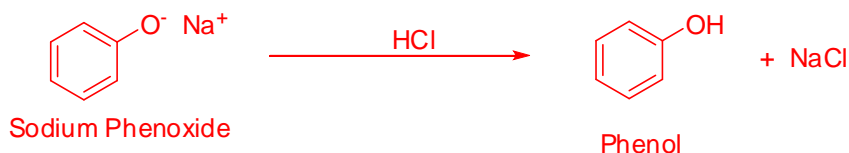
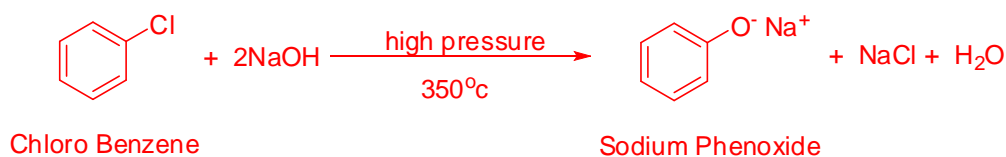


HANDOUT

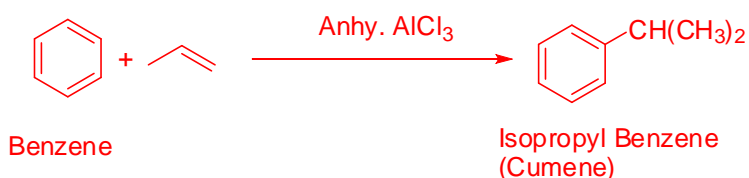
Preparations and properties of phenol

Methods of preparation of phenol:

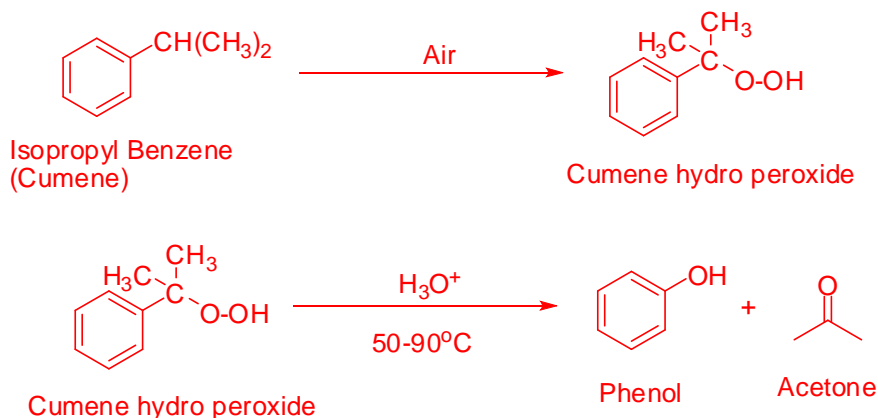
1) Hydrolysis of chloro benzene (Dow Process): Chloro benzene on reaction with aqueous sodium hydroxide at 350°C, under high pressure sodium phenoxide is produced. Sodium phenoxide on acidification yields phenol.



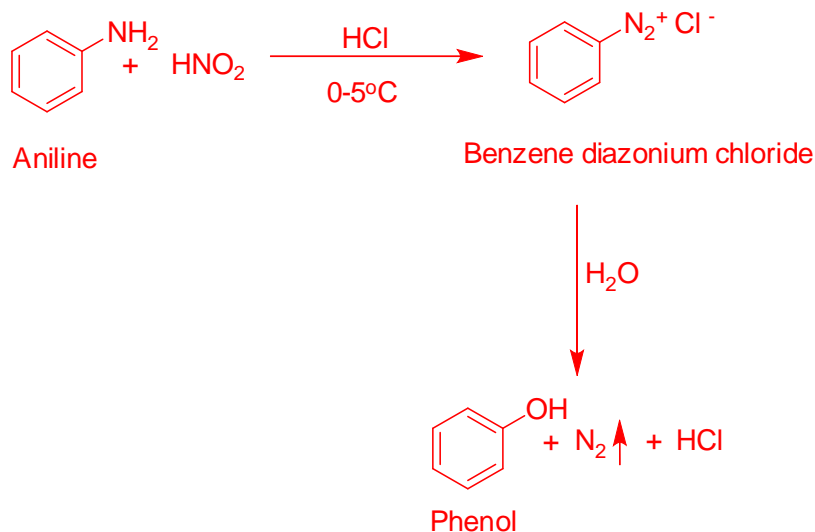
2) From Cumene: Most of the world wide production of phenol is based on this method. Cumene is prepared by Friedel-Craft alkylation of benzene with propene.



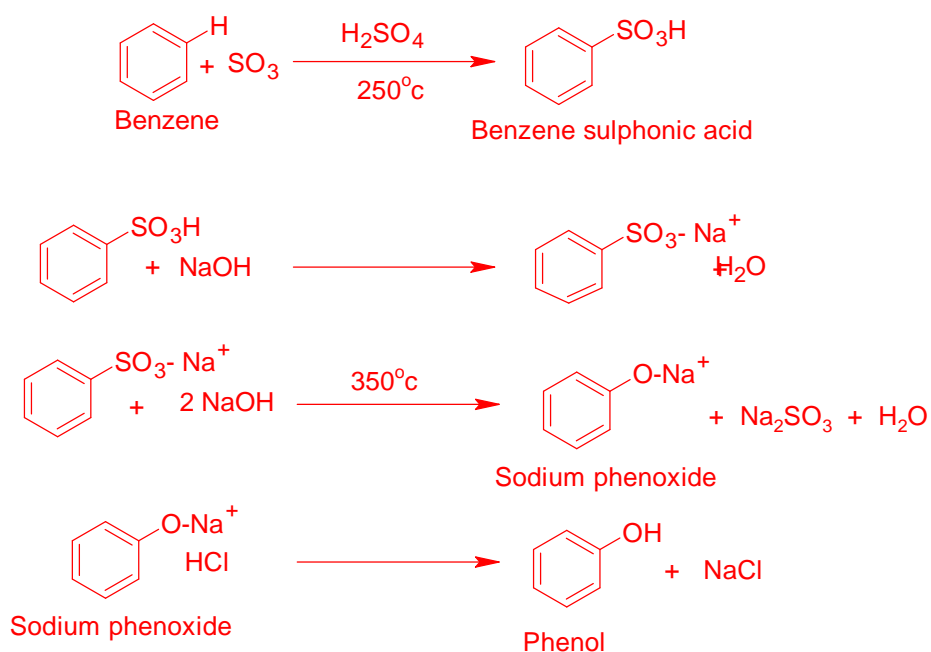
The cumene hydroperoxide which is formed by bubbling air through cumene, on treatment with strong acid forms phenol and acetone as additional product.



3) From benzene Diazonium salts: Aniline on reaction with nitrous acid in the presence of acid (HCl) forms benzene diazonium chloride, this on hydrolysis phenol is formed.



4) From aryl sulphate: Benzene on reaction with sulphur trioxide in the presence of sulphuric acid forms benzene sulphonic acid. This benzene sulphonic acid on reaction with excess sodium hydroxide forms sodium phenoxide. Sodium phenoxide in the presence of acid (HCl) forms phenol.



Physical properties:

1. It is a colorless solid with low melting point. It acquires light color on exposure to air or light. It is due to its oxidation.
2. Phenol is sparingly soluble in H₂O. Inter molecular hydrogen bonding existing in between phenol molecules.
3. Due to inter molecular hydrogen bonding phenols have high boiling point as compared to corresponding hydrocarbons.

Some physical properties of phenols

Name	m.p(K)	b.p(K)	Solubility(298 K) (gm/100 gm H ₂ O)	Acidity constant K _a x 10 ⁻¹⁹
Phenol	314	455	9.3	1.1
<i>O</i> -cresol	304	464	2.5	0.63
<i>m</i> -cresol	284	474	2.6	0.98
<i>p</i> -cresol	396	475	2.3	0.67
Catechol	377	519	45	1
Resorcinol	383	554	123	3

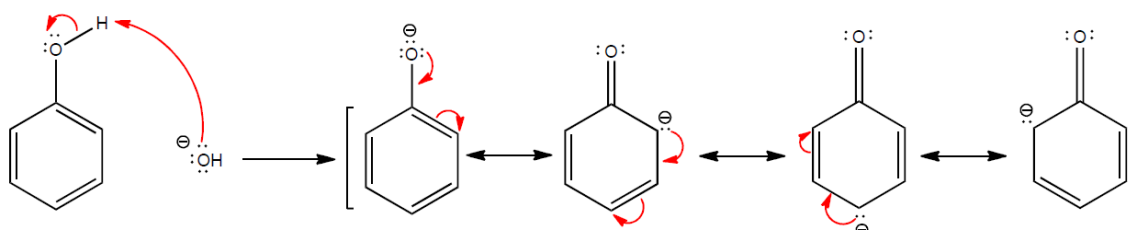
Chemical properties: Both phenols and alcohols have –OH group, but they differ widely in their properties.

Phenols show two types of reactions

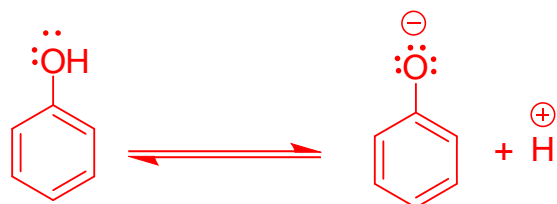
1. Reactions involving phenolic –OH group
2. Reactions involving benzene ring

1) Reactions involving phenolic -OH group

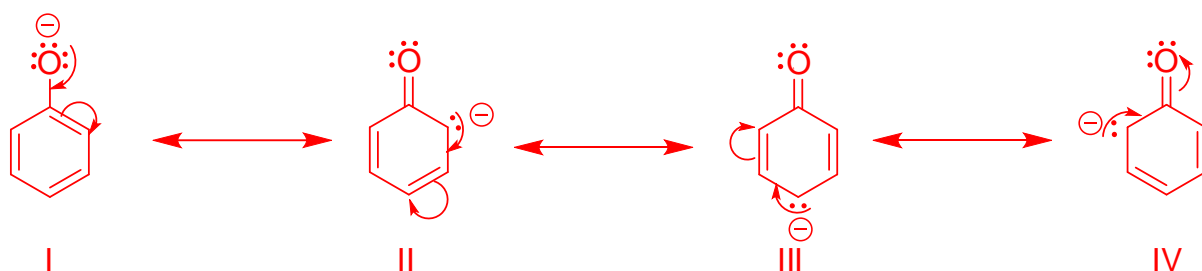
a) **Acidic nature:** Acidic nature of phenols can be explained on the basis of resonance.



Due to resonance, the oxygen atom in hydroxyl group acquires partial positive charge and attracts the bond pair of O-H bond towards itself.

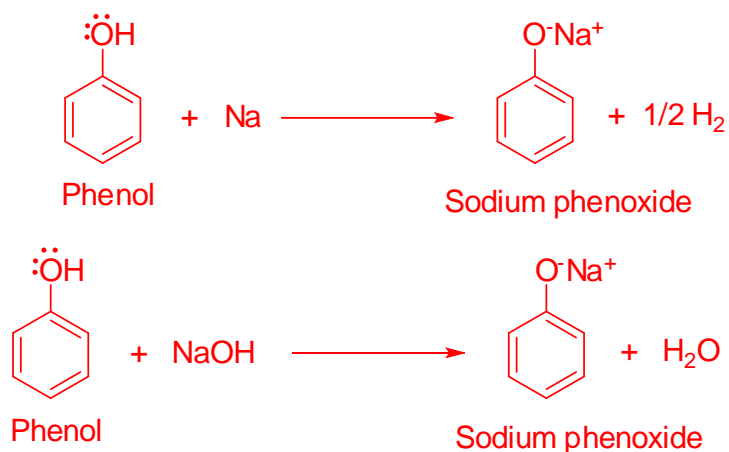


Phenoxide is more stable than phenol. Phenoxide ion stability can be explained on the basis of resonance.

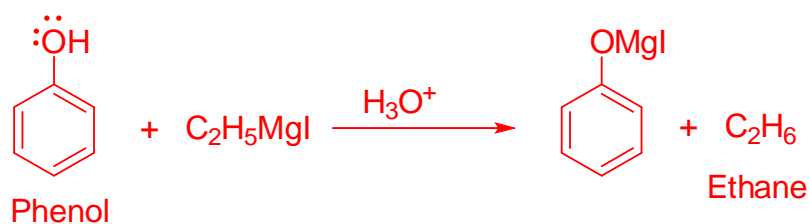


Phenols are more acidic than alcohols, but less acidic than carboxylic acids. Phenols does not react with weak bases like Na_2CO_3 , NaHCO_3 .

b) Action with alkali metal and metal hydroxides: Phenols react with alkali metal and their metal hydroxides and form metal phenoxide.



c) Action with Grignard reagent: Due to acidic nature of phenol, it reacts with Grignard reagent and forms addition product, which on hydrolysis gives ethane.



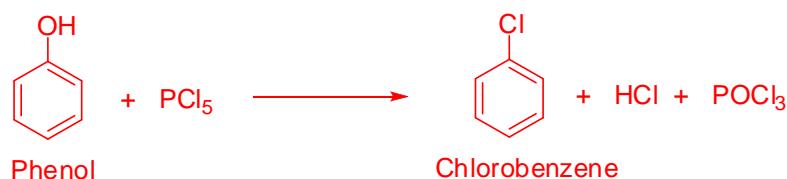
d) Action with ferric chloride: Since phenol is mostly enolic, it forms colored complex with FeCl_3 solution. The reaction of phenol with FeCl_3 solution is one of the identification tests for phenolic compounds.



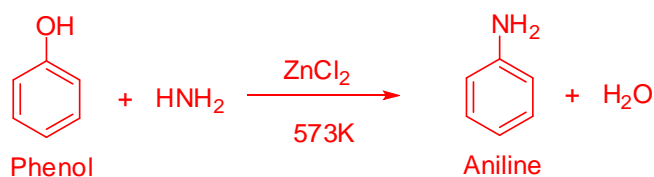
e) Reaction with Zinc dust: Benzene is formed on distillation of phenol with Zinc dust.



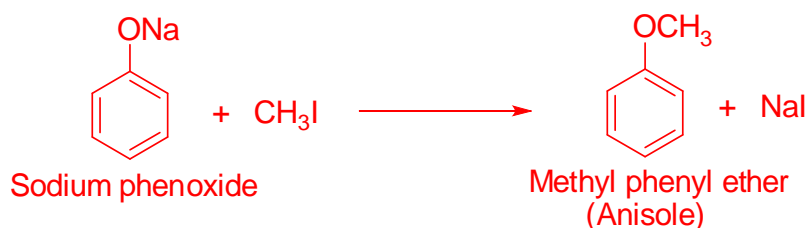
f) Reaction with PCl_5 : Phenol on reaction with PCl_5 forms chlorobenzene.



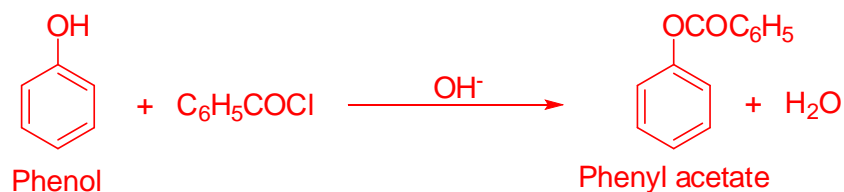
g) Reaction with ammonia: Aniline is formed on reaction of phenol with ammonia in presence of zinc chloride at 573K.



h) Williamson's synthesis: This is well known reaction for the preparation of alkyl-aryl ethers. Sodium phenoxide forms anisole on reaction with methyl iodide.

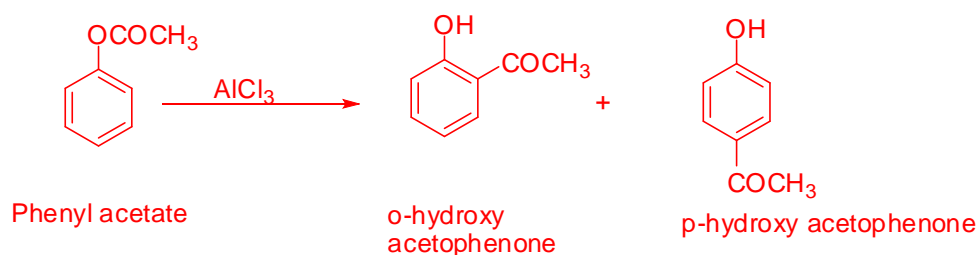


i) Esterification: Phenyl esters are prepared in good yield by the reaction of acid chloride or anhydride with phenol.

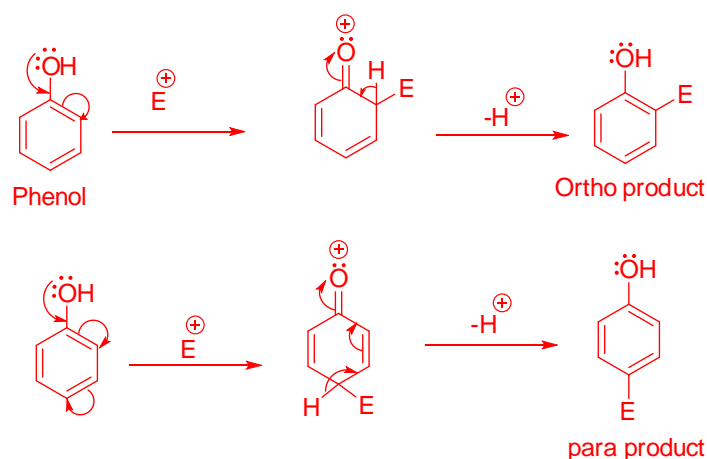


The reaction of phenol with aromatic acid chlorides is known as *Schotten Baumann* Reaction.

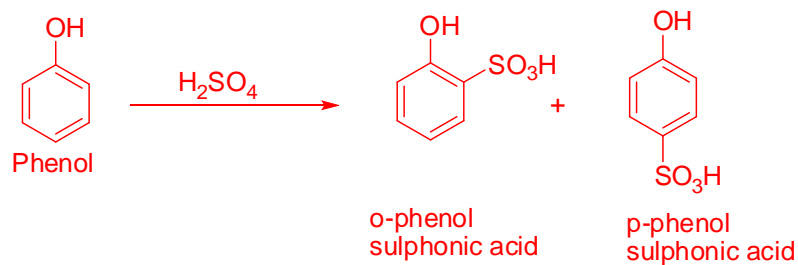
j) Fries rearrangement: On heating phenyl esters with anhydrous AlCl₃ undergoes internal rearrangement, this rearrangement is known as Fries rearrangement. Above 160°C ortho, below 50°C para isomer predominates.



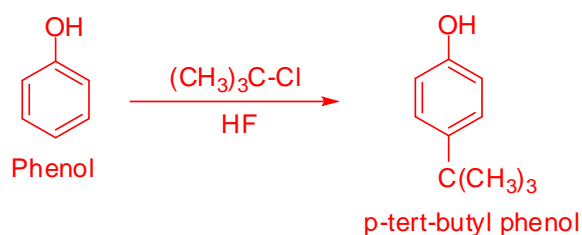
2) Reactions involving Benzene ring: The -OH group present on the ring activates benzene for electrophilic attack. Phenol undergoes electrophilic substitution reactions at ortho and para positions.



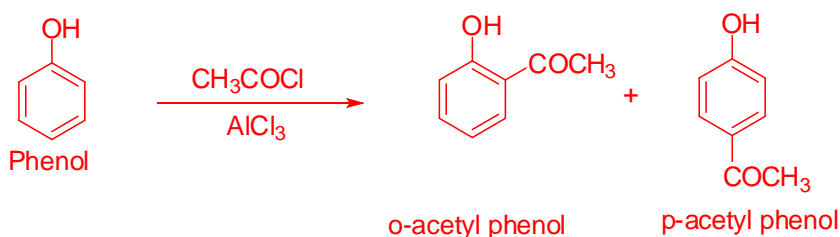
a) Halogenation: Phenol forms 2, 4, 6-tribromo phenol on addition with bromine water.



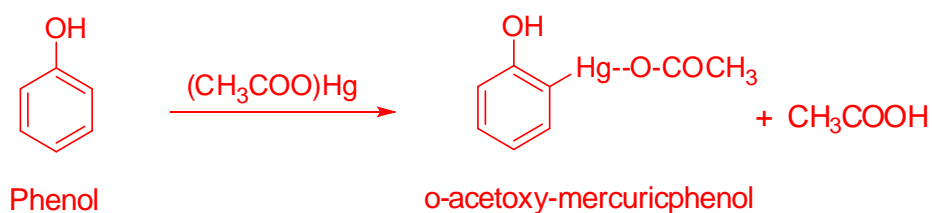
d) **Friedel-Craft's Alkylation:** *p*-tert-butyl phenol is formed on reaction of phenol with tert-butyl chloride in presence of HF.



e) **Friedel-Craft's Acylation:** Phenol forms o-acetyl phenol and p-acetyl phenol on reaction with acetylchloride in presence of anhydrous AlCl_3 .



f) **Mercuration:** Phenol on reacting with aqueous mercuric acetate forms o-acetoxy mercuricphenol.



List of Reference Books:

- 1) Organic Chemistry (English, Paperback, 10th edition) by T W Graham Solomons, John Wiley and Sons Ltd.
- 2) Organic Chemistry (English, Paperback, 7th edition) by Paula Y Bruice, Pearson Education.

3) Organic Chemistry (English, Paperback, 3rd edition) by Janice Gorzynski Smith, McGraw-Hill.

4) Organic Chemistry (English, Paperback, 2nd edition) by Jonathan Clayden, Nick Greeves and Stuart Warren, Oxford University Press.

Web Links:

1. <https://youtu.be/8p6R5yJjAGE>
2. <https://www.britannica.com/science/phenol>
3. <https://youtu.be/CDK3IBaJNNo>
4. <https://en.wikipedia.org/wiki/Phenol>

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