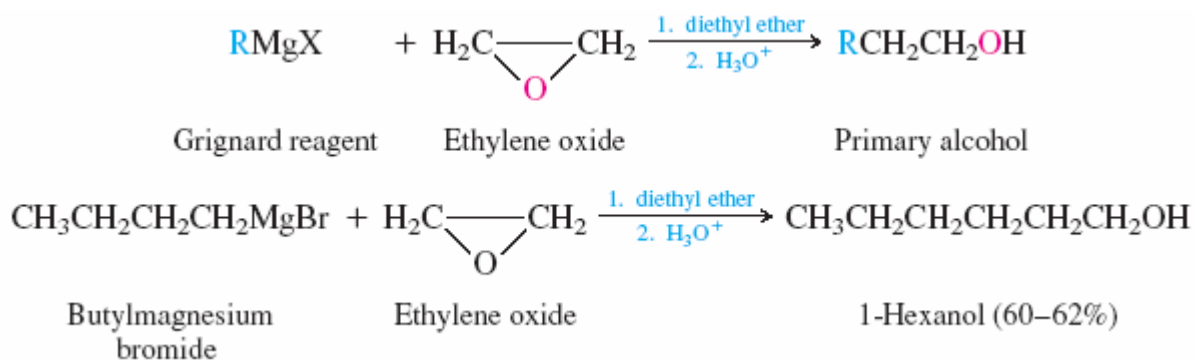


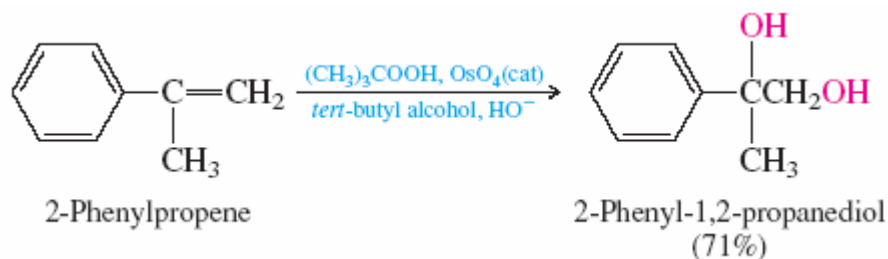
Alcohols, Diols, and Thiols

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.



- Section 15.5 Osmium tetroxide 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. Osmium-based reagents that bear chiral ligands catalyze enantioselective hydroxylation 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
- Section 15.10 See Table 15.5

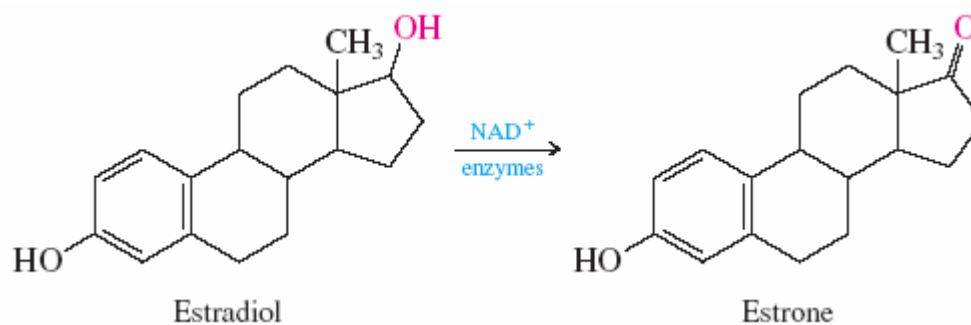
Reaction (section) and comments	General equation and specific example
<p>Conversion to dialkyl ethers (Section 15.7) On being heated in the presence of an acid catalyst, two molecules of a primary alcohol combine to form an ether and water. Diols can undergo an intramolecular condensation if a five-membered or six-membered cyclic ether results.</p>	$2\text{RCH}_2\text{OH} \xrightarrow[\text{heat}]{\text{H}^+} \text{RCH}_2\text{OCH}_2\text{R} + \text{H}_2\text{O}$ <p>Alcohol Dialkyl ether Water</p> $2(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH} \xrightarrow[150^\circ\text{C}]{\text{H}_2\text{SO}_4} (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$ <p>3-Methyl-1-butanol Di-(3-methylbutyl) ether (27%)</p>
<p>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.</p>	$\text{ROH} + \text{R}'\text{COH} \xrightarrow{\text{H}^+} \text{R}'\text{COR} + \text{H}_2\text{O}$ <p>Alcohol Carboxylic acid Ester Water</p> $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{COH} \xrightarrow{\text{H}^+} \text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ <p>1-Pentanol Acetic acid Pentyl acetate (71%)</p>
<p>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.</p>	$\text{ROH} + \text{R}'\text{COCl} \longrightarrow \text{R}'\text{COR} + \text{HCl}$ <p>Alcohol Acyl chloride Ester Hydrogen chloride</p> $(\text{CH}_3)_3\text{COH} + \text{CH}_3\text{COCl} \xrightarrow{\text{pyridine}} \text{CH}_3\text{COOC}(\text{CH}_3)_3$ <p><i>tert</i>-Butyl alcohol Acetyl chloride <i>tert</i>-Butyl acetate (62%)</p>
<p>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.</p>	$\text{ROH} + \text{R}'\text{COOCR}' \longrightarrow \text{R}'\text{COR} + \text{R}'\text{COH}$ <p>Alcohol Carboxylic acid anhydride Ester Carboxylic acid</p> $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{OH} + \text{CH}_3\text{COCCH}_3 \xrightarrow{\text{pyridine}} \text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{OCCH}_3$ <p><i>m</i>-Methoxybenzyl alcohol Acetic anhydride <i>m</i>-Methoxybenzyl acetate (99%)</p>
<p>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.</p>	$\text{ROH} + \text{HONO}_2 \xrightarrow{\text{H}^+} \text{RONO}_2 + \text{H}_2\text{O}$ <p>Alcohol Nitric acid Alkyl nitrate Water</p> $\text{Cyclopentanol} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \text{Cyclopentyl nitrate}$ <p>Cyclopentanol Cyclopentyl nitrate (69%)</p>

TABLE 15.5 Oxidation of Alcohols

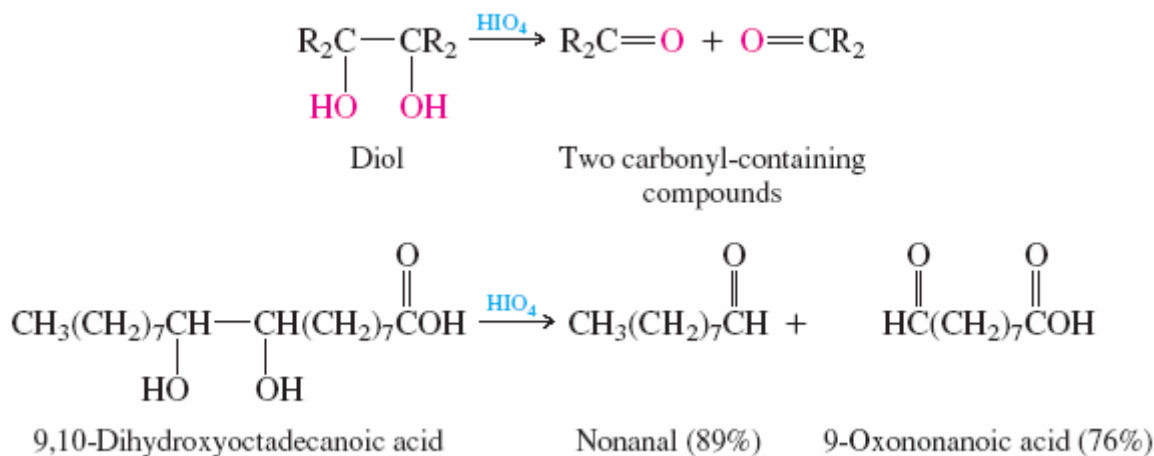
Class of alcohol	Desired product	Suitable oxidizing agent(s)
Primary, RCH_2OH	Aldehyde $\text{RCH}=\text{O}$	PCC* PDC*
Primary, RCH_2OH	Carboxylic acid RCOOH	$\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4, \text{H}_2\text{O}$ H_2CrO_4
Secondary, $\text{RCHR}'\text{OH}$	Ketone $\text{RCR}'=\text{O}$	PCC* PDC* $\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4, \text{H}_2\text{O}$ H_2CrO_4

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

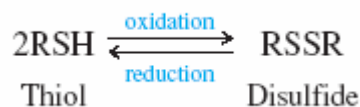
Section 15.11 Oxidation of alcohols to aldehydes and ketones is a common biological reaction. Most require a coenzyme such as the oxidized form of nicotinamide adenine dinucleotide (NAD^1).



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 OOH and COO stretching vibrations at 3200–3650 and 1025–1200 cm⁻¹, respectively.

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

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:

