Phenols

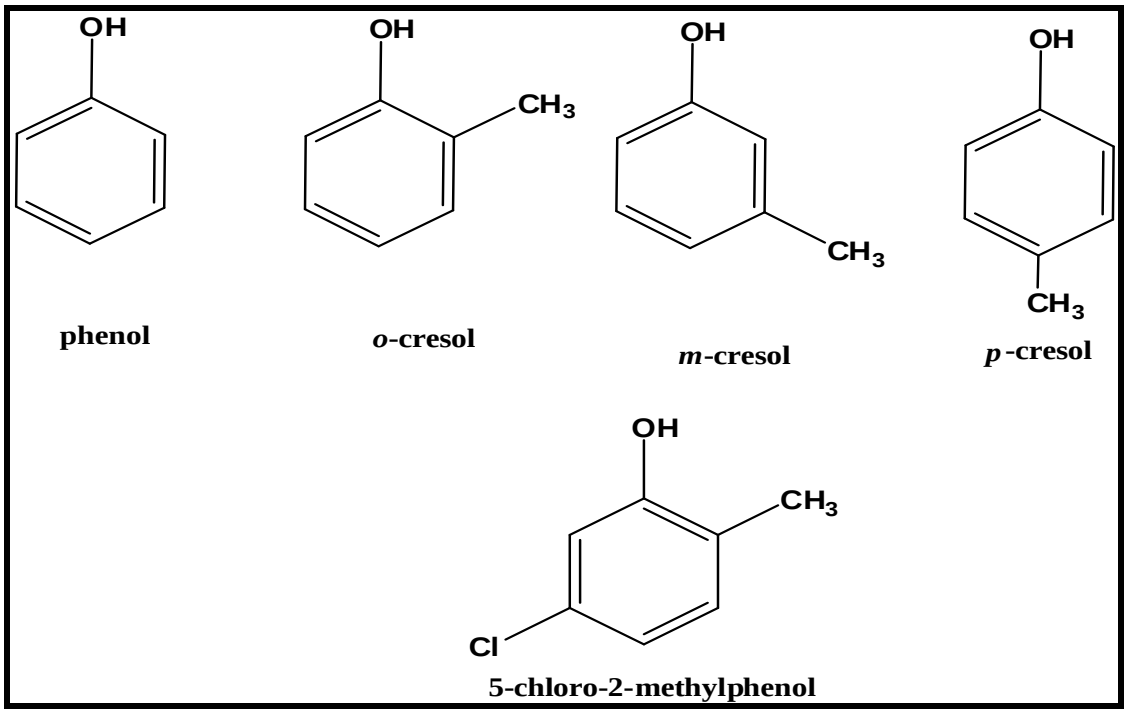
Phenols are compounds that have a hydroxyl group bond directly benzene or benzenoid ring. The parent compound of this group , C_6H_5OH,called simply phenol , is an important industrial chemical and pharmaceutical chemistry.

Phenols are compounds of the general formula Ar-OH ,when Ar=phenyl ,substituted phenyl. Phenols differ alcohols in having the hydroxyl group attached directly to an aromatic ring(phenyl or substituted phenyl).but the hydroxyl group in alcohol compounds are attached directly to an aliphatic group

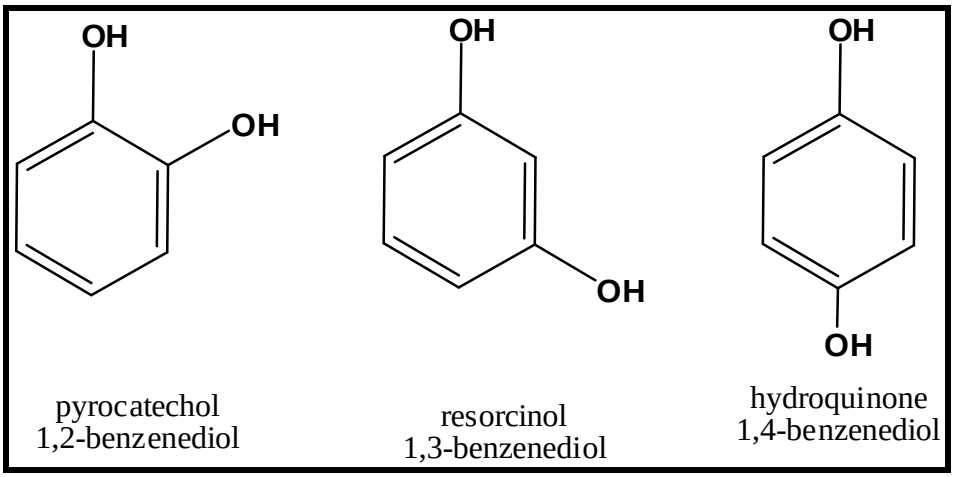
Nomenclature

An old name for benzene was phene , and its hydroxyl derivative came to be called phenol ,the systematic name for phenol is benzenol =(C_6H_5OH).this, like many other entrenched common names , is an acceptable IUPAC name.

(International Union of Pure and Applied Chemistry). Likewise ,o-,m- ,and p-cresol are acceptable names for the various ring-substituted hydroxyl derivatives of toluene **.** more highly substituted compounds are named as derivatives of phenols . numbering of the ring begins at the hydroxyl-substituted carbon and proceeds in the direction that gives the lower number to the next substituted carbon. Substituent are cited in alphabetical order.



the three dihydroxy derivatives of benzene may be named as 1,2- , 1,3 and 1,4-benzenediol ,respectively ,but each is more known by the common name .



Problem

Write structural formulas for each of the following compounds :

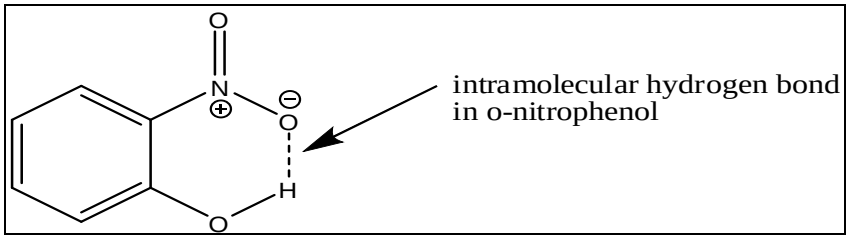
(a) Pyrogallol
(b) O-benzylphenol
(c) 3-nitro-1-naphthol
(d) 4-chlororesorcinol

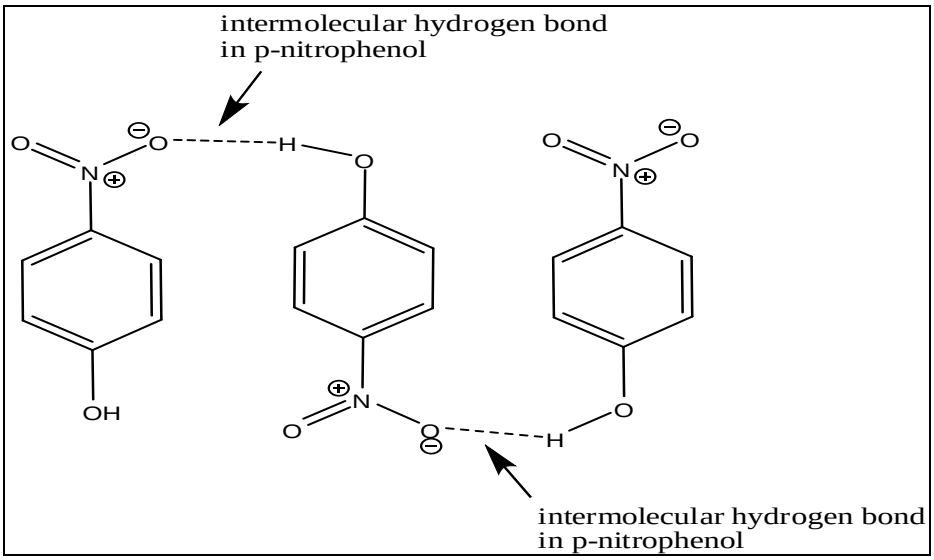
(e) salicylic acid (f) 1-naphthol

(g) B-naphthol (h) p-hydroxy benzoicacid

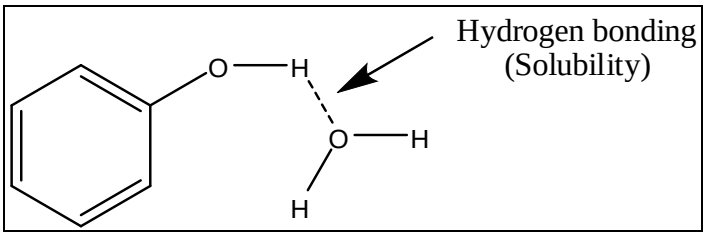
Physical properties of phenols

The physical properties of phenols are strongly influenced by the hydroxyl group. The simplest phenols are liquids or low- melting points solids, because of hydrogen bonding ,they have quite high boiling points. Some ortho-substituted phenols ,such as o-nitrophenol, have significantly lower boiling points than those of the meta and para isomers.this is because the intramolecular hydrogen bond that forms between the hydroxyl group and nitro group.



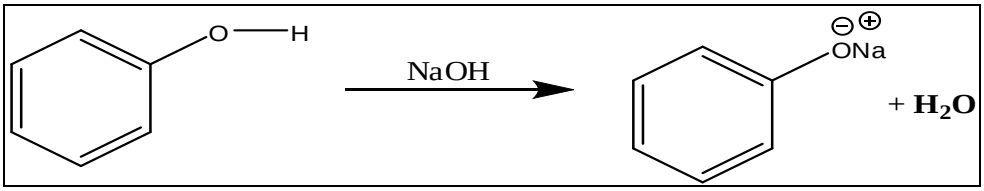


Phenols are soluble in water because of hydrogen bonding between hydroxyl group in phenols and water.

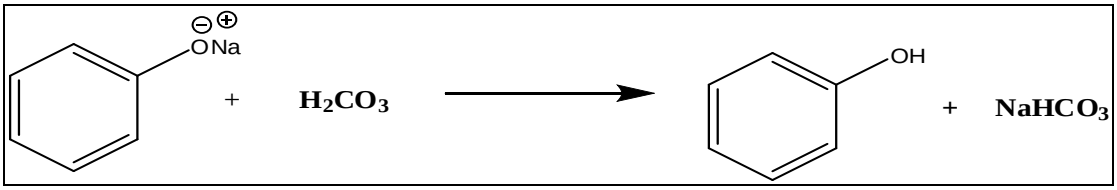


Acidity of phenols

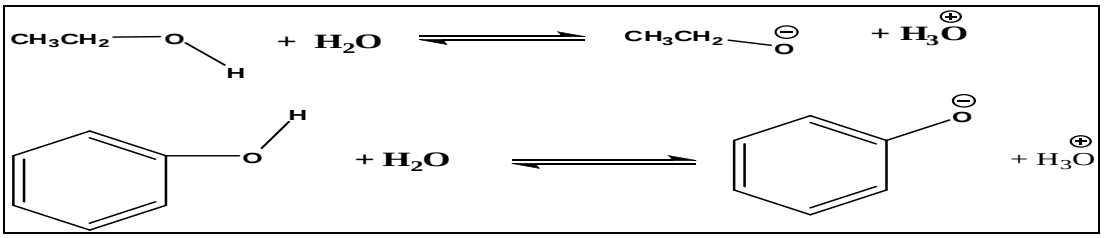
The most characteristic property of phenols is their acidity. Phenols are more acidic than alcohols but less acidic than carboxylic acids. Phenols are converted into their salts by aqueous hydroxide.



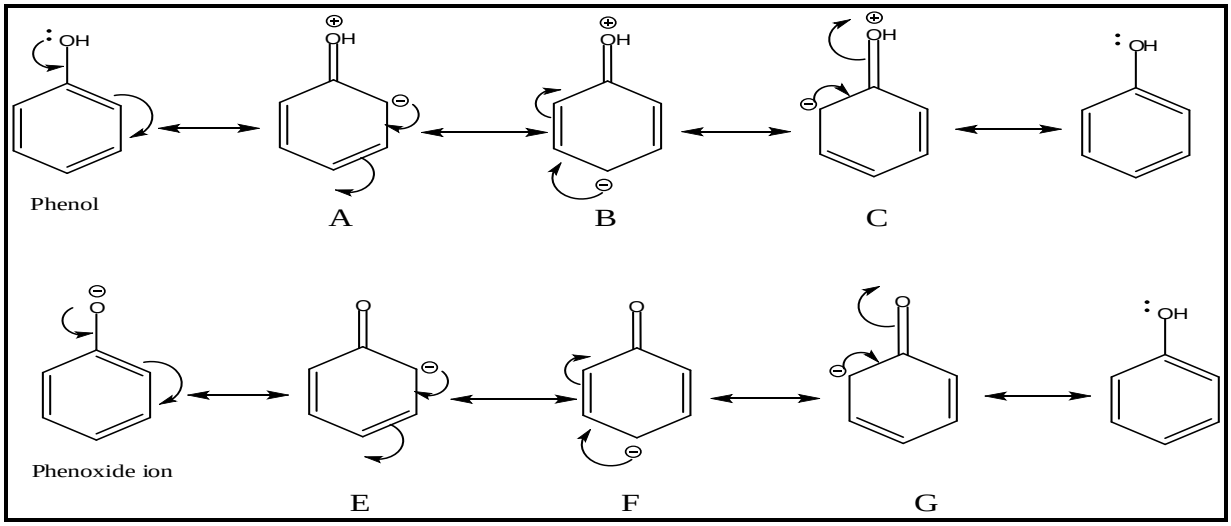
Most phenols are weaker than carbonic acid see below:



Now to help us understand why phenols are more acidic than alcohols ,let's compare the ionization equilibria for phenol and ethanol. In particular, consider the differences in charge delocalization in ethoxide ion and in phenoxide ion. The negative charge in ethoxide ion is localized on oxygen and is stabilized only by salvation forces. But the negative charge in phenoxide ion is stabilized both by salvation and by electron delocalization into the ring.



Resonance of phenols



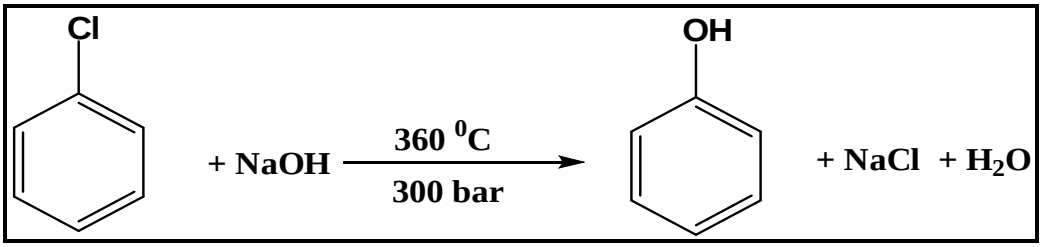
Structures A,B,C for phenol carry both positive and negative charges ; structures E,F,G for phenoxide ions carry only negative charges, the structure of phenol should contain more energy and hence the less stable than the structure of phenoxide ion. We have already encountered the effect of separation of charges on stability , the net effect of resonance is there for to stabilize the phenoxide ion to greater extent than the phenol.

Preparation of phenols

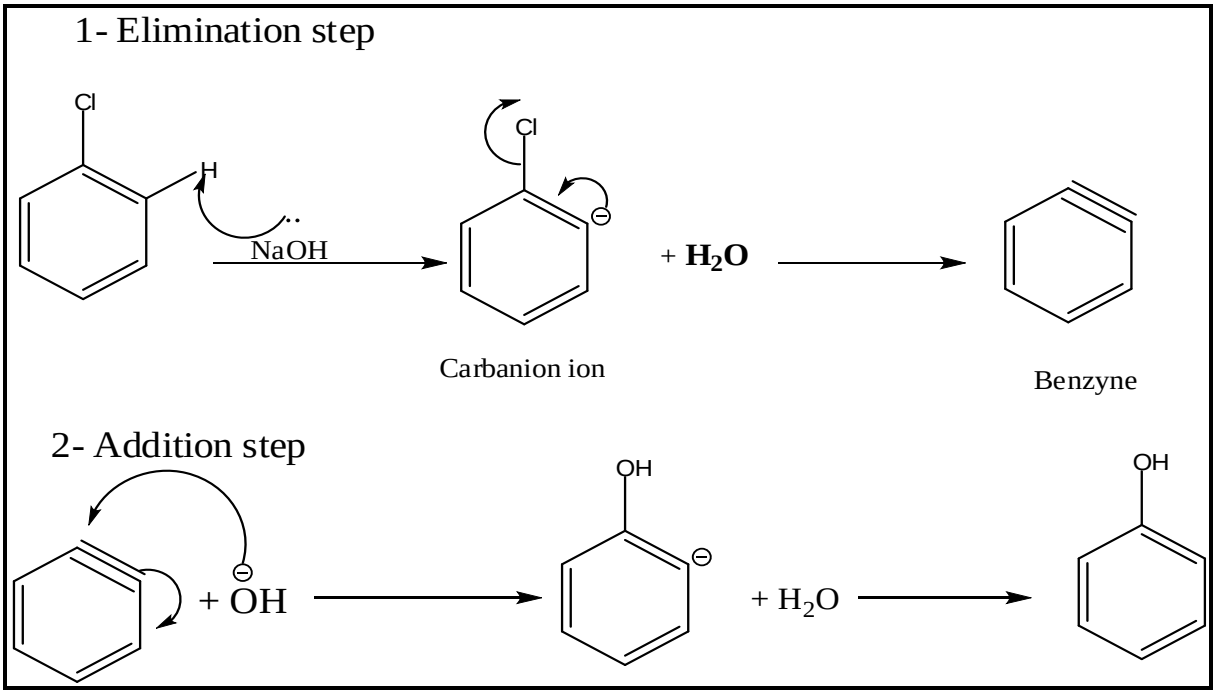
Industrial source :

1-Dow process:

This process was referred to the preparation of phenol from chlorobenzene . chlorobenzene is treated with dilute sodium hydroxide at 360 °C and 300 bar to convert it to phenol.

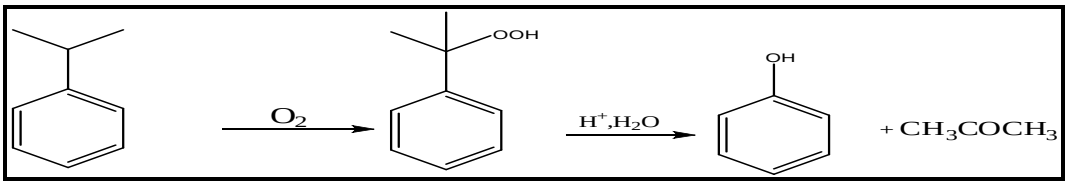


Mechanism:



2- Nearly all phenol is made today ,however ,by a newer process that starts with cumene,isopropylbenzene. Cumene is converted by air

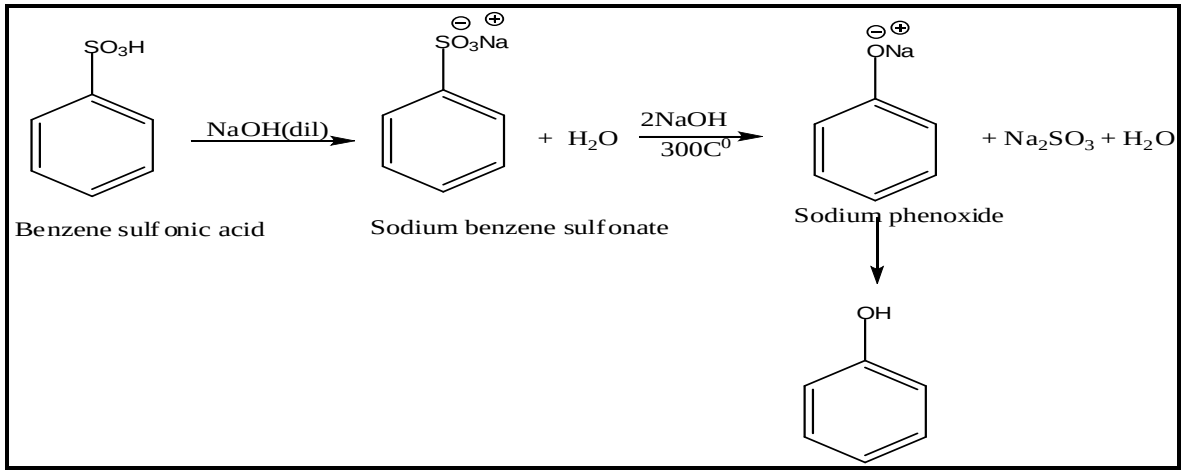
oxidation into cumene hydroperoxide , which is converted by aqueous acid into phenol and acetone.



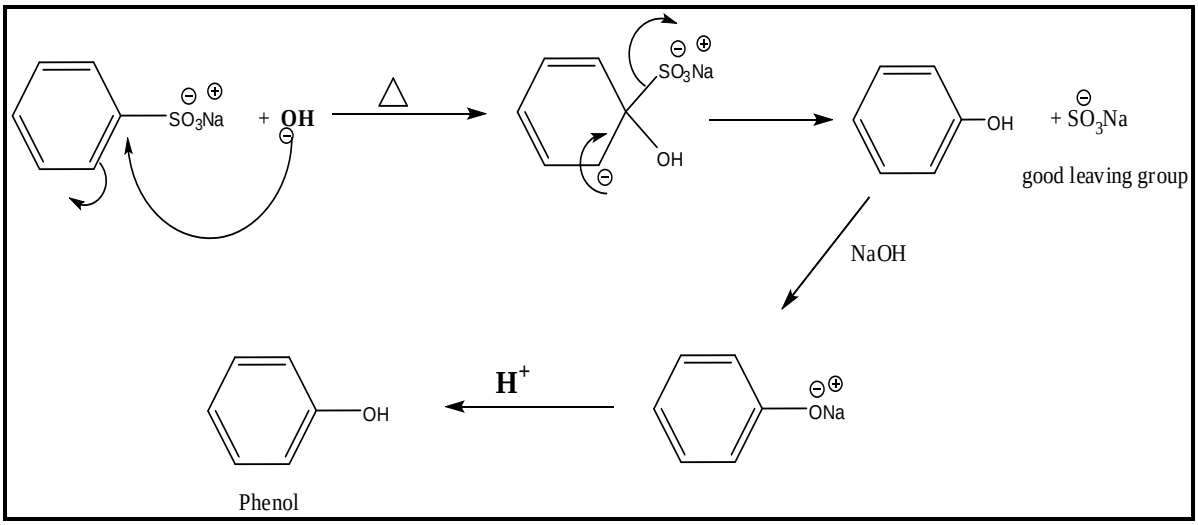
In the laboratory

1- Alkali fusion of sulfonates :

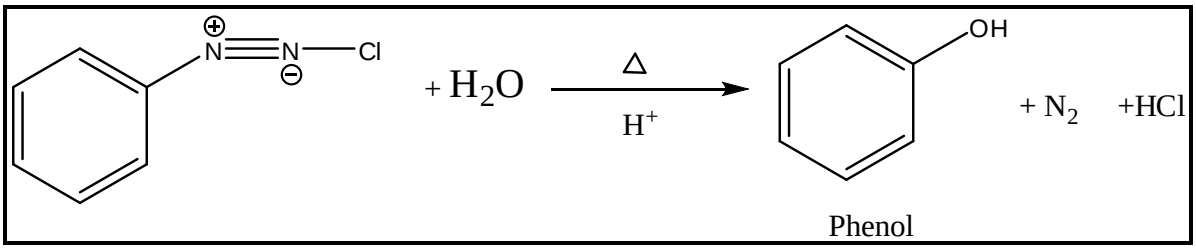
One of the synthetic processes used is the fusion of sodium benzene sulfonate with alkali medium.



Mechanism

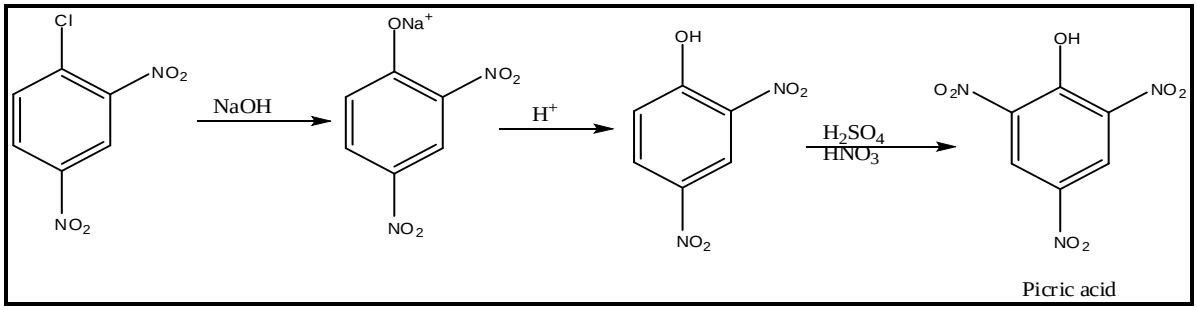


2- Hydrolysis of diazonium salt



Benzenediazonium salt

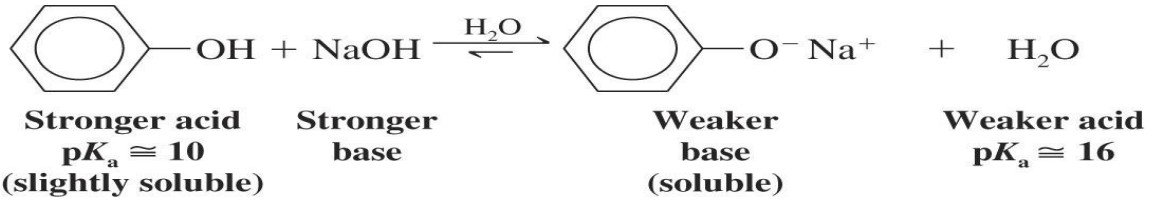
- The hydrolysis of aryl halides containing strongly electron with drawing groups ortho and para to the halogen ; 2,4-di nitro phenol are produced in this way on a large scale:

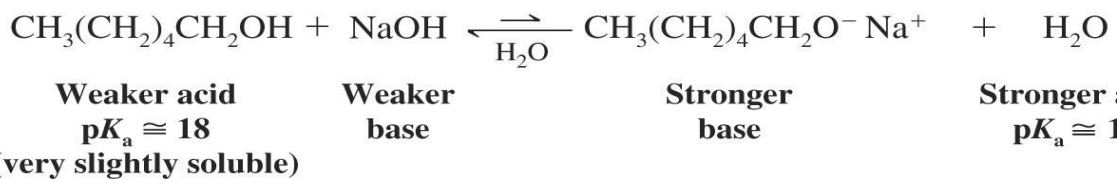


Reactions of phenols:

1- Reaction of phenols as acid

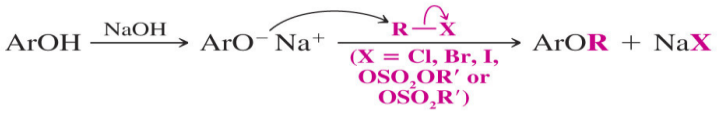
-Separating Phenols from Alcohols and Carboxylic Acids. Phenols are soluble in aqueous sodium hydroxide because of their relatively high acidity - most alcohols are not.



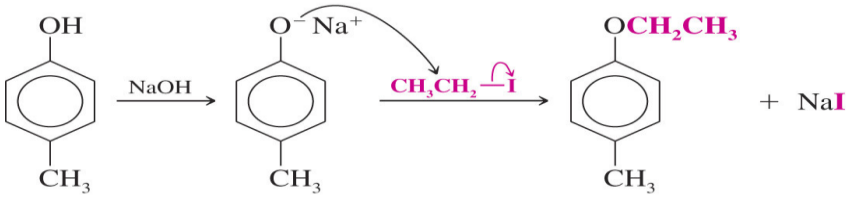


2 -Phenols in the Williamson Ether Synthesis. Phenoxides (phenol anions) react with primary alkyl halides to form ethers by an SN2 mechanism.

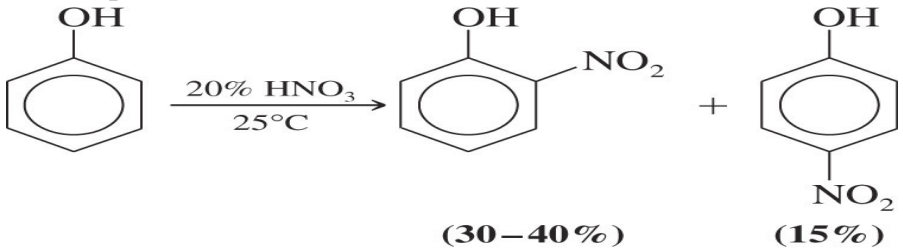
General Reaction



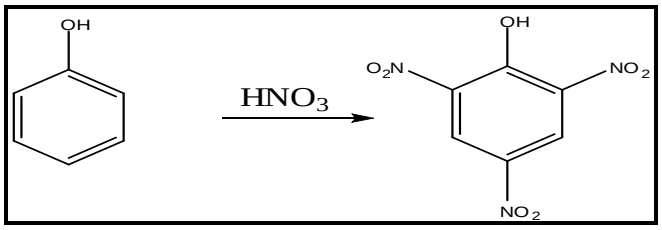
Specific Examples



2- Nitration of phenols

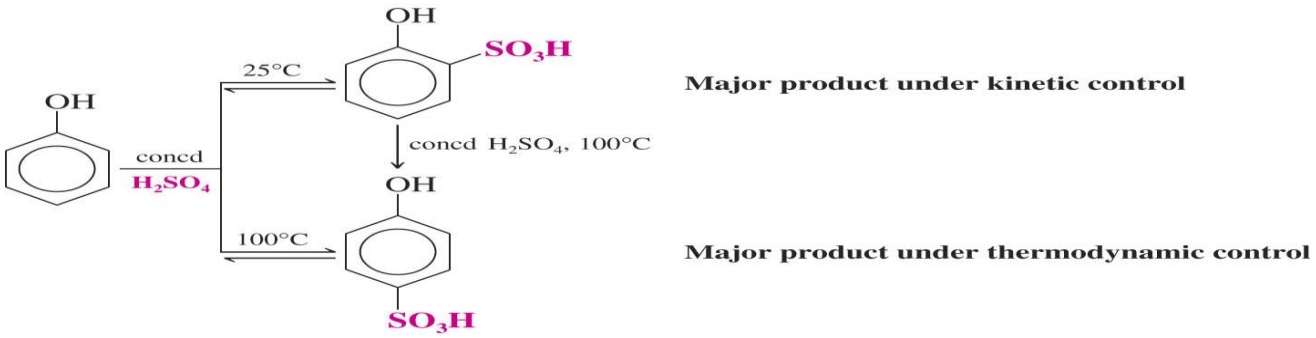


Synthesis of picric acid:-



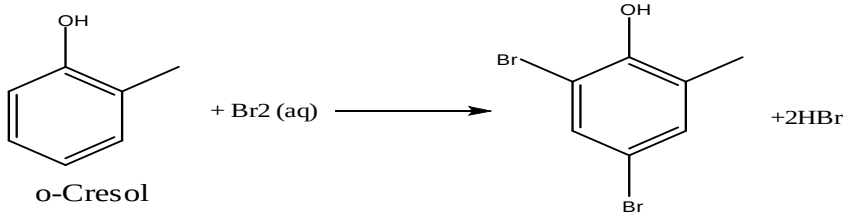
Sulfonation

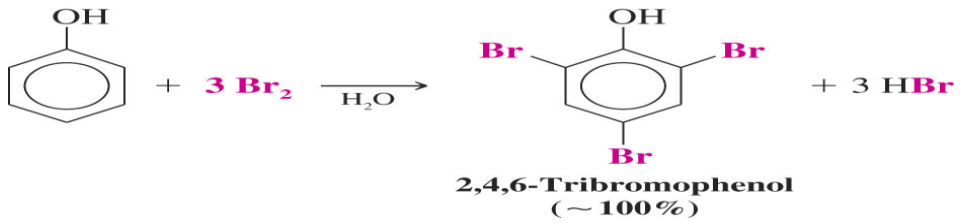
• Sulfonation gives mainly the ortho (kinetic) product at low temperature and the para (thermodynamic) product at high temperature.(ortho or para phenol sulfonic acid).



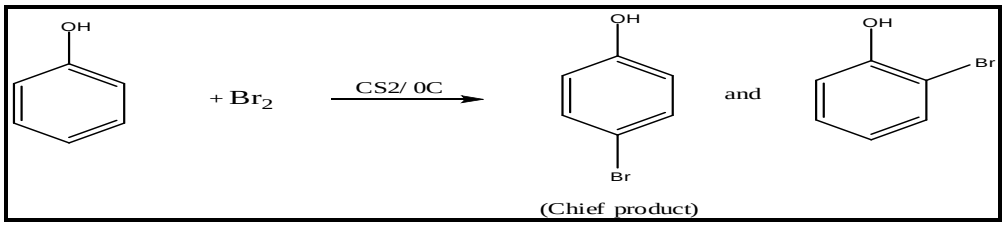
- Haloganation

Treatment of phenol with aqueous solution of bromine results in replacement of every hydrogen (ortho or para)to the –OH group ; and may even cause displacement of certain other groups.

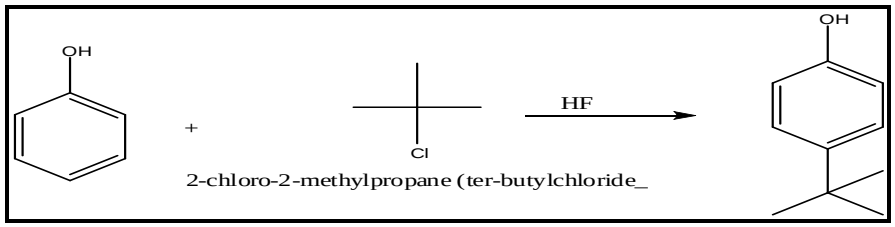




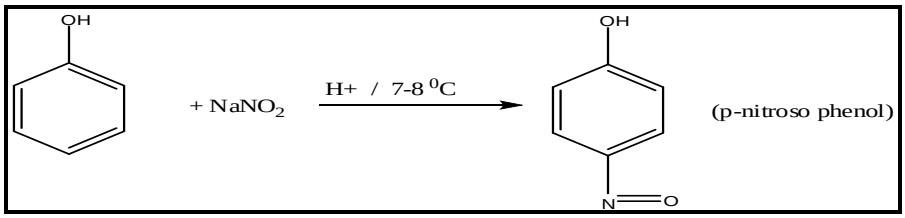
If halogenation is carried out in a solvent of low polarity such as chloroform, CCL_4, CS_2 reaction can be limited to mono halogenations.



- Friedl – crafts alkylation:

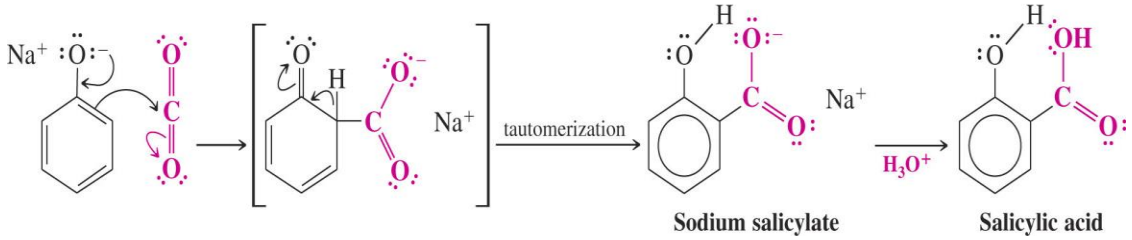


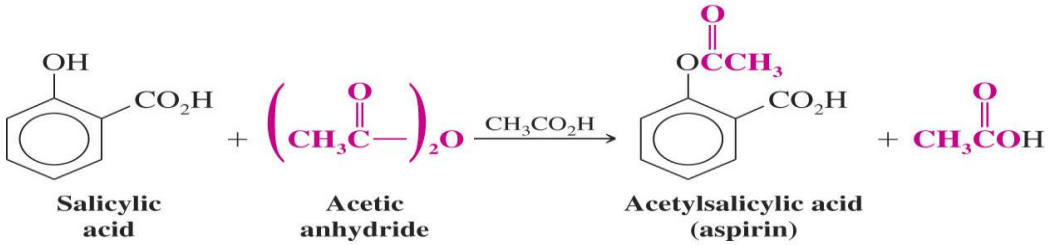
-Nitrosation:-



- Kolbe reaction
- Carbon dioxide is the electrophile for an electrophilic aromatic
- substitution with phenoxide anion
- – The phenoxide anion reacts as an enolate
- – The initial keto intermediate undergoes tautomerization to the phenol

- – Kolbe reaction of sodium phenoxide results in salicyclic acid, a
- synthetic precursor to acetylsalicylic acid (aspirin).

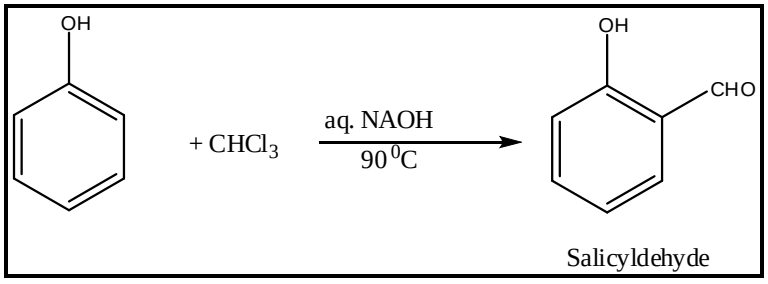




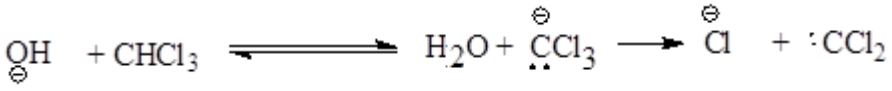
Rimer-tiemann reaction

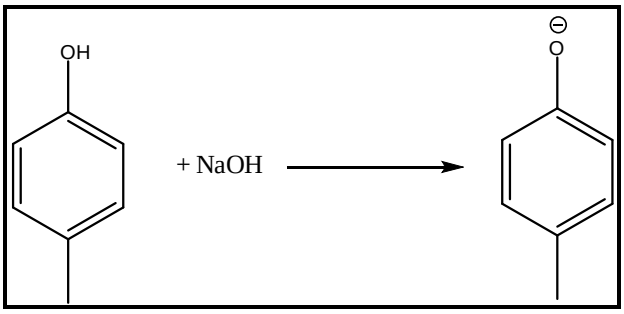
Treatement of a phenol with chloroform and aqueous hydroxide introduces an aldehyde group- CHO ,into the aromatic ,generally (ortho) to the –OH .

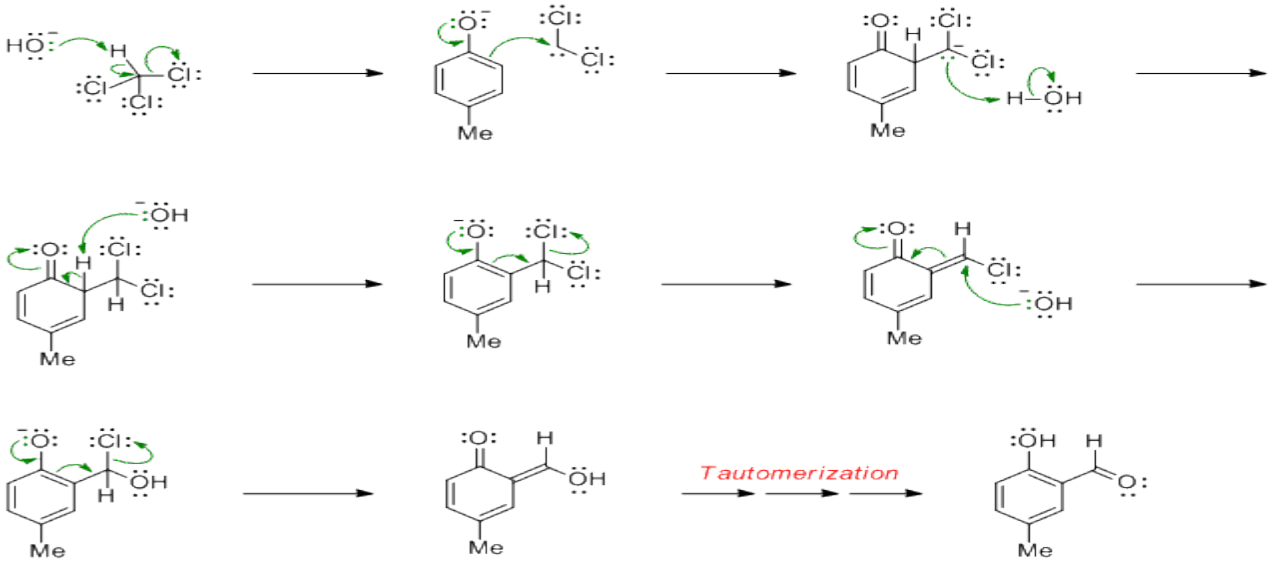
This reaction is known as the rimer tiemann reaction .



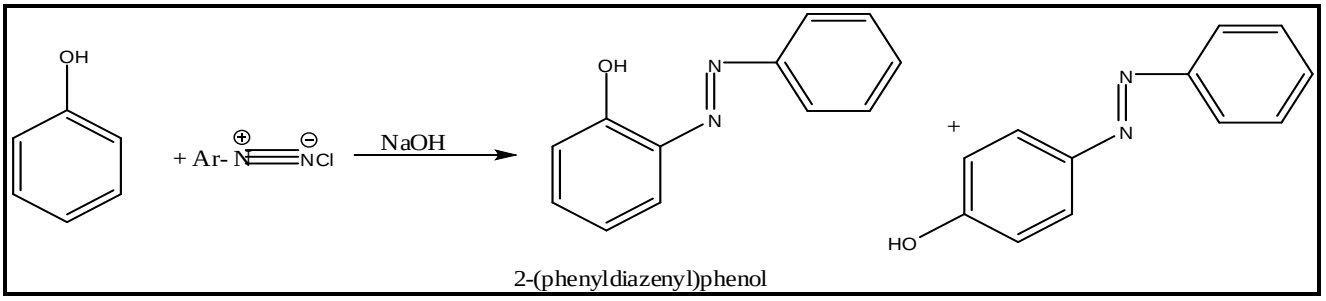
Mechanism:

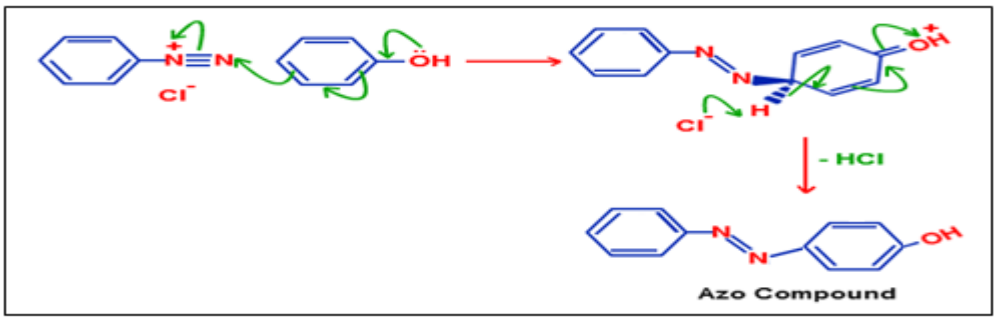






Azo compound formation





Identified of phenol

Many but not all phenols form colored complexes (ranging from green through blue and violet to red)with ferric chloride.