

## CHAPTER 19

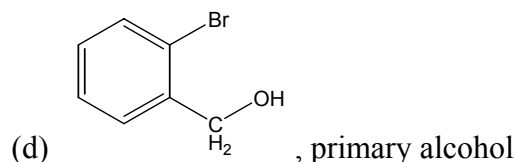
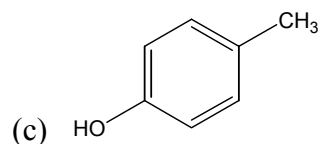
### ORGANIC CHEMISTRY II: FUNCTIONAL GROUPS

**19.2** (a) R-O-R; (b) R-CO-R; (c) R-CO-OR; (d) R-CHO

**19.4** (a) aldehyde; (b) carboxylic acid; (c) amide; (d) alcohol

**19.6** (a) 3-bromo-1-propene; (b) 1,1-difluoro-1,3-butadiene;  
(c) 1-bromo-2-pentyne; (d) 1,1,1-trichloro-2-butanone

**19.8** (a)  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ , primary alcohol; (b)  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ , secondary alcohol;

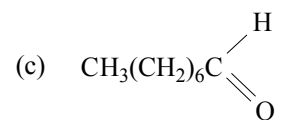
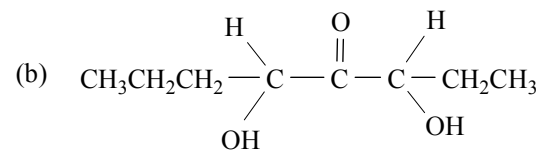
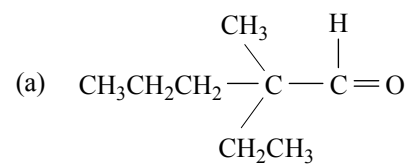


**19.10** (a)  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ ; (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ;  
(c)  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$

**19.12** (a) ethyl propyl ether; (b) butyl methyl ether; (c) dipropyl ether

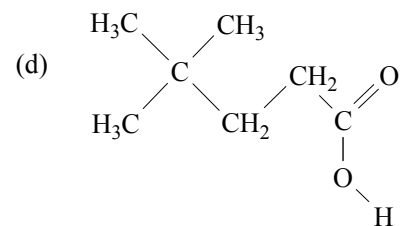
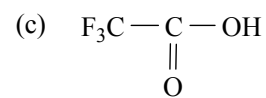
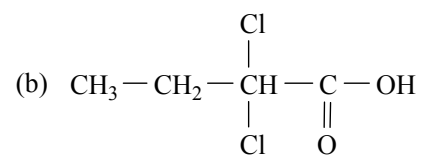
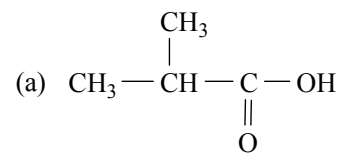
**19.14** (a) aldehyde, propanal; (b) aldehyde, 4-methylbenzaldehyde;  
(c) ketone, 4-ethyl-2-hexanone

**19.16**



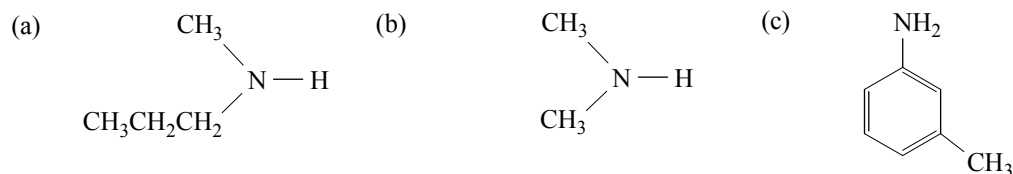
**19.18** (a) propanoic acid; (b) 2, 2- dichloroethanoic acid; (c) nonanoic acid

**19.20**



**19.22** (a) propylamine; (b) tetraethylammonium ion; (c) *p*-chloroaniline or 4-chloroaniline

**19.24**

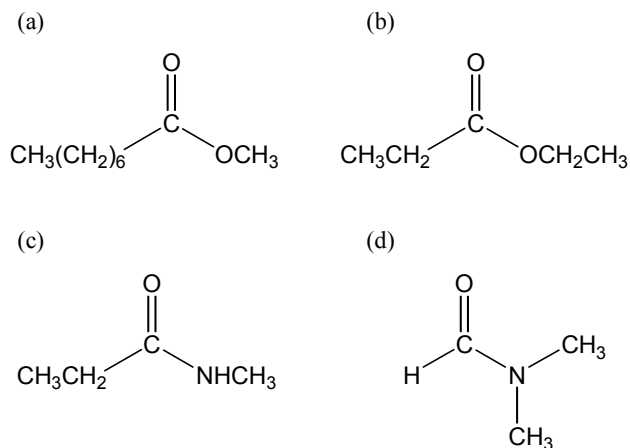


**19.26** (a), (b) and (d) may function as nucleophiles. All these molecules have lone pairs of electrons that will be attracted to a positively charged carbon center.  $\text{NH}_4^+$  does not have lone pairs of electrons and is positively charged, making it less likely to function as a nucleophile. If it is deprotonated first to give  $\text{NH}_3$ , however, it could function as a nucleophile.

**19.28** (a)  $\text{CH}_3\text{OH}$   
(b)  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$   
(c)  $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{CH}(\text{OH})(\text{CH}_2)_3\text{CH}_3$

These reactions are accomplished with an oxidizing agent, such as  $\text{Na}_2\text{Cr}_2\text{O}_7$ , in an acidified solution.

**19.30**



**19.32** (1)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{base (aq)}} \text{(dissolves)}$

(2)  $\text{CH}_3(\text{CH}_2)_3\text{CH}_3 \xrightarrow{\text{base (aq)}} \text{(does not dissolve)}$

(3)  $\text{CH}_3\text{COOH} \xrightarrow{\text{base (aq)}} \text{(dissolves)}$

(4)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{indicator}} \text{no color change}$

(5)  $\text{CH}_3\text{COOH} \xrightarrow{\text{indicator}} \text{color change to acidic}$

(1), (2), and (3) distinguish pentane from the others. (4) and (5) distinguish propanol from ethanoic acid.

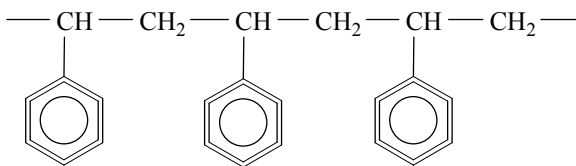
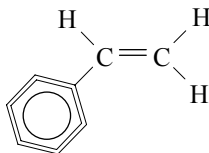
**19.34** The weakest base is methylamine, followed by dimethylamine. The strongest base is diethylamine. The basicity of amines increases with increased substitution on the nitrogen atom. In acting as a base the nitrogen atom develops a positive charge, which is stabilized by the electron-donating alkyl groups. Hence, the primary amine, methylamine, is a weaker base than the other two secondary amines. Diethylamine is a stronger base than dimethylamine because the larger ethyl group is a better electron donor than the smaller methyl group.

**19.36**

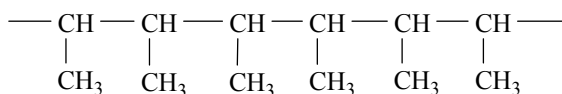
(a) tetrafluoroethene:  $\text{CF}_2=\text{CF}_2$



(b) phenylethene (styrene):



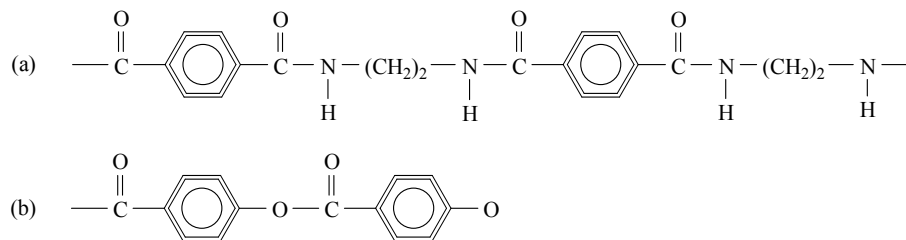
(c)  $\text{CH}_3\text{CH}=\text{CHCH}_3$



**19.38**

(a)  $\text{HO—C(CH}_3)_2\text{—COOH}$  (b)  $\begin{array}{c} \text{CH}=\text{CH}_2 \\ | \\ \text{CH}_3 \end{array}$  (c)  $\text{NH}_2\text{CH}_2\text{COOH}$

**19.40**



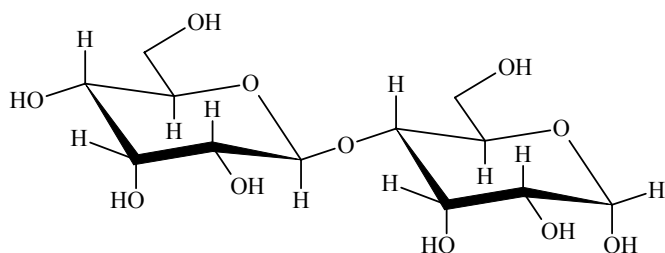
**19.42** The regular alternation of the placement of the substituents in a syndiotactic polymer (as opposed to the random attachments of substituents in an atactic polymer) permits the molecules to fit together snugly, forming a highly crystalline and dense material.

**19.44** Random copolymer.

**19.46** The more polar functional groups present, the greater the intermolecular forces. Greater intermolecular forces result in (a) higher softening point, (b) greater viscosity, and (c) greater mechanical strength.

**19.48** When polymer chains are cross-linked, the polymer does not soften as much as it otherwise would as the temperature is raised. It is also more resistant to deformation on stretching, because the cross-links pull it back. However, extensive cross linking can produce a rigid network that resists stretching.

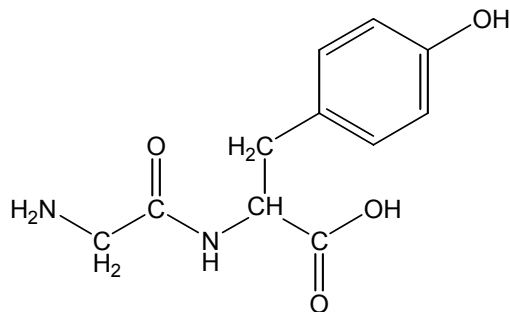
**19.50** (a)



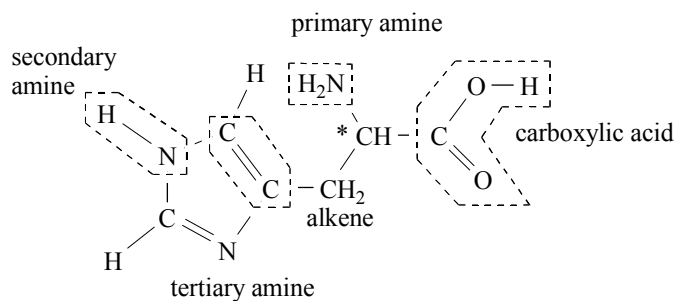
(b) The functional group formed acetal linkage; (c) the polymerization is a condensation reaction.

**19.52** Glycine, alanine, phenylalanine, valine, leucine, isoleucine, tryptophan, and methionine contain nonpolar side groups

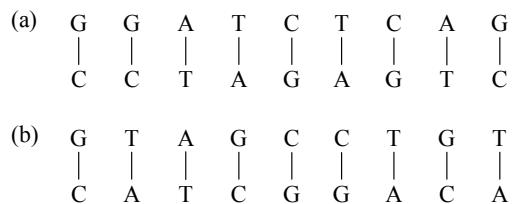
**19.54**



**19.56** (a) The functional groups include primary, secondary, and tertiary amines, as well as a carboxylic acid function. Histidine is an essential amino acid. There is one chiral carbon atom. It is labeled by an asterisk (\*) in the following structure.



**19.58**



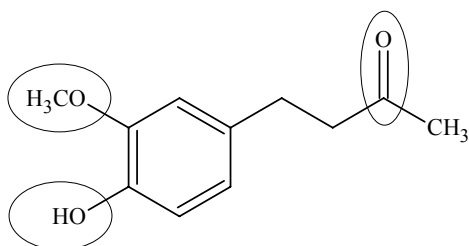
**19.60** (a)  $\text{C}_3\text{H}_7\text{NO}_2\text{S}$  (b)  $\text{C}_5\text{H}_5\text{N}_5$  (c)  $\text{C}_9\text{H}_{10}\text{O}_2$

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\* Chiral atoms are marked with an asterisk.

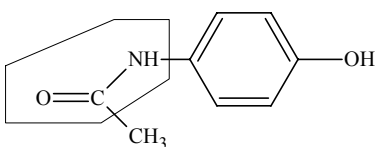
**19.62** All the functional groups are circled in the figures.

(a)



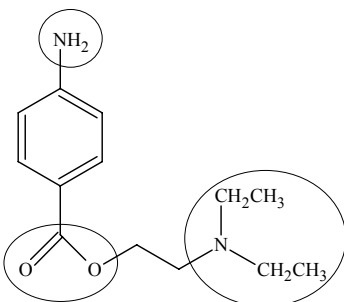
ether ( $-\text{OCH}_3$ ), alcohol ( $-\text{OH}$ ), ketone  $\left( \begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array} \right)$  aromatic ring  $\left( \text{benzene ring} \right)$

(b)



amide  $\left( \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N}-\text{R}' \\ | \\ \text{H} \end{array} \right)$ , phenol ( $-\text{OH}$ ), aromatic ring  $\left( \text{benzene ring} \right)$

(c)

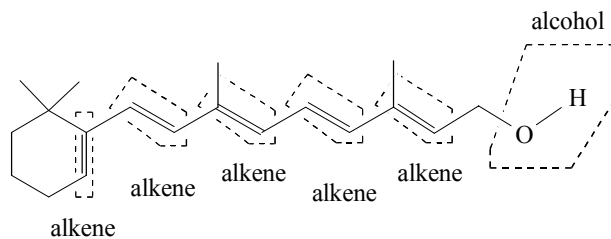


amine ( $-\text{NH}_2$ ), ester  $\left( \begin{array}{c} \diagup \\ \text{O}=\text{C} \\ \diagdown \end{array} \right)$ , tertiary amine  $\left( -\text{H}_2\text{C}-\text{N} \begin{array}{l} \diagup \text{CH}_2\text{CH}_3 \\ \diagdown \text{CH}_2\text{CH}_3 \end{array} \right)$

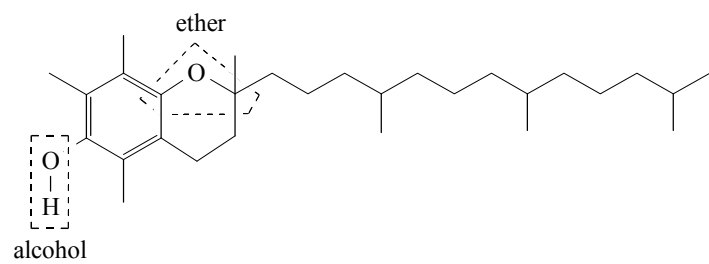


## 19.64

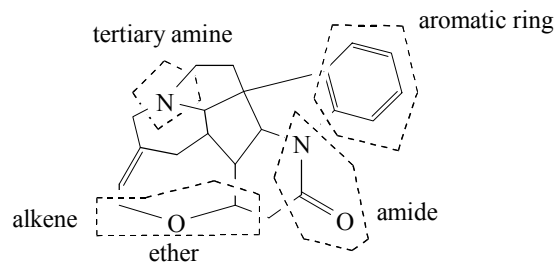
(a) alkene and alcohol



(b) ether, alcohol

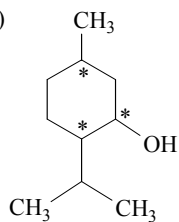


(c)

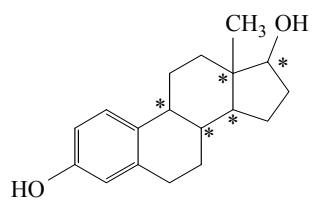


## 19.66

(a)



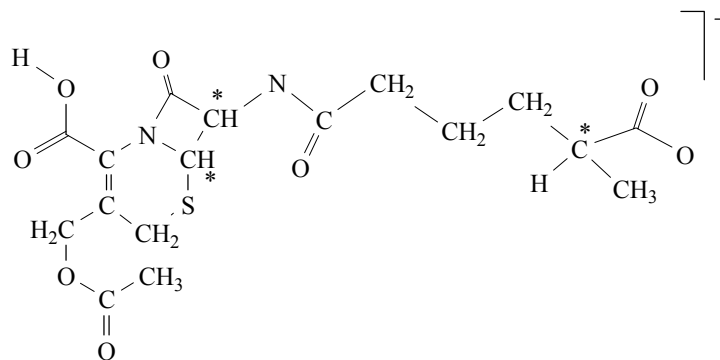
(b)



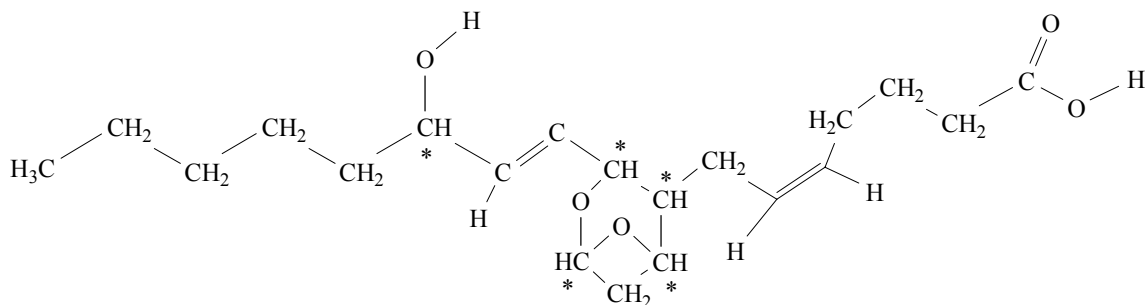
\*Indicates the chiral carbon atoms.

# 19.68

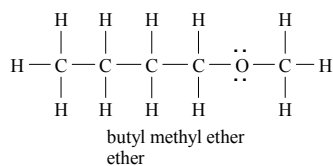
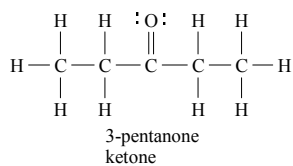
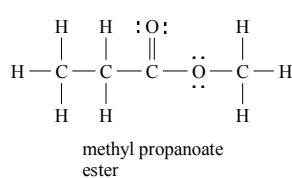
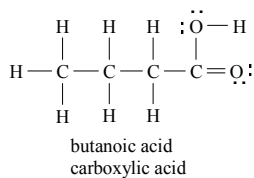
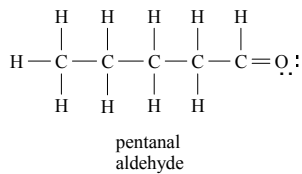
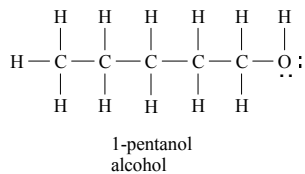
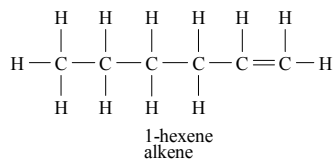
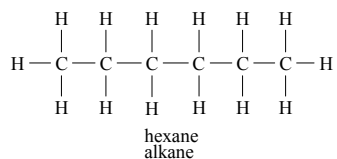
(a)



(b)



# 19.70 (a)



(b) 1-pentanol and butyl methyl ether are isomers. Pentanal and 3-pentanone are isomers. Butanoic acid and methyl propanoate are isomers. None of these molecules are chiral.

(c) Hexane – London forces

1-hexene – London forces

1-pentanol – hydrogen bonding, dipole-dipole interactions, London forces

Pentanal – dipole-dipole interactions, London forces

butanoic acid – hydrogen bonding, London forces, dipole-dipole interactions

methyl propanoate – London forces, dipole-dipole interactions

3-pentanone – London forces, dipole-dipole interactions

butyl methyl ether – London forces, weak dipole-dipole forces

(d) We can classify the molecules in the list into three categories based upon their intermolecular interactions: (1) those with London forces only, (2) those with London forces and dipole-dipole interactions, and (3) those with London forces, dipole-dipole interactions, and hydrogen bonding. The boiling point should increase with the increase in the types of intermolecular forces available, so compounds of type (1) will boil at a lower temperature than compounds of type (2), which will in turn boil at a lower temperature than compounds of type (3).

Type (1) molecules: hexane and 1-hexene

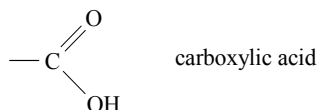
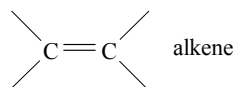
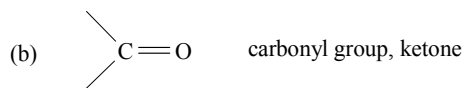
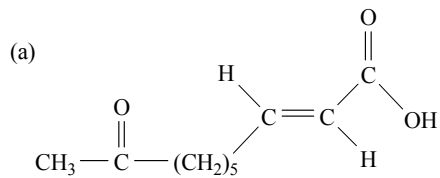
Type (2) molecules: pentanal, methyl propanoate, 3-pentanone, and butyl methyl ether

Type (3) molecules: pentanol and butanoic acid.

Within these classifications, it is more difficult to order the molecules; however, we can make some generalizations. The C=O in an aldehyde or a ketone will have a larger dipole moment than the C—O—C linkage in an ether, because of the geometry around the O atom. Thus we expect the ether to boil at a lower temperature. Among the molecules of Type (3), carboxylic acids generally exhibit stronger H-bonding than alcohols, so we would expect butanoic acid to boil at a higher temperature than pentanol.

Compound	Observed Boiling Point (°C)
hexane	69
1-hexene	64
pentanol	119–120
butanoic acid	103
methyl propanoate	79
3-pentanone	102
butyl methyl ether	70–71

### 19.72



**19.74** (a) condensation; (b) Because the sodium hydroxide is concentrated, the elimination reaction should dominate; however, nucleophilic substitution may also occur. (c) nucleophilic substitution; (d) condensation; (e) electrophilic substitution

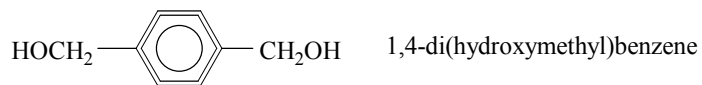
**19.76** Polymers generally do not have definite molecular masses because there is no fixed point at which the chain-lengthening process will cease. The chain stops growing due to lack of nearby monomer units of the

appropriate kind or a lack of properly oriented smaller polymeric aggregates.

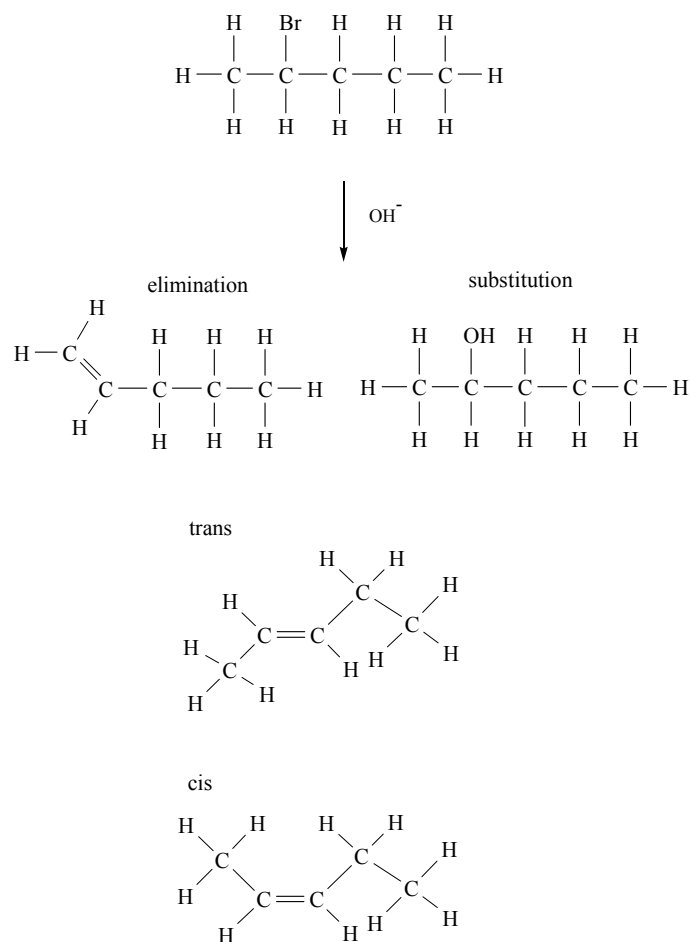
A polymer is, in a sense, not a pure compound, but rather a mixture of similar compounds of different chain length. There is no fixed molar mass, only an average molar mass. Because there is no one unique compound, there is no one unique melting point, rather a range of melting points.

Thus, there is no sharp transition between solid and liquid, and we say the solid softens rather than melts.

### 19.78

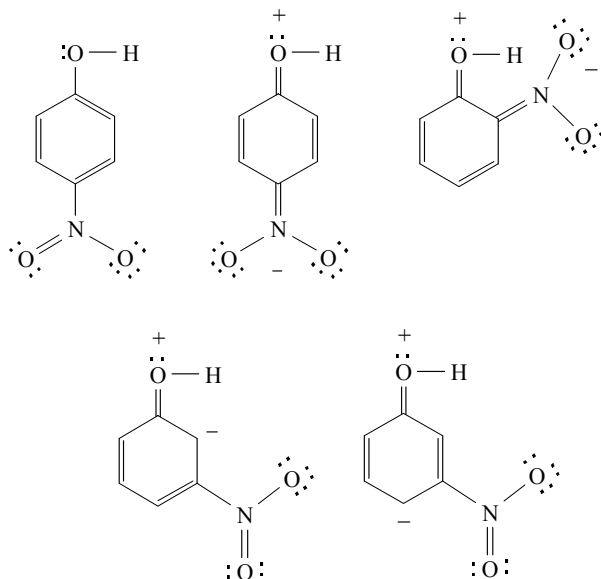


**19.80 (a)**



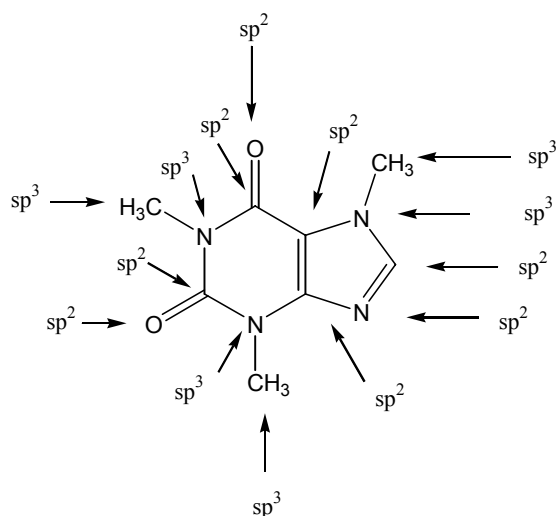
(b) Substitution will be favored over elimination if the hydroxide solution is dilute.

**19.82** The nitro group in general is an electron-withdrawing group and would normally be expected to enhance the acidity of the phenol, simply by pulling electron density away from the phenol oxygen atom. This happens by two processes. One is the simple inductive effect of having the electronegative groups attached to the aromatic ring. The second effect is through the resonance interaction of the nitro group with the aromatic ring, which reinforces the resonance interaction with the oxygen atom for the o- and p-isomers. The m-isomer, however, does not have a reinforcing resonance interaction. The appropriate resonance forms are shown below:



- 19.84** There is one nucleotide every 340 pm, or  $3.40 \times 10^{-10}$  m. Over the course of 0.299 m, there will be  $8.79 \times 10^8$  nucleotides. Each nucleotide has a molar mass of 625 g/mol on average, so the molar mass of the DNA molecule will be  $5.50 \times 10^{11}$  g/mol.
- 19.86** (a) The  $\text{Fe}^{2+}$  ions exit the ferritin protein through the “three-fold channel,” as this channel is lined with the polar amino acids aspartate and glutamate. This hydrophilic channel allows  $\text{Fe}^{2+}$  ions, complexed with water molecules, to exit the protein. The “four-fold channel” is lined with hydrophilic leucine, which prevents the water-soluble ion from exiting through this route.
- 19.88** (a) The nitrogen atoms as drawn are  $\text{sp}^3$  hybridized. (b) The polymer absorbs light due to the long chain of alternating single bonds and double bonds in the structure.

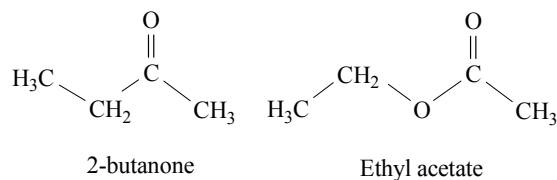
**19.90 (a)**



(b) Bond angles for  $sp^3$ -hybridized atoms should be around  $109.5^\circ$ .  
Bond angles for  $sp^2$ -hybridized atoms should be  $120^\circ$ .

**19.92** Two peaks with relative overall intensities 3:1. The larger peak is due to the six methyl protons and is split into three lines with intensities in the ratio 1:2:1. The smaller peak is due to the two methylene protons and is split into seven lines with relative intensities 1:6:15:20:15:6:1.

**19.94** The structures of the two compounds are shown below.



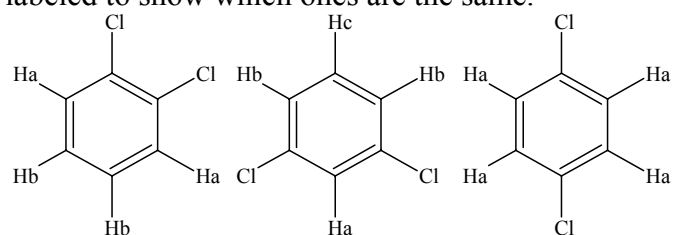
Both molecules contain an ethyl and a methyl group. The quartets are assigned to the  $\text{CH}_2$  groups of the ethyl unit. They have an intensity of two, and the fine structure arises from coupling to the three protons on the adjacent methyl group. Similarly, the triplet peaks in each spectrum correspond to the  $\text{CH}_3$  part of the ethyl unit. They have an intensity of three and are triplets, owing to coupling to the two  $\text{CH}_2$  protons. The peaks that have no coupling arise from the isolated methyl groups. The



major difference between the two spectra is the chemical shift, especially for the CH<sub>2</sub> groups. The CH<sub>2</sub> group of ethyl acetate is found farthest downfield because it is attached directly to an electronegative oxygen atom that acts to pull electron density away from the atoms attached to it. The C=O group is also somewhat electron-withdrawing but not nearly so much as an oxygen atom. The CH<sub>3</sub> parts of the ethyl groups are not much influenced by the change in molecular structure because they are removed from the electronegative center and the influence is not felt as strongly. Similarly, the isolated CH<sub>3</sub> groups are both attached to carbonyl functions and occur at similar chemical shifts.

**19.96** <sup>31</sup>P, <sup>19</sup>F, <sup>13</sup>C, <sup>15</sup>N, <sup>29</sup>Si, <sup>103</sup>Rh, <sup>107</sup>Ag, <sup>109</sup>Ag, <sup>77</sup>Se, <sup>111</sup>Cd, <sup>113</sup>Cd, <sup>117</sup>Sn, <sup>119</sup>Sn, <sup>125</sup>Te, <sup>207</sup>Pb, <sup>203</sup>Tl, <sup>205</sup>Tl, <sup>129</sup>Xe, <sup>183</sup>W, <sup>195</sup>Pt, <sup>187</sup>Os, <sup>89</sup>Y, etc.

**19.98** All the H atoms in benzene are equivalent and so there is only one peak observed, which contains no fine structure due to H—H interactions. The structures of the dichlorobenzenes are given below. The H atoms are labeled to show which ones are the same.



*o*-dichlorobenzene    *m*-dichlorobenzene    *p*-dichlorobenzene

As can be seen from the diagrams, *o*-dichlorobenzene will have two peaks in a 1:1 ratio, *m*-dichlorobenzene will have three signals in a 1:2:1 ratio, and *p*-dichlorobenzene will have only one signal. This alone is enough to distinguish between the three isomers. Coupling of H atoms attached to aromatic rings to other H atoms attached to the same ring is sometimes not simple. The degree of splitting of the signals is often small and may not be

resolvable unless one is using a spectrometer with a very large magnetic field strength. For the molecules in question, it is possible to say definitively that all the  $^1\text{H}$  atoms of *p*-dichlorobenzene are equivalent and will show no splitting. The  $\text{H}_a$  and  $\text{H}_b$  atoms of *o*-dichlorobenzene will couple to each other, but the pattern will be more complicated. An even more complicated fine structure is expected for the *m*-dichlorobenzene, in which there are three different types of protons attached to the aromatic ring.