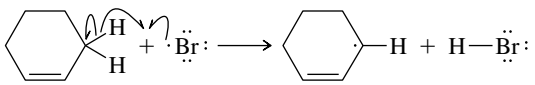
(c)



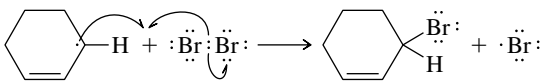
(d)



10.4 (Propagation step 1)



(Propagation step 2)



10.5 2,3,3-Trimethyl-1-butene gives only $(CH_3)_3CC(CH_2Br){=}CH_2$. 1-Octene gives a mixture of $CH_2{=}CHCH(Br)(CH_2)_4CH_3$ as well as the cis and trans stereoisomers of $BrCH_2CH{=}CH(CH_2)_4CH_3$.

10.6 (b) All the double bonds in humulene are isolated. (c) Two of the double bonds in cembrene are conjugated to each other but isolated from the remaining double bonds in the molecule. (d) The CH═C═CH unit is a cumulated double bond; it is conjugated to the double bond at C-2.

10.7 1,2-Pentadiene (3251 kJ/mol, 777.1 kcal/mol); (*E*)-1,3-pentadiene (3186 kJ/mol, 761.6 kcal/mol); 1,4-pentadiene (3217 kJ/mol, 768.9 kcal/mol)

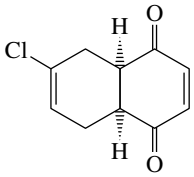
10.8 2-Methyl-2,3-pentadiene is achiral. 2-Chloro-2,3-pentadiene is chiral.

10.9 $CH_2{=}CHCH_2C(CH_3){=}CHCH_3$ (*cis* + *trans*) and $CH_2{=}CHCH_2C(=CH_2)CH_2CH_3$

10.10 $(CH_3)_2CClCH{=}CH_2$

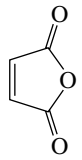
10.11 3,4-Dibromo-3-methyl-1-butene; 3,4-dibromo-2-methyl-1-butene; and 1,4-dibromo-2-methyl-2-butene

10.12

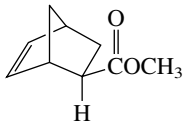


10.13 (b) $CH_2{=}CHCH{=}CH_2$ + *cis*-$N{\equiv}CCH{=}CHC{\equiv}N$

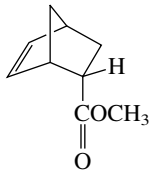
(c) $CH_3CH{=}CHCH{=}CH_2$ +



10.14



and

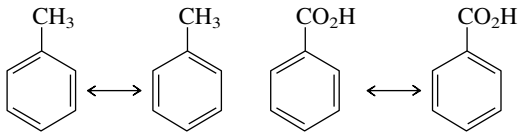


10.15 π

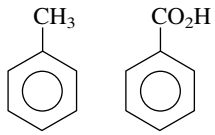
10.16 There is a mismatch between the ends of the HOMO of one 1,3-butadiene molecule and the LUMO of the other (Fig. 10.9). The reaction is forbidden.

CHAPTER 11

11.1 (a)

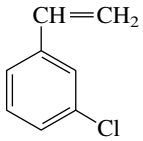


(b)

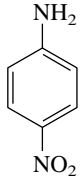


11.2 1,3,5-Cycloheptatriene resonance energy = 25 kJ/mol (5.9 kcal/mol). It is about six times smaller than the resonance energy of benzene.

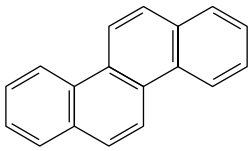
11.3 (b)



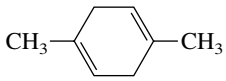
(c)



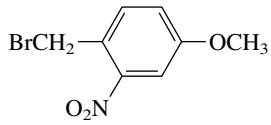
11.4



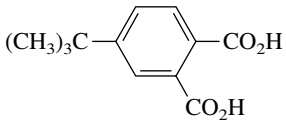
11.5



11.6 (b)



11.7



11.8 (b) $C_6H_5CH_2OC(CH_3)_3$ (c) $C_6H_5CH_2\ddot{N}{=}\overset{+}{N}{=}\ddot{N}:^-$ (d) $C_6H_5CH_2SH$ (e) $C_6H_5CH_2I$

11.9 1,2-Dihydronaphthalene, 101 kJ/mol (24.1 kcal/mol); 1,4-dihydronaphthalene, 113 kJ/mol (27.1 kcal/mol)

11.10 (b) $C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$ (c) $C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}HCH_2Br$ (d) $C_6H_5CH\!-\!CH_2 + C_6H_5CO_2H$ (O bridge)

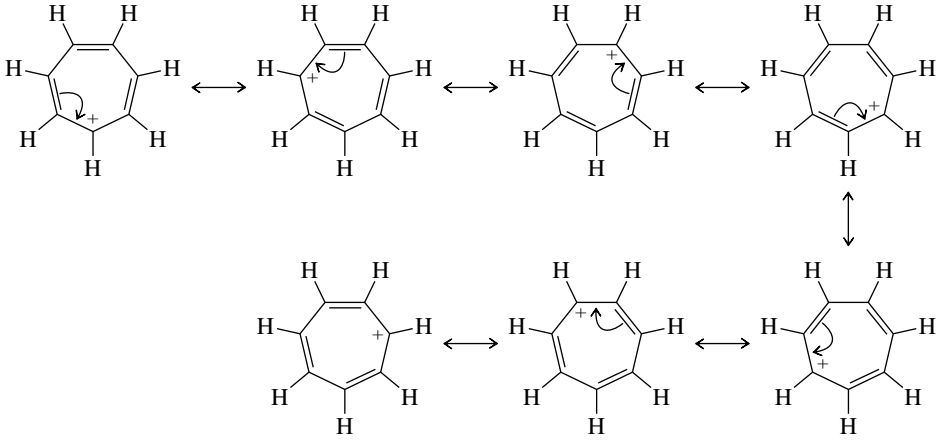
11.11 Styrene, 4393 kJ/mol (1050 kcal/mol); cyclooctatetraene, 4543 kJ/mol (1086 kcal/mol)

11.12 Diels–Alder reaction

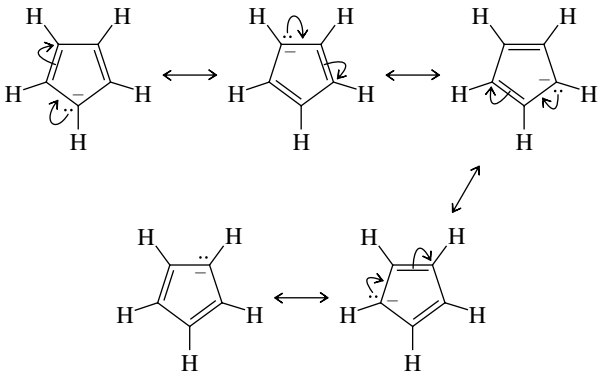
11.13 (b) Five doubly occupied bonding orbitals plus two half-filled nonbonding orbitals plus five vacant antibonding orbitals

11.14 Divide the heats of combustion by the number of carbons. The two aromatic hydrocarbons (benzene and [18]-annulene) have heats of combustion per carbon that are less than those of the nonaromatic hydrocarbons (cyclooctatetraene and [16]-annulene). On a per carbon basis, the aromatic hydrocarbons have lower potential energy (are more stable) than the nonaromatic hydrocarbons.

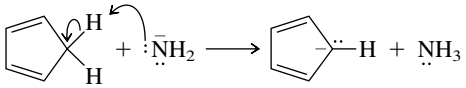
11.15



11.16



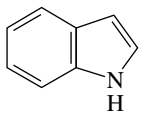
11.17



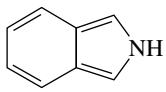
11.18 (b) Cyclononatetraenide anion is aromatic.

11.19 Indole is more stable than isoindole.

Six-membered ring corresponds to benzene.



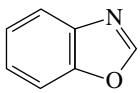
Indole: more stable



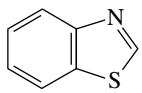
Isoindole: less stable

Six-membered ring does not have same pattern of bonds as benzene.

11.20

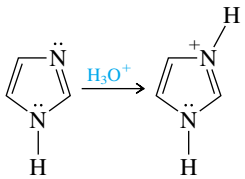


Benzoxazole



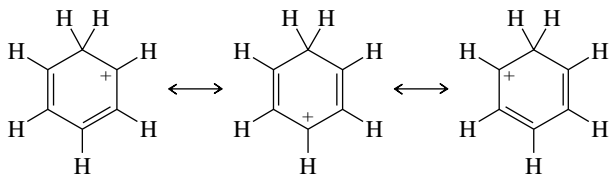
Benzothiazole

11.21



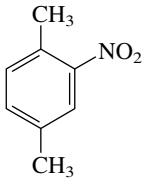
CHAPTER 12

12.1 The positive charge is shared by the three carbons indicated in the three most stable resonance structures:

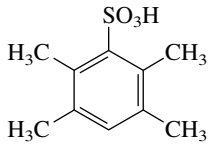


Provided that these structures contribute equally, the resonance picture coincides with the MO treatment in assigning one third of a positive charge (+ 0.33) to each of the indicated carbons.

12.2

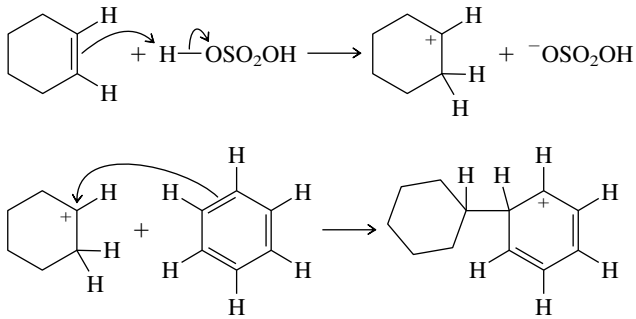


12.3

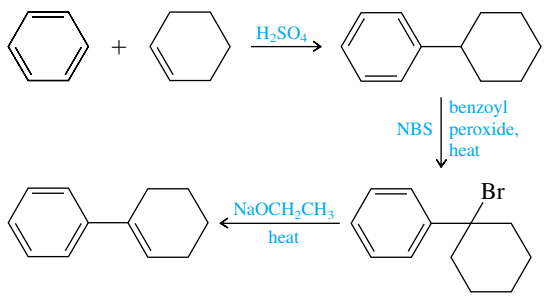


12.4 The major product is isopropylbenzene. Ionization of 1-chloropropane is accompanied by a hydride shift to give $CH_3\overset{+}{C}HCH_3$, which then attacks benzene.

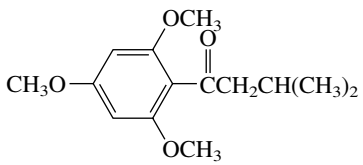
12.5



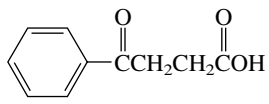
12.6



12.7



12.8



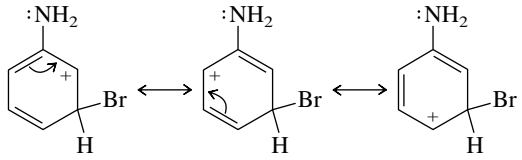
12.9 (b) Friedel–Crafts acylation of benzene with $(CH_3)_3CC(=O)Cl$, followed by reduction with Zn(Hg) and hydrochloric acid

12.10 (b) Toluene is 1.7 times more reactive than *tert*-butylbenzene. (c) Ortho (10%), meta (6.7%), para (83.3%)

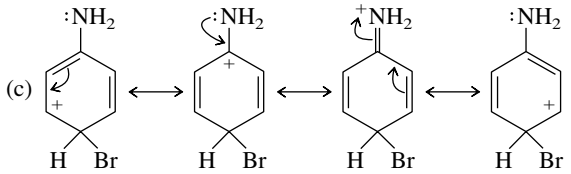
12.11

$-CH_2Cl$	$-CHCl_2$	$-CCl_3$
Deactivating ortho, para-directing	Deactivating ortho, para-directing	Deactivating meta-directing

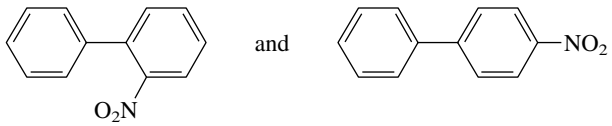
12.12 (b)



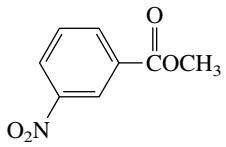
(c)



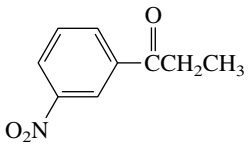
12.13



12.14 (b)

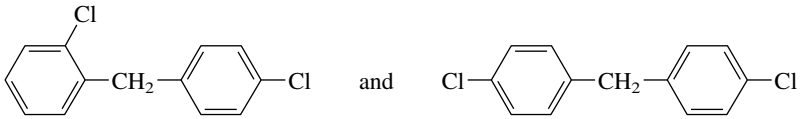


(c)

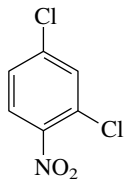


12.15 The group $-\overset{+}{N}(CH_3)_3$ is strongly deactivating and meta-directing. Its positively charged nitrogen makes it a powerful electron-withdrawing substituent. It resembles a nitro group.

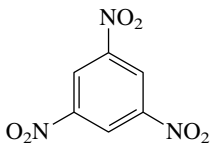
12.16



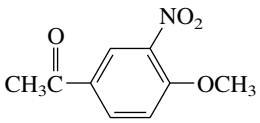
12.17 (b)



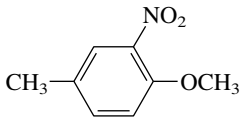
(c)



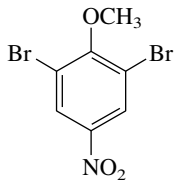
(d)



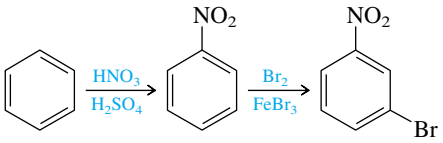
(e)



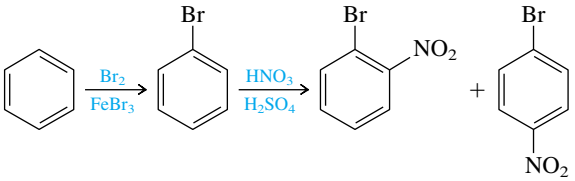
(f)



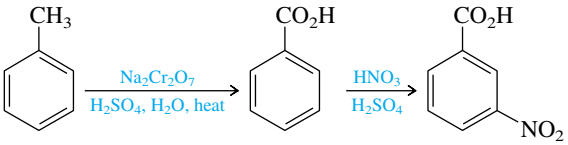
12.18 *m*-Bromonitrobenzene:



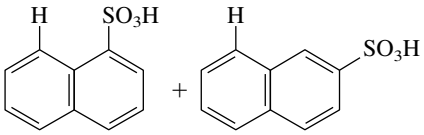
p-Bromonitrobenzene:



12.19



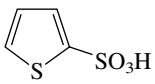
12.20



Formed faster More stable

The hydrogen at C-8 (the one shown in the structural formulas) crowds the $-SO_3H$ group in the less stable isomer.

12.21



CHAPTER 13

13.1 1.41 T

13.2 25.2 MHz

13.3 (a) 6.88 ppm; (b) higher field; more shielded

13.4 H in CH_3CCl_3 is more shielded than H in $CHCl_3$. If H in $CHCl_3$ appears at δ 7.28 ppm, then H in CH_3CCl_3 appears 4.6 ppm upfield of 7.28 ppm. Its chemical shift is δ 2.7 ppm.

13.5 The chemical shift of the methyl protons is δ 2.2 ppm. The chemical shift of the protons attached to the aromatic ring is δ 7.0 ppm.

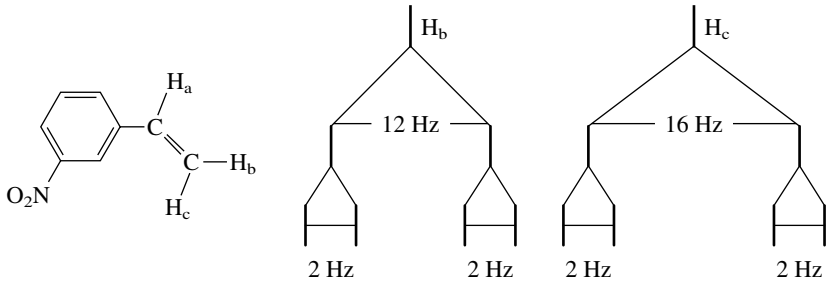
13.6 (b) Five; (c) two; (d) two; (e) three; (f) one; (g) four; (h) three

13.7 (b) One; (c) one; (d) one; (e) four; (f) four

13.8 (b) One signal (singlet); (c) two signals (doublet and triplet); (d) two signals (both singlets); (e) two signals (doublet and quartet)

13.9 (b) Three signals (singlet, triplet, and quartet); (c) two signals (triplet and quartet); (d) three signals (singlet, triplet, and quartet); (e) four signals (three triplets and quartet)

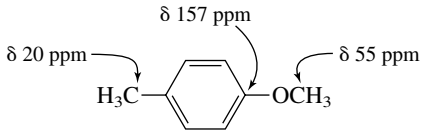
13.10 Both H_b and H_c appear as doublets of doublets:



13.11 (b) The signal for the proton at C-2 is split into a quartet by the methyl protons, and each line of this quartet is split into a doublet by the aldehyde proton. It appears as a doublet of quartets.

13.12 (b) Six; (c) six; (d) nine; (e) three

13.13



13.14 1,2,4-Trimethylbenzene

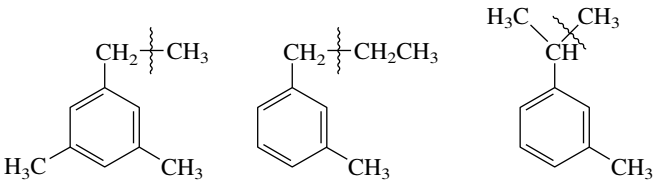
13.15 Benzyl alcohol. Infrared spectrum has peaks for O—H and sp^3 C—H; lacks peak for C=O.

13.16 HOMO–LUMO energy difference in ethylene is greater than that of *cis,trans*-1,3-cyclooctadiene.

13.17 2-Methyl-1,3-butadiene

13.18 (b) Three peaks (*m/z* 146, 148, and 150); (c) three peaks (*m/z* 234, 236, and 238); (d) three peaks (*m/z* 190, 192, and 194)

13.19



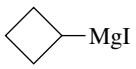
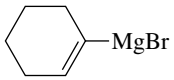
Base peak $C_9H_{11}^+$ (*m/z* 119) | Base peak $C_8H_9^+$ (*m/z* 105) | Base peak $C_9H_{11}^+$ (*m/z* 119)

13.20 (b) 3; (c) 2; (d) 3; (e) 2; (f) 2

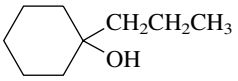
CHAPTER 14

14.1 (b) Cyclohexylmagnesium chloride

14.2 (b) $CH_3\underset{\underset{Br}{|}}{C}HCH_2CH_3 + 2Li \longrightarrow CH_3\underset{\underset{Li}{|}}{C}HCH_2CH_3 + LiBr$

14.3 (b) $CH_2{=}CHCH_2MgCl$ (c)  (d) 

14.4 (b) $CH_3(CH_2)_4CH_2OH + CH_3CH_2CH_2CH_2Li \longrightarrow CH_3CH_2CH_2CH_3 + CH_3(CH_2)_4CH_2OLi$
(c) $C_6H_5SH + CH_3CH_2CH_2CH_2Li \longrightarrow CH_3CH_2CH_2CH_3 + C_6H_5SLi$

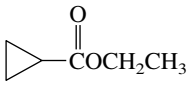
14.5 (b) $C_6H_5CHCH_2CH_2CH_3$ (OH) (c)  (d) $CH_3CH_2CH_2C(CH_3)(CH_2CH_3)OH$

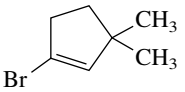
14.6 $CH_3\ddot{C}H_2^- + H-C\equiv CCH_2CH_2CH_2CH_3 \longrightarrow CH_3CH_3 + :\bar{C}\equiv CCH_2CH_2CH_2CH_3$

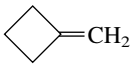
Ethyl anion — 1-Hexyne — Ethane — Conjugate base of 1-hexyne

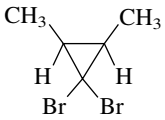
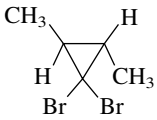
14.7 (b) $CH_3MgI + C_6H_5CCH_3(=O) \xrightarrow[2.\ H_3O^+]{1.\ \text{diethyl ether}} C_6H_5C(CH_3)(OH)CH_3$

and $C_6H_5MgBr + CH_3CCH_3(=O) \xrightarrow[2.\ H_3O^+]{1.\ \text{diethyl ether}} C_6H_5C(CH_3)(OH)CH_3$

14.8 (b) $2C_6H_5MgBr +$ 

14.9 (b) $LiCu(CH_3)_2 +$ 

14.10 (b) 

14.11 *cis*-2-Butene $\longrightarrow$  *trans*-2-Butene $\longrightarrow$ 

14.12 $Fe(CO)_5$

CHAPTER 15

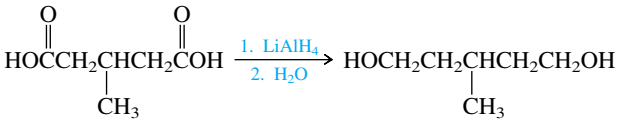
15.1 The primary alcohols $CH_3CH_2CH_2CH_2OH$ and $(CH_3)_2CHCH_2OH$ can each be prepared by hydrogenation of an aldehyde. The secondary alcohol $CH_3CH(OH)CH_2CH_3$ can be prepared by hydrogenation of a ketone. The tertiary alcohol $(CH_3)_3COH$ cannot be prepared by hydrogenation.

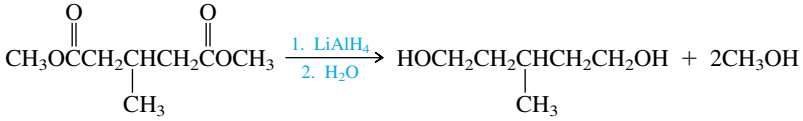
15.2 (b) $CH_3CD(OD)CH_3$ (c) $C_6H_5CH(OH)D$ (d) DCH_2OD

15.3 $CH_3CH_2COCH(CH_3)_2$

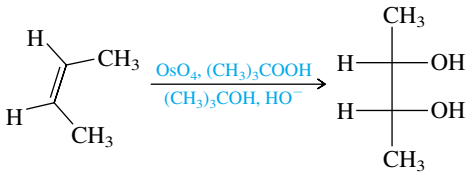
15.4 (b) 

15.5

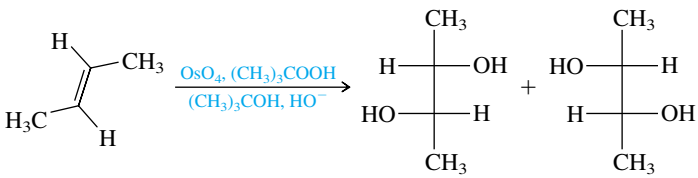




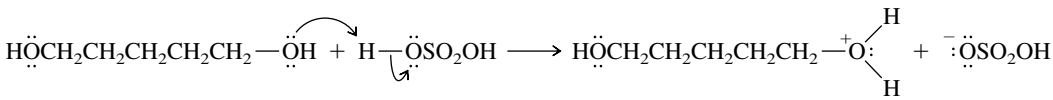
15.6 *cis*-2-Butene yields the meso stereoisomer of 2,3-butanediol:



trans-2-Butene gives equal quantities of the two enantiomers of the chiral diol:



15.7 Step 1:



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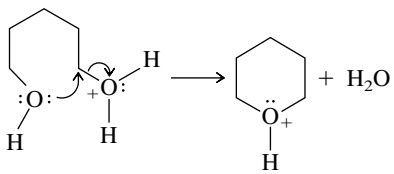

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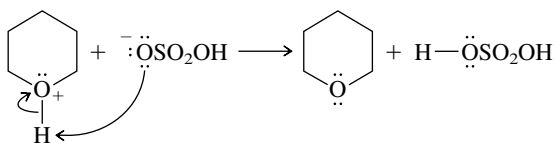
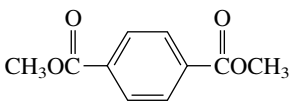
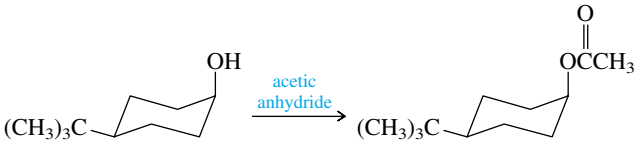
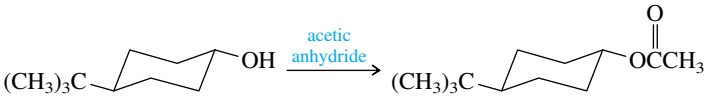


15.8 (b)



15.9

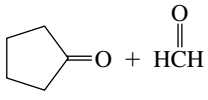




15.10 $O_2NOCH_2CHCH_2ONO_2$ (ONO$_2$ on the CH)

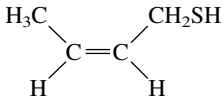
15.11 (b) $CH_3C(=O)(CH_2)_5CH_3$ (c) $CH_3(CH_2)_5CH(=O)$

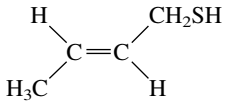
15.12 (b) One; (c) none

15.13 (b) $(CH_3)_2CHCH_2C(=O)H + C_6H_5CH_2C(=O)H$ (c) 

15.14 $CH_3(CH_2)_4CH_2OH \xrightarrow[\text{heat}]{HBr} CH_3(CH_2)_4CH_2Br \xrightarrow[2.\ NaOH]{1.\ (H_2N)_2C{=}S} CH_3(CH_2)_4CH_2SH$

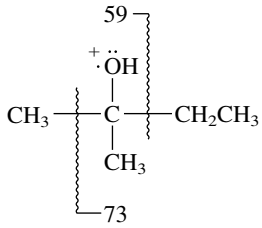
1-Hexanol 1-Bromohexane 1-Hexanethiol

15.15 $CH_3CH(CH_3)CH_2CH_2SH$ 

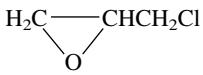


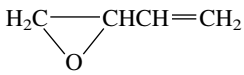
3-Methyl-1-butanethiol *cis*-2-Butene-1-thiol *trans*-2-Butene-1-thiol

15.16 The peak at *m/z* 70 corresponds to loss of water from the molecular ion. The peaks at *m/z* 59 and 73 correspond to the cleavages indicated:

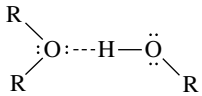


CHAPTER 16

16.1 (b) 

(c) 

16.2 1,2-Epoxybutane, 2546 kJ/mol (609.1 kcal/mol); tetrahydrofuran, 2499 kJ/mol (597.8 kcal/mol)

16.3 

16.4 1,4-Dioxane

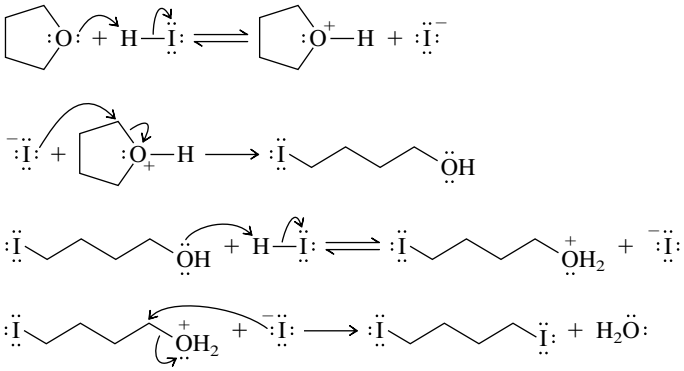
16.5 $(CH_3)_2C{=}CH_2 \xrightarrow{H^+} (CH_3)_2\overset{+}{C}{-}CH_3 \xrightarrow{HOCH_3} (CH_3)_3C{-}\overset{+}{O}(H)CH_3 \xrightarrow{-H^+} (CH_3)_3COCH_3$

16.6 $C_6H_5CH_2ONa + CH_3CH_2Br \longrightarrow C_6H_5CH_2OCH_2CH_3 + NaBr$
and $CH_2CH_2ONa + C_6H_5CH_2Br \longrightarrow C_6H_5CH_2OCH_2CH_3 + NaBr$

16.7 (b) $(CH_3)_2CHONa + CH_2{=}CHCH_2Br \longrightarrow CH_2{=}CHCH_2OCH(CH_3)_2 + NaBr$
(c) $(CH_3)_3COK + C_6H_5CH_2Br \longrightarrow (CH_3)_3COCH_2C_6H_5 + KBr$

16.8 $CH_3CH_2OCH_2CH_3 + 6O_2 \longrightarrow 4CO_2 + 5H_2O$

16.9 (b) $C_6H_5CH_2OCH_2C_6H_5$ (c) 

16.10 

16.11 Only the trans epoxide is chiral. As formed in this reaction, neither product is optically active.

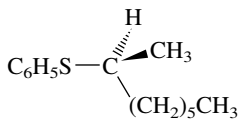
16.12 (b) $N_3CH_2CH_2OH$ (c) $HOCH_2CH_2OH$ (d) $C_6H_5CH_2CH_2OH$
(e) $CH_3CH_2C{\equiv}CCH_2CH_2OH$

16.13 Compound B

16.14 Compound A

16.15 *trans*-2-Butene gives *meso*-2,3-butanediol on epoxidation followed by acid-catalyzed hydrolysis. *cis*-2-Butene gives *meso*-2,3-butanediol on osmium tetraoxide hydroxylation.

16.16 The product has the *S* configuration.



16.17 Phenyl vinyl sulfoxide is chiral. Phenyl vinyl sulfone is achiral.

16.18 $CH_3SCH_3 + CH_3(CH_2)_{10}CH_2I$ will yield the same sulfonium salt. This combination is not as effective as $CH_3I + CH_3(CH_2)_{10}CH_2SCH_3$, because the reaction mechanism is S_N2 and CH_3I is more reactive than $CH_3(CH_2)_{10}CH_2I$ in reactions of this type because it is less crowded.

16.19 $CH_2{=}\overset{+}{O}(CH_3)CHCH_2CH_3$

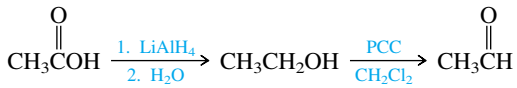
CHAPTER 17

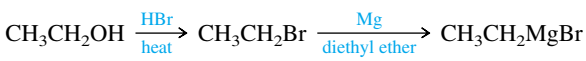
17.1 (b) Pentanedial; (c) 3-phenyl-2-propenal; (d) 4-hydroxy-3-methoxybenzaldehyde

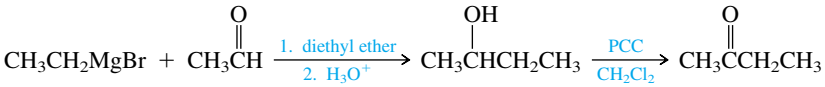
17.2 (b) 2-Methyl-3-pentanone; (c) 4,4-dimethyl-2-pentanone; (d) 4-penten-2-one

17.3 No. Carboxylic acids are inert to catalytic hydrogenation.

17.4



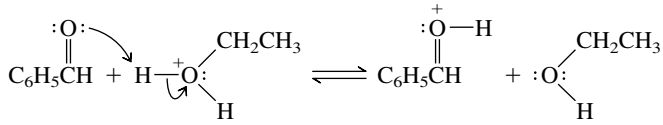




17.5 $Cl_3CCH(OH)_2$

17.6 $CH_2{=}C(CH_3)C{\equiv}N$

17.7 **Step 1:**



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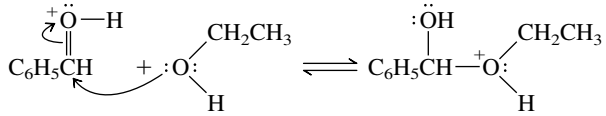

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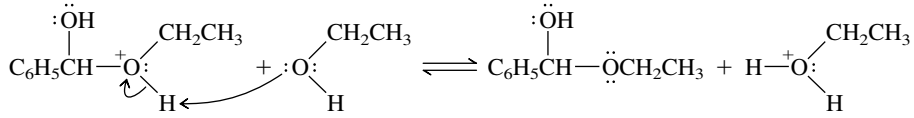
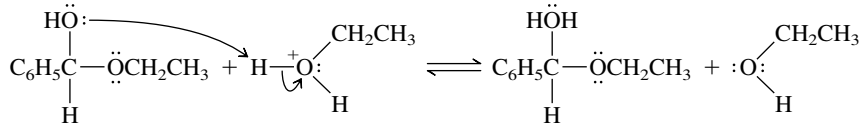
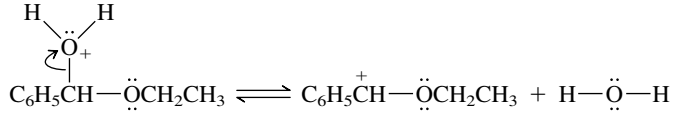


Formation of the hemiacetal is followed by loss of water to give a carbocation.

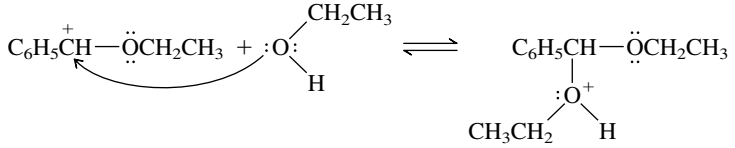
Step 4:



Step 5:



Step 6:



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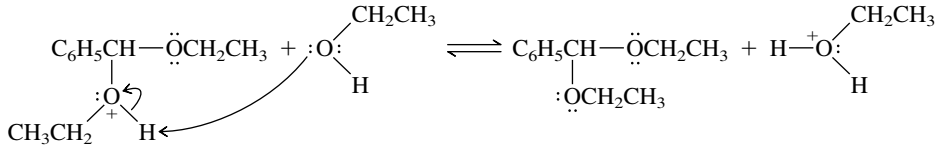
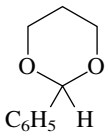
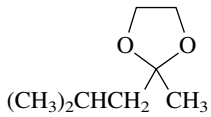


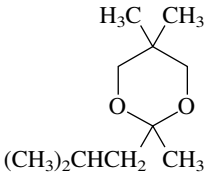
17.8 (b)



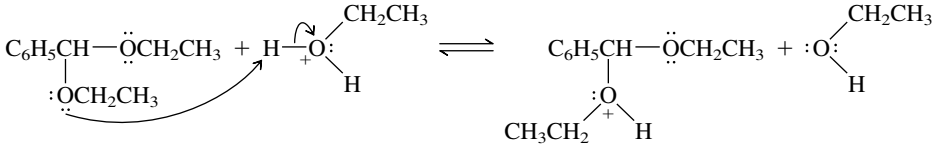
(c)



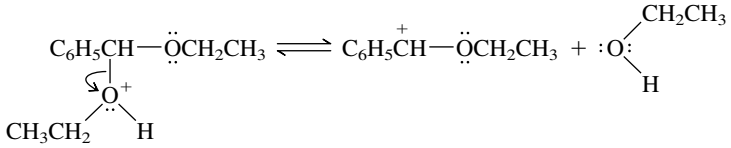
(d)



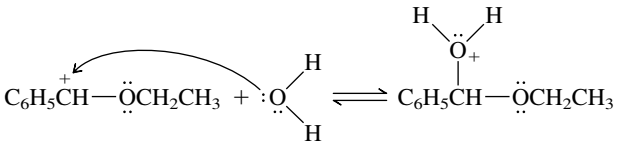
17.9 **Step 1:**



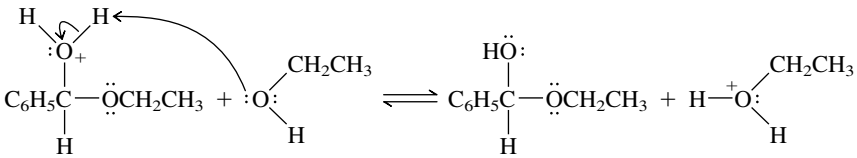
Step 2:



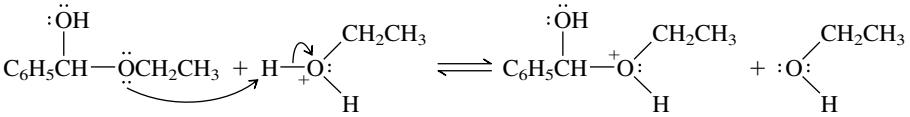
Step 3:



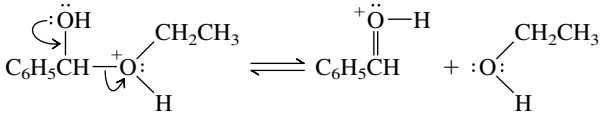
Step 4:



Step 5:



Step 6:



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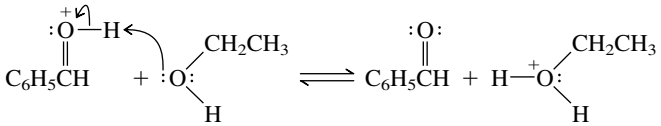
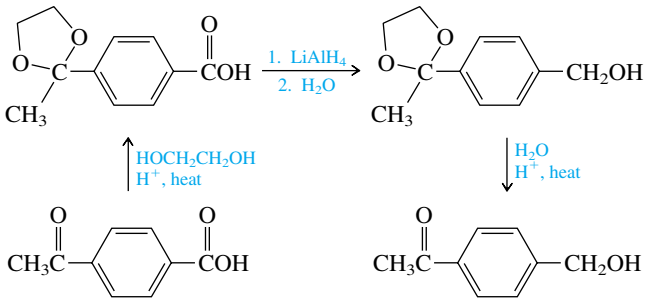
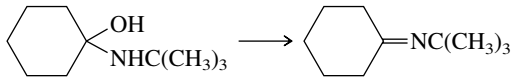


17.10

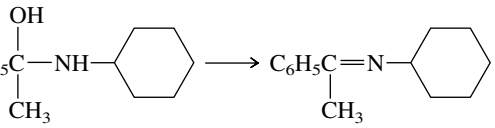


17.11 (b) $C_6H_5CH(OH)NHCH_2CH_2CH_2CH_3 \longrightarrow C_6H_5CH{=}NCH_2CH_2CH_2CH_3$

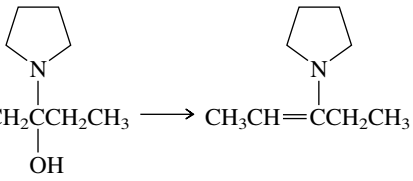
(c)



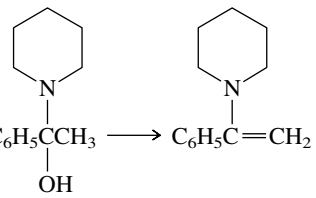
(d)



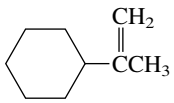
17.12 (b)



(c)



17.13 (b) $CH_3CH_2CH_2CH{=}CHCH{=}CH_2$ (c)



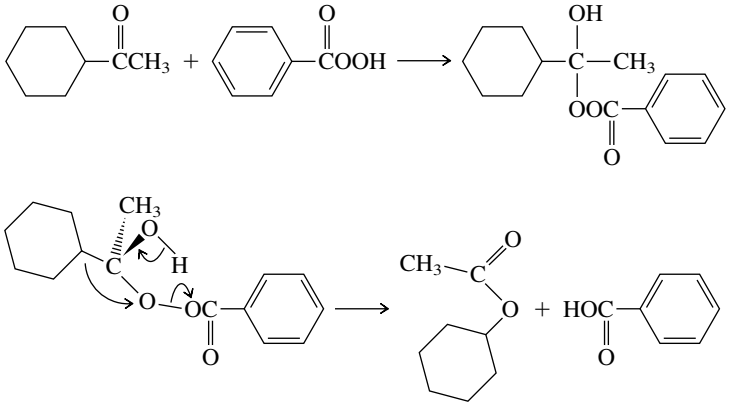
17.14 $(C_6H_5)_3P{=}CH_2$

17.15 (b) $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H + (C_6H_5)_3\overset{+}{P}-\ddot{\overset{-}{C}}H_2$ or $H\overset{O}{\overset{\|}{C}}H + CH_3CH_2CH_2\ddot{\overset{-}{C}}H-\overset{+}{P}(C_6H_5)_3$

17.16 $CH_3\underset{Br}{CH}CH_2CH_3 + (C_6H_5)_3P: \longrightarrow CH_3\underset{{}^{+}P(C_6H_5)_3}{CH}CH_2CH_3\ Br^-$

$CH_3\underset{{}^{+}P(C_6H_5)_3}{CH}CH_2CH_3\ Br^- \xrightarrow[DMSO]{NaCH_2\overset{O}{\overset{\|}{S}}CH_3} CH_3\ddot{\overset{-}{C}}HCH_2CH_3$ (${}^{+}P(C_6H_5)_3$)

17.17



17.18 Hydrogen migrates to oxygen (analogous to a hydride shift in a carbocation).

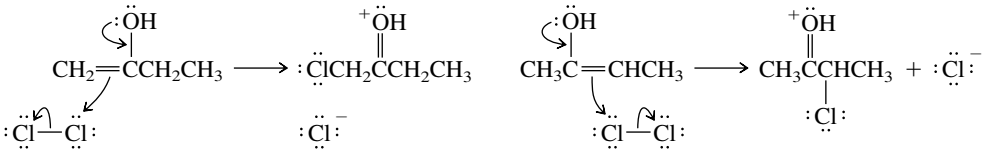
CHAPTER 18

18.1 (b) Zero; (c) five; (d) four

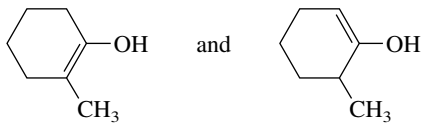
18.2 $ClCH_2CCH_2CH_3$ and CH_3CCHCH_3 (Cl)

18.3 $CH_2{=}CCH_2CH_3 \xrightarrow{Cl_2} ClCH_2CCH_2CH_3$ $\quad$ $CH_3C{=}CHCH_3 \xrightarrow{Cl_2} CH_3CCHCH_3$ (Cl)

18.4



18.5 (b) $C_6H_5C{=}CH_2$ (OH) (c)

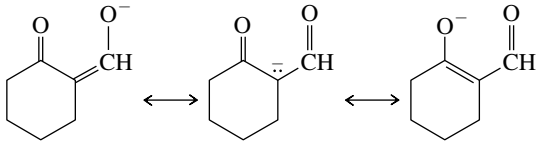


and

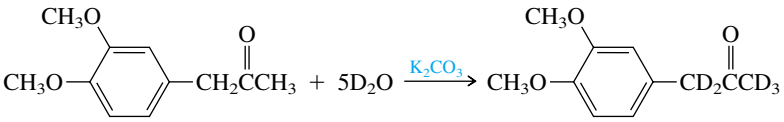
18.6 (b) $C_6H_5CCH{=}CCH_3$ (O, HO) and $C_6H_5C{=}CHCCH_3$ (OH, O)

18.7 (b) $C_6H_5CCH{=}CCH_3 \longleftrightarrow C_6H_5CCHCCH_3 \longleftrightarrow C_6H_5C{=}CHCCH_3$ (O, O⁻)

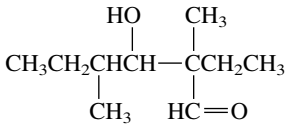
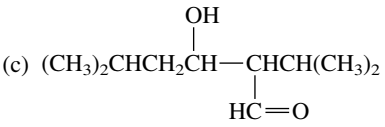
(c)

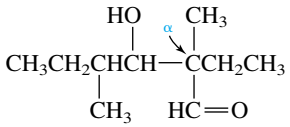


18.8 Hydrogen–deuterium exchange at α carbons via enolate:

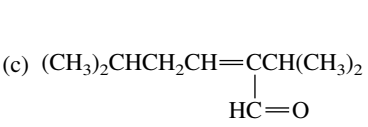


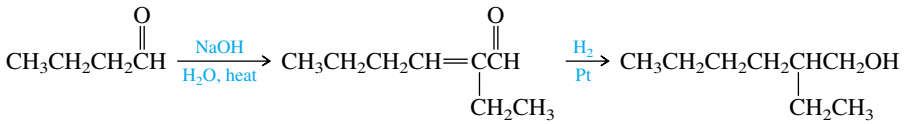
18.9 Product is chiral, but is formed as a racemic mixture because it arises from an achiral intermediate (the enol); it is therefore not optically active.

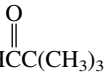
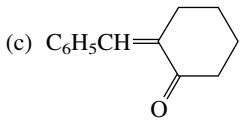
18.10 (b)  (c) 

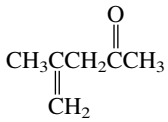
18.11 (b) 

Cannot dehydrate; no protons on α-carbon atom

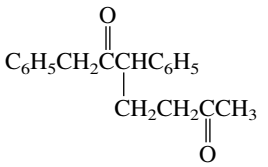
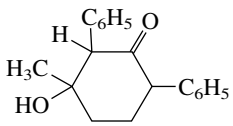
(c) 

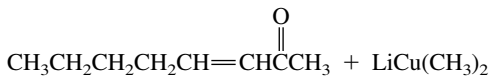
18.12 

18.13 (b)  (c) 

18.14 

18.15 Acrolein ($CH_2{=}CHCH{=}O$) undergoes conjugate addition with sodium azide in aqueous solution to give $N_3CH_2CH_2CH{=}O$. Propanal is not an α,β-unsaturated carbonyl compound and cannot undergo conjugate addition.

18.16  and 

18.17 

CHAPTER 19

19.1 (b) (*E*)-2-butenoic acid; (c) ethanedioic acid; (d) *p*-methylbenzoic acid or 4-methylbenzoic acid.

19.2 The negative charge in $CH_3\overset{\overset{O}{\|}}{C}OO^-$ cannot be delocalized into the carbonyl group.

19.3 (b) $CH_3CO_2H + (CH_3)_3CO^- \rightleftharpoons CH_3CO_2^- + (CH_3)_3COH$
(The position of equilibrium lies to the right.)
(c) $CH_3CO_2H + Br^- \rightleftharpoons CH_3CO_2^- + HBr$
(The position of equilibrium lies to the left.)
(d) $CH_3CO_2H + HC{\equiv}C{:}^- \rightleftharpoons CH_3CO_2^- + HC{\equiv}CH$
(The position of equilibrium lies to the right.)
(e) $CH_3CO_2H + NO_3^- \rightleftharpoons CH_3CO_2^- + HNO_3$
(The position of equilibrium lies to the left.)
(f) $CH_3CO_2H + H_2N^- \rightleftharpoons CH_3CO_2^- + NH_3$
(The position of equilibrium lies to the right.)

19.4 (b) $CH_3\underset{\underset{OH}{|}}{C}HCO_2H$ (c) $CH_3\overset{\overset{O}{\|}}{C}CO_2H$ (d) $CH_3\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}CH_2CO_2H$

19.5 $HC{\equiv}CCO_2H$

19.6 The "true K_1" for carbonic acid is 1.4×10^{-4}.

19.7 (b) The conversion proceeding by way of the nitrile is satisfactory.

$$HOCH_2CH_2Cl \xrightarrow{NaCN} HOCH_2CH_2CN \xrightarrow{\text{hydrolysis}} HOCH_2CH_2CO_2H$$

Since 2-chloroethanol has a proton bonded to oxygen, it is not an appropriate substrate for conversion to a stable Grignard reagent.

(c) The procedure involving a Grignard reagent is satisfactory.

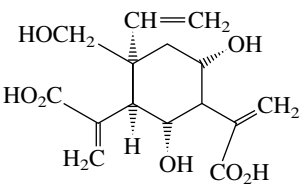
$$(CH_3)_3CCl \xrightarrow{Mg} (CH_3)_3CMgCl \xrightarrow[2.\ H_3O^+]{1.\ CO_2} (CH_3)_3CCO_2H$$

The reaction of *tert*-butyl chloride with cyanide ion proceeds by elimination rather than substitution.

19.8 Water labeled with ^{18}O adds to benzoic acid to give the tetrahedral intermediate shown. This intermediate can lose unlabeled H_2O to give benzoic acid containing ^{18}O.

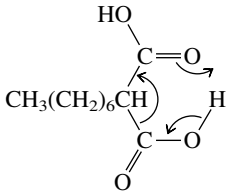
$$\overset{\overset{^{18}O}{\|}}{C_6H_5COH} \xleftarrow{-H_2O} C_6H_5\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}{-}{}^{18}OH \xrightarrow{-H_2O} \overset{\overset{O}{\|}}{C_6H_5C}{-}{}^{18}OH$$

19.9 (b) $HOCH_2(CH_2)_{13}CO_2H$; (c)

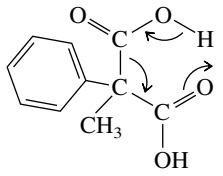


19.10 $CH_3(CH_2)_{15}CH_2CO_2H \xrightarrow[PCl_3]{Br_2} CH_3(CH_2)_{15}\underset{\underset{Br}{|}}{C}HCO_2H \xrightarrow[acetone]{NaI} CH_3(CH_2)_{15}\underset{\underset{I}{|}}{C}HCO_2H$

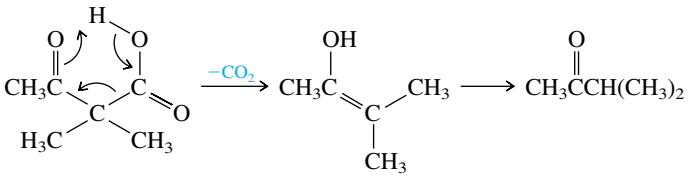
19.11 (b) $CH_3(CH_2)_6CH_2CO_2H$ via



(c) $C_6H_5CHCO_2H$ (CH$_3$ on the α-carbon) via



19.12 (b)



CHAPTER 20

20.1 (b) $CH_3CH_2CH(C_6H_5)COC(C_6H_5)CHCH_2CH_3$ (c) $CH_3CH_2CH(C_6H_5)COCH_2CH_2CH_2CH_3$

(d) $CH_3CH_2CH_2COCH_2CH(C_6H_5)CH_2CH_3$ (e) $CH_3CH_2CH(C_6H_5)CNH_2$

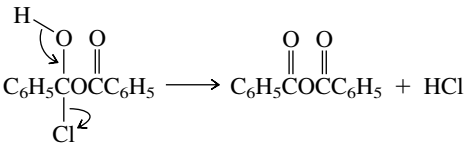
(f) $CH_3CH_2CH(C_6H_5)CNHCH_2CH_3$ (g) $CH_3CH_2CH(C_6H_5)C{\equiv}N$

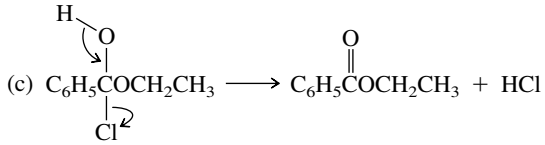
20.2 Rotation about the carbon–nitrogen bond is slow in amides. The methyl groups of *N,N*-dimethylformamide are nonequivalent because one is cis to oxygen, the other cis to hydrogen.

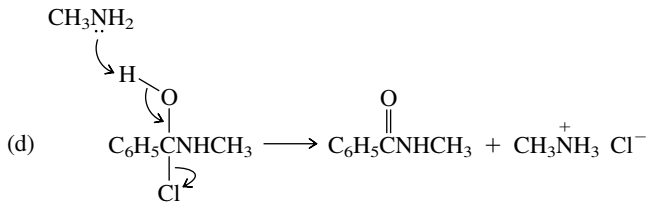
20.3 (b) $C_6H_5COCOC_6H_5$ (c) $C_6H_5COCH_2CH_3$ (d) $C_6H_5CNHCH_3$

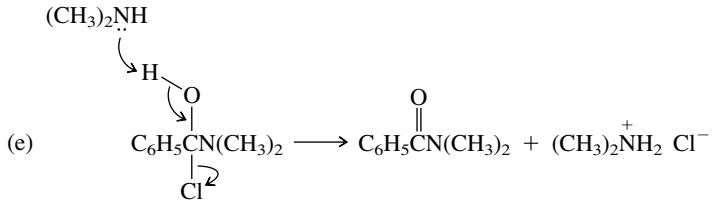
(e) $C_6H_5CN(CH_3)_2$ (f) C_6H_5COH

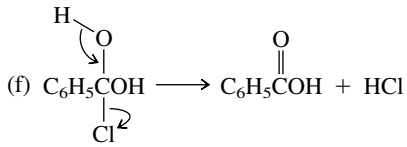
20.4 (b)

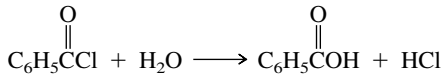


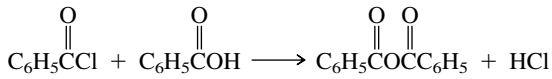
(c) 

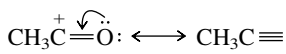
(d) 

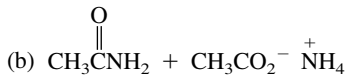
(e) 

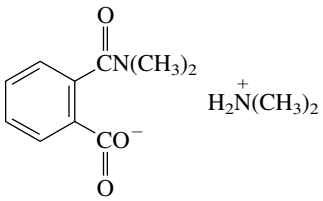
(f) 

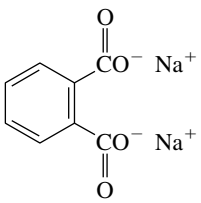
20.5 



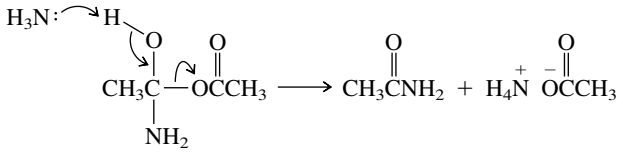
20.6 

20.7 (b) 

(c) 

(d) 

20.8 (b)



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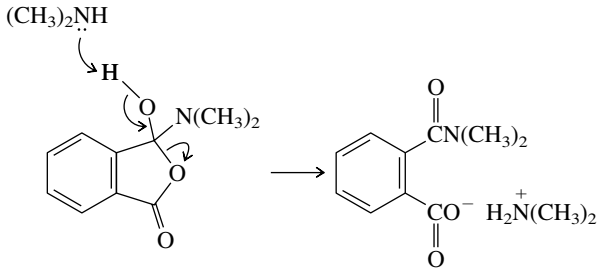

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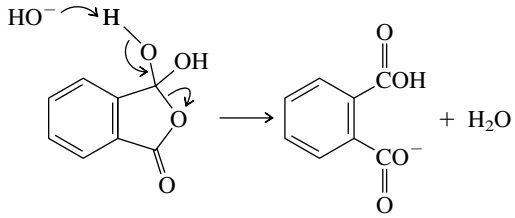
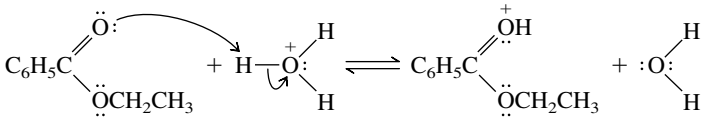
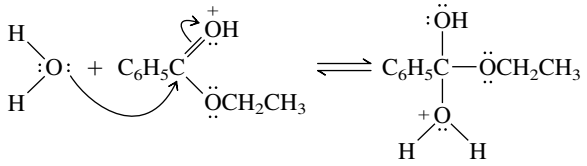


20.9 $HOCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_2CH_2OH$ ($C_5H_{12}O_3$) and CH_3CO_2H

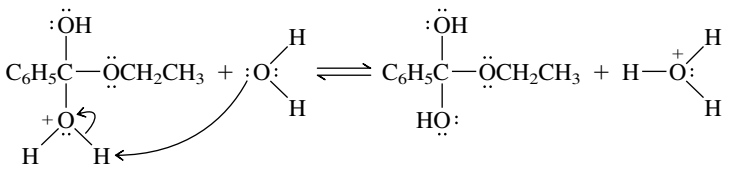
20.10 **Step 1:** Protonation of the carbonyl oxygen



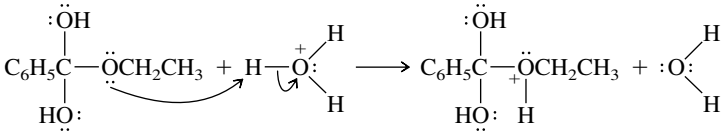
Step 2: Nucleophilic addition of water



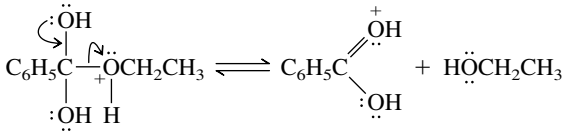
Step 3: Deprotonation of oxonium ion to give neutral form of tetrahedral intermediate



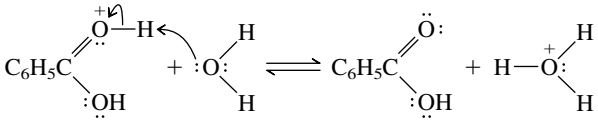
Step 4: Protonation of ethoxy oxygen



Step 5: Dissociation of protonated form of tetrahedral intermediate

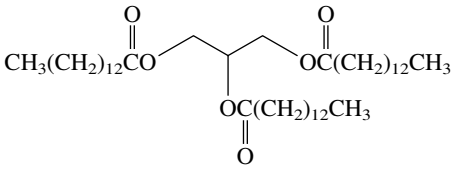


Step 6: Deprotonation of protonated form of benzoic acid



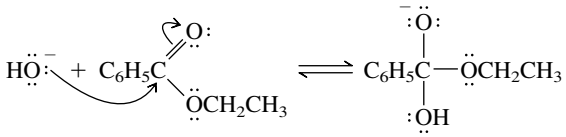
20.11 The carbonyl oxygen of the lactone became labeled with ^{18}O.

20.12

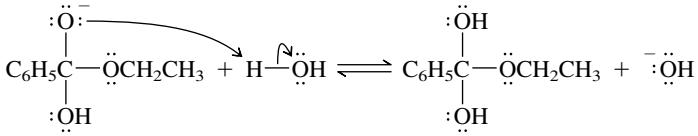


20.13 The isotopic label appeared in the acetate ion.

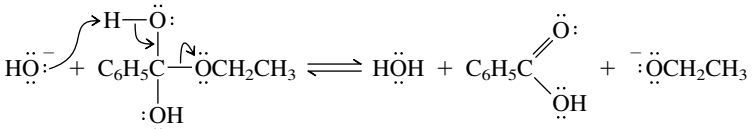
20.14 Step 1: Nucleophilic addition of hydroxide ion to the carbonyl group



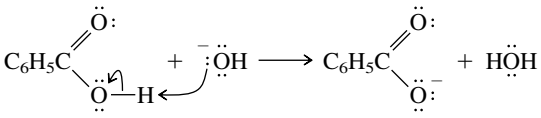
Step 2: Proton transfer from water to give neutral form of tetrahedral intermediate



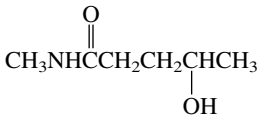
Step 3: Hydroxide ion-promoted dissociation of tetrahedral intermediate



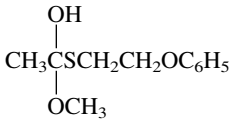
Step 4: Proton abstraction from benzoic acid



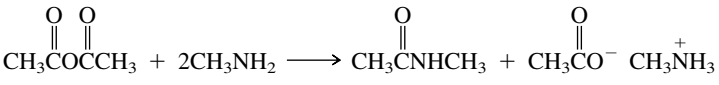
20.15



20.16

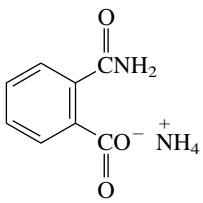


20.17 (b)

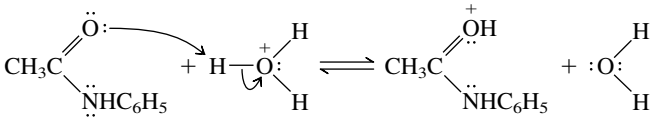


(c)

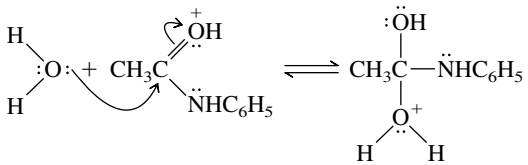
20.18



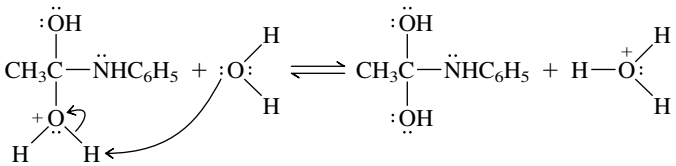
20.19 Step 1: Protonation of the carbonyl oxygen



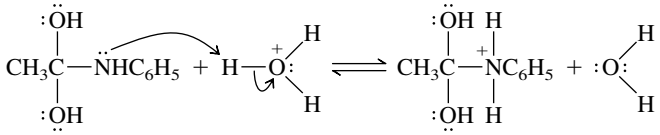
Step 2: Nucleophilic addition of water



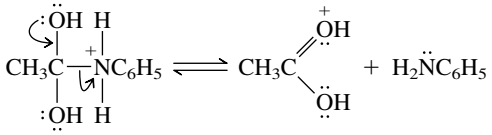
Step 3: Deprotonation of oxonium ion to give neutral form of tetrahedral intermediate



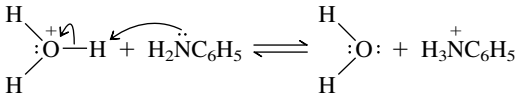
Step 4: Protonation of amino group of tetrahedral intermediate

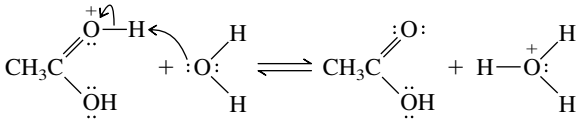


Step 5: Dissociation of N-protonated form of tetrahedral intermediate

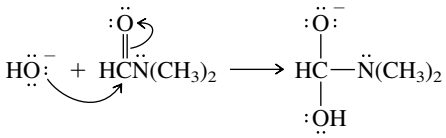


Step 6: Proton-transfer processes

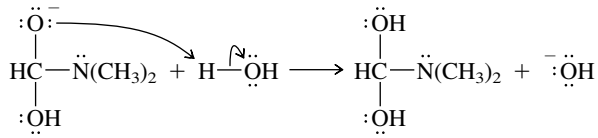




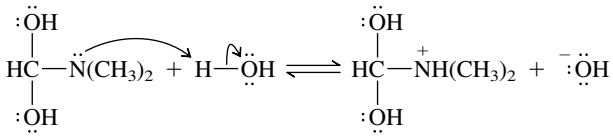
20.20 Step 1: Nucleophilic addition of hydroxide ion to the carbonyl group



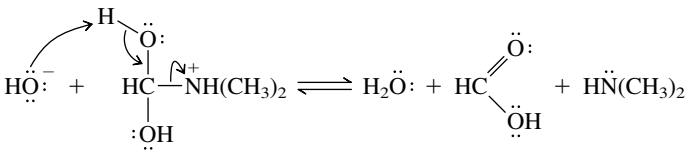
Step 2: Proton transfer to give neutral form of tetrahedral intermediate



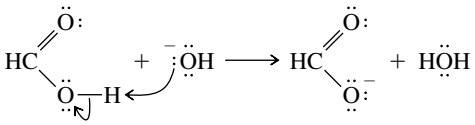
Step 3: Proton transfer from water to nitrogen of tetrahedral intermediate



Step 4: Dissociation of N-protonated form of tetrahedral intermediate



Step 5: Irreversible formation of formate ion

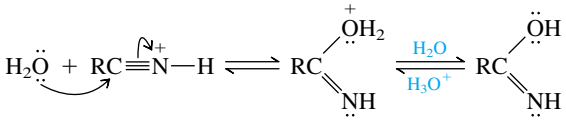


20.21 $CH_3CH_2CH_2CO_2H \xrightarrow[2.\ NH_3]{1.\ SOCl_2} CH_3CH_2CH_2CNH_2 \xrightarrow[H_2O,\ NaOH]{Br_2} CH_3CH_2CH_2NH_2$

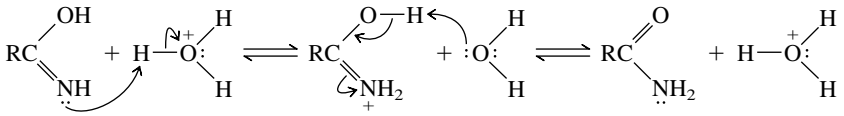
20.22 $CH_3CH_2OH \xrightarrow[H_2SO_4,\ heat]{Na_2Cr_2O_7,\ H_2O} CH_3COH \xrightarrow[2.\ NH_3]{1.\ SOCl_2} CH_3CNH_2 \xrightarrow{P_4O_{10}} CH_3C{\equiv}N$

$CH_3CH_2OH \xrightarrow[or\ HBr]{PBr_3} CH_3CH_2Br \xrightarrow{NaCN} CH_3CH_2CN$

20.23 In acid, the nitrile is protonated on nitrogen. Nucleophilic addition of water yields an imino acid.



A series of proton transfers converts the imino acid to an amide.



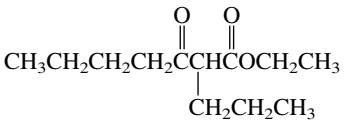
20.24 $CH_3CH_2CN + C_6H_5MgBr \xrightarrow[2.\ H_2O,\ H^+,\ heat]{1.\ diethyl\ ether} C_6H_5CCH_2CH_3$

The imine intermediate is $C_6H_5\overset{\overset{NH}{\|}}{C}CH_2CH_3$.

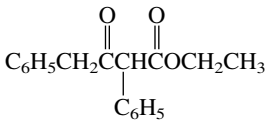
CHAPTER 21

21.1 Ethyl benzoate cannot undergo the Claisen condensation.

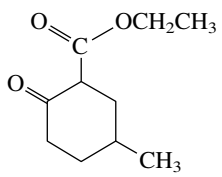
Claisen condensation product of ethyl pentanoate:



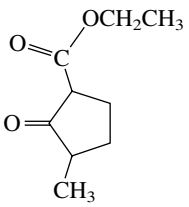
Claisen condensation product of ethyl phenylacetate:



21.2 (b)

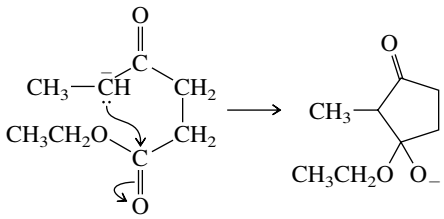


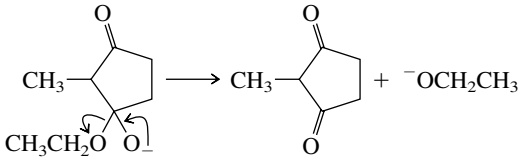
(c)



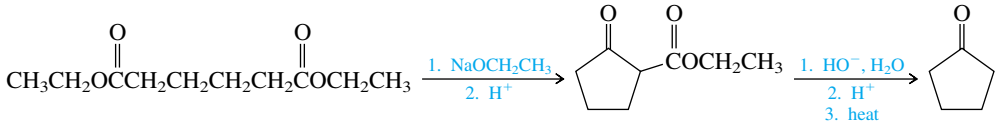
21.3 (b) $C_6H_5CHCCOCH_2CH_3$ (with $COCH_2CH_3$ and O) (c) C_6H_5CHCH (with $COCH_2CH_3$ and O)

21.4





21.5



21.6 (b) $C_6H_5CH_2Br + CH_3CCH_2COCH_2CH_3$ → (1. $NaOCH_2CH_3$; 2. HO^-, H_2O; 3. H^+; 4. heat) → $C_6H_5CH_2CH_2CCH_3$

(c) $CH_2{=}CHCH_2Br + CH_3CCH_2COCH_2CH_3$ → (1. $NaOCH_2CH_3$; 2. HO^-, H_2O; 3. H^+; 4. heat) → $CH_2{=}CHCH_2CH_2CCH_3$

21.7 (b) $CH_3(CH_2)_5CH_2Br + CH_2(COOCH_2CH_3)_2$ → ($NaOCH_2CH_3$, ethanol) → $CH_3(CH_2)_5CH_2CH(COOCH_2CH_3)_2$ → (1. HO^-, H_2O; 2. H^+; 3. heat) → $CH_3(CH_2)_5CH_2CH_2COH$

(c) $CH_3CH_2CHCH_2Br + CH_2(COOCH_2CH_3)_2$ → ($NaOCH_2CH_3$, ethanol) → $CH_3CH_2CHCH_2CH(COOCH_2CH_3)_2$ → (1. HO^-, H_2O; 2. H^+; 3. heat) → $CH_3CH_2CHCH_2CH_2COH$

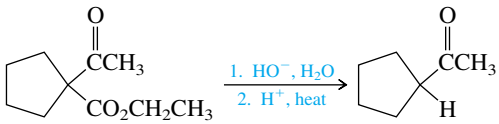
(d) $C_6H_5CH_2Br + CH_2(COOCH_2CH_3)_2 \xrightarrow[\text{ethanol}]{NaOCH_2CH_3}$

$$C_6H_5CH_2CH(COOCH_2CH_3)_2 \xrightarrow[3.\ \text{heat}]{1.\ HO^-,\ H_2O;\ 2.\ H^+} C_6H_5CH_2CH_2COH$$

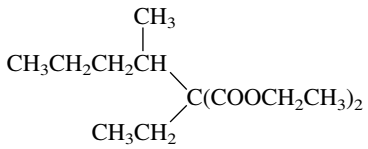
21.8 $CH_3CCH_2COCH_2CH_3 \xrightarrow[CH_3Br]{NaOCH_2CH_3} CH_3CCHCOCH_2CH_3 \xrightarrow[CH_3Br]{NaOCH_2CH_3}$ (CH$_3$ branch)

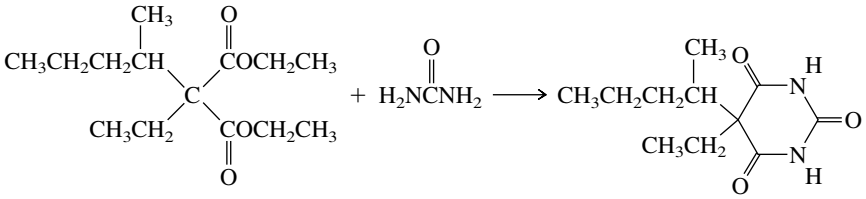
$$CH_3CCCOCH_2CH_3 \xrightarrow[3.\ \text{heat}]{1.\ HO^-,\ H_2O;\ 2.\ H^+} CH_3CCH(CH_3)_2$$
(H$_3$C, CH$_3$ branch)

21.9 $CH_3CCH_2COCH_2CH_3 + BrCH_2CH_2CH_2CH_2Br \xrightarrow{NaOCH_2CH_3}$

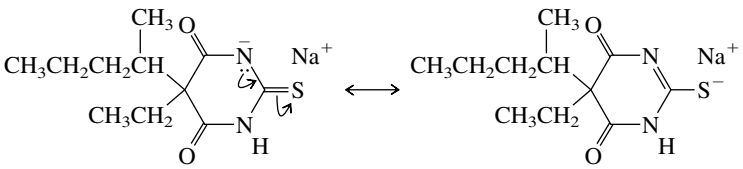


21.10 $CH_2(COOCH_2CH_3)_2 \xrightarrow[2.\ NaOCH_2CH_3,\ CH_3CH_2Br]{1.\ NaOCH_2CH_3,\ CH_2CH_2CH_2CHCH_3(Br)}$



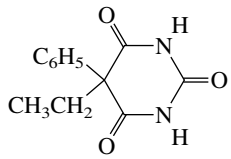


21.11

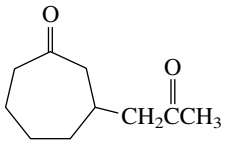


21.12 $C_6H_5CH_2COCH_2CH_3 + CH_3CH_2OCOCH_2CH_3 \xrightarrow{NaOCH_2CH_3} C_6H_5CH(COOCH_2CH_3)_2$

$$C_6H_5CH(COOCH_2CH_3)_2 \xrightarrow[CH_3CH_2Br]{NaOCH_2CH_3} C_6H_5C(COOCH_2CH_3)_2 \xrightarrow{H_2NCNH_2}$$
(CH$_2$CH$_3$ branch)

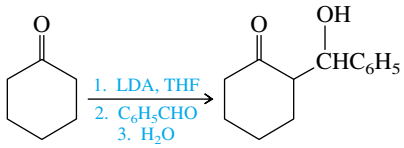


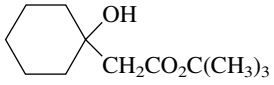
21.13



21.14 (b) $C_6H_5CH_2CO_2CH_3 \xrightarrow[2.\ CH_3I]{1.\ LDA,\ THF} C_6H_5CHCO_2CH_3$ (with CH_3 branch)

(c)



(d) $CH_3CO_2C(CH_3)_3 \xrightarrow[2.\ \text{cyclohexanone}\ 3.\ H_2O]{1.\ LDA,\ THF}$ 

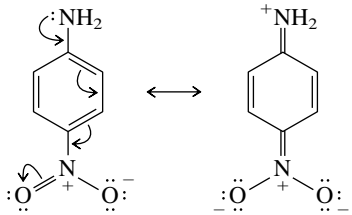
CHAPTER 22

22.1 (b) 1-Phenylethanamine or 1-phenylethylamine; (c) 2-propen-1-amine or allylamine

22.2 *N,N*-Dimethylcycloheptanamine

22.3 Tertiary amine; *N*-ethyl-4-isopropyl-*N*-methylaniline

22.4

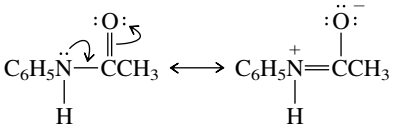


22.5 $pK_b = 6$; K_a of conjugate acid $= 1 \times 10^{-8}$; pK_a of conjugate acid $= 8$

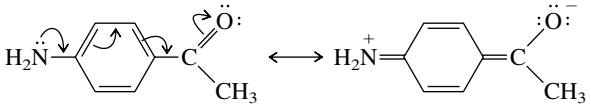
22.6 $\log (CH_3NH_3^+/CH_3NH_2) = 10.7 - 7 = 3.7$; $(CH_3NH_3^+/CH_3NH_2) = 10^{3.7} = 5000$

22.7 Tetrahydroisoquinoline is a stronger base than tetrahydroquinoline. The unshared electron pair of tetrahydroquinoline is delocalized into the aromatic ring, and this substance resembles aniline in its basicity, whereas tetrahydroisoquinoline resembles an alkylamine.

22.8 (b) The lone pair of nitrogen is delocalized into the carbonyl group by amide resonance.

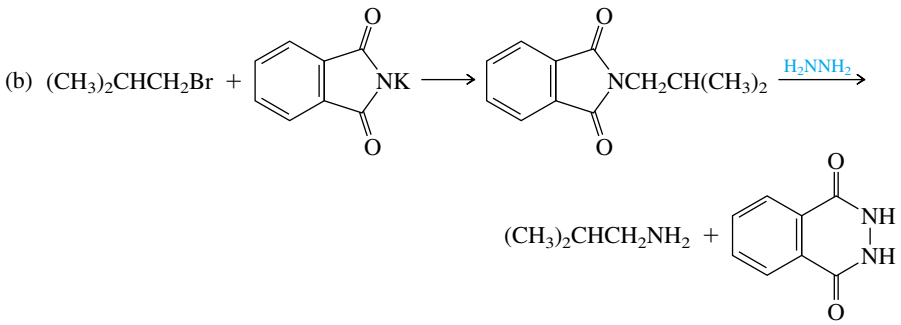


(c) The amino group is conjugated to the carbonyl group through the aromatic ring.



22.9 $CH_2{=}CHCH_3 \xrightarrow[400°C]{Cl_2} CH_2{=}CHCH_2Cl \xrightarrow{NH_3} CH_2{=}CHCH_2NH_2$

22.10 Isobutylamine and 2-phenylethylamine can be prepared by the Gabriel synthesis; *tert*-butylamine, *N*-methylbenzylamine, and aniline cannot.



22.11 (b) Prepare *p*-isopropylnitrobenzene as in part (a); then reduce with H_2, Ni (or Fe + HCl or Sn + HCl, followed by base). (c) Prepare isopropylbenzene as in part (a); then dinitrate with HNO_3 + H_2SO_4; then reduce both nitro groups. (d) Chlorinate benzene with Cl_2 + $FeCl_3$; then nitrate (HNO_3, H_2SO_4), separate the desired para isomer from the unwanted ortho isomer, and reduce. (e) Acetylate benzene by a Friedel–Crafts reaction (acetyl chloride + $AlCl_3$); then nitrate (HNO_3, H_2SO_4); then reduce the nitro group.

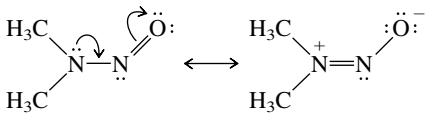
22.12 (b) $C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}H + C_6H_5CH_2NH_2 \xrightarrow{H_2,\ Ni} C_6H_5CH_2NHCH_2C_6H_5$

(c) $C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}H + (CH_3)_2NH \xrightarrow{H_2,\ Ni} C_6H_5CH_2N(CH_3)_2$

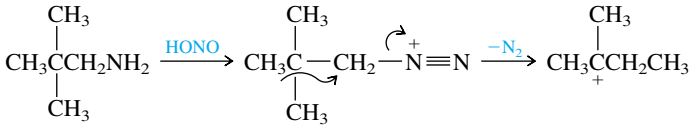
(d) $C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}H$ +  $\xrightarrow{H_2,\ Ni}$ $C_6H_5CH_2-N$ 

22.13 (b) $(CH_3)_3CCH_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$ (c) $CH_2{=}CH_2$

22.14 (b) Prepare acetanilide as in part (a); dinitrate (HNO_3, H_2SO_4); then hydrolyze the amide in either acid or base. (c) Prepare *p*-nitroacetanilide as in part (a); then reduce the nitro group with H_2 (or Fe + HCl or Sn + HCl, followed by base).

22.15 

22.16 The diazonium ion from 2,2-dimethylpropylamine rearranges via a methyl shift on loss of nitrogen to give 1,1-dimethylpropyl cation.



22.17 Intermediates: benzene to nitrobenzene to *m*-bromonitrobenzene to *m*-bromoaniline to *m*-bromophenol. Reagents: HNO_3, H_2SO_4; Br_2, $FeBr_3$; Fe, HCl then HO^-; $NaNO_2$, H_2SO_4, H_2O, then heat in H_2O.

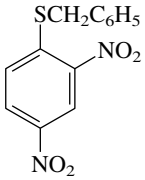
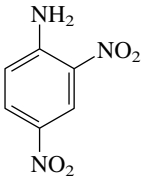
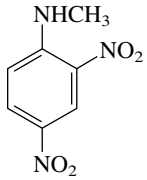
22.18 Prepare *m*-bromoaniline as in Problem 22.17; then $NaNO_2$, HCl, H_2O followed by KI.

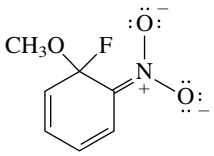
22.19 Intermediates: benzene to ethyl phenyl ketone to ethyl *m*-nitrophenyl ketone to *m*-aminophenyl ethyl ketone to ethyl *m*-fluorophenyl ketone. Reagents: propanoyl chloride, $AlCl_3$; HNO_3, H_2SO_4; Fe, HCl, then HO^-; $NaNO_2$, H_2O, HCl, then HBF_4, then heat.

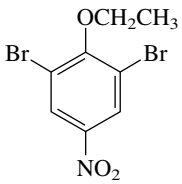
22.20 Intermediates: isopropylbenzene to *p*-isopropylnitrobenzene to *p*-isopropylaniline to *p*-isopropylacetanilide to 4-isopropyl-2-nitroacetanilide to 4-isopropyl-2-nitroaniline to *m*-isopropylnitrobenzene. Reagents: HNO_3, H_2SO_4; Fe, HCl, then HO^-; acetyl chloride; HNO_3, H_2SO_4; acid or base hydrolysis; $NaNO_2$, HCl, H_2O, and CH_3CH_2OH or H_3PO_2.

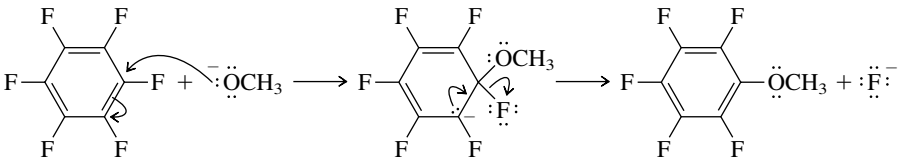
CHAPTER 23

23.1 $C_6H_5CH_2Cl$

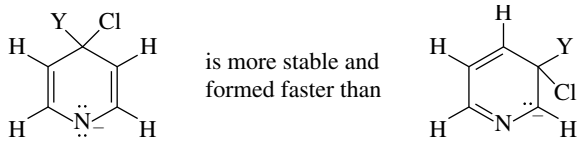
23.2 (b)  (c)  (d) 

23.3 

23.4 

23.5 

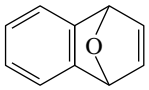
23.6 Nitrogen bears a portion of the negative charge in the anionic intermediate formed in the nucleophilic addition step in 4-chloropyridine, but not in 3-chloropyridine.



23.7 A benzyne intermediate is impossible because neither of the carbons ortho to the intended leaving group bears a proton.

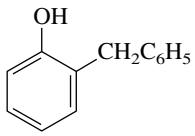
23.8 3-Methylphenol and 4-methylphenol (*m*-cresol and *p*-cresol)

23.9

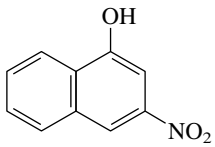


CHAPTER 24

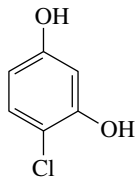
24.1 (b)



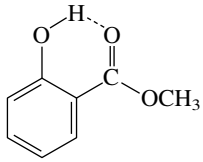
(c)



(d)

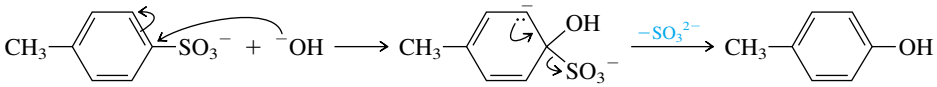


24.2 Methyl salicylate is the methyl ester of *o*-hydroxybenzoic acid. Intramolecular (rather than intermolecular) hydrogen bonding is responsible for its relatively low boiling point.

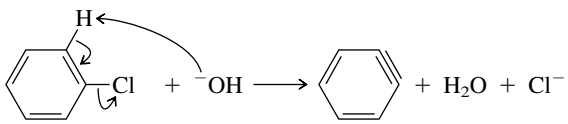


24.3 (b) *p*-Cyanophenol is stronger acid because of conjugation of cyano group with phenoxide oxygen. (c) *o*-Fluorophenol is stronger acid because electronegative fluorine substituent can stabilize negative charge better when fewer bonds intervene between it and the phenoxide oxygen.

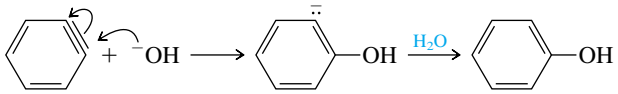
24.4



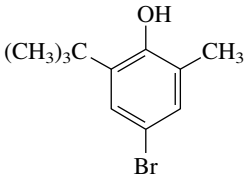
24.5



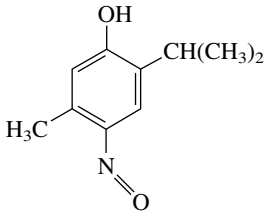
then



24.6 (b)



(c)



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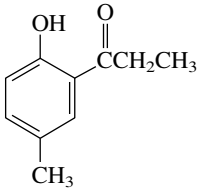
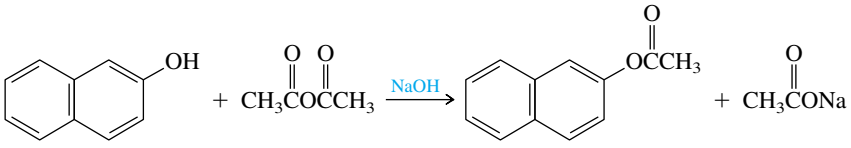


24.7 (b)

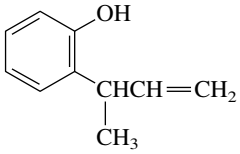


(c) $C_6H_5OH + C_6H_5CCl \longrightarrow C_6H_5OCC_6H_5 + HCl$

24.8 $C_6H_5OCH_2CHCH_3$ (OH)

24.9 *p*-Fluoronitrobenzene and phenol (as its sodium or potassium salt)

24.10

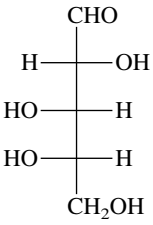


CHAPTER 25

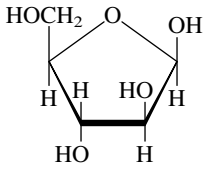
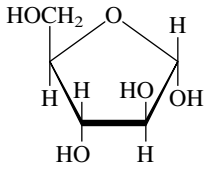
25.1 (b) L-Glyceraldehyde; (c) D-glyceraldehyde

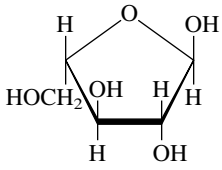
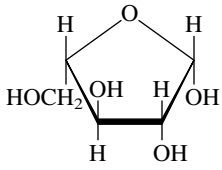
25.2 L-Erythrose

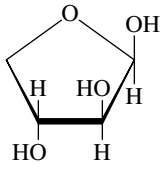
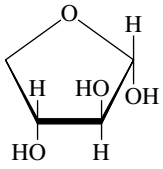
25.3

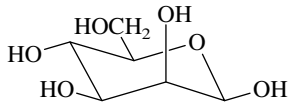
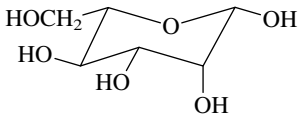


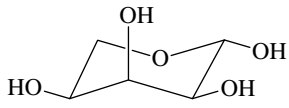
25.4 L-Talose

25.5 (b)  and 

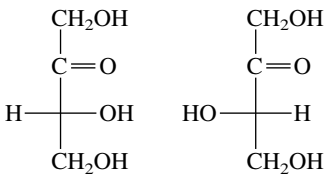
(c)  and 

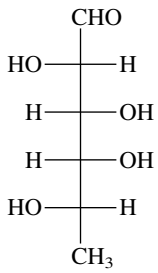
(d)  and 

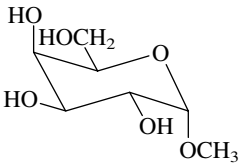
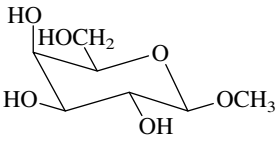
25.6 (b)  (c) 

(d) 

25.7 67% α, 33% β

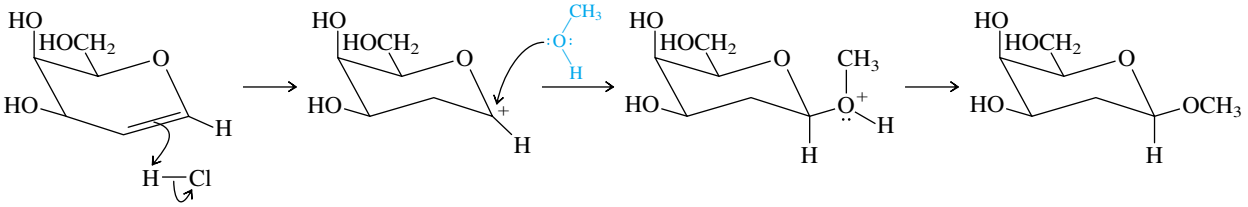
25.8 

25.9 (b) 

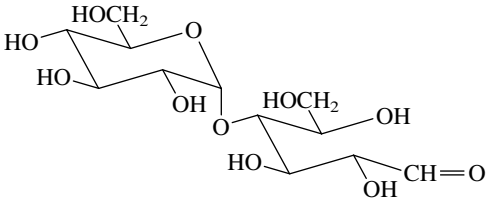
25.10  

α β

25.11 The mechanism for formation of the β-methyl glycoside is shown. The mechanism for formation of the α isomer is the same except that methanol approaches the carbocation from the axial direction.



25.12



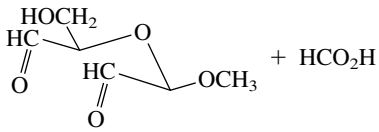
25.13 No. The product is a meso form.

25.14 All (b) through (f) will give positive tests.

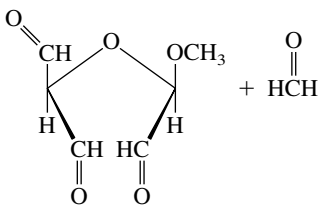
25.15 L-Gulose

25.16 The intermediate is an enediol, $HOCH{=}CCH_2OP(OH)_2$ (with OH on the central carbon).

25.17 (b) Four equivalents of periodic acid are required. One molecule of formaldehyde and four molecules of formic acid are formed from each molecule of D-ribose.
(c) Two equivalents



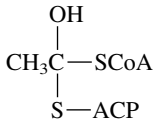
(d) Two equivalents



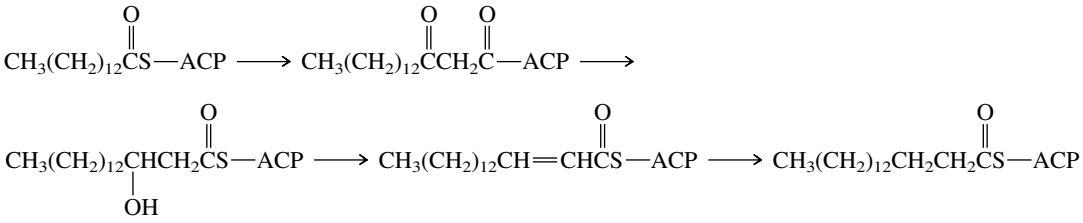
CHAPTER 26

26.1 Hydrolysis gives $CH_3(CH_2)_{16}CO_2H$ (2 mol) and (*Z*)-$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$ (1 mol). The same mixture of products is formed from 1-oleyl-2,3-distearylglycerol.

26.2

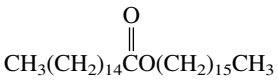


26.3

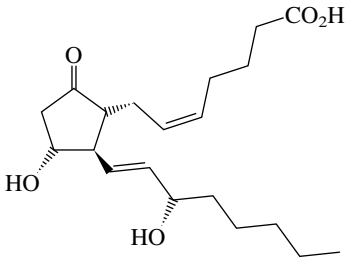


26.4 *R* in both cases

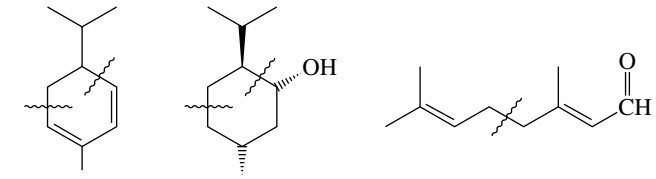
26.5



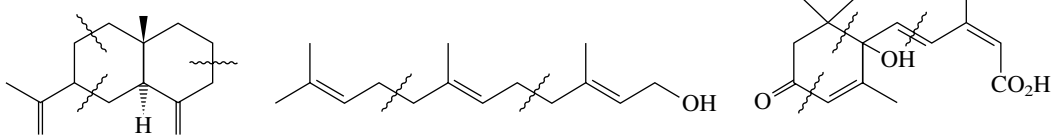
26.6



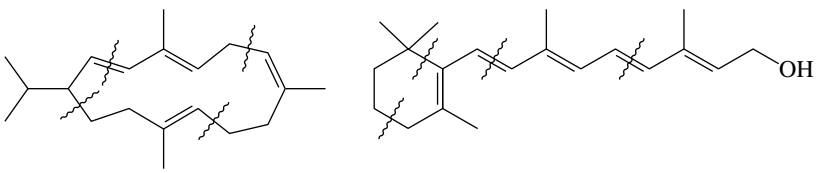
26.7



α-Phellandrene Menthol Citral

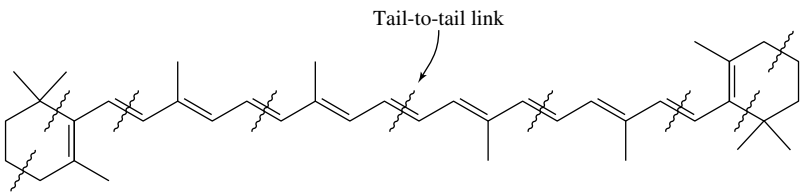


α-Selinene Farnesol Abscisic acid

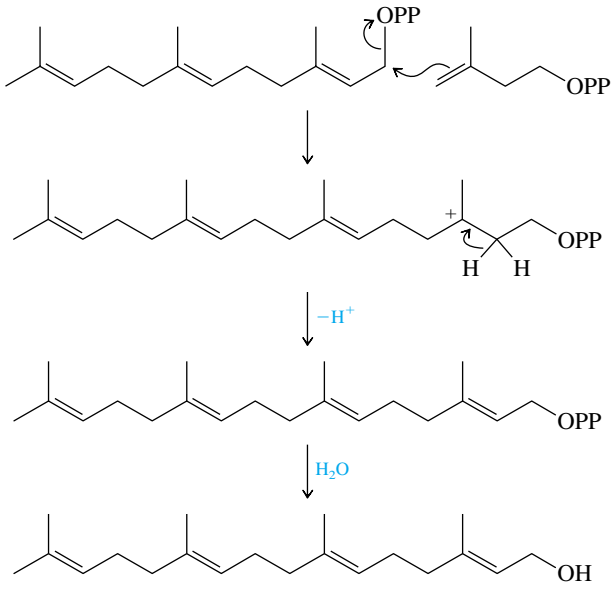


Cembrene Vitamin A

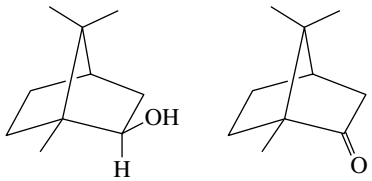
26.8



26.9



26.10



Isoborneol Camphor

26.11 Four carbons would be labeled with ^{14}C; they are C-1, C-3, C-5, and C-7.

26.12 (b) Hydrogens that migrate are those originally attached to C-13 and C-17 (steroid numbering); (c) the methyl group attached to C-15 of squalene 2,3-epoxide; (d) the methyl groups at C-2 and C-10 plus the terminal methyl group of squalene 2,3-epoxide.

26.13 All the methyl groups are labeled, plus C-1, C-3, C-5, C-7, C-9, C-13, C-15, C-17, C-20, and C-24 (steroid numbering).

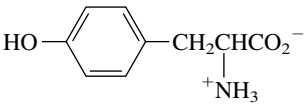
26.14 The structure of vitamin D_2 is the same as that of vitamin D_3 except that vitamin D_2 has a double bond between C-22 and C-23 and a methyl substituent at C-24.

CHAPTER 27

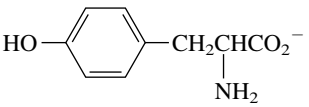
27.1 (b) *R;* (c) *S*

27.2 Isoleucine and threonine

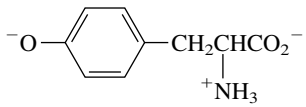
27.3 (b)



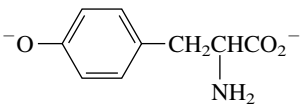
(c)



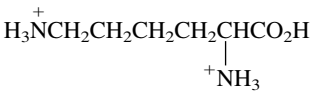
or



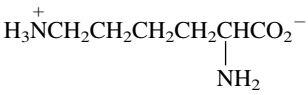
(d)



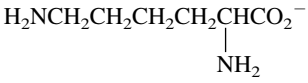
27.4 At pH 1:



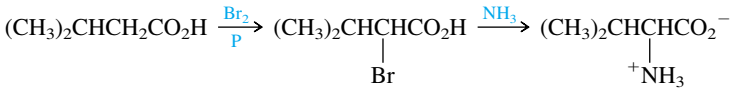
At pH 9:



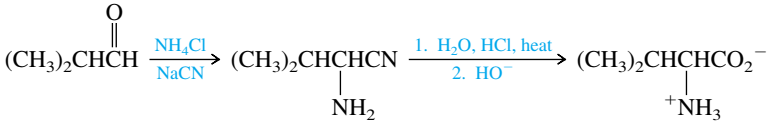
At pH 13:



27.5

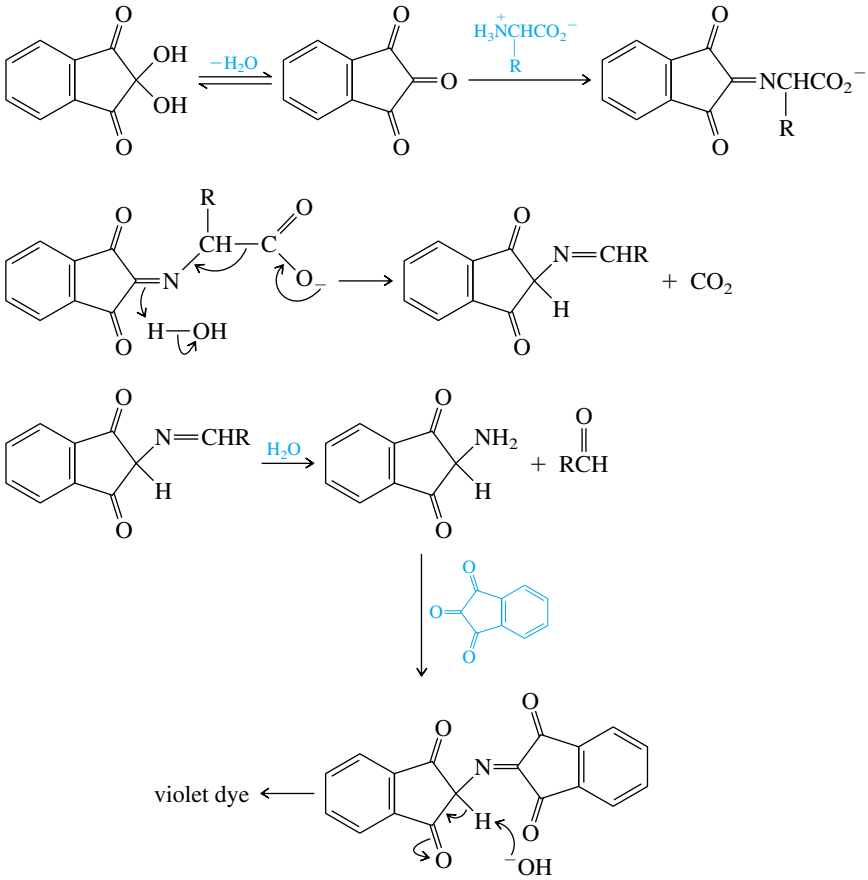


27.6

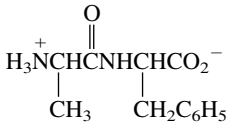


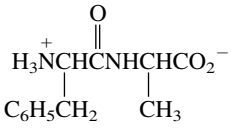
27.7 Treat the sodium salt of diethyl acetamidomalonate with isopropyl bromide. Remove the amide and ester functions by hydrolysis in aqueous acid; then heat to cause $(CH_3)_2CHC(CO_2H)_2$ (with $^+NH_3$) to decarboxylate to give valine. The yield is low because isopropyl bromide is a secondary alkyl halide, because it is sterically hindered to nucleophilic attack, and because elimination competes with substitution.

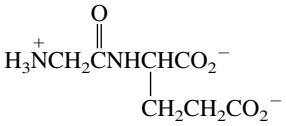
27.8

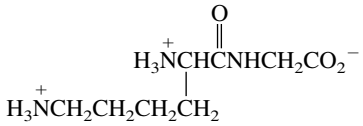


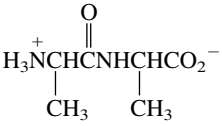
27.9 Glutamic acid

27.10 (b) 

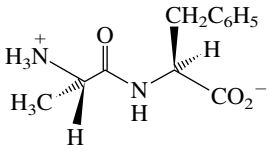
(c) 

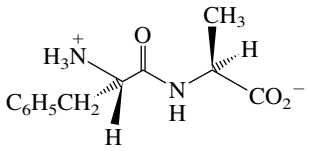
(d) 

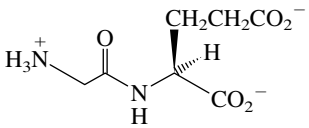
(e) 

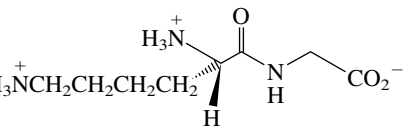
(f) 

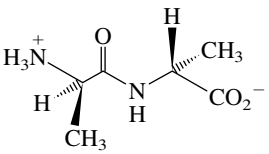
One-letter abbreviations: (b) AF; (c) FA; (d) GE; (e) KG; (f) D-A-D-A

27.11 (b) 

(c) 

(d) 

(e) 

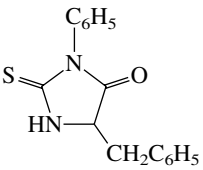
(f) 

27.12 Tyr-Gly-Gly-Phe-Met; YGGFM

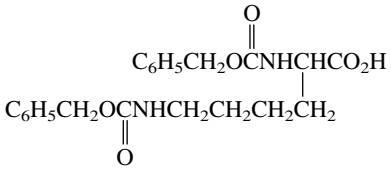
27.13

Ala-Gly-Phe-Val	Gly-Ala-Phe-Val	Phe-Gly-Ala-Val	Val-Gly-Phe-Ala
Ala-Gly-Val-Phe	Gly-Ala-Val-Phe	Phe-Gly-Val-Ala	Val-Gly-Ala-Phe
Ala-Phe-Gly-Val	Gly-Phe-Ala-Val	Phe-Ala-Gly-Val	Val-Phe-Gly-Ala
Ala-Phe-Val-Gly	Gly-Phe-Val-Ala	Phe-Ala-Val-Gly	Val-Phe-Ala-Gly
Ala-Val-Gly-Phe	Gly-Val-Ala-Phe	Phe-Val-Gly-Ala	Val-Ala-Gly-Phe
Ala-Val-Phe-Gly	Gly-Val-Phe-Ala	Phe-Val-Ala-Gly	Val-Ala-Phe-Gly

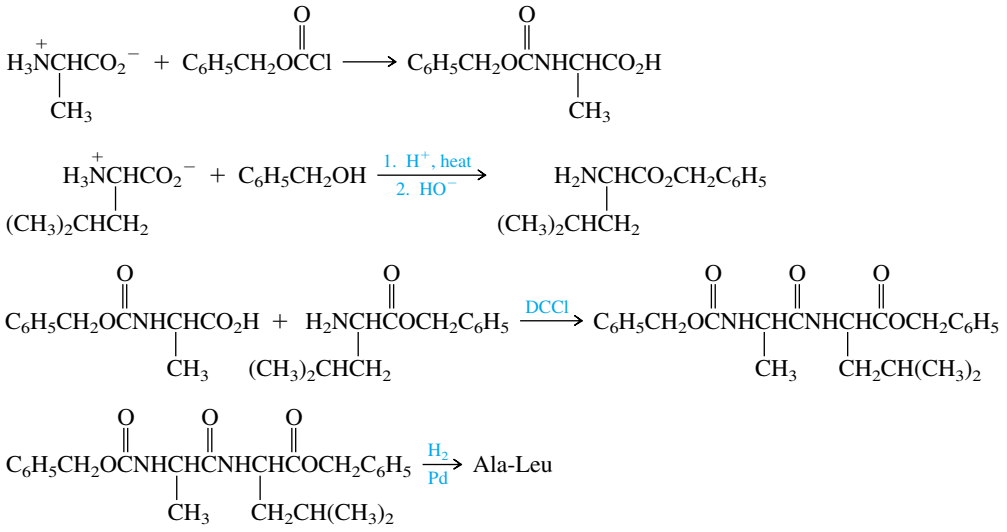
27.14 Val-Phe-Gly-Ala Val-Phe-Ala-Gly

27.15 

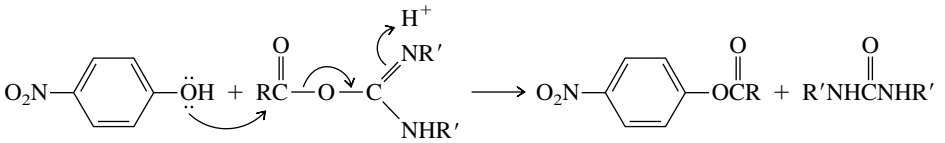
27.16



27.17



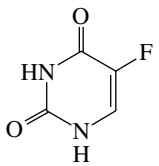
27.18 An *O*-acylisourea is formed by addition of the Z-protected amino acid to *N,N′*-dicyclohexylcarbodiimide, as shown in Figure 27.13. This *O*-acylisourea is attacked by *p*-nitrophenol.



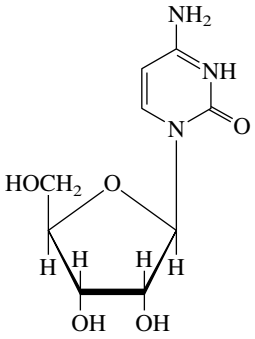
27.19 Remove the Z protecting group from the ethyl ester of Z-Phe-Gly by hydrogenolysis. Couple with the *p*-nitrophenyl ester of Z-Leu; then remove the Z group of the ethyl ester of Z-Leu-Phe-Gly.

27.20 Protect glycine as its Boc derivative and anchor this to the solid support. Remove the protecting group and treat with Boc-protected phenylalanine and DCCI. Remove the Boc group with HCl; then treat with HBr in trifluoroacetic acid to cleave Phe-Gly from the solid support.

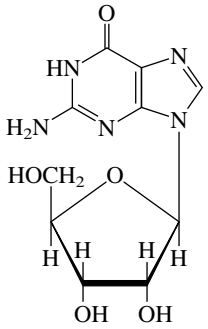
27.21



27.22 (b) Cytidine



(c) Guanosine



27.23 The codons for glutamic acid (GAA and GAG) differ by only one base from two of the codons for valine (GUA and GUG).

APPENDIX 3

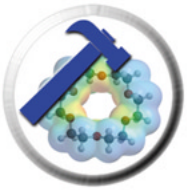
LEARNING CHEMISTRY WITH MOLECULAR MODELS: USING *SPARTANBUILD* AND *SPARTANVIEW*

Alan J. Shusterman, Department of Chemistry, Reed College, Portland, OR
Warren J. Hehre, Wavefunction, Inc., Irvine, CA

SpartanBuild: AN ELECTRONIC MODEL KIT

SpartanBuild is a program for building and displaying molecular models. It gives detailed information about molecular geometry (bond lengths and angles) and stability (strain energy). The program is located on the CD *Learning By Modeling* included with your text and may be run on any Windows (95/98/NT) or Power Macintosh computer.

SpartanBuild is intended both to assist you in solving problems in the text (these problems are matched with the following icon)



and more generally as a "replacement" to the plastic "model kits" that have been a mainstay in organic chemistry courses.

The tutorials that follow contain instructions for using *SpartanBuild*. Each tutorial gives instructions for a related group of tasks (install software, change model display, etc.). Computer instructions are listed in the left-hand column, and comments are listed in the right-hand column. Please perform these instructions on your computer as you read along.

Installing *SpartanBuild*	*SpartanBuild* is "CD-protected." The CD must remain in the drive at all times.
1. Insert *Learning By Modeling* CD.	
2. Double-click on the CD's icon.	
Starting *SpartanBuild*	Starting the program opens a large *SpartanBuild* window (blank initially), a model kit, and a tool bar. Models are assembled in the window.
3. Double-click on the *SpartanBuild* icon.	
Quitting *SpartanBuild*	Restart *SpartanBuild* to continue.
4. Select **Quit** from the **File** menu.	

BUILDING A MODEL WITH ATOMS

One way to build a model is to start with one atom and then add atoms one at a time as needed. For example, propanal, $CH_3CH_2CH{=}O$, can be assembled from four "atoms" (sp^3 C, sp^3 C, sp^2 C, and sp^2 O).

Starting to build propanal, $CH_3CH_2CH{=}O$
If necessary, start *SpartanBuild.*

1. Click on  in the model kit.
2. Click anywhere in the window.

The  button becomes highlighted.

A carbon atom with four unfilled valences (white) appears in the *SpartanBuild* window as a ball-and-wire model.

You start building propanal using an sp^3 C from the model kit. Note that five different types of carbon are available. Each is defined by a particular number of *unfilled valences* (these are used to make bonds) and a particular "idealized geometry." Valences that are not used for bonds are automatically turned into hydrogen atoms, so it is normally unnecessary to build hydrogens into a model.

Atom button					
Atom label	sp^3 C	sp^2 C	sp C	delocalized C	trigonal C
Unfilled valences	4 single	2 single 1 double	1 single 1 triple	1 single 2 partial double	3 single
Ideal bond angles	109.5°	120°	180°	120°	120°

You can rotate a model (in this case, just an sp^3 C), move it around the screen, and change its size using the mouse in conjunction with the keyboard (see the following table). Try these operations now.

Operation	**PC**	**Mac**
Rotate	Move mouse with left button depressed.	Move mouse with button depressed.
Translate	Move mouse with right button depressed.	Press **option** key, and move mouse with button depressed.
Scale	Press **shift** key, and move mouse with right button depressed.	Simultaneously press **option** and **control** keys, and move mouse with button depressed.

To finish building propanal, you need to add two carbons and an oxygen. Start by adding another sp^3 C (it should still be selected), and continue by adding an sp^2 C and an sp^2 O. Atoms are added by clicking on unfilled valences in the model (the valences turn into bonds).

If you make a mistake at any point, you can undo the last operation by selecting **Undo** from the **Edit** menu, or you can start over by selecting **Clear** from the **Edit** menu.

To finish building propanal, $CH_3CH_2CH{=}O$

3. If necessary, click on sp^3 C in the model kit.

This selects the carbon atom with four single valences.

4. Click on the tip of any unfilled valence in the window.	This makes a carbon–carbon single bond (the new bond appears as a dashed line).
5. Click on sp^2 C in the model kit.	This selects the carbon atom with one double and two single valences.
6. Click on the tip of any unfilled valence in the window.	This makes a carbon–carbon single bond. Bonds can only be made between valences of the same type (single + single, double + double, etc.).
7. Click on sp^2 O in the model kit.	This selects the oxygen atom with one double valence.
8. Click on the tip of the double unfilled valence in the window.	This makes a carbon–oxygen double bond. *Note:* If you cannot see which valence is the double valence, then rotate the model first.

MEASURING MOLECULAR GEOMETRY

Three types of geometry measurements can be made using *SpartanBuild:* distances between pairs of atoms, angles involving any three atoms, and dihedral angles involving any four atoms. These are accessible from the **Geometry** menu and from the toolbar. Try these operations now.

Geometry Menu	PC	Mac
Distance		
Angle		
Dihedral		

CHANGING MODEL DISPLAY

The ball-and-wire display is used for model building. Although it is convenient for this purpose, other model displays show three-dimensional molecular structure more clearly and may be preferred. The space-filling display is unique in that it portrays a molecule as a set of atom-centered spheres. The individual sphere radii are taken from experimental data and roughly correspond to the size of atomic electron clouds. Thus, the space-filling display attempts to show how much space a molecule takes up.

Changing the Model Display

1. One after the other, select **Wire, Tube, Ball and Spoke,** and **Space Filling** from the **Model** menu.

BUILDING A MODEL USING GROUPS

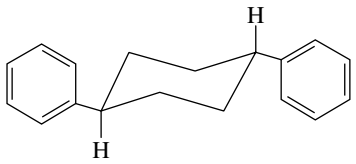
Organic chemistry is organized around "functional groups," collections of atoms that display similar structures and properties in many different molecules. *SpartanBuild* simplifies the construction of molecular models that contain functional groups by providing a small library of prebuilt groups. For example, malonic acid, $HO_2C—CH_2—CO_2H$, is easily built using the **Carboxylic Acid** group.

Building malonic acid, $HO_2C—CH_2—CO_2H$

1. Select **Clear** from the **Edit** menu	This removes the existing model from the *SpartanBuild* window.
2. Click on sp^3 C in the model kit, then click in the *SpartanBuild* window.	
3. Click on the **Groups** button in the model kit.	This indicates that a functional group is to be selected
4. Select **Carboxylic Acid** from the **Groups** menu.	This makes this group appear in the model kit.
5. Examine the unfilled valences of the carboxylic acid group, and find the one marked by a small circle. If necessary, click on the group to make this circle move to the valence on carbon.	The carboxylic acid group has two structurally distinct valences that can be used to connect this group to the model. The "active" valence is marked by a small circle and can be changed by clicking anywhere on the group.
6. Click on the tip of any unfilled valence in the window.	A new carbon–carbon bond forms and an entire carboxylic acid group is added to the model.
7. Click on the tip of any unfilled valence on carbon.	This adds a second carboxylic acid group to the model.

BUILDING A MODEL USING RINGS

Many organic molecules contain one or more rings. *SpartanBuild* contains a small library of prebuilt structures representing some of the most common rings. For example, *trans*-1,4-diphenylcyclohexane can be constructed most easily using **Benzene** and **Cyclohexane** rings.



trans-1,4-Diphenylcyclohexane

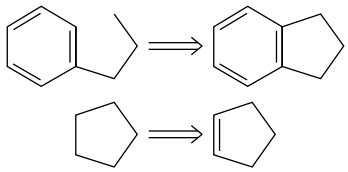
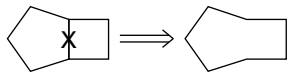
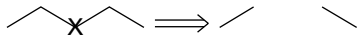
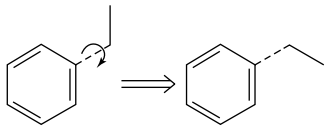
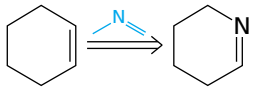
Building *trans*-1,4-phenylcyclohexane

1. Select **Clear** from the **Edit** menu.	This removes the existing model from the *SpartanBuild* window.
2. Click on the **Rings** button.	This indicates that a ring is to be selected.
3. Select **Cyclohexane** from the **Rings** menu.	This makes this ring appear in the model kit.
4. Click anywhere in the *SpartanBuild* window.	This places an entire cyclohexane ring in the window.

5. Select **Benzene** from the **Rings** menu. — This makes this ring appear in the model kit.
6. Click on the tip of any equatorial unfilled valence. — This adds an entire benzene ring to the model.
7. Click on the tip of the equatorial unfilled valence directly across the ring (the valence on C-4). — This adds a second benzene ring to the model.

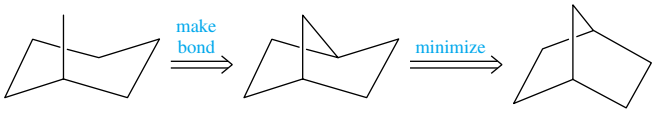
ADDITIONAL TOOLS

Many models can be built with the tools that have already been described. Some models, however, require special techniques (or are more easily built) using some of the *SpartanBuild* tools described in the following table.

Tool	PC	Mac	Use	Example
Make Bond			Click on two unfilled valences. The valences are replaced by a bond.	
Break Bond			Click on bond. The bond is replaced by two unfilled valences.	
Delete			Click on atom or unfilled valence. Deleting an atom removes all unfilled valences associated with atom.	
Internal Rotation			Click on bond to select it for rotation. Press **Alt** key (PC) or **space bar** (Mac), and move mouse with button depressed (left button on PC). One part of the model rotates about the selected bond relative to other part.	
Atom Replacement			Select atom from model kit, then double-click on atom in model. Valences on the new atom must match bonds in the model or replacement will not occur.	

MINIMIZE: GENERATING REALISTIC STRUCTURES AND STRAIN ENERGY

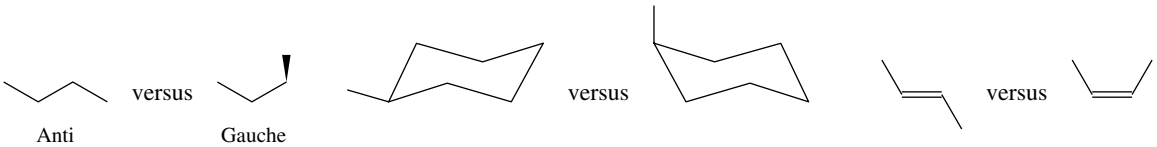
In some cases, the model that results from building may be severely distorted. For example, using **Make Bond** to transform *axial* methylcyclohexane into bicyclo[2.2.1]heptane (norbornane) gives a highly distorted model (the new bond is too long and the ring has the wrong conformation).



The distorted structure can be replaced by a "more reasonable" structure using an empirical "molecular mechanics" calculation. This calculation, which is invoked in *SpartanBuild* by clicking on **Minimize,** automatically finds the structure with the smallest strain energy (in this case, a structure with "realistic" bond distances and a boat conformation for the six-membered ring).

It is difficult to tell which models contain structural distortions. You should "minimize" all models after you finish building them.

Molecular mechanics strain energies have another use. They can also be used to compare the energies of models that share the same molecular formula, that is, models that are either stereoisomers or different conformations of a single molecule (allowed comparisons are shown here).



SpartanBuild reports strain energies in kilocalories per mole (1 kcal/mol = 4.184 kJ/mol) in the lower left-hand corner of the *SpartanBuild* window.

SpartanView: VIEWING AND INTERPRETING MOLECULAR-MODELING DATA

Learning By Modeling contains a program, *SpartanView*, which displays preassembled molecular models, and also a library of *SpartanView* models to which you can refer. These models differ in two respects from the models that you can build with *SpartanBuild*. Some models are animations that show how a molecule changes its shape during a chemical reaction, vibration, or conformation change. Others contain information about electron distribution and energy that can only be obtained from sophisticated quantum chemical calculations. The following sections describe how to use *SpartanView*.

SpartanView models are intended to give you a "molecule's eye view" of chemical processes and to help you solve certain text problems. The text uses the following icon to alert you to corresponding models on the CD.

Each icon corresponds to a model or a group of models on the CD. All of the models for a given chapter are grouped together in the same folder. For example, the models for this appendix are grouped together in a folder named "Appendix." The location

of models within each folder can be determined by paying attention to the context of the icon. When an icon accompanies a numbered figure or problem, the figure or problem number is used to identify the model on the CD. When an icon appears next to an unnumbered figure, the name of the model is listed next to the icon.

Some *SpartanView* procedures are identical to *SpartanBuild* procedures and are not described in detail. In particular, the same mouse button-keyboard combinations are used to rotate, translate, and scale models. Also, the same menu commands are used to change the model display and obtain geometry data. Please refer back to the *SpartanBuild* instructions for help with these operations.

START *SpartanView*, OPEN AND CLOSE MODELS, SELECT AND MOVE "ACTIVE" MODEL

One difference between *SpartanView* and *SpartanBuild* is the number of models that the two programs can display. *SpartanBuild* can display only a single model, but *SpartanView* allows the simultaneous display of several models. Only one *SpartanView* model can be "active" at any time, and most mouse and menu operations affect only the "active" model.

The following tutorials contain instructions for using *SpartanView*. Please perform these operations on your computer as you read along.

Installing *Spartan View*

1. Insert *SpartanView* CD.
2. Double-click on the CD's icon.

SpartanView and *SpartanBuild* are located on *Learning By Modeling.* Both programs are "CD-protected."

Starting *SpartanView*

3. Double-click on the *SpartanView* icon.

This causes the *SpartanView* window to open. The window is blank initially.

Opening models

4. Select **Open** from the File menu.
5. Double-click on "Appendix," then double-click on "Appendix A."

"Appendix A" in the Appendix folder contains three models: water, methanol, and hydrogen chloride.

Making hydrogen chloride, HCl, the "active" model

6. Move the cursor to any part of the hydrogen chloride model, and click on it.

This makes hydrogen chloride the active model. The name of the active model is displayed at the top of the *SpartanView* window. Only one model can be active at any time.

Moving a model

7. Rotate, translate, and scale the active model using the same mouse and keyboard operations as those used with *SpartanBuild*.

Rotation and translation affect only the active model, but scaling affects all models on the screen.

Closing model

8. Select **Close** from the **File** menu.

Close affects only the active model.

QUANTUM MECHANICAL MODELS

Most of the *SpartanView* models on the CD have been constructed using quantum mechanical calculations, although some simplifications have been used to accelerate the calculations. This means that the models, although closely resembling real molecules, never precisely duplicate the properties of real molecules. Even so, the models are sufficiently similar to real molecules that they can usually be treated as equivalent. This is important because models can contain more types of information, and models can be constructed for molecules that cannot be studied in the laboratory. Also, models can be joined together to make "animations" that show how molecules move.

MEASURING AND USING MOLECULAR PROPERTIES

SpartanView models provide information about molecular energy, dipole moment, atomic charges, and vibrational frequencies (these data are accessed from the **Properties** menu). Energies and charges are available for all quantum mechanical models, whereas dipole moments and vibrational frequencies are provided for selected models only.

Energy is the most useful molecular property because changes in energy indicate whether or not a chemical reaction is favorable and how fast it can occur. *SpartanView* reports energies in "atomic units," or au (1 au = 2625.5 kJ/mol). The energy of any system made up of infinitely separated (and stationary) nuclei and electrons is exactly 0 au. A molecule's energy can therefore be thought of as the energy change that occurs when its component nuclei and electrons are brought together to make the molecule. The "assembly" process releases a vast amount of energy, so molecular energies are always large and negative.

The energies of two molecules (or two groups of molecules) can be compared as long as they contain exactly the same nuclei and exactly the same number of electrons, a condition that is satisfied by isomers. It is also satisfied by the reactants and products of a balanced chemical reaction. For example, the energy change, ΔE, for a chemical reaction, $A + B \rightarrow C + D$, is obtained by subtracting the energies of the reactant molecules from the energies of the product molecules: $\Delta E = E_C + E_D - E_A - E_B$. ΔE is roughly equivalent to the reaction enthalpy, $\Delta H°$. The same type of computation is used to calculate the activation energy, E_{act}. This energy is obtained by subtracting the energies of the reactant molecules from that of the transition state.

Making water the active model

1. Move the cursor to any part of the water model, and click on it.

Measuring the calculated energy

2. Select **Energy** from the **Properties** menu.
3. Click on **Done** when finished.

The calculated energy of water (−75.5860 au) is displayed at the bottom of the screen.

Measuring the dipole moment

4. Select **Dipole Moment** from the **Properties** menu.
5. Click on **Done** when finished.

The calculated magnitude of the dipole moment of water (2.39 D) is displayed at the bottom of the screen. The calculated direction is indicated by a yellow arrow.

DISPLAYING MOLECULAR VIBRATIONS AND MEASURING VIBRATIONAL FREQUENCIES

Molecular vibrations are the basis of infrared (IR) spectroscopy. Certain groups of atoms vibrate at characteristic frequencies and these frequencies can be used to detect the presence of these groups in a molecule.

SpartanView displays calculated vibrations and frequencies for selected models. Calculated frequencies are listed in units of (cm^{-1}) and are consistently larger than observed frequencies (observed frequency $= 0.9 \times$ calculated frequency is a good rule of thumb).

Displaying a list of vibrational frequencies for water

1. Select **Frequencies** from the **Properties** menu.

Frequencies (in cm^{-1}) are listed in numerical order from smallest (or imaginary) at the top to largest at the bottom.

Displaying a vibration

2. *Double-click* on a frequency to make it active.
3. Click on **OK** to close the window.

A checkmark indicates the active vibration (only one vibration can be displayed at a time). Atom motions are exaggerated to make them easier to see.

4. Select **Ball and Spoke** from the **Model** menu.

Vibrations appear most clearly when a molecule is displayed as a ball-and-spoke model.

Stopping the display of a vibration

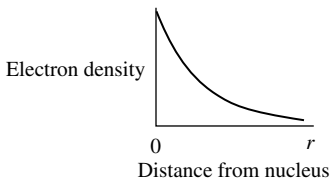
5. Repeat step 1, double-click on the active vibration, and click on **OK.**

Double-clicking on an active vibration deactivates it.

DISPLAYING ELECTROSTATIC POTENTIAL MAPS

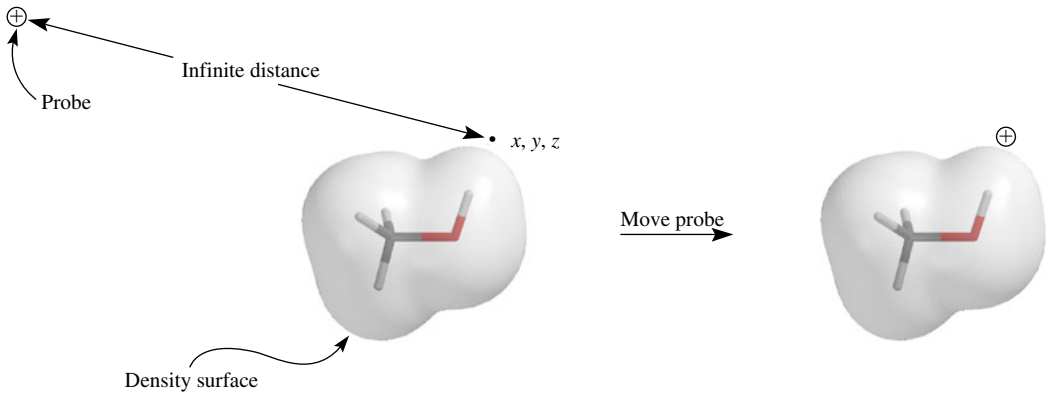
One of the most important uses of models is to show how electrons are distributed inside molecules. The "laws" of quantum mechanics state that an electron's spatial location cannot be precisely specified, but the likelihood of detecting an electron at a particular location can be calculated (and measured). This likelihood is called the "electron density" (see Chapter 1), and *SpartanView* can display three-dimensional graphs that show regions of high and low electron density inside a molecule.

The electron density at a given location is equivalent to the amount of negative charge at that location. Thus, a hydrogen atom, which consists of a proton and an electron, can be thought of as a proton embedded in a "cloud" of negative charge. The total amount of charge in the cloud exactly equals the charge on a single electron, but the charge at any given point in the cloud is considerably smaller and varies as shown in the following graph.



The graph shows that negative charge (or electron density) falls off as one goes farther away from the nucleus. It also shows that the charge cloud lacks a sharp boundary, or "edge." The apparent lack of an edge is problematic because we know from experimental observations that molecules do, in fact, possess a characteristic size and shape. *SpartanView* models solve this problem by using an arbitrarily selected value of the electron density to define the edge of a molecule's electron cloud. The program searches for all of the locations where the electron density takes on this edge value. Then it connects these locations together to make a smooth surface called a "size density surface," or more simply, a "density surface." Such density surfaces can be used as quantum mechanical "space-filling" models. The size and shape of density surfaces are in good agreement with the size and shape of empirical space-filling models, and the amount of electron density that lies outside the density surface is usually inconsequential.

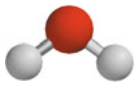
A density surface marks the edge of a charge cloud, but it does not tell us how electron density is distributed inside the cloud. We can get a feel for the latter by calculating the electrostatic potential at different points on the density surface. The electrostatic potential at any point *(x, y, z)* on the density surface is defined as the change in energy that occurs when a "probe" particle with +1 charge is brought to this point starting from another point that is infinitely far removed from the molecule (see figure). If the energy rises (positive potential), the probe is repelled by the molecule at point *(x, y, z)*. If the energy falls (negative potential), the probe is attracted by the molecule.

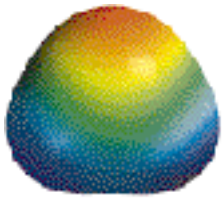


The electrostatic potential gives us information about the distribution of electron density in the molecule because the potential at point *(x, y, z)* is usually influenced most by the atom closest to this point. For example, if a molecule is neutral and the potential at point *(x, y, z)* is positive, then it is likely that the atom closest to this point has a net positive charge. If the potential at *(x, y, z)* is negative, then it is likely that the closest atom has a net negative charge. The size of the potential is also useful. The larger the potential at a given point, the larger the charge on the nearest atom.

These rules for assigning atomic charges work well for most neutral molecules, but they do not work for ions. This is because an ion's overall charge dominates the potential near the ion. For example, positive ions generate a positive potential everywhere around the ion. The rules also fail for atoms with highly distorted electron clouds. In such cases, positive and negative potentials are both found near the atom, and the charge is ambiguous.

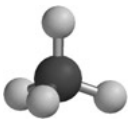
SpartanView uses color to display the value of the electrostatic potential on the density surface. These colored diagrams are called "electrostatic potential maps" or just "potential maps." Different potentials are assigned different colors as follows: red (most negative potential on the map) < orange < yellow < (green) < blue (most positive potential on the map). The following potential map of water shows how this works (refer to the ball-and-spoke model for the molecule's orientation). The most negative potential (red) is found near oxygen, and the most positive potentials (blue) are found near the hydrogens. Thus, we can assign a partial negative charge to oxygen and partial positive charges to the hydrogens.

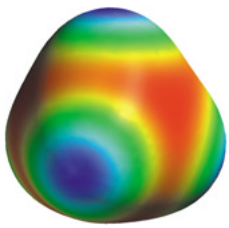




The potential map of water tells us the relative charges on oxygen and hydrogen, but it does not tell us if these charges are large or small. To discover this, we need to know the *magnitude* of the potentials. As it turns out, the most positive potentials (the blue regions) on this map are about 250 kJ/mol—a large value for a neutral molecule—so the atomic charges must be fairly large.

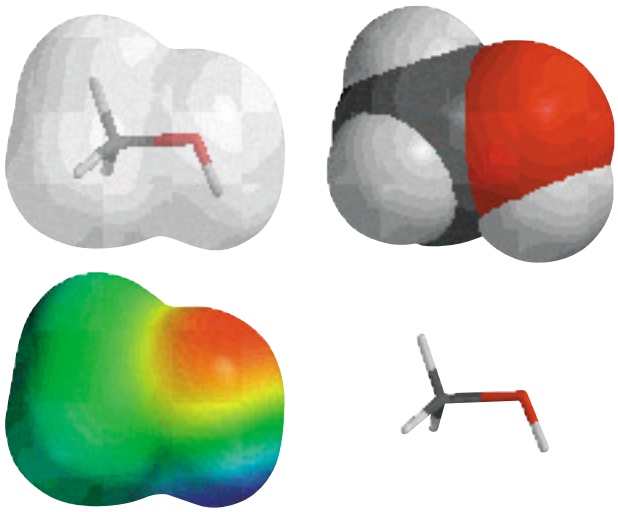
Potential maps can be used to compare electron distributions in different molecules providing *all of the maps assign the same color to the same potential*, that is, the maps all use the same color–potential scale. A "normal" potential map for methane (CH_4) is shown on the left (by "normal" we mean that the map displays the most negative potential as red and the most positive potential as blue). This map tells us that carbon carries a partial negative charge and the hydrogens carry partial positive charges. But, just like before, the map does not tell us the magnitude of these charges. One way to get at this information is to reassign the colors using the color–potential scale that was previously used to make water's potential map (see preceding discussion). This gives a new map that looks more or less green everywhere. This fact, along with the total absence of red and blue, tells us that the potentials, and the atomic charges, in methane are much smaller than those in water. (The most positive potential on methane's map is only 50 kJ/mol.)





normal color assignments

color assignments based on water molecule's potential map (see above)



Size density surface *(top left),* space-filling model *(top right),* potential map *(bottom left),* and tube model *(bottom right)* for methanol.

Making methanol the active model

1. Move the cursor to any part of the methanol model, and click on it.

Displaying a size density surface

2. Select **Density** from the **Surfaces** menu, then select **Transparent** from the sub-menu.

SpartanView uses the word "density" to identify size density surfaces. The size density surface is similar in size and shape to a space-filling model.

Stopping the display of a surface

3. Select **Density** from the **Surfaces** menu, then select **None** from the sub-menu.

This removes the size density surface.

Displaying an electrostatic potential map

4. Select **Potential Map** from the **Surfaces** menu, then select **Solid** from the sub-menu.

The red part of the map identifies oxygen as a negatively charged atom, and the blue part identifies the most positively charged hydrogen atom.

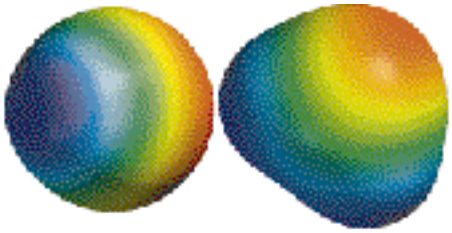
Closing all of the models.

5. Select **Close All** from the **File** menu.

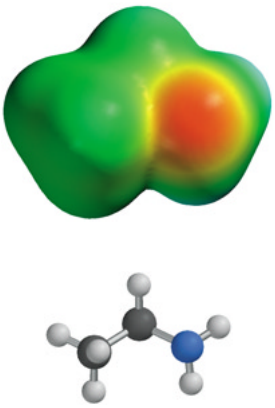
CHEMICAL APPLICATIONS OF ELECTROSTATIC POTENTIAL MAPS

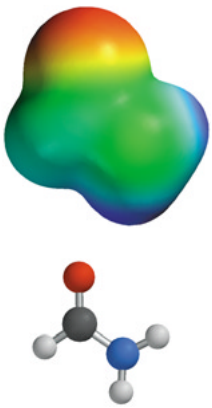
Potential maps are a very powerful tool for thinking about a variety of chemical and physical phenomena. For example, water's potential map suggests that two water molecules will be attracted to each other in a way that brings a positive hydrogen in one molecule close to the negative oxygen in the other molecule (see figure). This type of intermolecular bonding is called a "hydrogen bond." Significant hydrogen bonding does not

occur between methane molecules because methane molecules create much smaller potentials.

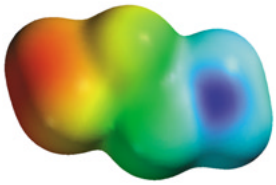


Potential maps can also be useful predictors of chemical reactivity. For example, the nitrogen atoms in ethylamine, $CH_3CH_2NH_2$, and in formamide, $O{=}CHNH_2$, appear to be identical, and we might therefore predict similar chemical reactivity patterns, but the potential maps of these compounds tell a different story. The potential map of ethylamine (see following figure, *left*) shows a region of negative potential that coincides with the location of the lone-pair electron density. This nitrogen is a good electron donor and can act as a base or nucleophile. Formamide's map (see figure, *right*), on the other hand, shows that the oxygen atom might act as an electron donor, but not the nitrogen atom. The nitrogen atoms in these compounds are very different, and they will display different chemical behavior as well.

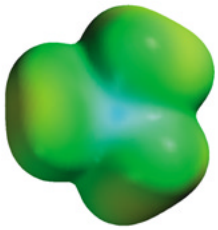




The same kinds of comparisons can also be applied to the short-lived (and therefore hard-to-observe) molecules that form during a chemical reaction. The potential maps of *n*-butyl cation, $CH_3CH_2CH_2CH_2^+$, and *tert*-butyl cation, $(CH_3)_3C^+$, show us that these highly reactive species differ in significant ways. The electrostatic potentials for *n*-butyl cation vary over a wider range, and the positive charge is clearly associated with the end carbon (see following figure, *left*). *tert*-Butyl cation's map, by comparison, shows a much smaller range of potentials (see figure, *right*). The central carbon is positively charged, but the potential never becomes as positive as those found in *n*-butyl cation. This tells us that some of the electron density normally associated with the methyl groups has been transferred to the central carbon.



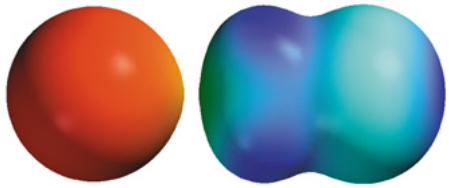
$CH_3CH_2CH_2\overset{+}{C}H_2$



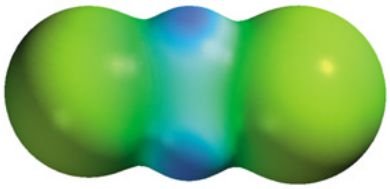
$(CH_3)_3C^+$

As a final example, we compare potential maps of the reactants, transition state, and products for an S_N2 reaction, $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$. The reactant and product maps show negatively charged chloride and bromide ions, respectively; therefore, this reaction causes electron density to shift from one atom to another. The transition state map is distinctive in that it shows *partial* negative charges on both Cl and Br, that is, the negative charge is delocalized over Cl and Br in the transition state.

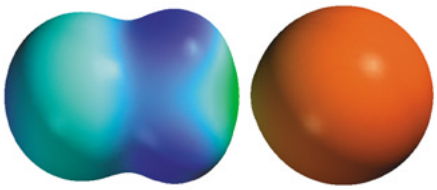
$Cl^- + CH_3—Br$



$[Cl{-}{-}{-}CH_3{-}{-}{-}Br]^-$



$Cl—CH_3 + Br^-$

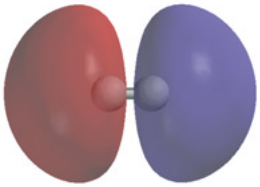


DISPLAYING MOLECULAR ORBITAL SURFACES

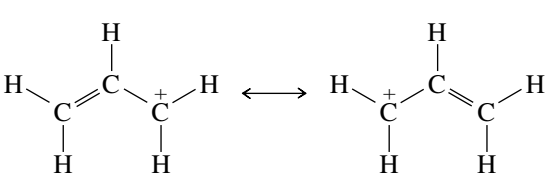
SpartanView displays molecular orbitals as colored surfaces. An orbital surface connects points in space where the selected orbital has a particular numerical *magnitude,* and different colors are used to indicate surfaces corresponding to negative and positive values of the orbital.

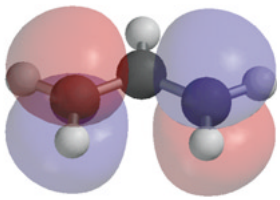
The most important molecular orbitals are the so-called frontier molecular orbitals. These are the highest (energy) occupied molecular orbital (HOMO), and lowest (energy) unoccupied molecular orbital (LUMO). The following picture shows the LUMO surface for the hydrogen molecule, H_2. The LUMO consists of two separate surfaces, a red

surface surrounding one hydrogen and a blue surface surrounding the other. The colors tell us that the orbital's value is negative near one hydrogen, and positive near the other. We can also tell from this that the orbital's value must pass through zero somewhere in the empty space between the two surfaces (the "zero" region is called a "node"). Any node that crosses the bonding region makes an orbital "antibonding" and raises the orbital's energy. As a rule, electrons are only found in low-energy bonding orbitals, but this can change during a chemical reaction.



Molecular orbitals are useful tools for identifying reactive sites in a molecule. For example, the positive charge in allyl cation is delocalized over the two terminal carbon atoms, and both atoms can act as electron acceptors. This is normally shown using two resonance structures, but a more "compact" way to see this is to look at the shape of the ion's LUMO (the LUMO is a molecule's electron-acceptor orbital). Allyl cation's LUMO appears as four surfaces. Two surfaces are positioned near each of the terminal carbon atoms, and they identify allyl cation's electron-acceptor sites.

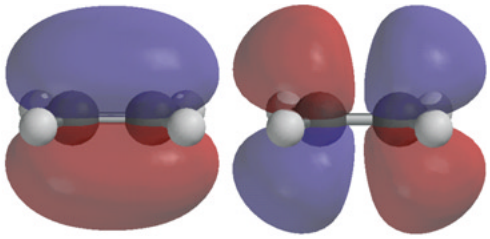




Moving into "Appendix B" and making ethylene the active model

1. Select **Open** from the **File** menu and double click on "Appendix B." Move the cursor to any part of the ethylene model, and click on it.

Appendix B contains two models: ethylene and butane.



The HOMO *(left)* and LUMO *(right)* of ethylene.

Displaying an orbital surface

2. Select **LUMO** from the **Surfaces** menu, then select **Transparent** from the sub-menu.

This displays the LUMO of ethylene. This is an unoccupied antibonding molecular orbital.

Stopping the display of an orbital surface

3. Select **LUMO** again from the **Surfaces** menu, then select **None** from the sub-menu.

The orbital is no longer displayed.

4. Select **HOMO** from the **Surfaces** menu, then select **Transparent** from the sub-menu.

This displays the HOMO of ethylene. This is an occupied bonding molecular orbital.

DISPLAYING *SpartanView* SEQUENCES (ANIMATIONS)

SpartanView can display atom motions that occur during a conformational change or chemical reaction.

Making butane the active model

1. Move the cursor to any part of the butane model, and click on it.

Animating a sequence

2. Click on the "arrow" button in the lower left-hand corner of the window.

The scroll bar slides back and forth, and the "step" label is updated during the animation. You can rotate, translate, and scale the model at any point during the animation.

Stopping the animation

3. Click on the "double bar" button in the lower left-hand corner of the window.

The animation and the scroll bar stop at the current step in the sequence.

Stepping through a sequence

4. Click on the "bar-arrows" at the right end of the scroll bar.

The scroll bar jumps to a new position, and the step label is updated, to show the current location in the sequence.

Measuring a property for a sequence

5. Select **Energy** from the Properties menu.
6. Repeat step 4 to see other energies.

All properties (energy, dipole moment, atomic charges) and geometry parameters (distance, angle, dihedral angle) can be animated or stepped through.

Quitting *SpartanView*

7. Select **Quit** from the **File** menu.

CREDITS

INTRODUCTION

Pages 3, 4, 5 Stamps are courtesy of James O. Schreck, Professor of Chemistry, University of Northern Colorado.

CHAPTER 11

Page 410 (Figure 11.5) was generated using crystallographic coordinates obtained from the Center for Computational Materials Science at the United States Naval Research Laboratory via http://cst-www.nrl.navy.mil/lattice/struk/a9.html.

Page 411 (Figure 11.7) was obtained from the Center for Nanoscale Science and Technology at Rice University via http://cnst.rice.edu/images/Tube1010a.tif.

CHAPTER 13

Page 488 (Figure 13.1) is from M. Silberberg, *Chemistry,* 2nd ed., p. 260. McGraw-Hill, New York, 2000.

Page 517 (Figure 13.24) is courtesy of Simon Fraser/Science Photo Library/Photo Researchers, Inc. Newcastle upon Tyne.

Page 524 (Figure 13.32) is adapted from R. Isaksson, J. Roschester, J. Sandstrom, and L. G. Wistrand, *Journal of the American Chemical Society,* 1985, 107, 4074–4075 with permission of the American Chemical Society.

Page 527 (Figure 13.34) is from M. Silberberg, *Chemistry,* 2nd ed., p. 56. McGraw-Hill, New York, 2000.

Page 530 (Figure 13.38) is adapted from H. D. Durst and G. W. Gokel, *Experimental Organic Chemistry,* 2nd ed., McGraw-Hill, New York, 1987.

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CHAPTER 25

Page 994 (Figure 25.8) is adapted from crystallographic coordinates deposited with the Protein Data Bank. PDB ID: 4TF4. Sakon, J., Irwin, D., Wilson, D. B., Karplus, P. A., Structure and Mechanism of Endo/Exocellulase E4 from Thermomonospora Fusca. To be published.

CHAPTER 26

Page 1035 (Figure 26.9c) is adapted from crystallographic coordinates deposited with the Protein Data Bank. PDB ID: 1CLE. Ghosh, D., Wawrzak, Z., Pletnev, V. Z., Li, N., Kaiser, R., Pangborn, W., Jornvall, H., Erman, M., Duax, W. L., Structure of Uncomplexed and Linoleate-Bound Candida Cholesterol Esterase. To be published.

CHAPTER 27

Page 1084 is adapted from crystallographic coordinates deposited with the Protein Data Bank. PDB ID: 1PID. Brange, J., Dodson, G. G., Edwards, D. J., Holden, P. H., Whittingham, J. L., A Model of Insulin Fibrils Derived from the X-Ray Crystal Structure of a Monomeric Insulin (Despentapeptide Insulin). To be published.

Page 1085 (Figure 27.16) is adapted from crystallographic coordinates deposited with the Protein Data Bank. PDB ID: 2SLK. Fossey S. A., Nemethy, G., Gibson, K. D., Scheraga, H. A., Conformational Energy Studies of Beta-Sheets of Model Silk Fibroin Peptides. I. Sheets of Poly(Ala-Gly) Chains. Biopolymers 31, pp. 1529 (1991).

Page 1087 (Figure 27.18) is adapted from crystallographic coordinates deposited with the Protein Data Bank. PDB ID: 2CTB. Teplyakov, A., Wilson, K. S., Orioli, P., Mangani S., The High Resolution Structure of the Complex between Carboxypeptidase A and L-Phenyl Lactate. To be published.

Page 1089 (Figure 27.21) is adapted from crystallographic coordinates deposited with the Protein Data Bank. PDB ID: 1VXH. Yang, F., Phillips Jr., G. N., Structures of Co-, Deoxy- and met-Myoglobins at Various Ph Values. To be published.

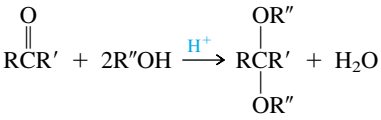
Page 1090 and page 1097 (Figure 27.25) is adapted from crystallographic coordinates deposited with the Protein Data Bank. PDB ID: 1DDN. White, A., Ding, X., Vanderspek, J. C., Murphy J. R., Ringe, D., Structure of the Metal-Ion-Activated Diphtheria Toxin Repressor/Tox Operator Complex. Nature 394, pp. 502, (1998).

Page 1100 (Figure 27.28) is adapted from crystallographic coordinates deposited with the Protein Data Bank. PDB ID: 6TNA. Sussman, J. L., Holbrook, S. R., Warrant, R. W., Church, G. M., Kim, S. H., Crystal Structure of Yeast Phenylalanine T-RNA. I. Crystallographic Refinement. J.Mol.Biol. 123, pp. 607, (1978).

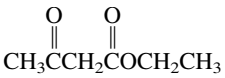
GLOSSARY

Absolute configuration (Section 7.5): The three-dimensional arrangement of atoms or groups at a stereogenic center.

Acetal (Section 17.8): Product of the reaction of an aldehyde or a ketone with two moles of an alcohol according to the equation

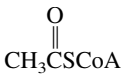


Acetoacetic ester synthesis (Section 21.6): A synthetic method for the preparation of ketones in which alkylation of the enolate of ethyl acetoacetate



is the key carbon–carbon bond-forming step.

Acetyl coenzyme A (Section 26.1): A thiol ester abbreviated as



that acts as the source of acetyl groups in biosynthetic processes involving acetate.

Acetylene (Sections 1.18 and 9.1): The simplest alkyne, HC≡CH.

Achiral (Section 7.1): Opposite of *chiral*. An achiral object is superimposable on its mirror image.

Acid (Section 4.6): According to the Arrhenius definition, a substance that ionizes in water to produce protons. According to the Brønsted–Lowry definition, a substance that donates a proton to some other substance. According to the Lewis definition, an electron-pair acceptor.

Acid anhydride (Sections 2.3 and 20.1): Compound of the type

Both R groups are usually the same, although they need not always be.

Acid dissociation constant K_a (Section 4.6): Equilibrium constant for dissociation of an acid:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Activating substituent (Sections 12.10 and 12.12): A group that when present in place of a hydrogen causes a particular reaction to occur faster. Term is most often applied to substituents that increase the rate of electrophilic aromatic substitution.

Active site (Section 27.20): The region of an enzyme at which the substrate is bound.

Acylation (Section 12.7 and Chapter 20): Reaction in which an acyl group becomes attached to some structural unit in a molecule. Examples include the Friedel–Crafts acylation and the conversion of amines to amides.

Acyl chloride (Sections 2.3 and 20.1): Compound of the type

R may be alkyl or aryl.

Acyl group (Sections 12.7 and 20.1): The group

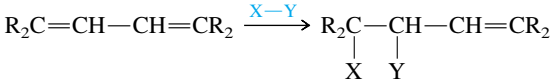
R may be alkyl or aryl.

Acylium ion (Section 12.7): The cation $R-C\equiv\overset{+}{O}:$.

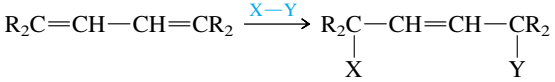
Acyl transfer (Section 20.3): A nucleophilic acyl substitution. A reaction in which one type of carboxylic acid derivative is converted to another.

Addition (Section 6.1): Reaction in which a reagent X—Y adds to a multiple bond so that X becomes attached to one of the carbons of the multiple bond and Y to the other.

1,2 Addition (Section 10.10): Addition of reagents of the type X—Y to conjugated dienes in which X and Y add to adjacent doubly bonded carbons:



1,4 Addition (Section 10.10): Addition of reagents of the type X—Y to conjugated dienes in which X and Y add to the termini of the diene system:



Addition–elimination mechanism (Section 23.6): Two-stage mechanism for nucleophilic aromatic substitution. In the