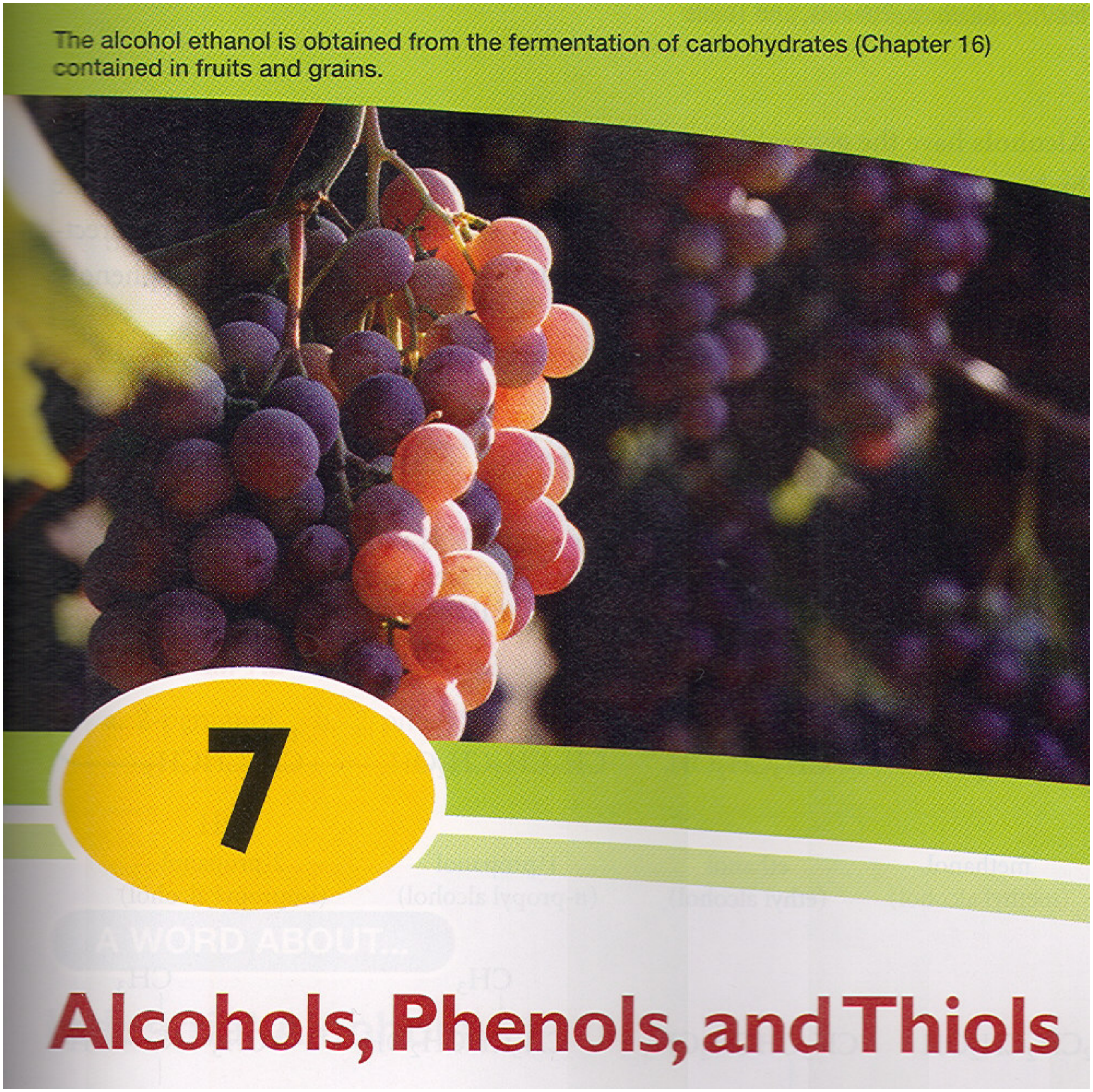
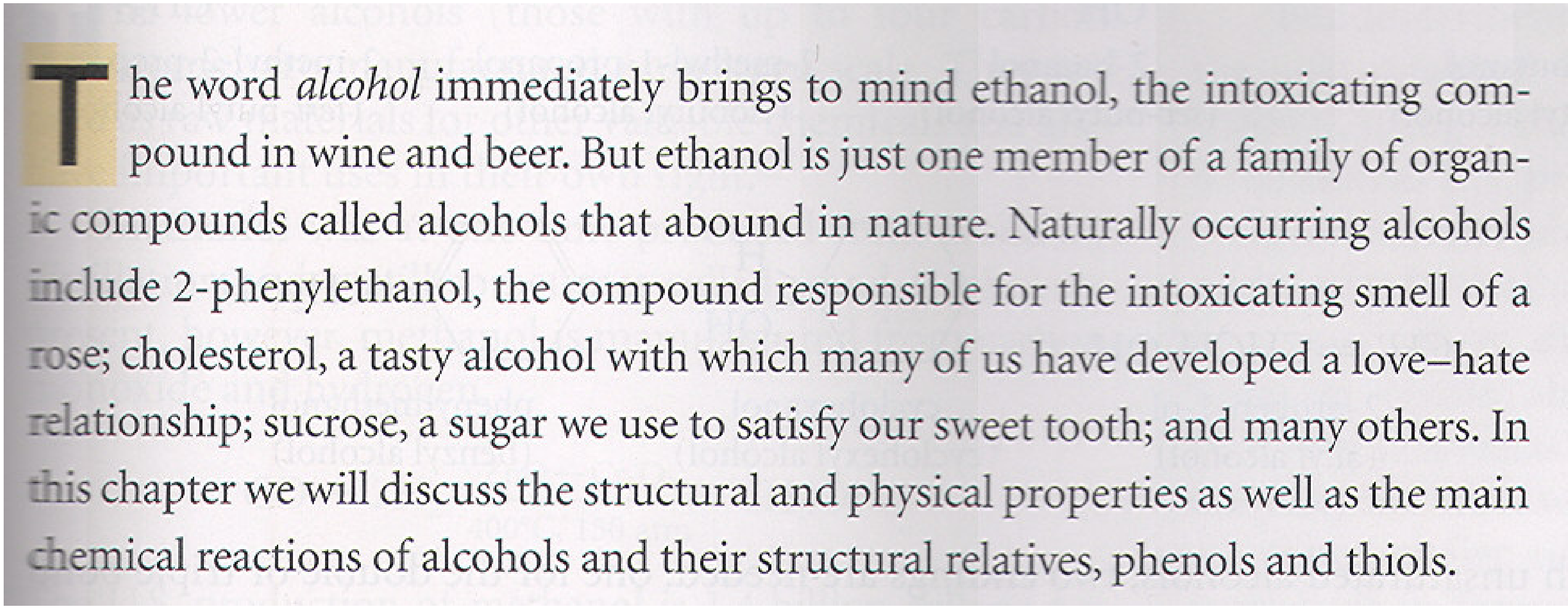


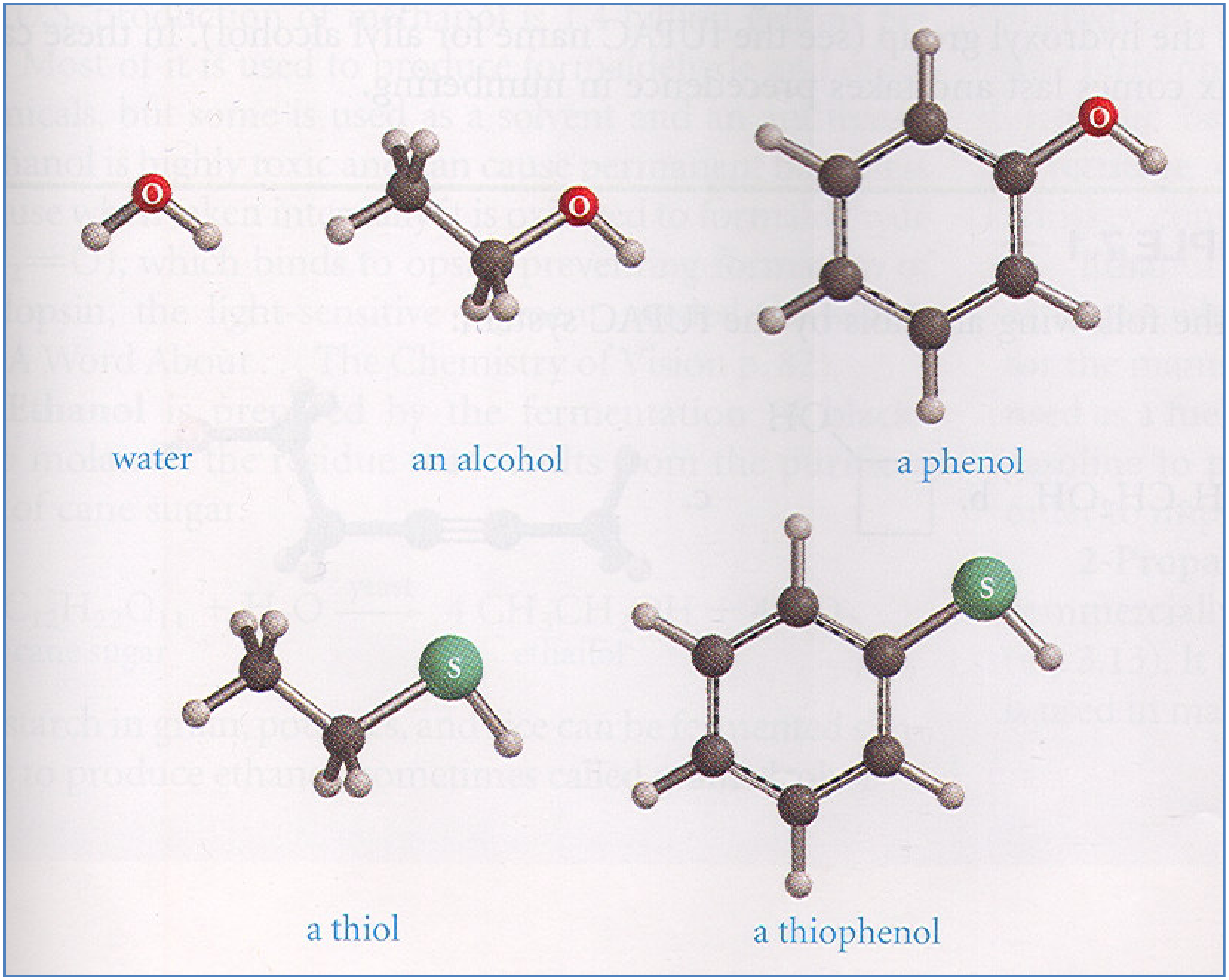
The alcohol ethanol is obtained from the fermentation of carbohydrates (Chapter 16) contained in fruits and grains.

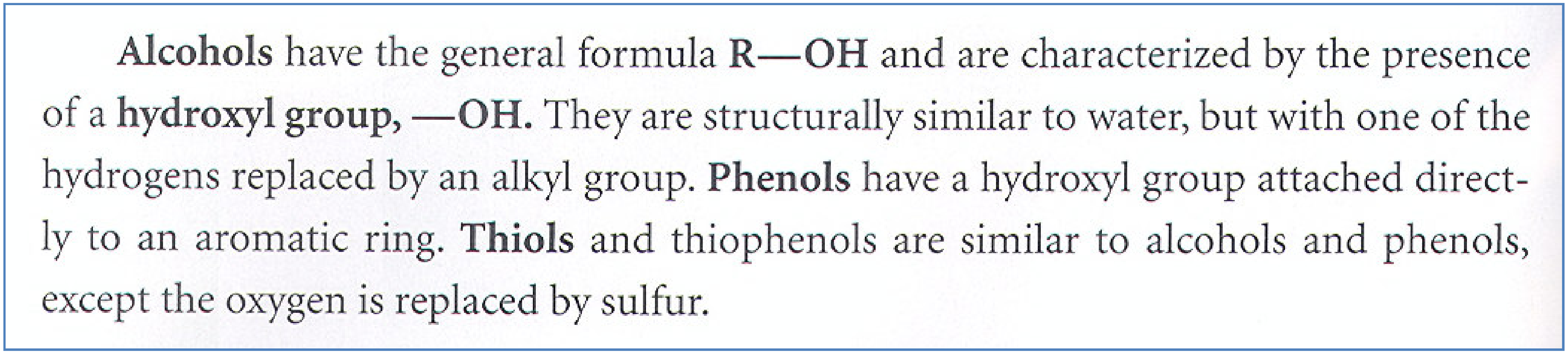
7

Alcohols, Phenols, and Thiols

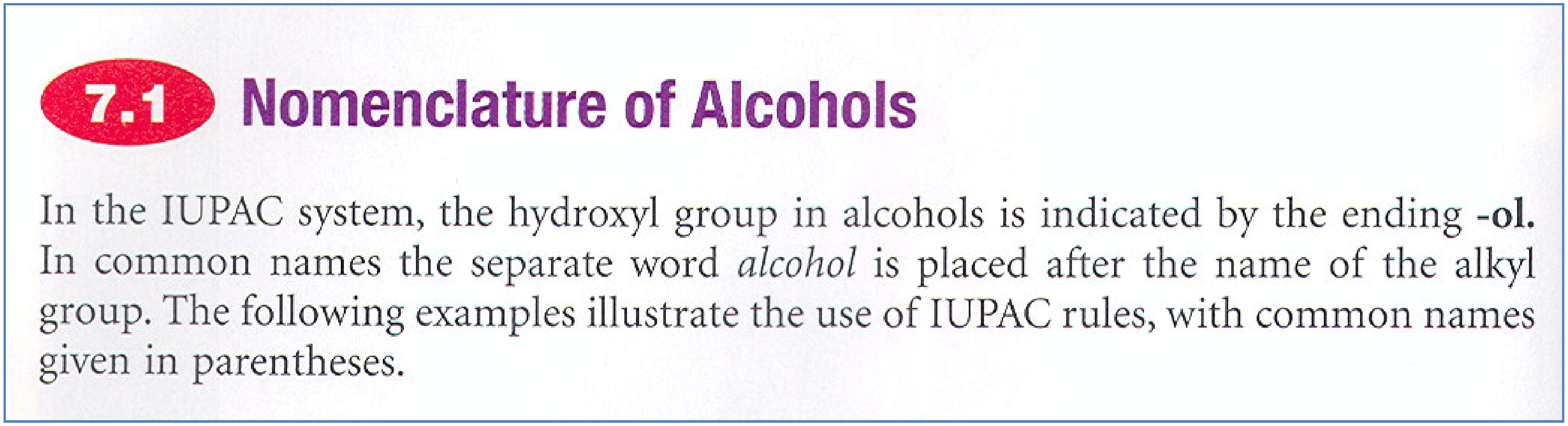


The word *alcohol* immediately brings to mind ethanol, the intoxicating compound in wine and beer. But ethanol is just one member of a family of organic compounds called alcohols that abound in nature. Naturally occurring alcohols include 2-phenylethanol, the compound responsible for the intoxicating smell of a rose; cholesterol, a tasty alcohol with which many of us have developed a love–hate relationship; sucrose, a sugar we use to satisfy our sweet tooth; and many others. In this chapter we will discuss the structural and physical properties as well as the main chemical reactions of alcohols and their structural relatives, phenols and thiols.


water
an alcohol
a phenol
a thiol
a thiophenol

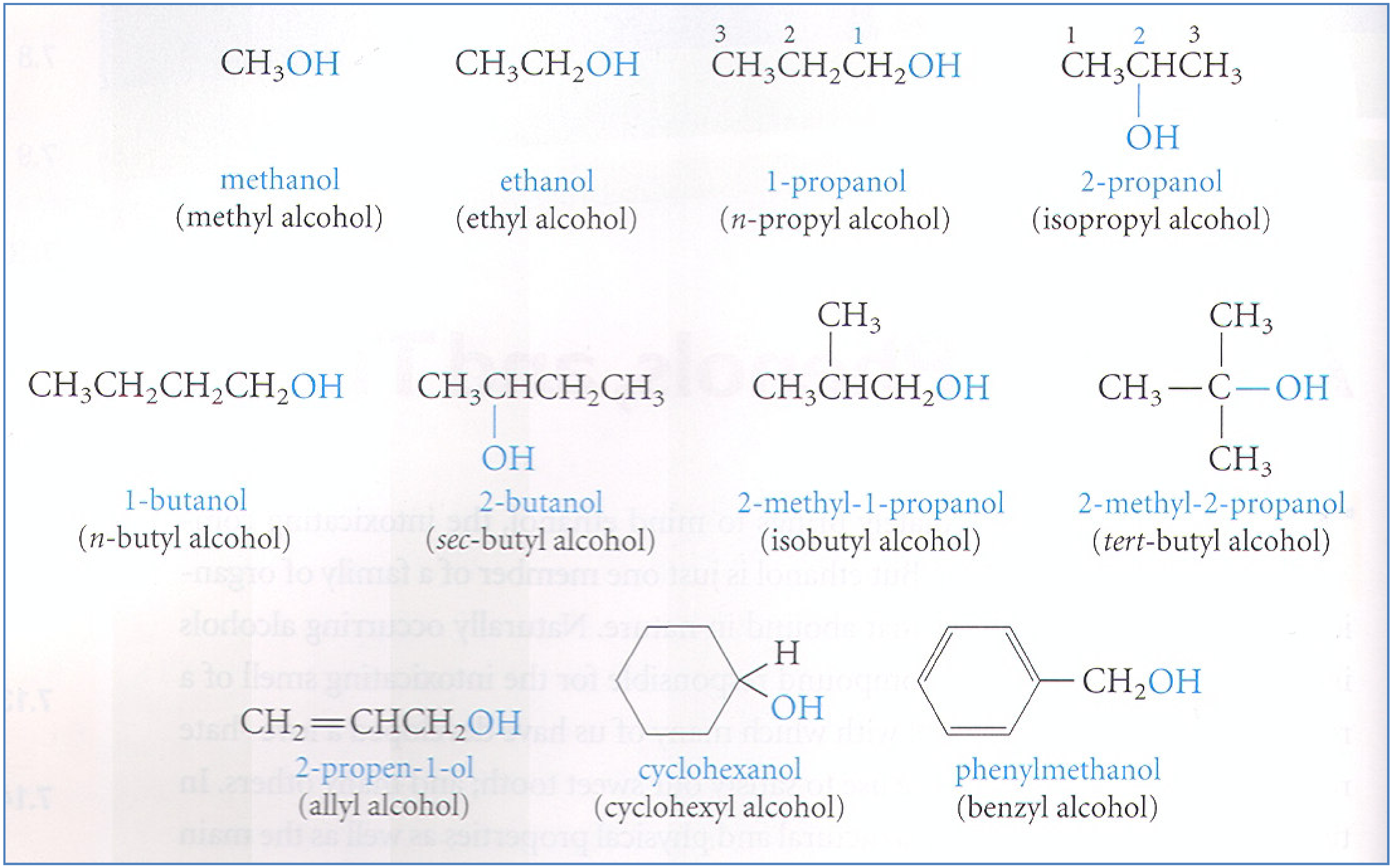


Alcohols have the general formula **R—OH** and are characterized by the presence of a **hydroxyl group, —OH.** They are structurally similar to water, but with one of the hydrogens replaced by an alkyl group. **Phenols** have a hydroxyl group attached directly to an aromatic ring. **Thiols** and thiophenols are similar to alcohols and phenols, except the oxygen is replaced by sulfur.



7.1 Nomenclature of Alcohols

In the IUPAC system, the hydroxyl group in alcohols is indicated by the ending **-ol.** In common names the separate word *alcohol* is placed after the name of the alkyl group. The following examples illustrate the use of IUPAC rules, with common names given in parentheses.



CH_3OH

methanol
(methyl alcohol)

CH_3CH_2OH

ethanol
(ethyl alcohol)

$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2OH$

1-propanol
(*n*-propyl alcohol)

$\overset{1}{C}H_3\overset{2}{C}H(OH)\overset{3}{C}H_3$

2-propanol
(isopropyl alcohol)

$CH_3CH_2CH_2CH_2OH$

1-butanol
(*n*-butyl alcohol)

$CH_3CH(OH)CH_2CH_3$

2-butanol
(*sec*-butyl alcohol)

$CH_3CH(CH_3)CH_2OH$

2-methyl-1-propanol
(isobutyl alcohol)

$CH_3-C(CH_3)_2-OH$

2-methyl-2-propanol
(*tert*-butyl alcohol)

$CH_2{=}CHCH_2OH$

2-propen-1-ol
(allyl alcohol)

cyclohexanol
(cyclohexyl alcohol)

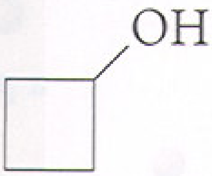
phenylmethanol
(benzyl alcohol)

With unsaturated alcohols, two endings are needed: one for the double or triple bond and one for the hydroxyl group (see the IUPAC name for allyl alcohol). In these cases, the *-ol* suffix comes last and takes precedence in numbering.

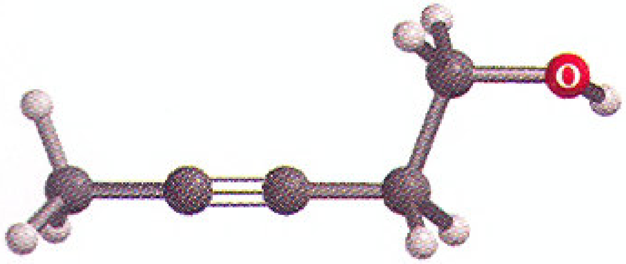
EXAMPLE 7.1

Name the following alcohols by the IUPAC system:

a. $ClCH_2CH_2OH$ b.

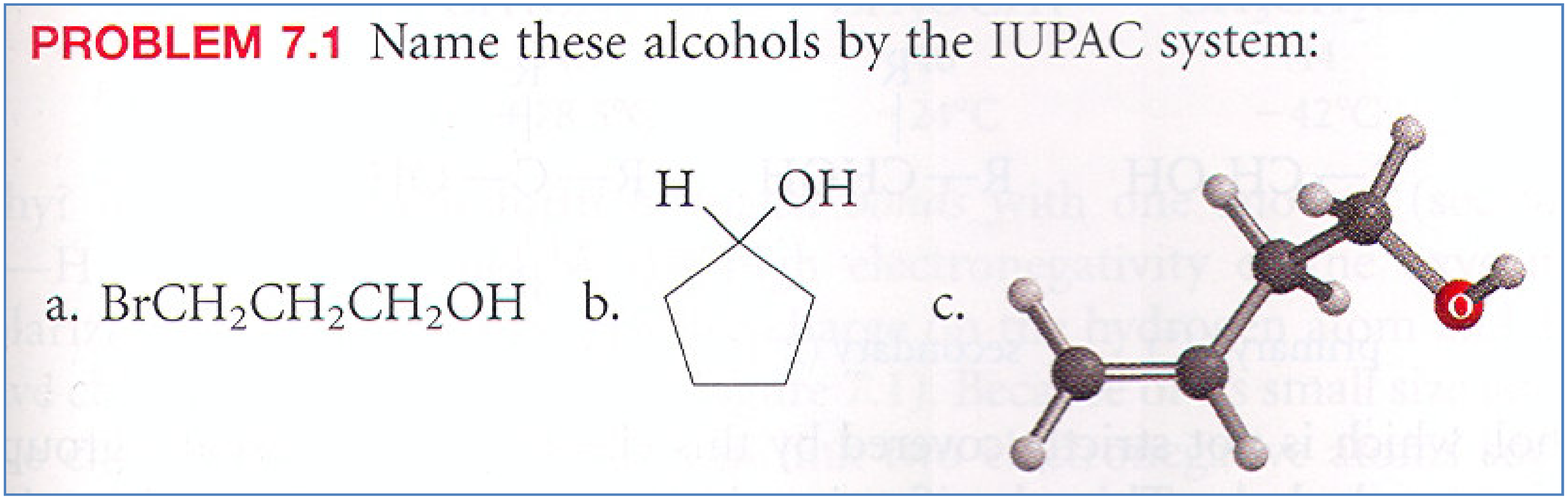


c.



SOLUTION

a. 2-chloroethanol (number from the hydroxyl-bearing carbon)
b. cyclobutanol
c. 3-pentyne-1-ol (*not* 2-pentyne-5-ol)



PROBLEM 7.1 Name these alcohols by the IUPAC system:

a. $BrCH_2CH_2CH_2OH$ b. c.

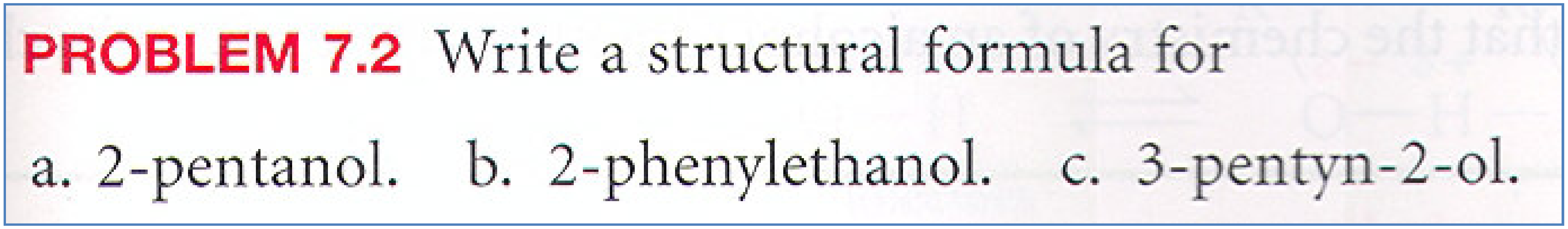
7.1 a. Number from the hydroxyl-bearing carbon:

$\text{Br}\overset{3}{\text{C}}\text{H}_2\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{H}_2\text{OH}$ 3-bromo-1-propanol or just 3-bromopropanol

b. cyclopentanol

c. The alcohol takes precedence over the double bond.

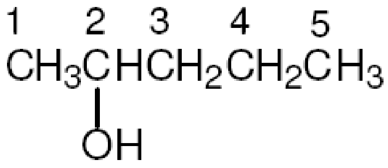
$\text{H}_2\overset{4}{\text{C}}{=}\overset{3}{\text{C}}\text{H}\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{H}_2\text{OH}$ 3-buten-1-ol



PROBLEM 7.2 Write a structural formula for

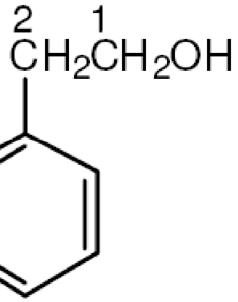
a. 2-pentanol. b. 2-phenylethanol. c. 3-pentyn-2-ol.

a.



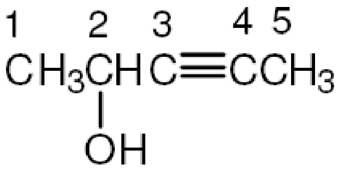
$$\underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_2CH_2CH_3}$$

b.

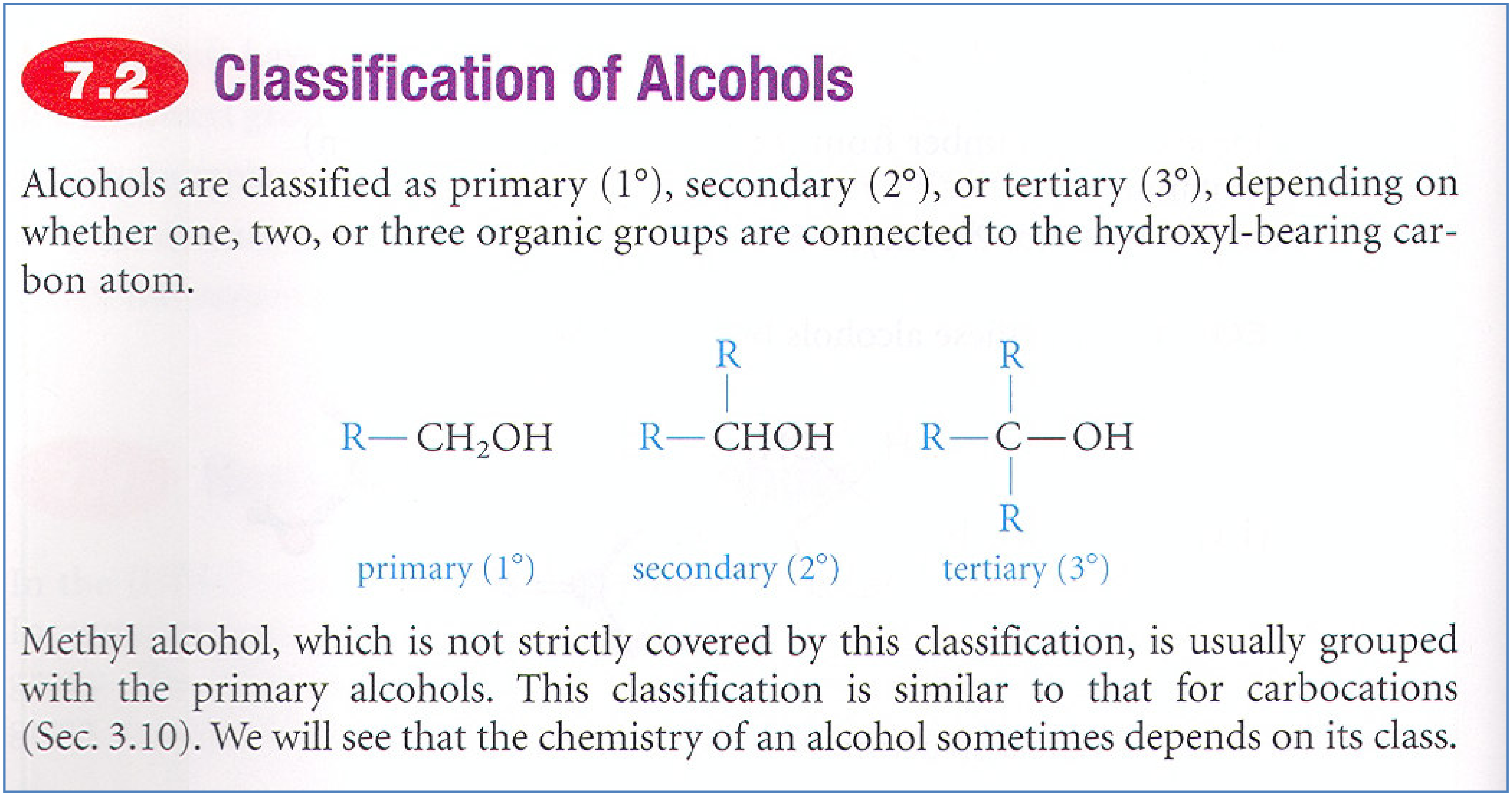


$C_6H_5CH_2CH_2OH$

c.



$$\underset{\displaystyle OH}{CH_3\underset{|}{C}HC{\equiv}CCH_3}$$



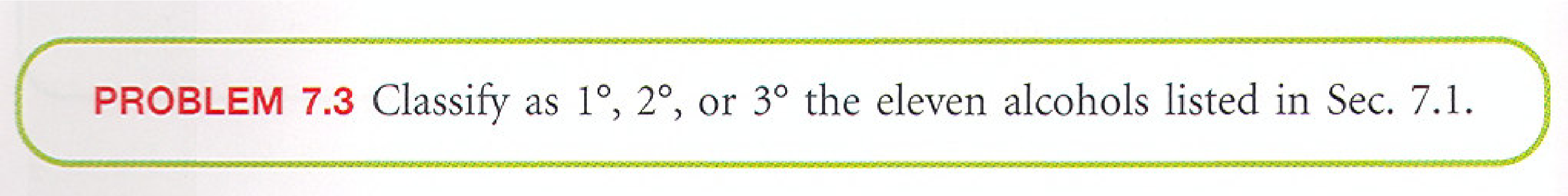
7.2 Classification of Alcohols

Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°), depending on whether one, two, or three organic groups are connected to the hydroxyl-bearing carbon atom.

$$\mathrm{R{-}CH_2OH} \qquad \mathrm{R{-}\overset{\displaystyle R \atop |}{C}HOH} \qquad \mathrm{R{-}\underset{\displaystyle | \atop R}{\overset{\displaystyle R \atop |}{C}}{-}OH}$$

primary (1°) secondary (2°) tertiary (3°)

Methyl alcohol, which is not strictly covered by this classification, is usually grouped with the primary alcohols. This classification is similar to that for carbocations (Sec. 3.10). We will see that the chemistry of an alcohol sometimes depends on its class.



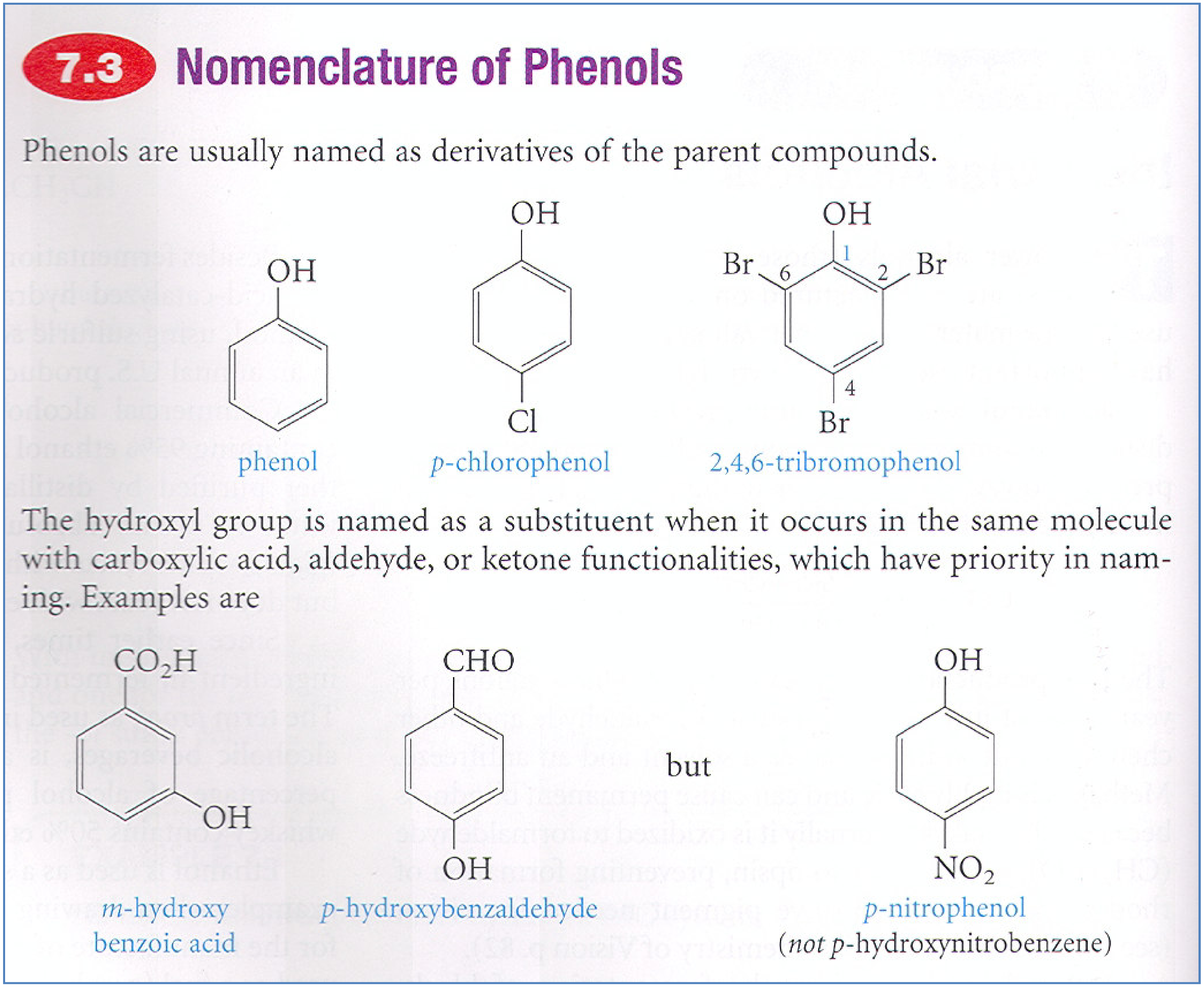
PROBLEM 7.3 Classify as 1°, 2°, or 3° the eleven alcohols listed in Sec. 7.1.

Methanol is usually grouped with the primary alcohols:

Primary: CH_3OH, CH_3CH_2OH, $CH_3CH_2CH_2OH$, $CH_3CH_2CH_2CH_2OH$, $(CH_3)_2CHCH_2OH$, $CH_2{=}CHCH_2OH$, $C_6H_5CH_2OH$ (all have a $-CH_2OH$ group)

Secondary: $(CH_3)_2CHOH$, $CH_3CH(OH)CH_2CH_3$, cyclohexanol (all have a CHOH group)

Tertiary: $(CH_3)_3COH$



7.3 Nomenclature of Phenols

Phenols are usually named as derivatives of the parent compounds.

phenol

p-chlorophenol

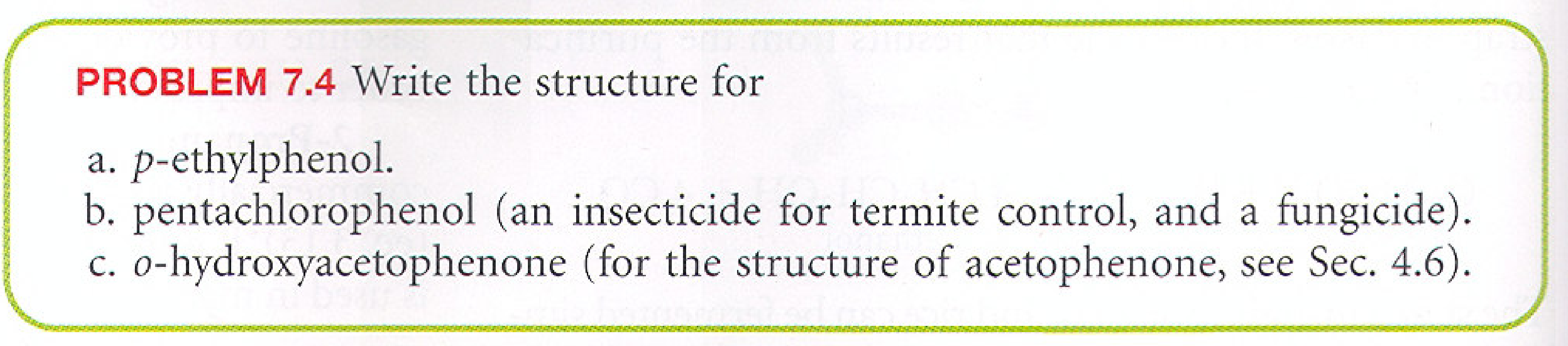
2,4,6-tribromophenol

The hydroxyl group is named as a substituent when it occurs in the same molecule with carboxylic acid, aldehyde, or ketone functionalities, which have priority in naming. Examples are

m-hydroxy benzoic acid

p-hydroxybenzaldehyde

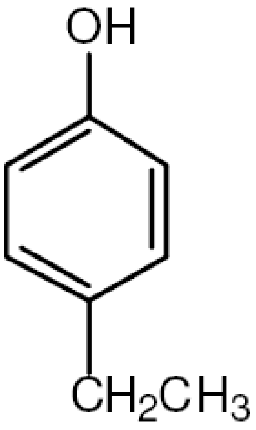
p-nitrophenol
(*not p*-hydroxynitrobenzene)



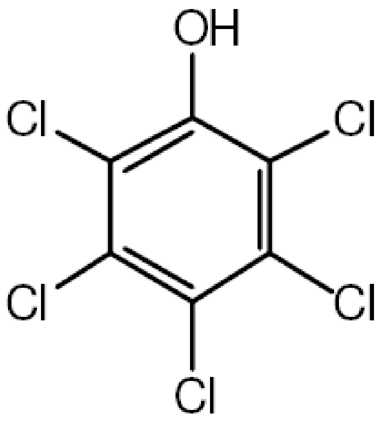
PROBLEM 7.4 Write the structure for

a. *p*-ethylphenol.
b. pentachlorophenol (an insecticide for termite control, and a fungicide).
c. *o*-hydroxyacetophenone (for the structure of acetophenone, see Sec. 4.6).

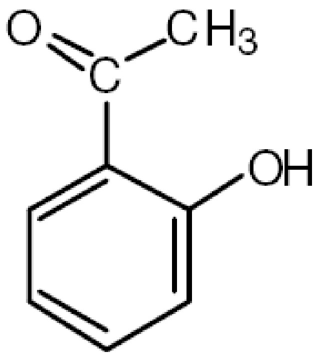
a.

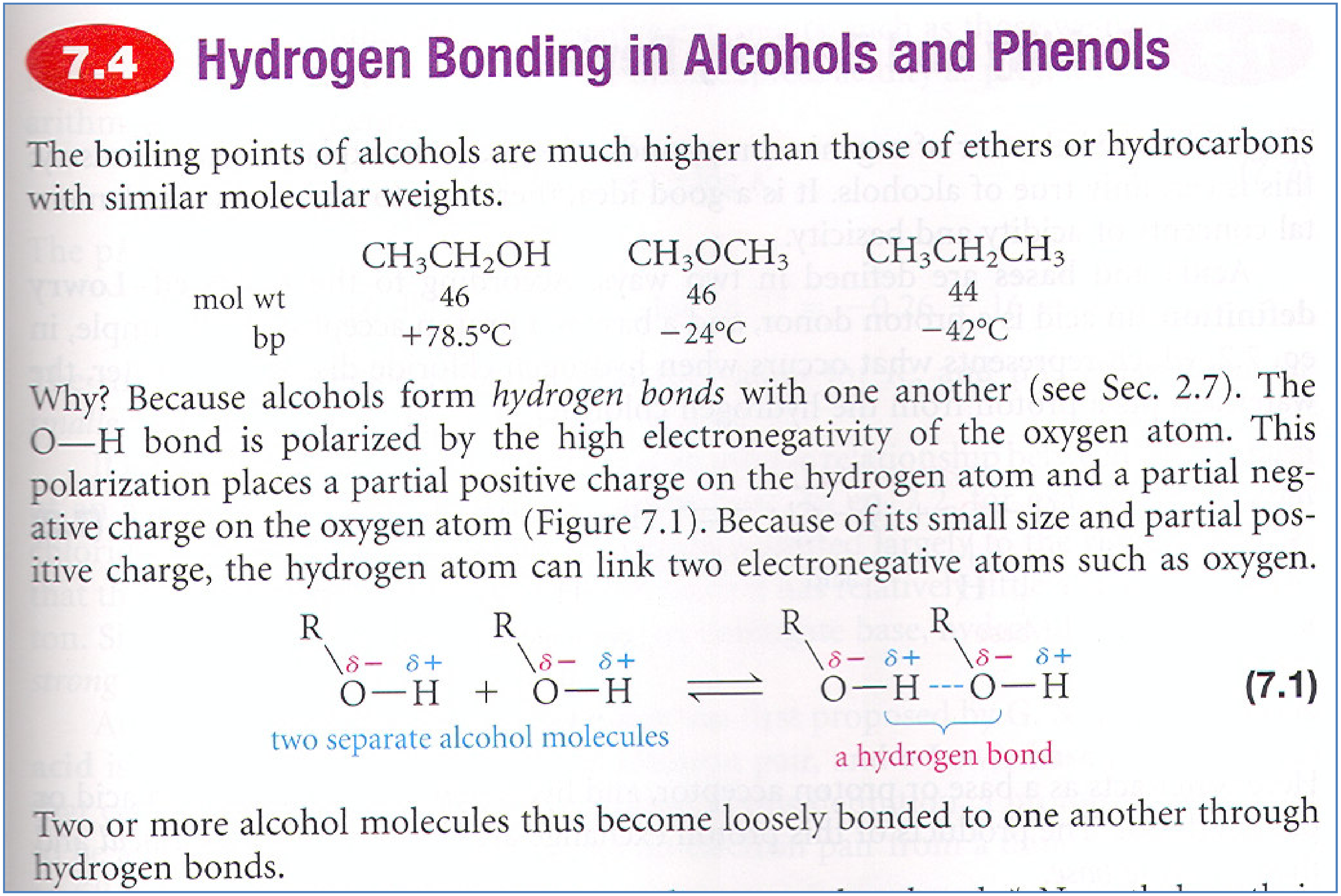


b.



c.





7.4 Hydrogen Bonding in Alcohols and Phenols

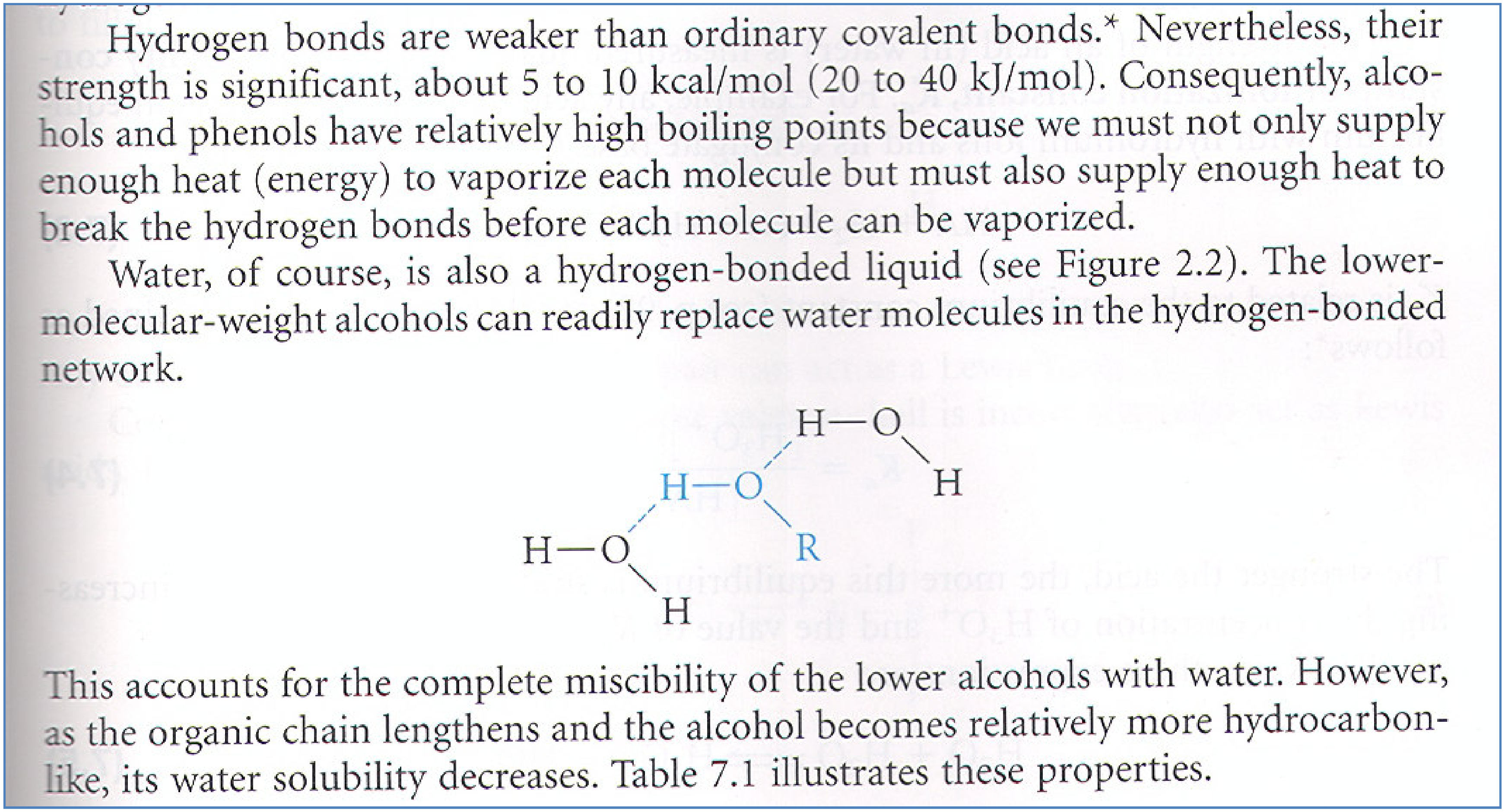
The boiling points of alcohols are much higher than those of ethers or hydrocarbons with similar molecular weights.

	CH_3CH_2OH	CH_3OCH_3	$CH_3CH_2CH_3$
mol wt	46	46	44
bp	+78.5°C	−24°C	−42°C

Why? Because alcohols form *hydrogen bonds* with one another (see Sec. 2.7). The O—H bond is polarized by the high electronegativity of the oxygen atom. This polarization places a partial positive charge on the hydrogen atom and a partial negative charge on the oxygen atom (Figure 7.1). Because of its small size and partial positive charge, the hydrogen atom can link two electronegative atoms such as oxygen.

$$\underbrace{\overset{R\backslash\ \delta-}{O}\overset{\delta+}{-H} + \overset{R\backslash\ \delta-}{O}\overset{\delta+}{-H}}_{\text{two separate alcohol molecules}} \rightleftharpoons \overset{R\backslash\ \delta-}{O}\overset{\delta+}{-}\underbrace{H \cdots O}_{\text{a hydrogen bond}}\overset{R\backslash\ \delta-\ \ \delta+}{-H} \qquad \textbf{(7.1)}$$

Two or more alcohol molecules thus become loosely bonded to one another through hydrogen bonds.



Hydrogen bonds are weaker than ordinary covalent bonds.* Nevertheless, their strength is significant, about 5 to 10 kcal/mol (20 to 40 kJ/mol). Consequently, alcohols and phenols have relatively high boiling points because we must not only supply enough heat (energy) to vaporize each molecule but must also supply enough heat to break the hydrogen bonds before each molecule can be vaporized.

Water, of course, is also a hydrogen-bonded liquid (see Figure 2.2). The lower-molecular-weight alcohols can readily replace water molecules in the hydrogen-bonded network.

This accounts for the complete miscibility of the lower alcohols with water. However, as the organic chain lengthens and the alcohol becomes relatively more hydrocarbon-like, its water solubility decreases. Table 7.1 illustrates these properties.

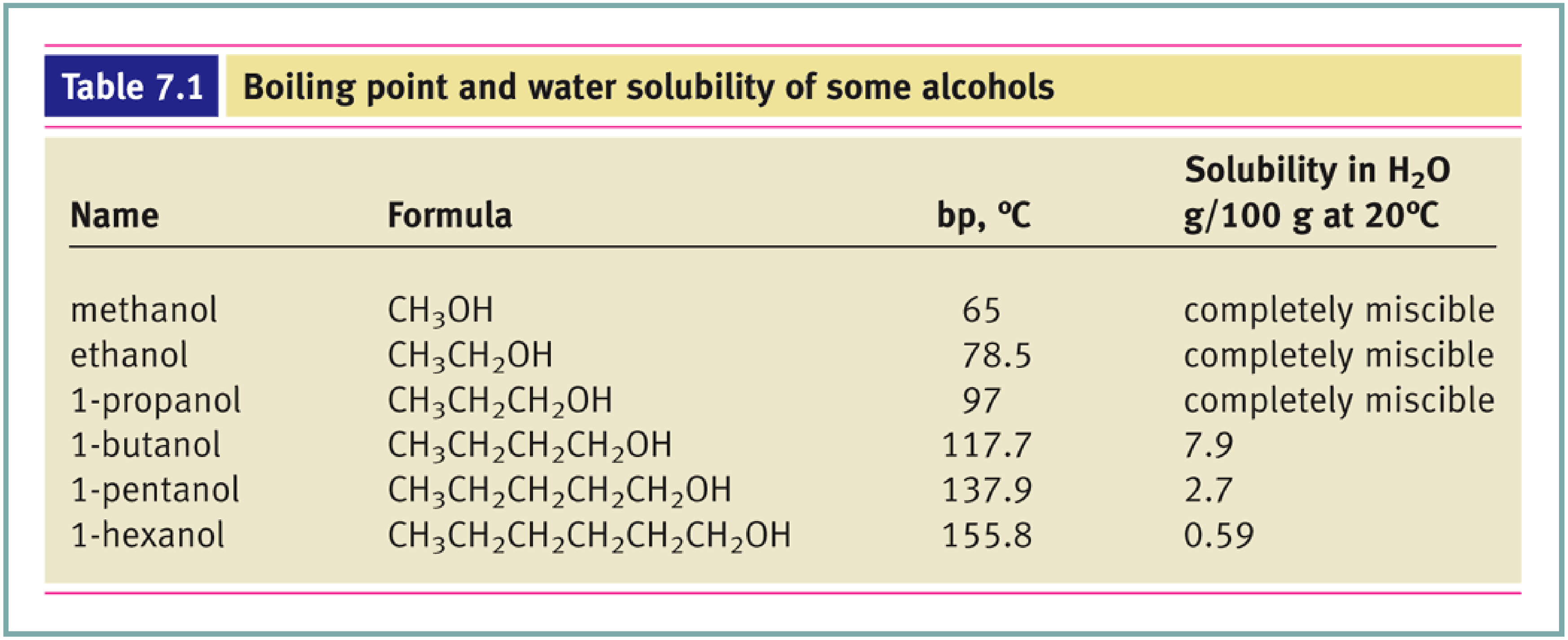


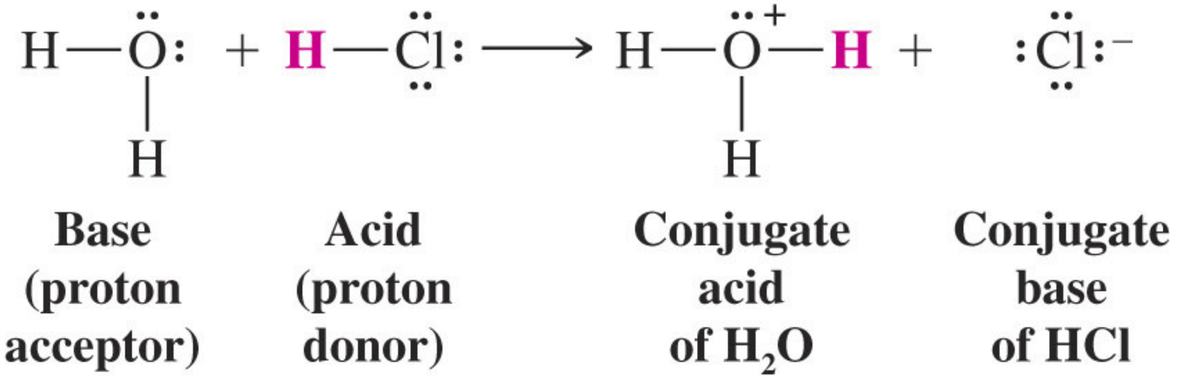
Table 7.1 Boiling point and water solubility of some alcohols

Name	Formula	bp, °C	Solubility in H_2O g/100 g at 20°C
methanol	CH_3OH	65	completely miscible
ethanol	CH_3CH_2OH	78.5	completely miscible
1-propanol	$CH_3CH_2CH_2OH$	97	completely miscible
1-butanol	$CH_3CH_2CH_2CH_2OH$	117.7	7.9
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	137.9	2.7
1-hexanol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	155.8	0.59

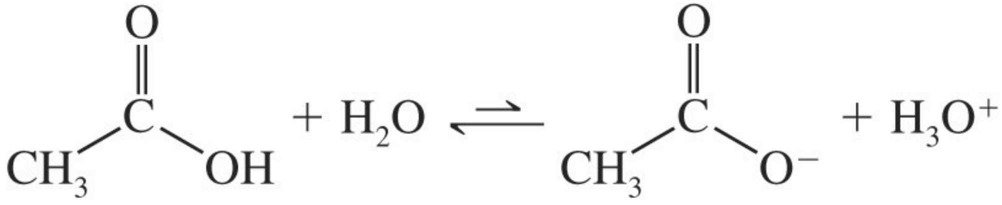
7.5 Acidity & Basicity Reviewed

Brønsted-Lowry Definition of Acids and Bases

- Acid: a substance that can donate a proton
- Base: a substance that can accept a proton
- Example
  - Hydrogen chloride is a very strong acid and essentially all hydrogen chloride molecules transfer their proton to water



- Strengths of Acids and Bases
  - K_a and pK_a
    - Acetic acid is a relatively weak acid and a 0.1M solution is only able to protonate water to the extent of about 1%



    - The equilibrium equation for this reaction is:

$$K_{eq} = \frac{[H_3O^+]\,[CH_3CO_2^-]}{[CH_3CO_2H][H_2O]}$$

- Dilute acids have a constant concentration of water (about 55.5 M) and so the concentration of water can be factored out to obtain the acidity constant (K_a)
- K_a for acetic acid is 1.76 X 10^{-5}

$$\boxed{K_a = K_{eq}[H_2O] = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]}}$$

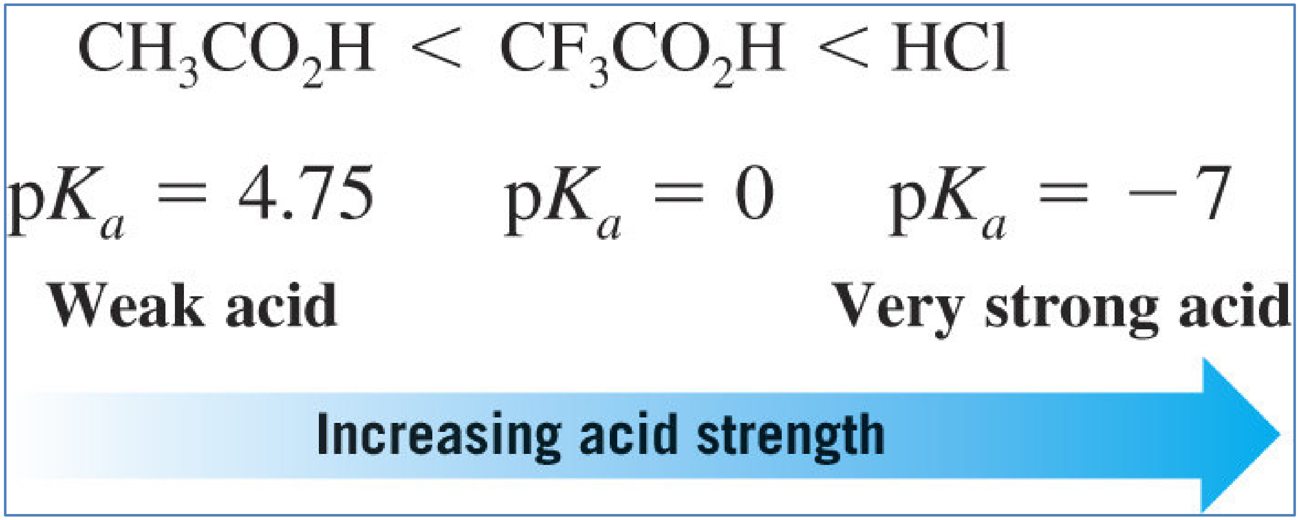
- Any weak acid (HA) dissolved in water fits the general K_a expression
  - The stronger the acid, the larger the K_a

$$\boxed{K_a = \frac{[H_3O^+][A^-]}{[HA]}}$$

- Acidity is usually expressed in terms of pK_a
  - pK_a is the negative log of K_a
  - The pK_a for acetic acid is 4.75

$$pK_a = -\log K_a$$

  - The larger the pK_a, the weaker the acid



$$CH_3CO_2H < CF_3CO_2H < HCl$$

$$pK_a = 4.75 \qquad pK_a = 0 \qquad pK_a = -7$$

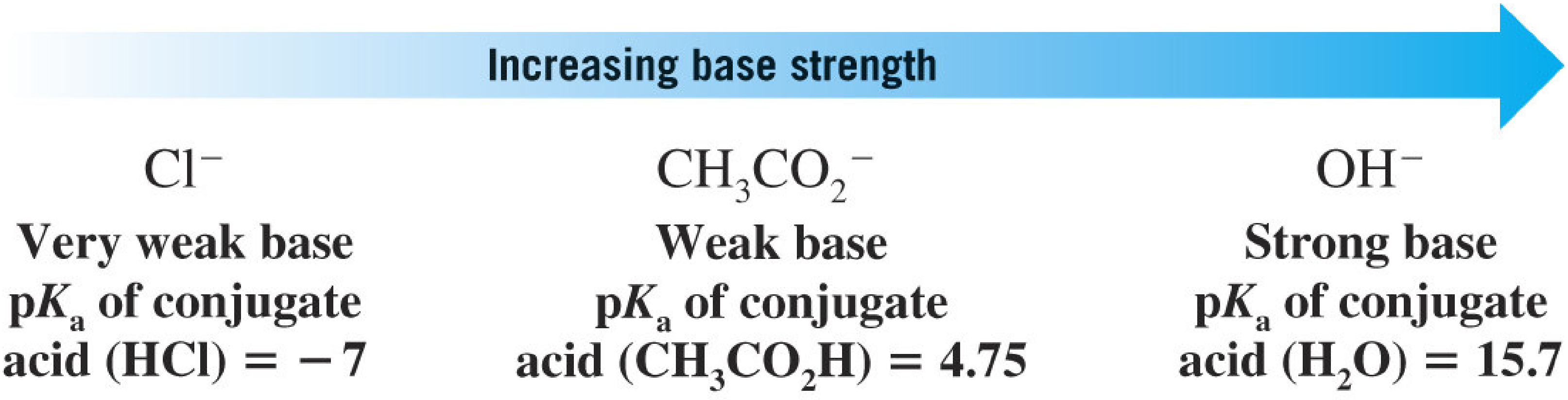
Weak acid **Very strong acid**

	Acid	**Approximate pK_a**	**Conjugate Base**	
Strongest acid	$HSbF_6$	< -12	SbF_6^-	Weakest base
	HI	-10	I^-	
	H_2SO_4	-9	HSO_4^-	
	HBr	-9	Br^-	
	HCl	-7	Cl^-	
	$C_6H_5SO_3H$	-6.5	$C_6H_5SO_3^-$	
	$(CH_3)_2\overset{+}{O}H$	-3.8	$(CH_3)_2O$	
	$(CH_3)_2C{=}\overset{+}{O}H$	-2.9	$(CH_3)_2C{=}O$	
	$CH_3\overset{+}{O}H_2$	-2.5	CH_3OH	
	H_3O^+	-1.74	H_2O	
	HNO_3	-1.4	NO_3^-	
	CF_3CO_2H	0.18	$CF_3CO_2^-$	
	HF	3.2	F^-	
	CH_3CO_2H	4.75	$CH_3CO_2^-$	
	H_2CO_3	6.35	HCO_3^-	
	$CH_3COCH_2COCH_3$	9.0	$CH_3CO\overset{-}{C}HCOCH_3$	
	NH_4^+	9.2	NH_3	
	C_6H_5OH	9.9	C_6H_5O-	
	HCO_3^-	10.2	CO_3^{2-}	
	$CH_3NH_3^+$	10.6	CH_3NH_2	
	H_2O	15.7	OH^-	
	CH_3CH_2OH	16	$CH_3CH_2O^-$	
	$(CH_3)_3COH$	18	$(CH_3)_3CO^-$	
	CH_3COCH_3	19.2	$^-CH_2COCH_3$	
	$HC{\equiv}CH$	25	$HC{\equiv}C^-$	
	H_2	35	H^-	
	NH_3	38	NH_2^-	
	$CH_2{=}CH_2$	44	$CH_2{=}CH^-$	
Weakest acid	CH_3CH_3	50	$CH_3CH_2^-$	Strongest base

Increasing acid strength

Increasing base strength

- Predicting the Strengths of Bases
  - The stronger the acid, the weaker its conjugate base will be
    - An acid with a low pK_a will have a weak conjugate base
    - Chloride is a very weak base because its conjugate acid HCl is a very strong acid



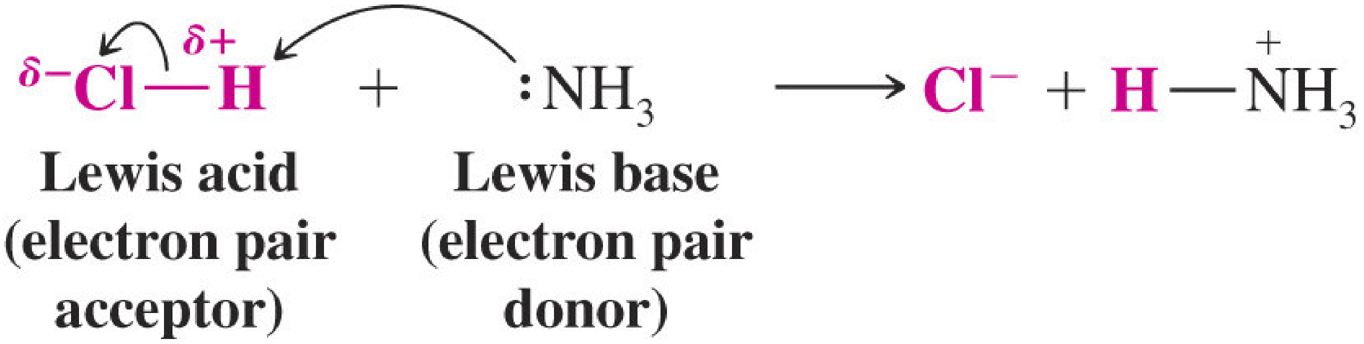
Cl^-
Very weak base
pK_a of conjugate acid (HCl) = −7

$CH_3CO_2^-$
Weak base
pK_a of conjugate acid (CH_3CO_2H) = 4.75

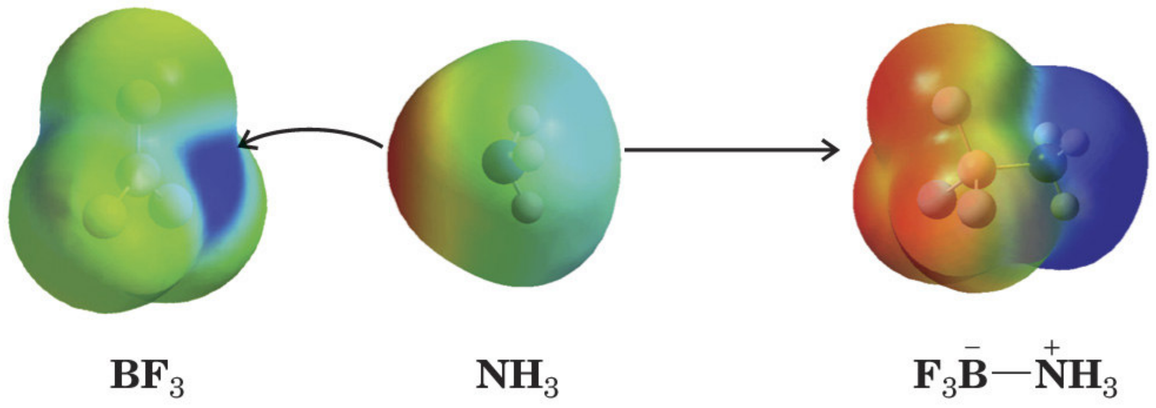
OH^-
Strong base
pK_a of conjugate acid (H_2O) = 15.7

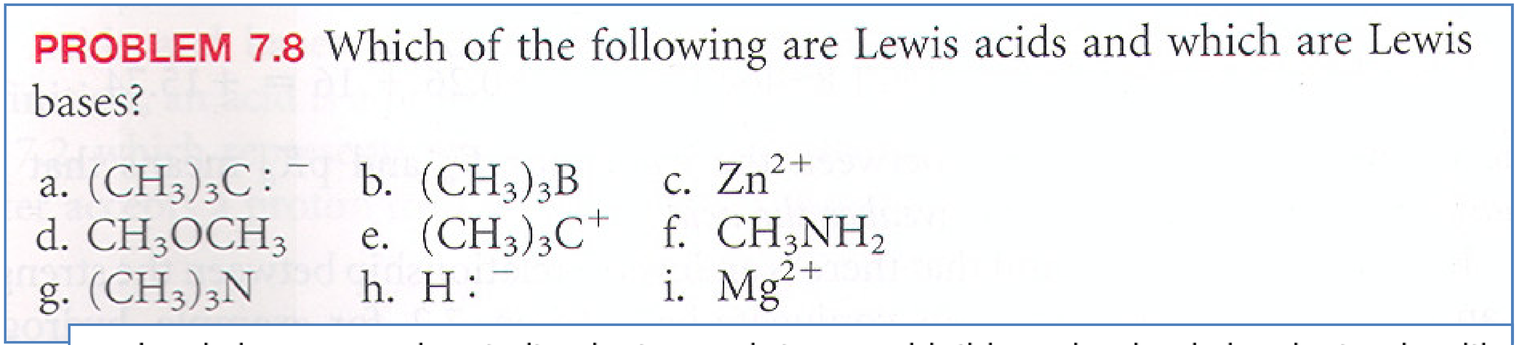
– Lewis Definition of Acids and Bases

- Lewis Acid: electron pair acceptor
- Lewis Base: electron pair donor
- Curved arrows show movement of electrons to form and break bonds



- Opposite Charges Attract and React
  - BF$_3$ and NH$_3$ react based on their relative electron densities
    - BF$_3$ has substantial positive charge on the boron
    - NH$_3$ has substantial negative charge localized at the lone pair

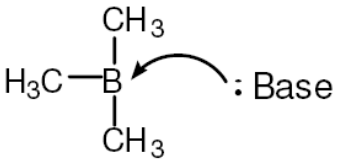



PROBLEM 7.8 Which of the following are Lewis acids and which are Lewis bases?

a. $(CH_3)_3C:^-$
b. $(CH_3)_3B$
c. Zn^{2+}
d. CH_3OCH_3
e. $(CH_3)_3C^+$
f. CH_3NH_2
g. $(CH_3)_3N$
h. $H:^-$
i. Mg^{2+}

a. Lewis base; can donate its electron pair to an acid; this carbanion is isoelectronic with $(CH_3)_3N$**:** (part g).

b. Lewis acid; the boron has only six valence electrons around it and can accept two more:



c. Lewis acid, can accept electron pairs to neutralize the positive charge.

d. Lewis base, because of the unshared electron pairs on the oxygen:

$CH_3\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}CH_3$

e. Lewis acid; this carbocation is isoelectronic with $(CH_3)_3B$ (part b).

f. Lewis base, because of the unshared electron pair on the nitrogen.

g. Lewis base, again because of the unshared electron pair on the nitrogen.

h. Lewis base; hydride can donate its electron pair to an acid.

i. Lewis acid; can accept electron pairs to neutralize the positive charge.