

FIGURE 15.9 The 200-MHz ¹H NMR spectrum of 2-phenylethanol (C₆H₅CH₂CH₂OH).

hydroxyl-bearing carbon to form a stable cation. Thus, the mass spectra of most primary alcohols exhibit a prominent peak at m/z 31.

PROBLEM 15.16 Three of the most intense peaks in the mass spectrum of 2-methyl-2-butanol appear at *m/z* 59, 70, and 73. Explain the origin of these peaks.

Interpreting the mass spectra of sulfur compounds is aided by the observation of an M+2 peak because of the presence of the mass-34 isotope of sulfur. The major cleavage pathway of *thiols* is analogous to that of alcohols.

15.15 SUMMARY

- Section 15.1 Functional group interconversions involving alcohols either as reactants or as products are the focus of this chapter. Alcohols are commonplace natural products. Table 15.1 summarizes reactions discussed in earlier sections that can be used to prepare alcohols.
- Section 15.2 Alcohols can be prepared from carbonyl compounds by reduction of aldehydes and ketones. See Table 15.3.
- Section 15.3 Alcohols can be prepared from carbonyl compounds by reduction of carboxylic acids and esters. See Table 15.3.

ABLE 15.3

Preparation of Alcohols by Reduction of Carbonyl Functional Groups

	Product of reduction of carbonyl compound by specified reducing agent			
Carbonyl compound	Lithium aluminum hydride (LiAlH ₄)	Sodium borohydride (NaBH ₄)	Hydrogen (in the presence of a catalyst)	
O Aldehyde RCH (Section 15.2)	Primary alcohol RCH₂OH	Primary alcohol RCH₂OH	Primary alcohol RCH₂OH	
O Ketone RCR' (Section 15.2)	Secondary alcohol RCHR'	Secondary alcohol RCHR' OH	Secondary alcohol RCHR' OH	
O Carboxylic acid RCOH (Section 15.3)	Primary alcohol RCH ₂ OH	Not reduced	Not reduced	
Carboxylic ester RCOR' (Section 15.3)	Primary alcohol RCH₂OH plus R'OH	Reduced too slowly to be of practical value	Requires special catalyst, high pressures and temperatures	

Section 15.4 Grignard and organolithium reagents react with ethylene oxide to give primary alcohols.

$$RMgX + H_2C \xrightarrow{CH_2} CH_2 \xrightarrow{1. \text{ diethyl ether}} RCH_2CH_2OH$$

$$Grignard \ reagent \qquad Ethylene \ oxide \qquad Primary \ alcohol$$

$$CH_3CH_2CH_2CH_2MgBr + H_2C \xrightarrow{O} CH_2 \xrightarrow{1. \text{ diethyl ether}} CH_3CH_2CH_2CH_2CH_2CH_2OH$$

$$Butylmagnesium \qquad Ethylene \ oxide \qquad 1-Hexanol \ (60-62\%)$$

$$bromide$$

Section 15.5 Osmium tetraoxide is a key reactant in the conversion of alkenes to vicinal diols.

The reaction is called **hydroxylation** and proceeds by syn addition to the double bond.

Section 15.6 Table 15.2 summarizes reactions of alcohols that were introduced in earlier chapters.

Section 15.7 See Table 15.4

Section 15.8 See Table 15.4

Section 15.9 See Table 15.4

Section 15.10 See Table 15.5

Section 15.11 Oxidation of alcohols to aldehydes and ketones is a common biological reaction. Most require a coenzyme such as the oxidized form of nicotinamide adenine dinucleotide (NAD⁺).

Section 15.12 Periodic acid cleaves vicinal diols; two aldehydes, two ketones, or an aldehyde and a ketone are formed.

$$R_{2}C - CR_{2} \xrightarrow{HIO_{4}} R_{2}C = O + O = CR_{2}$$

$$HO OH$$

$$Diol Two carbonyl-containing compounds$$

$$O O O O$$

$$\parallel CH_{3}(CH_{2})_{7}CH - CH(CH_{2})_{7}COH \xrightarrow{HIO_{4}} CH_{3}(CH_{2})_{7}CH + HC(CH_{2})_{7}COH$$

$$HO OH$$

$$9,10-Dihydroxyoctadecanoic acid Nonanal (89%) 9-Oxononanoic acid (76%)$$

Section 15.13 **Thiols** are compounds of the type RSH. They are more acidic than alcohols and are readily deprotonated by reaction with aqueous base. Thiols can be oxidized to sulfenic acids (RSOH), sulfinic acids (RSO₂H), and sulfonic acids (RSO₃H). The redox relationship between thiols and disulfides is important in certain biochemical processes.

$$\begin{array}{c}
2RSH & \xrightarrow{\text{oxidation}} & RSSR \\
\hline
\text{Thiol} & Disulfide
\end{array}$$

Section 15.14 The hydroxyl group of an alcohol has its O—H and C—O stretching vibrations at 3200–3650 and 1025–1200 cm⁻¹, respectively.

The chemical shift of the proton of an O—H group is variable (δ 1–5) and depends on concentration, temperature, and solvent. Oxygen deshields both the proton and the carbon of an H—C—O unit. Typical NMR chemical shifts are δ 3.3–4.0 for ¹H and δ 60–75 for ¹³C of H—C—O.

ABLE 15.4

ether results.

Summary of Reactions of Alcohols Presented in This Chapter

Reaction (section) and comments

Conversion to dialkyl ethers (Section 15.7) On being heated in the presence of an acid catalyst, two molecules of a primary alcohol combine to form an ether and water. Diols can undergo an intramolecular condensation if a fivemembered or six-membered cyclic

Fischer esterification (Section 15.8) Alcohols and carboxylic acids yield an ester and water in the presence of an acid catalyst. The reaction is an equilibrium process that can be driven to completion by using either the alcohol or the acid in excess or by removing the water as it is formed.

Esterification with acyl chlorides (Section 15.8) Acyl chlorides react with alcohols to give esters. The reaction is usually carried out in the presence of pyridine.

Esterification with carboxylic acid anhydrides (Section 15.8) Carboxylic acid anhydrides react with alcohols to form esters in the same way that acyl chlorides do.

Formation of esters of inorganic acids (Section 15.9) Alkyl nitrates, dialkyl sulfates, trialkyl phosphites, and trialkyl phosphates are examples of alkyl esters of inorganic acids. In some cases, these compounds are prepared by the direct reaction of an alcohol and the inorganic acid.

General equation and specific example

$$2RCH_{2}OH \xrightarrow{H^{+}} RCH_{2}OCH_{2}R + H_{2}O$$
Alcohol Dialkyl ether Water
$$2(CH_{3})_{2}CHCH_{2}CH_{2}OH \xrightarrow{H_{2}SO_{4}} (CH_{3})_{2}CHCH_{2}CH_{2}CH_{2}CH_{2}CH(CH_{3})_{2}$$

$$3-Methyl-1-butanol Di-(3-methylbutyl) ether (27\%)$$

$$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}OH + CH_{3}COH \xrightarrow{H^{+}} CH_{3}COCH_{2}CH_{2}CH_{2}CH_{2}CH_{3}$$
1-Pentanol Acetic acid Pentyl acetate (71%)
$$O \qquad O \qquad O$$

ROH + R'ČCI
$$\longrightarrow$$
 R'ČOR + HCI

Alcohol Acyl Ester Hydrogen chloride

O O

(CH₃)₃COH + CH₃CCI $\xrightarrow{\text{pyridine}}$ CH₃COC(CH₃)₃

$$(CH_3)_3COH$$
 + CH_3CCI \longrightarrow $CH_3COC(CH_3)_3$
 $tert$ -Butyl alcohol Acetyl $tert$ -Butyl acetate (62%)

$$\begin{array}{c|cccc} & O & O & O & O \\ \parallel & \parallel & & \parallel & \\ ROH & + & R'COCR' & \longrightarrow R'COR + R'COH \\ \\ Alcohol & Carboxylic & Ester & Carboxylic \\ acid anhydride & acid \\ \end{array}$$

$$\begin{array}{c|cccc} CH_3O & CH_3O & CH_3O & O \\ & & \parallel & \parallel & \\ & & CH_2OH + CH_3COCCH_3 & \xrightarrow{pyridine} & CH_2OCCH_3 \end{array}$$

m-Methoxybenzyl alcohol

Acetic anhydride

m-Methoxybenzyl acetate (99%)

ROH + HONO₂
$$\xrightarrow{H^+}$$
 RONO₂ + H₂O
Alcohol Nitric acid Alkyl nitrate Water

OH $\xrightarrow{HNO_3}$ ONO₂

nitrate (69%)

Cyclopentanol Cyclopentyl

TABLE 15.5 Oxidation of Alcohols			
Class of alcohol Desired product	Suitable oxidizing agent(s)		
Primary, RCH ₂ OH Aldehyde RCH	PCC* PDC*		
Primary, RCH₂OH Carboxylic acid RCOH	$Na_2Cr_2O_7$, H_2SO_4 , H_2O H_2CrO_4		
Secondary, RCHR' Ketone RCR' OH	PCC* PDC* Na ₂ Cr ₂ O ₇ , H ₂ SO ₄ , H ₂ O H ₂ CrO ₄		

*PCC is pyridinium chlorochromate; PDC is pyridinium dichromate. Both are used in dichloromethane.

The most intense peaks in the mass spectrum of an alcohol correspond to the ion formed according to carbon-carbon cleavage of the type shown:

PROBLEMS

15.17 Write chemical equations, showing all necessary reagents, for the preparation of 1-butanol by each of the following methods:

- (a) Hydroboration-oxidation of an alkene
- (b) Use of a Grignard reagent
- (c) Use of a Grignard reagent in a way different from part (b)
- (d) Reduction of a carboxylic acid
- (e) Reduction of a methyl ester
- (f) Reduction of a butyl ester
- (g) Hydrogenation of an aldehyde
- (h) Reduction with sodium borohydride

15.18 Write chemical equations, showing all necessary reagents, for the preparation of 2-butanol by each of the following methods:

- (a) Hydroboration-oxidation of an alkene
- (b) Use of a Grignard reagent
- (c) Use of a Grignard reagent different from that used in part (b)
- (d-f) Three different methods for reducing a ketone