STUDY GUIDE AND SOLUTIONS MANUAL
TO ACCOMPANY

ORGANIC CHEMISTRY

TENTH EDITION

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are relatively positive and which are relatively negative—in other words, their **polarity**. Associations between molecules strongly depend on both shape and the complementarity of their electrostatic charges (polarity).

When it comes to organic chemistry it will be much easier for you to understand why organic molecules have certain properties and react the way they do if you have an appreciation for the structure of the molecules involved. Structure is, in fact, almost everything, in that whenever we want to know why or how something works we look ever more deeply into its structure. This is true whether we are considering a toaster, jet engine, or an organic reaction. If you can visualize the shape of the puzzle pieces in organic chemistry (molecules), you will see more easily how they fit together (react).

SOME EXAMPLES

In order to review some of the concepts that will help us understand the structure of organic molecules, let's consider three very important molecules—water, methane, and methanol (methyl alcohol). These three are small and relatively simple molecules that have certain similarities among them, yet distinct differences that can be understood on the basis of their structures. Water is a liquid with a moderately high boiling point that does not dissolve organic compounds well. Methanol is also a liquid, with a lower boiling point than water, but one that dissolves many organic compounds easily. Methane is a gas, having a boiling point well below room temperature. Water and methanol will dissolve in each other, that is, they are miscible. We shall study the structures of water, methanol, and methane because the principles we learn with these compounds can be extended to much larger molecules.

Water

HOH

Let's consider the structure of water, beginning with the central oxygen atom. Recall that the atomic number (the number of protons) for oxygen is eight. Therefore, an oxygen atom also has eight electrons. (An ion may have more or less electrons than the atomic number for the element, depending on the charge of the ion.) Only the valence (outermost) shell electrons are involved in bonding. Oxygen has six valence electrons—that is, six electrons in the second principal shell. (Recall that the number of valence electrons is apparent from the group number of the element in the periodic table, and the row number for the element is the principal shell number for its valence electrons.) Now, let's consider the electron configuration for oxygen. The sequence of atomic orbitals for the first three shells of any atom is shown below. Oxygen uses only the first two shells in its lowest energy state.

$$1s,\ 2s,\ 2p_x,\ 2p_y,\ 2p_z,\ 3s,\ 3p_x,\ 3p_y,\ 3p_z$$

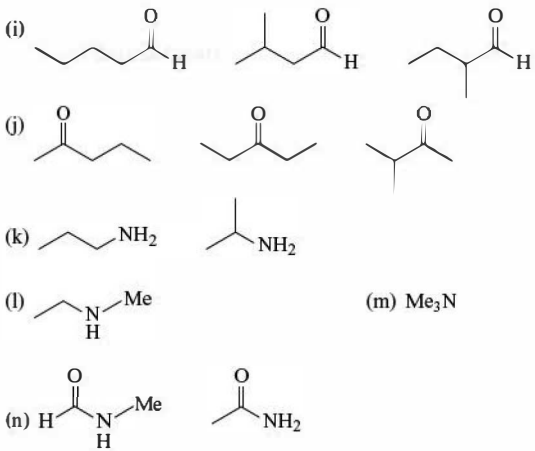
The *p* orbitals of any given principal shell (second, third, etc.) are of equal energy. Recall also that each orbital can hold a maximum of two electrons and that each equal energy orbital must accept one electron before a second can reside there (Hund's rule). So, for oxygen we place two electrons in the 1*s* orbital, two in the 2*s* orbital, and one in each of the 2*p* orbitals, for a subtotal of seven electrons. The final eighth electron is paired with another in one of the 2*p* orbitals. The configuration for the eight electrons of oxygen is, therefore

$$1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$$

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Physical Properties

2.36 (a) The O—H group of Vitamin A is the hydrophilic portion of the molecule, but the remainder of the molecule is not only hydrophobic but much larger. The multiple van der Waals attractions outweigh the effect of hydrogen bonding to water through a single hydroxyl group. Hence, Vitamin A is not expected to be water soluble.

(b) For Vitamin B_3, there are multiple hydrophilic sites. The carbonyl oxygen and the O—H of the acid function as well as the ring nitrogen can all hydrogen bond to water. Since the hydrophobic portion (the ring) of the molecule is modest in size, the molecule is expected to be water soluble.

2.37 The attractive forces between hydrogen fluoride molecules are the very strong dipole-dipole attractions that we call *hydrogen bonds*. (The partial positive charge of a hydrogen fluoride molecule is relatively exposed because it resides on the hydrogen nucleus. By contrast, the positive charge of an ethyl fluoride molecule is buried in the ethyl group and is shielded by the surrounding electrons. Thus the positive end of one hydrogen fluoride molecule can approach the negative end of another hydrogen fluoride molecule much more closely, with the result that the attractive force between them is much stronger.)

2.38 The cis isomer is polar while the trans isomer is nonpolar ($\mu = 0$ D). The intermolecular attractive forces are therefore greater in the case of the cis isomer, and thus its boiling point should be the higher of the two.

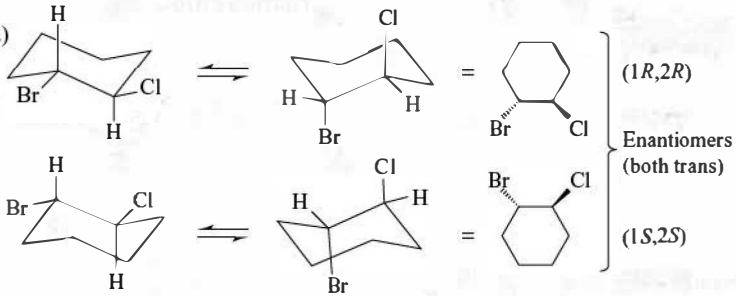
2.39 Because of its ionic character—it is a true salt—the compound is water-soluble. The organic cation and the bromide ion are well-solvated by water molecules in a fashion similar to sodium bromide. The compound also is soluble in solvents of low polarity such as diethyl ether (though less so than in water). The hydrophobic alkyl groups can now be regarded as lipophilic—groups that seek a nonpolar environment. Attractive forces between the alkyl groups of different cations can be replaced, in part, by attractive forces (van der Waals forces) between these alkyl groups and ether molecules.

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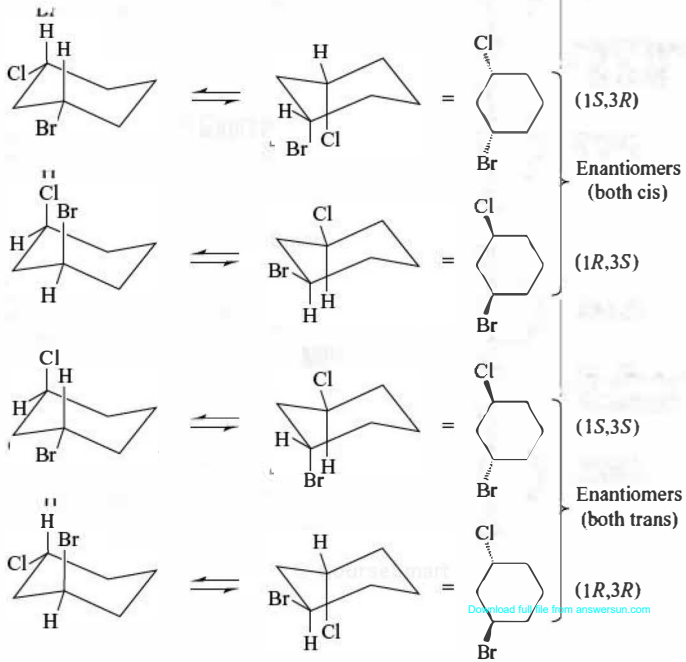
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5.29 (a)



(b)



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9.41 Compound J is *cis*-1,2-dichloroethene.

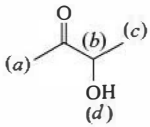


We can make the following IR assignments:

3125 cm^{-1}, alkene C—H stretching
1625 cm^{-1}, C=C stretching
695 cm^{-1}, out-of-plane bending of cis C—H bonds

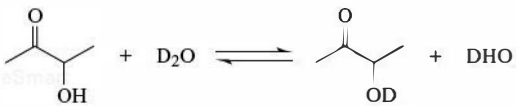
The ^1H NMR spectrum indicates the hydrogens are equivalent.

9.42 (a) Compound K is,



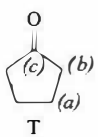
(a) Singlet, δ 2.15 C=O, near 1720 cm^{-1} (s)
(b) Quartet, δ 4.25
(c) Doublet, δ 1.35
(d) Singlet, δ 3.75

(b) When the compound is dissolved in D_2O, the —OH proton (*d*) is replaced by a deuteron, and thus the ^1H NMR absorption peak disappears.



9.43 The IR absorption band at 1745 cm^{-1} indicates the presence of a  group in a five-membered ring, and the signal at δ 220 can be assigned to the carbon of the carbonyl group.

There are only two other signals in the ^{13}C spectrum; the DEPT spectra suggest two equivalent sets of two —CH_2— groups each. Putting these facts together, we arrive at cyclopentanone as the structure for T.



(a) δ 23
(b) δ 38
(c) δ 220

9.44 (1) Molecular ion = 96 *m/z*

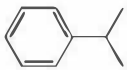
Potential molecular formula = C_7H_{14} or C_6H_8O

(2) The presence of a strong C=O absorption at 1685 cm^{-1} in the IR and the integrals of the ^1H NMR spectra totaling 8, and the appearance of 6 unique carbons in the ^{13}C spectra lead to C_6H_8O as the correct molecular formula.

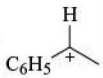
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27. 

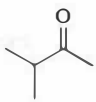
m/z 120 = M^+

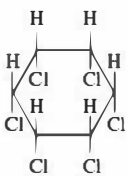
$105 = M^+ - 15(CH_3\cdot) =$ 

$77 = M^+ - 43(i - Pr\cdot) = C_6H_5^+$

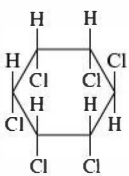
δ7.2–7.6	5 ring protons
2.95	CH of isopropyl group
1.29	equivalent CH_3s of isopropyl group

28. $C_5H_{10}O$ has IHD = 2
IR absorption indicates C=O
^{13}C NMR spectrum for **X** is consistent with structure

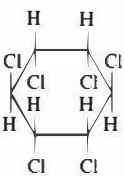


29. (a) 

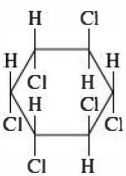
1 meso



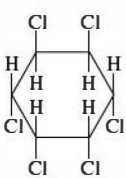
2 meso



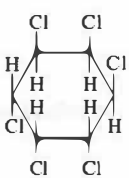
3 meso



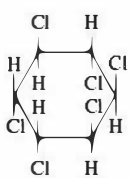
4 meso



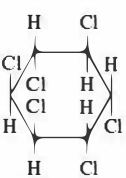
5 meso



6 meso

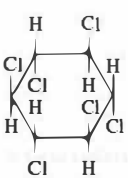


7



8

Enantiomers



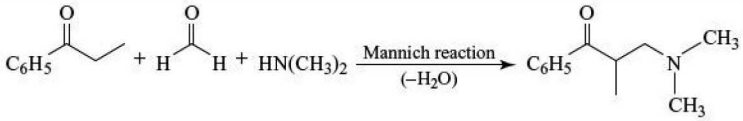
9 meso

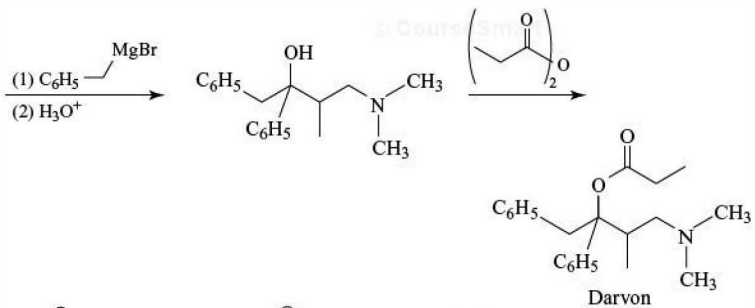
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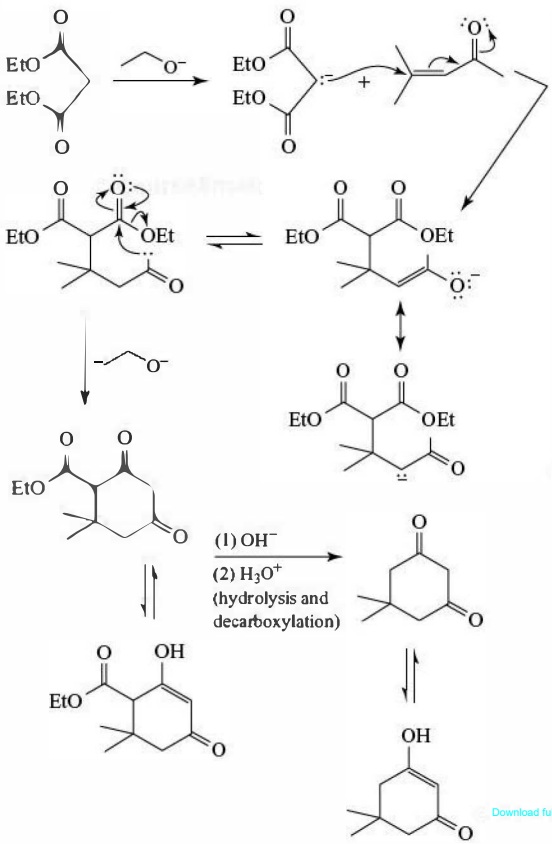
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19.51





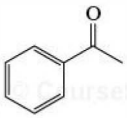
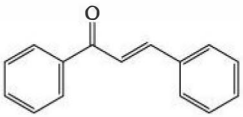
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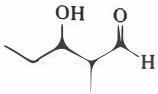
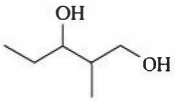
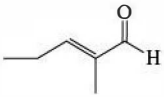


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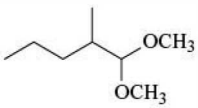
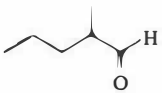
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19.7 (a)  (b)  (c) HCN

19.8 (a)  (b)  (c) 

(d) $LiAlH_4$, Et_2O (e) H_2, Ni, pressure (f) CH_3OH (excess), HA

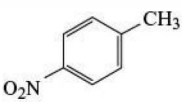
(g)  (h) 

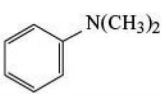
(i) (1) 
(2) H_2O

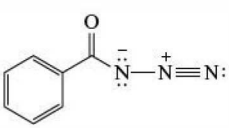
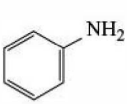
EXERCISE 20

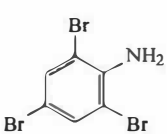
20.1 (d) 20.2 (e)

20.3 (a) (2) (b) (4) (c) (3)

20.4 (a) A = HNO_3/H_2SO_4 B =  C = $NaNO_2$, HCl, 0–5°C

D = CuCN E = $LiAlH_4$, Et_2O F = 

(b) A = NaN_3 B =  C = 

D =  E = H_3PO_2

20.5 (a) (2) (b) (2) (c) (1) (d) (1) (e) (2) (f) (2)

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