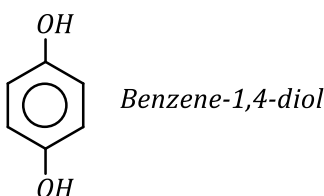
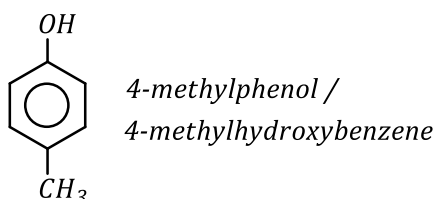
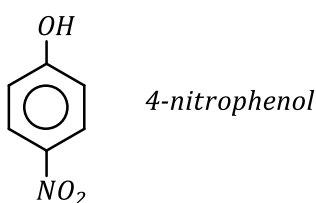
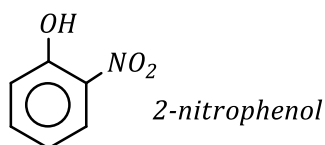
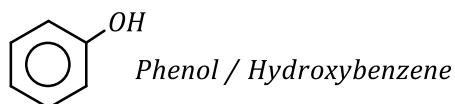


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Phenols

Phenols are a class of compounds that have one or more hydroxyl group bonded directly to a benzene ring.

Like alcohols, they may be monohydric, or polyhydric according to the number of hydroxyl groups that they contain.



The parent compound of this group, C_6H_5OH , called simply called *phenol*, is the most important member of the family.

Phenols are not alcohols even though they contain the hydroxyl group. They do not behave like alcohols in most of their reactions because the neighboring benzene ring has a profound effect on the behaviour the hydroxyl group.

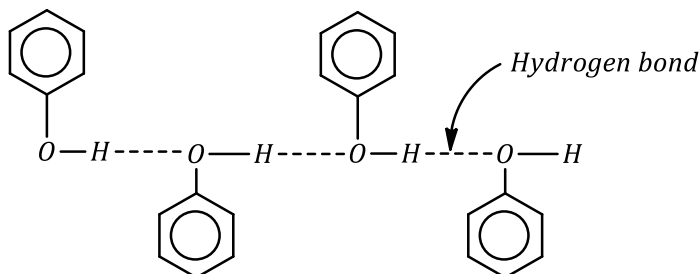
Physical properties of phenol

- When phenol is added to water at room temperature, two liquid layers are formed. If the temperature is raised to above $66^\circ C$, a single layer is formed because phenol and water are totally miscible above this temperature.
- Phenol dissolves in water because of the hydrogen bonds formed between phenol molecules and water molecules.
- It is not very soluble in water (unlike ethanol, which is totally miscible) because of the large hydrophobic benzene ring.
- Phenol is soluble in a variety of organic solvents.
- The boiling and melting point of phenol (molecular mass 94) is higher than methylbenzene (molecular mass 92).

	Molecular mass	Melting point	Boiling point
Phenol	94	42	181
methylbenzene	92	-95	111

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The reason for the high boiling point of phenol as compared to methylbenzene is that phenol forms intermolecular hydrogen bonds leading to association of its molecules in addition to the Van der Waal's forces of attraction. Additional energy is required to break the hydrogen bonds which raises its boiling point.



On the other hand, methylbenzene does not contain any strong electronegative atom attached to oxygen atom. Therefore, it does not form intermolecular hydrogen bonding. Hence its boiling point is lower than that of phenol.

- The boiling point of phenol is higher than that of corresponding alcohols of comparable molecular mass.

Phenol exhibits stronger intermolecular hydrogen bonding than the corresponding alcohols due to greater polarity of the $O - H$ bond in phenol which is caused by the interaction of the lone pair of electrons on the oxygen atom with the delocalized pi electrons of the benzene ring.

NOTE: the introduction of electron withdrawing groups e.g. nitro group into the benzene ring of phenol especially in the ortho and para positions results into significant increase in the boiling point of the compound. For example,

Compound	Melting point	Boiling point
Phenol	42	181
2-nitrophenol	45	217
4-nitrophenol	114	245

Explanation:

The nitro groups exert a negative inductive effect on the benzene ring. This increases the interaction of the lone pair of electrons on the oxygen atom of the hydroxyl group with the delocalized pi electrons of the benzene ring leading to an increase in the polarity of the $O - H$ bond and therefore an increase in the boiling points or melting points.

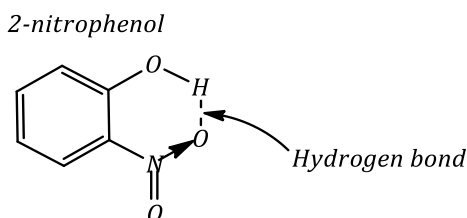
2-nitrophenol and 4-nitrophenol have different physical properties like boiling points and boiling points and solubility in water. This is shown in the table below.

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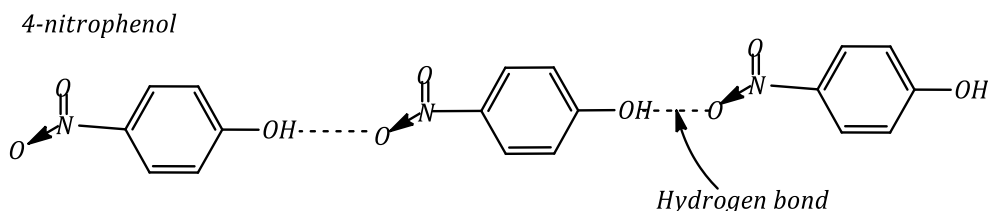
Compound	Melting point	Boiling point	Solubility in water
2-nitrophenol	45	217	Insoluble (immiscible)
4-nitrophenol	114	245	Very soluble (miscible)

Explanation:

In 2-nitrophenol (o-nitrophenol), the two functional groups are close to one another and facilitates the formation of intramolecular hydrogen bond within the molecule.



In 4-nitrophenol (p-nitrophenol), the two functional groups are far apart from each other facilitating the formation of extensive intermolecular hydrogen bond between the molecules. Therefore, a considerable amount of energy is required to break the several hydrogen bonds in 4-nitrophenol than in 2-nitrophenol leading to a high boiling and melting point of 4-nitrophenol.

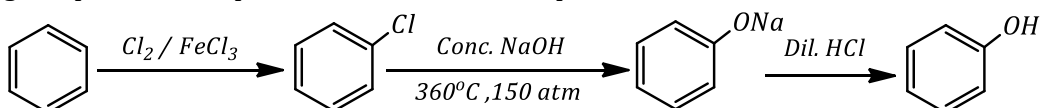


Similarly, the boiling point of 2-Nitrobenzoic acid is lower than that of 4-Nitrobenzoic acid.

Preparation of phenol

1. From chlorobenzene

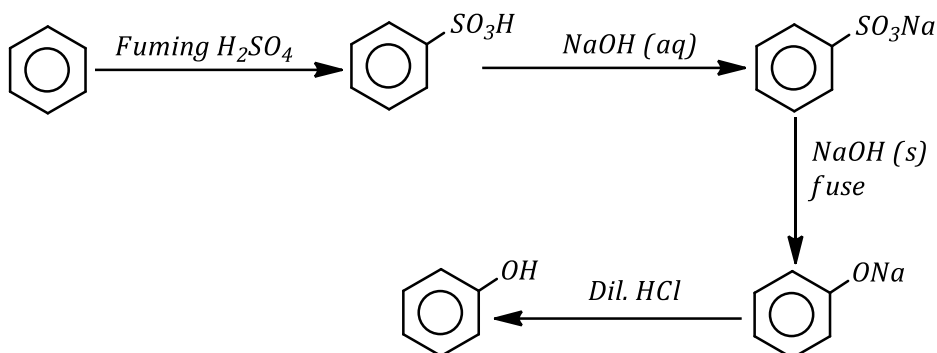
Chlorobenzene is treated with aqueous sodium hydroxide solution at 360°C under a pressure of 150-300 atmospheres to form sodium phenoxide, which on acidification gives phenol. This process is called the Dow process.



2. From benzene sulphonic acid

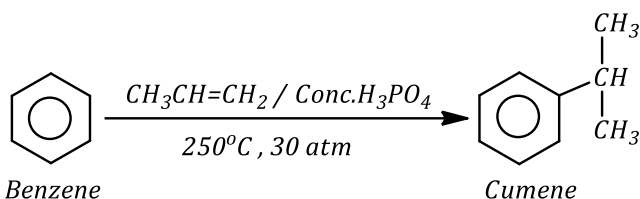
This involves sulphonation of benzene followed by fusion of the sodium salt of benzene sulphonic acid with sodium hydroxide at 350°C to form sodium phenoxide which is then hydrolysed by dilute hydrochloric acid to form phenol.

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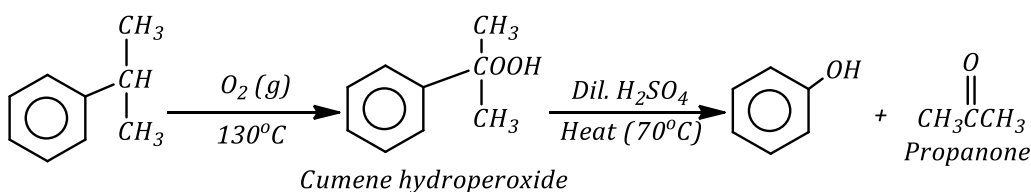


3. Cumene process

This involves air oxidation of cumene. Cumene is obtained by alkylation of benzene with propene in the presence of concentrated phosphoric acid or sulphuric acid at 250°C and a pressure of 30 atmosphere.

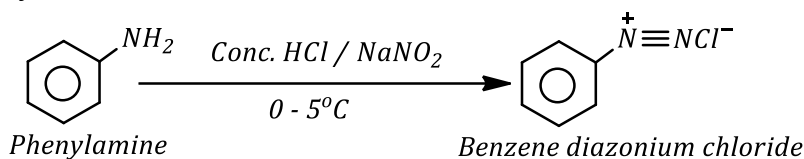


The oxidation of cumene results in the formation of cumene hydroperoxide which on acid-catalysed decomposition yields phenol. Propanone is a valuable by-product of this reaction.

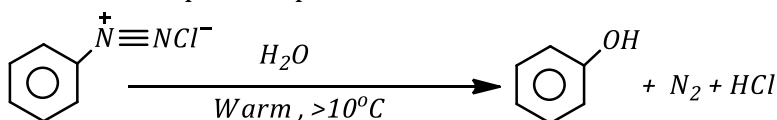


4. From benzene diazonium salt (hydrolysis of a diazonium salt)

Benzene diazonium salt is obtained by reacting phenylamine with concentrated hydrochloric acid and sodium nitrite at 0-5°C.



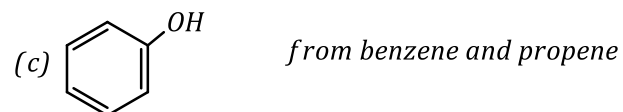
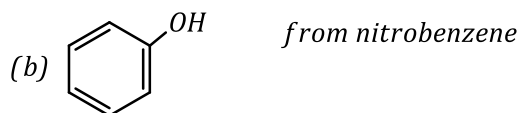
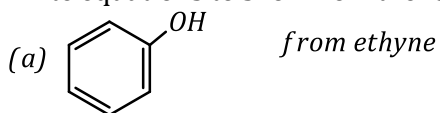
The diazonium salts are stable in cold aqueous solutions but lose nitrogen on boiling with water, to produce phenol.



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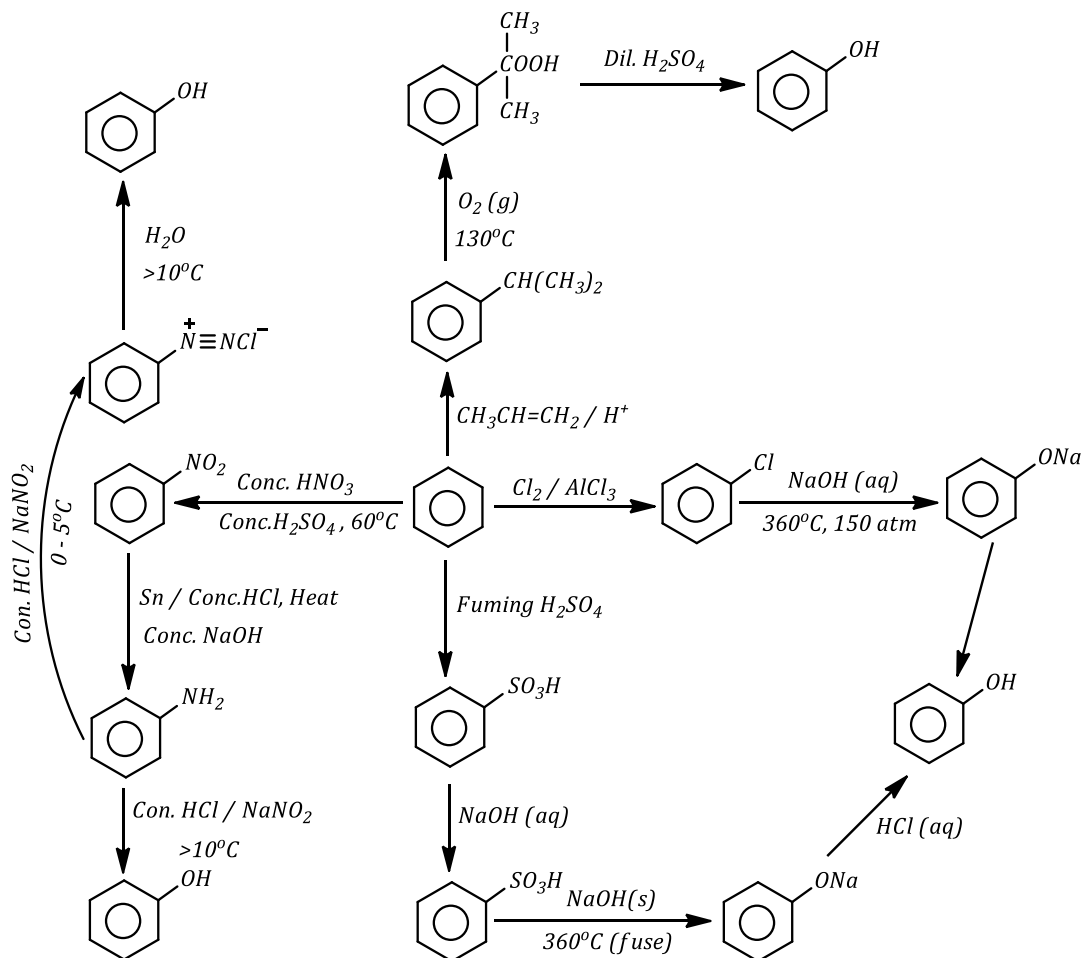
Task

Write equations to show how the following conversions can be achieved.



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Summary of preparation of phenol from benzene.



NOTE: some of the methods in the above scheme will be looked at in details under other topics a head.

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Reactions of phenol

Phenol generally give two types of reactions i.e. (i) the reactions due to the hydroxyl group and (ii) the reactions due to the aromatic ring.

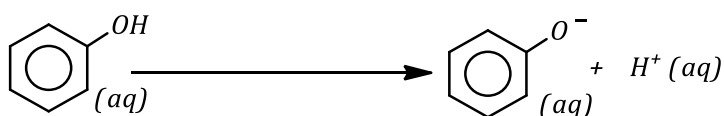
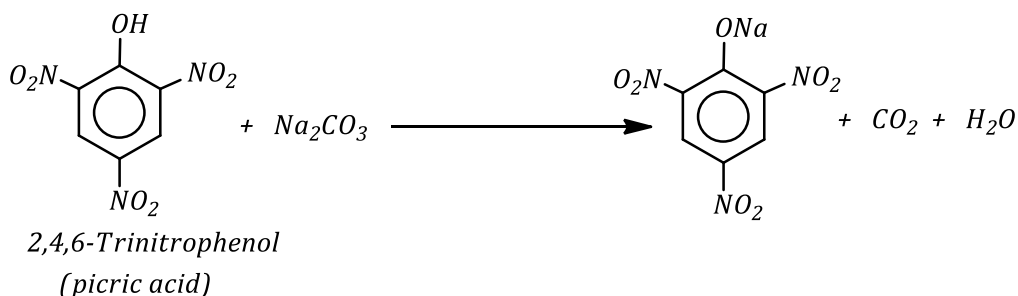
Acidity of phenol

Unlike alcohols which are neutral compounds, an aqueous solution of phenol is acidic. (I.e. turns blue litmus paper pink but aqueous solution of an alcohol is neutral to litmus paper).

Explanation:

In phenol, the lone pair of electrons on the oxygen atom interacts with the delocalized pi electrons of the benzene ring. This strengthens the carbon-oxygen bond and weakens the oxygen-hydrogen bond. Hence in aqueous solution, the oxygen-hydrogen bond easily breaks making phenol to release a proton in solution.

NOTE: Phenol is not acidic enough to release carbon dioxide from sodium carbonate. Electron withdrawing groups when introduced increases the acidity of phenol to liberate carbon dioxide i.e.



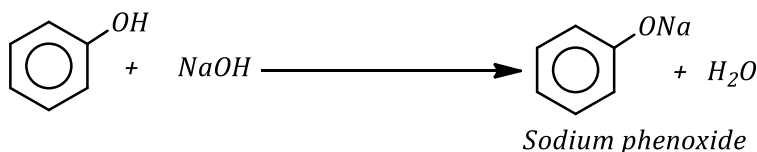
In alcohols, such interaction is not there and therefore the oxygen-hydrogen bond is much stronger hence in aqueous solution, a proton cannot be released making alcohols neutral.

1. Salt formation.

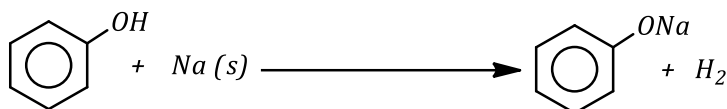
Phenol can react with sodium hydroxide to form sodium phenoxide (a salt) and water with alcohols.

NOTE: Alcohols do not react with sodium hydroxide to an appreciable extent.

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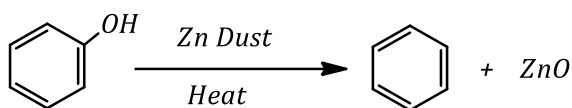


Phenol can react with sodium metal to yield sodium phenoxide and hydrogen gas.



2. Reaction with zinc dust

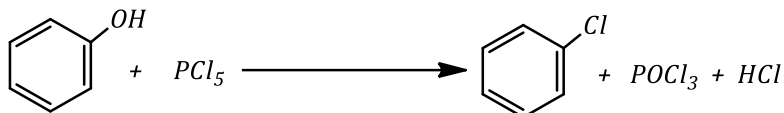
Phenol reacts with red hot zinc dust to form benzene.



The $-\text{OH}$ group of benzene is replaced by $-\text{H}$ in this reaction

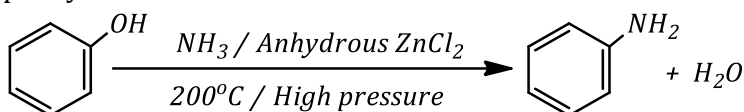
3. Reaction with phosphorous pentachloride.

Phenol reacts slowly with phosphorous pentachloride to form Chlorobenzene. The yield of Chlorobenzene formed is poor.



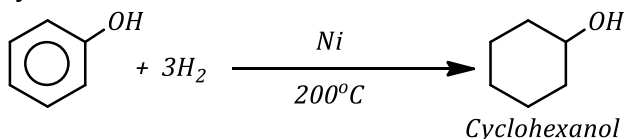
4. Reaction with ammonia

Phenol reacts with ammonia when heated under high pressure and temperature of about 200°C in the presence of anhydrous zinc chloride as a catalyst to form phenylamine.



5. Hydrogenation

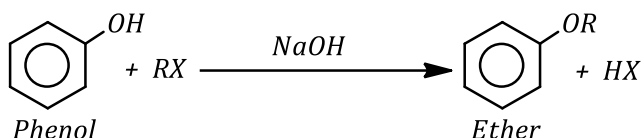
Phenol is reduced by hydrogen in the presence of nickel catalyst at 200°C to form cyclohexanol.



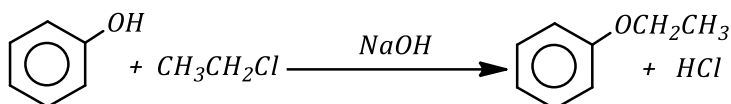
6. Reaction with alkyl halides (ether formation)

Phenol reacts with alkyl halides in the presence of aqueous sodium hydroxide solution to form an ether. This is known as Williamson ether synthesis.

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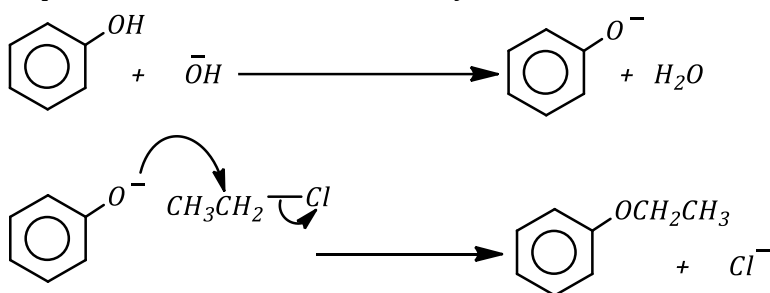


Example:



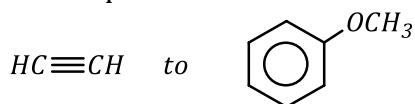
Mechanism

Phenol is first converted to a phenoxide ion which acts as a nucleophile and displaces the halide ion from the alkyl halide in an $\text{S}_{\text{N}}2$ reaction.



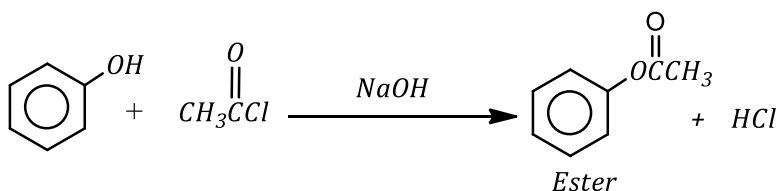
Task

Write equations to show how the conversion below can be effected.

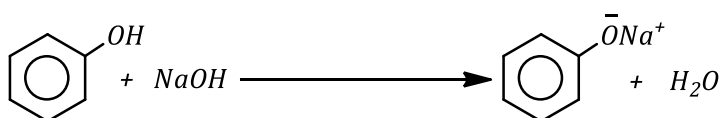


7. Reaction with acid (acyl) chlorides (ester formation)

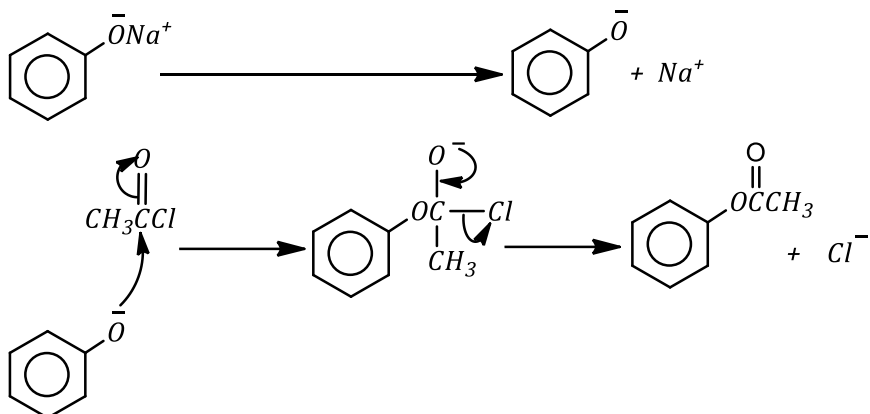
Phenol reacts with acyl compounds in the presence of sodium hydroxide to form ester.



Mechanism:

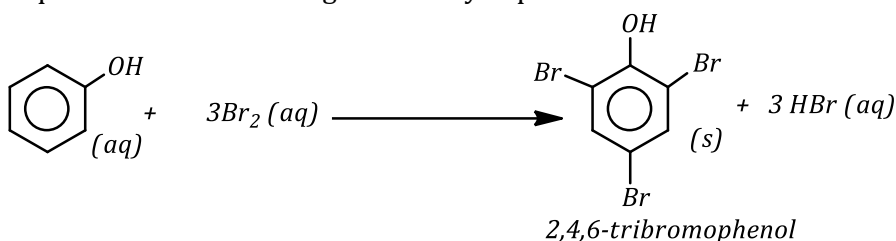


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8. Halogenation

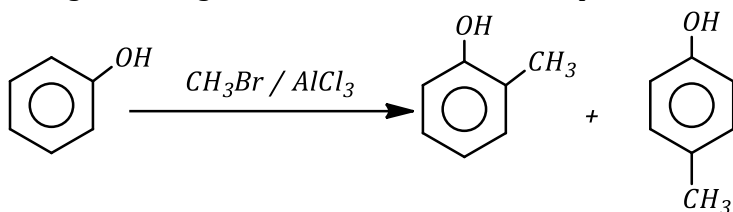
Phenol readily reacts with excess chlorine or bromine in aqueous solution to form trihalophenol, which is a white precipitate. No Lewis acid (halogen carrier) is required. This is due to high reactivity of phenol.



Observation: the aqueous solution of bromine turns from reddish-brown to colourless, a white precipitate is formed.

9. Alkylation

Phenol reacts with alkylhalides in the presence of a halogen carrier to form a ortho and para product. Two products are formed because the hydroxyl group in phenol is ring activating and substituents attached at positions 2,4 and or 6.

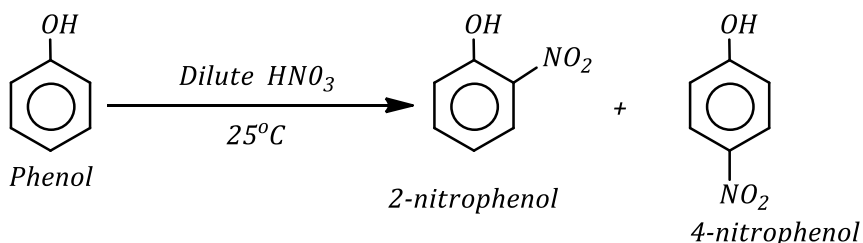


10. Nitration

Usually nitration is done using concentrated nitric acid in the presence of concentrated sulphuric acid at a temperature of $55\text{--}60^\circ\text{C}$.

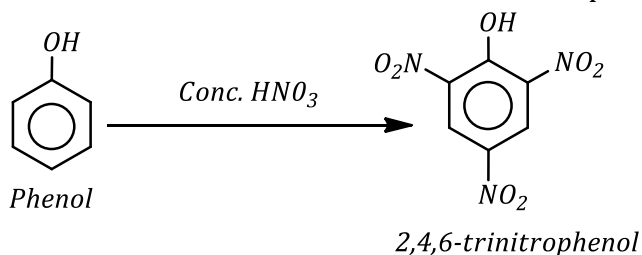
The mixed reagent is too strong to be used for a strongly activated benzene ring. In this case, nitration of phenol is done using simply dilute nitric acid at 25°C . The reaction yields a mixture of 2-nitrophenol and 4-nitrophenol.

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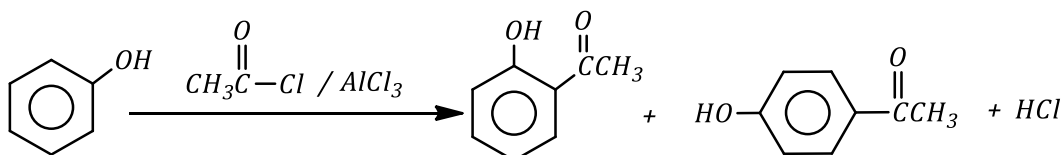
The two isomers can be separated by steam distillation.

If concentrated nitric acid is used 2,4,6-trinitrophenol (picric acid) is formed.



11. Acylation

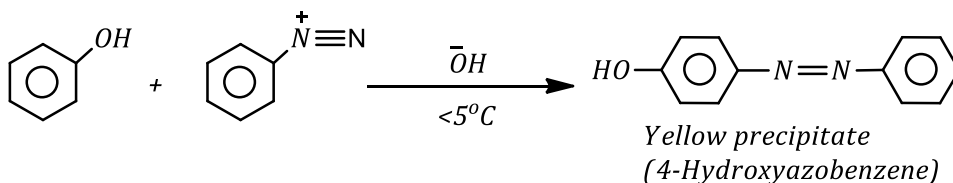
Phenol reacts with acid chlorides in the presence of a halogen carrier to form a mixture of products e.g.



12. Diazo coupling reactions of phenol

Phenol reacts with diazonium salts in alkaline solution to form an azo-dye which is a yellow precipitate (solid). This is called diazo coupling reaction.

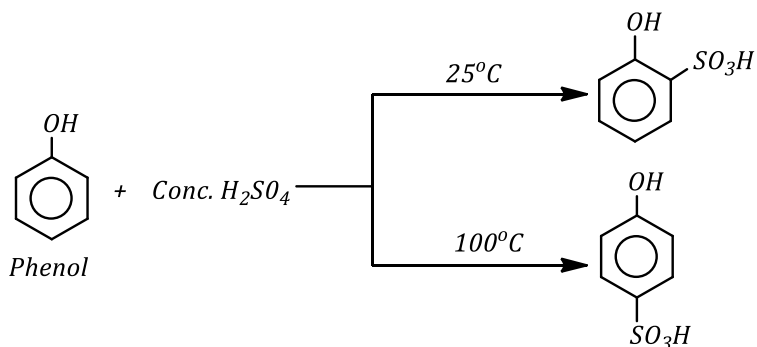
Coupling takes place at the para position, almost exclusively. However, if the para position is not free, coupling may occur at the ortho position.



13. Sulfonation

Phenol reacts concentrated sulphuric acid at 25°C at ortho position. However, if the reaction is carried out at 100°C , para isomer is the major product.

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Chemical tests for Phenol.

1. Phenol reacts with bromine water to form 2,4,6-tribromophenol which is seen as a white precipitate.
2. Phenol when treated with neutral iron(III) chloride gives a purple/ violet colouration.

Uses of phenol

- Used in the manufacture of dyes
- Used as antiseptic,
- Used in making drugs like aspirin and some herbicides.
- Used in the manufacture of plastics like Bakelite.
- Manufacture of detergents.

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Task

1. Both ethanol and phenol contain a common functional group.
 - (a) Name one reagent that can be used to distinguish the two compounds and state what would be observed if each of the compounds is treated with the reagent you have named and write the equation for the reaction that occurs if any.
 - (b) An aqueous solution of phenol is acidic whereas that of ethanol is neutral. Explain this observation.
 - (c) Phenol and ethanol react with ethanoyl chloride to give a similar product.
 - (i) Write equation for the reaction and name the organic product in each case.
 - (ii) Outline the mechanism for the reaction between phenol and ethanoyl chloride.
 - (d) Mention two uses of phenol.
2. An organic compound, P contains 76.32% carbon, 6.38% hydrogen and the rest being oxygen.
 - (a) Determine the empirical formula of P.
 - (b) A solution of 1.50 g of P in 20.90 g of benzene freezes at 1.3°C while pure benzene freezes at 5.5°C. (K_f of benzene is $5.5^\circ\text{C mol}^{-1}\text{kg}^{-1}$). Determine the:
 - (i) molecular mass of P.
 - (ii) molecular formula of P and write the structural formula of p.
 - (c) A solution of P in water is acidic but does not liberate carbon dioxide from carbonates. Briefly explain why a solution of P in water is acidic.
 - (d) Describe three ways in which the chemistry of P is similar to that of ethanol.
 - (e) Briefly describe the reaction of P with bromine water.
 - (f) Write equation and outline the mechanism for the reaction between P and:
 - (i) ethanoyl chloride
 - (ii) chloromethane in the presence of sodium hydroxide solution.
 - (g) Write equations to show how P can be:
 - (i) synthesized from benzene.
 - (ii) prepared from benzene and propene
 - (iii) converted to methylbenzene.
 - (h) Name a reagent that when separately added to both P and ethanol
 - (i) Gives similar observation
 - (ii) Can be used to differentiate between the two compounds.

(in each case state what would be observed)