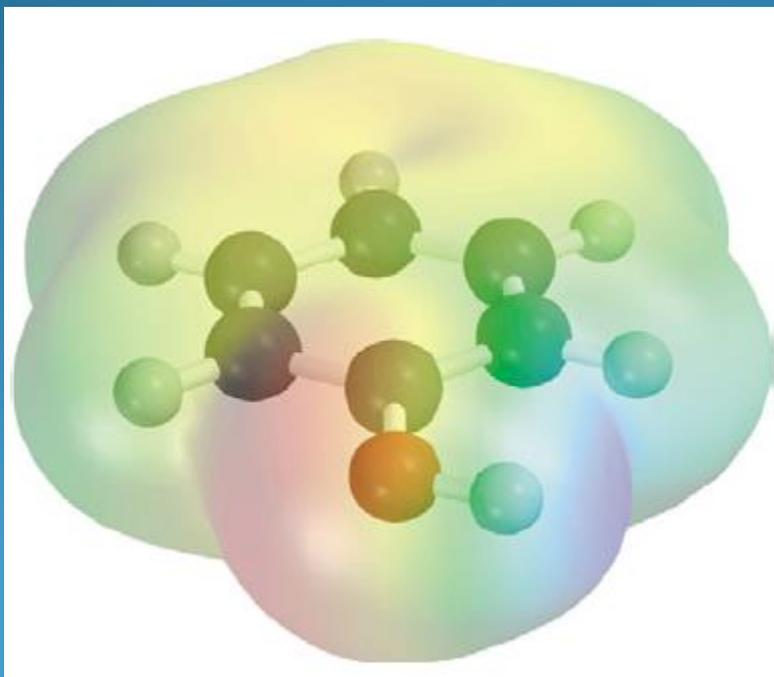


Chapter 2

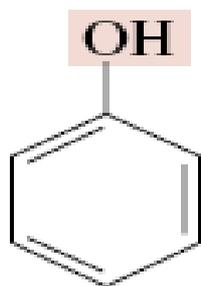
Phenols



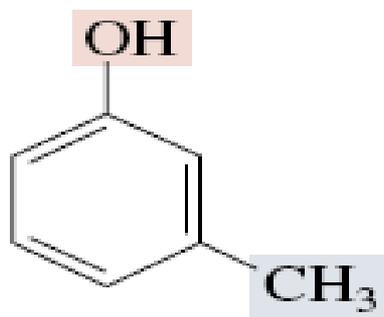
1-Nomenclature of Phenols

- Phenols are compounds that have hydroxyl group bonded directly to benzene ring.

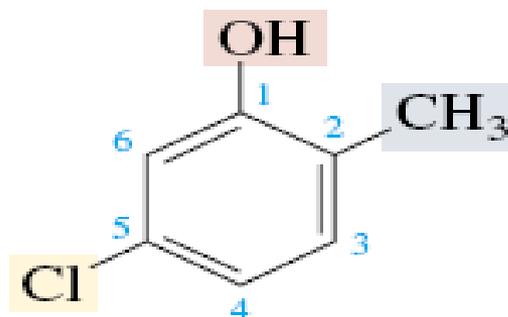
Named on basis of phenol as parent, substituents listed in alphabetical order.



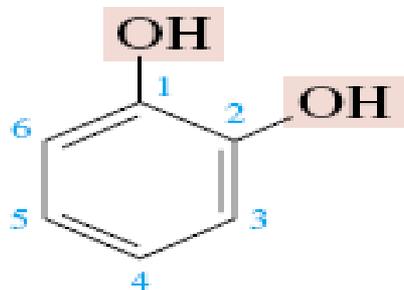
Phenol



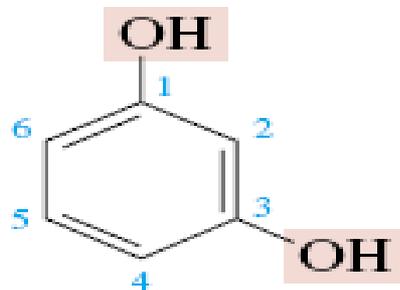
m-Cresol



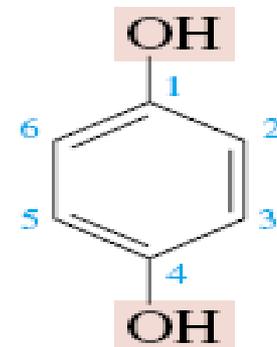
5-Chloro-2-methylphenol



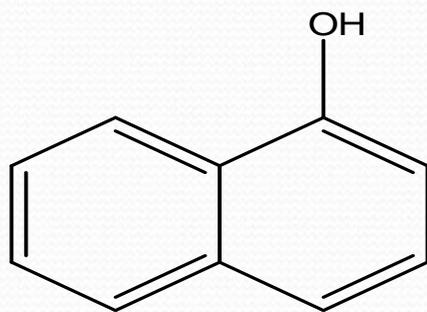
1,2-Benzenediol
(pyrocatechol)



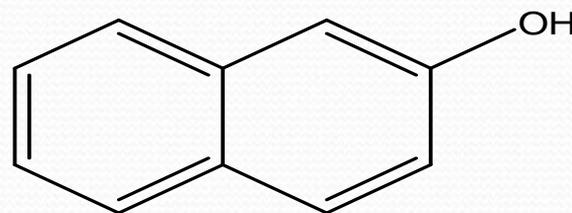
1,3-Benzenediol
(resorcinol)



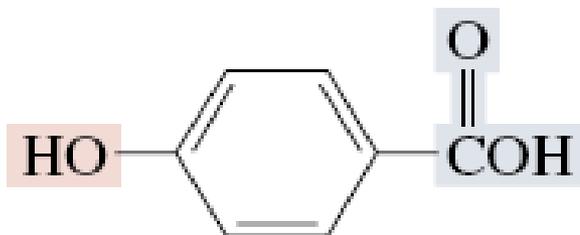
1,4-Benzenediol
(hydroquinone)



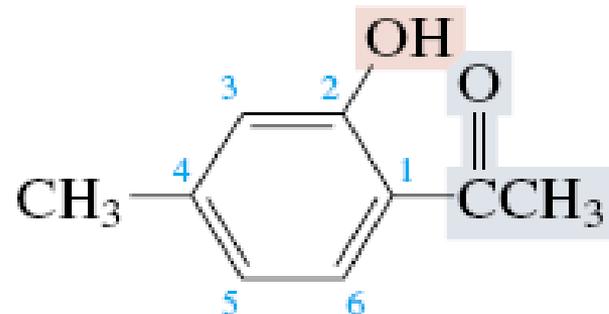
1- Naphthol



2- Naphthol



p-Hydroxybenzoic acid



2-Hydroxy-4-methylacetophenone

PROBLEM 24.1 Write structural formulas for each of the following compounds:

- (a) Pyrogallol (1,2,3-benzenetriol)
- (b) *o*-Benzylphenol
- (c) 3-Nitro-1-naphthol
- (d) 4-Chlororesorcinol

2-Physical Properties

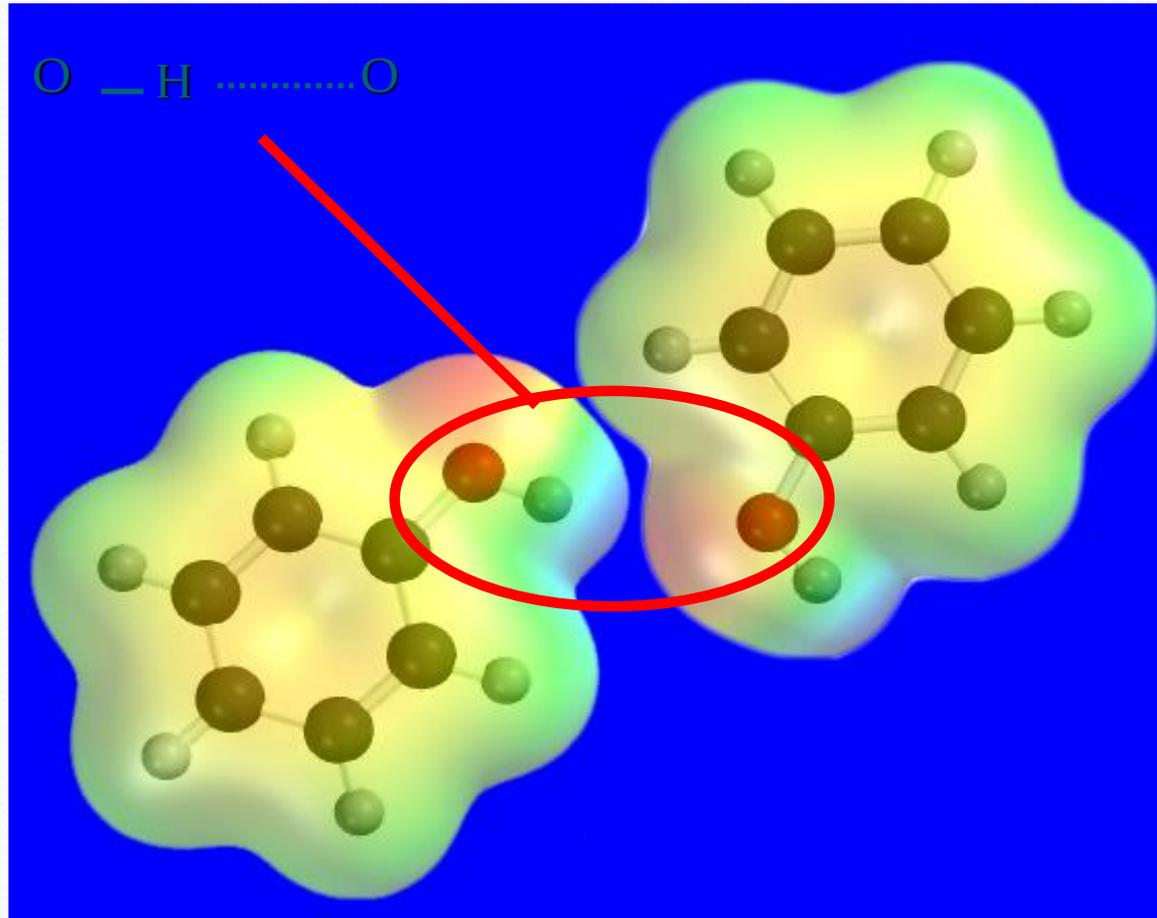
1-The OH group of phenols allows hydrogen bonding to other phenol molecules and to water.

2-Compared to compounds of similar size and molecular weight, hydrogen bonding in phenol raises its melting point, boiling point, and solubility in water.

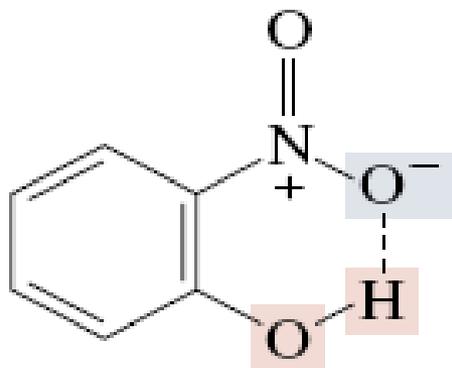
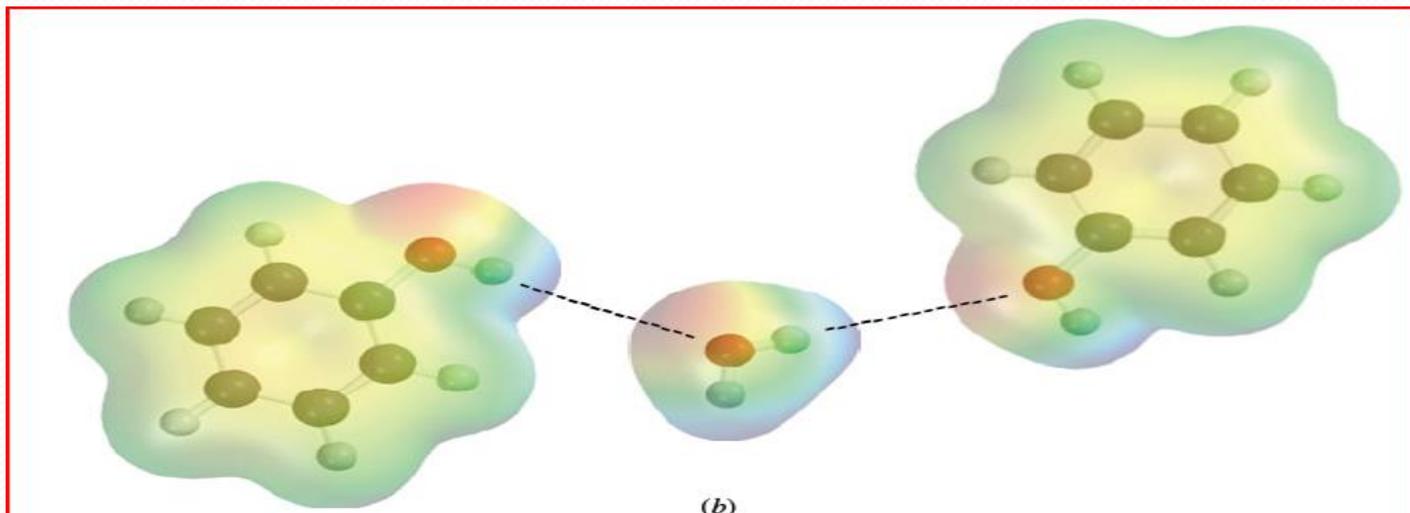
TABLE 24.1 Comparison of Physical Properties of an Arene, a Phenol, and an Aryl Halide

Physical property	Compound		
	Toluene, $C_6H_5CH_3$	Phenol, C_6H_5OH	Fluorobenzene, C_6H_5F
Molecular weight	92	94	96
Melting point	$-95^{\circ}C$	$43^{\circ}C$	$-41^{\circ}C$
Boiling point (1 atm)	$111^{\circ}C$	$132^{\circ}C$	$85^{\circ}C$
Solubility in water ($25^{\circ}C$)	0.05 g/100 mL	8.2 g/100 mL	0.2 g/100 mL

Hydrogen Bonding of Phenols



Hydrogen Bonding with Water

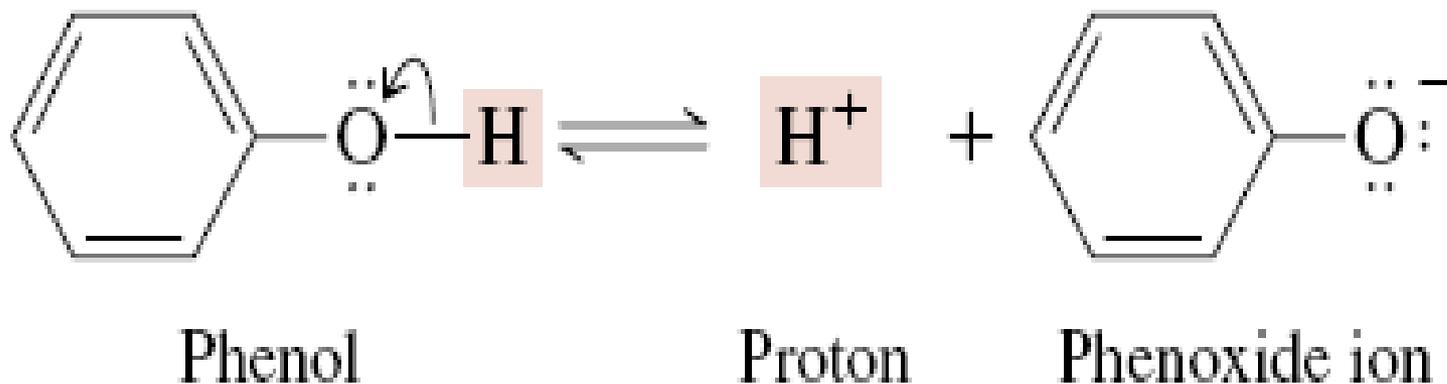
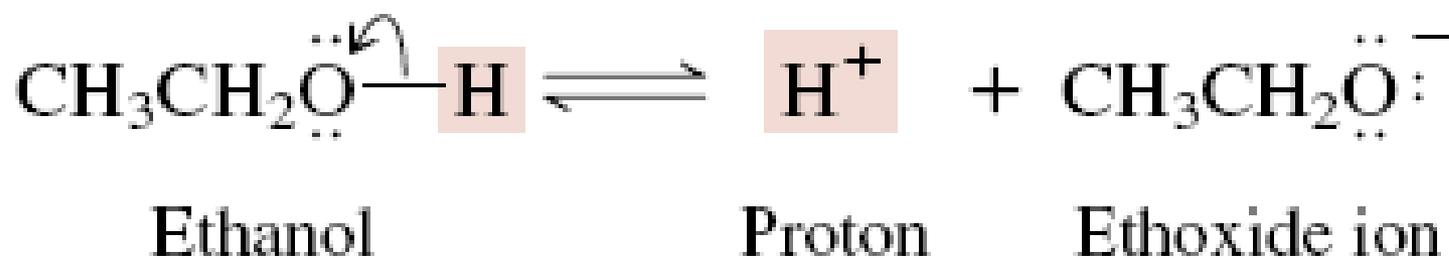


Intramolecular hydrogen bond
in *o*-nitrophenol

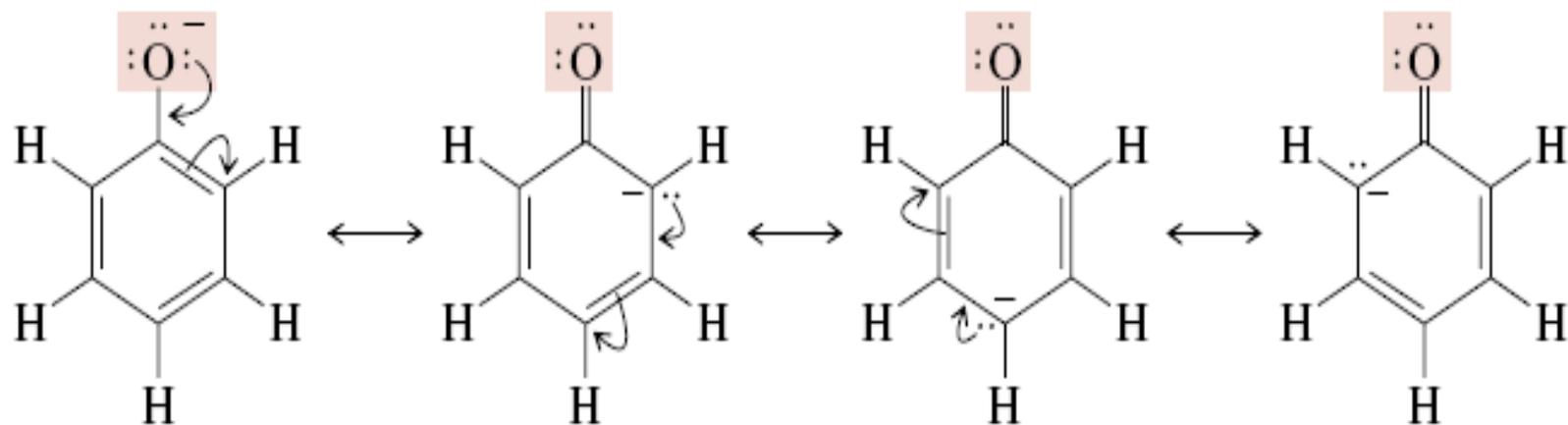
3- Acidity of Phenols

- Most characteristic property of phenols is their acidity.
- Phenols ($pK_a = 10$) are more acidic than alcohols ($pK_a = 16-20$) but less acidic than Carboxylic acids ($pK_a = 5$).

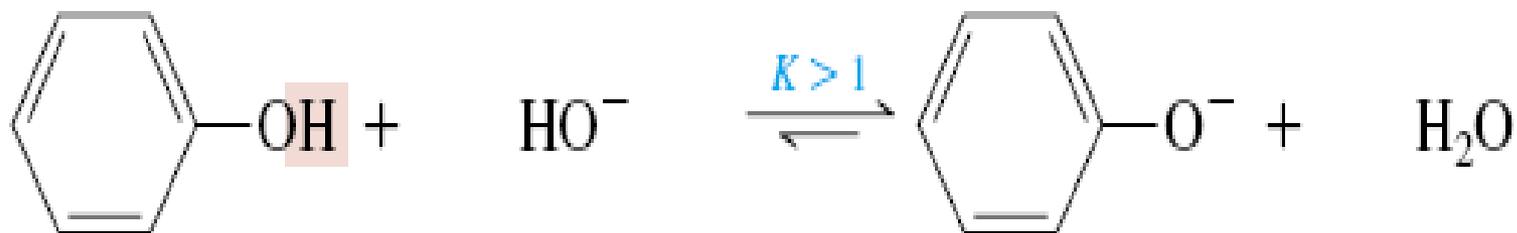
To explain why, let's compare the ionization of Ethanol and Phenols



Electron delocalization in phenoxide is represented by resonance among the structures:



The negative charge in phenoxide ion is shared by the oxygen and the carbons that are ortho and para to it. Delocalization of its negative charge strongly stabilizes phenoxide ion.

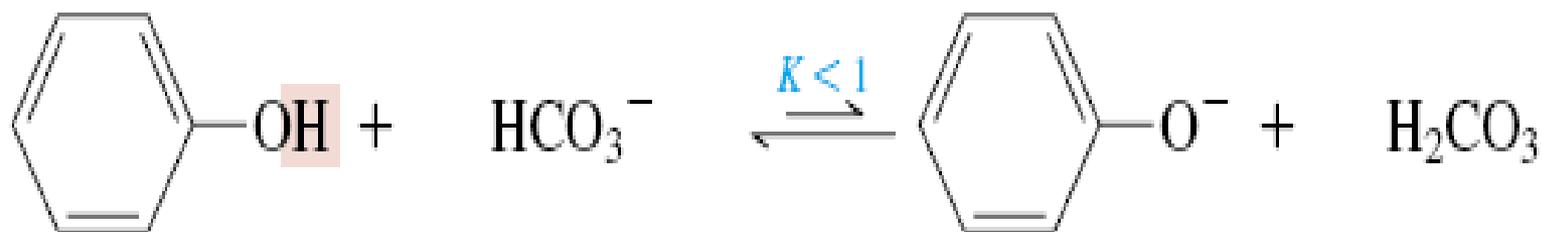


Phenol
(stronger acid)

Hydroxide ion
(stronger base)

Phenoxide ion
(weaker base)

Water
(weaker acid)



Phenol
(weaker acid)

Bicarbonate ion
(weaker base)

Phenoxide ion
(stronger base)

Carbonic acid
(stronger acid)

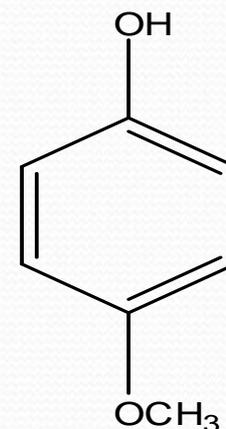
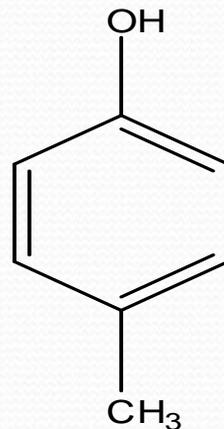
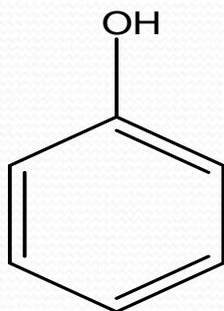
Substituent Effects on the Acidity of Phenols.

1-Electron-releasing groups (CH_3 , OCH_3) have little or no effect.

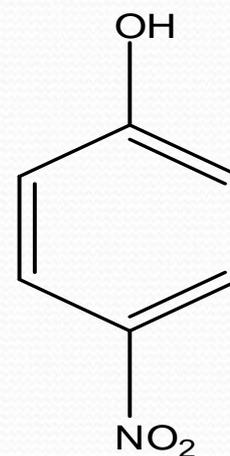
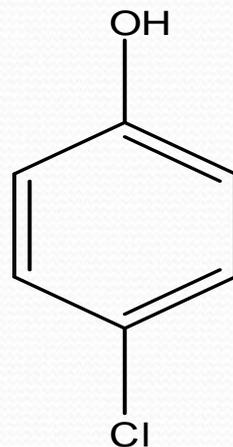
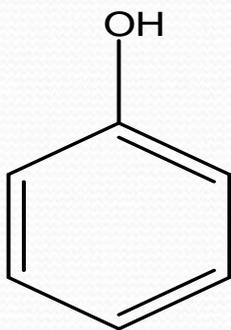
2-Electron-withdrawing groups (NO_2 , Cl , OH) increase acidity.

3- Multiple substituent of electron- withdrawing group greatly increase acidity of phenols.

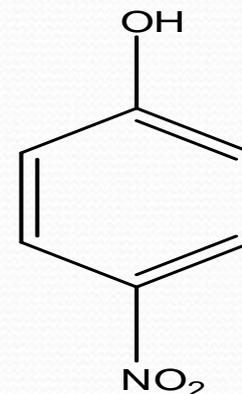
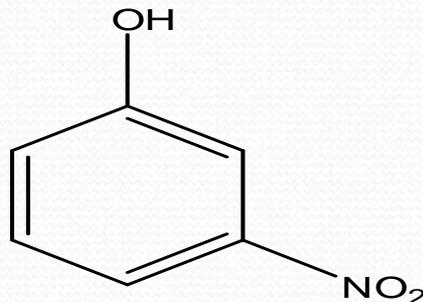
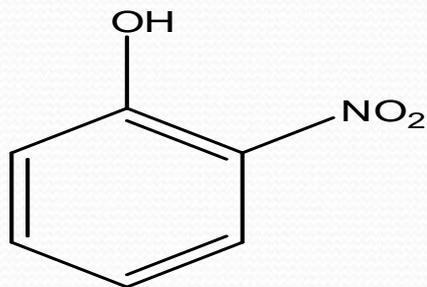
Electron-releasing groups have little or no effect.



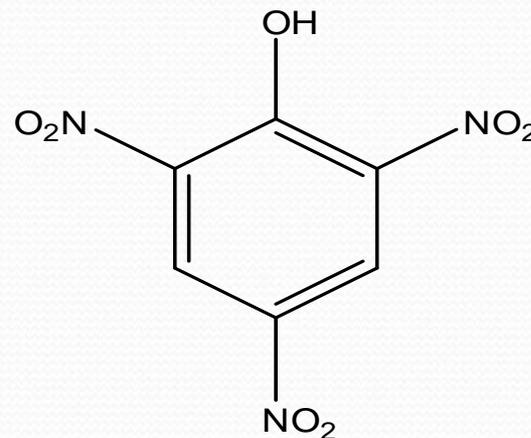
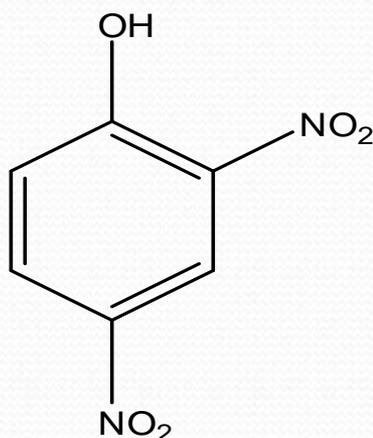
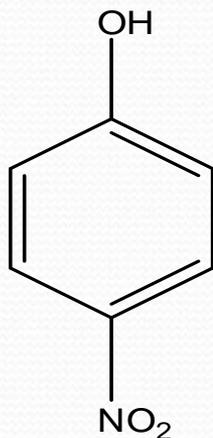
Electron-withdrawing groups increase acidity.



Effect of electron-withdrawing groups is most pronounced at ortho and para positions.



Effect of strong electron-withdrawing groups is cumulative.

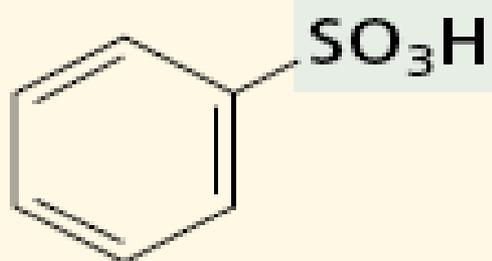


Compound name	Ionization constant K_a	pK_a
Monosubstituted phenols		
Phenol	1.0×10^{-10}	10.0
<i>o</i> -Cresol	4.7×10^{-11}	10.3
<i>m</i> -Cresol	8.0×10^{-11}	10.1
<i>p</i> -Cresol	5.2×10^{-11}	10.3
<i>o</i> -Chlorophenol	2.7×10^{-9}	8.6
<i>m</i> -Chlorophenol	7.6×10^{-9}	9.1
<i>p</i> -Chlorophenol	3.9×10^{-9}	9.4
<i>o</i> -Methoxyphenol	1.0×10^{-10}	10.0
<i>m</i> -Methoxyphenol	2.2×10^{-10}	9.6
<i>p</i> -Methoxyphenol	6.3×10^{-11}	10.2
<i>o</i> -Nitrophenol	5.9×10^{-8}	7.2
<i>m</i> -Nitrophenol	4.4×10^{-9}	8.4
<i>p</i> -Nitrophenol	6.9×10^{-8}	7.2
Di- and trinitrophenols		
2,4-Dinitrophenol	1.1×10^{-4}	4.0
3,5-Dinitrophenol	2.0×10^{-7}	6.7
2,4,6-Trinitrophenol	4.2×10^{-1}	0.4

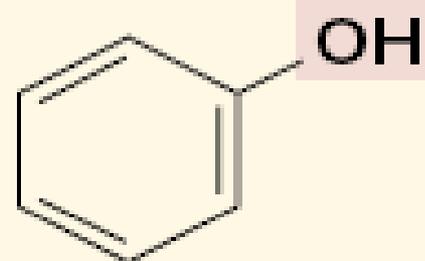
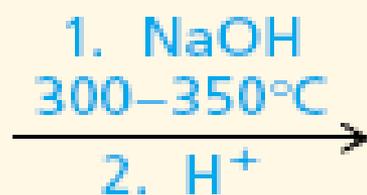
4-Sources of Phenols

- Phenols was first isolated from coal tar.
- Phenol is an important industrial chemical.
- Major use is in phenolic resins for adhesives and plastics.

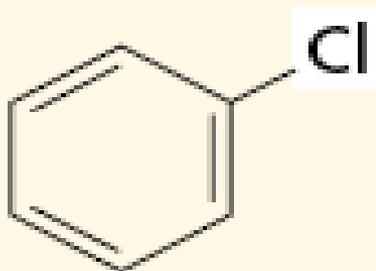
Industrial preparation of Phenols



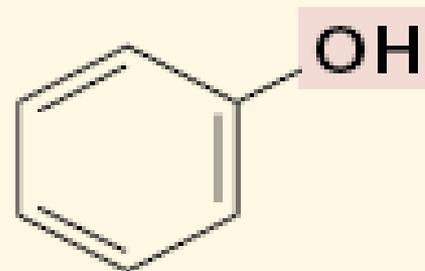
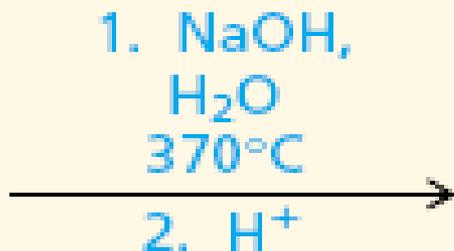
Benzenesulfonic acid



Phenol



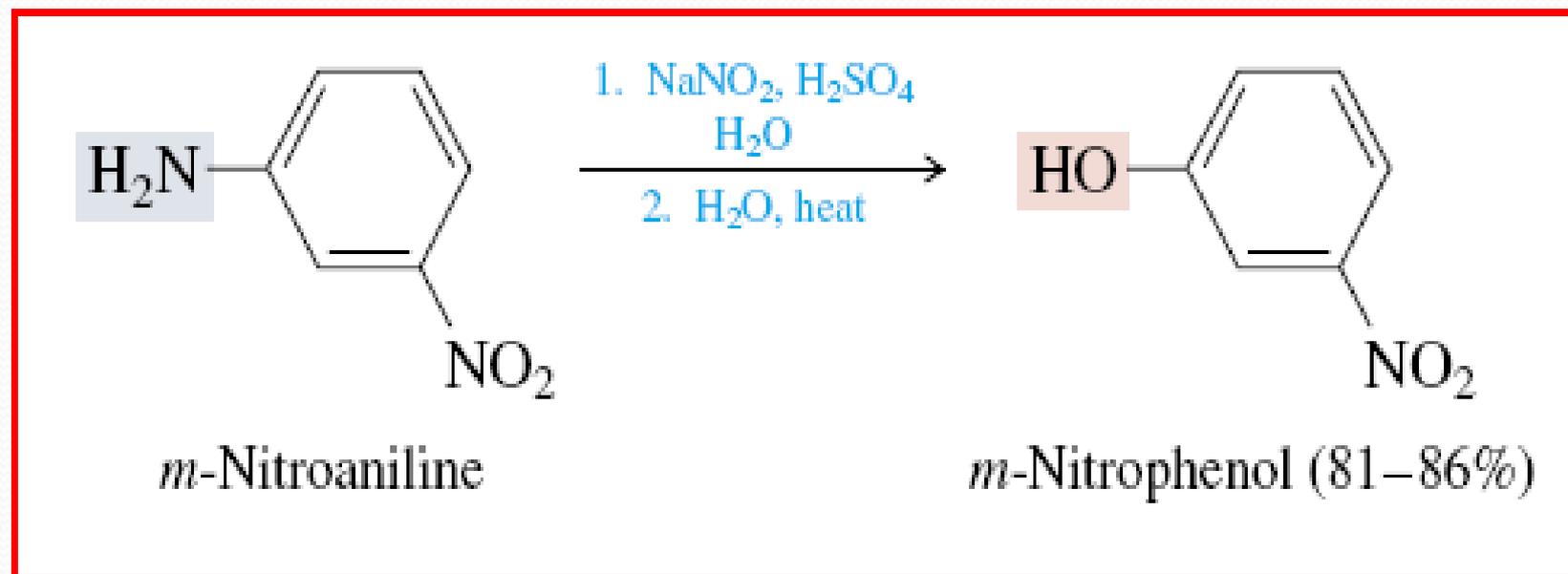
Chlorobenzene



Phenol

Laboratory Synthesis of Phenols

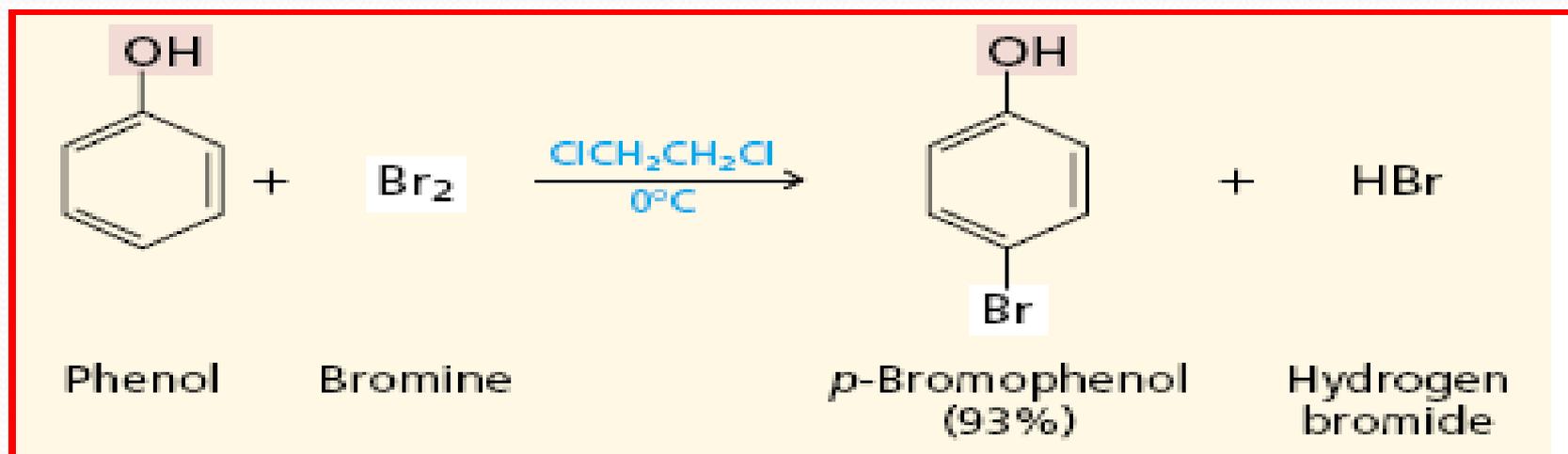
The most important synthesis of phenols in the laboratory is from amines by hydrolysis of their corresponding diazonium salts, as described in Section 22.18:

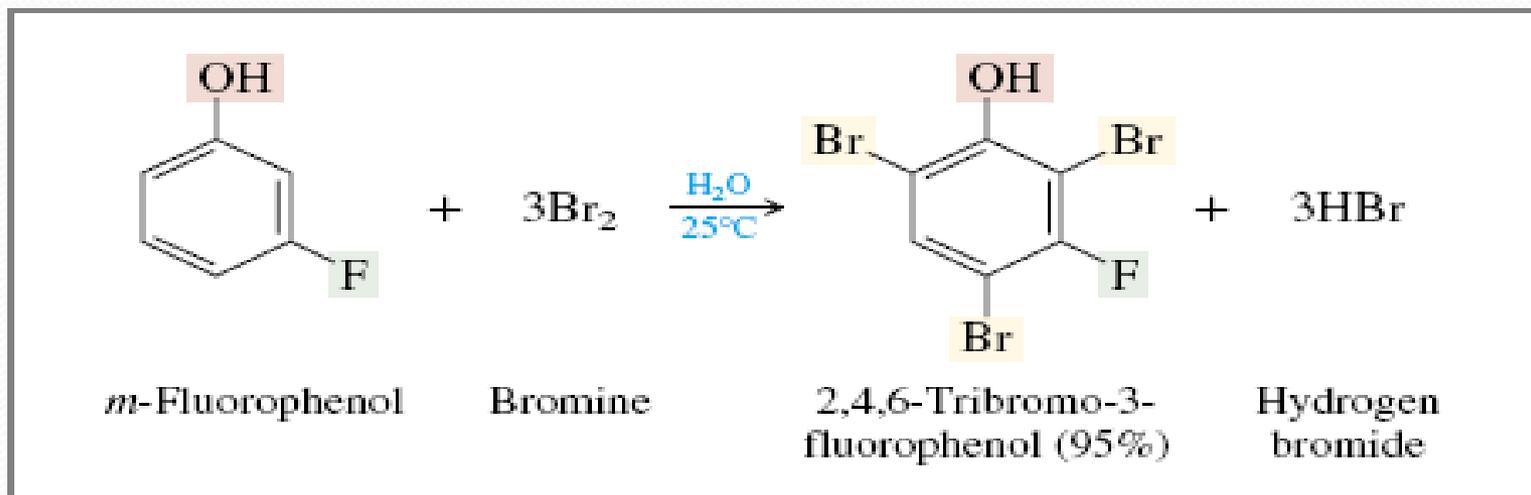


5- Reactions of Phenols

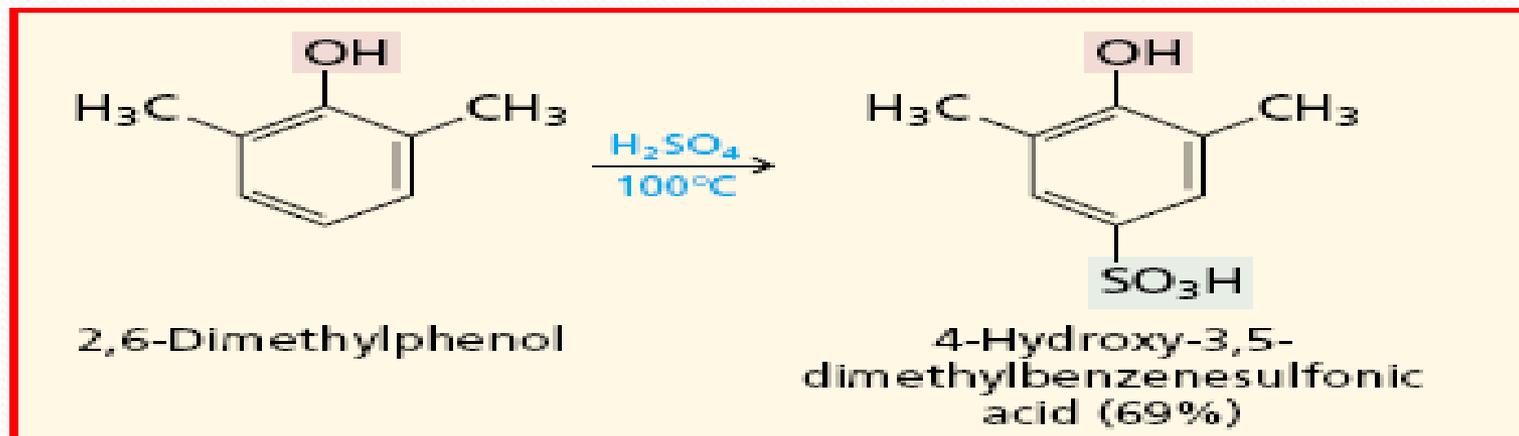
A hydroxyl group is very powerful activating substituent, and electrophilic aromatic substitution in phenol occurs far faster, and under milder condition, than in benzene.

a- Halogenation

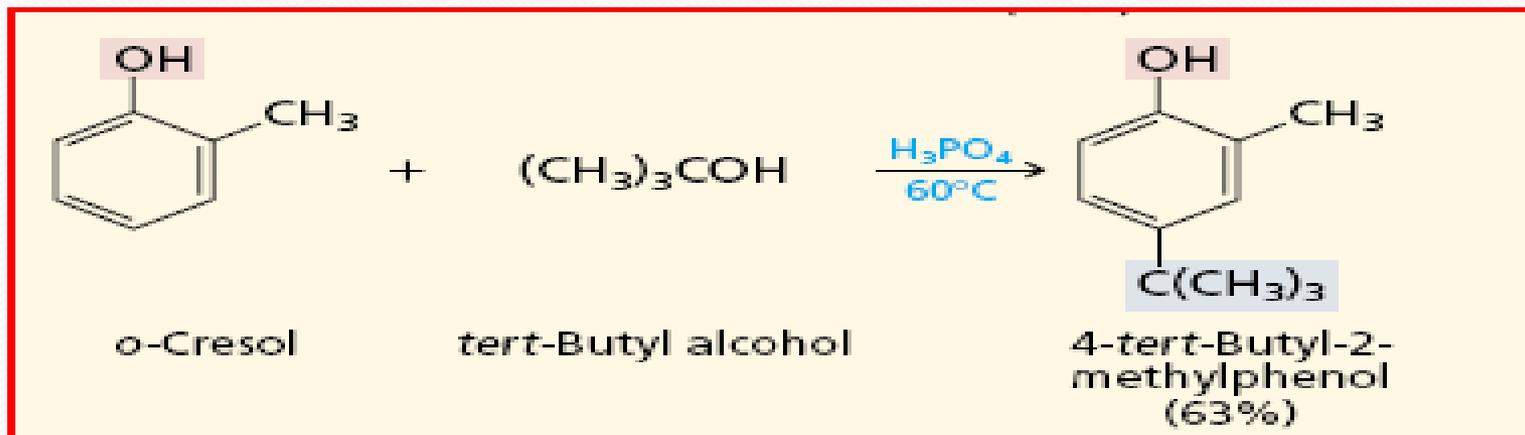




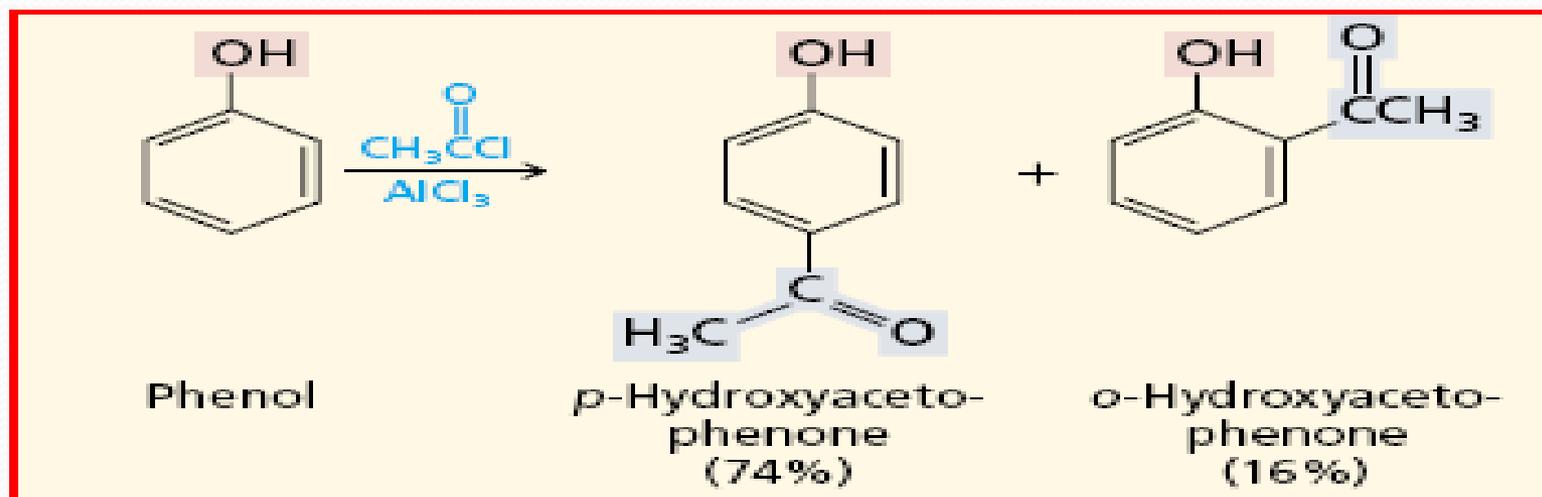
b- Sulfonation



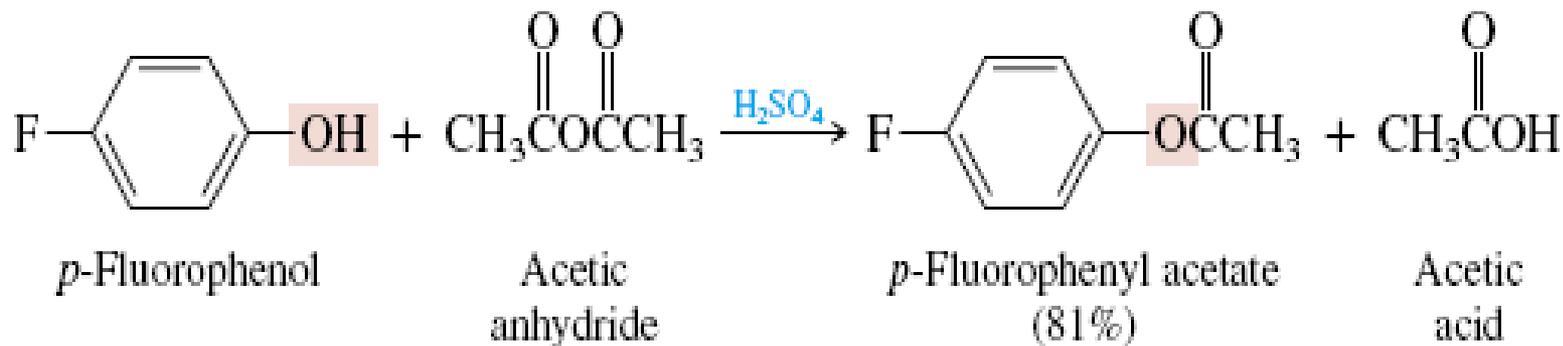
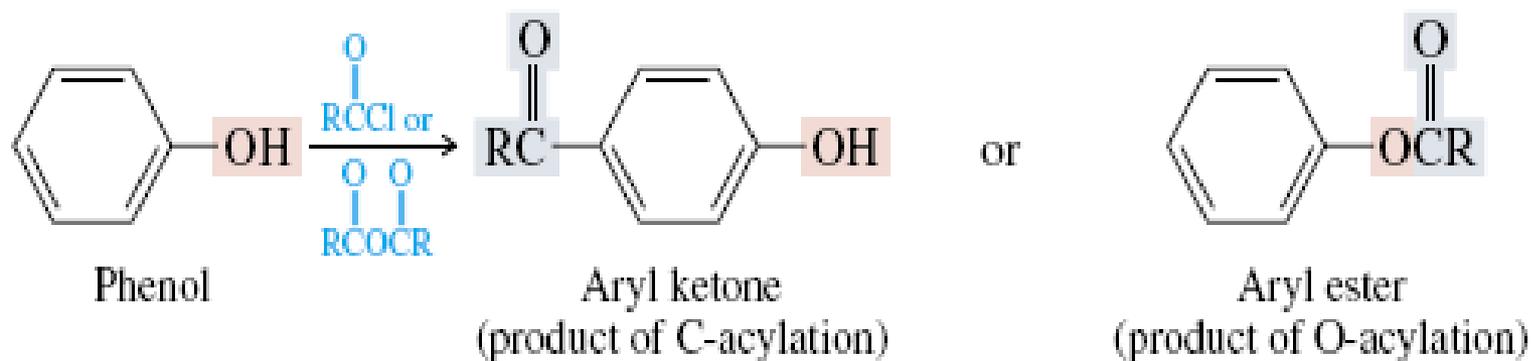
d-Friedal Crafts Alkylation



e-Friedal Crafts Acylation



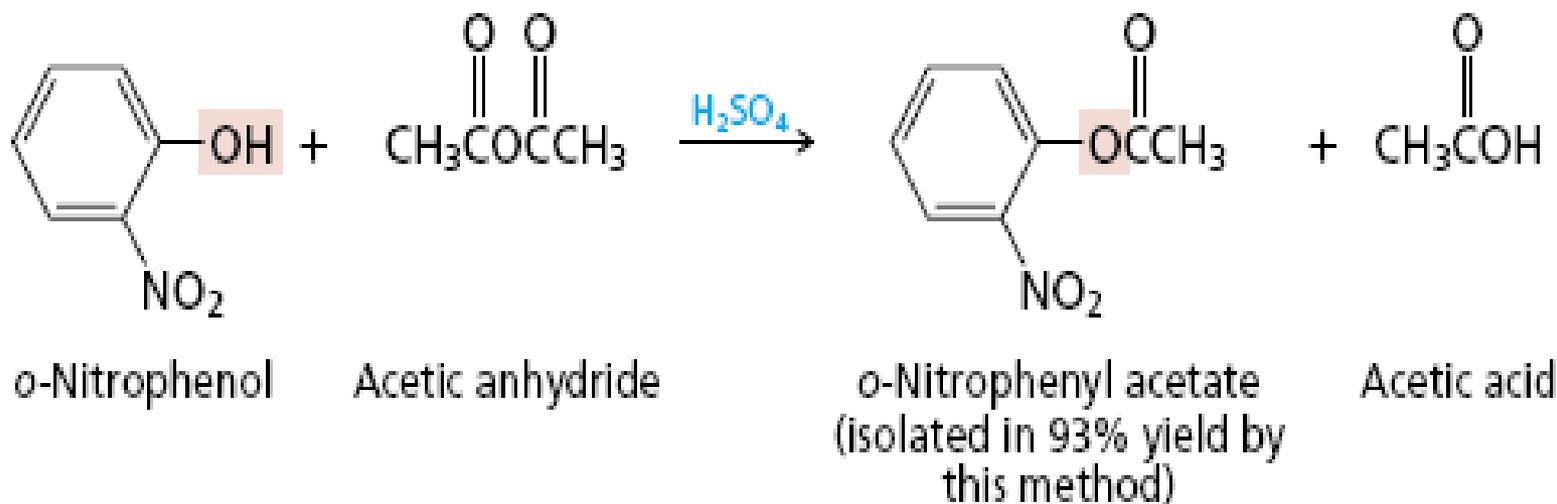
In the **absence of $AlCl_3$** , However **O-acylation** occurs instead.



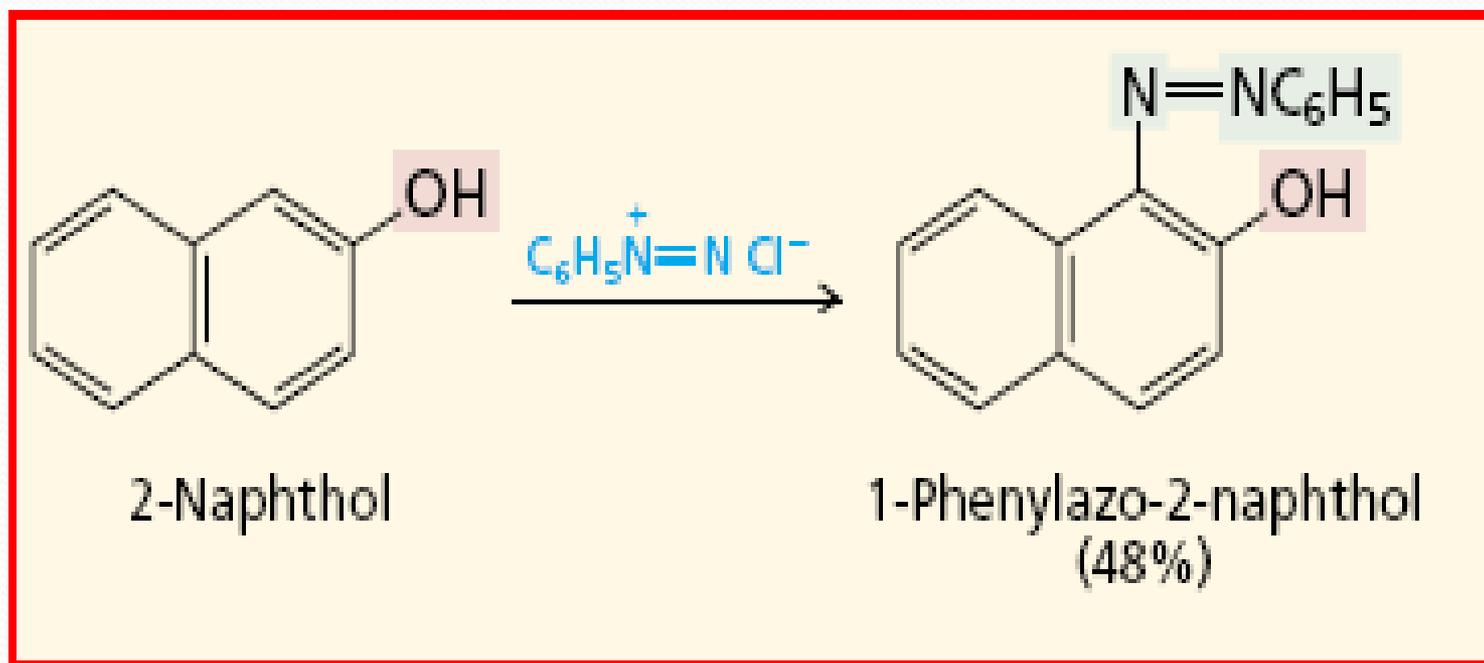
PROBLEM 24.7 Write chemical equations expressing each of the following:

- Preparation of *o*-nitrophenyl acetate by sulfuric acid catalysis of the reaction between a phenol and a carboxylic acid anhydride.
- Esterification of 2-naphthol with acetic anhydride in aqueous sodium hydroxide
- Reaction of phenol with benzoyl chloride

SAMPLE SOLUTION (a) The problem specifies that an acid anhydride be used; therefore, use acetic anhydride to prepare the acetate ester of *o*-nitrophenol:

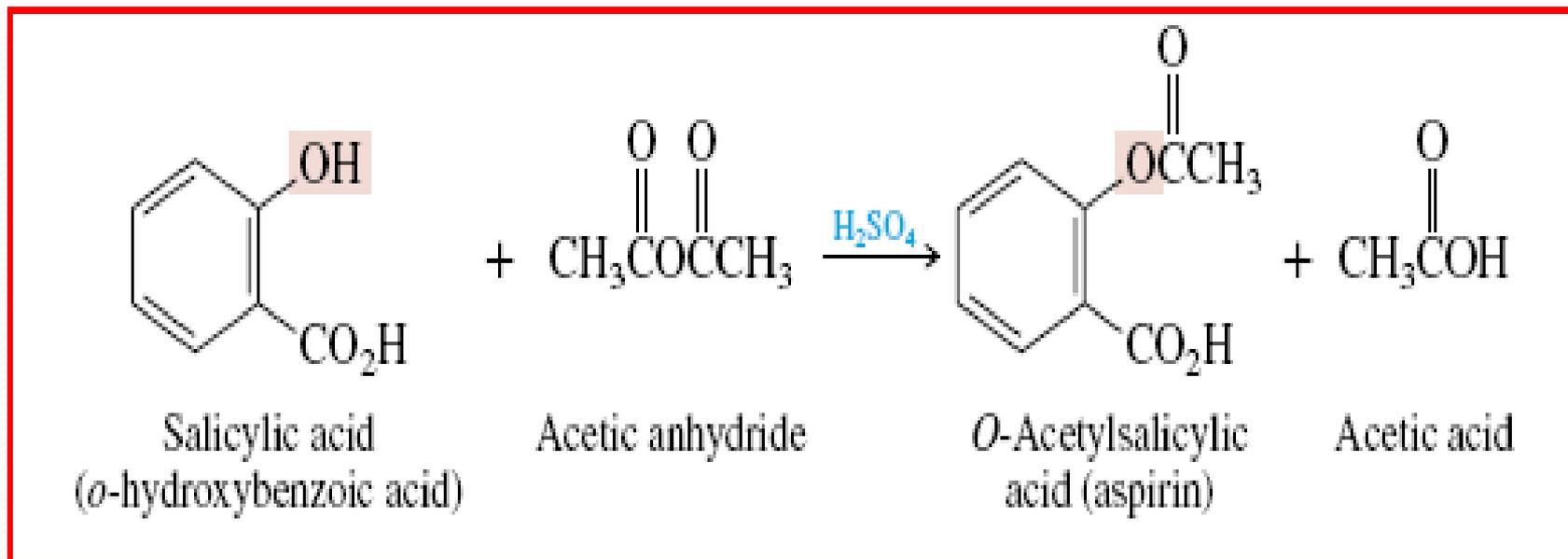


f- Reaction with arenediazonium salts.

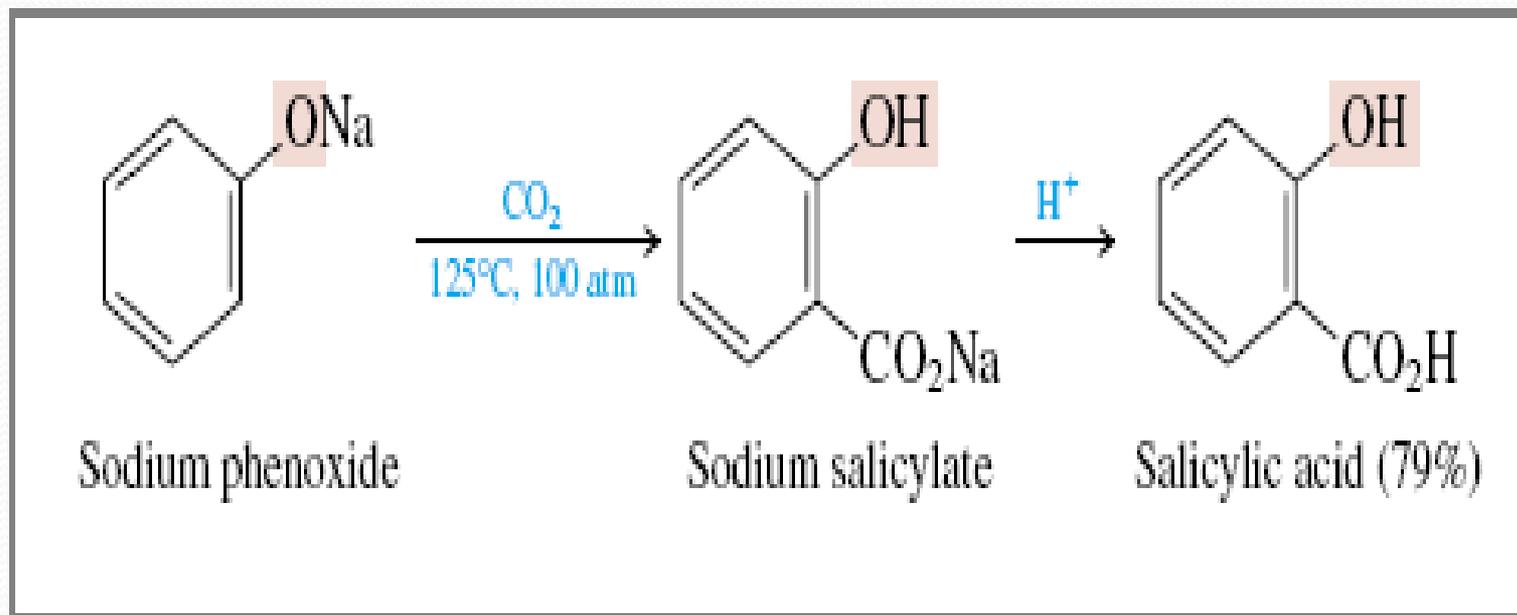


6- Aspirin and the Klobe – Schmitt Reaction.

The best known aryl ester is *O*-acetylsalicylic acid, better known as *aspirin*. It is prepared by acetylation of the phenolic hydroxyl group of salicylic acid:



Preparation of Salicylic Acid



This reaction is called the **Kolbe- Schmitt reaction**. Acidification converts the sodium salt shown above to salicylic acid.