

Phenols

Phenols are Compounds Containing an -OH group attached directly to an aromatic ring.

In organic chemistry Phenols Sometimes Called Phenolics. The Simplest of the class is Phenol, which is also Carboxylic acid (C_6H_5OH). Phenolic Compounds are classified as simple Phenols or Polyphenols based on the number of Phenol units in the molecule.

Synonyms are arnols or aryl alcohol.

Phenolic Compounds are synthesized industrially, they also produced by plants and micro organism.

Although Similar to alcohols, Phenols have unique Properties and are not classified as alcohols (since the hydroxyl group is not bonded to a saturated Carbon atom). They have higher acidity due to the aromatic ring's tight coupling with the oxygen and relatively loose bonds between the oxygen and hydrogen. The acidity of the hydroxyl group in Phenols is commonly intermediate between that of aliphatic alcohols and Carboxylic acids. Their pK_a is usually between 10 and 12.

Loss of a Positive hydrogen ion (H^+) from the hydroxyl gp. of a Phenol forms a corresponding negative Phenolate ion or Phenoxide ion and the corresponding salts are called Phenolates or Phenoxides. Although the term aryloxides is preferred according to IUPAC.

Phenols can have two or more hydroxyl gp bonded to the aromatic ring in the same molecule. The simplest examples are the benzene diols, each having two hydroxy gps on a benzene ring.

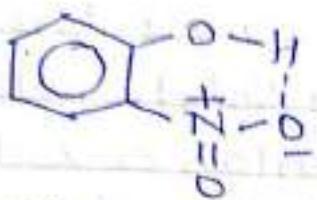
Physical Properties of Phenols - most pure Phenols are colorless liquids or solids, although they are often found to contain a red tint owing to the presence of oxidation products.

- ② Phenols have a characteristic Carbolic odour which in case of Phenol itself is highly toxic.
- 3. The boiling Points of Phenol are higher than all phatic Alcohols of comparable molecular weight. This is due to stronger intramolecular hydrogen bonding in Phenols relatively to alcohols.

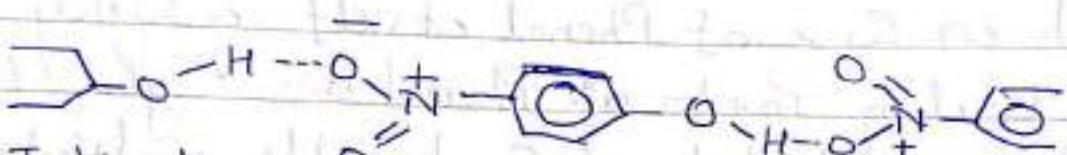
The introduction of a hydroxy group into an already substituted aromatic ring, especially in the para position, to methyl, halogen or nitro group, produces a marked increase in the boiling point.

Compound	m.p. ^o C	b.p. ^o C
Phenol	42°	181
Nitrobenzene	5.5	210
O-nitroPhenol	45	217
m-nitroPhenol	96	-
P-nitroPhenol	114	245

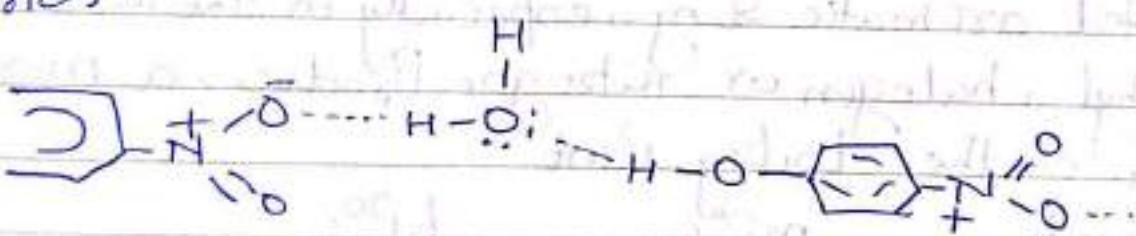
The greater volatility of the ortho isomer is due to intramolecular hydrogen bonding whereas the higher boiling point of the para isomer is due to intermolecular hydrogen bonding.



Intramolecular
hydrogen bonding
in o-nitroPhenol.

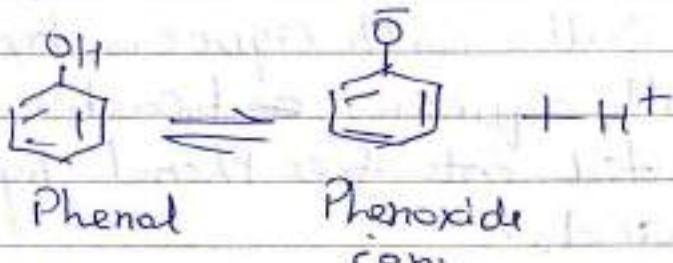


Intermolecular hydrogen bonding in p-nitrophenol
p-nitrophenol is more soluble in water than o-nitrophenol. This is because p-nitrophenol can associate with itself and also with water molecules. o-nitrophenol cannot form intramolecular hydrogen bonds.

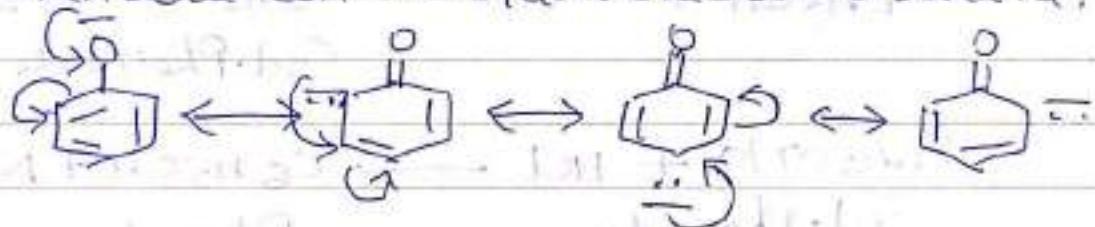


Intermolecular hydrogen bonding between
water & p-nitrophenol.

Acidity of Phenols → Phenols are much more acidic than alcohols but less so than carboxylic acids or even carbonic acid. Phenols are acidic due to the formation of stable phenoxide ions in aqueous solutions. e.g. Phenol itself gives Phenoxide ion on dissociation.

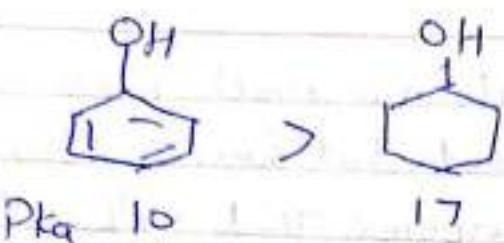


The Phenoxide ion is stable due to resonance.



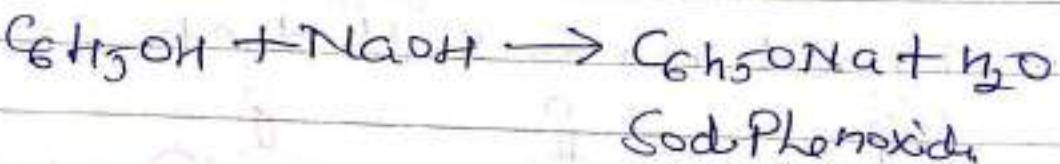
The negative charge is spread throughout the benzene ring and thereby effectively dispersed. This charge delocalization is a stabilizing factor in the Phenoxide ion. No resonance is possible in alkoxide ions (RO^-) derived from alcohols. The negative charge is concentrated (localized) on a single oxygen atom. Consequently, alcohols are much weaker acids than Phenols. e.g.

pKa of Phenol is 10, but that of cyclohexanol is about 17. Thus Phenol is 10^7 times more acidic than cyclohexanol.

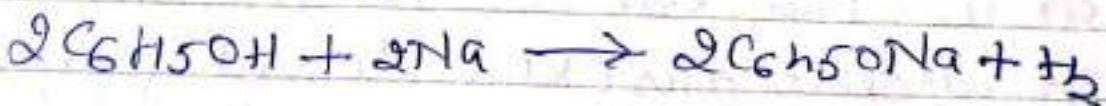


Phenol is more acidic than cyclohexanol.

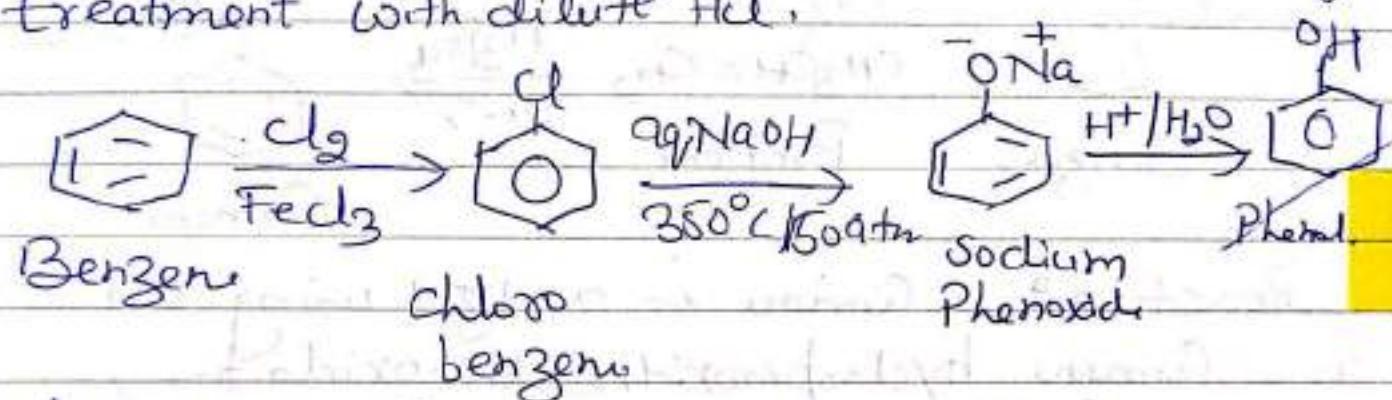
They form salts with aqueous hydroxide but not with aqueous ~~or~~ bicarbonate. The salts are converted into free Phenol by aqueous mineral acids.



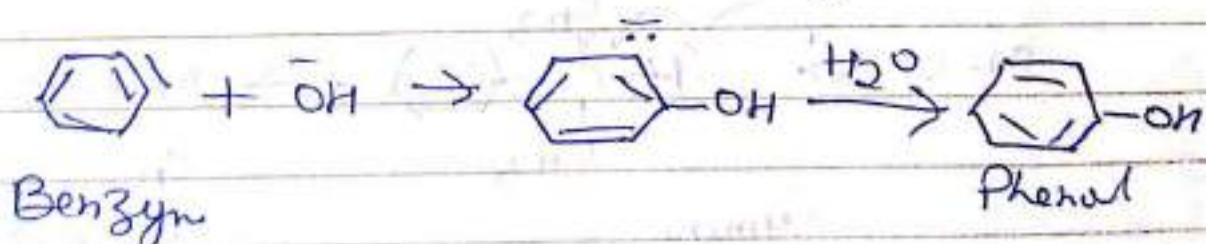
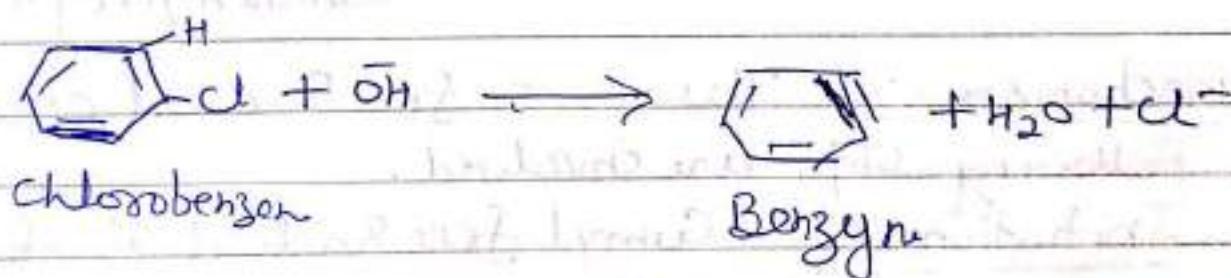
As in the case of alcohol, Phenol, react with Sodium metal to give hydrogen gas producing Sodium Phenoxide.



Preparation → Phenol is obtained by the following methods. First introduced in 1928 by the Dow Chemical Company U.S.A. from Chlorobenzene (Dow Process) This involves the hydrolysis of chlorobenzene with aqueous NaOH at high temperature and pressure followed by treatment with dilute HCl.

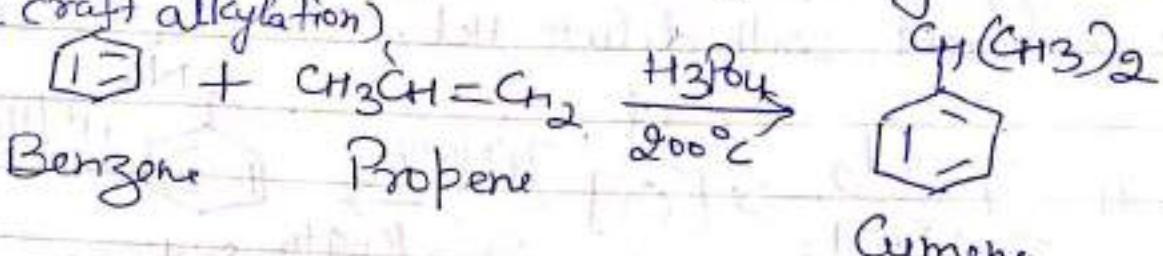


Mechanism → The base catalyzed hydrolysis of chlorobenzene follows the following elimination-addition mechanism.

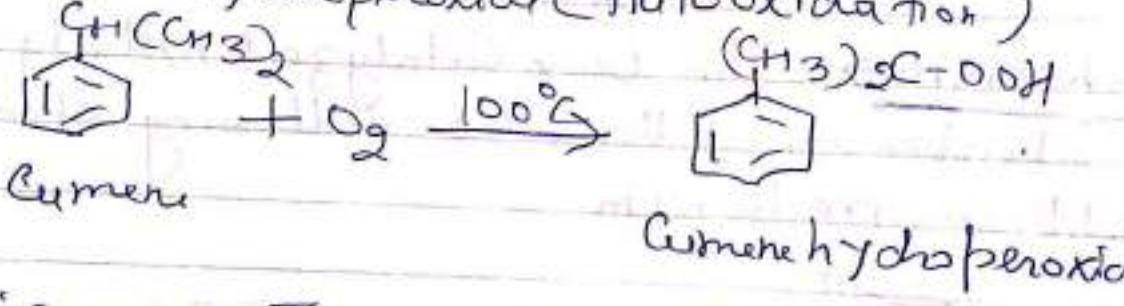


From Cumene - (Cumene Process) This involves three reactions.

Reaction 1 - Benzene is treated with propene in the presence of H_3PO_4 or H_2SO_4 to form Cumene. This is Friedel-Crafts alkylation reaction (Friedel-Crafts alkylation).



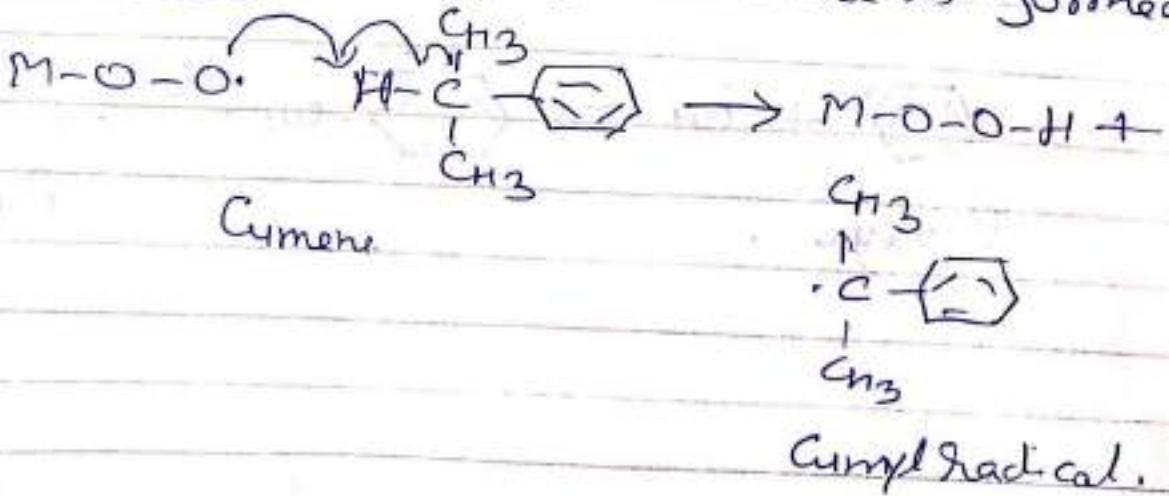
Reaction 2:- Cumene is oxidized using air to give Cumene hydroperoxide (autooxidation)



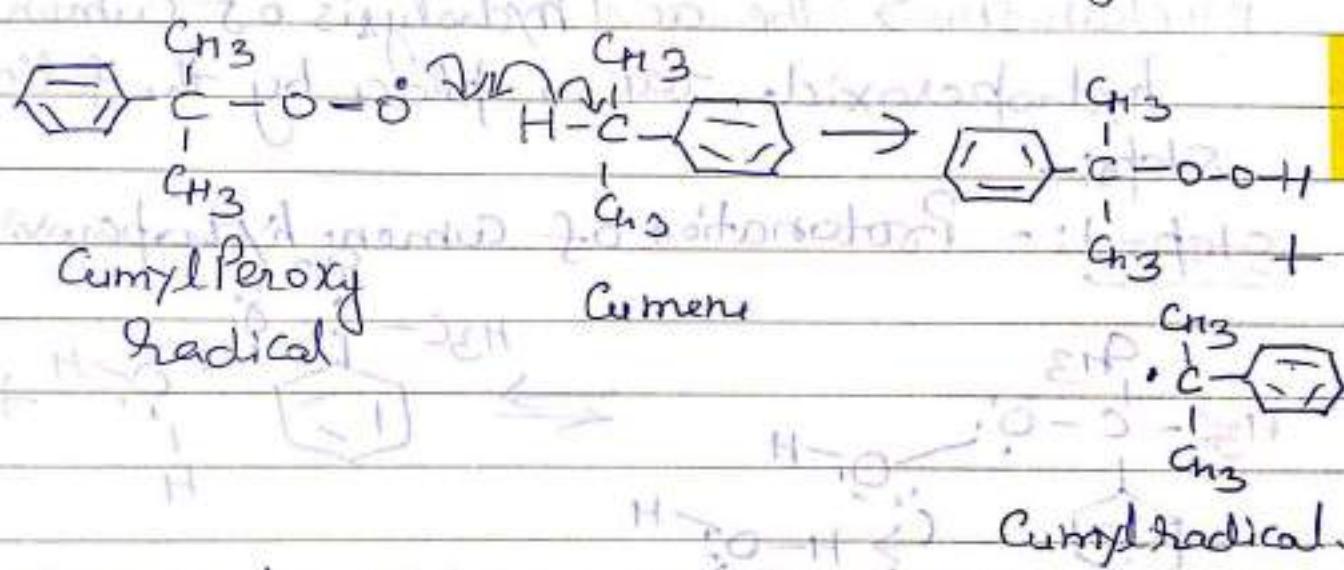
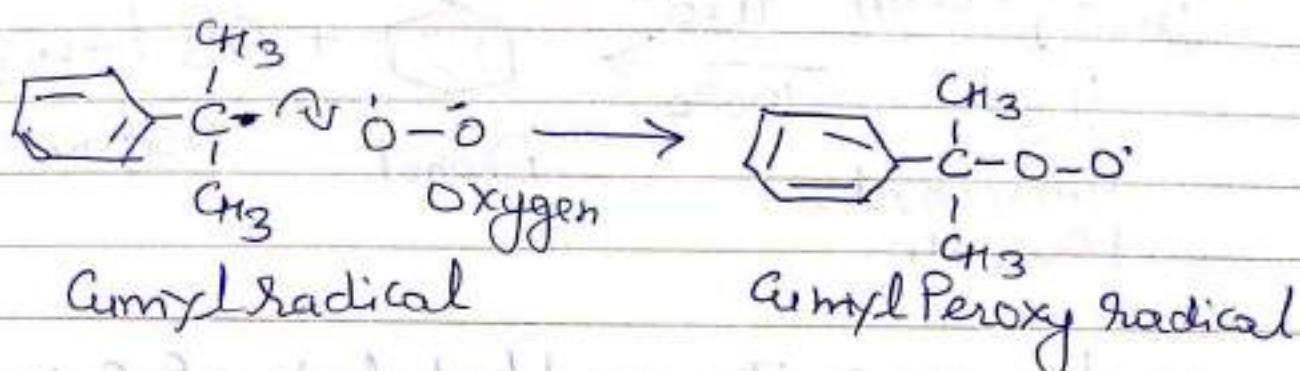
Mechanism → This is a free radical chain reaction.
Following steps are involved.

Training steps are showed.

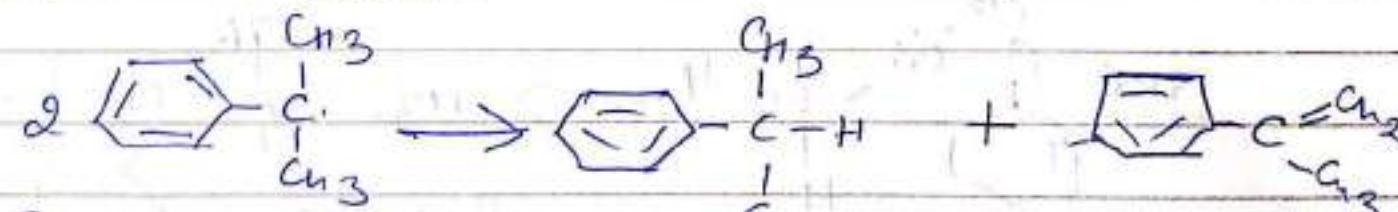
Initiation Step: Cumyl free radical is formed.



Propagation Step \rightarrow Cumyl radical Propagates the chain, Cumene hydroperoxide is formed.

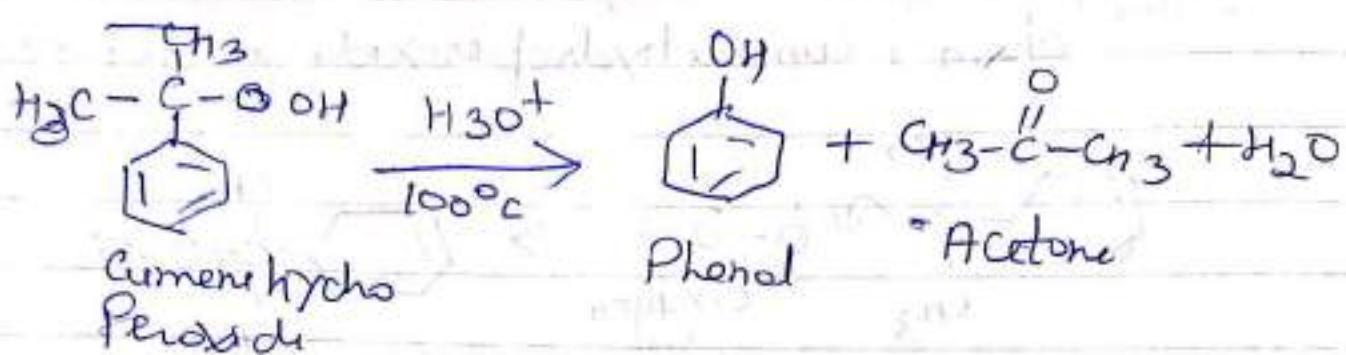


Termination Steps → Any two free radicals can combine. Only one of many possible termination reactions is shown.



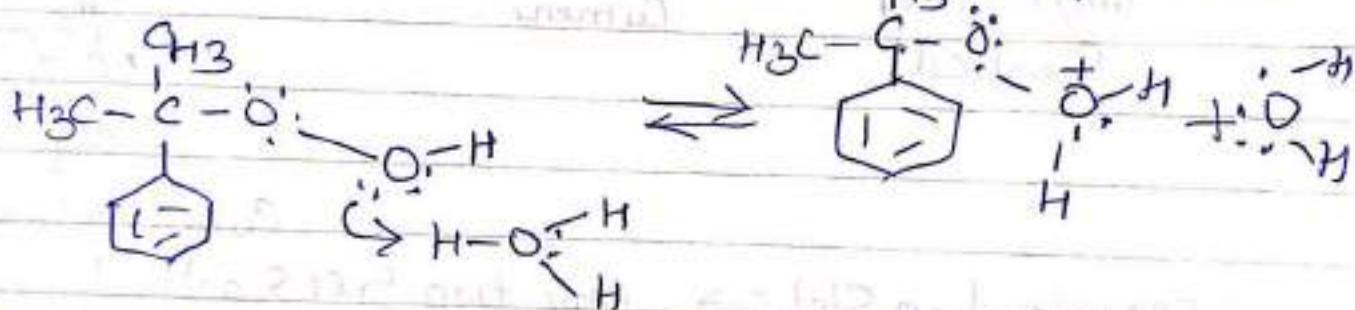
Reaction 3 Cimene h, C_3

Hydroperoxide is treated with dilute HCl to yield Phenol and acetone.

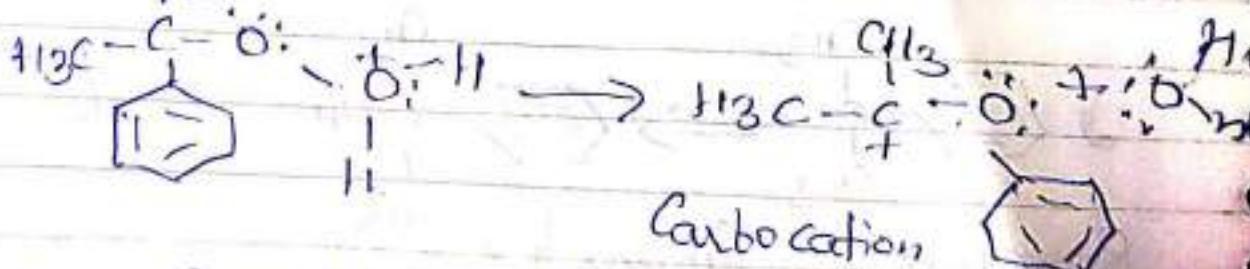


Mechanism → The acid hydrolysis of Cumene hydroperoxide takes place by the following steps:

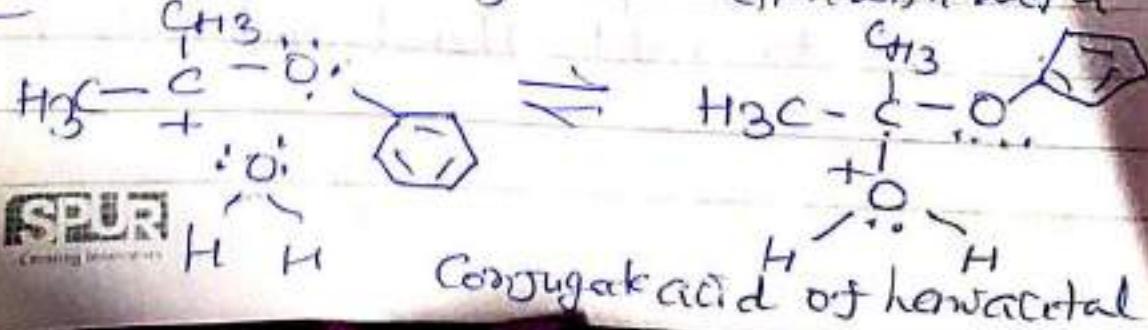
Step-1:- Protonation of Cumene hydroperoxide



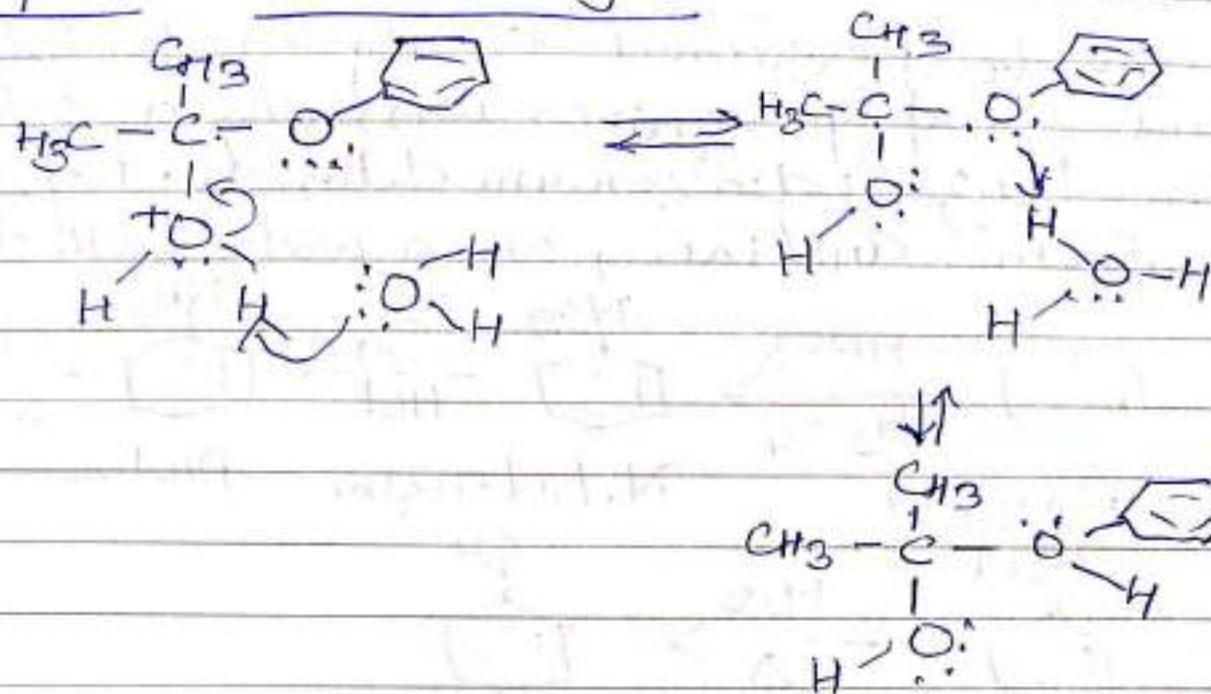
Step-2:- Migration of the Phenyl gp. to form a Carbocation.



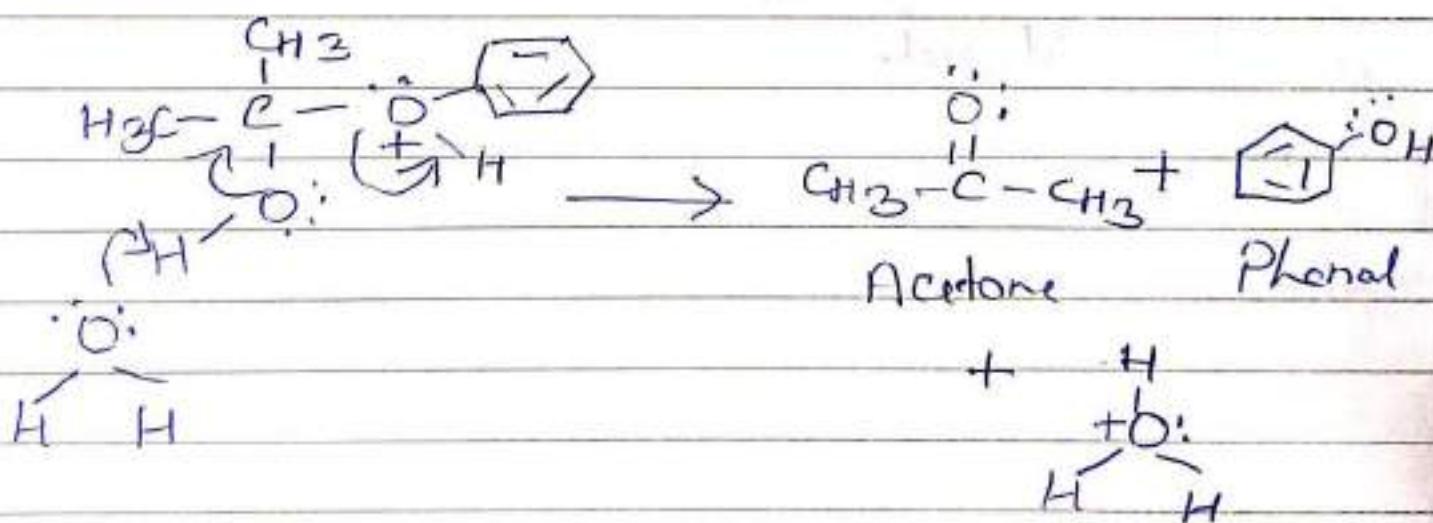
Step-3 - Reaction of Carbocation with water



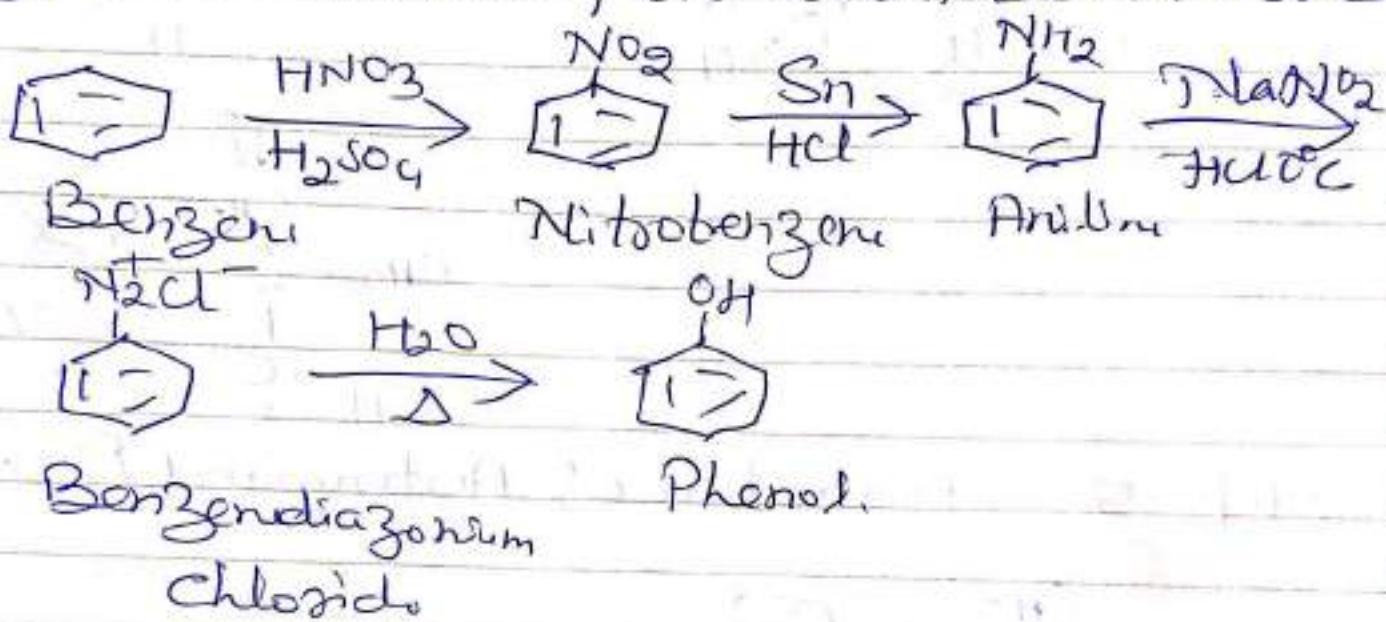
Step-4 - Proton transfer



Step-5 - Formation of Acetone and Phenol.

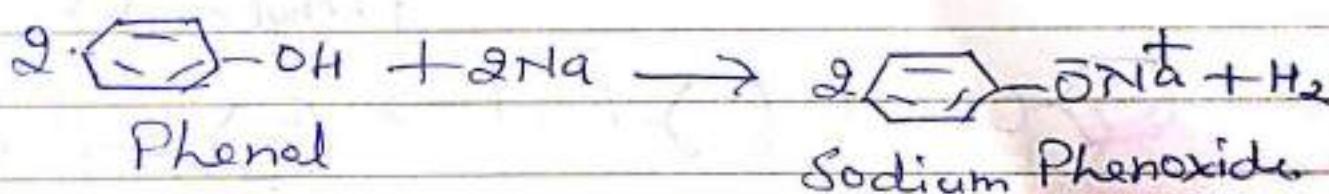
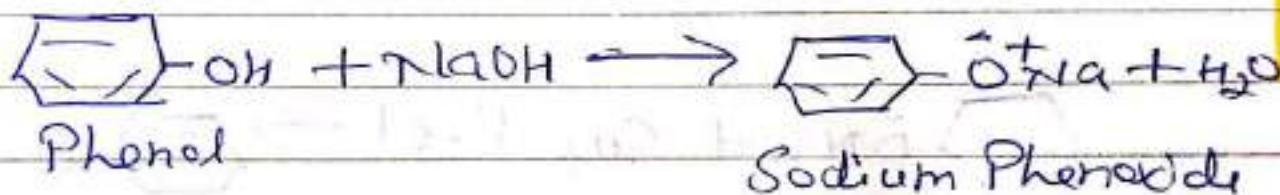


From Benzene diazonium Salts → This reaction can be performed easily in the laboratory and simply requires warming a solution of benzene diazonium chloride, prepared from Aniline, on a water bath at 50°C .

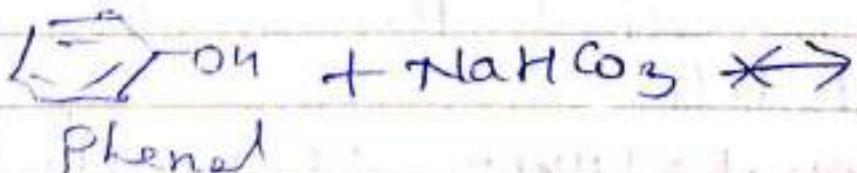
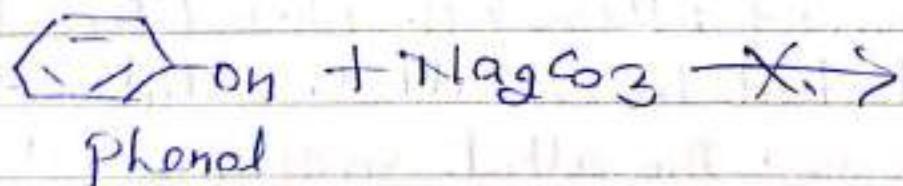


Properties → (Chemical) The reactions of Phenol are the reactions of the -OH group and the benzene ring.

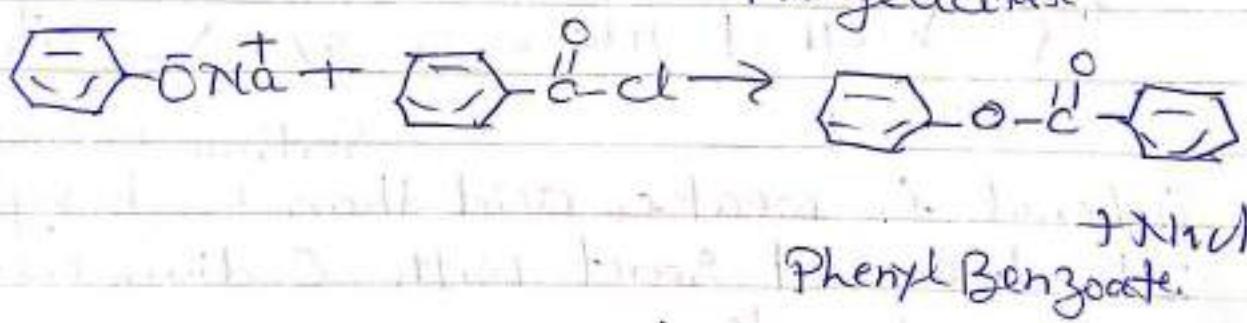
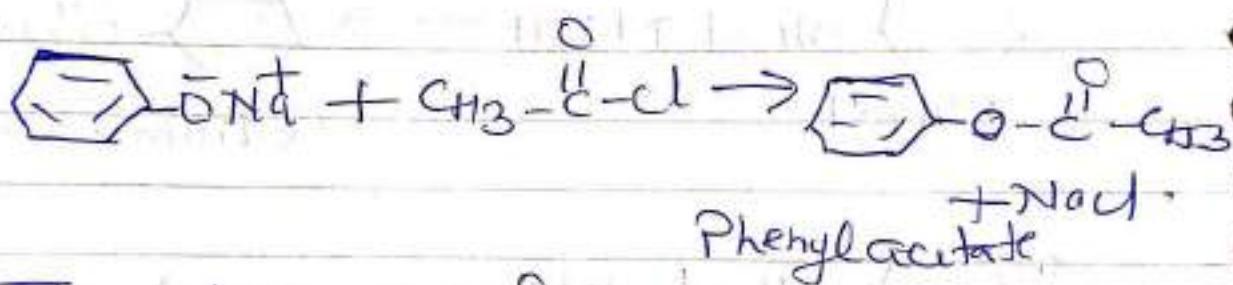
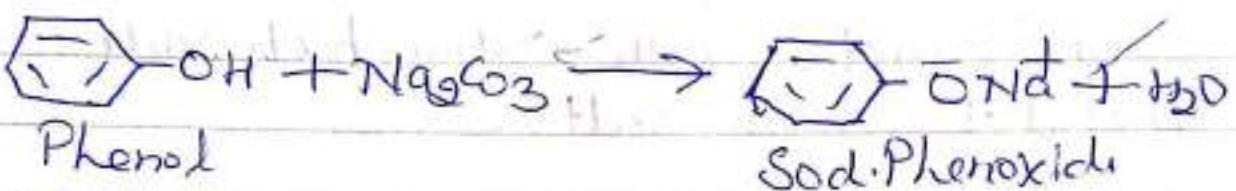
① Formation of Salts → Phenol is acidic.
It reacts with Sodium hydroxide or Sodium metal to form salts.



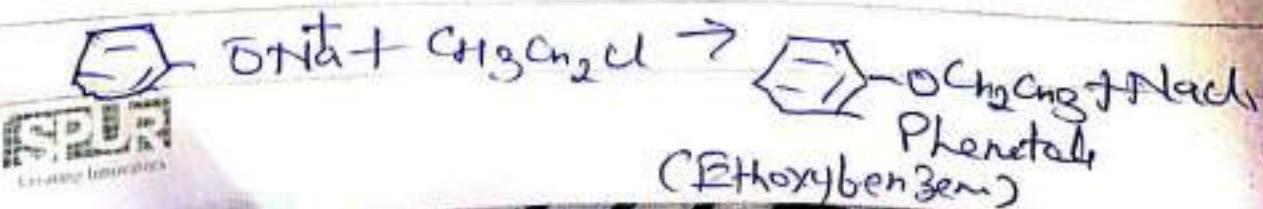
Phenol is weaker acid than carboxylic acids.
It does not react with sodium carbonate or bicarbonate.



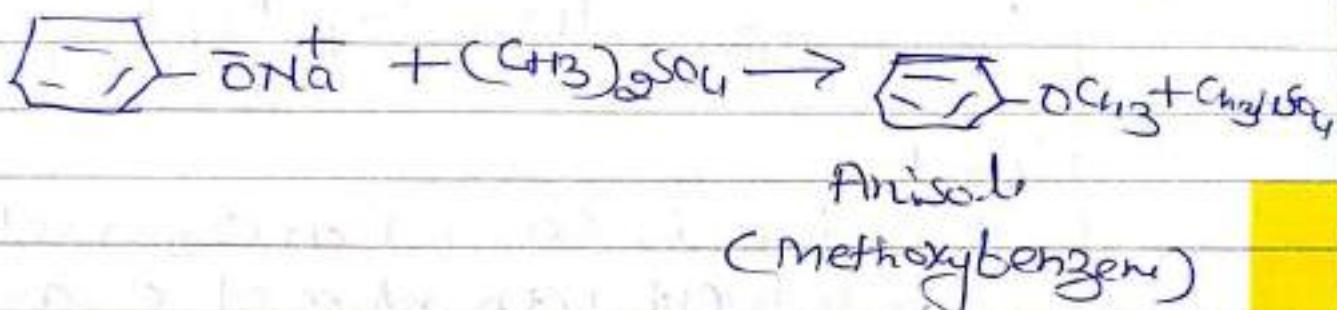
Formation of Esters \rightarrow Phenol reacts with acid chlorides in aqueous alkali solution to give Phenyl esters. The alkali first forms the Phenoxyde ion which then reacts with acid chloride.



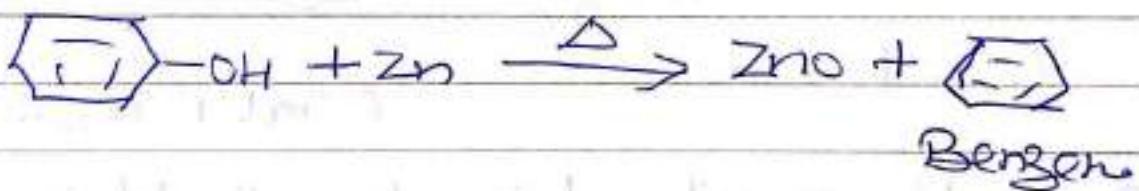
Formation of Ethers \Rightarrow (1) Phenol reacts with alkyl halides in alkali solution to form Phenyl ethers. The alkali first forms the phenoxide ion which then reacts with the alkyl halide.



⑪ Phenol reacts with dimethyl sulfate in alkali solution to form anisole (methoxy benzene)

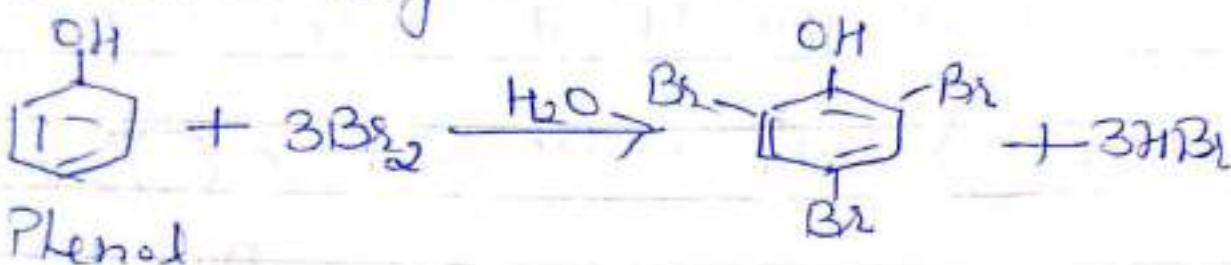


Reaction with Zinc dust \rightarrow When Phenol is distilled with Zinc dust, low yield of benzene is obtained.

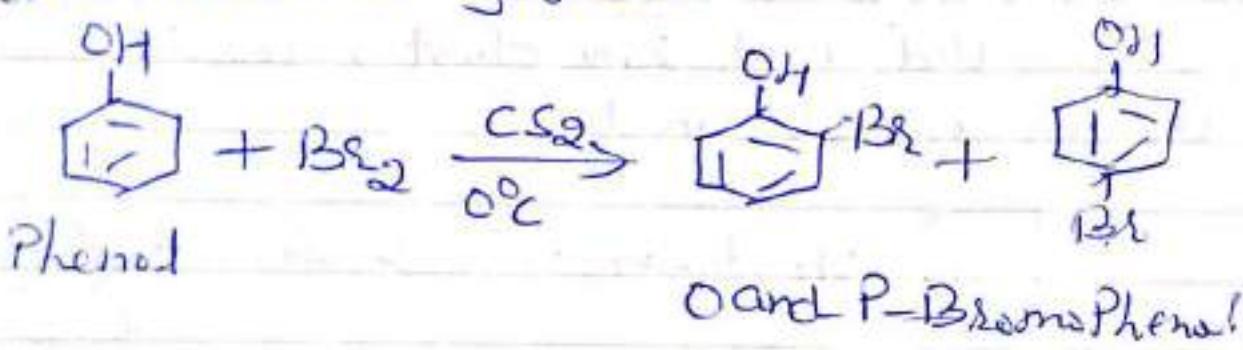


Reactions of Benzene Ring \rightarrow Phenol under goes electrophilic substitution reactions much more readily as compared to benzene ring. The reaction condition used for monosubstitution in Benzene ring give to substitution with Phenol. By moderating the reaction conditions, however we can obtain the monosubstitution product. The $-\text{OH}$ group in Phenol is an α -P director and activator.

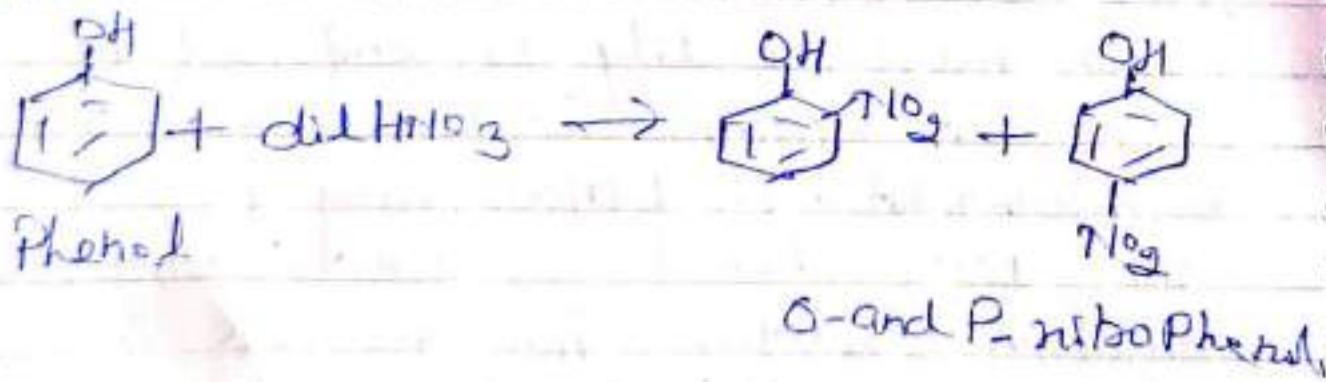
Halogenation → Phenol reacts with bromine water (aqueous bromine) to give precipitate of 2,4,6-tribromoPhenol. chlorine reacts in the same way.



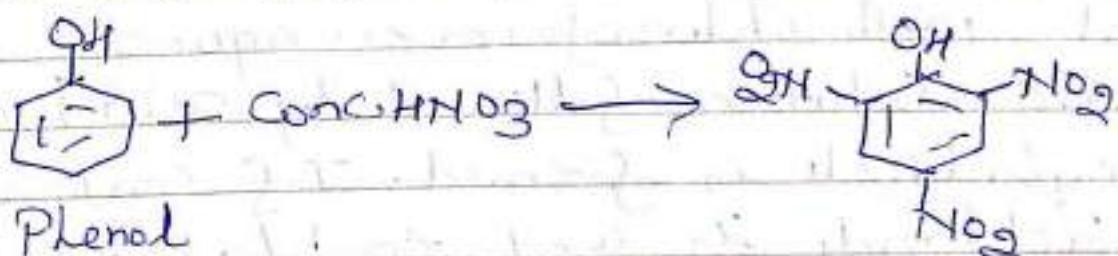
If the reaction is carried in CS_2 or CCl_4 (non polar solvent) a mixture of O-and P-bromoPhenol is formed.



Nitration → Phenol reacts with dilute nitric acid to give a mixture of O-and P-nitro Phenol.

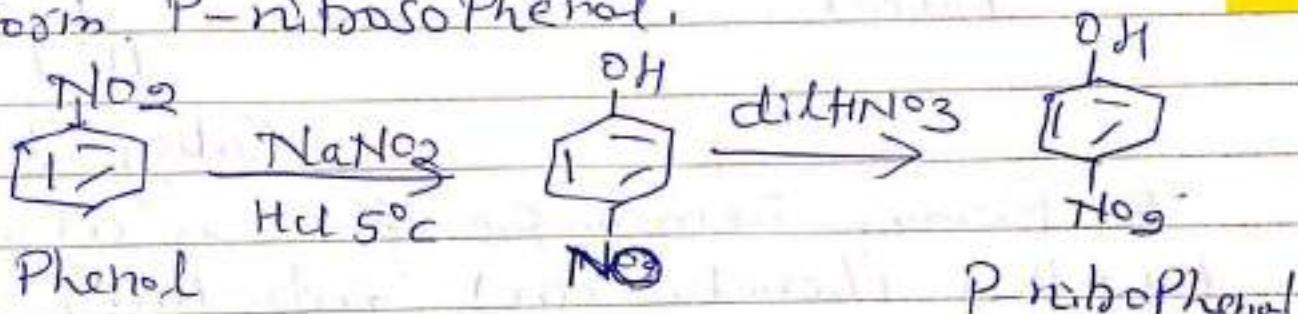


with Conc. nitric acid Picric acid is formed



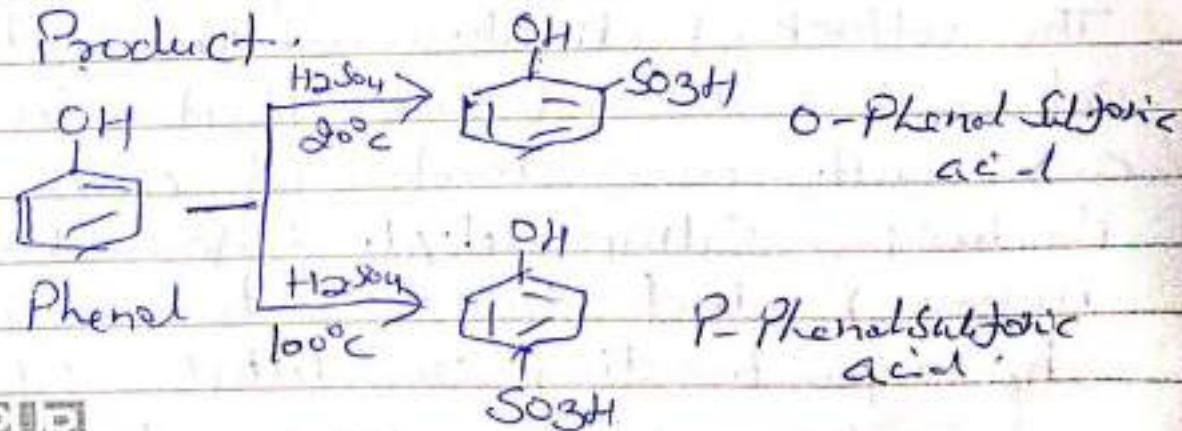
Picric acid (2,4,6-trinitrophenol)

Nitrosation Phenol reacts with nitrous acid (obtained from NaNO_2/HCl at 5°C) to form P-nitroso Phenol.

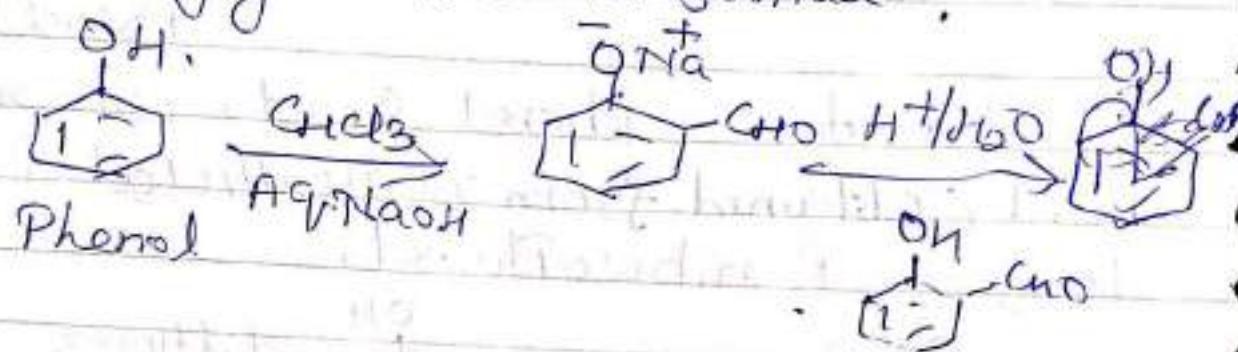


P-nitroso Phenol on oxidation with dilute nitric acid gives P-nitro Phenol.

Sulfonation → When Phenol is treated with Conc. Sulfuric acid at 20°C O-Phenol Sulfonic acid is the main Product At 100°C P-Phenol Sulfonic acid is the main Product.



Reimer-Tiemann Reaction → The treatment of Phenol with chloroform in aqueous sodium hydroxide solution followed by acid hydrolysis Salicylaldehyde is formed. If carbon tetrachloride is used in place of chloroform, salicylic acid is formed.



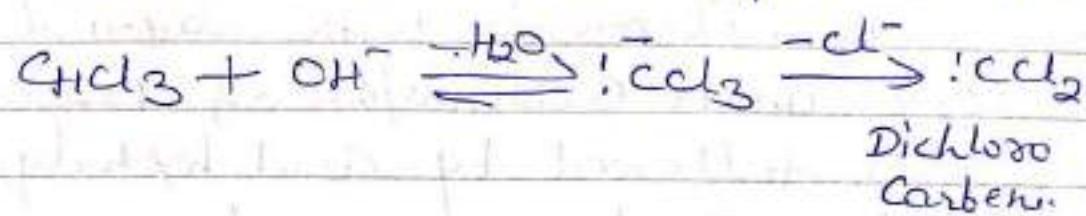
Salicylaldehyde

The Reimer-Tiemann reaction is also given by other Phenols and introduces - CHO in the ortho Position.

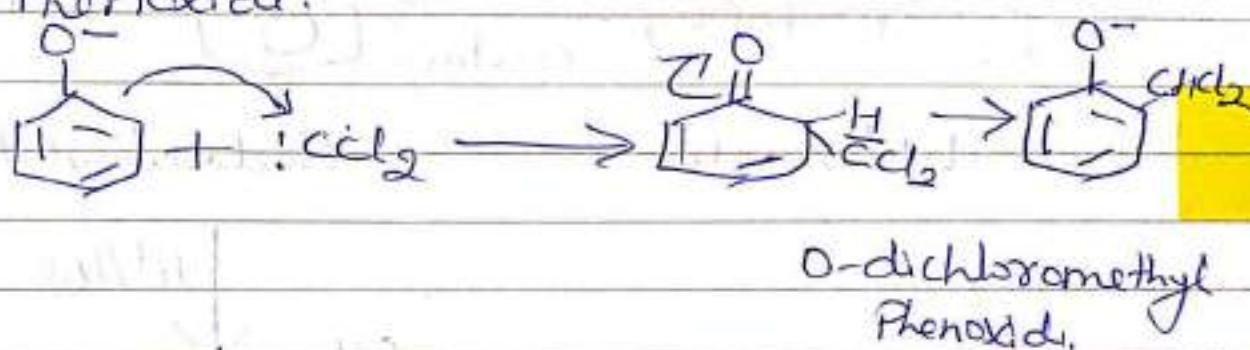
Mechanism → The reaction of chloroform and base produces dichlorocarbene, a reactive species. The carbene is electron deficient and behaves like an electrophile toward the electron rich aromatic ring.

The attack of dichlorocarbene at strongly activated ortho and para position in Phenoxide can results in formation of ortho and para Products. Salicylaldehyde is formed as a major Product due to intramolecular hydrogen bonding. The details of reaction mechanism are as follows.

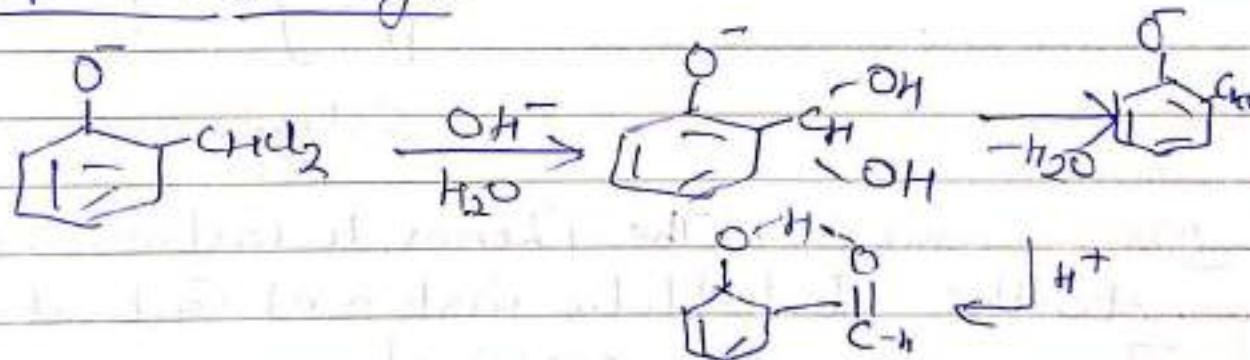
Step-1 - Generation of electrophile (1,1 elimination)



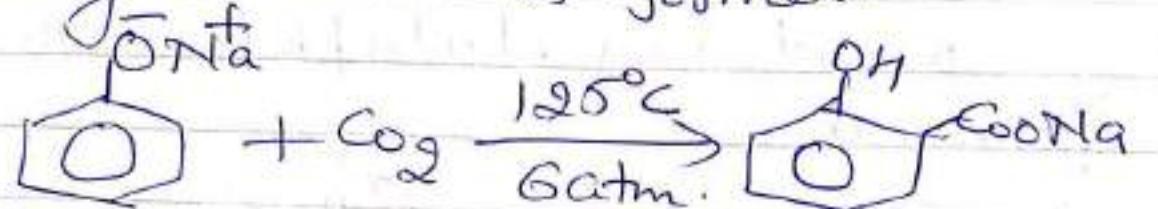
Step-2:- Reaction of electrophile with Phenoxide.



Step 3- Hydrolysis

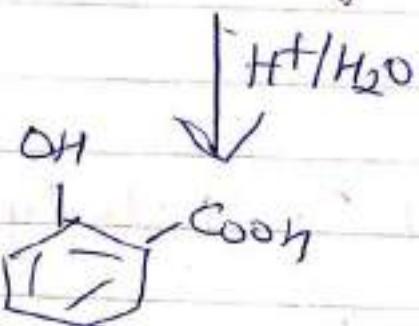


Kolbe Reaction \rightarrow This involves the treatment of Sodium Phenoxide with Carbon Dioxide at 125°C under 6 atmospheres of Pressure followed by acid hydrolysis. Salicylic acid is formed.



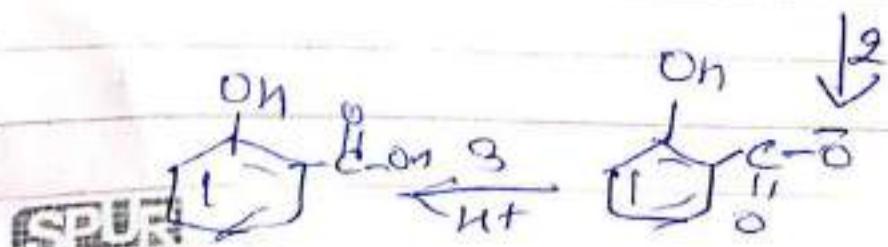
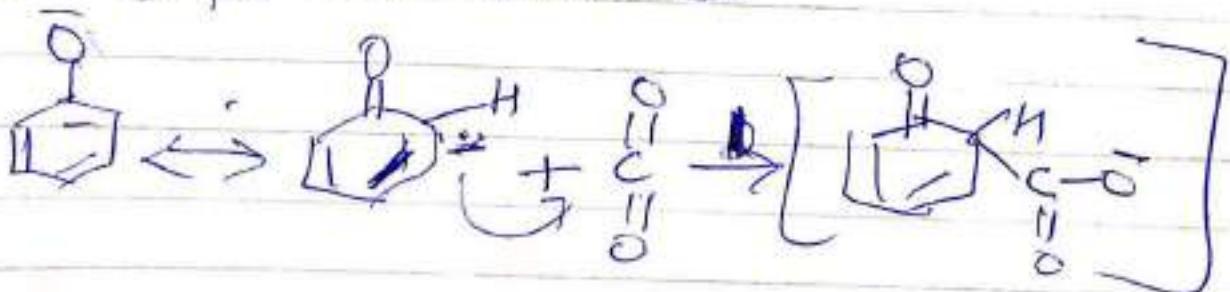
Sod Phenoxide

Sod Salicylate



Salicylic acid

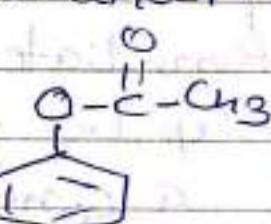
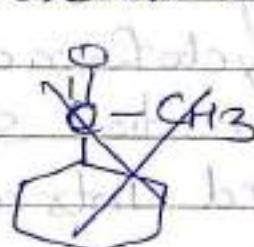
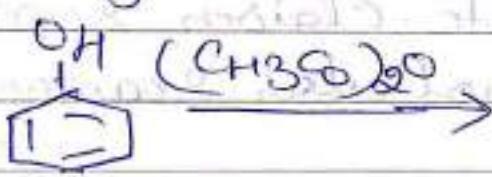
Mechanism \rightarrow The Phenoxide Carbanion adds to the electrophilic Carbon of Carbon dioxide. Three steps are involved.



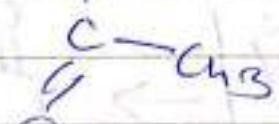
The Kolbe reaction is also given by other Phenols and introduces $-COOCH_3$ group in the ortho position. This reaction is called Kolbe-Schmidt Reaction.

Fries Rearrangement \rightarrow The Phenol is first treated with acetic anhydride in the presence of aqueous Sodium hydroxide to give Phenyl acetate. The ester is then heated with aluminium chloride catalyst when the acyl group migrates from the Phenolic oxygen to an ortho or Para Position of the ring.

The Product is a mixture of O-and P-hydroxyacetophenone.

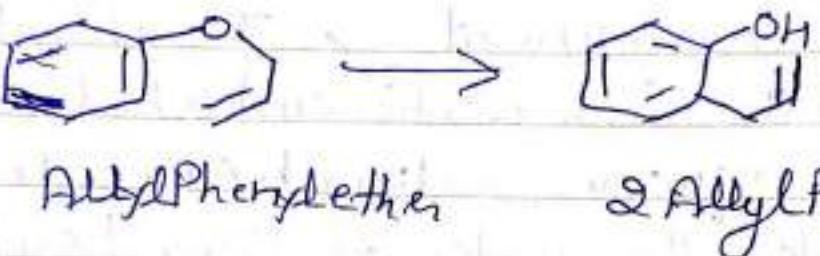


O-and P-hydroxyacetophenone

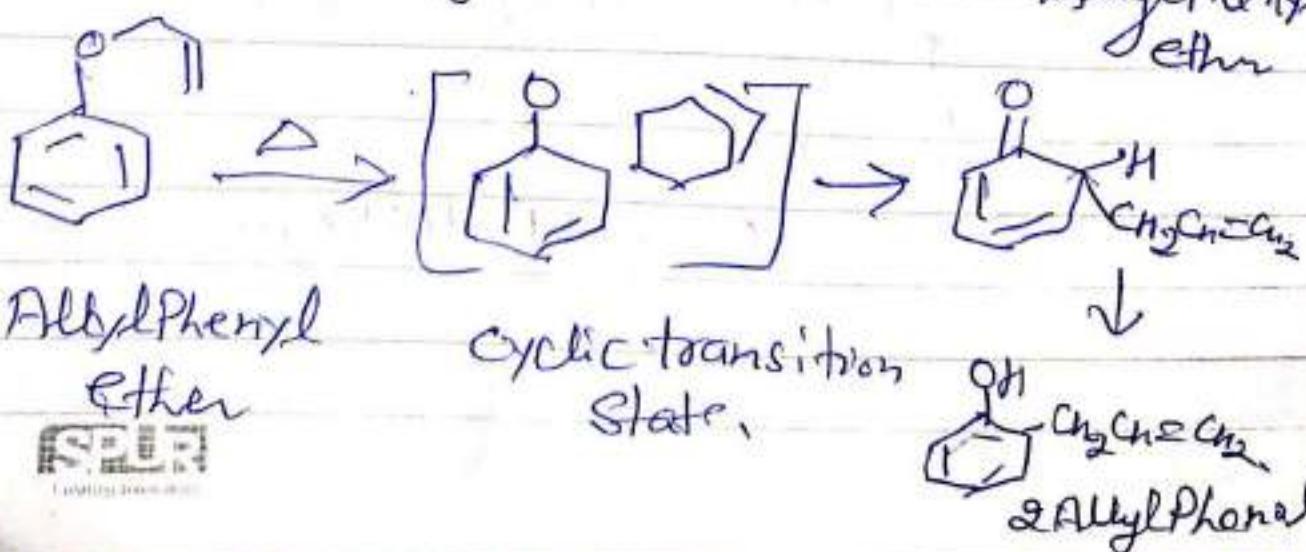
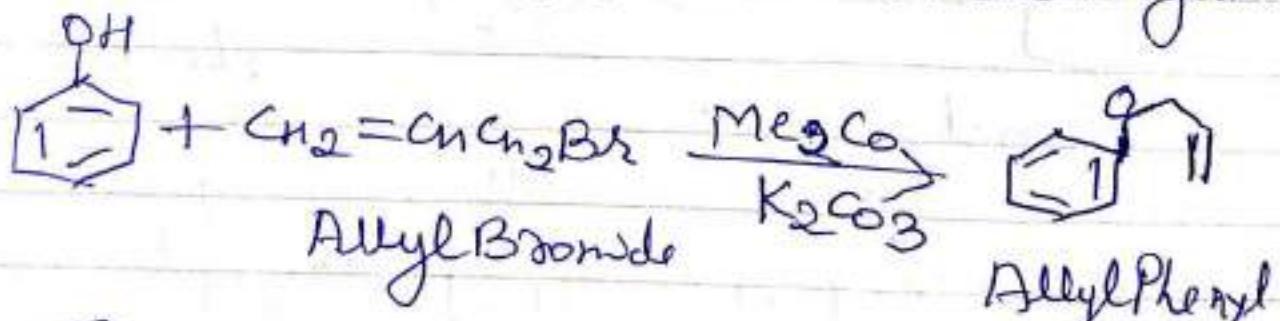


O- and P-hydroxyacetophenone

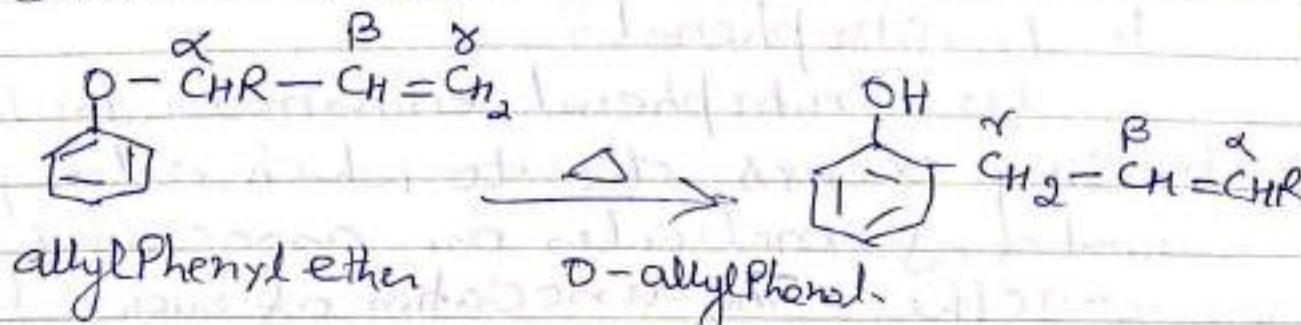
Rearrangement $\xrightarrow{\text{heat}}$ is an example of Pericyclic Reaction.
Claisen Condensation \rightarrow The allyl Phenyl ethers on heating undergo thermal rearrangement to give 2-allyl Phenols. This is known as Claisen Rearrangement.



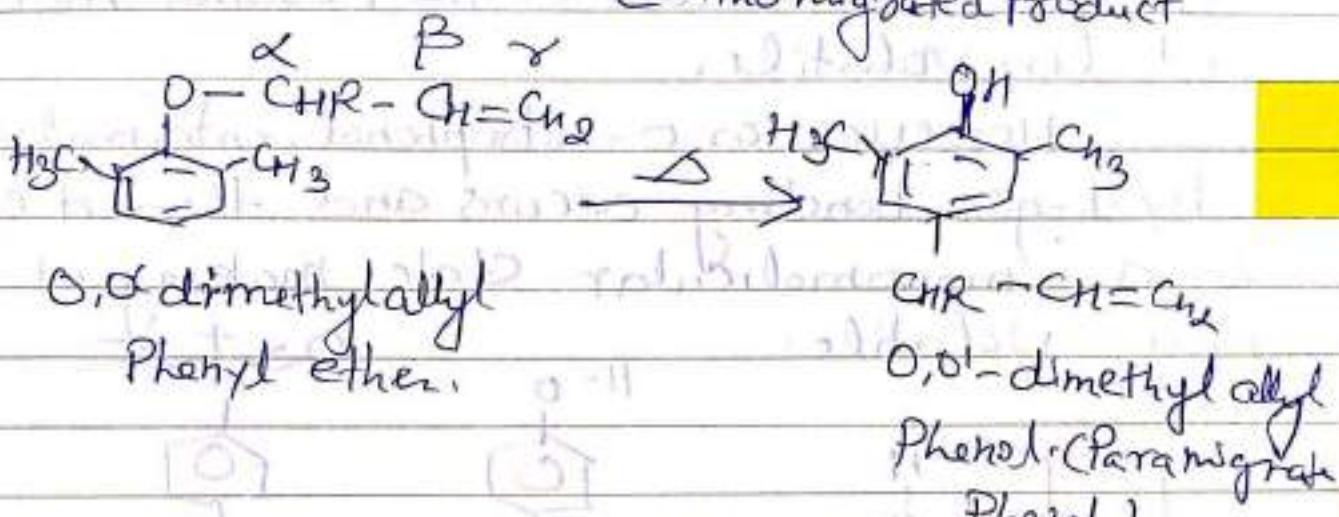
In Claisen rearrangement the allyl groups migrates from oxygen to the ring, preferably at ortho position. It is a [3,3]-sigma tropic rearrangement which leads to an intermediate, cyclohexadienone and proceeds via a cyclic transition state. Claisen rearrangement is a concerted intramolecular rearrangement.



Gaffermann Synthesis



(Ortho-migrated product)



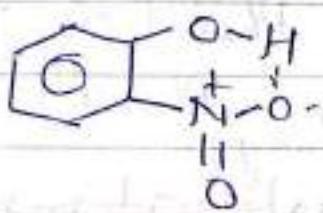
During ~~ortho~~ migration the allyl group always undergoes an allylic shift. The carbon atom to the ethereal oxygen atom in the substrate becomes γ to the ring in the product. However in para-migration the allylic group is found exactly as it was in the starting ether. When the para and both ortho position are filled there is no reaction to all - migration to the meta position has not been observed.

The intramolecular mechanistic approach is evidenced from the following facts (i) that the reaction (ii) requires no catalyst (iii) is of first order kinetics

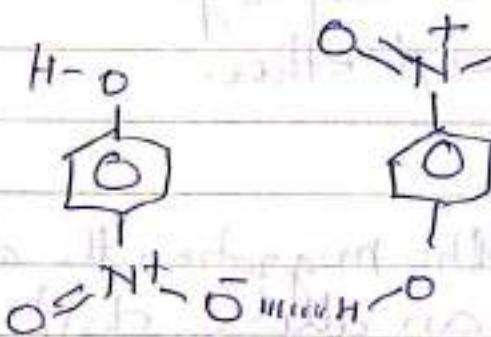
why is o-nitrophenol more volatile compared to p-nitrophenol?

In P-nitrophenol intramolecular hydrogen bonding occurs due to which a large number of molecules are associated together. The association of such a large number of molecules in the P-isomer makes it less volatile.

However in o-nitrophenol, intramolecular hydrogen bonding occurs and thus it exists in a monomeric state making it more volatile.



Intramolecular
hydrogen bonding
m.p. 97°C.



Intermolecular hybr.
m.p. 114°C