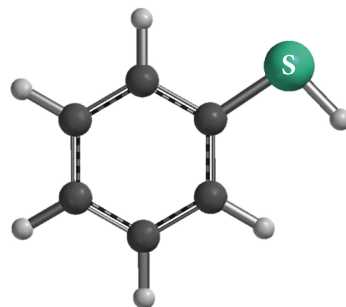
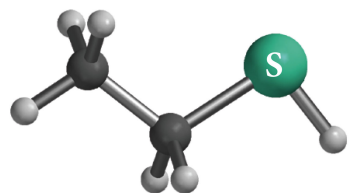
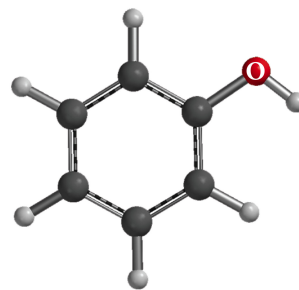
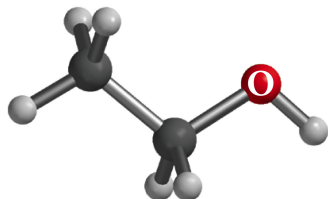


# Chapter 7: Alcohols, Phenols and Thiols

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





# 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.



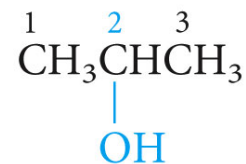
methanol  
(methyl alcohol)



ethanol  
(ethyl alcohol)



1-propanol  
(*n*-propyl alcohol)



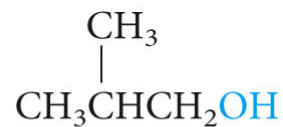
2-propanol  
(isopropyl alcohol)



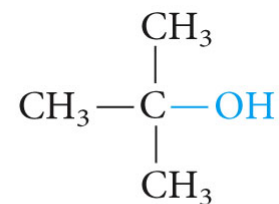
1-butanol  
(*n*-butyl alcohol)



2-butanol  
(*sec*-butyl alcohol)



2-methyl-1-propanol  
(isobutyl alcohol)



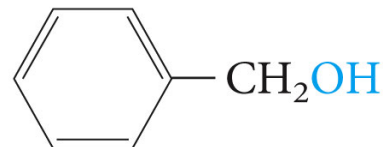
2-methyl-2-propanol  
(*tert*-butyl alcohol)



2-propen-1-ol  
(allyl alcohol)

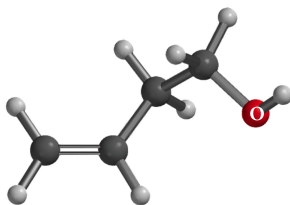
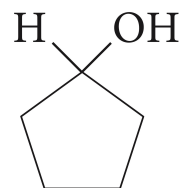
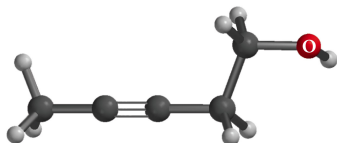
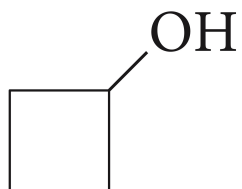


cyclohexanol  
(cyclohexyl alcohol)



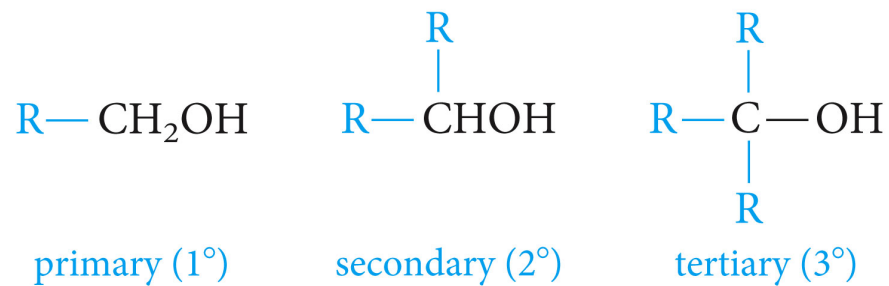
phenylmethanol  
(benzyl alcohol)

Name the following alcohols

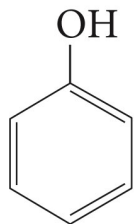




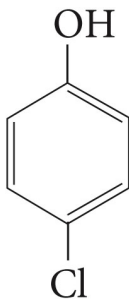
# Classification of Alcohols



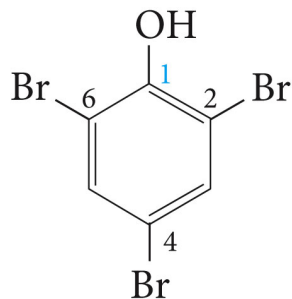
# Nomenclature of Phenols



phenol



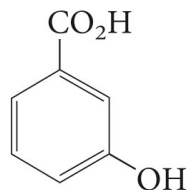
*p*-chlorophenol



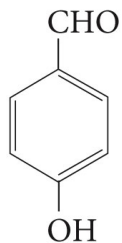
2,4,6-tribromophenol



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

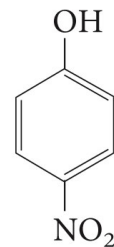


*m*-hydroxy  
benzoic acid



*p*-hydroxybenzaldehyde

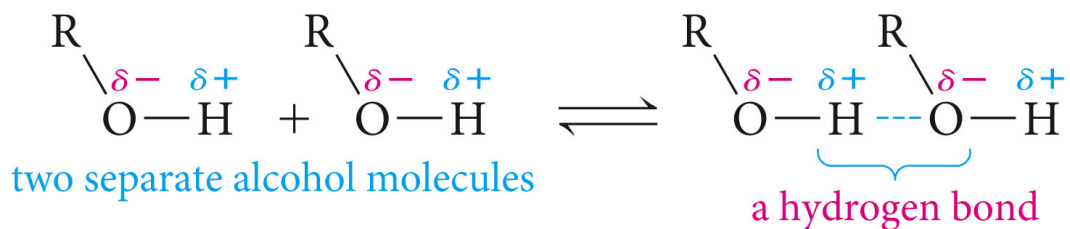
but

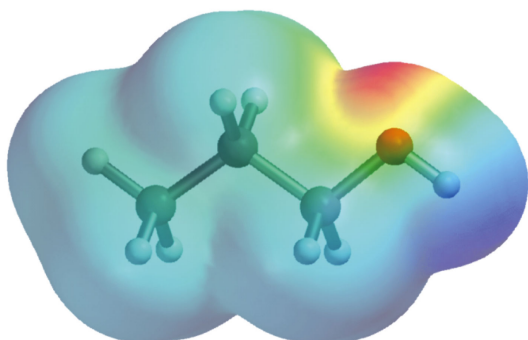


*p*-nitrophenol  
(*not p*-hydroxynitrobenzene)

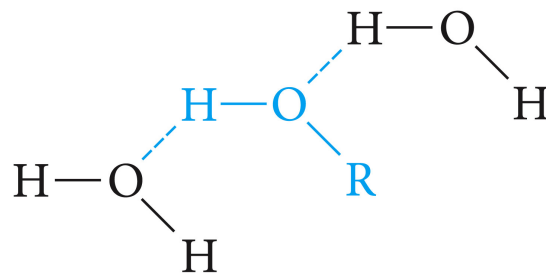
# Hydrogen bonding in Alcohols and Phenols

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





Electronic potential map for 1-propanol

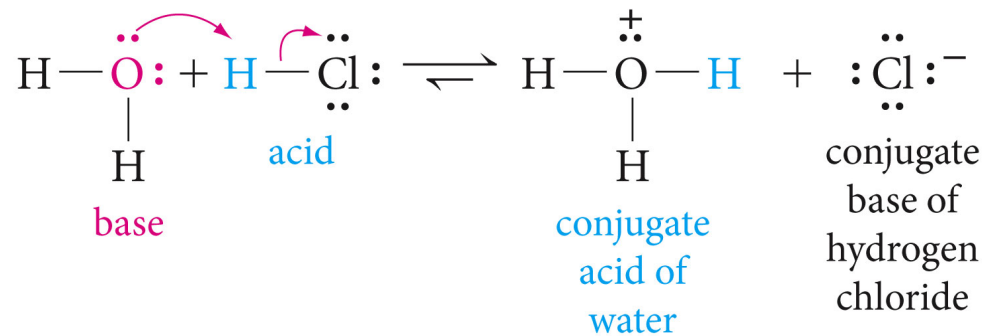


The lower-molecular-weight alcohols can readily replace water molecules in the hydrogen-bonded network. This accounts for the complete miscibility of such alcohols with water.

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

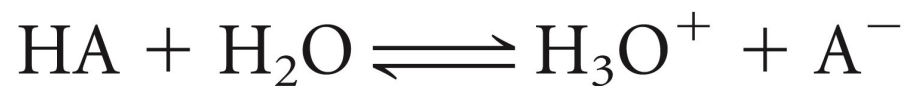
<b>Name</b>	<b>Formula</b>	<b>bp, °C</b>	<b>Solubility in H<sub>2</sub>O g/100 g at 20°C</b>
methanol	CH <sub>3</sub> OH	65	completely miscible
ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	78.5	completely miscible
1-propanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	97	completely miscible
1-butanol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

# Review of Acidity and Basicity



Bronsted-Lowry definition, Acid proton donor, and base proton acceptor

For a generic acid HA, the dissociation/ionization constant  $K_a$  expression is;



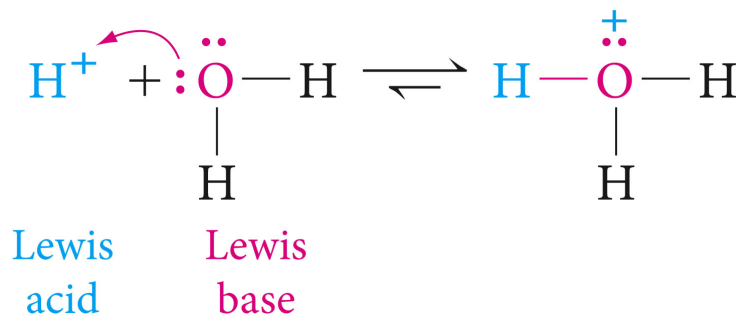
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{p}K_a = -\log K_a$$

# Lewis definition:

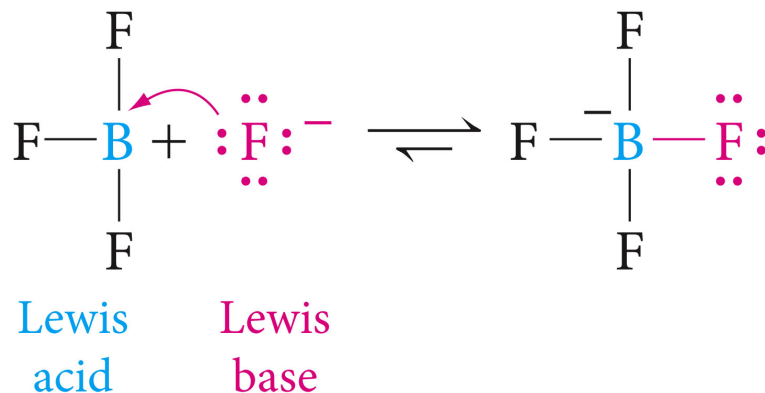
A Lewis Acid is a substance that can accept an electron pair

While a Lewis base is a substance that can donate an electron pair



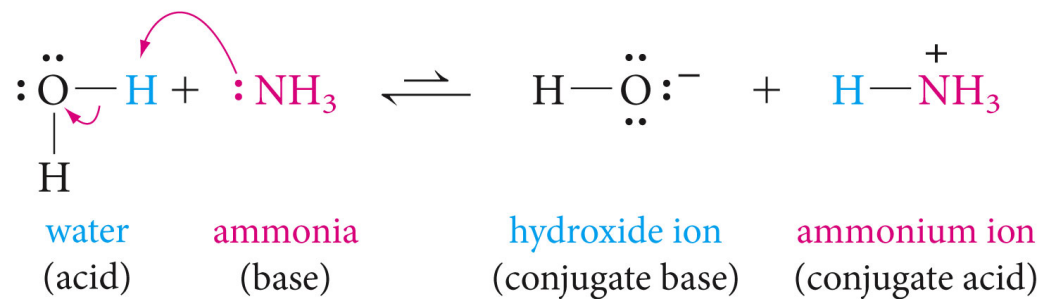


Compounds with an element whose valence shell is incomplete also act as Lewis acids.

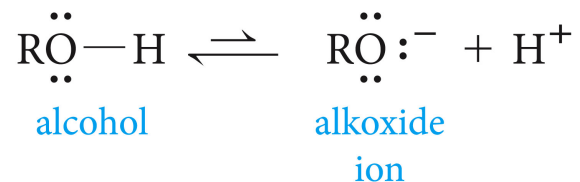


Similarly, when  $\text{FeCl}_3$  and  $\text{AlCl}_3$  acts as catalysts for electrophilic aromatic chlorination or Friedel-Crafts reactions, they are acting as Lewis acids: where the metal atoms accepts an electron pair from chlorine to form an alkyl or acyl chloride

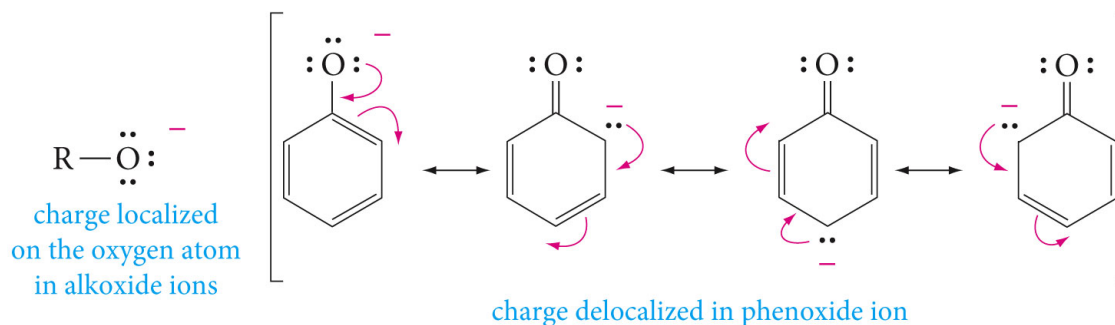
Finally some substances can react as acids or bases depending on other reactants



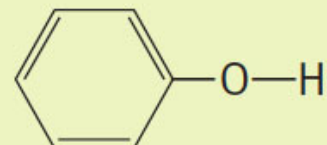
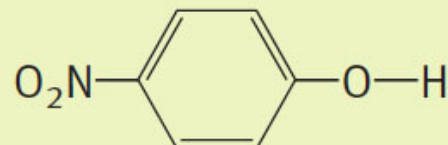
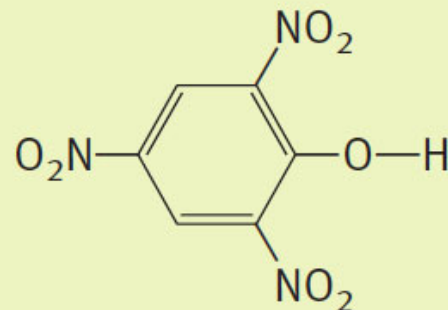
# The Acidity of Alcohols and Phenols



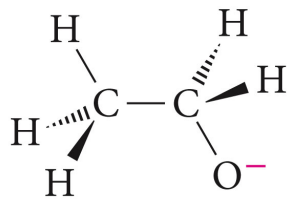
Phenols are much stronger acids than alcohols mainly because the corresponding phenoxide ions are stabilized by resonance. The negative charge of an alkoxide ion is concentrated on the oxygen atom, while the negative charge on the phenoxide ion can be delocalized to the *ortho* and *para* ring positions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



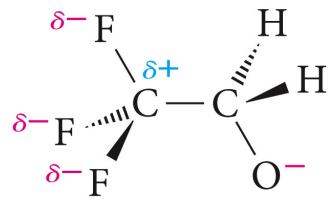
**Table 7.2** ■  $pK_a$ 's of Selected Alcohols and Phenols in Aqueous Solution

Name	Formula	$pK_a$
water	HO—H	15.7
methanol	CH <sub>3</sub> O—H	15.5
ethanol	CH <sub>3</sub> CH <sub>2</sub> O—H	15.9
<i>t</i> -butyl alcohol	(CH <sub>3</sub> ) <sub>3</sub> CO—H	18
2,2,2-trifluoroethanol	CF <sub>3</sub> CH <sub>2</sub> O—H	12.4
phenol		10.0
<i>p</i> -nitrophenol		7.2
picric acid		0.25

## Stabilization by inductive effect

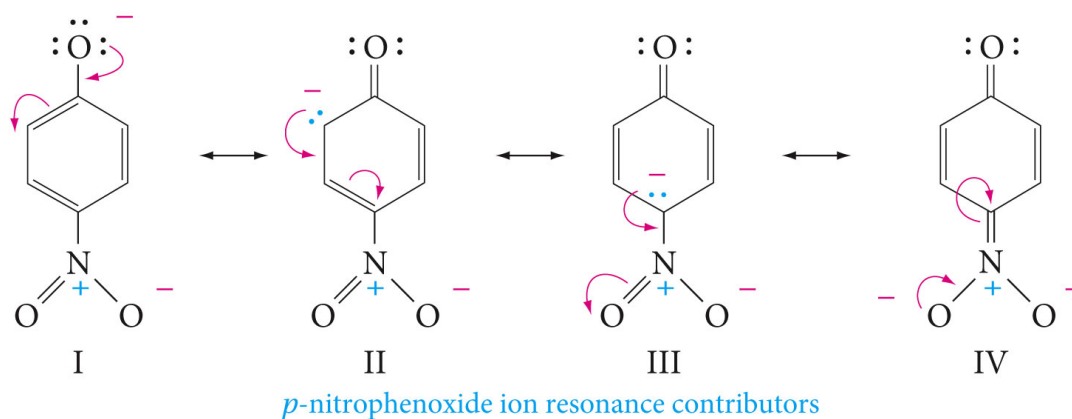


ethoxide ion



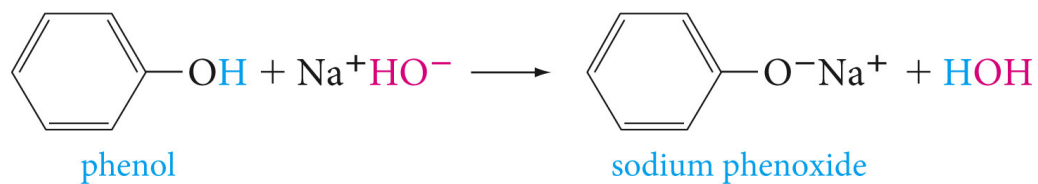
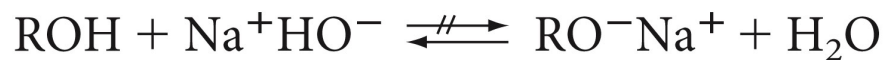
2,2,2-trifluoroethoxide ion

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



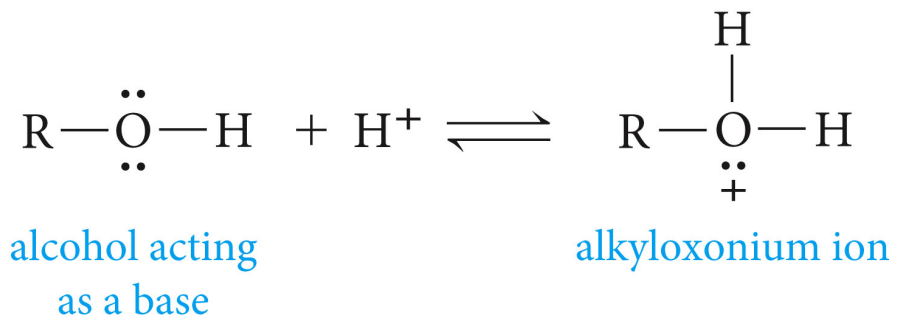


Ordinary treatment of alcohols with sodium hydroxide does not convert them to their alkoxides. This is because alkoxides are stronger bases than hydroxide ion, so the reaction goes in the reverse direction. Phenols, however, can be converted to phenoxides ions in this way.

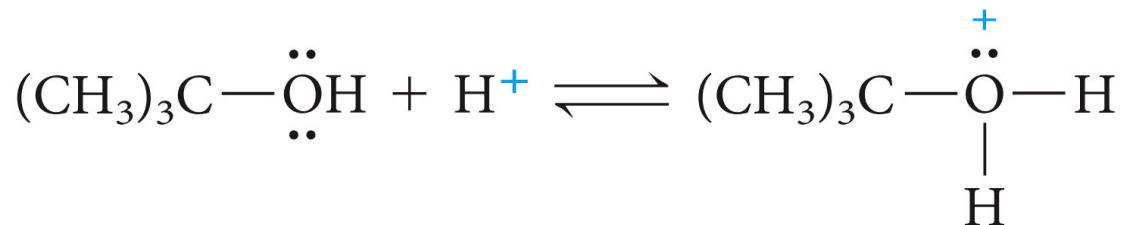
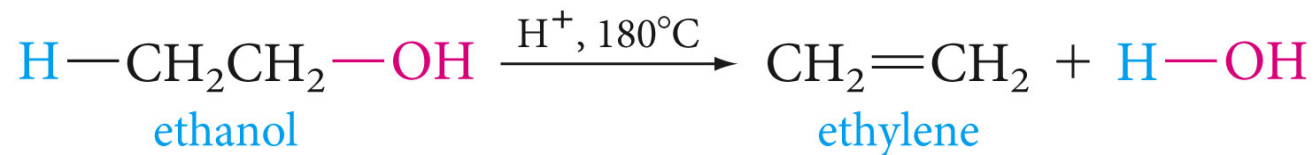


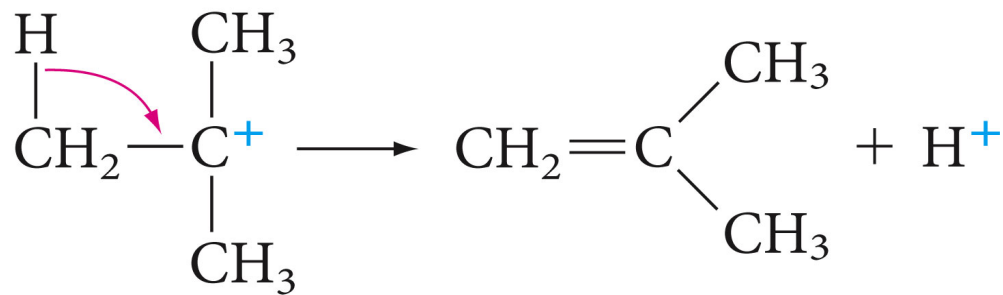
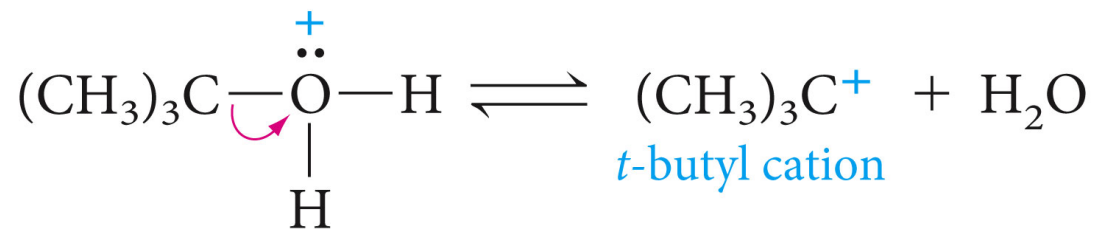


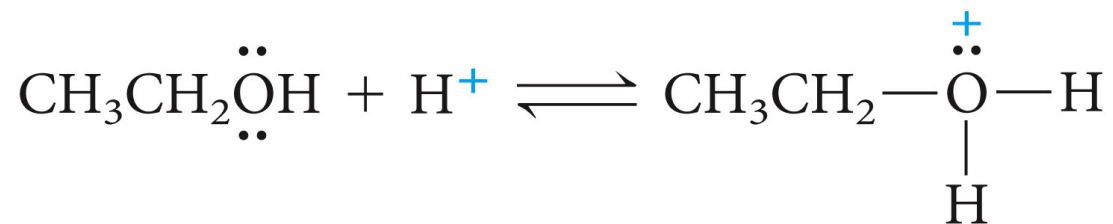
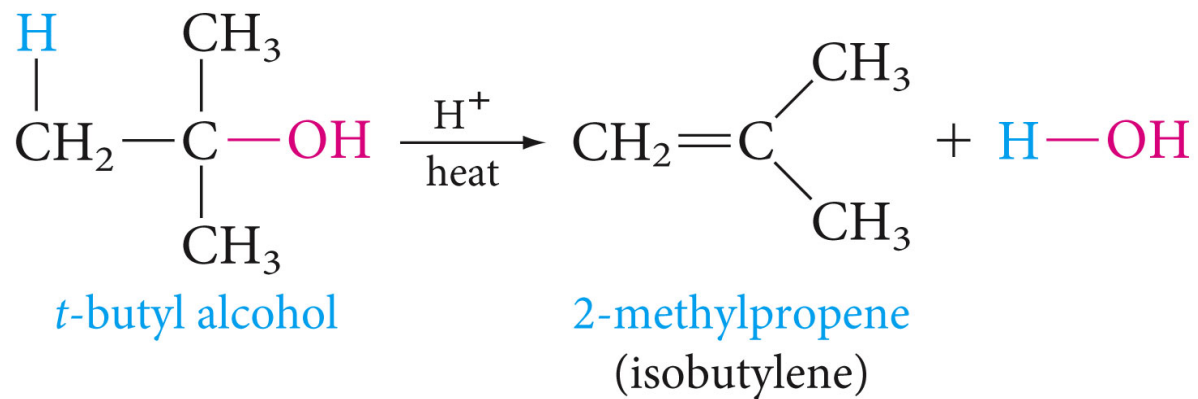
# The Basicity of Alcohols and Phenols

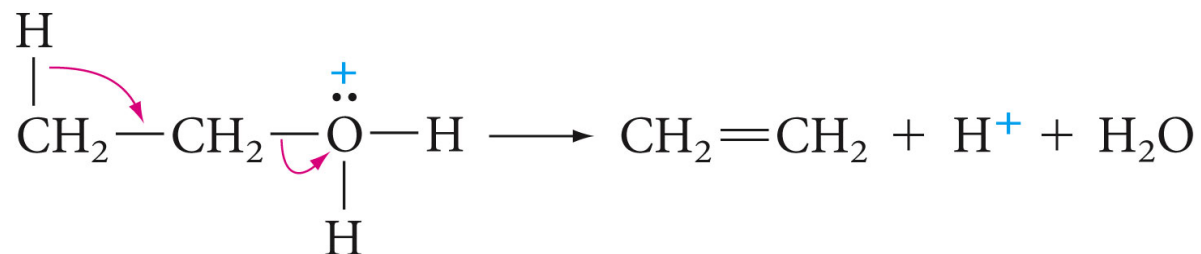


## Dehydration of Alcohols to Alkenes

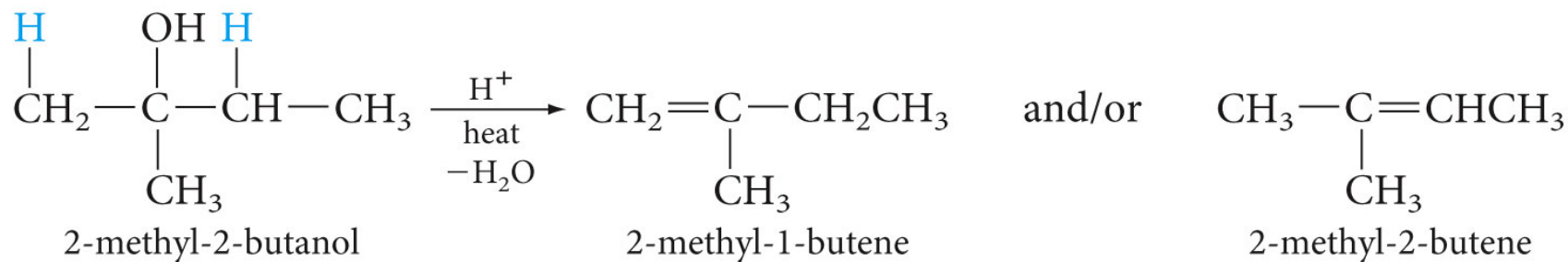




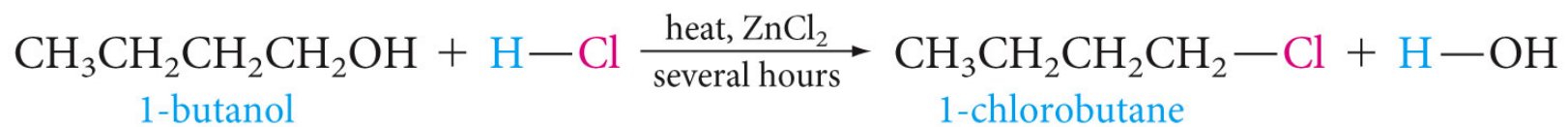
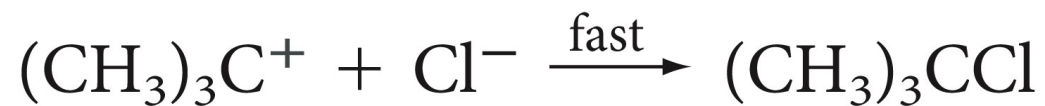




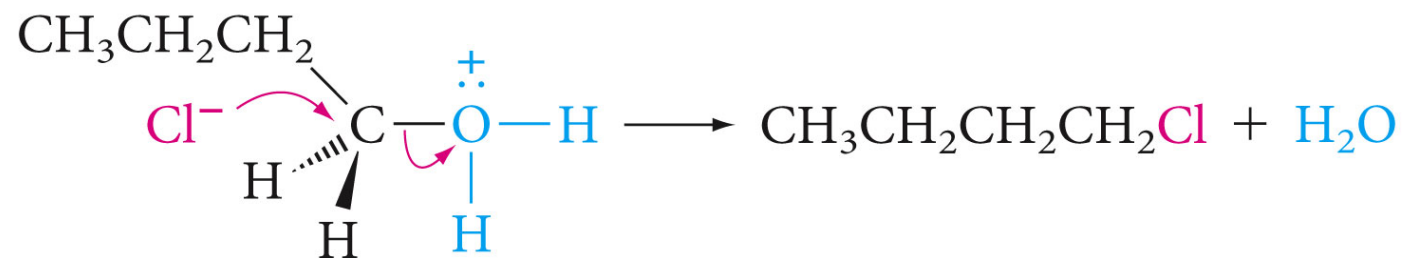
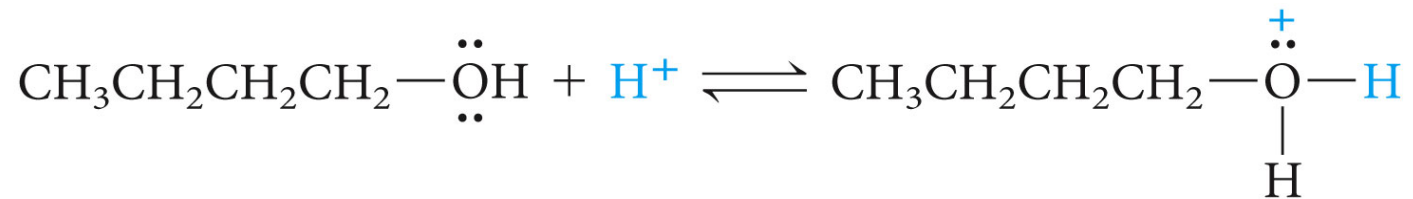
Sometimes a single alcohol gives two or more alkenes





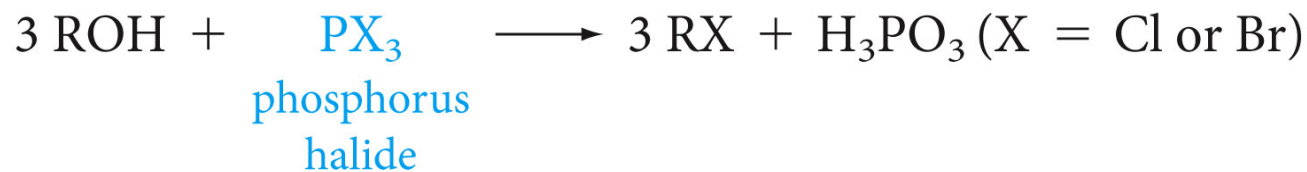
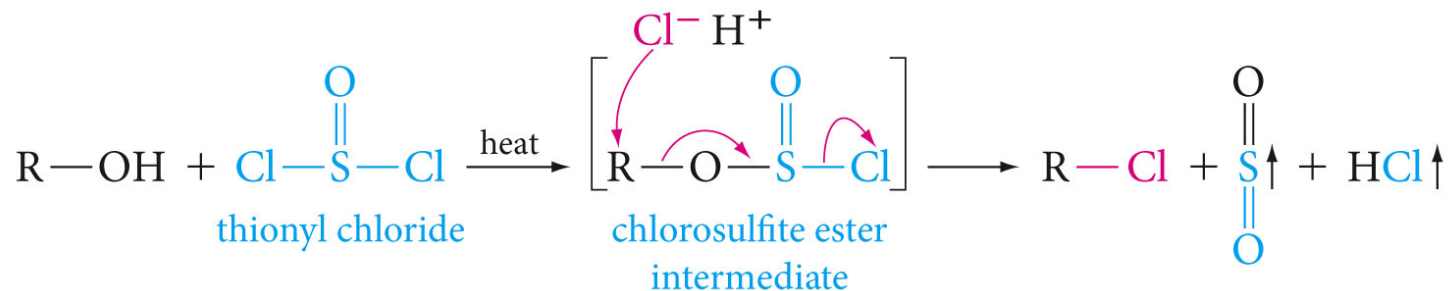


Reaction occurs by an S<sub>N</sub>2 mechanism when the alcohol is protonated by an acid.

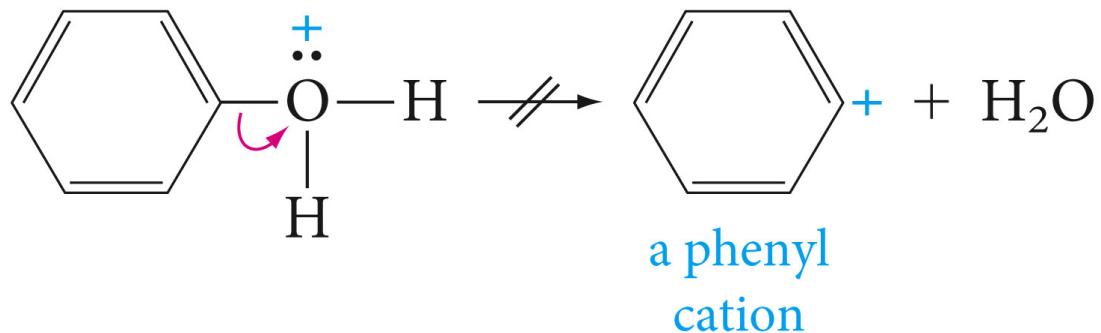




## Other Ways to Prepare Alkyl Halides from Alcohols

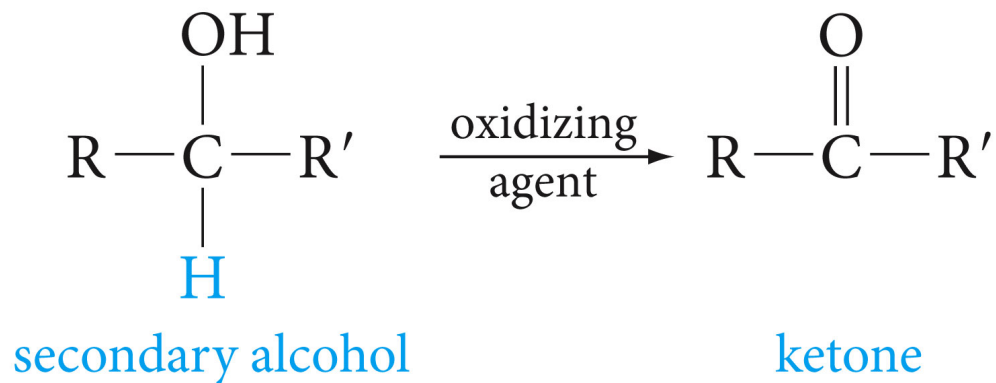
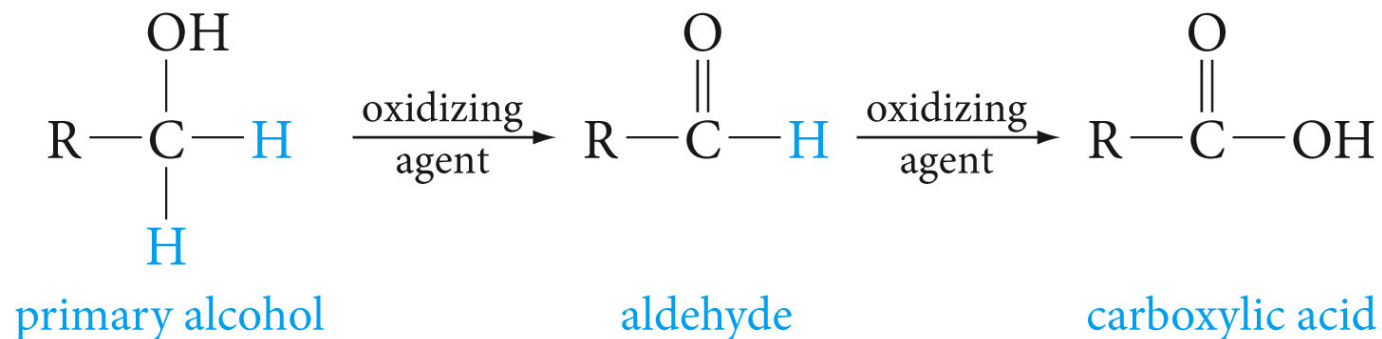


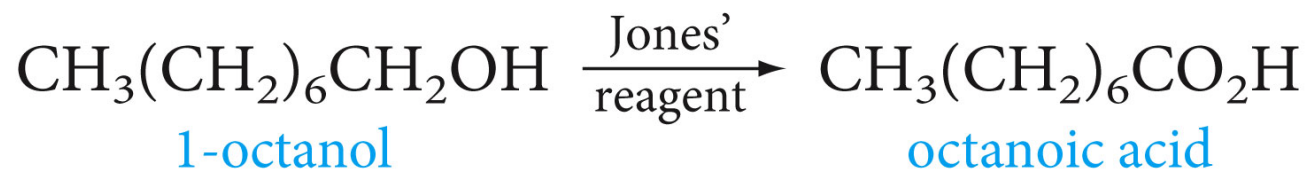
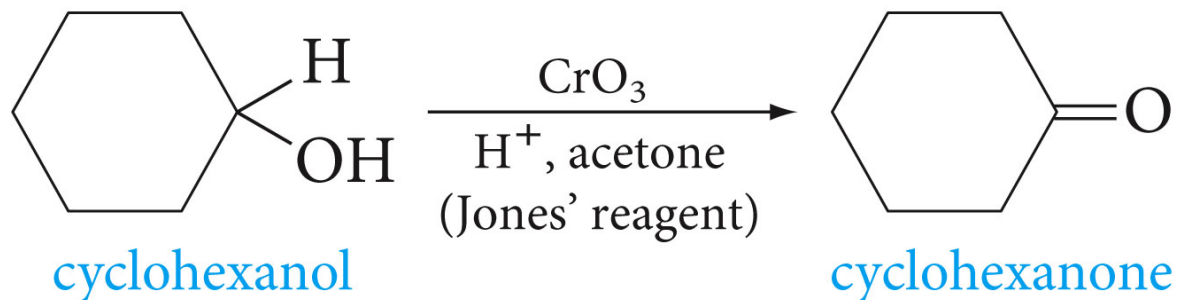
## A Comparison of Alcohols and Phenols



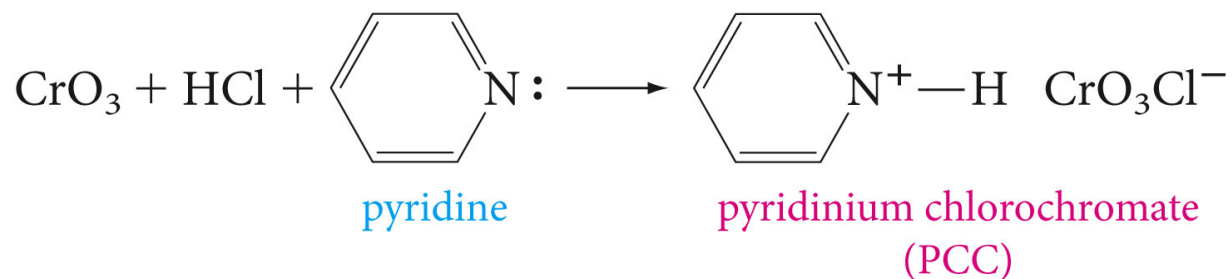
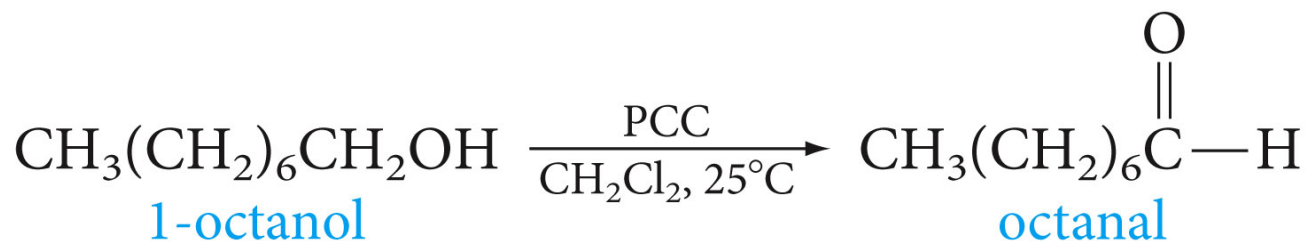
Phenyl cations are energetically unstable and are difficult to form. Phenols can also never undergo displacement by the  $S_N2$  mechanism

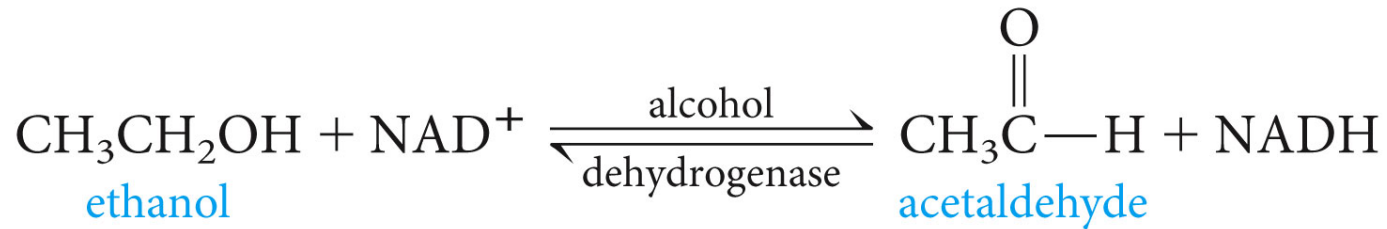
# Oxidation of Alcohols to Aldehydes, Ketones, and Carboxylic Acids



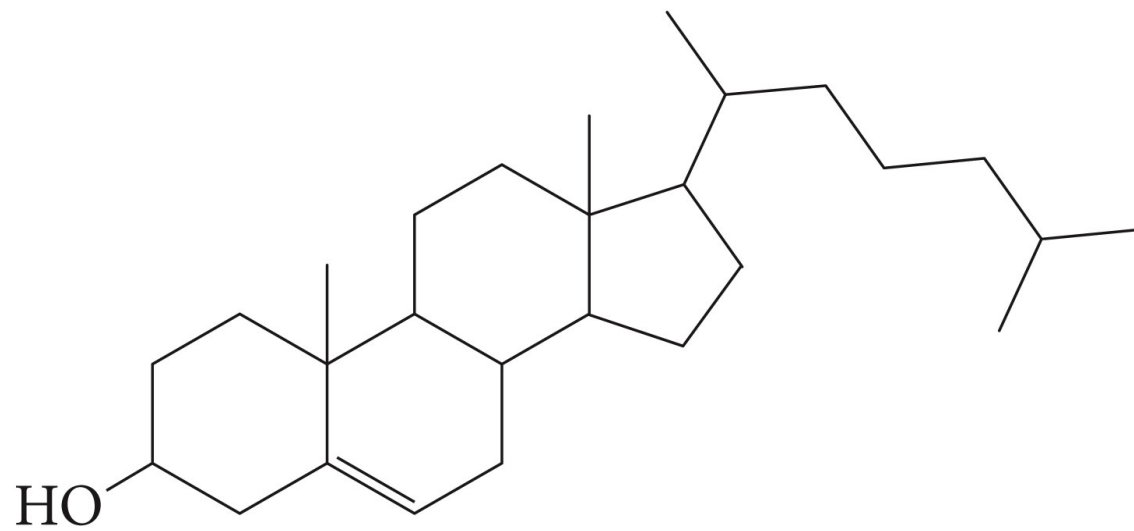


With primary alcohols, oxidation can be stopped at the aldehyde stage by special reagents, such as Pyridinium Chlorochromate (PCC)



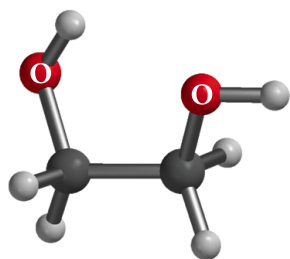


In the body, similar oxidation are accomplished by enzymes, together with rather complex coenzyme called nicotinamide adenine dinucleotide,  $\text{NAD}^+$ . This reaction takes place in the liver and is a key step in the body's attempt to rid itself of imbibed alcohol. The resulting acetaldehyde is also toxic and is further oxidized to acetic acid and eventually carbon dioxide and water.

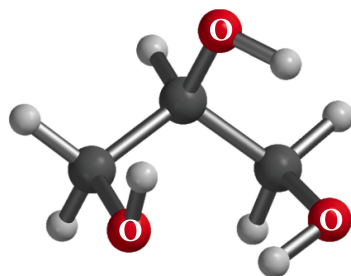


cholesterol

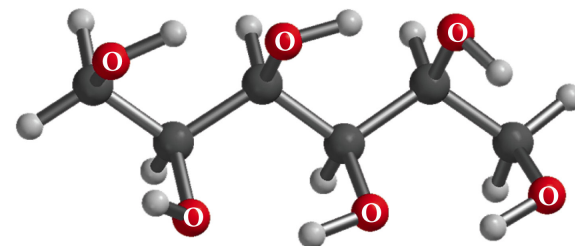
# Alcohols with More Than One Hydroxyl Group



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

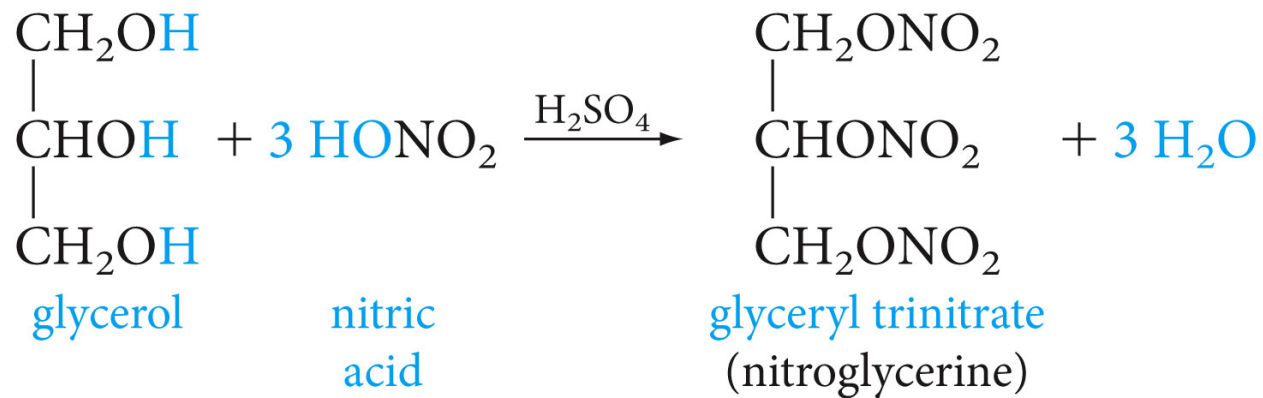


Glycerol (glycerine)  
1,2,3-propanetriol  
bp 290 °C

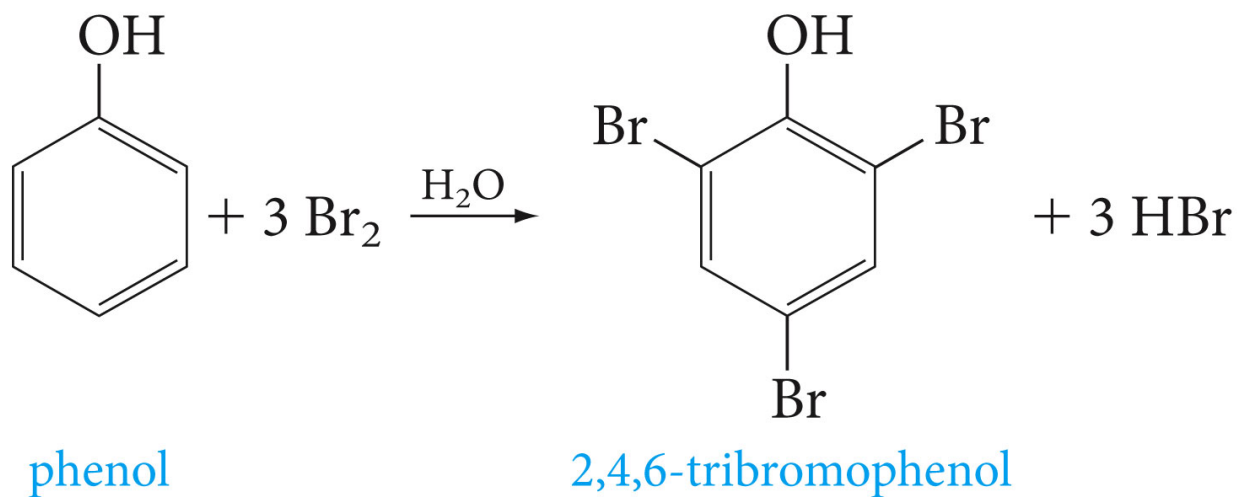
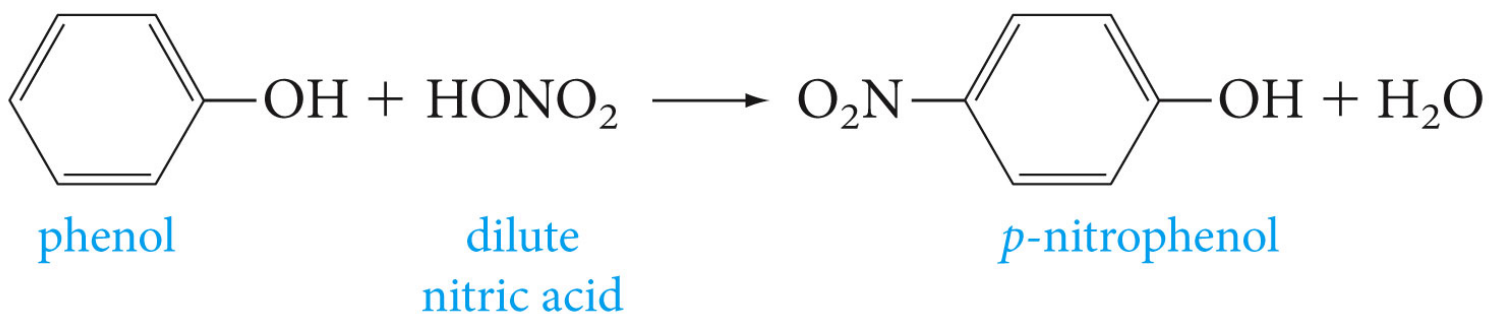


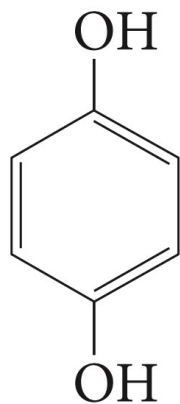
Sorbitol  
1,2,3,4,5,6-hexanehexaol  
Mp 110-112 °C



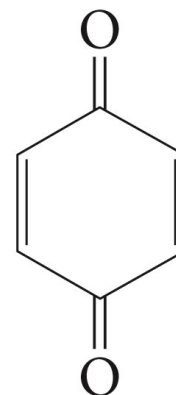
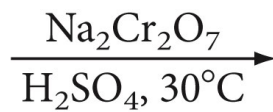


# Aromatic Substitutions in Phenols



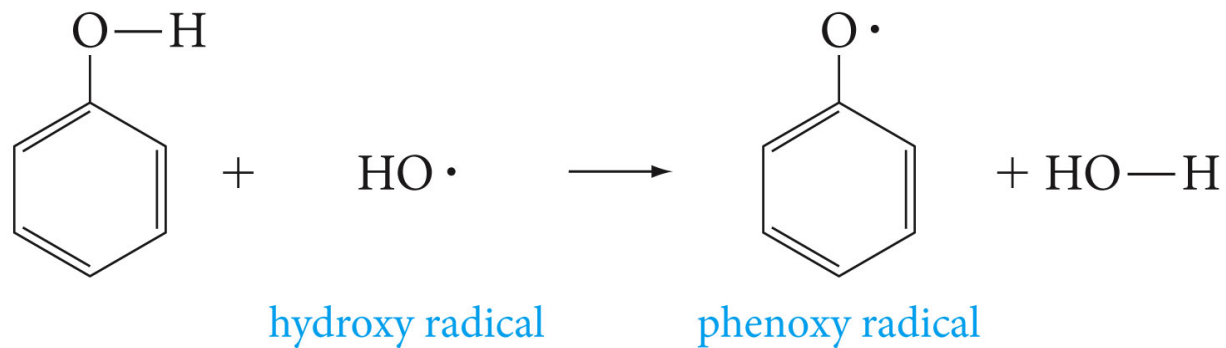


hydroquinone  
colorless, mp 171°C



1,4-benzoquinone  
yellow, mp 116°C

# Phenols and Antioxidants



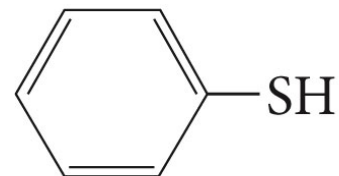
# Thiols, the Sulfur Analogs of Alcohols and Phenols



methanethiol  
(methyl mercaptan)



1-butanethiol  
(*n*-butyl mercaptan)



thiophenol  
(phenyl mercaptan)





Thymol is an antibacterial oil obtained from thyme (*Thymus vulgaris*). The IUPAC name of this compound is 2-isopropyl-5-methylphenol. Draw the structure of thymol.