Phenols

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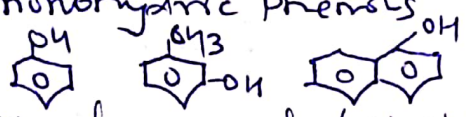
Aromatic hydroxy compounds are called phenols. Phenols are compounds containing one or more hydroxyl groups directly linked to the aromatic nucleus.

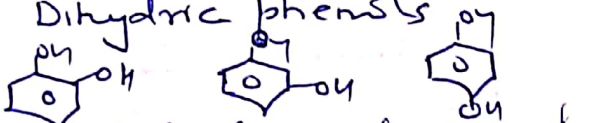
Phenols are termed as monohydric, dihydric, trihydric etc according to the no. of hydroxyl group linked to the nucleus.

Monohydric phenols



Phenol m-cresol α-Naphthol

Dihydric phenols

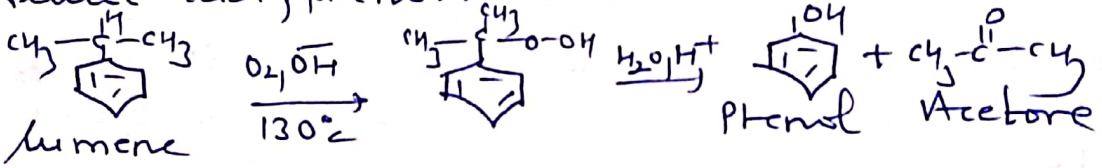


Catechol Resorcinol Quinol

Preparations

1) From cumene

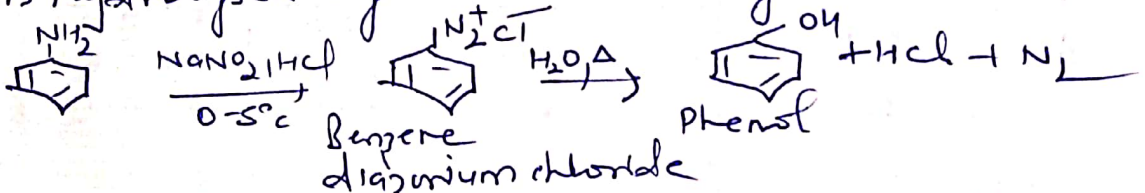
Cumene is isopropyl benzene, it is oxidized to cumene hydroperoxide by oxygen in the presence of alkali. When this compound is decomposed with dilute acid, phenol & acetone are formed.



Cumene Phenol Acetone

2) From benzene diazonium salts

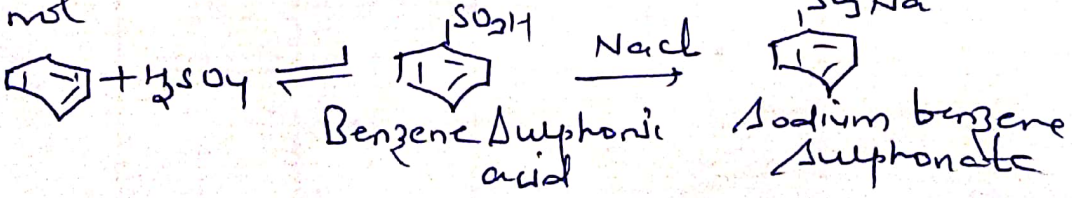
Phenols are produced when diazonium salt solution is hydrolysed by acidified boiling water



Benzene diazonium chloride

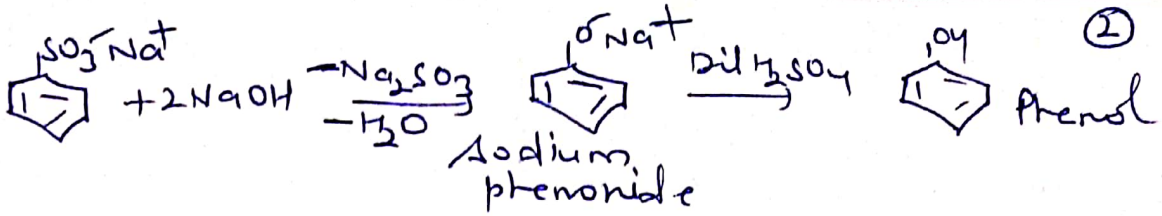
3) From benzene sulphonic acids

Benzene sulphonic acid is prepared by heating benzene with conc. H_2SO_4. After it, NaCl is added to the reaction mixture & sodium benzene sulphonate separates out. Dry benzenesulphonate is then mixed with NaOH & the mixture is heated at 300-350°C. Sodium phenoxide is formed which on acidification with cold dil H_2SO_4 forms phenol



Benzene Sulphonic acid

Sodium benzene Sulphonate



Electrophilic Substitution Reactions of Phenols

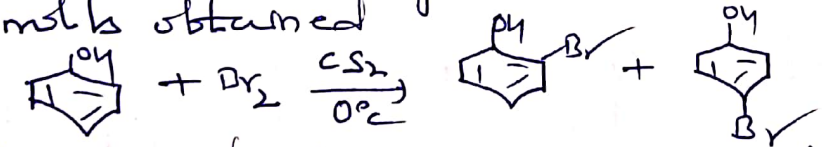
Phenol give electrophilic aromatic substitution reactions due to the benzene ring.

-OH is ortho, para directing group due to presence of lone pair on oxygen atom. -OH group is strongly activating group for aromatic Electrophilic Substitution reaction. Phenol undergoes electrophilic substitution reactions much more readily as compare to benzene

1 Halogenation

Phenol reacts with Bromine Water in aqueous medium to give 2,4,6-tribromophenol. Phenol similarly forms 2,4,6-trichlorophenol with chlorine Water.

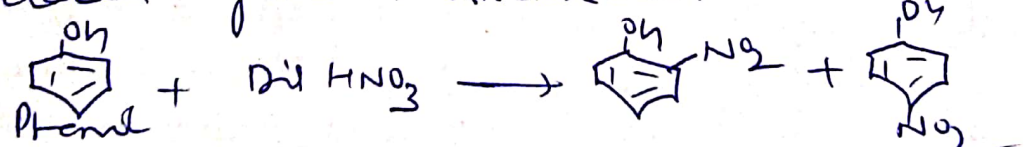
In non-polar solvents (such as CS_2, CCl_4, $CHCl_3$) the substitution is regulated and monobromo phenol is obtained

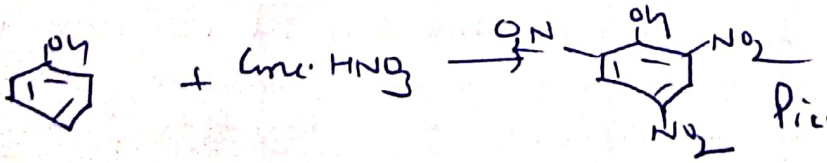


→ In presence of a polar solvent, phenol gets ionized to form phenoxide which is more activating thus trisubstitution occurs.

2 Nitration

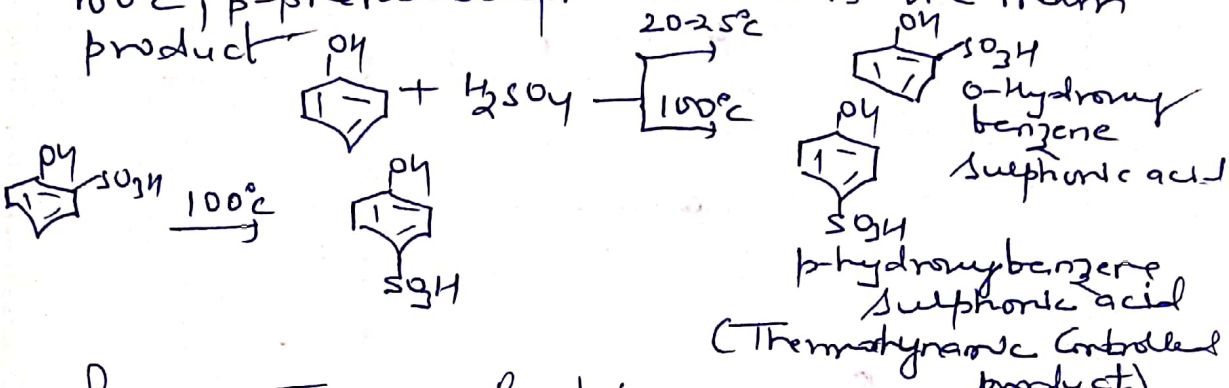
Phenol forms o- and p-nitrophenols with cold dil HNO_3 at room temperature, the former can be seperated by Steam distillation.





3 Sulphonation

When phenol is treated with conc. H_2SO_4 at 20°C, o-phenol sulphonic acid is the main product, At 100°C, p-phenol sulphonic acid is the main product

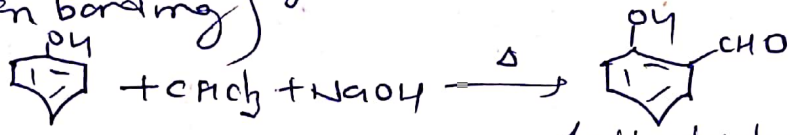


(Thermodynamic Controlled product)

4 Reimer–Tiemann Reaction

When phenol is treated with chloroform and aqueous solution of sodium hydroxide followed by acidification o-hydroxy benzaldehyde is formed

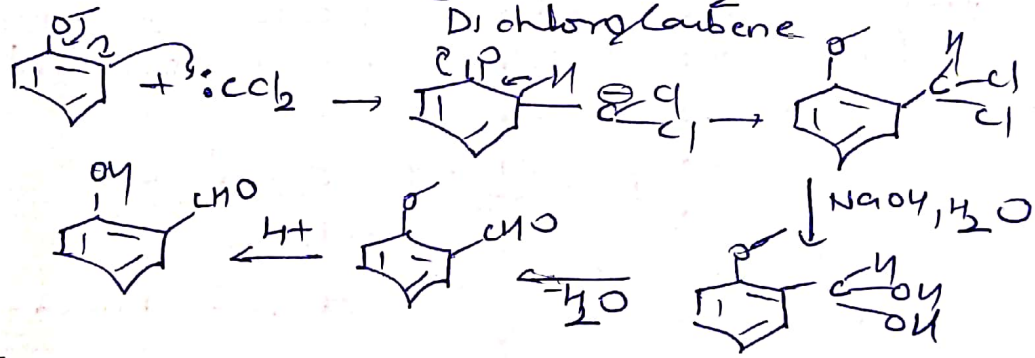
(Ortho pdt is stablized by intramolecular hydrogen bonding)



mechanism

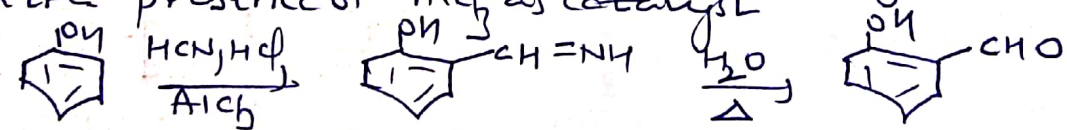
1) $CHCl_3 + OH^- \rightarrow \ominus CCl_3 \xrightarrow{-Cl^-} :CCl_2$

Dichlorocarbene

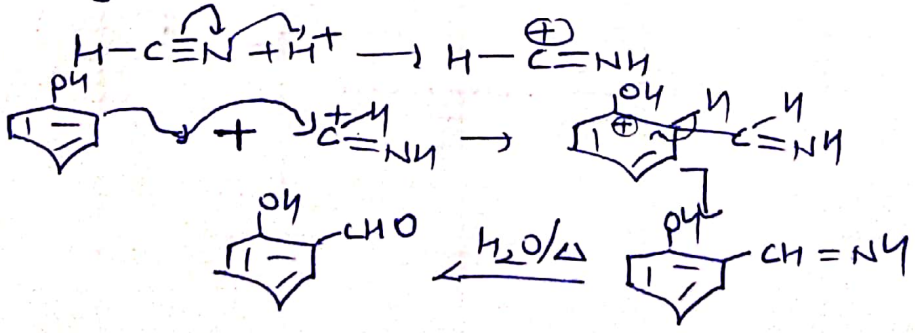


5 Gatterman Aldehyde Synthesis

Formylation of Aromatic Compound by HCN/HCl in the presence of $AlCl_3$ as catalyst

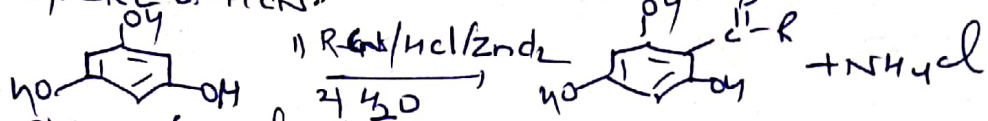


mechanism

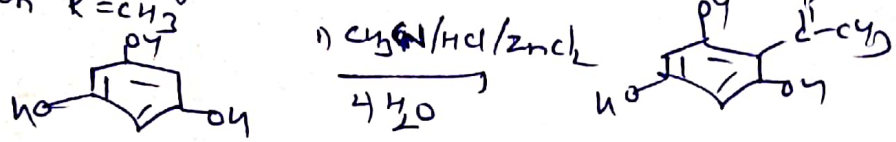


6 Houben–Hoesch Reaction

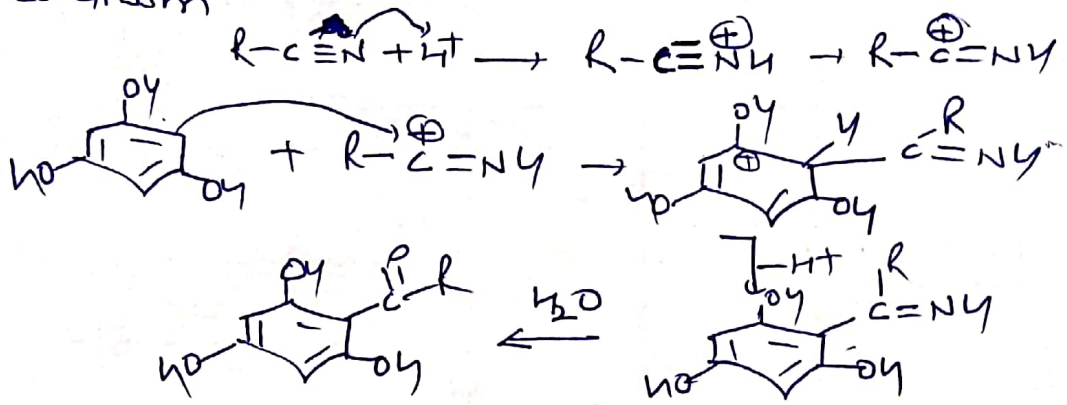
This reaction is an extension of Gatterman aldehyde synthesis. In this reaction, alkyl cyanide is used in the place of HCN.



When R = CH_3

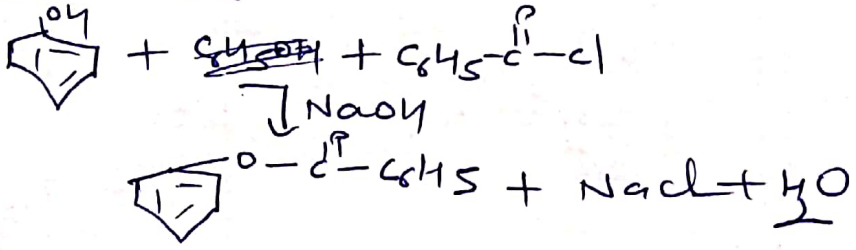


mechanism

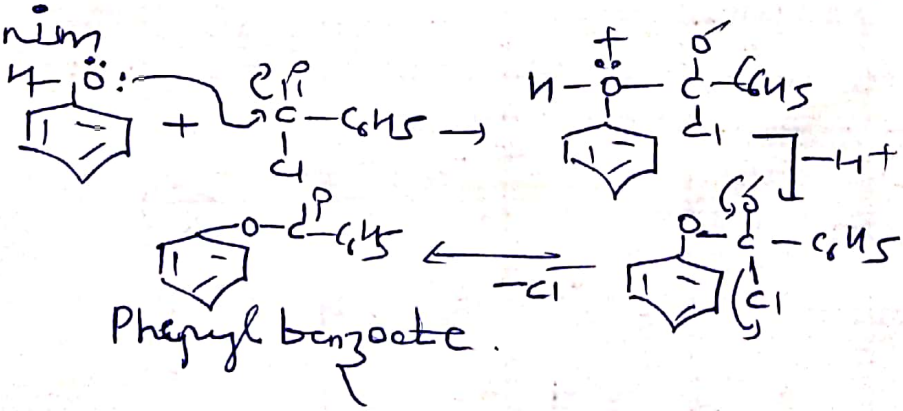


7 Schotten–Baumann Reaction

Phenols react with acid chlorides/anhydrides to form phenyl ester. This rxn occurs in the presence of base

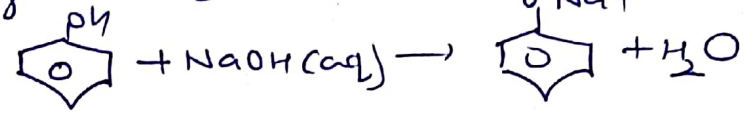


mechanism

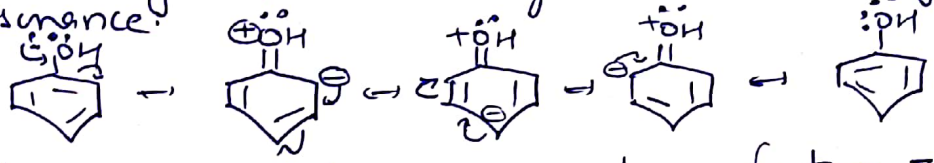


Acidity of Phenols

Phenols are weakly acidic in nature (pKa = 10). They are however more acidic than aliphatic hydroxy compounds i.e. alcohols but less acidic than carboxylic acids.

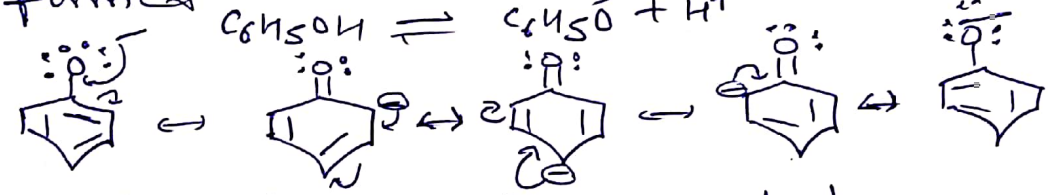


The acidity of phenol may be explained by resonance.



1) Due to resonance, the oxygen atom of the -OH group acquires a positive charge and the oxygen atom acquires or attract bonding pair of electron of the -OH group. As a result, the tendency of hydrogen atom to dissociate as proton increases.

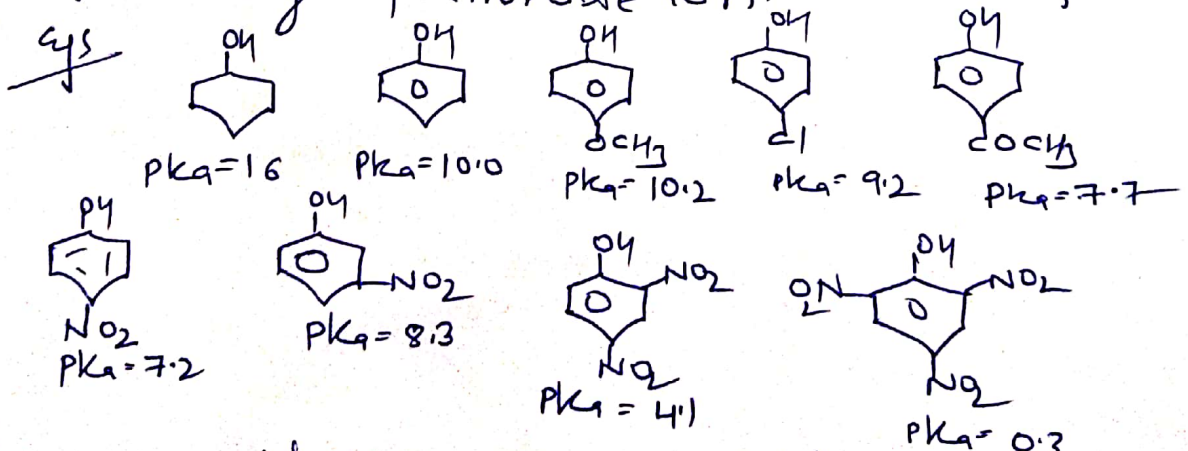
11) When phenol ionizes, the phenoxide ion is formed



Resonating structures of phenoxide ion are monopolar and therefore more stable than those of phenol.

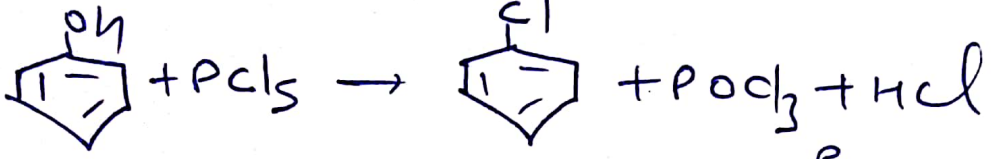
Acidity of substituted phenols is found to be dependent on the nature of substituents. An electron withdrawing group on the phenol is acid strengthening as it will stabilize the resulting phenoxide ion.

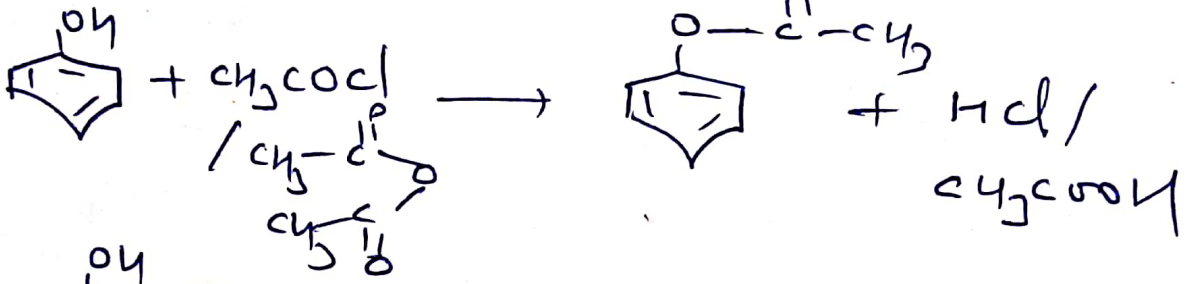
eg:

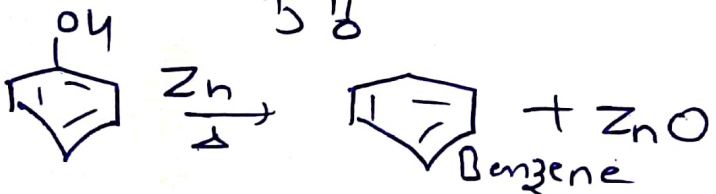


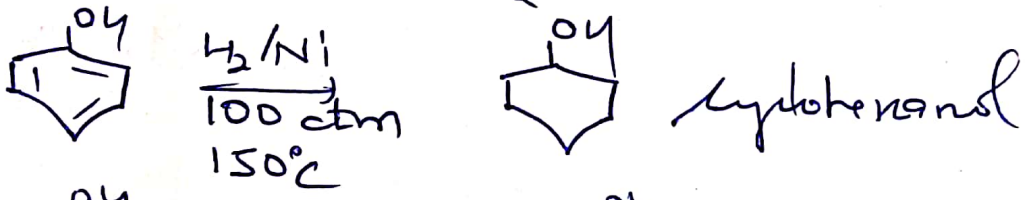
(less pKa, more acidity)

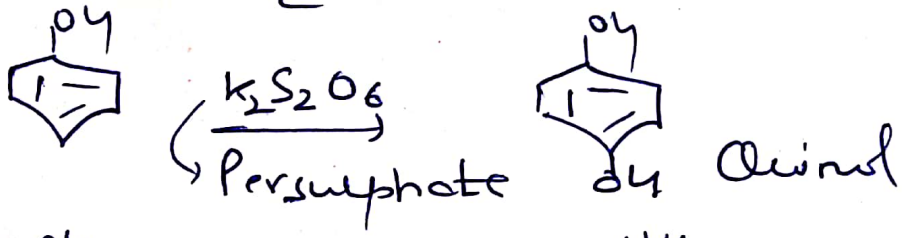
Reactions of –OH group

1) 

2) 

3) 

4) 

5) 

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