Phenols

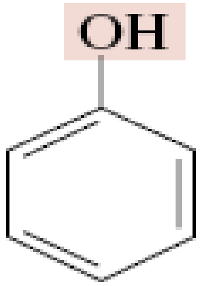
Lecturer:hiba mushtaq ahmed

1-Nomenclature of Phenols

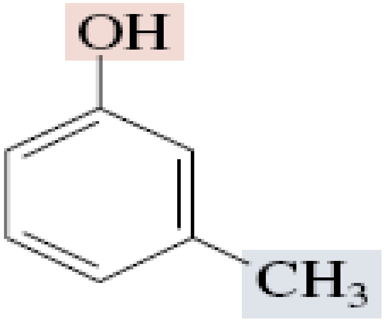
- Phenols are compounds that have hydroxyl group bonded directly to benzene ring.

Named on basis of phenol as parent,

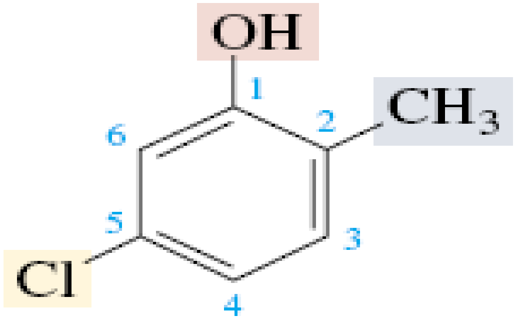
substituents listed in alphabetical order.



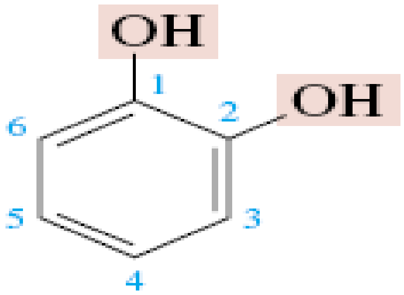
Phenol



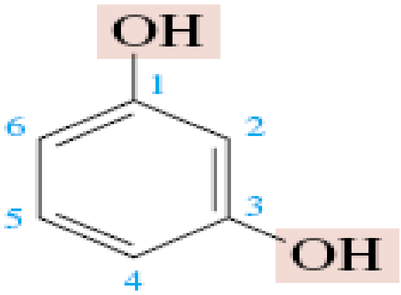
m-Cresol



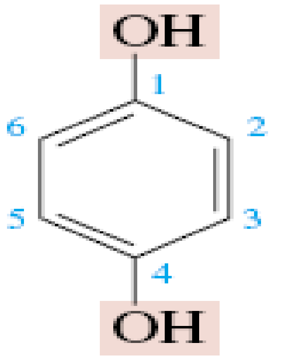
5-Chloro-2-methylphenol



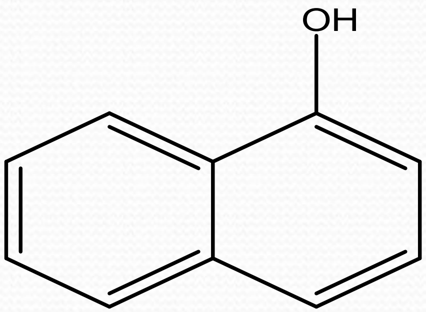
1,2-Benzenediol
(pyrocatechol)



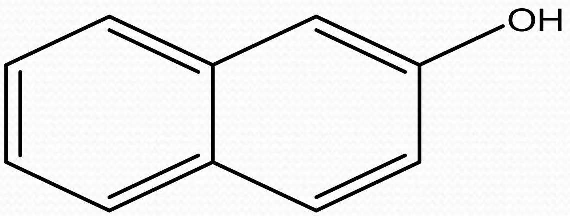
1,3-Benzenediol
(resorcinol)



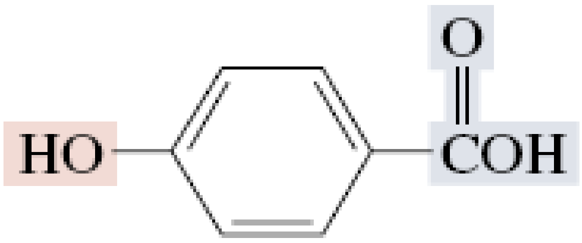
1,4-Benzenediol
(hydroquinone)



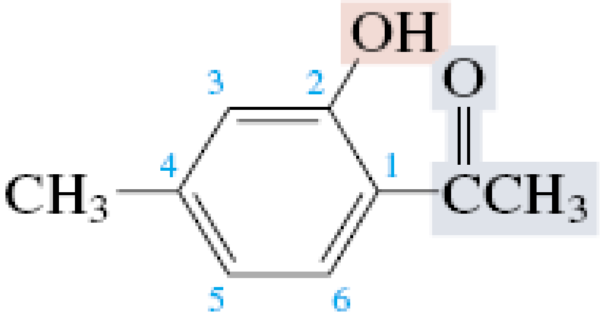
1- Naphthol



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.

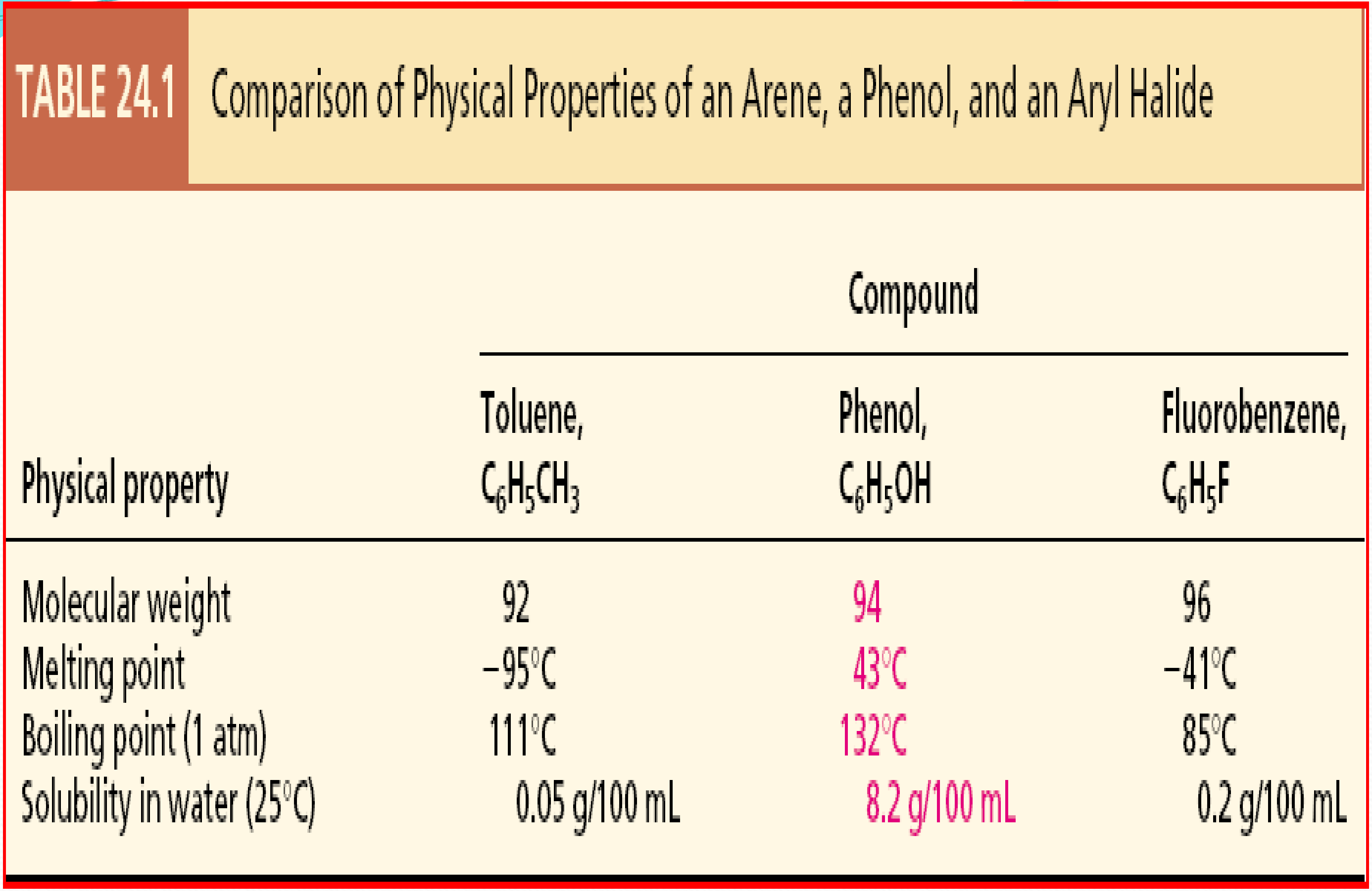
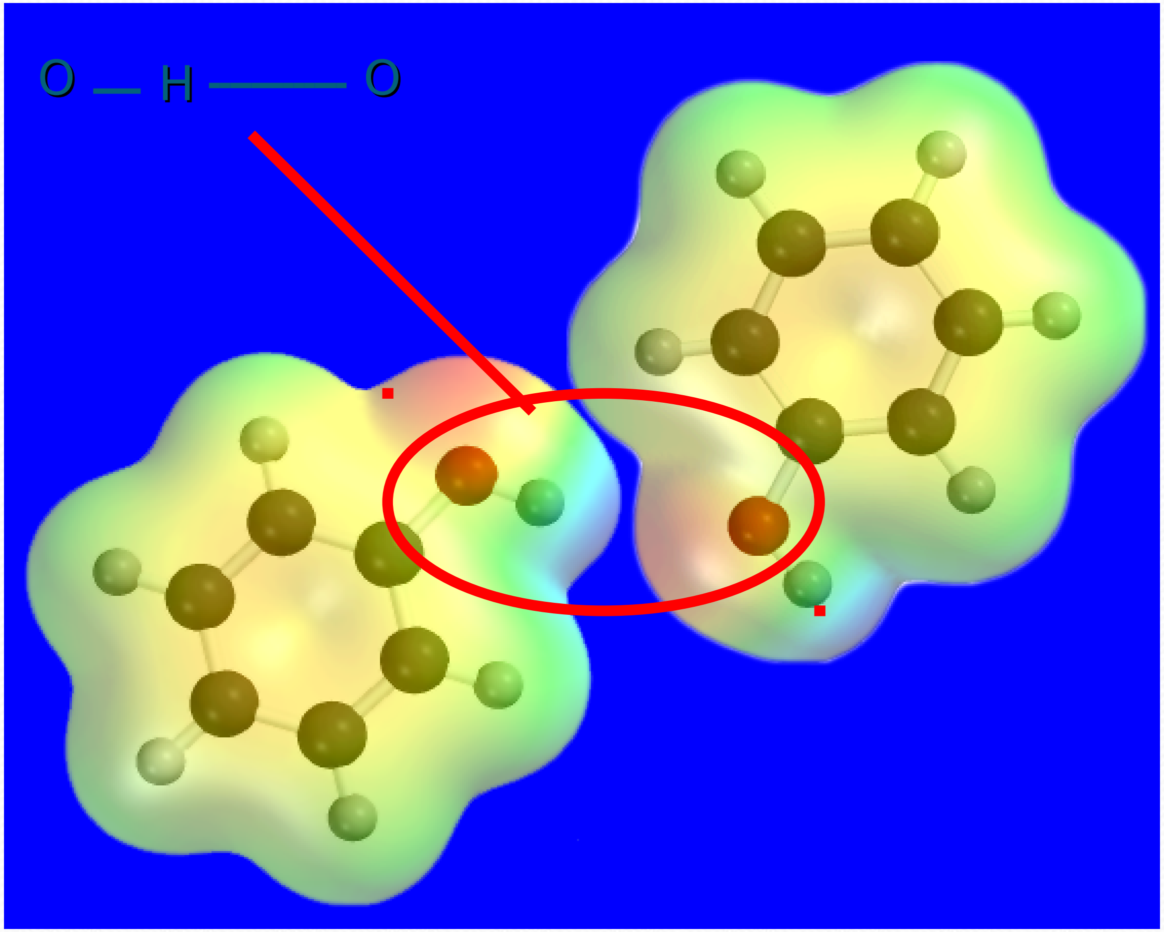


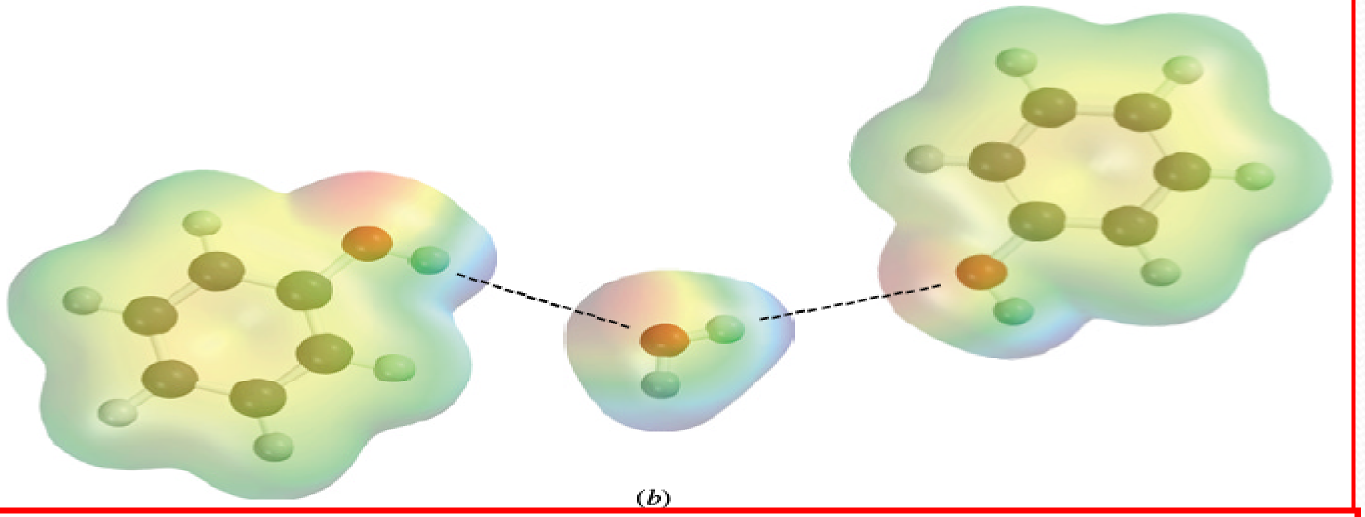
TABLE 24.1 Comparison of Physical Properties of an Arene, a Phenol, and an Aryl Halide

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

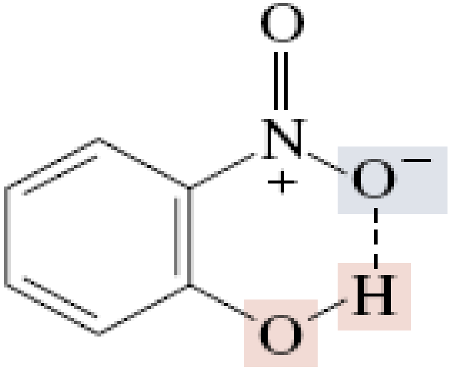
Hydrogen Bonding of Phenols



Hydrogen Bonding with Water



(b)

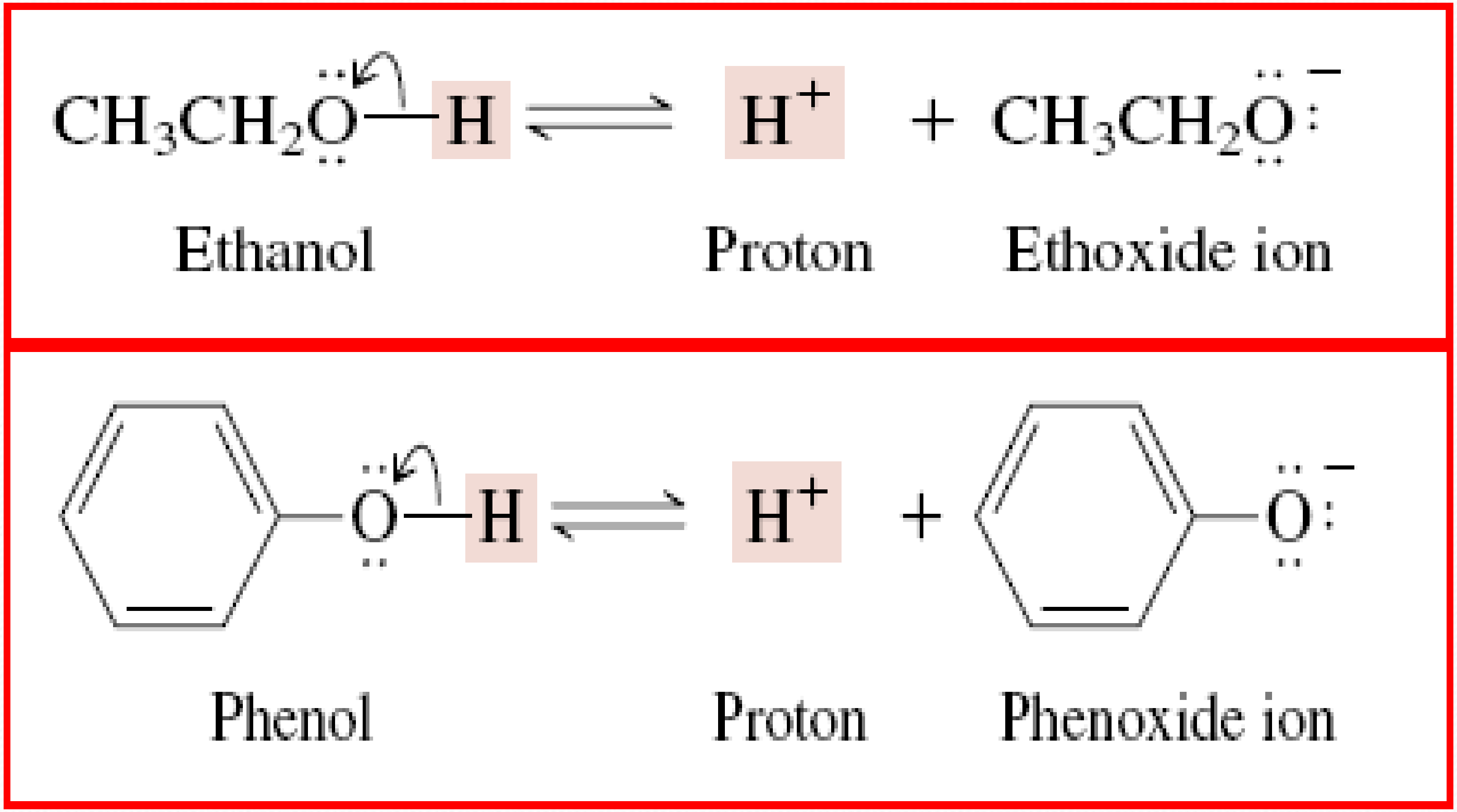


Intramolecular hydrogen bond in *o*-nitrophenol

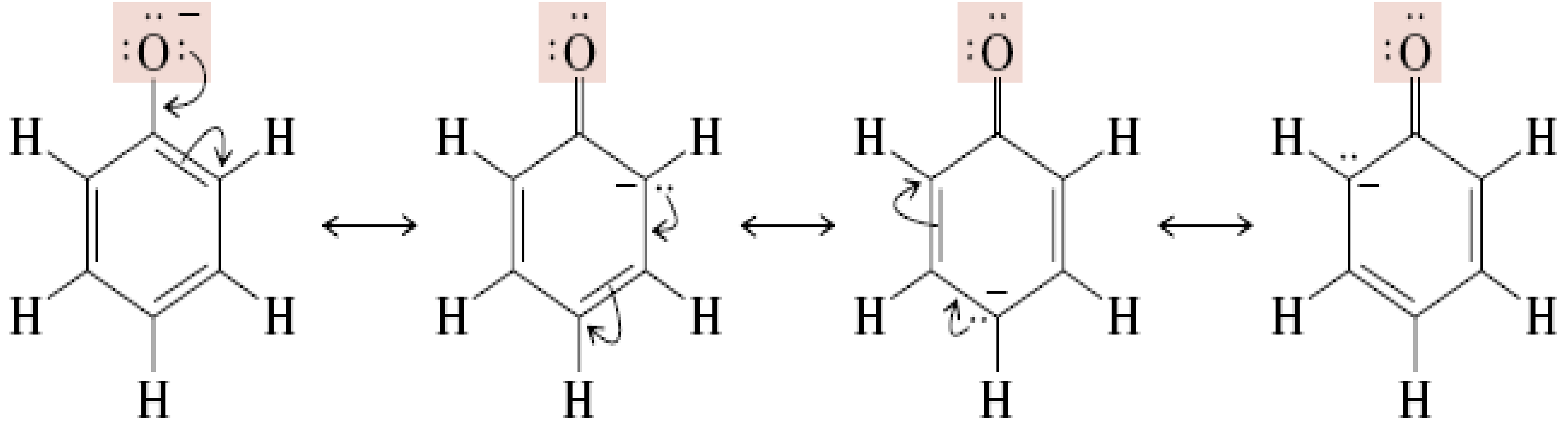
3- Acidity of Phenols

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

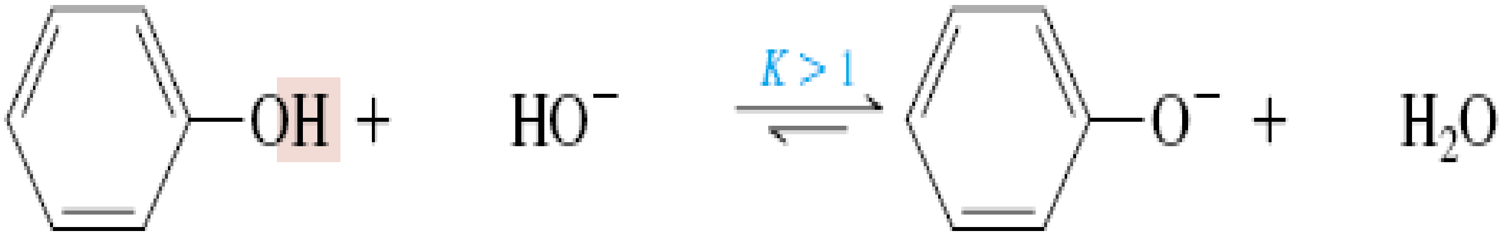
To explain why, let's compare the ionization of Ethanol and Phenols



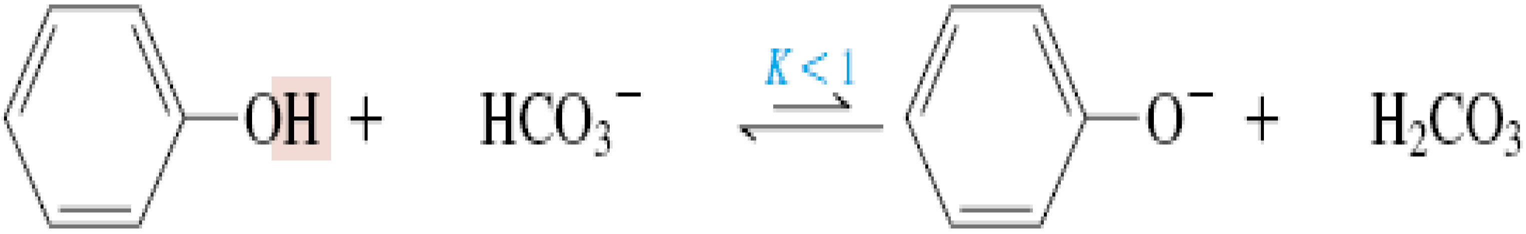
Electron delocalization in phenoxide is represented by resonance among the structures:



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	Hydroxide ion	Phenoxide ion	Water
(stronger acid)	(stronger base)	(weaker base)	(weaker acid)



Phenol	Bicarbonate ion	Phenoxide ion	Carbonic acid
(weaker acid)	(weaker base)	(stronger base)	(stronger acid)

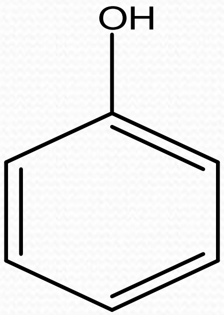
Substituent Effects on the Acidity of Phenols.

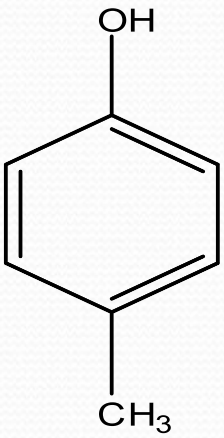
1-Electron-releasing groups (CH3, OCH3) have little or no effect.

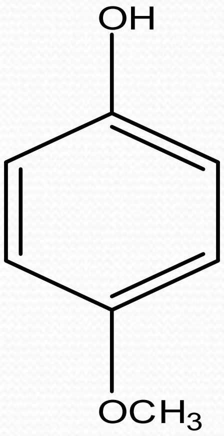
2-Electron-withdrawing groups (NO2, Cl, OH) increase acidity.

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

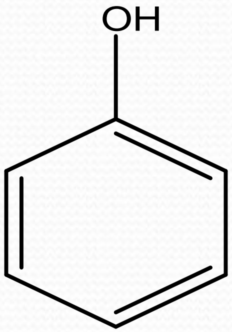
Electron-releasing groups have little or no effect.

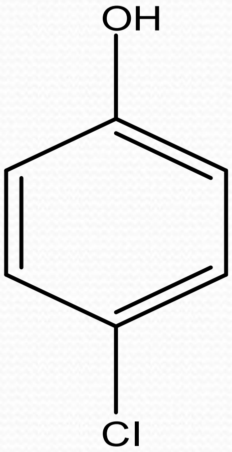


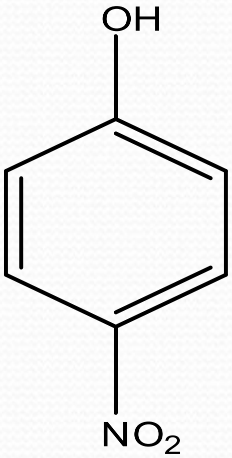




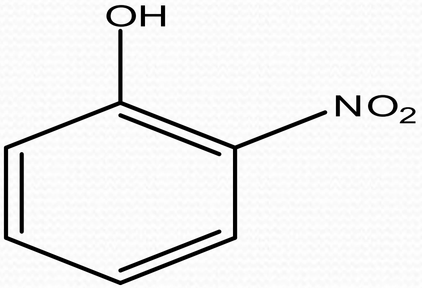
Electron-withdrawing groups increase acidity.

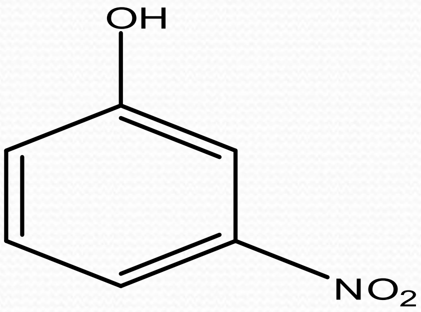


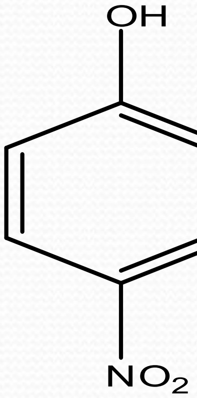




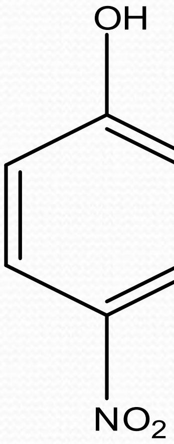
Effect of electron-withdrawing groups is most pronounced at ortho and para positions.

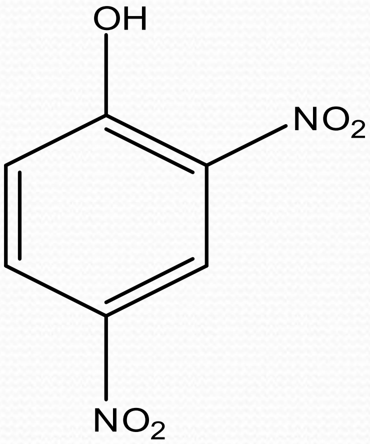


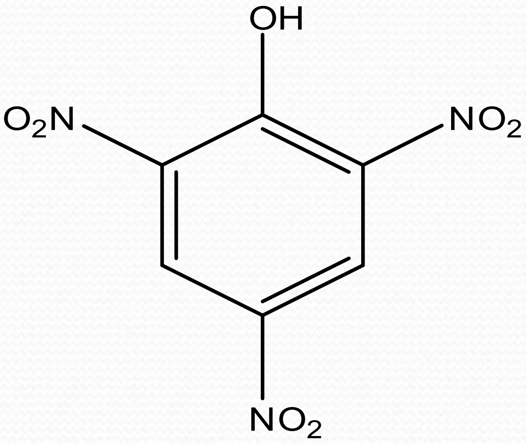


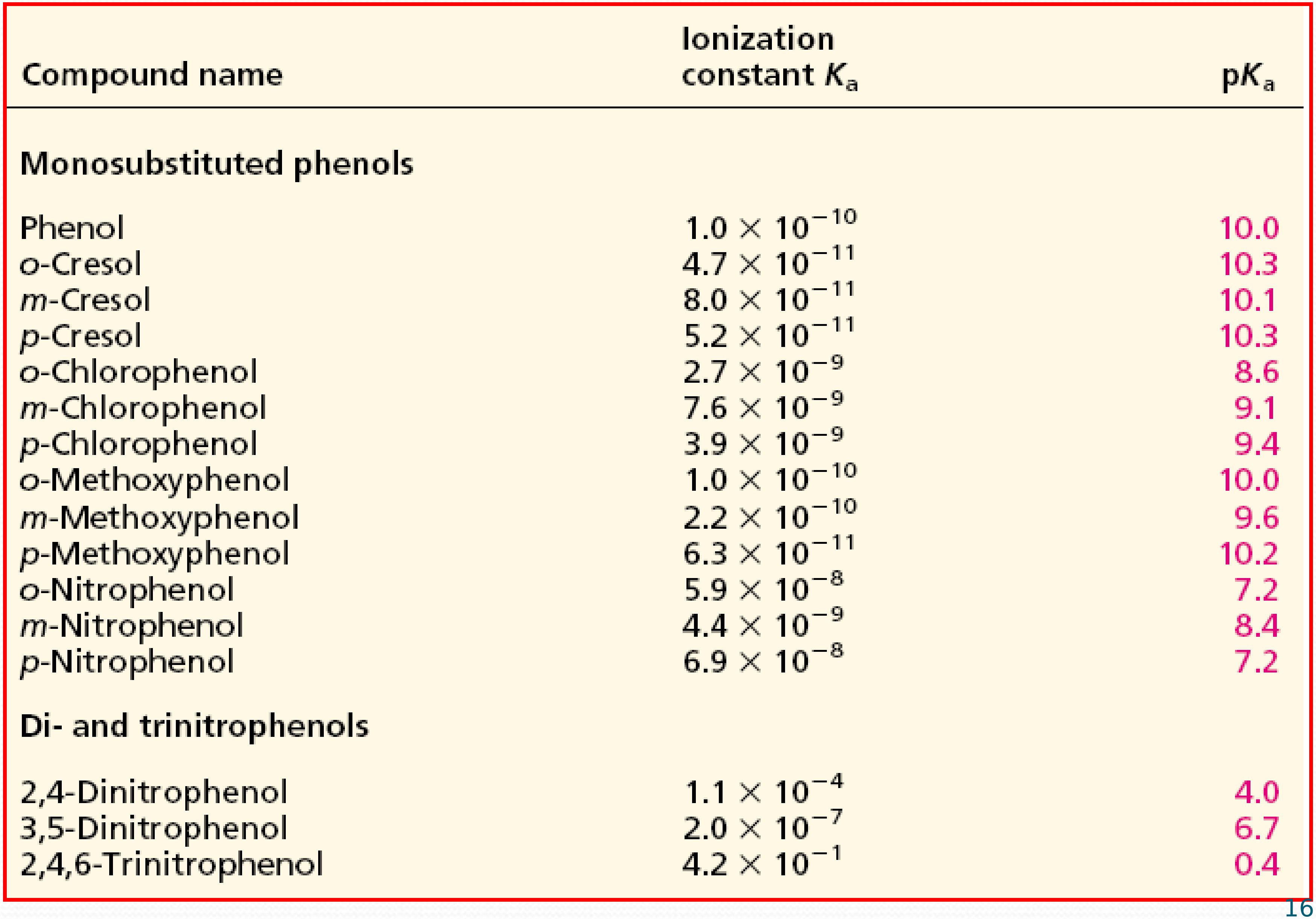


Effect of strong electron-withdrawing groups is cumulative.







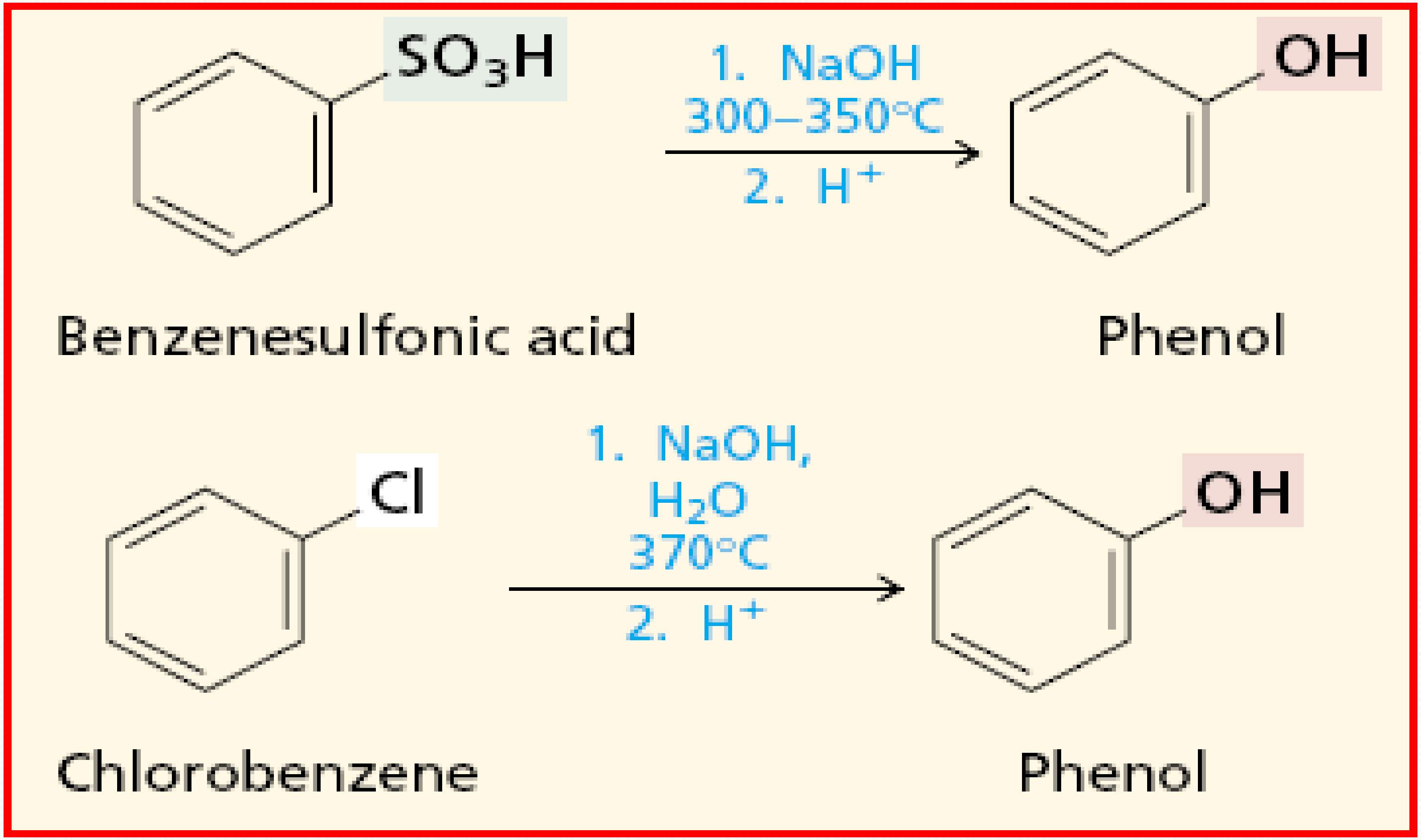


Compound name	Ionization constant K_a	pK_a
Monosubstituted phenols		
Phenol	1.0×10^{-10}	10.0
o-Cresol	4.7×10^{-11}	10.3
m-Cresol	8.0×10^{-11}	10.1
p-Cresol	5.2×10^{-11}	10.3
o-Chlorophenol	2.7×10^{-9}	8.6
m-Chlorophenol	7.6×10^{-9}	9.1
p-Chlorophenol	3.9×10^{-9}	9.4
o-Methoxyphenol	1.0×10^{-10}	10.0
m-Methoxyphenol	2.2×10^{-10}	9.6
p-Methoxyphenol	6.3×10^{-11}	10.2
o-Nitrophenol	5.9×10^{-8}	7.2
m-Nitrophenol	4.4×10^{-9}	8.4
p-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

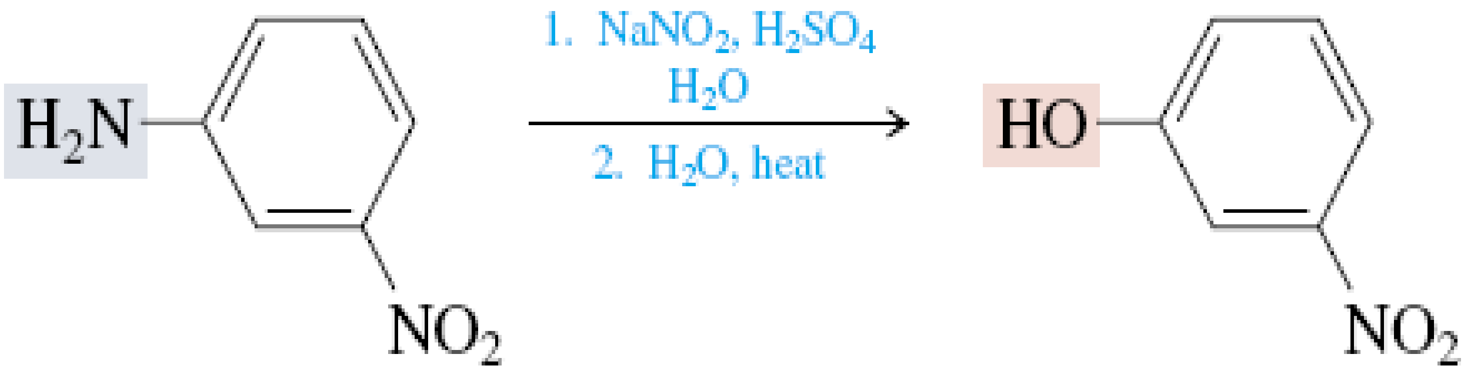
- Phenols was first isolated from coal tar.
- Phenol is an important industrial chemical.
- Major use is in phenolic resins for adhesives and plastics.

Industrial preparation of Phenols



Laboratory Synthesis of Phenols

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



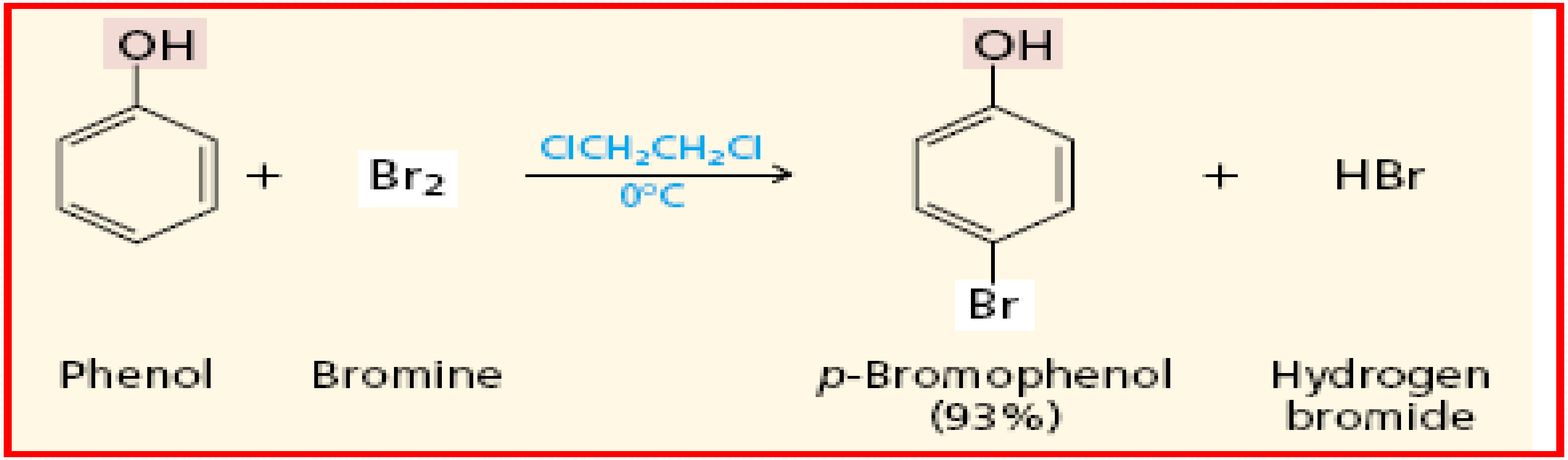
m-Nitroaniline

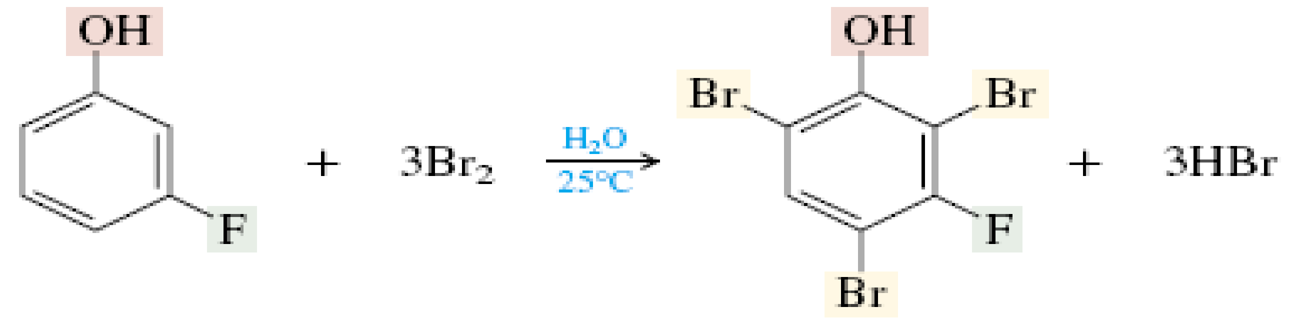
m-Nitrophenol (81–86%)

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





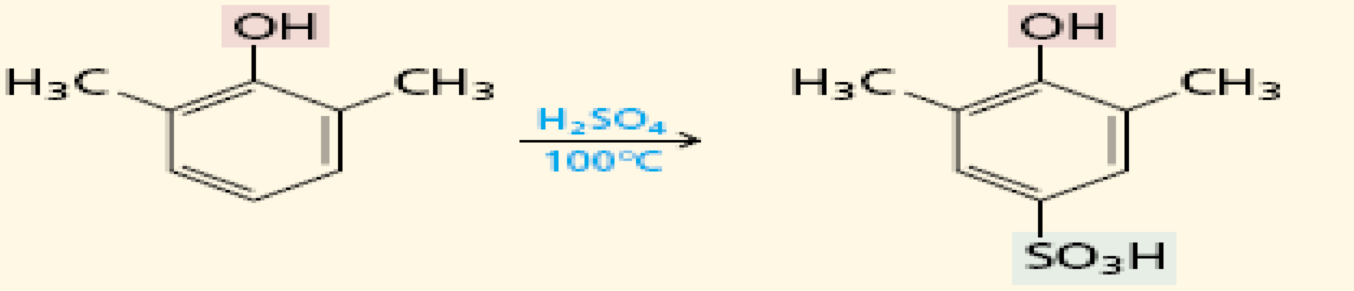
m-Fluorophenol

Bromine

2,4,6-Tribromo-3-fluorophenol (95%)

Hydrogen bromide

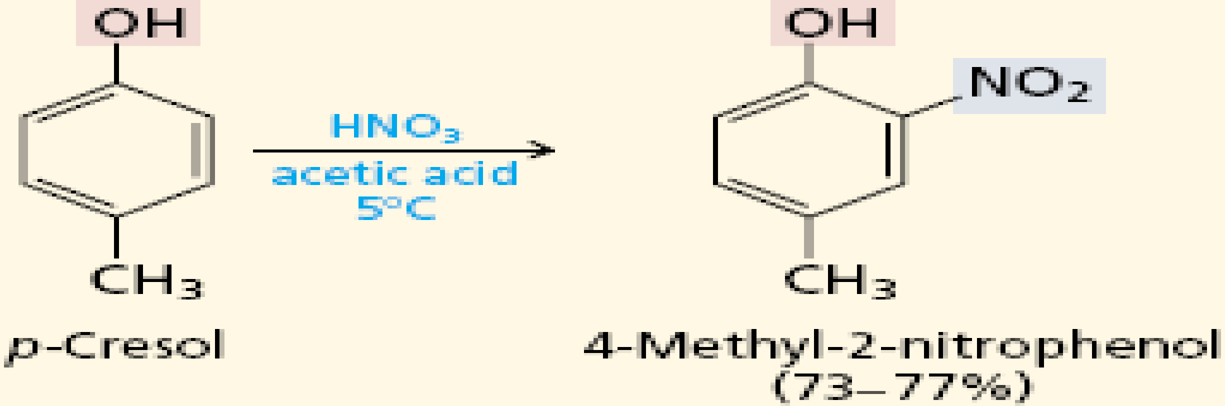
b- Sulfonation



2,6-Dimethylphenol

4-Hydroxy-3,5-dimethylbenzenesulfonic acid (69%)

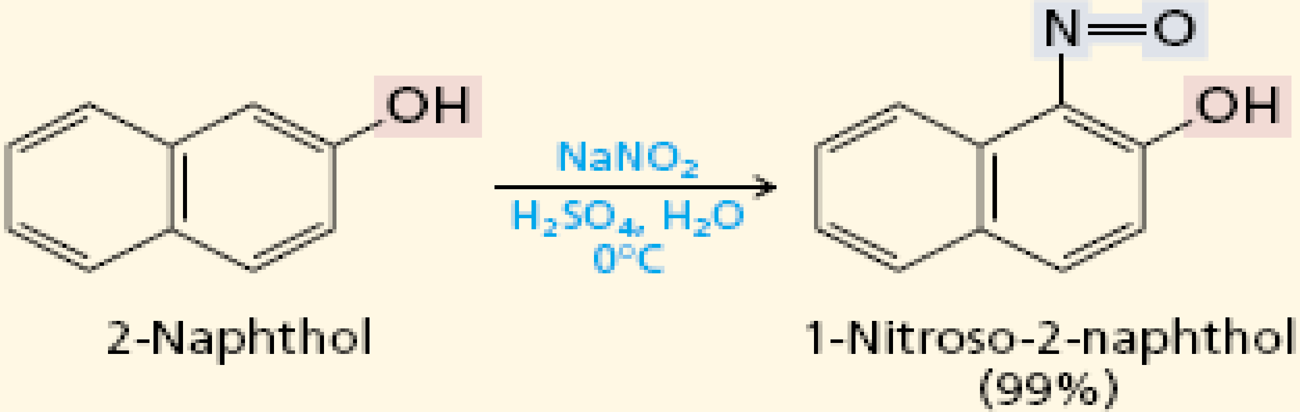
c- Nitration



p-Cresol

4-Methyl-2-nitrophenol
(73–77%)

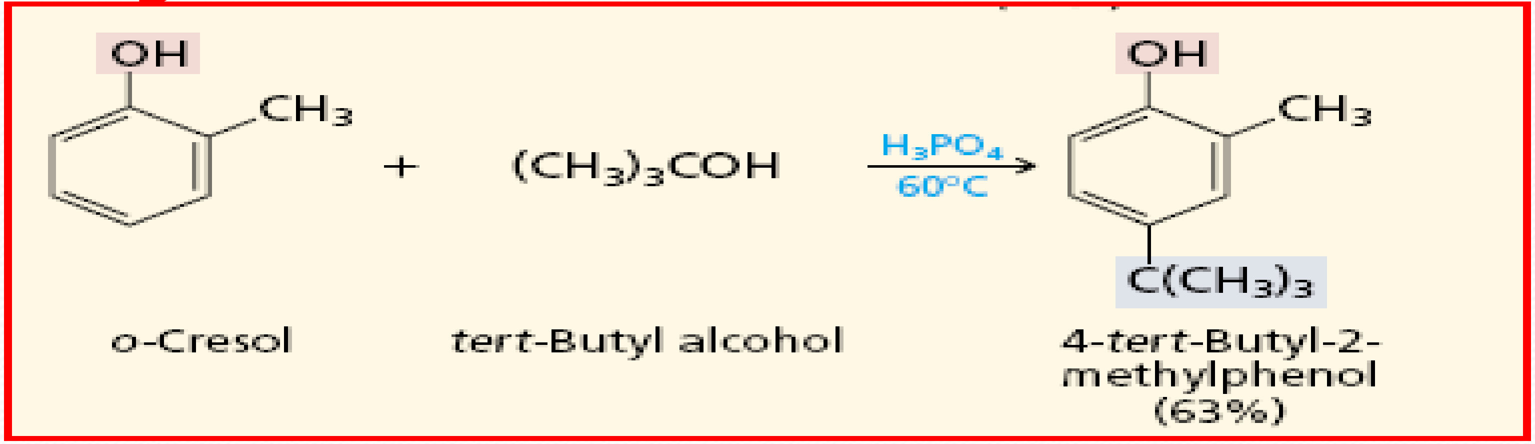
d- Nitrosation



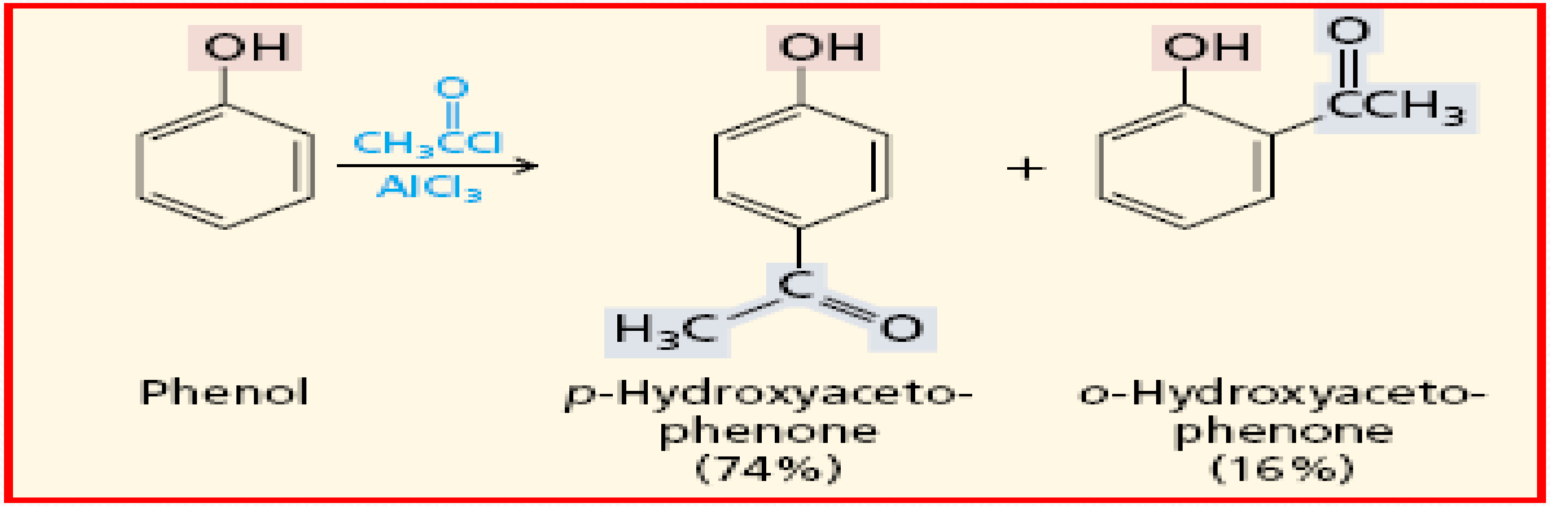
2-Naphthol

1-Nitroso-2-naphthol
(99%)

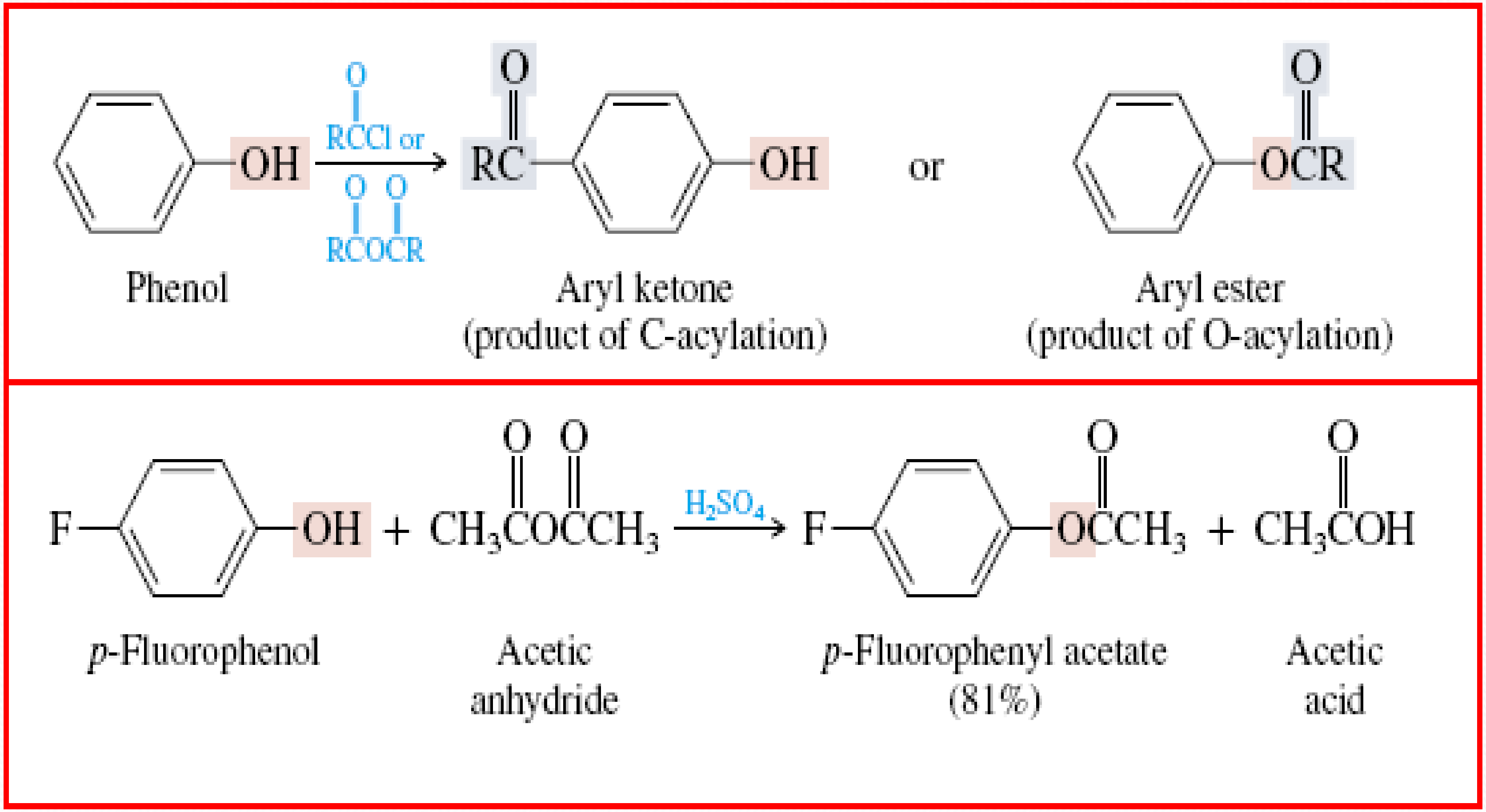
d-Friedal Crafts Alkylation

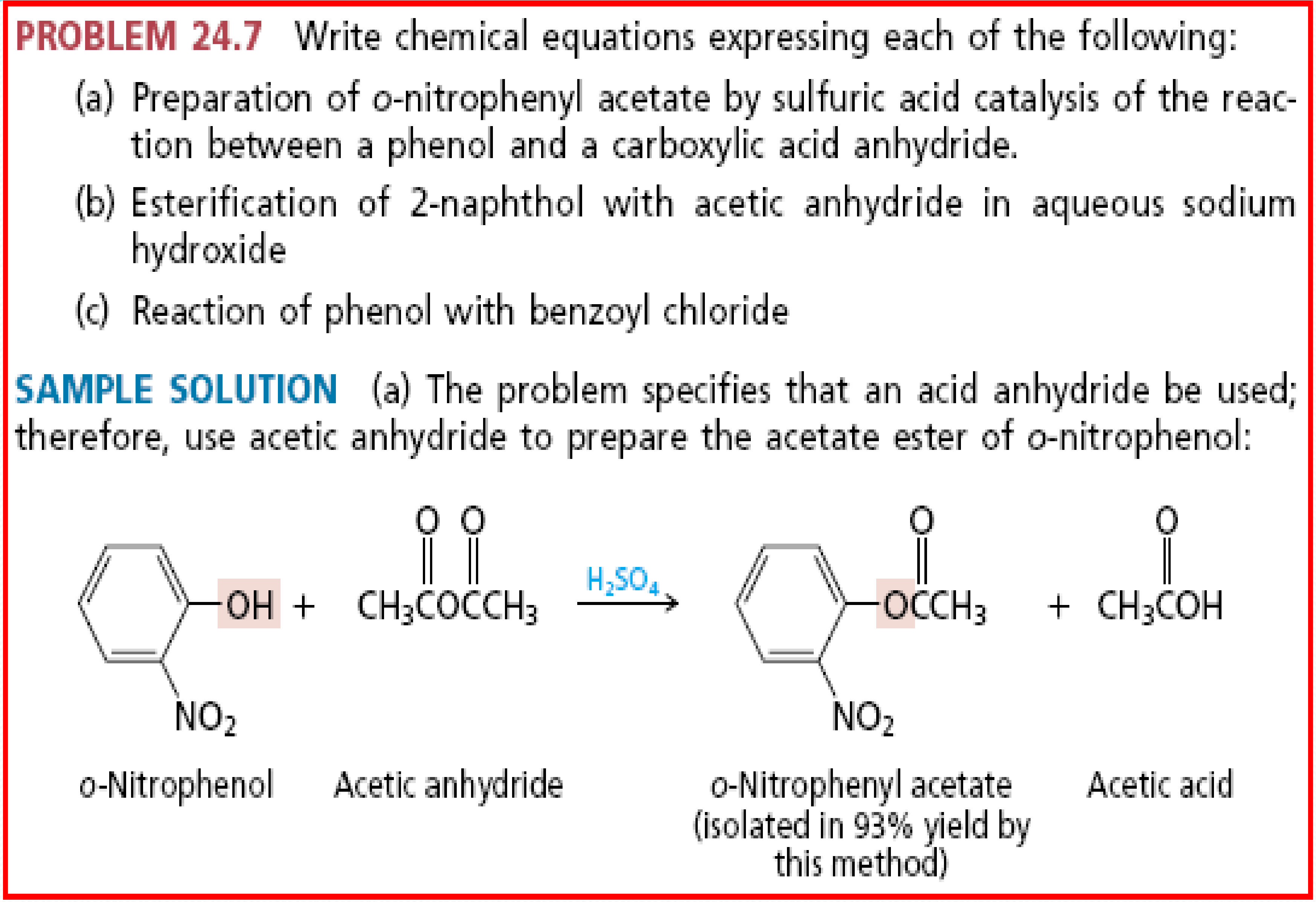


e-Friedal Crafts Acylation



In the absence of ALCL3, However O-acylation occurs instead.





PROBLEM 24.7 Write chemical equations expressing each of the following:

(a) Preparation of *o*-nitrophenyl acetate by sulfuric acid catalysis of the reaction between a phenol and a carboxylic acid anhydride.

(b) Esterification of 2-naphthol with acetic anhydride in aqueous sodium hydroxide

(c) 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:

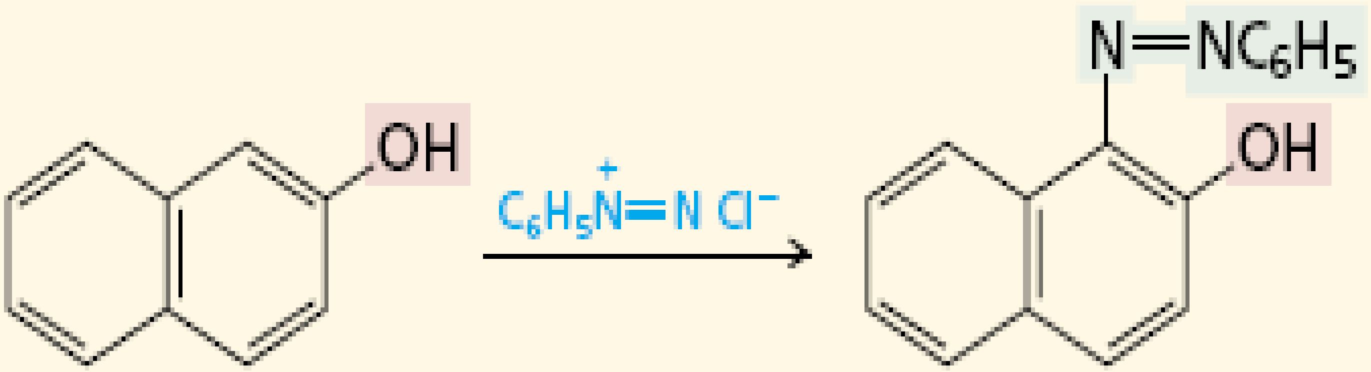
o-Nitrophenol

Acetic anhydride

o-Nitrophenyl acetate (isolated in 93% yield by this method)

Acetic acid

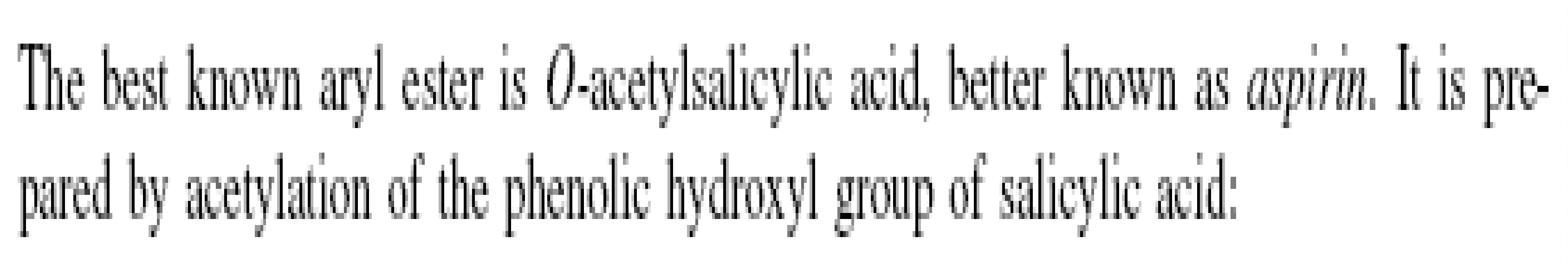
f- Reaction with arenediazonium salts.



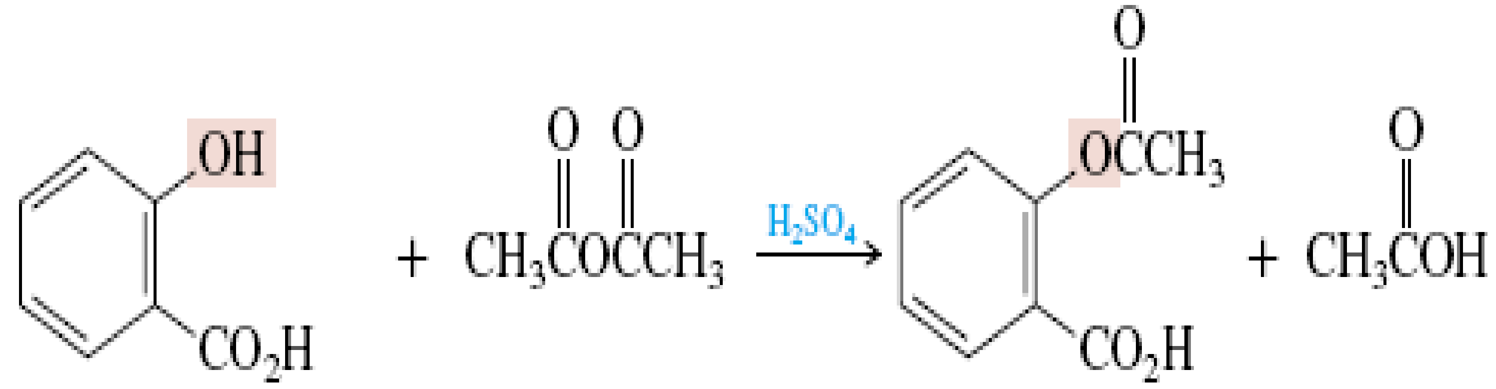
2-Naphthol

1-Phenylazo-2-naphthol
(48%)

6- Aspirin and the Klobe – Schmitt Reaction.

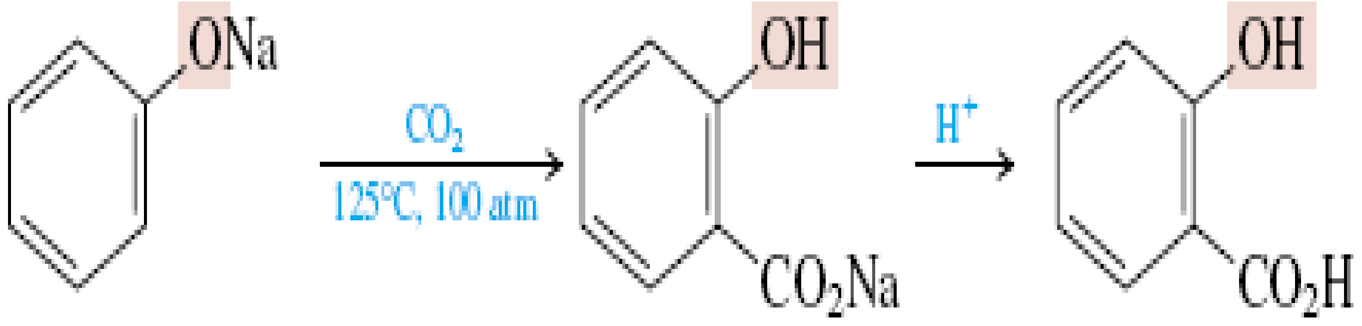


The best known aryl ester is *O*-acetylsalicylic acid, better known as *aspirin*. It is prepared by acetylation of the phenolic hydroxyl group of salicylic acid:



Salicylic acid (*o*-hydroxybenzoic acid) + Acetic anhydride $\xrightarrow{H_2SO_4}$ *O*-Acetylsalicylic acid (aspirin) + Acetic acid

Preparation of Salicylic Acid



Sodium phenoxide — Sodium salicylate — Salicylic acid (79%)

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