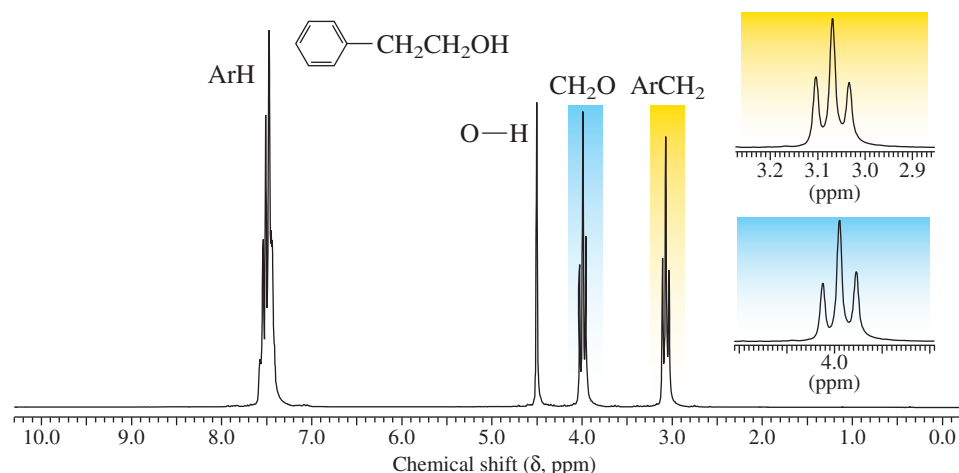


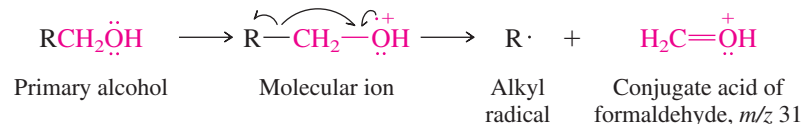
FIGURE 15.5

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



UV-VIS: Unless the molecule has other chromophores, alcohols are transparent above about 200 nm; λ_{max} for methanol, for example, is 177 nm.

Mass Spectrometry: The molecular ion peak is usually quite small in the mass spectrum of an alcohol. A peak corresponding to loss of water is often evident. Alcohols also fragment readily by a pathway in which the molecular ion loses an alkyl group from the 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 15.17**

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.

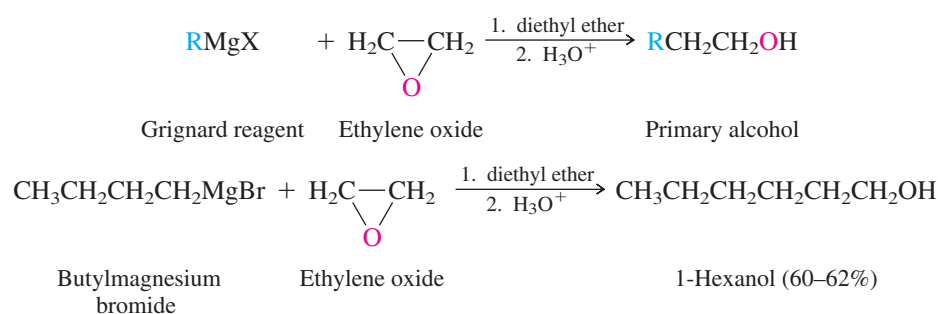
Interpreting the mass spectra of sulfur compounds is aided by the observation of an $M+2$ peak because of the presence of the mass-34 isotope of sulfur. The major cleavage pathway of *thiols* is analogous to that of alcohols.

15.15 SUMMARY

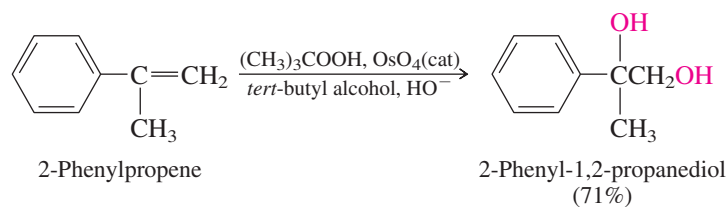
- Section 15.1 Functional group interconversions involving alcohols either as reactants or as products are the focus of this chapter. Alcohols are commonplace natural products. Table 15.1 summarizes reactions discussed in earlier sections that can be used to prepare alcohols.
- Section 15.2 Alcohols 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 15.4 Grignard and organolithium reagents react with ethylene oxide to give primary alcohols.

TABLE 15.3 Preparation of Alcohols by Reduction of Carbonyl Functional Groups

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



Section 15.5 Osmium tetroxide is a key reagent in the conversion of alkenes to vicinal diols.



The reaction is called **dihydroxylation** and proceeds by syn addition to the double bond. Osmium-based reagents that bear chiral ligands catalyze enantioselective dihydroxylation of alkenes.

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

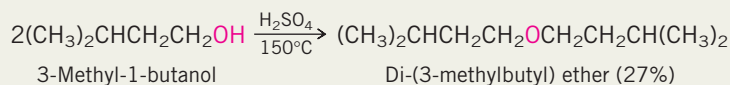
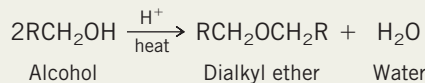
Section 15.7 See Table 15.4

Section 15.8 See Table 15.4

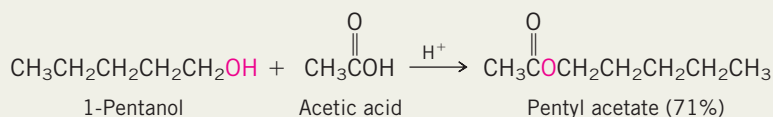
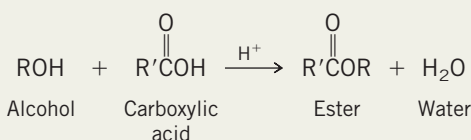
Section 15.9 See Table 15.4

TABLE 15.4 Summary of Reactions of Alcohols Presented in This Chapter**Reaction (section) and comments****General equation and specific example**

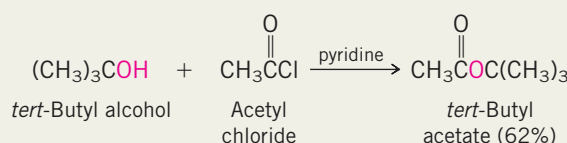
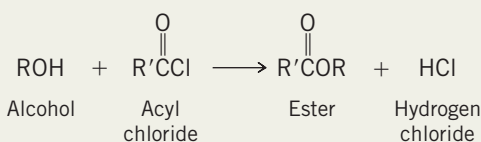
Conversion to dialkyl ethers (Section 15.7) On being heated in the presence of an acid catalyst, two molecules of a primary alcohol combine to form an ether and water. Diols can undergo an intramolecular condensation if a five-membered or six-membered cyclic ether results.

**Fischer esterification (Section 15.8)**

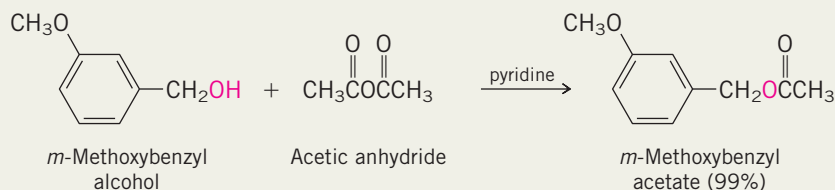
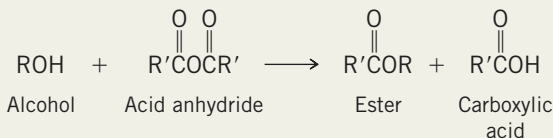
Alcohols and carboxylic acids yield an ester and water in the presence of an acid catalyst. The reaction is an equilibrium process that can be driven to completion by using either the alcohol or the acid in excess or by removing the water as it is formed.

**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 acid anhydrides (Section 15.8)**

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.

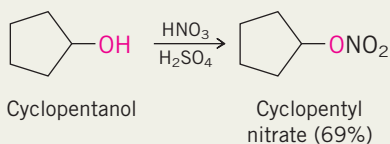
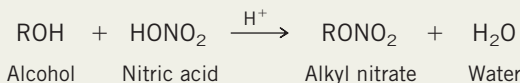


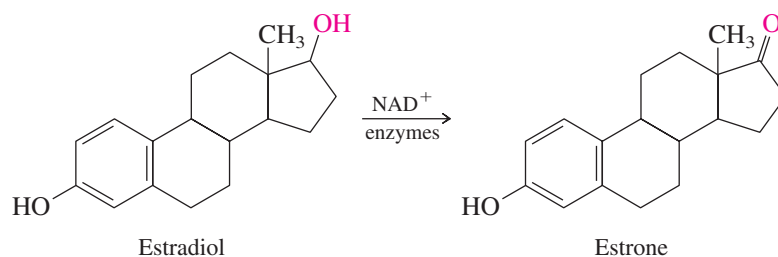
TABLE 15.5 Oxidation of Alcohols

Class of alcohol	Desired product	Suitable oxidizing agent(s)
Primary, RCH ₂ OH	Aldehyde $\text{RCH}=\text{O}$	PCC* PDC*
Primary, RCH ₂ OH	Carboxylic acid $\text{RCO}=\text{O}$	Na ₂ Cr ₂ O ₇ , H ₂ SO ₄ , H ₂ O H ₂ CrO ₄
Secondary, RCHR' OH	Ketone $\text{RCR}'=\text{O}$	PCC* PDC* Na ₂ Cr ₂ O ₇ , H ₂ SO ₄ , H ₂ O H ₂ CrO ₄

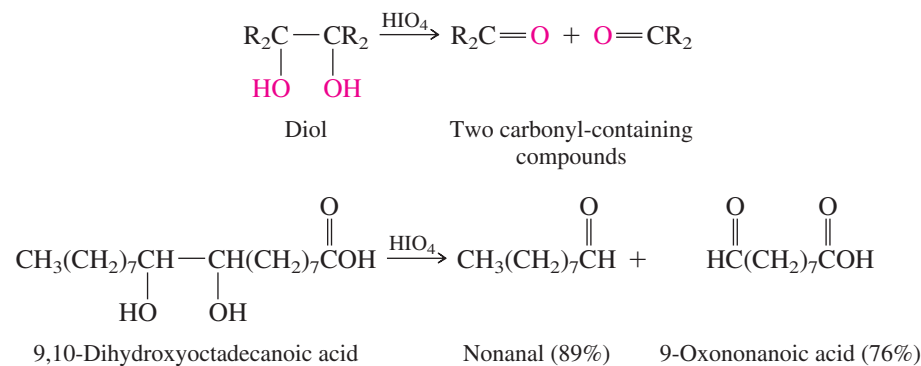
*PCC is pyridinium chlorochromate; PDC is pyridinium dichromate. Both are used in dichloromethane.

Section 15.10 See Table 15.5

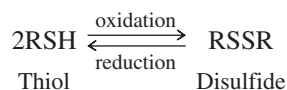
Section 15.11 Oxidation of alcohols to aldehydes and ketones is a common biological reaction. Most require a coenzyme such as the oxidized form of nicotinamide adenine dinucleotide (NAD⁺).



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



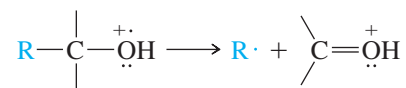
Section 15.13 **Thiols** are compounds of the type RSH. They are more acidic than alcohols and are readily deprotonated by reaction with aqueous base. Thiols can be oxidized to sulfenic acids (RSOH), sulfinic acids (RSO₂H), and sulfonic acids (RSO₃H). The redox relationship between thiols and disulfides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



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 ^{13}C of H—C—O.

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

15.18 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

15.19 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

15.20 Write chemical equations, showing all necessary reagents, for the preparation of *tert*-butyl alcohol by:

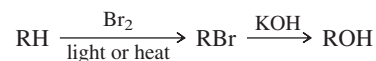
- Reaction of a Grignard reagent with a ketone

- Reaction of a Grignard reagent with an ester of the type RCOCH_3

15.21 Which of the isomeric $\text{C}_5\text{H}_{12}\text{O}$ alcohols can be prepared by lithium aluminum hydride reduction of:

- An aldehyde
- A ketone
- A carboxylic acid
- An ester of the type RCOCH_3

15.22 Evaluate the feasibility of the route



as a method for preparing

- 1-Butanol from butane
- 2-Methyl-2-propanol from 2-methylpropane
- Benzyl alcohol from toluene
- (*R*)-1-Phenylethanol from ethylbenzene

15.23 Sorbitol is a sweetener often substituted for cane sugar, because it is better tolerated by diabetics. It is also an intermediate in the commercial synthesis of vitamin C. Sorbitol is prepared by high-pressure hydrogenation of glucose over a nickel catalyst. What is the structure (including stereochemistry) of sorbitol?