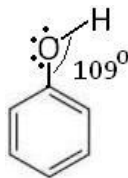


PHENOLS

PHENOL

- Phenols are the aromatic compounds having hydroxyl group (-OH) directly attached to benzene ring.

ELECTRONIC STRUCTURE OF PHENOL

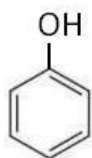


- In phenols the -OH group is attached to sp^2 hybrid carbon of an aromatic ring and the oxygen atom of the hydroxyl group has two lone pairs of electrons and the bond angle in phenol is 109° . The C-O bond length in phenol (136pm) is slightly less than in methanol(142pm) due to resonance in aromatic ring of phenol
- Phenol has dipole moment 1.54D where as methanol has dipole moment 1.71D. This smaller dipole moment of phenol is due to the electron attracting effect of phenyl group in contrast to the electron releasing effect of methyl (or alkyl) group in alcohol

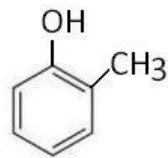
CLASSIFICATION OF PHENOL

- Phenols are classified as mono, di and trihydric phenols according to the number of hydroxyl groups attached to the aromatic ring.

1. Monohydric phenols

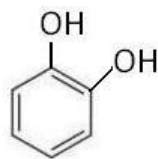


Phenol

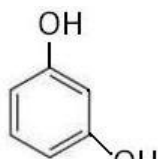


2-methyl phenol
o-cresol

2. Dihydric phenols



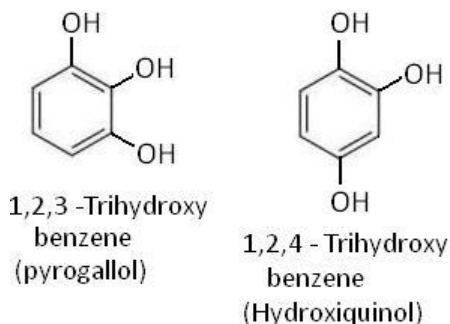
Phenol
1,2-Dihydroxy
benzene
(catechol)



1,3-Dihydroxy
benzene
(resorcinol)

3. Trihydric phenols

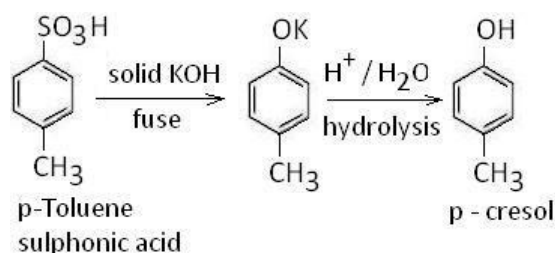
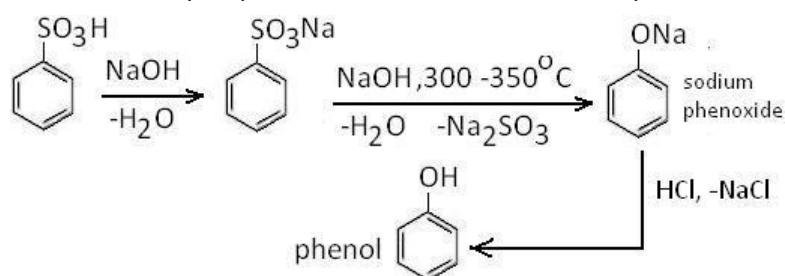
PHENOLS



GENERAL METHODS OF PREPARATION OF PHENOLS

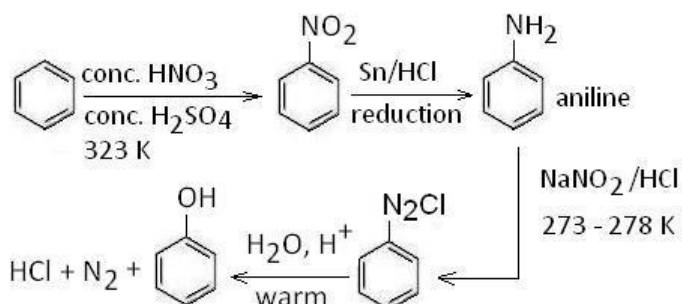
1. Alkali fusion of sulphonates

Sodium salt of aryl sulphonic acids on fusion with sodium hydroxide at 300-350°C yield phenol



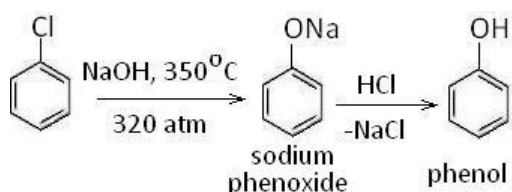
The above reaction is laboratory method for preparation of phenol

2. Hydrolysis of diazonium salt

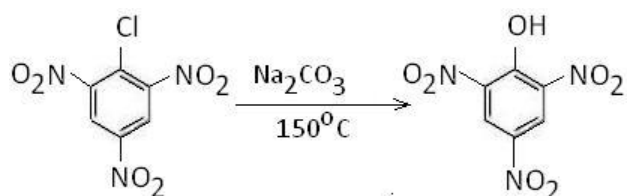
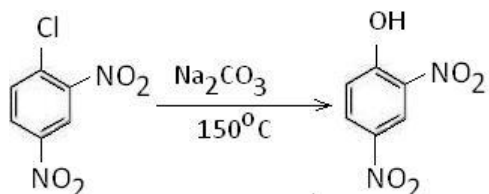
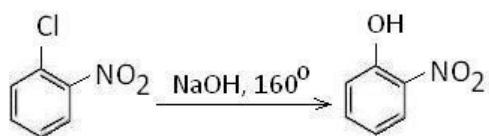


3. Hydrolysis of aryl halides (Dow's process)

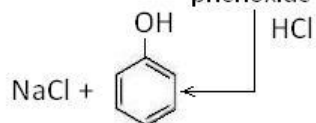
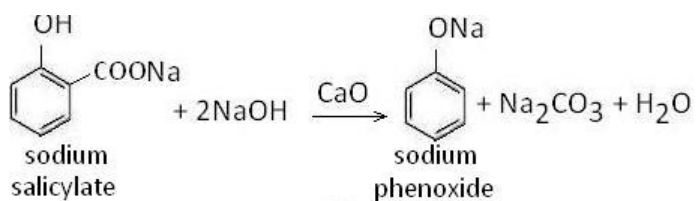
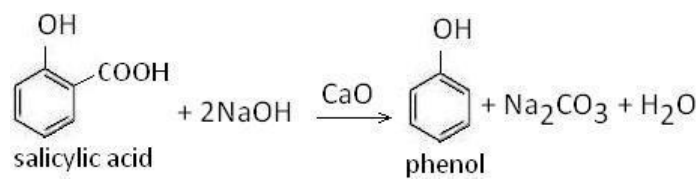
- Aryl halides on hydrolysis yield phenol but the process is not so simple because halogen atom attached to benzene ring does not undergo S_N2 reaction since C-X bond is resonance stabilized. Hence reaction takes place at high pressure and elevated pressure.



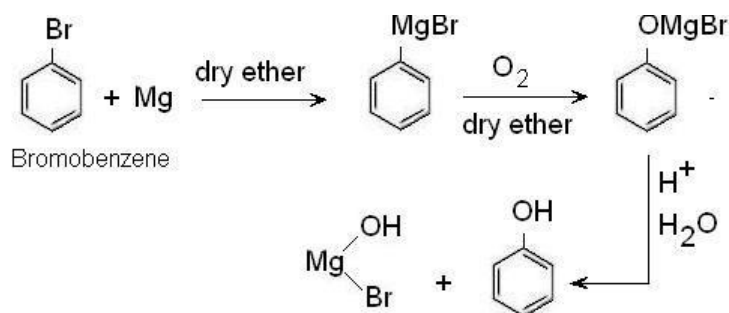
- However if some electron withdrawing group is attached to benzene ring, then reaction conditions get relaxed



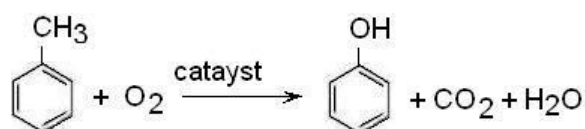
4. Decarboxylation of salicylic acid



5. Oxidation of Grignard reagent



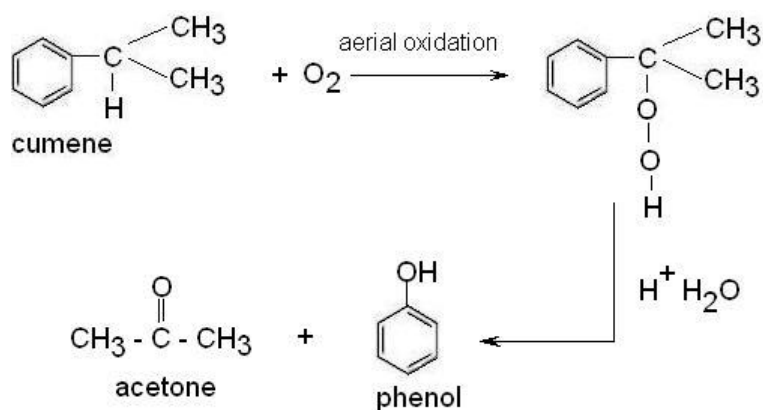
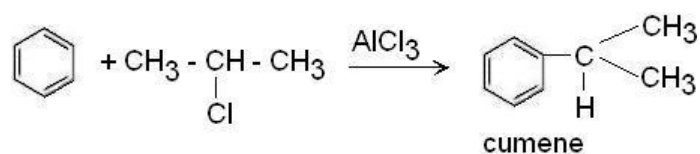
6. Oxidation of aromatic hydrocarbons



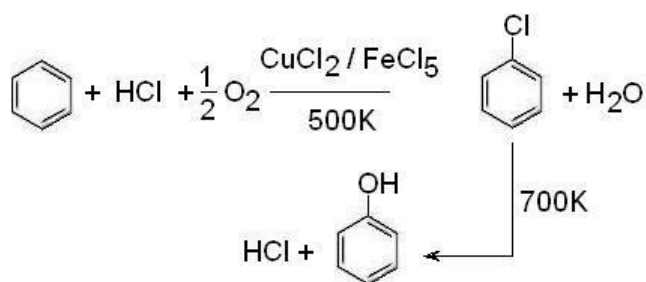
Catalyst used in this reaction is cupric salt.

7. Oxidation of iso-propyl benzene (Cumene)

Cumene is prepared by Friedel Crafts alkylation of benzene with 2-Chloropropane.



8. Rasching's process



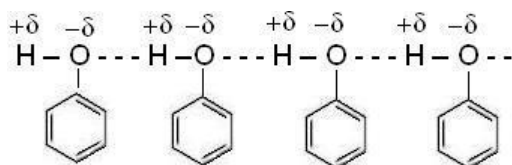
PHYSICAL PROPERTIES OF PHENOL

1. Physical state

- Phenols are colourless liquids or low melting point solids, but they reddish brown due to auto oxidation on exposure to air and light.
- Phenols are poisonous in nature but act as disinfectant and antiseptic.

2. Solubility

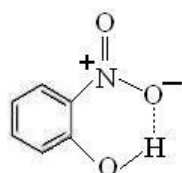
Phenols form H-Bonds with water molecule and hence soluble in water, but their solubility is lower than that of alcohols because of large hydrocarbon part



Intermolecular H-bonding among water and phenol molecules

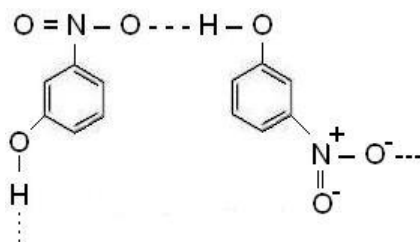
3. Boiling point

- Phenols have much higher boiling point than their corresponding hydrocarbons due to intermolecular hydrogen bonding
- Amongst the isomeric nitrophenols, O-nitrophenol has much lower melting point and solubility than meta and para isomers of nitrophenol because of intramolecular H-bonding. Thus it does not undergo association with other molecules. In fact ortho-nitrophenol is steam volatile

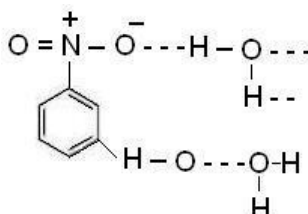


Intramolecular
H-bonding

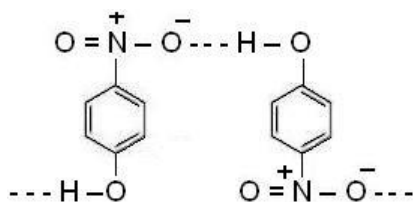
- On the other hand meta and para nitrophenol exhibit intermolecular H-bonding with their own molecules as well as with water molecules and hence show comparatively higher melting and solubility.
 - Intermolecular H-bonding (m -nitrophenol)



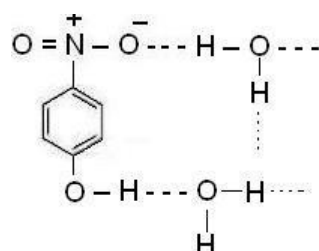
ii) H- bonding with water molecules (m-nitrophenol)



iii) Intermolecular H- bonding (p -nitrophenol)



iv) H – bonding with water molecules (p – nitrophenol)

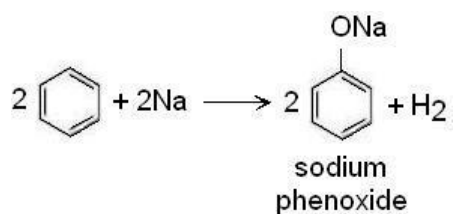


CHEMICAL PROPERTIES OF PHENOL

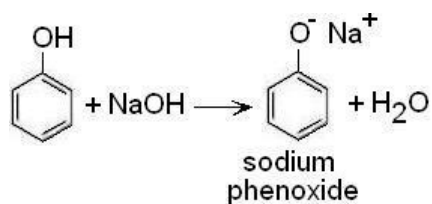
(A) Reactions involving cleavage of O-H bond

1. Acidic character of phenol

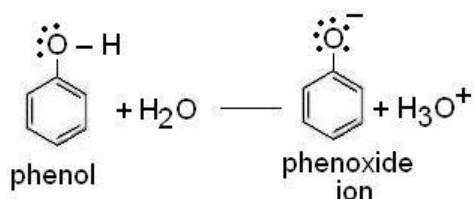
(i) Reaction with active metals



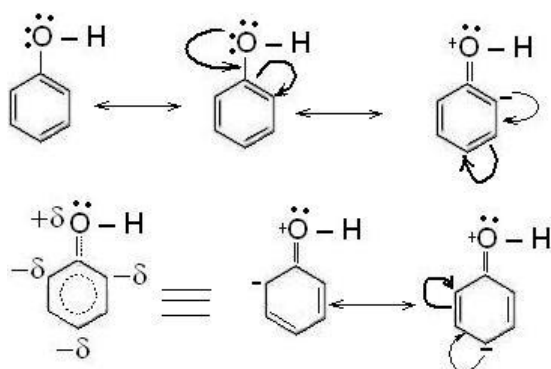
(ii) Reaction with alkalis



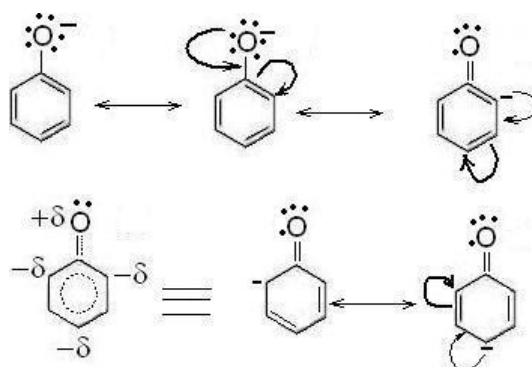
- They do not react with carbonates and bicarbonates. Phenols are weaker acid as compared to carboxylic acid because of polar O-H group in them. The acidic nature of phenol is due to formation of stable phenoxide ion in solution to give H^+ ions



- Phenol behaves as stronger acid than alcohol
 - The greater acidity of phenol is due to stability of phenoxide ion is resonance stabilised .
 - Resonance structure of phenol



- As a result of resonance it weakens the polar O-H bond and thus facilitates the release of proton (H^+) to give phenoxide ion which is also stable due to resonance
- Resonating structure of phenoxide ion

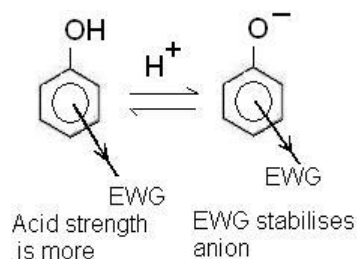


- Both phenol and phenoxide ion are stable due to resonance. But phenoxide ion is more stabilized than phenol because the resonating structure of phenoxide ion carry only negative structure of phenol involves separation of positive and negative charge. This charge delocalization is a stabilizing factor in phenoxide ion and increases acidity of phenol.

vi. Effect of substituent on the acidity of phenols

a. Electron withdrawing group (EWG)

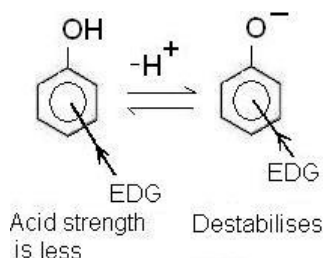
1. Electron withdrawing groups NO_2 , $-\text{X}$, $-\text{CHO}$, $-\text{COOH}$, $-\text{CN}$ etc stabilizes the phenoxide ion more by dispersing the negative charge relative to phenol (i.e. proton release become easy) and thus increases the acidic strength of phenols



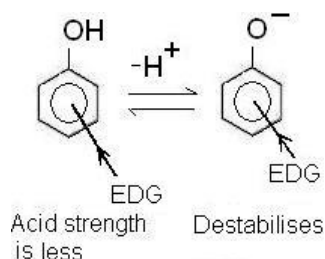
2. Particular effect is more when the substituent is present on o- and p- positions than in m- position. Thus acidic strength of nitrophenol decreases in the order p-nitrophenol > o-nitrophenol > m-nitrophenol > phenol
3. Further greater the number of electron withdrawing groups at o- and p- position, more acidic the phenol.

b. Electron donating group (EDG)

- (i) Electron donating group $-\text{R}$, $-\text{NH}_2$, $-\text{OR}$ etc destabilize the phenoxide ion by donating electrons and intensify the negative charge relative to phenol (i.e. proton release become difficult) and thus decreases the acidic strength of phenol.



- (ii) The effect is more when the substituent is present on o- and p- position than on m- position with respect to $-\text{OH}$ group. Thus cresol are less acidic than phenol.

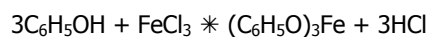
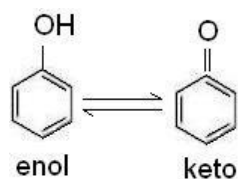


m- methoxy and m-amino phenols are stronger acid than phenols because of $-\text{I}$ effect (of $-\text{OCH}_3$ and $-\text{NH}_2$ groups) and absence of $+\text{R}$ effect.

m- methoxy phenol > m-amino phenol > phenol > O-methoxy phenol > p-methoxy phenol

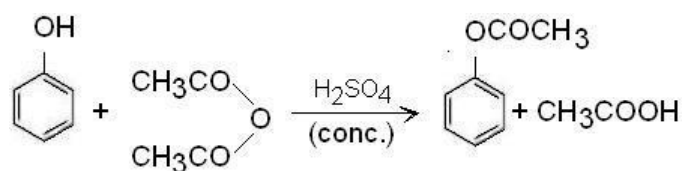
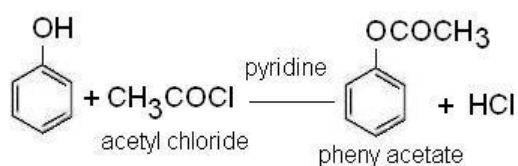
vii) Reaction of $-\text{OH}$ group

- i. Reaction with FeCl_3 is the test of phenol

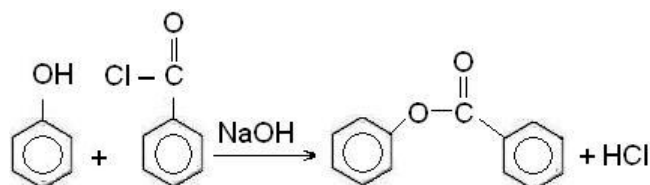


$(\text{C}_6\text{H}_5\text{O})_3\text{Fe}$: Ferric phenoxide (violet complex)

ii. Ester formation

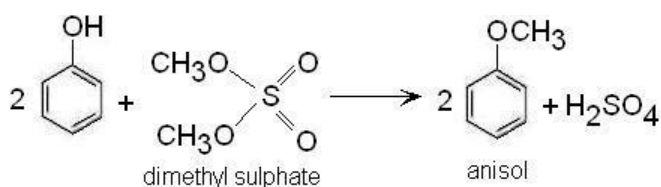
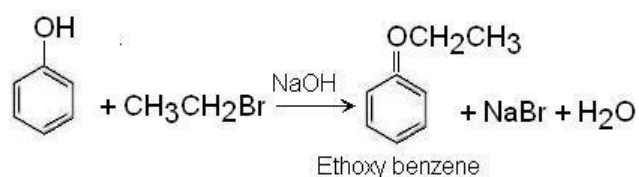


Reaction with benzoyl chloride is known as benzylation

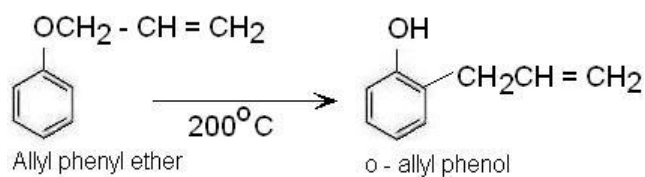


Benzylation of alcohols or phenols in presence of NaOH is called Schotten-Baumann reaction.

iii. Ether formation

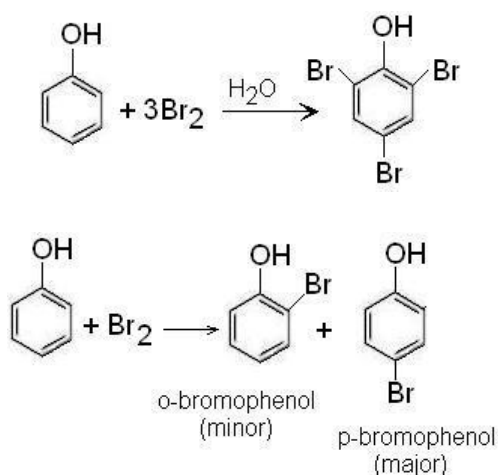


- Claisen rearrangement



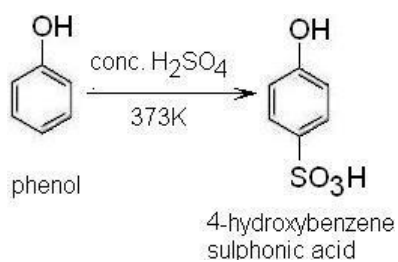
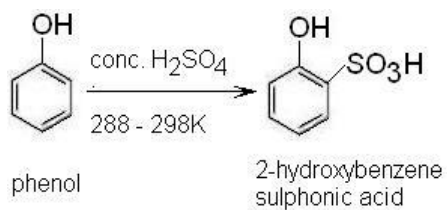
(B) Electrophilic aromatic substitution reaction

1. Halogenation

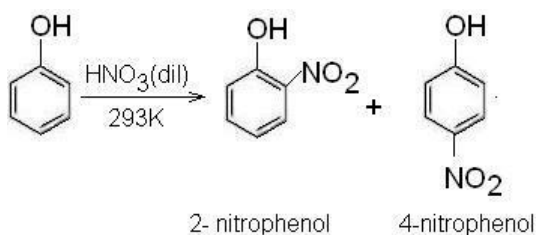


Due to steric hindrance at ortho position, para-product predominates

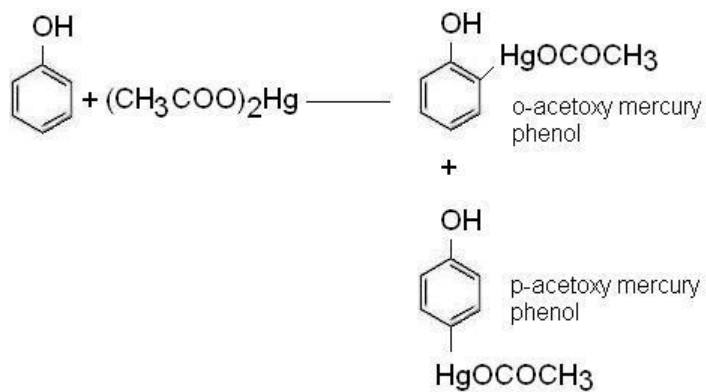
2. Sulphonation



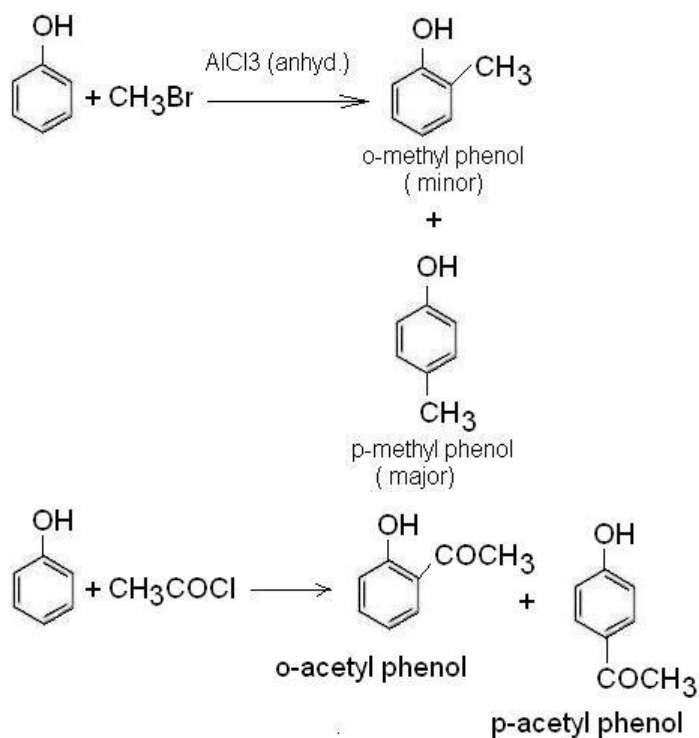
3. Nitration



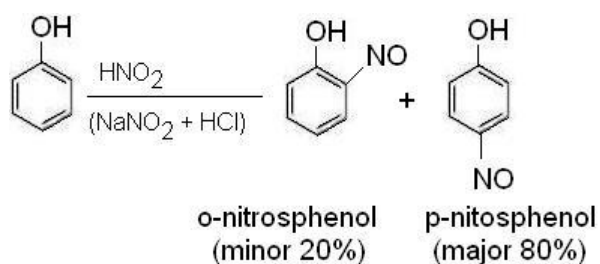
4. Mercuration



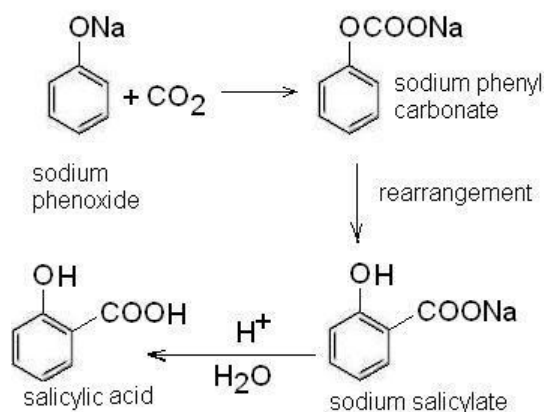
5. Friedel crafts alkylation and acylation



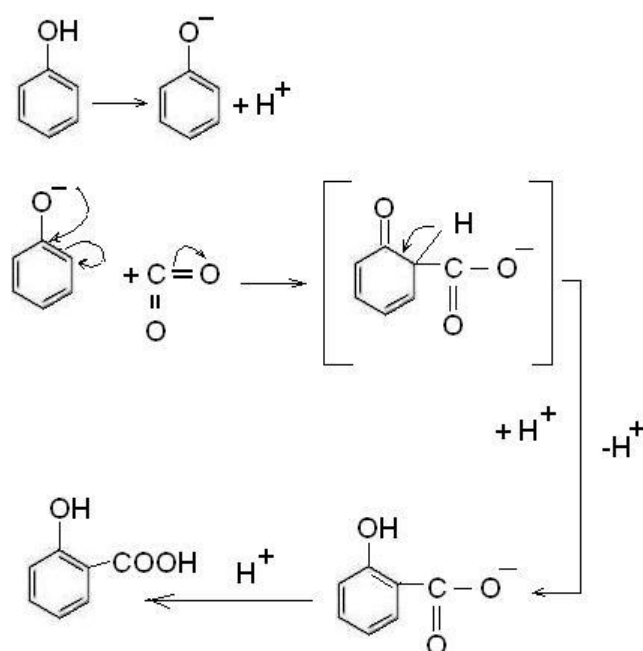
6. Nitrosation



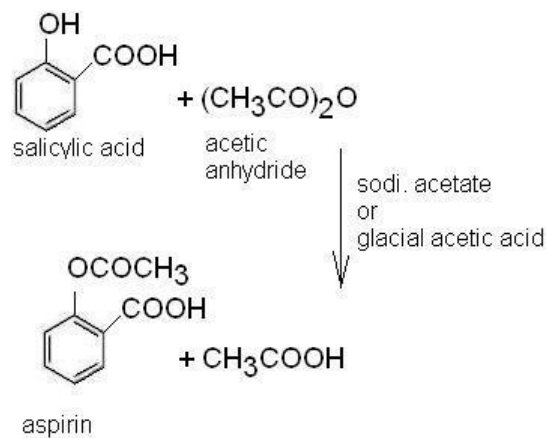
7. Kolbe's reaction



Mechanism

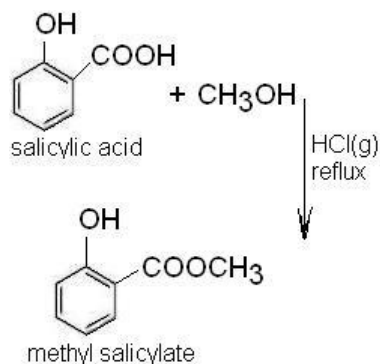


(a) Acetyl salicylic acid (Aspirin)



It is a white solid (m.pt. 408K) and is used for relieving pain (analgesic) and to bring down the body temperature (antipyretic during fever)

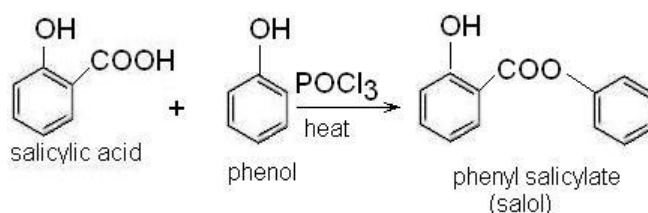
(b) Methyl salicylate



It is an oily liquid (b.pt. 495K) with pleasant odour (oil of wintergreen) used in perfumery and flavouring agent.

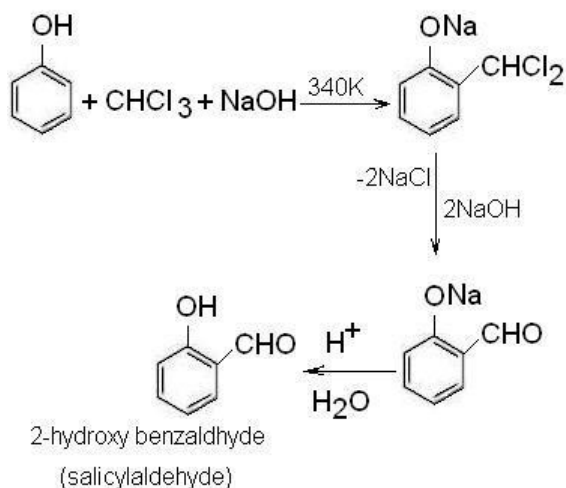
It is also used in medicine in the treatment of rheumatic pain and as a remedy for aches, sprains and bruises.

(c) phenyl salicylate (salol)



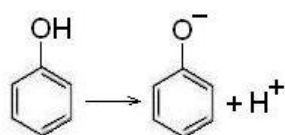
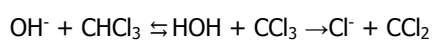
It is white solid (m.pt 316K) and is used as an intestinal antiseptic.

8. Reimer-Tiemann reaction

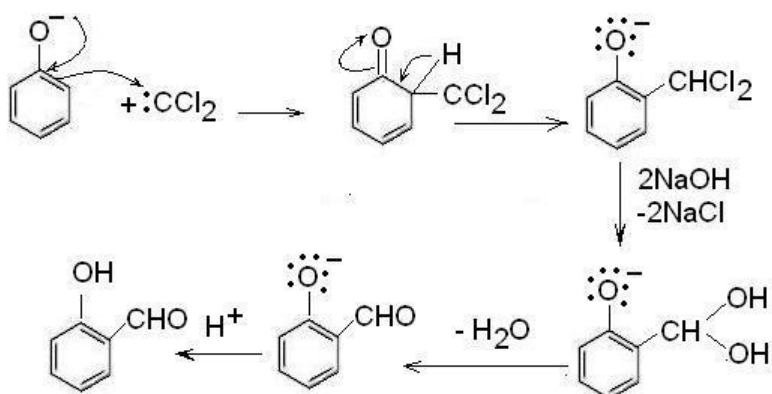


Mechanism

The electrophile, dichloromethylene CCl₂ is generated from chloroform by action of base

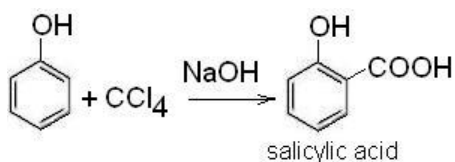


Attack of electrophile (:CCl_2) on phenoxide ion



Salicylaldehyde

If the reaction is carried out with carbon tetrachloride (CCl_4) instead of chloroform, o-hydroxy benzoic acid (salicylic acid) is formed.



TESTS TO DISTINGUISH BETWEEN ALCOHOLS AND PHENOLS

1. Litmus test

Phenol turns blue litmus red being acidic in nature but alcohol do not.

2. Ferric chloride test

Phenol react with neutral ferric chloride solution to form violet or green coloured solution where as alcohol do not undergo such reactions.

3. Bromine water test

Aqueous solution of phenol forms white precipitate of 2,4,6-tribromo phenol, when treated with bromine water. However alcohol so not give such precipitation.