



# **Chapter 7**

**Alcohols**

**Phenols**

**and**

**Thiols**

## 7.1 Nomenclature of Alcohols

IUPAC: hydroxyl group : **-ol** (**alkanols**)

Common names : **alkyl alcohols**



methanol

(methyl alcohol)



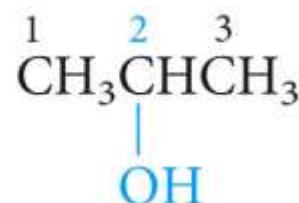
ethanol

(ethyl alcohol)



1-propanol

(*n*-propyl alcohol)



2-propanol

(isopropyl alcohol)



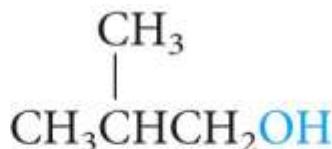
1-butanol

(*n*-butyl alcohol)



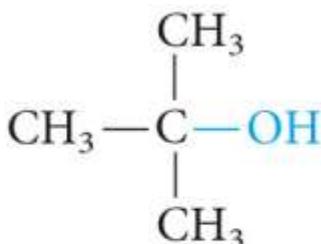
2-butanol

(*sec*-butyl alcohol)



2-methyl-1-propanol

(isobutyl alcohol)



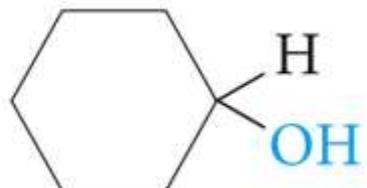
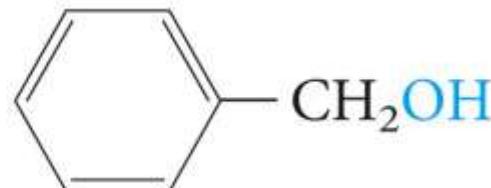
2-methyl-2-propanol

(*tert*-butyl alcohol)

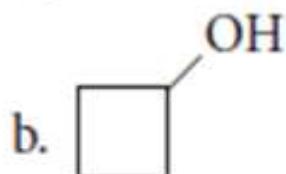


2-propen-1-ol

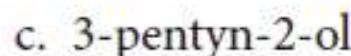
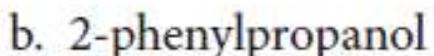
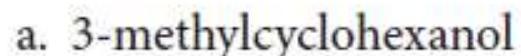
(allyl alcohol)

cyclohexanol  
(cyclohexyl alcohol)phenylmethanol  
(benzyl alcohol)

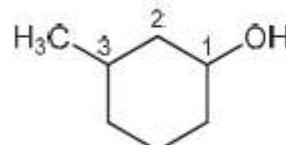
Name the following alcohols by the IUPAC



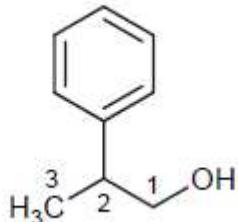
PROBLEM 7.2 Write a structural formula for



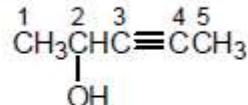
a.



b.



c.



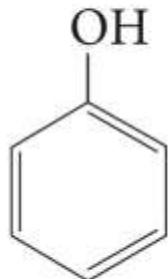
## 7.2 Classification of Alcohols

primary ( $1^\circ$ )     $\text{R}-\text{CH}_2\text{OH}$

secondary ( $2^\circ$ )     $\begin{array}{c} \text{R} \\ | \\ \text{R}-\text{CHOH} \end{array}$

tertiary ( $3^\circ$ )     $\begin{array}{c} \text{R} \\ | \\ \text{R}-\text{C}-\text{OH} \\ | \\ \text{R} \end{array}$

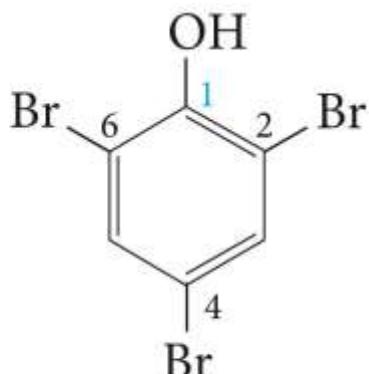
## 7.3 Nomenclature of Phenols



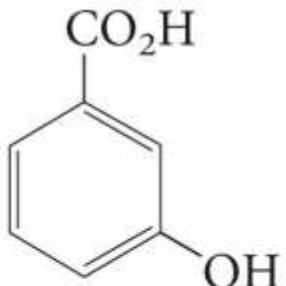
phenol



*p*-chlorophenol



2,4,6-tribromophenol



*m*-hydroxy  
benzoic acid



*p*-hydroxybenzaldehyde

but

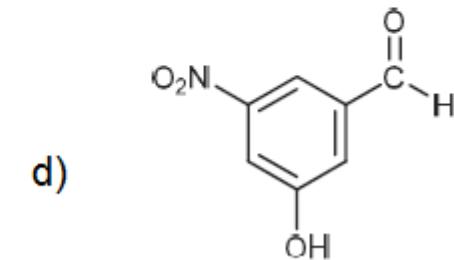
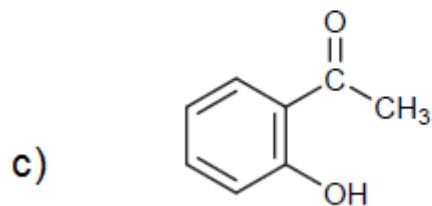
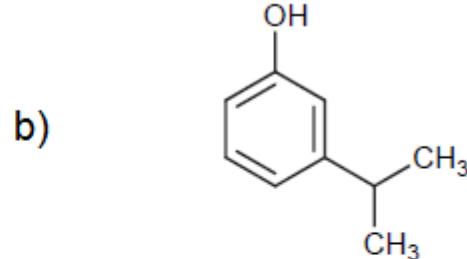
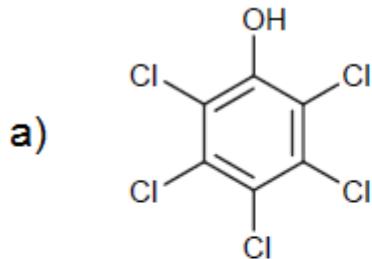


*p*-nitrophenol  
(not *p*-hydroxynitrobenzene)

## PROBLEM 7.4

Write the structure for

- a. pentachlorophenol.
- b. *m*-isopropylphenol
- c. *o*-hydroxyacetophenone
- d. 3-hydroxy-5-nitrobenzaldehyde

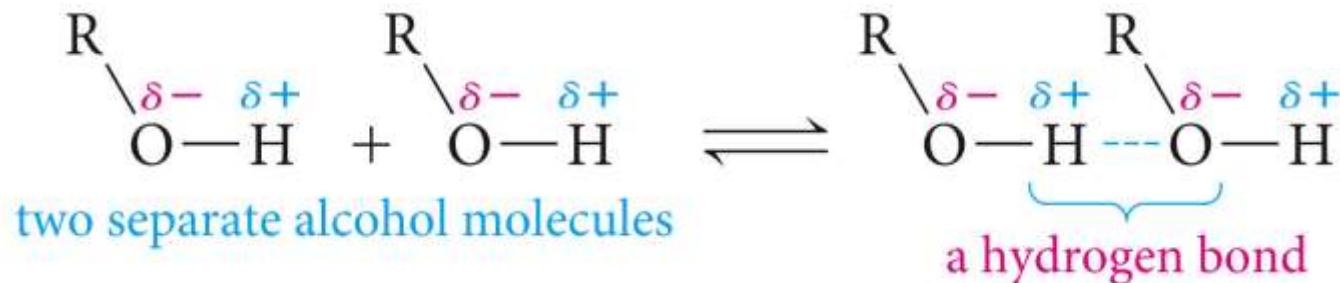


## 4.4 Hydrogen bonding in Alcohols and Phenols

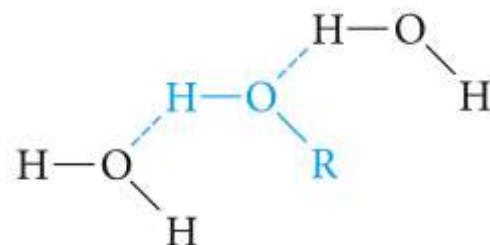
Boiling points of alcohols are much higher than those of ethers or hydrocarbons with similar molecular weights.

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

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



Solubility : Alcohols form hydrogen-bonds with water.

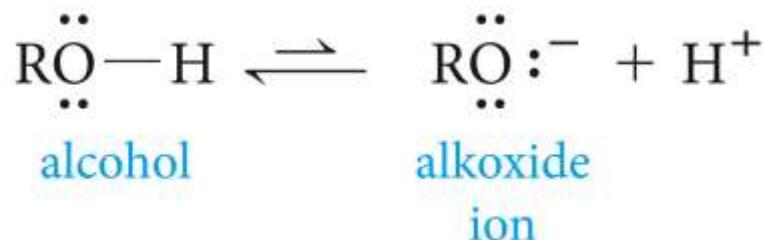


So they are water-soluble up to about 5C atoms per OH group.  
As number of C atoms increases, water solubility decreases.

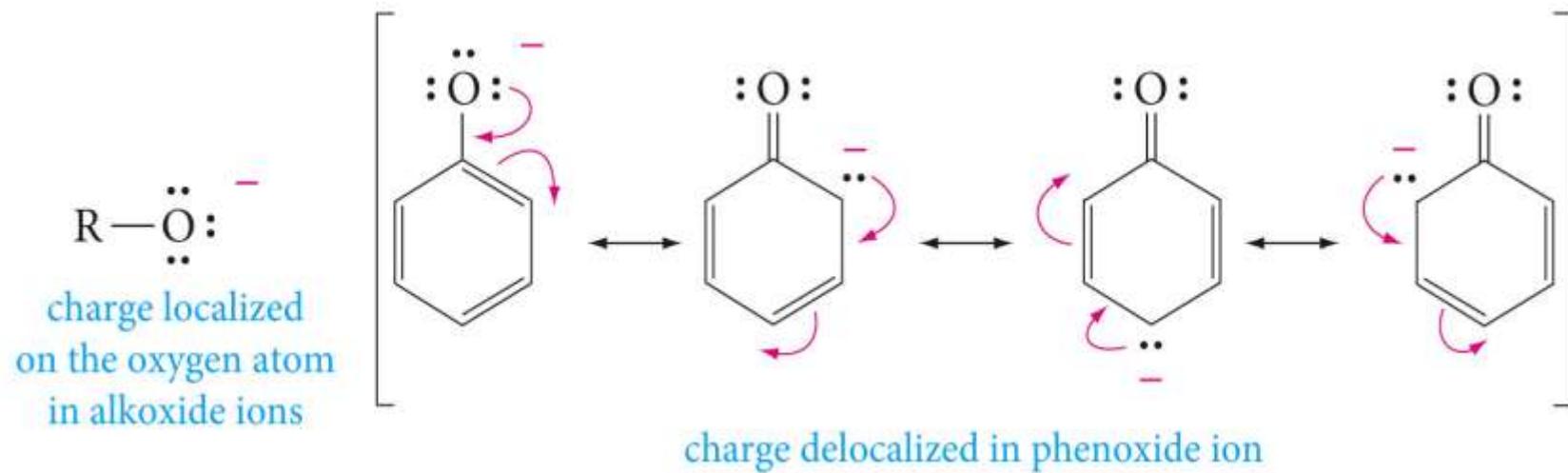
Name	Formula	bp, °C	Solubility in H <sub>2</sub> O g/100 g at 20°C
methanol	CH <sub>3</sub> OH	65	completely miscible
ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	78.5	completely miscible
1-propanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	97	completely miscible
1-butanol	CH <sub>3</sub> CH <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

## 7.6 Acidity of Alcohols and Phenols

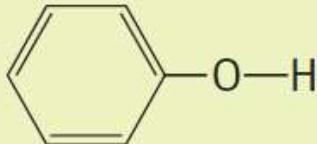
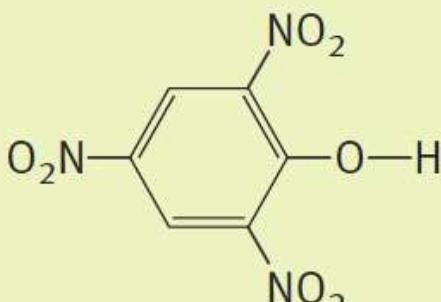
The hydroxyl group shows acidic character:



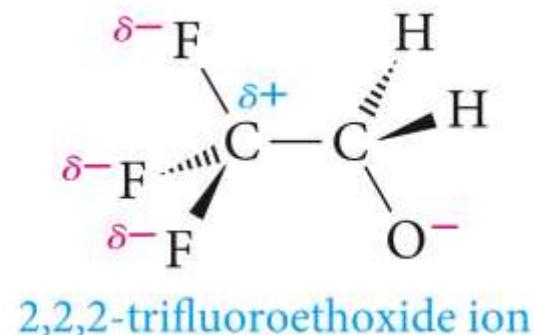
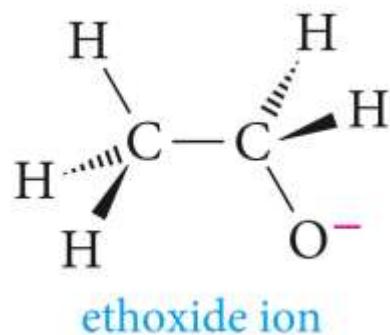
Phenols are more acidic than alcohols because phenoxide ions are stabilized by resonance ( $-ve$  charge delocalized over ortho and para positions). In alkoxides it is localized on the oxygen atom.



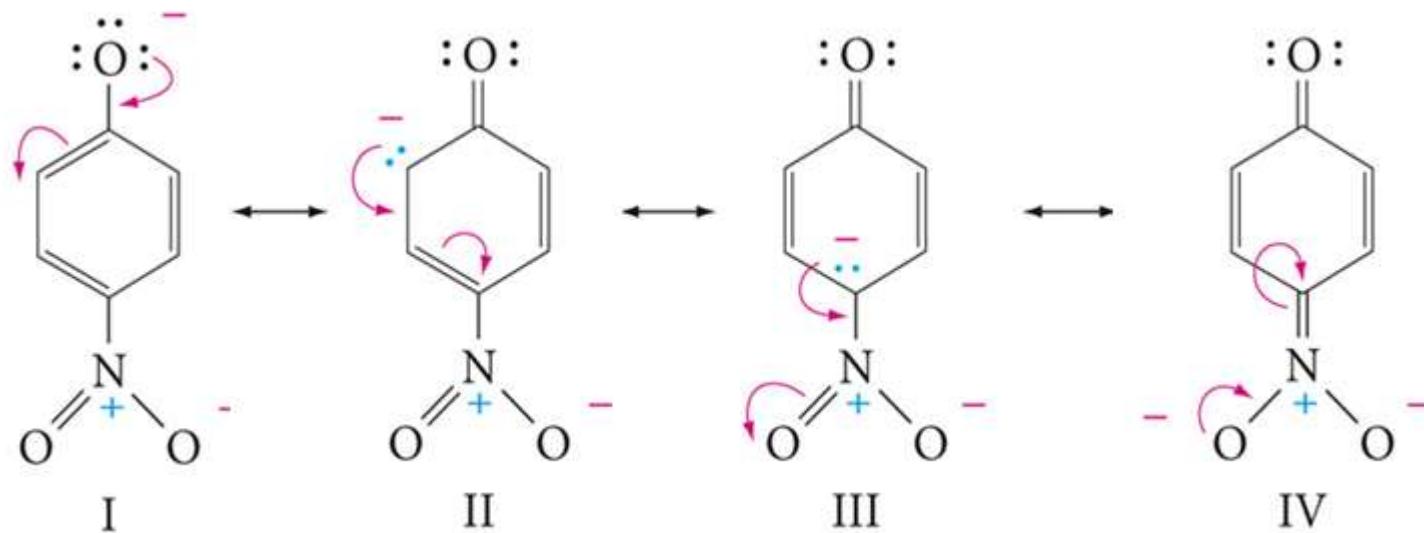
**Table 7.2** ■  $pK_a$ 's of Selected Alcohols and Phenols in Aqueous Aolution

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

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

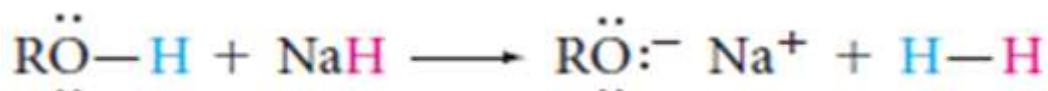


**-ve charge stabilized  
by inductive effect**



**-ve charge  
stabilized  
by resonance**

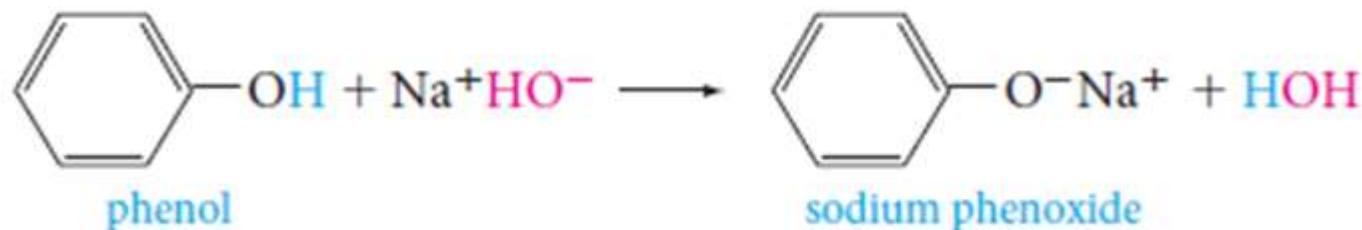
Formation of Alkoxides : Alcohol + very strong base (Na, K, NaH, NaNH<sub>2</sub>)



Sodium hydroxide (NaOH) is not strong enough to react with R-OH.  
(alkoxides are stronger bases than hydroxide ion)

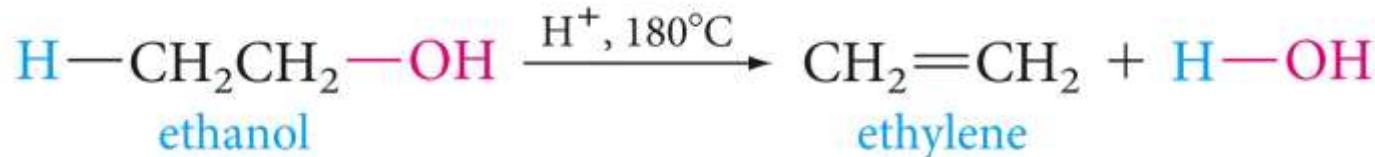


Phenols are more acidic and react with NaOH :

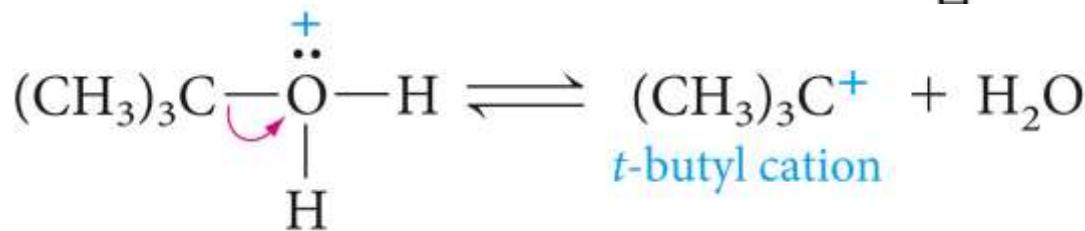
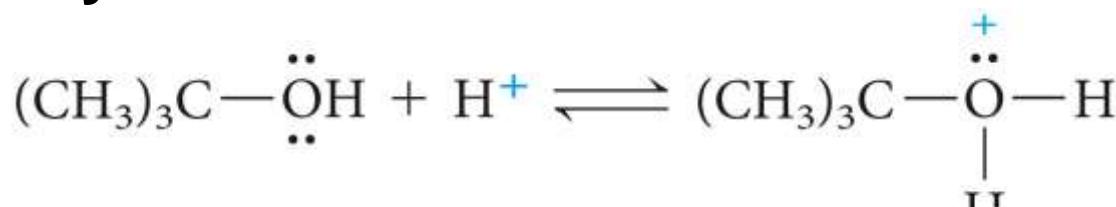


## 7.8 Dehydration of Alcohols to Alkenes

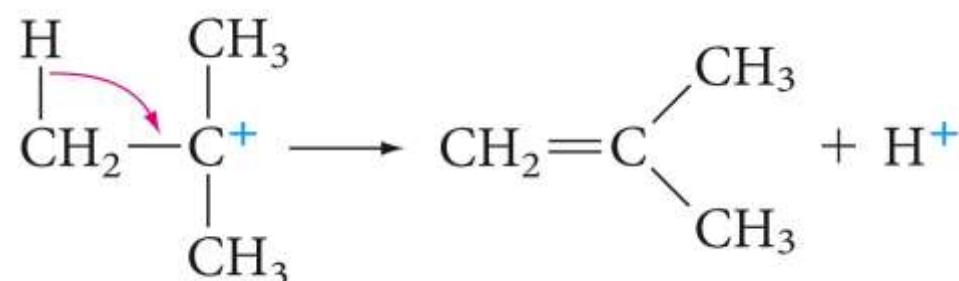
Dehydration by heating with acid (Elimination of H<sub>2</sub>O : E1 or E2)

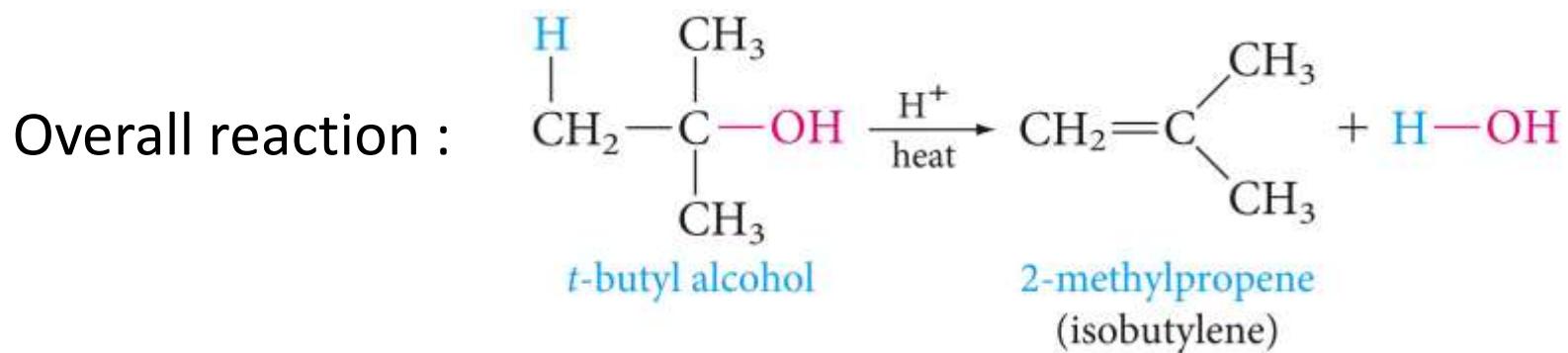


**Tertiary : E1**

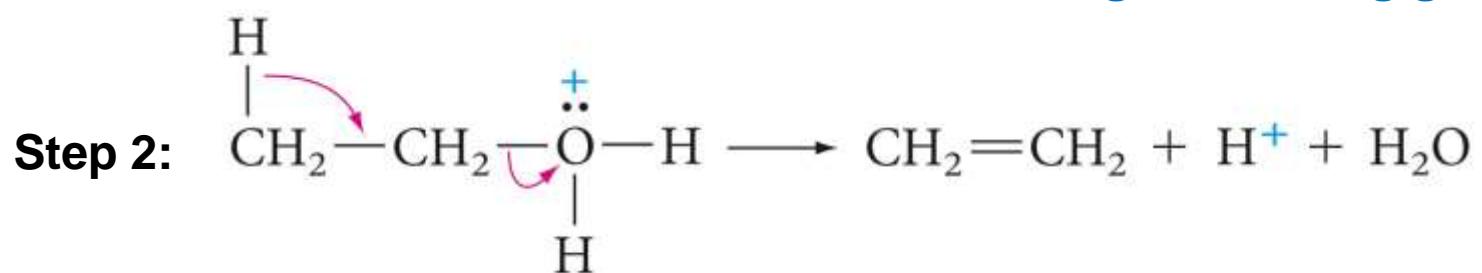
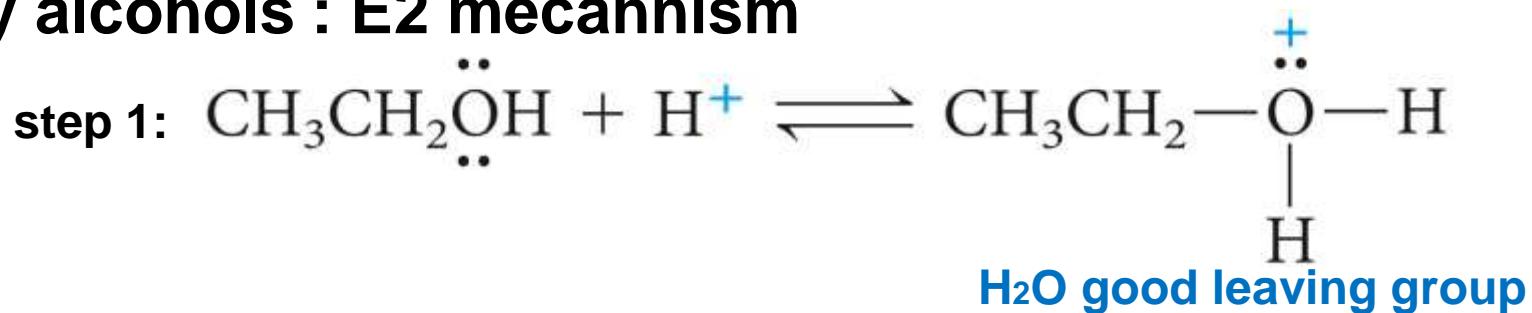


H<sub>2</sub>O is a good leaving group

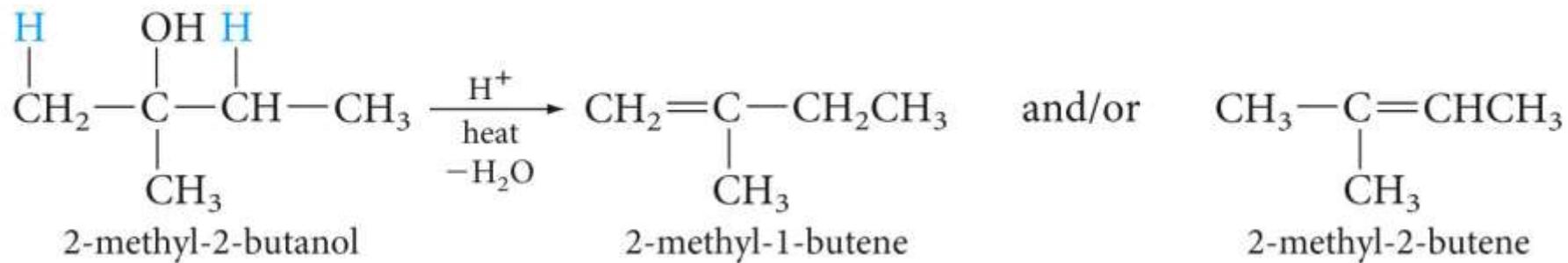




## Primary alcohols : E2 mechanism



Some alcohols give more than one alkene:

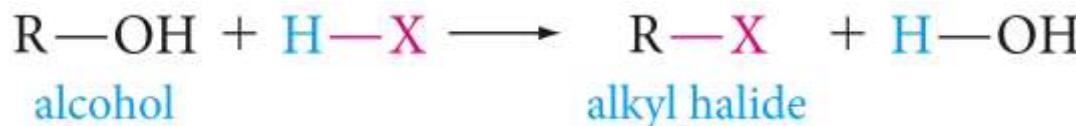


**Rule :**

**The alkene with the most substituted double bond  
is major product**

## 7.9 Reaction of Alcohols with Hydrogen Halides (H-X)

Alcohols react with hydrogen halides (HCl, HBr, and HI) in **S<sub>N</sub>1** mechanism.

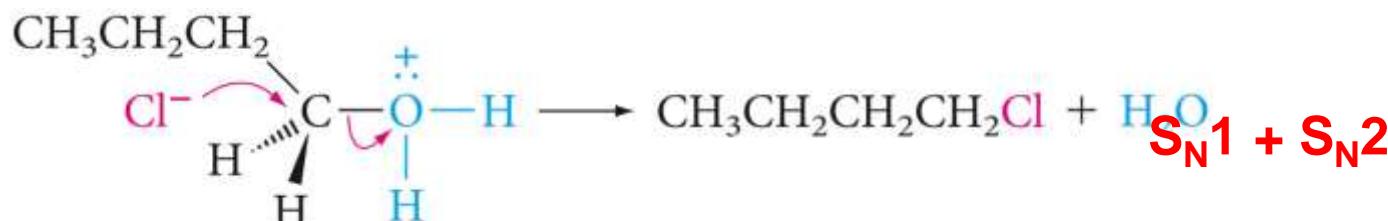
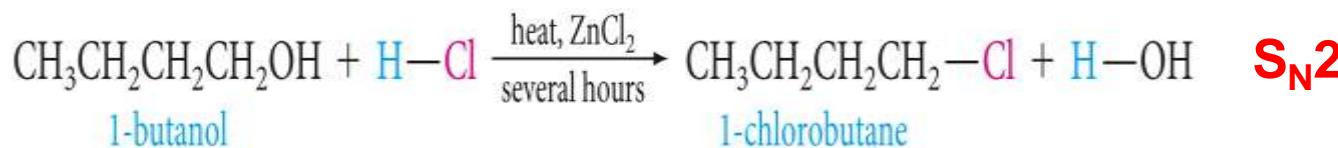
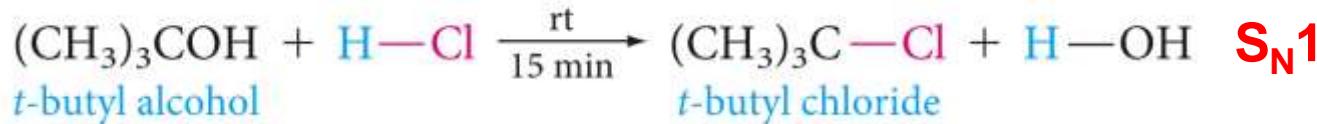


Halide ions are nucleophilic but not basic, so we get only substitution products. Rate and mechanism depend only on alcohol (tertiary, secondary, or primary).

### Mechanism :

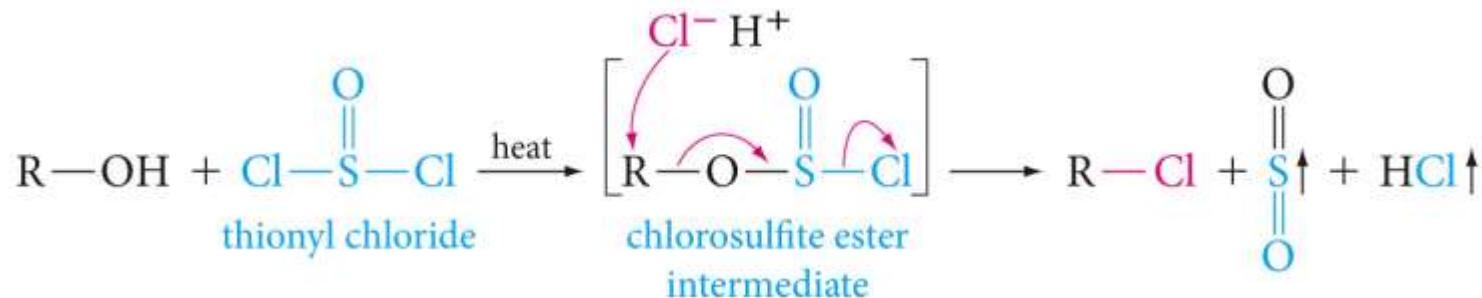
**S<sub>N</sub>1** : with secondary and tertiary (carbocation formed).

**S<sub>N</sub>2** : with primary and methyl, slow, require (conc **HCl + ZnCl<sub>2</sub>**)

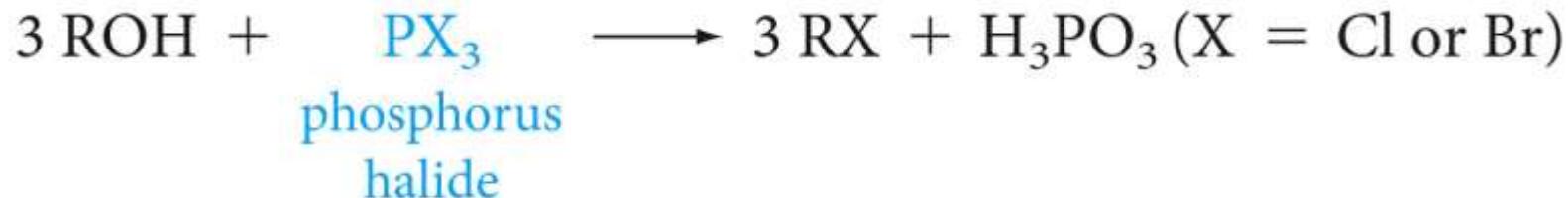


## 7.10 Other Ways to Prepare Alkyl Halides from Alcohols :

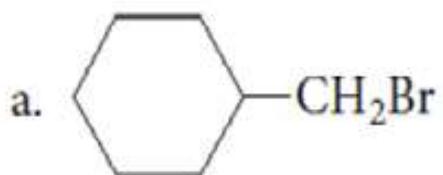
1) Thionyl chloride ( $\text{SOCl}_2$ ).



2) Phosphorus halides ( $\text{PX}_3$ ).



Write equations for the preparation of the following alkyl halides from the corresponding alcohol and  $\text{SOCl}_2$ ,  $\text{PCl}_3$ , or  $\text{PBr}_3$ .

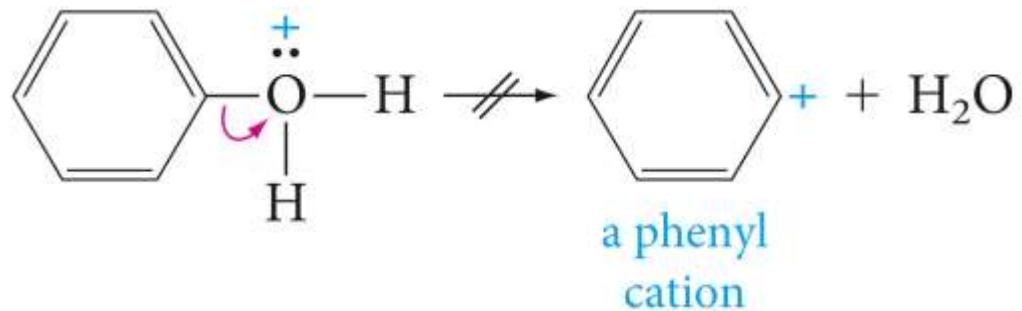


## 7.11 Comparison of Alcohols and Phenols :

Phenyl cations are unstable (No S<sub>N</sub>1) .

Phenols do not undergo S<sub>N</sub>2 reactions (no backside attack).

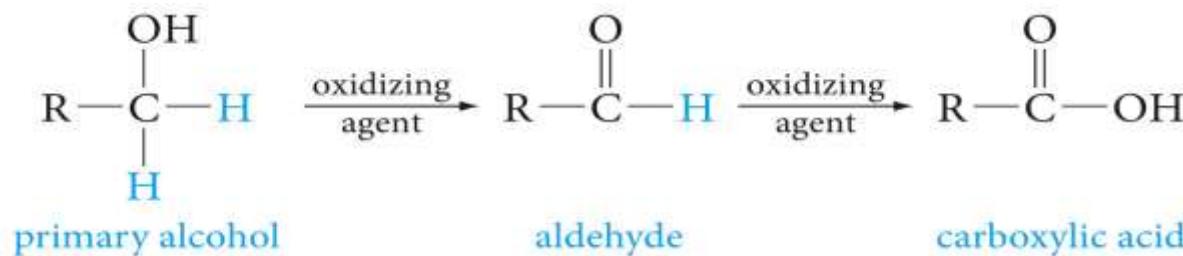
Phenols do not undergo elimination (E1 or E2)



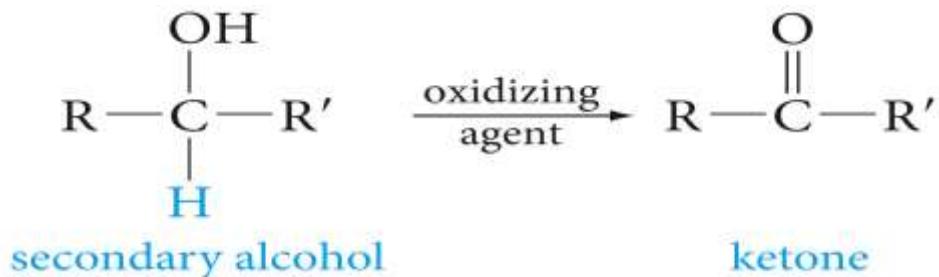
## 7.12 Oxidation of Alcohols :

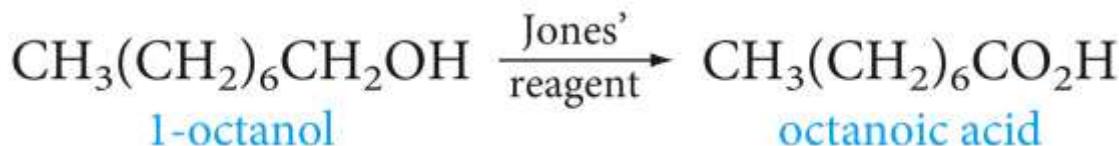
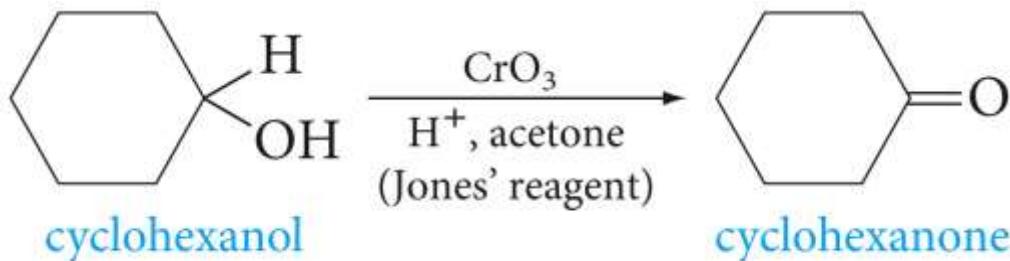
**1°** and **2°** alcohols can be oxidized to carbonyl compounds.  
**3°** alcohols are not oxidized.

**1°** alcohols give aldehydes, then carboxylic acids:

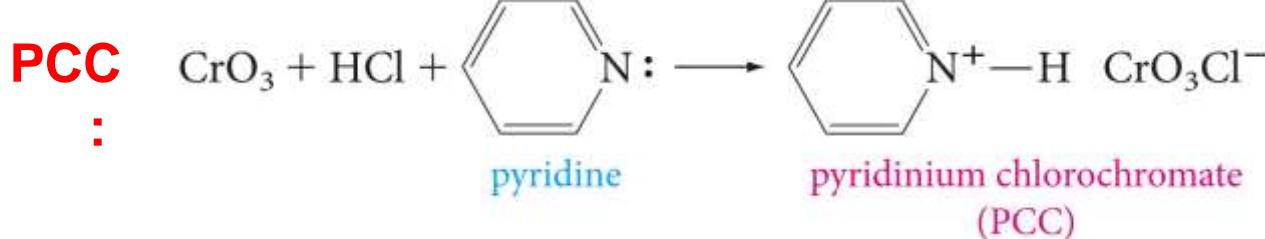
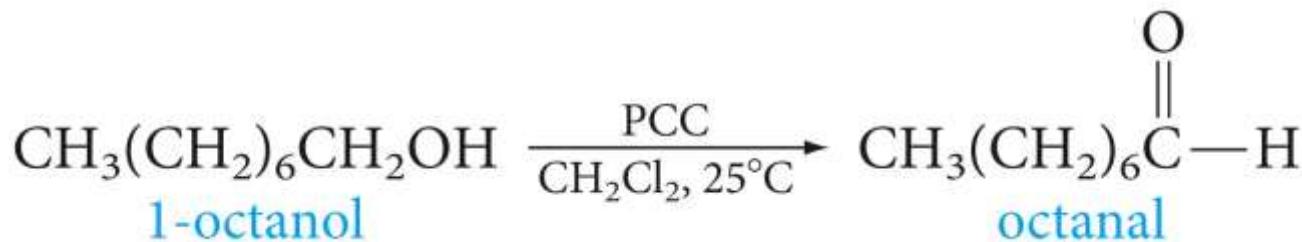


**2°** alcohols give ketones:





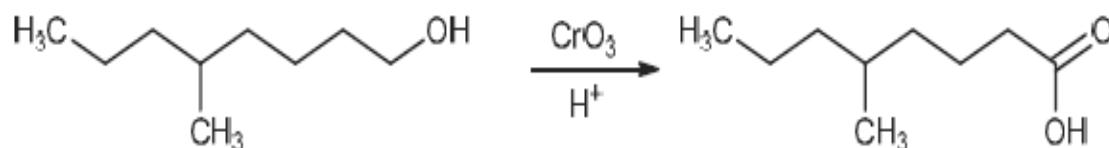
Oxidation of  $1^\circ$  alcohols to aldehydes by Pyridinium Chlorochromate (**PCC**) :



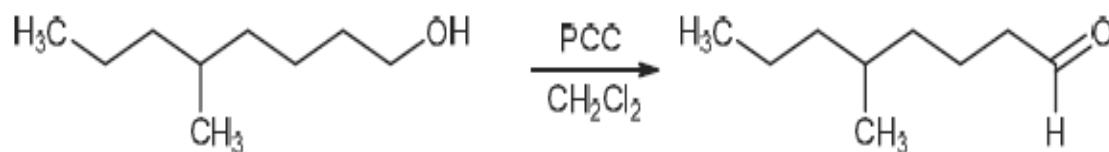
Write an equation for the oxidation of

- 4-methyl-1-octanol with Jones' reagent
- 4-methyl-1-octanol with PCC
- 4-phenyl-2-butanol with Jones' reagent
- 4-phenyl-2-butanol with PCC

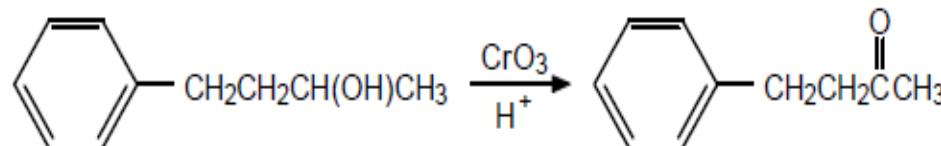
a. The alcohol is primary and gives a carboxylic acid.



b. The alcohol is primary and gives an aldehyde.

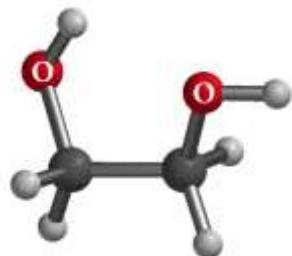


c. The alcohol is secondary and gives a ketone.



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

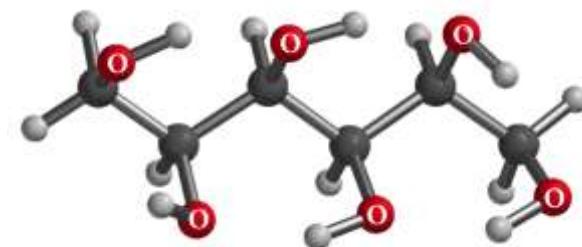
## 7.13 Alcohols with More Than One Hydroxyl Group :



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



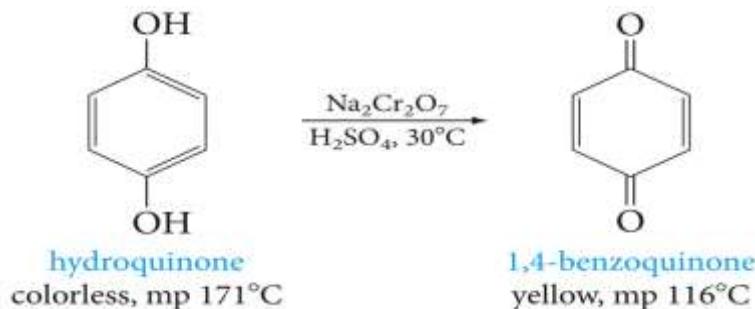
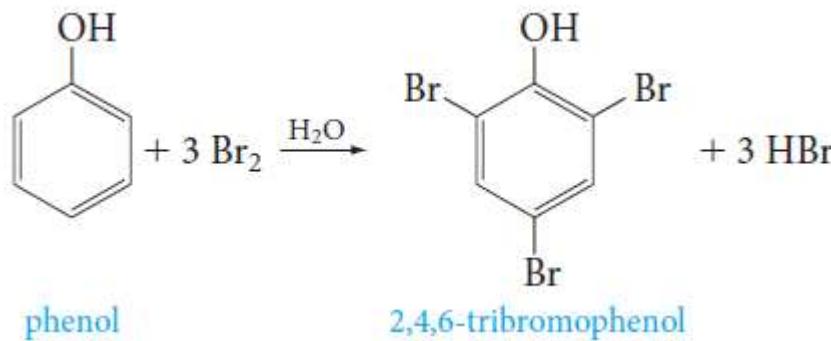
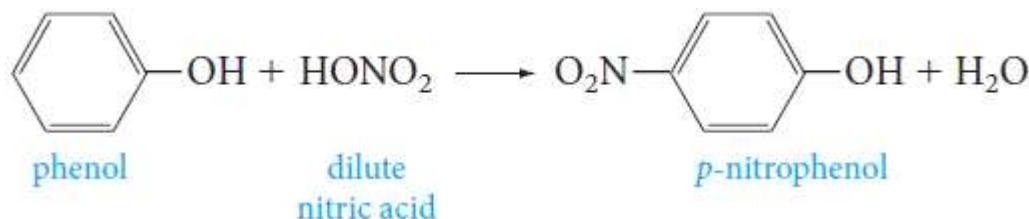
Glycerol (glycerine)  
1,2,3-propanetriol  
bp 290 °C



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

## 7.14 Electrophilic Aromatic Substitution in Phenols :

Phenols undergo electrophilic aromatic substitution easily because -OH is strong activating.



**Oxidation to quinone:**

## 7.17 Thiols the Sulfur Analog of Alcohols and Phenols

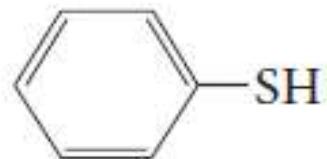
The **-SH** group, called the **sulphydryl group**, is the functional group of thiols .Thiols are named as follows:



**methanethiol**  
(methyl mercaptan)



**1-butanethiol**  
(*n*-butyl mercaptan)



**thiophenol**  
(phenyl mercaptan)

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



Preparation of R-SH (thiols) :



## Acidity :

Thiols are more acidic than alcohols and they react with NaOH :

