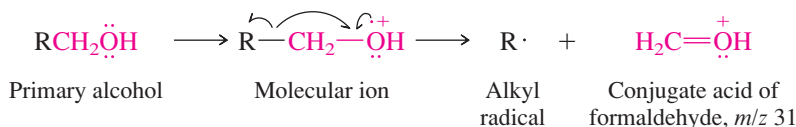


FIGURE 15.9 The 200-MHz ^1H NMR spectrum of 2-phenylethanol ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$).

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.

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

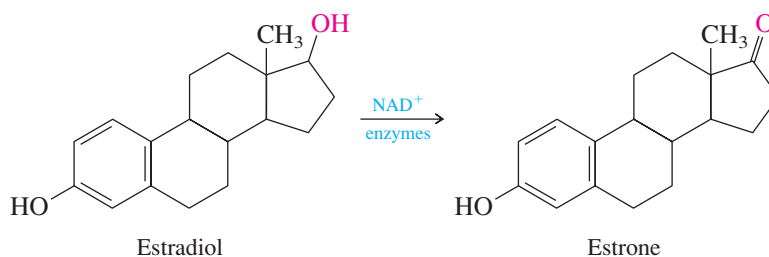
Section 15.7 See Table 15.4

Section 15.8 See Table 15.4

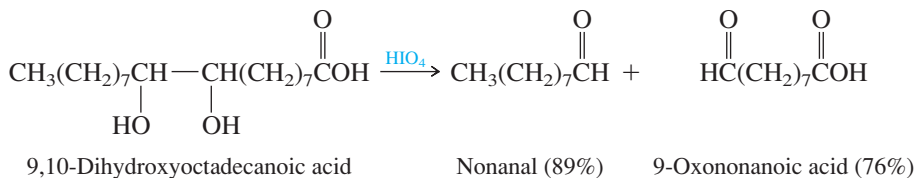
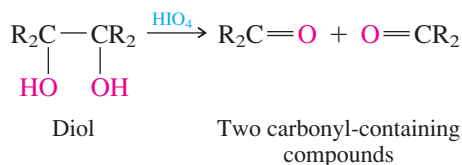
Section 15.9 See Table 15.4

Section 15.10 See Table 15.5

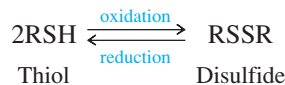
Section 15.11 Oxidation of alcohols to aldehydes and ketones is a common biological reaction. Most require a coenzyme such as the oxidized form of nicotinamide adenine dinucleotide (NAD^+).



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



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 (RSO_2H), and sulfonic acids (RSO_3H). The redox relationship between thiols and disulfides is important in certain biochemical processes.



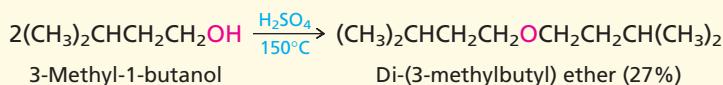
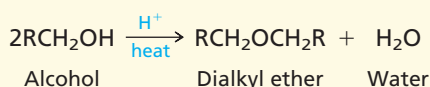
Section 15.14 The hydroxyl group of an alcohol has its $\text{O}-\text{H}$ and $\text{C}-\text{O}$ stretching vibrations at $3200-3650$ and $1025-1200 \text{ cm}^{-1}$, respectively.

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

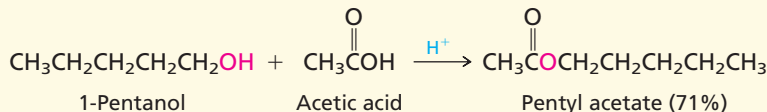
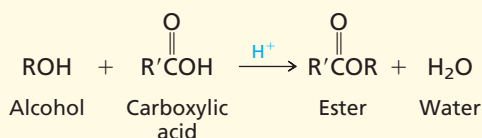
TABLE 15.4 Summary of Reactions of Alcohols Presented in This Chapter

Reaction (section) and comments
General equation and specific example

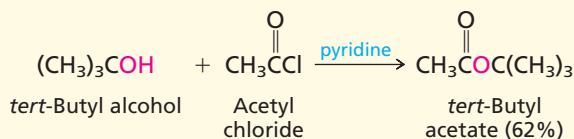
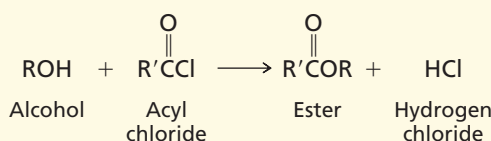
Conversion to dialkyl ethers (Section 15.7) On being heated in the presence of an acid catalyst, two molecules of a primary alcohol combine to form an ether and water. Diols can undergo an intramolecular condensation if a five-membered or six-membered cyclic ether results.



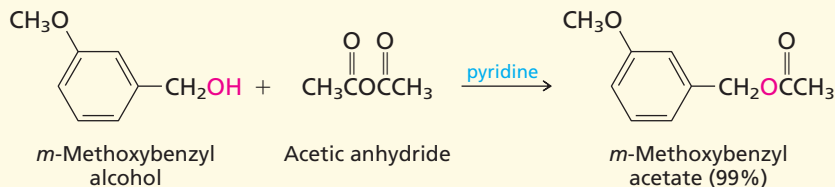
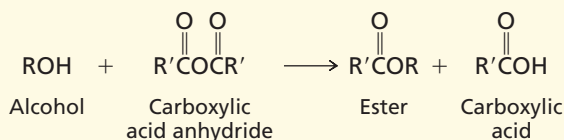
Fischer esterification (Section 15.8) Alcohols and carboxylic acids yield an ester and water in the presence of an acid catalyst. The reaction is an equilibrium process that can be driven to completion by using either the alcohol or the acid in excess or by removing the water as it is formed.



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.

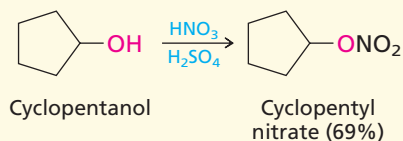
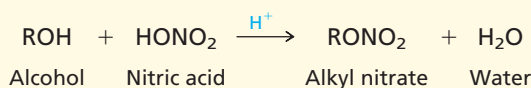
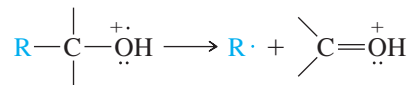


TABLE 15.5 Oxidation of Alcohols

Class of alcohol	Desired product	Suitable oxidizing agent(s)
Primary, RCH ₂ OH	Aldehyde $\text{R}\overset{\text{O}}{\parallel}\text{CH}$	PCC* PDC*
Primary, RCH ₂ OH	Carboxylic acid $\text{R}\overset{\text{O}}{\parallel}\text{COH}$	Na ₂ Cr ₂ O ₇ , H ₂ SO ₄ , H ₂ O H ₂ CrO ₄
Secondary, RCHR' OH	Ketone $\text{R}\overset{\text{O}}{\parallel}\text{CR}'$	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:

- Hydroboration–oxidation of an alkene
- Use of a Grignard reagent
- Use of a Grignard reagent in a way different from part (b)
- Reduction of a carboxylic acid
- Reduction of a methyl ester
- Reduction of a butyl ester
- Hydrogenation of an aldehyde
- 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:

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