ALCOHOLS, PHENOLS AND ETHERS

PHEONOLS

(INTRODUCTION, PREPARATION METHOD AND PROPERTIES)

PHENOL PHENOLS - GENERAL METHOD OF PREPERATION Formula C₆H₅OH



Structure

Phenol, known by alternative names such as carbolic acid, benzenol, or hydroxy benzene, has an -OH group linked to a carbon atom with sp² hybridization. It was first discovered by Runge in the middle oil fraction obtained from the distillation of coal tar. Initially, it was termed "carbolic acid," combining "carbo" for coal and "oleum" for oil. Interestingly, trace quantities of phenol are also detectable in human urine.

GENERAL METHODS OF PREPARATION

(1) From benzene sulphonic acid

When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.

 $C_6H_5SO_3Na \ + \ NaOH \ \longrightarrow \ C_6H_5OH \ + \ Na_2SO_3$

(2) From benzene diazonium chloride

Warming a solution of benzene diazonium chloride results in the production of phenol, accompanied by the release of nitrogen gas.



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Chemistry

(3) By distilling a phenolic acid with soda lime (decarboxylation)



(4) **From Grignard reagent:** Phenol can be obtained by reacting the Grignard reagent with oxygen, followed by hydrolysis in an acidic environment.

$$C_6H_5MgBr \xrightarrow{[0]} C_6H_5OMgBr \xrightarrow{[0]} C_6H_5OH + Mg \xrightarrow{Br}_{OH}$$

(5) From benzene



- (6) From chloro benzene
 - $\begin{array}{ccc} Ph \longrightarrow Cl & \xrightarrow{Aq. \ NaOH} & No \ NSR \ at \ normal \ condition \\ \hline \textbf{Stable by resonance} \\ R \longrightarrow Cl & \xrightarrow{Aq. \ NaOH} & R \longrightarrow OH \ [NSR] \end{array}$

Ph—Cl
$$\xrightarrow{Aq. NaOH}$$
 Ph—ONa $300^{\circ}C$

Order of NSR



$Class-12^{th}$

(7) Industrial preparation of phenol

Phenol can be industrially synthesized through the following methods:

- (a) Middle oil fraction from coal tar distillation
- (b) Cumene
- (c) Raschig process
- d) Dow's process

(a) Middle oil fraction from coal tar distillation



(b) From cumene (Isopropyl benzene): Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst. This is decomposed by dil. H₂SO₄ into phenol and acetone.



(c) Raschig process: Chlorobenzene is formed by the interaction of benzene, HCl and air at 300^o C in presence of catalyst CuCl₂ + FeCl₃.

Chemistry

It is hydrolyzed by superheated steam at 425° C to form phenol and HCl.

$$C_{6}H_{6} + HCl + \frac{1}{2}O_{2} \xrightarrow{CaCl_{2}/FeCl} C_{6}H_{5}Cl + H_{2}O$$

$$C_{6}H_{6} + HCl + \frac{1}{2}O_{2} \xrightarrow{CaCl_{2}/FeCl_{3}} C_{6}H_{5}Cl + H_{2}O$$

$$C_{6}H_{5}Cl + H_{2}O \xrightarrow{425^{\circ}C} C_{6}H_{5}OH + HCl$$

(super-heated steam)

(d) **Dow process:** This process involves alkaline hydrolysis of chloro benzene-(large quantities of phenol formed).

$$C_{6}H_{5}Cl + NaOH$$
 $\xrightarrow{Cu - Fe}_{300^{\circ}C}$ $+ Nacl$

PHYSICAL PROPERTIES OF PHENOLS

- (i) Phenol is a transparent, moisture-absorbing crystalline solid.
- (ii) When exposed to air and light, it gradually undergoes oxidation, turning pink in color.

Phenoquinone (pink colour)

- (iii) While it possesses toxic properties, it serves as an antiseptic and disinfectant.
- (iv) Phenol exhibits limited solubility in water, but readily dissolves in organic solvents.
- (v) The solubility of phenol in water is significantly lower than that of alcohols, primarily due to the larger hydrocarbon component within its molecule.
- (vi) Thanks to intermolecular hydrogen bonding, phenol has a higher boiling point than corresponding hydrocarbons and aryl halides. In contrast, intermolecular hydrogen bonding in ortho-derivatives is utilized in the production of dyes, drugs, bakelite. Its melting point (MP) is 43°C, and its boiling point (BP) is 182°C.

Chemistry

CHEMICAL PROPERTIES OF PHENOLS

(A) REACTIONS DUE TO -OH GROUP

Acidic Nature

Phenol displays modest acidity, which can be attributed to the creation of a stable phenoxide ion in solution. The stability of the phenoxide ion is achieved through resonance, which disperses the negative charge across the benzene ring, enhancing its stability. Electron-withdrawing groups like -NO₂ and -Cl amplify the acidity of phenol, while electron-releasing groups such as -CH₃ diminish its acidity.

$$C_6H_5OH \rightarrow C_6H_5O + H_3O$$

Phenol exhibits greater acidity compared to alcohols but is less acidic than carboxylic acids and even carbonic acid.

This acidic nature of phenol is evident in the following ways:

- (i) Phenol changes blue litmus to red.
- (ii) Highly electro positive metals react with phenol.

 $2C_6H_5OH + 2Na \longrightarrow 2C_6H_5ONa + H_2$

(iii) Phenol reacts with strong alkalies to form phenoxides.

(iv) However, phenol does not decompose Na₂CO₃ or NaHCO₃ because phenol is weaker than carbonic acid.

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 $C_6H_5ONa+H_2O$

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 $C_6H_5OH + Na_2CO_3 \text{ or } NaHCO_3$ No reaction Ph — Oh + NaHCO₃ Ph-ONa + H_2CO_3 Acid-I Base-I Base-II Acid-II Acid-I < Acid-II Reaction in reverse direction Base-I <Base-II

(v) Phenol does not react with NaHCO₃.

Chemistry

(vi) Acetic acid reacts with NaHCO₃ and gives effervescence of CO₂.
 Reaction with PCl₅: Phenol reacts with PCl₅ to form chloro benzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.

$$C_{6}H_{5}OH + PCl_{5} \longrightarrow C_{6}H_{5}Cl + POCl_{3} + HCl$$

$$3C_{6}H_{5}OH + POCl_{3} \longrightarrow (C_{6}H_{5})_{3}PO_{4} + 3HCl$$

Reaction with Zn dust: When phenol is distilled with zinc dust benzene is obtained.

$$C_6H_5OH + Zn \longrightarrow C_6H_6 + ZnO$$

Reaction with NH₃(Butcherer reaction): Phenol reacts with NH₃ in presence of anhydrous ZnCl₂ to form aniline.

$$C_{6}H_{5}OH + NH_{3} \xrightarrow{Anhydrous ZnCl_{2} \text{ or } (NH_{4})_{2}SO_{3}/NH_{3}150^{\circ}C} C_{6}H_{5}NH_{2} + H_{2}O$$

Reaction with FeCl3: Phenol gives violet colouration with FeCl3 solution (neutral) due to formation of a complex.

$$C_6H_5OH + FeCl_3 \longrightarrow Voilet colour$$

This reaction is used to differentiate phenol from alcohols.

Acetylation (Schotten-Baumann reaction): Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.

$$C_{6}H_{5}OH + CICOCH_{3} \xrightarrow{\text{NaOH}} C_{6}H_{5}O \xrightarrow{\text{C}} C_{6}H_{5}O \xrightarrow{\text{C}} C_{6}H_{3}$$

$$C_{6}H_{5}OH + \underbrace{\text{C}}_{0} C_{6}H_{5} \xrightarrow{\text{NaOH}} C_{6}H_{5}O \xrightarrow{\text{C}} C_{6}H_{5}O \xrightarrow{\text{C}} C_{6}H_{5}$$

Ether formation (Alkylation): Phenol reacts with alkyl halides in alkali solution to form phenyl ethers.

(Williamson's synthesis)

$$C_{6}H_{5}OH + NaOH \xrightarrow{alkali \text{ solution}} C_{6}H_{5}ONa \xrightarrow{RX} C_{6}H_{5}OR$$
Sodium phenoxide
$$C_{6}H_{5}OH + CH_{2}N_{2} \longrightarrow C_{6}H_{5}OCH_{3} + N_{2}\uparrow$$
Reaction with P₂S₅: 5C₆H₅OH + P₂S₅ \xrightarrow{\Delta} 5C₆H₅SH + P₂O₅

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(B) REACTION OF BENZENE RING: The -OH group exhibits ortho and para directing effects, effectively activating the benzene ring.



Halogenation: Phenol reacts with bromine in CCl₄ to form mixture of o–and p–bromo phenol.



Phenol reacts with bromine water to form a white ppt. of 2,4,6 tribromo phenol.



Nitration: when exposed to diluted HNO₃ at temperatures ranging from 0°C to 10°C, undergoes a reaction that leads to the formation of both o- and p-nitro phenols.



[2, 4, 6–Trinitrophenol (Picric acid)]

Additionally, when phenol is subjected to a nitrating mixture, it results in the production of 2,4,6-trinitro phenol, also known as picric acid.

Sulphonation: Phenol reacts with fuming H₂SO₄ to form o–and p–hydydroxy benzene sulphonic acid at different temperatures.



Friedel-Craft's reaction: Phenol when treated with methyl chloride in presence of anhydrous AlCl₃ p-cresol is main product.



o – and p – hydroxy acetophenone

Gattermann aldehyde synthesis: The treatment of phenol with liquid HCN and HCl gas in the presence of anhydrous AlCl₃ primarily results in the formation of p-hydroxy benzaldehyde through a formylation reaction.

HCl + HCN
$$\xrightarrow{\text{AIC}_3}$$
 HNCHCl

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Chemistry



Riemer-Tiemann reaction: When phenol is subjected to reflux with chloroform and aqueous NaOH, followed by acid hydrolysis, it produces o-hydroxy benzaldehyde. However, if CCl₄ is employed, salicylic acid is generated instead.



MECHANISM

CCl₂ is neutral attacking electrophile (formed by α , α – elimination reaction)



Kolbe 's Schmidt reaction: This process entails the reaction of C₆H₅ONa with CO₂ at 140°C, and it is followed by the formation of salicylic acid through acid hydrolysis.



Hydrogenation: When phenol is subjected to hydrogenation in the presence of nickel catalyst at a temperature range of 150-200°C, it transforms into cyclohexanol.



Cyclohexanol. (C₆H₁₁OH) (used as a good solvent)

Fries' rearrangement reaction



Duff 's reaction: This approach exclusively yields the o-compound due to the hindrance caused by the presence of a -I group within the ring.



Coupling reactions: Phenol, in the presence of an alkaline solution, undergoes coupling with benzene diazonium chloride, resulting in the creation of a red dye known as p-hydroxy azobenzene.



Phenol couples with phthalic anhydride in presence of conc. H₂SO₄ to form a dye (phenol phthalein) used as an indicator.



Phenol (2molecules)



Phenol phthalien (Colorless in acidic Medium and pink in alkaline medium)

Lederer Manasse (Condensation with formaldehyde): Phenol can polymerize when it reacts with an excess of formaldehyde in the presence of either NaOH or a weak acid



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(H⁺), leading to the formation of a polymer commonly referred to as bakelite or a resin.

Leibermann's nitroso reaction: When phenol undergoes a reaction with NaNO₂ in the presence of concentrated H₂SO₄, it results in a profound green or blue hue, which subsequently shifts to red when diluted with water. Upon alkaline treatment with NaOH, the initial green or blue color is reinstated.

This reaction is used as a test of phenol.



Reaction with acetone: (Condensation with acetone)



Oxidation



TESTS OF PHENOL

- (i) Phenol causes blue litmus paper to turn red.
- (ii) An aqueous solution of phenol exhibits a violet color when a drop of ferric chloride is added.
- (iii) Phenol undergoes Liebermann's nitroso test, resulting in red color in concentrated H₂SO₄ and blue color in dilute H₂SO₄.
- (iv) When an aqueous phenol solution is exposed to bromine water, it forms a white precipitate of 2,4,6-tribromophenol.
- (v) In the presence of concentrated H₂SO₄, phenol reacts with phthalic anhydride to produce phenolphthalein, which exhibits a pink color in the presence of an alkali.
- (vi) When phenol is treated with ammonia and sodium hypochlorite, it produces a blue color.

Differences between phenol and alcohol (C₂H₅OH)

- (i) Phenol exhibits greater acidity compared to aliphatic alcohols due to the presence of resonance in the phenoxide ion.
- (ii) When treated with FeCl3, phenol develops a violet color, whereas aliphatic alcohols do not exhibit this reaction.
- (iii) Phenol reacts with PCl5 to form triphenyl phosphate, whereas aliphatic alcohols yield alkyl chlorides.
- (iv) Phenol is characterized by a phenolic odor, whereas alcohols have a pleasant odor.
- (v) Upon oxidation, phenol yields quinone, while alcohols produce aldehydes, ketones, or acids.

Uses of Phenol: Phenol is used

- (a) Utilized as an antiseptic in soap and lotion formulations, "Dettol" contains 2,4-Dichloro-3,5-dimethyl phenol.
- (b) Employed in the production of azo dyes, phenolphthalein, picric acid (an explosive), cyclohexanol (used as a solvent for rubber), plastics (such as bakelite), and more.
- (c) Employed in the synthesis of pharmaceuticals like aspirin, salol, phenacetin, and other drugs.
- (d) Serves as a preservative for ink products.