

Chapter 7: Alcohols, Phenols and Thiols

45

$\text{CH}_3\text{CH}_2\text{OH}$
ethanol





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, $-OH$** .

-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.



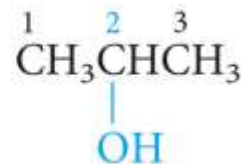
methanol
(methyl alcohol)



ethanol
(ethyl alcohol)



1-propanol
(*n*-propyl alcohol)



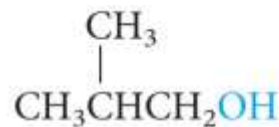
2-propanol
(isopropyl alcohol)



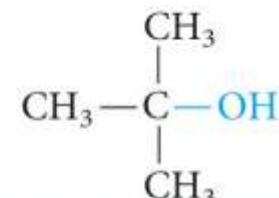
1-butanol
(*n*-butyl alcohol)



2-butanol
(*sec*-butyl alcohol)



2-methyl-1-propanol
(isobutyl alcohol)



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



2-propen-1-ol
(allyl alcohol)



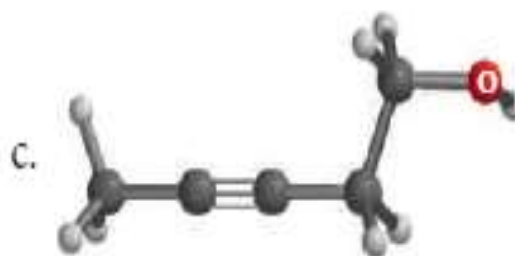
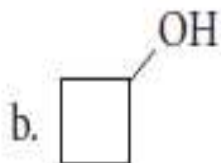
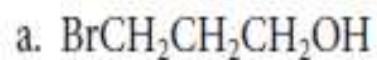
cyclohexanol
(cyclohexyl alcohol)



phenylmethanol
(benzyl alcohol)

EXAMPLE 7.1

Name the following alcohols by the IUPAC system:

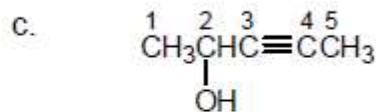
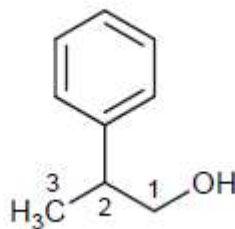
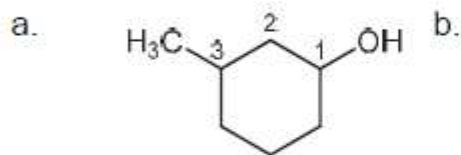


Solution

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

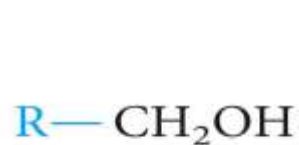
PROBLEM 7.2 Write a structural formula for

- a. 3-methylcyclohexanol
- b. 2-phenylpropanol
- c. 3-pentyn-2-ol



7.2 Classification of Alcohols

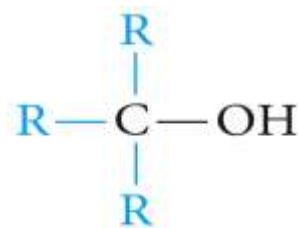
Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°), depending on whether one, two, or three organic groups are connected to the hydroxyl-bearing carbon atom



primary (1°)

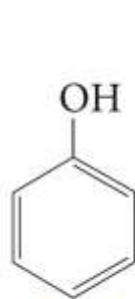


secondary (2°)



tertiary (3°)

7.3 Nomenclature of Phenols



phenol

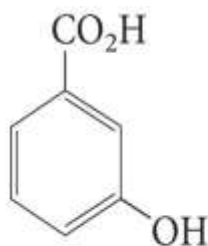


p-chlorophenol



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

but



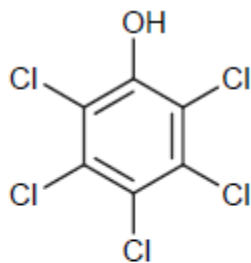
p-nitrophenol
(not *p*-hydroxynitrobenzene)

PROBLEM 7.4

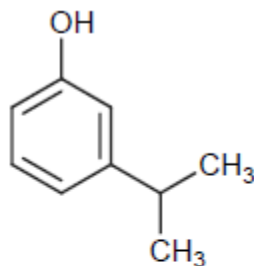
Write the structure for

- pentachlorophenol.
- m*-isopropylphenol
- o*-hydroxyacetophenone
- 3-hydroxy-5-nitrobenzaldehyde

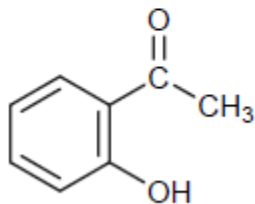
a.



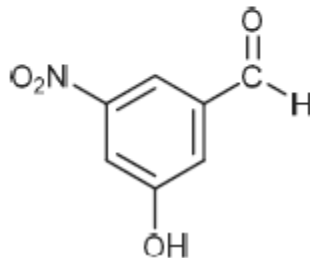
b.



c.



d.

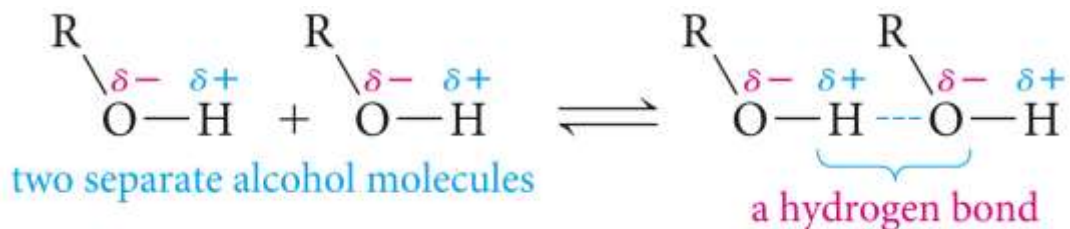


4.4 Hydrogen bonding in Alcohols and Phenols

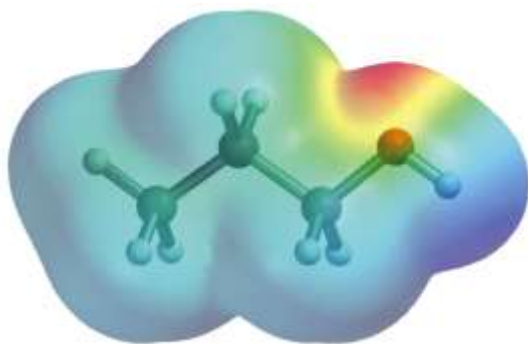
The boiling points of alcohols are much higher than those of ethers or hydrocarbons with similar molecular weights.

| | | | |
|--------|-----------------------------------|---------------------------|-------------------------------------|
| | $\text{CH}_3\text{CH}_2\text{OH}$ | CH_3OCH_3 | $\text{CH}_3\text{CH}_2\text{CH}_3$ |
| mol wt | 46 | 46 | 44 |
| bp | +78.5°C | -24°C | -42°C |

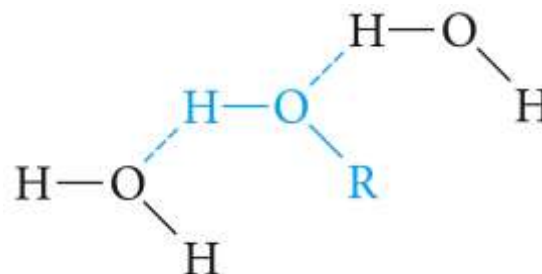
Why? Because alcohols form *hydrogen bonds* with one another



The lower-molecular-weight alcohols can readily replace water molecules in the hydrogen-bonded network. This accounts for the complete miscibility of such alcohols with water.



Electronic potential map for 1-propanol



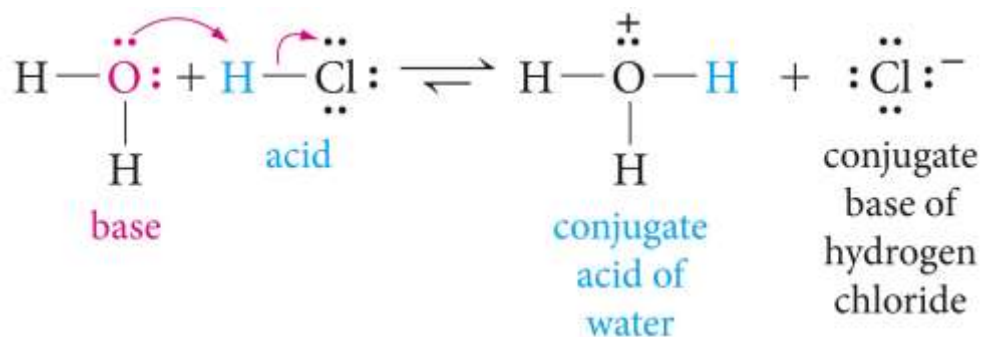
However, as the organic chain lengthens and the alcohol becomes relatively more hydrocarbon like, its water solubility decreases.

Table 7.1  **Boiling Point and Water Solubility of Some Alcohols**

| Name | Formula | bp, °C | Solubility in H₂O g/100 g at 20°C |
|-------------|--|---------------|---|
| methanol | CH ₃ OH | 65 | completely miscible |
| ethanol | CH ₃ CH ₂ OH | 78.5 | completely miscible |
| 1-propanol | CH ₃ CH ₂ CH ₂ OH | 97 | completely miscible |
| 1-butanol | CH ₃ CH ₂ CH ₂ CH ₂ OH | 117.7 | 7.9 |
| 1-pentanol | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH | 137.9 | 2.7 |
| 1-hexanol | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH | 155.8 | 0.59 |

7.5 Acidity and Basicity reviewed

Brønsted–Lowry acid is a proton donor, **Brønsted–Lowry base** is a proton acceptor.



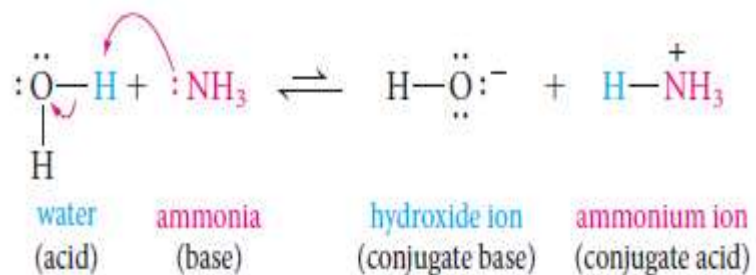
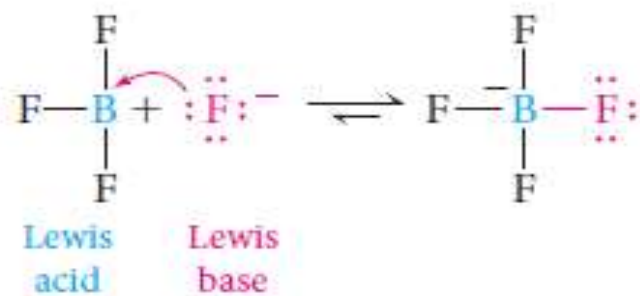
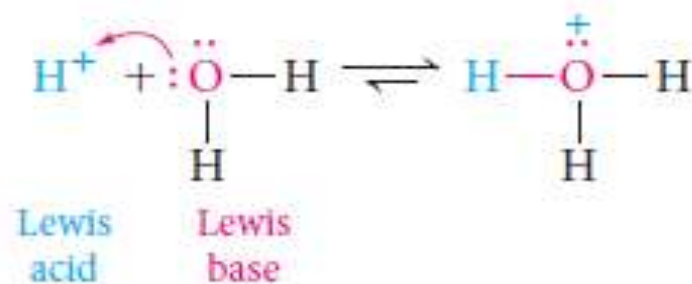
The strength of an acid (in water) is measured quantitatively by its acidity constant, or ionization constant, K_a .



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

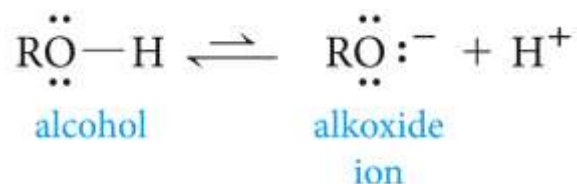
A **Lewis acid** is an electron pair acceptor;
a **Lewis base** is an electron pair donor.

Examples



7.6 The Acidity of Alcohols and Phenols

The hydroxyl group can act as a proton donor, and dissociation occurs in a manner similar to that for water:



Phenols are much stronger acids than alcohols mainly because the corresponding phenoxide ions are stabilized by resonance. The negative charge of an alkoxide ion is concentrated on the oxygen atom, while the negative charge on the phenoxide ion can be delocalized to the *ortho* and *para* ring positions through resonance

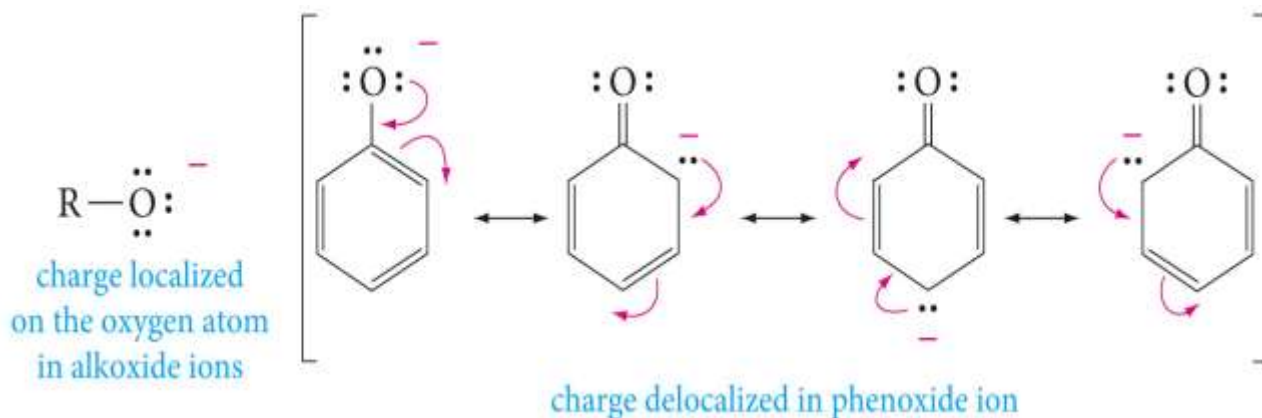
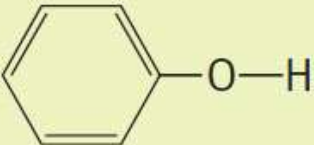

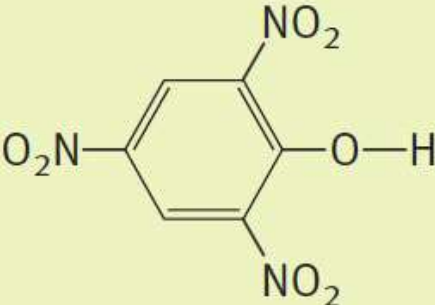
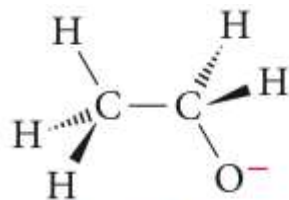


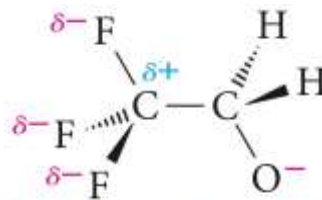
Table 7.2 $\text{p}K_a$'s of Selected Alcohols and Phenols in Aqueous Solution

| Name | Formula | $\text{p}K_a$ |
|-------------------------|--|---------------|
| water | HO—H | 15.7 |
| methanol | $\text{CH}_3\text{O—H}$ | 15.5 |
| ethanol | $\text{CH}_3\text{CH}_2\text{O—H}$ | 15.9 |
| <i>t</i> -butyl alcohol | $(\text{CH}_3)_3\text{CO—H}$ | 18 |
| 2,2,2-trifluoroethanol | $\text{CF}_3\text{CH}_2\text{O—H}$ | 12.4 |
| phenol |  | 10.0 |
| <i>p</i> -nitrophenol |  | 7.2 |
| picric acid |  | 0.25 |

Stabilization by inductive effect

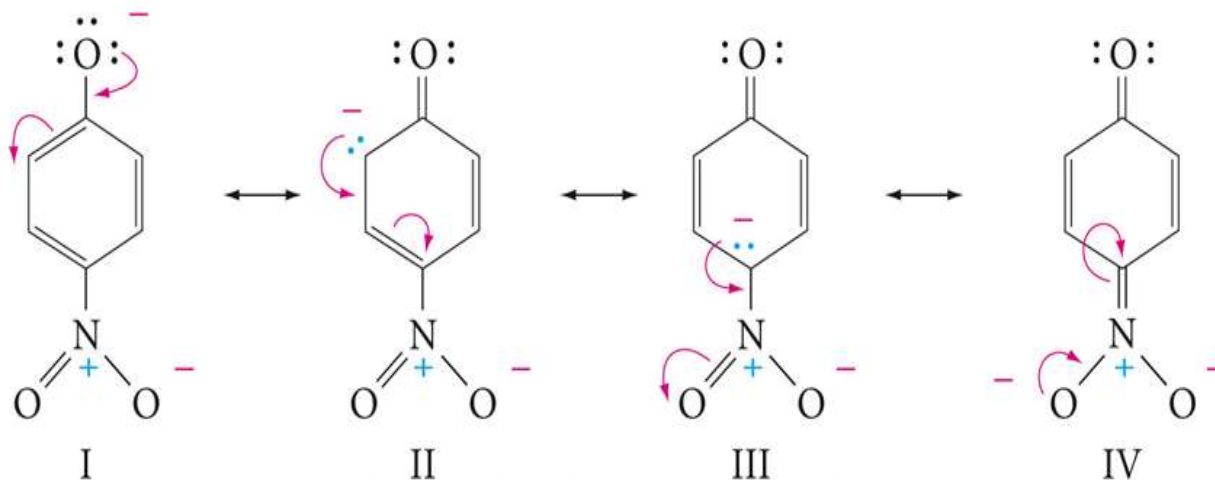


ethoxide ion



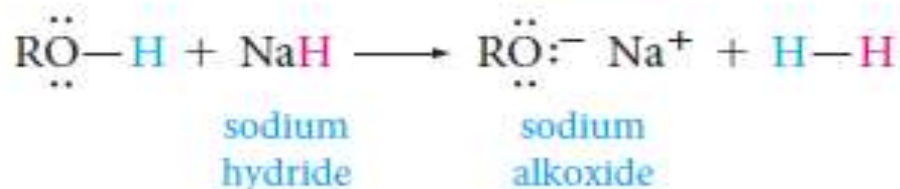
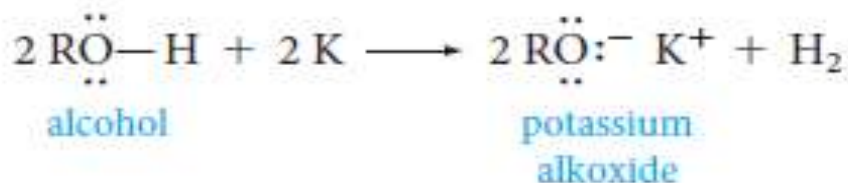
2,2,2-trifluoroethoxide ion

All electron-withdrawing groups increase acidity by stabilizing the conjugate base. Electron-donating groups decrease acidity because they destabilize the conjugate base.

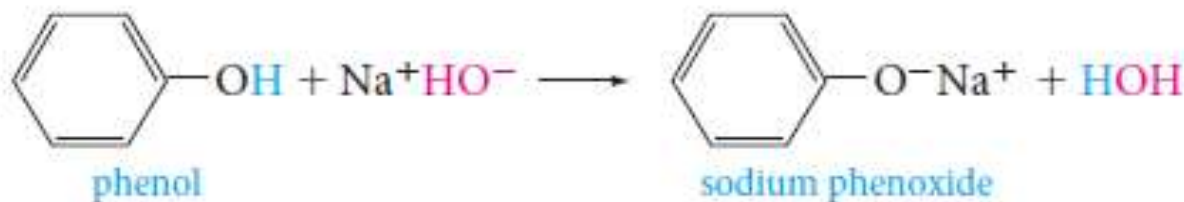
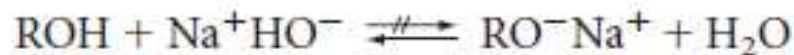


p-nitrophenoxide ion resonance contributors

Alkoxides can be prepared by the reaction of an alcohol with sodium or potassium metal or with a metal hydride

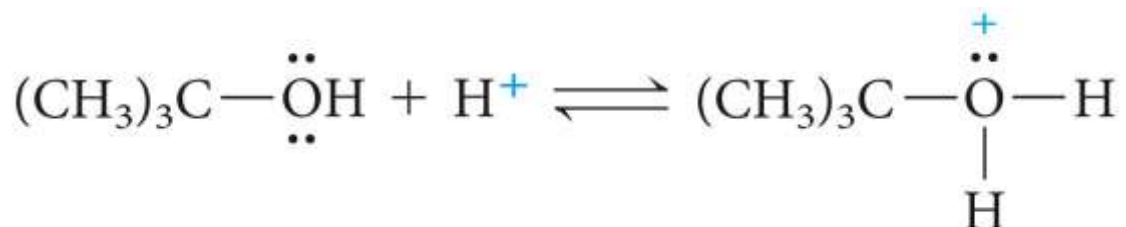


The treatment of alcohols with sodium hydroxide does not convert them to their alkoxides. This is because alkoxides are stronger bases than hydroxide ion. Phenols, however, can be converted to phenoxide ions in this way.

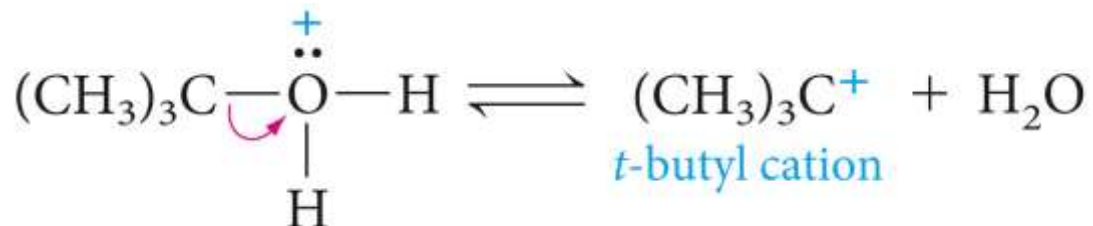


Tertiary alcohols dehydrate by the E1 mechanism.

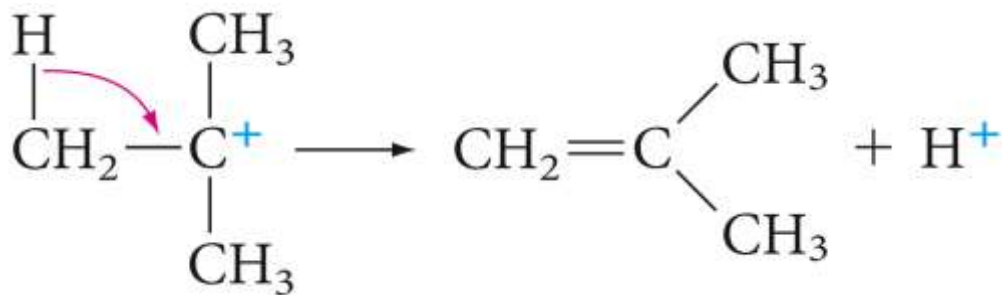
The first step involves rapid and reversible protonation of the hydroxyl group.



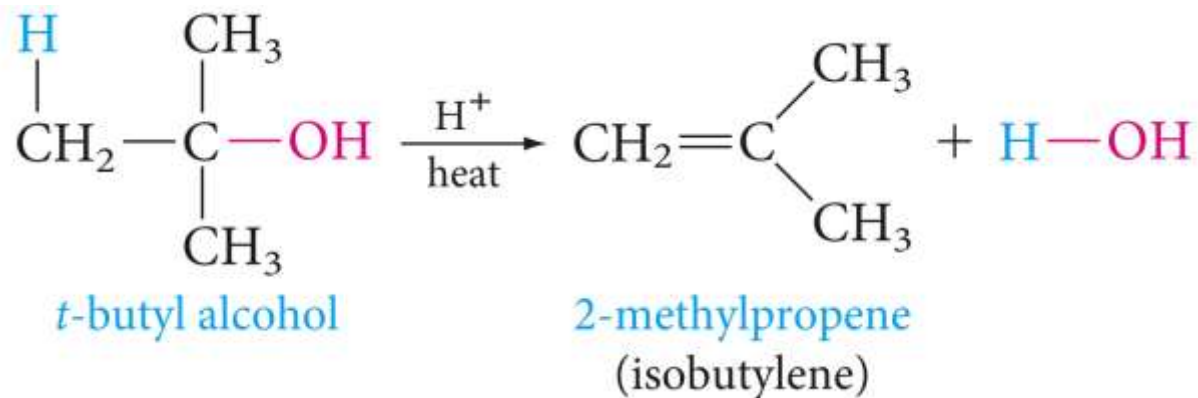
Ionization (the rate-determining step), with water as the leaving group, occurs readily because the resulting carbocation is tertiary.



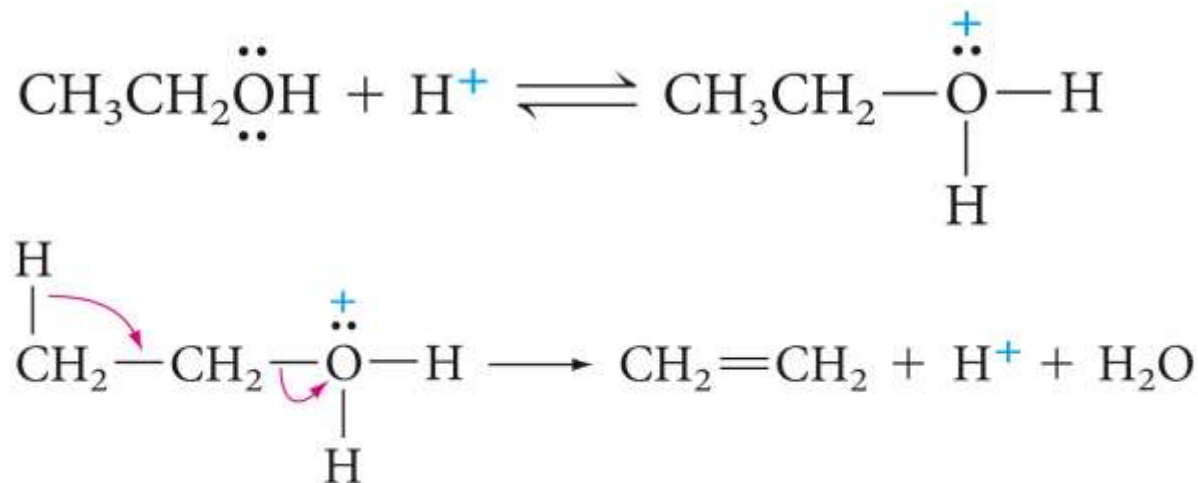
Proton loss from a carbon atom adjacent to the positive carbon completes the reaction.



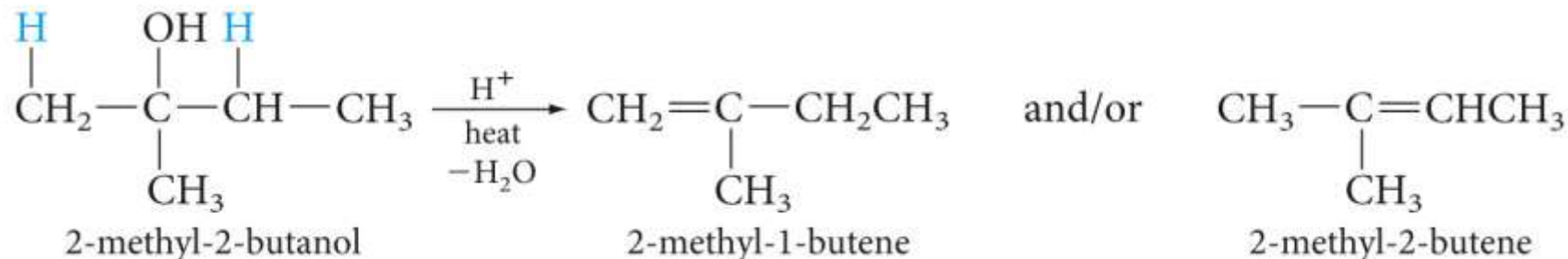
The overall reaction is



With a primary alcohol, a primary carbocation intermediate is avoided by combining the last two steps of the mechanism. The loss of water and an adjacent proton occurs simultaneously in an E2 mechanism.



Sometimes a single alcohol gives two or more alkenes



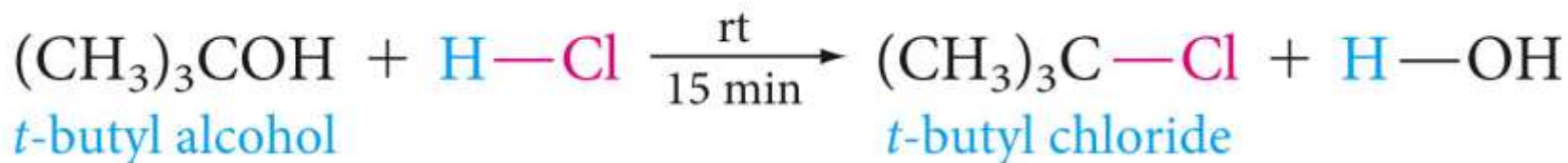
In these cases, *the alkene with the most substituted double bond usually predominates*. By “most substituted,” we mean the alkene with the greatest number of alkyl groups on the doubly bonded carbons.

7.9 The Reaction of Alcohols with Hydrogen Halides

Alcohols react with hydrogen halides (HCl, HBr, and HI) to give alkyl halides

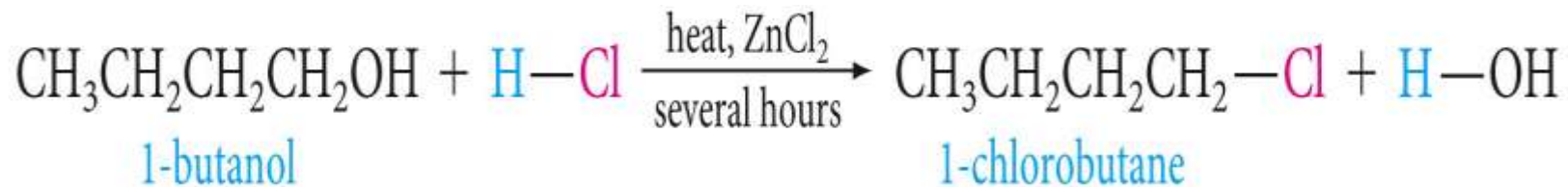


Because halide ions are good nucleophiles, we obtain mainly substitution products instead of dehydration. Once again, the reaction rate and mechanism depend on the class of alcohol (tertiary, secondary, or primary).

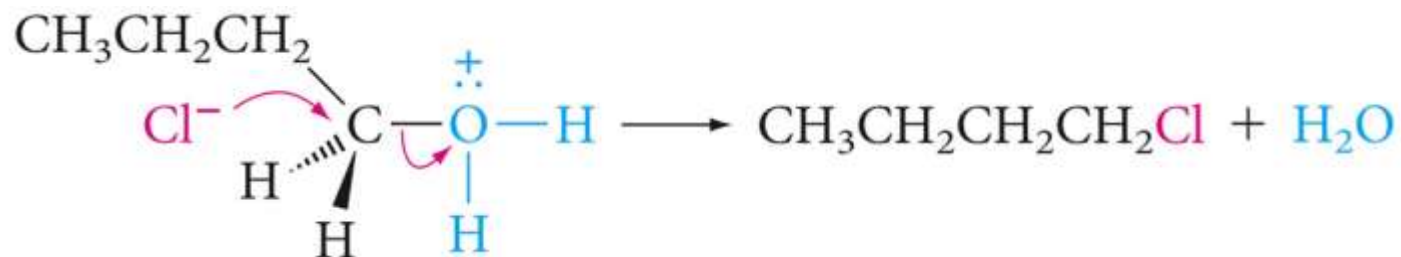


The reaction occurs by an S_N1 mechanism and involves a carbocation intermediate.

On the other hand, 1-butanol, a primary alcohol, reacts slowly and must be heated for several hours with a mixture of concentrated hydrochloric acid and a Lewis acid catalyst such as zinc chloride to accomplish the same type of reaction.



The reaction occurs by an S_N2 mechanism.

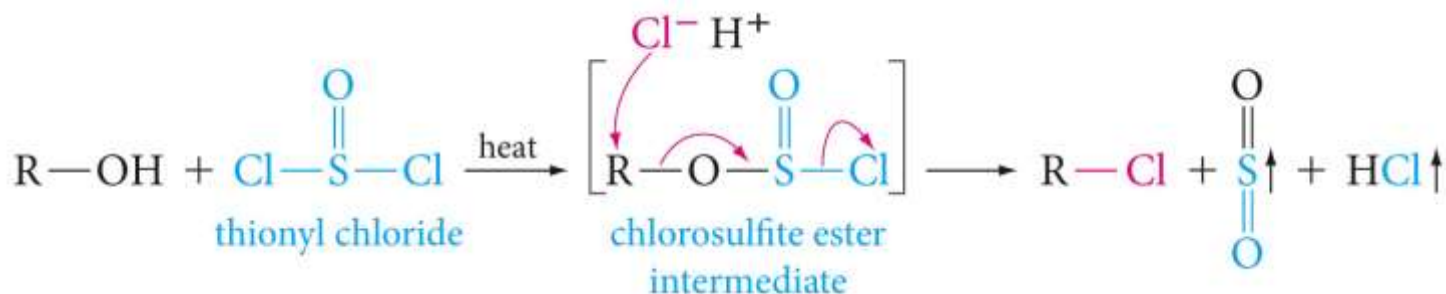


Secondary alcohols react at intermediate rates by both S_N1 and S_N2 mechanisms.

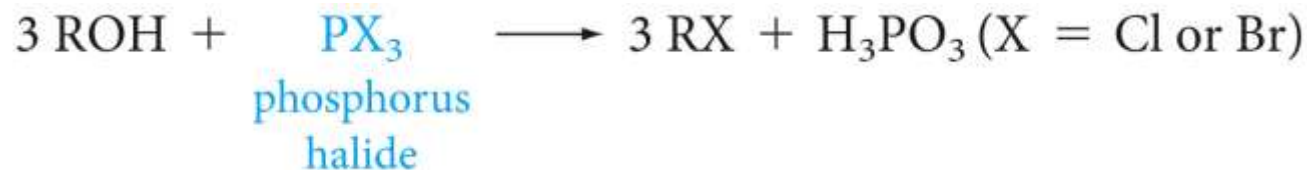
7.10 Other Ways to Prepare Alkyl Halides from Alcohols

Since alkyl halides are extremely useful in synthesis, it is not surprising that chemists have devised several ways to prepare them from alcohols.

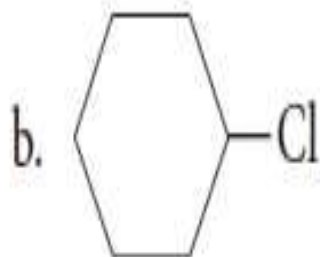
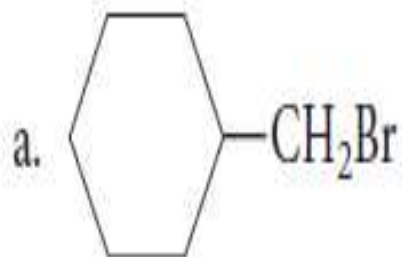
1. Thionyl chloride reacts with alcohols to give alkyl chlorides.

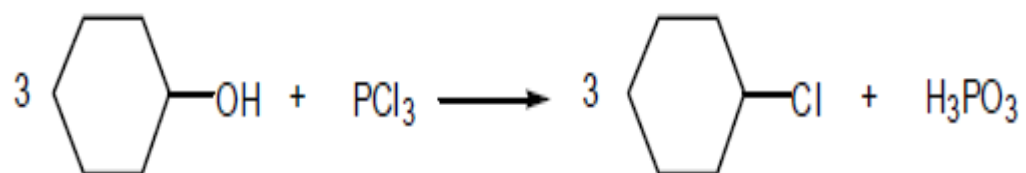
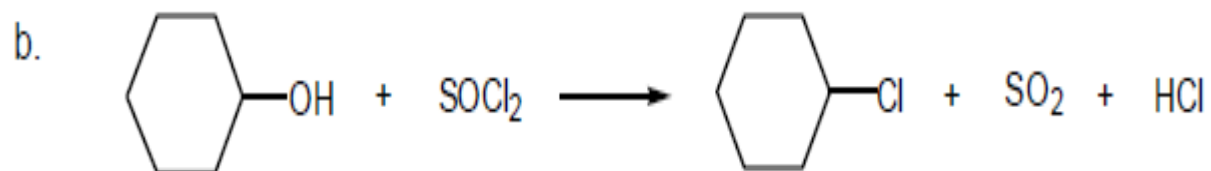
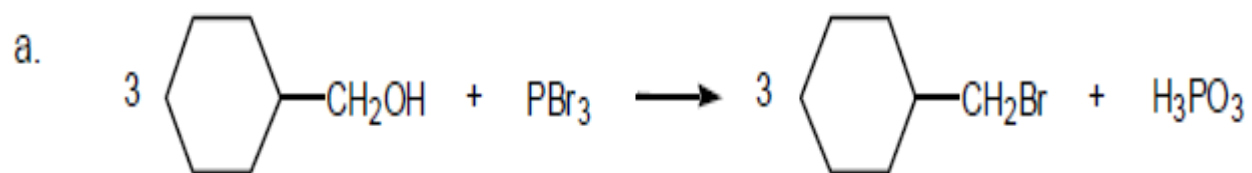


2. Phosphorus halides also convert alcohols to alkyl halides.



PROBLEM 7.17 Write balanced equations for the preparation of the following alkyl halides from the corresponding alcohol and SOCl_2 , PCl_3 , or PBr_3 .

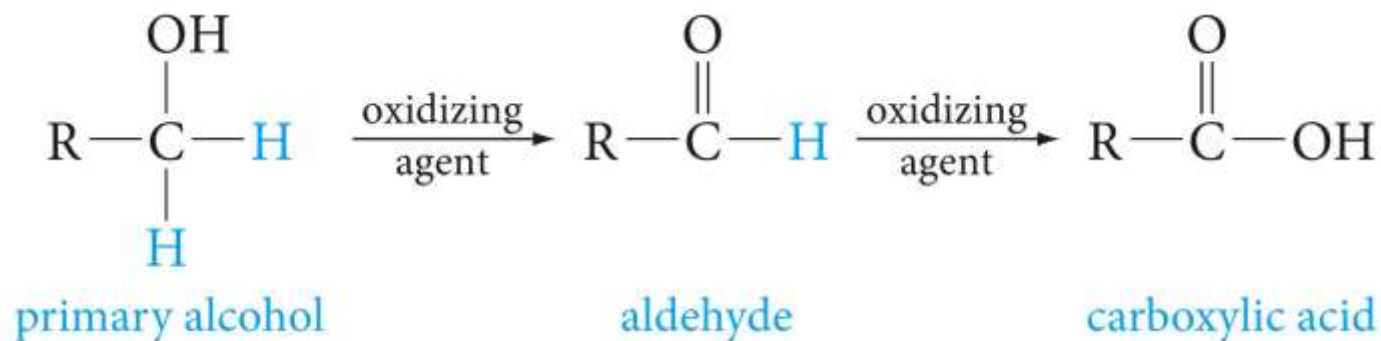




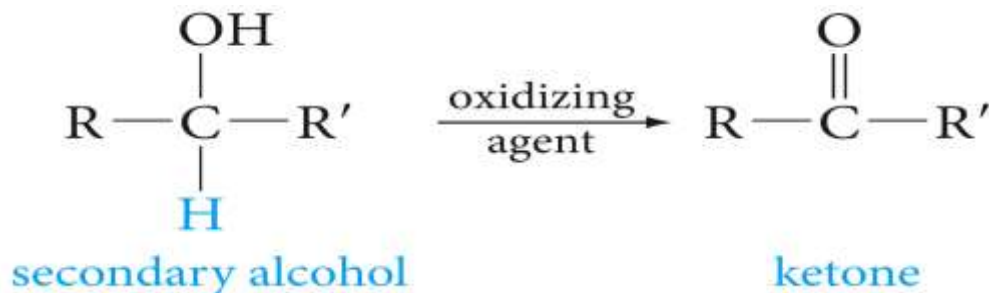
7.12 Oxidation of Alcohols to Aldehydes, Ketones, and Carboxylic Acids

Alcohols with at least one hydrogen attached to the hydroxyl-bearing carbon can be oxidized to carbonyl compounds.

Primary alcohols give aldehydes, which may be further oxidized to carboxylic acids.

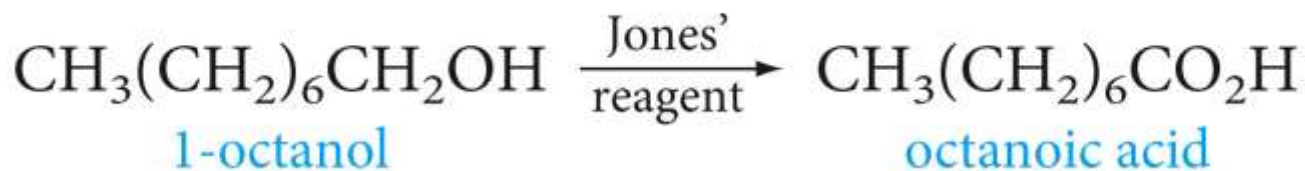
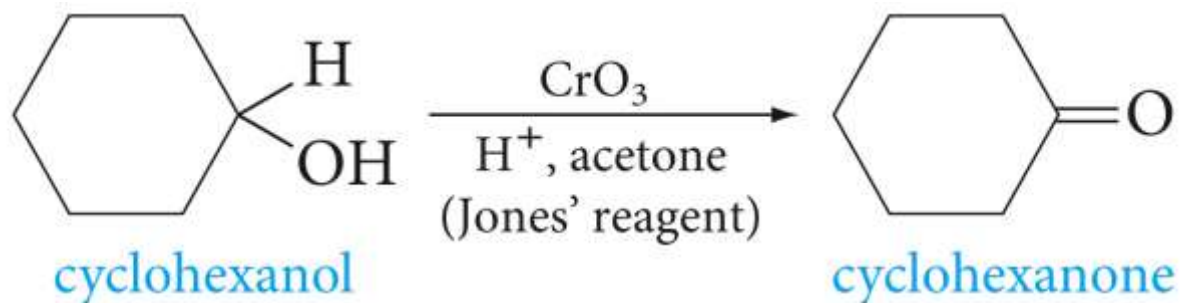


Secondary alcohols give ketones.

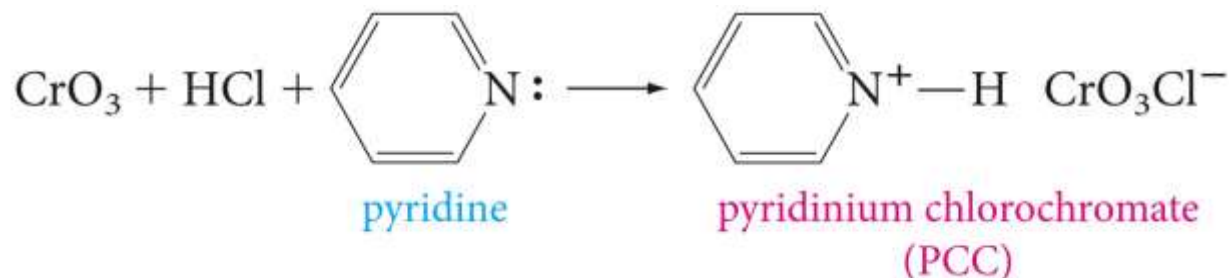
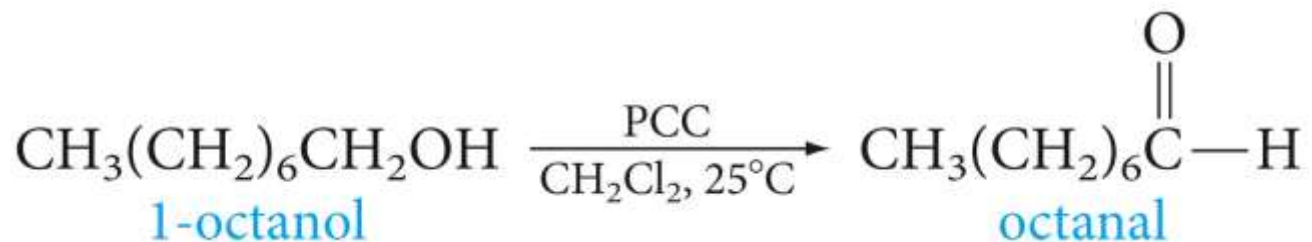


Tertiary alcohols, having no hydrogen atom on the hydroxyl-bearing carbon, do not undergo this type of oxidation.

A common laboratory oxidizing agent for alcohols is chromic anhydride, CrO_3 , dissolved in aqueous sulfuric acid (**Jones' reagent**). Acetone is used as a solvent in such oxidations.



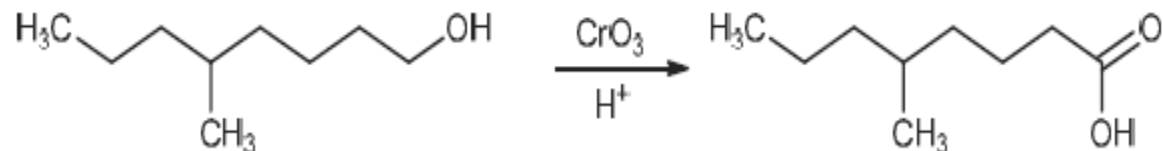
With primary alcohols, oxidation can be stopped at the aldehyde stage by special reagents, such as Pyridinium Chlorochromate (PCC)



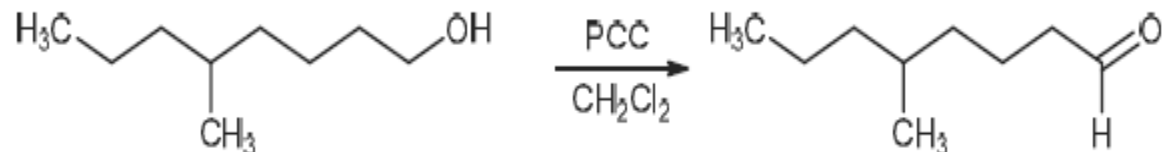
PROBLEM 7.19 Write an equation for the oxidation of

- a. 4-methyl-1-octanol with Jones' reagent
- b. 4-methyl-1-octanol with PCC
- c. 4-phenyl-2-butanol with Jones' reagent
- d. 4-phenyl-2-butanol with PCC

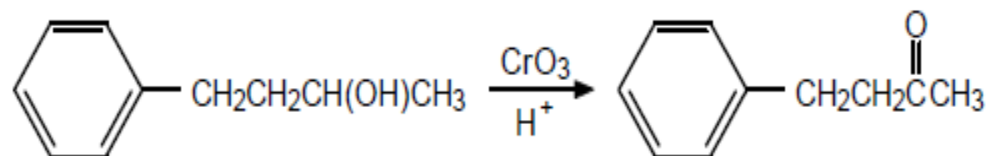
- a. The alcohol is primary and gives a carboxylic acid.



- b. The alcohol is primary and gives an aldehyde.

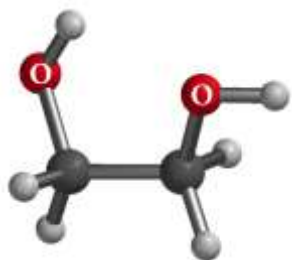


- c. The alcohol is secondary and gives a ketone.

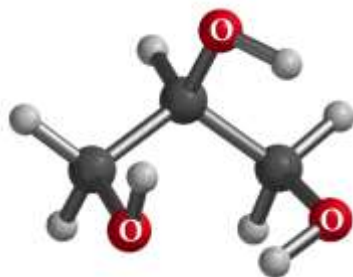


- d. The alcohol is secondary and gives a ketone, regardless of the oxidizing agent. The product is the same as in part c.

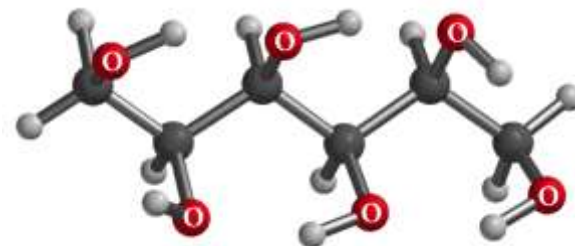
7.13 Alcohols with More Than One Hydroxyl Group



Ethylene glycol
(1,2-ethanediol)
bp 198 °C



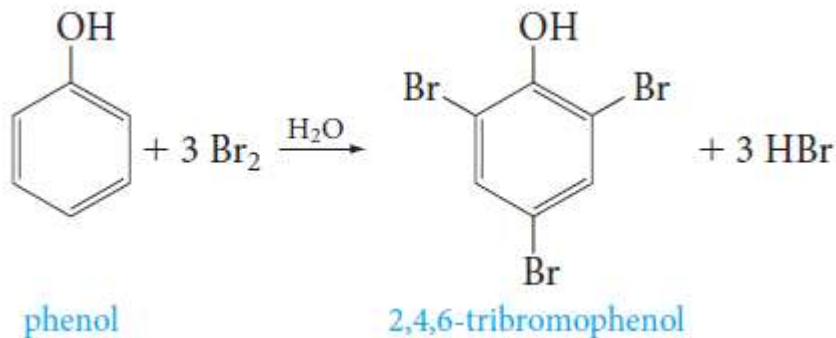
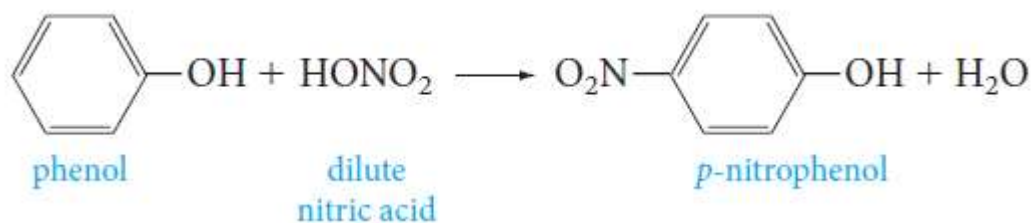
Glycerol (glycerine)
1,2,3-propanetriol
bp 290 °C



Sorbitol
1,2,3,4,5,6-hexanehexaol
Mp 110-112 °C

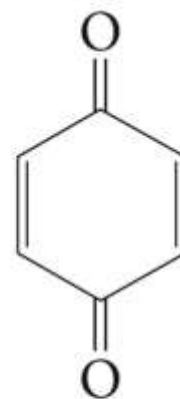
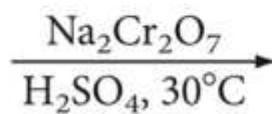
7.14 Aromatic Substitution in Phenols

Phenols undergo electrophilic aromatic substitution under very mild conditions because the hydroxyl group is strongly ring activating.





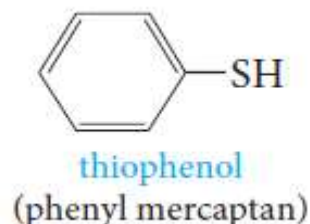
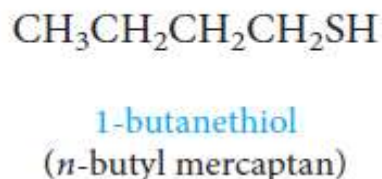
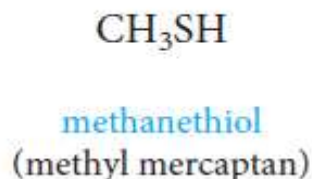
hydroquinone
colorless, mp 171°C



1,4-benzoquinone
yellow, mp 116°C

7.17 Thiols the Sulfur Analog of Alcohols and Phenols

- The **-SH** group, called the **sulfhydryl group**, is the functional group of thiols. Thiols are named as follows:



Thiols are sometimes called **mercaptans**, a name that refers to their reaction with mercuric ion to form mercury salts, called **mercaptides**.



- Alkyl thiols can be made from alkyl halides by nucleophilic displacement with sulfhydryl ion



- Thiols are more acidic than alcohols. The pK_a of ethanethiol, for example, is 10.6 whereas that of ethanol is 15.9. Hence, thiols react with aqueous base to give thiolate

