PHENOLS

INTRODUCTION, STRUCTURE, AND PROPERTIES

1.1 Definition of Phenols

Phenols are aromatic organic compounds in which a hydroxyl group (–OH) is directly attached to a benzene ring.

General formula: Ar–OH

Example:

- Phenol (C_6H_5OH)

1.2 Nomenclature of Phenols

IUPAC Naming Rules

1. Parent compound is **phenol**
2. Number the ring so that –OH gets position 1
3. Name substituents with positions

Examples:

- 2-methylphenol (o-cresol)
- 3-nitrophenol (m-nitrophenol)
- 4-chlorophenol (p-chlorophenol)

1.3 Structure and Bonding

- Oxygen is **sp^2 hybridized (partially)** due to resonance
- Lone pair on oxygen overlaps with benzene π-system

1.4 Resonance in Phenol

Phenol exhibits resonance due to interaction between:

- Lone pair on oxygen
- π-electrons of benzene ring

Effect:

- Increases electron density at ortho and para positions
- Enhances reactivity of the ring

1.5 Physical Properties

(a) Hydrogen Bonding

- Both intermolecular and intramolecular hydrogen bonding
- Leads to higher boiling points than hydrocarbons

(b) Boiling Point

- Higher than benzene due to hydrogen bonding

(c) Solubility

- Moderately soluble in water
- Forms hydrogen bonds with water

(d) Acidity

- More acidic than alcohols
- Forms phenoxide ion ($C_6H_5O^-$)

1.6 Comparison: Phenols vs Alcohols

Property	Phenols	Alcohols
Acidity	Higher	Lower
Structure	Aromatic	Aliphatic
Reactivity	High (ring activated)	Moderate

PREPARATION AND CHEMICAL REACTIONS

2.1 Preparation of Phenols

(a) From Haloarenes (Dow Process)

- Chlorobenzene + NaOH → Phenol
- High temperature and pressure

(b) From benzene Sulfonic Acid

- Fusion with NaOH → Sodium phenoxide → Phenol

(c) From Diazonium Salts

- Benzene diazonium salt + water → Phenol + N_2

(d) From Cumene (Industrial Method)

- Oxidation of cumene → Phenol + acetone

2.2 Chemical Reactions of Phenols

(a) Acidic Reactions

Phenol reacts with:

- NaOH → Sodium phenoxide
- Does NOT react with $NaHCO_3$ (weak acid)

(b) Electrophilic Substitution Reactions

Due to resonance, phenol is highly activated.

1. Nitration

- Dilute HNO_3 → o- and p-nitrophenol
- Concentrated HNO_3 → picric acid (2,4,6-trinitrophenol)

2. Halogenation

- Bromine water → white precipitate (2,4,6-tribromophenol)

3. Sulfonation

- Phenol + H_2SO_4 → o- and p-phenolsulfonic acid

(c) Esterification

Phenol + acid chloride → ester

(d) Ether Formation

- Williamson synthesis (less common for phenols)

ACIDITY, MECHANISMS, AND APPLICATIONS

3.1 Acidity of Phenols

Why phenols are acidic:

- Phenoxide ion is stabilized by resonance

Resonance structures distribute negative charge over ring

3.2 Factors Affecting Acidity

(a) Electron-withdrawing groups (increase acidity)

- $–NO_2$, –Cl

(b) Electron-donating groups (decrease acidity)

- $–CH_3$, –OH

3.3 Mechanism of Electrophilic Substitution

Steps:

1. Formation of electrophile
2. Attack on ring (ortho/para position)
3. Formation of sigma complex
4. Deprotonation → restore aromaticity

3.4 Important Named Reactions

(a) Kolbe Reaction

- Sodium phenoxide + CO_2 → salicylic acid

(b) Reimer–Tiemann Reaction

- Phenol + $CHCl_3$/NaOH → salicylaldehyde

3.5 Tests for Phenols

(a) Ferric Chloride Test

- Violet/blue color confirms phenol

(b) Bromine Water Test

- White precipitate (tribromophenol)

3.6 Uses of Phenols

Industrial Uses

- Antiseptics (phenol itself)

- Manufacture of plastics (Bakelite)
- Pharmaceuticals

Biological Importance

- Present in amino acids (e.g., tyrosine)
- Antioxidants

3.7 Safety and Toxicity

- Phenol is corrosive
- Can cause burns
- Toxic if ingested

REVISION QUESTIONS

QUESTION 1: BASIC STRUCTURES AND NOMENCLATURE (20 MARKS)

(a) Draw the structural formula of phenol and label all functional groups. *(4 marks)*

(b) Draw the structures of the following compounds: *(8 marks)*

- 2-methylphenol
- 3-nitrophenol
- 4-chlorophenol
- 2,4-dinitrophenol

(c) Identify the ortho, meta, and para positions on a benzene ring using phenol as an example. *(4 marks)*

(d) Explain how the position of substituents affects the structure and properties of phenols. *(4 marks)*

QUESTION 2: RESONANCE STRUCTURES (20 MARKS)

(a) Draw all possible resonance structures of phenol. *(8 marks)*

(b) Draw the resonance structures of the phenoxide ion. *(6 marks)*

(c) Using your structures, explain why phenol is more acidic than ethanol. *(6 marks)*

QUESTION 3: ELECTROPHILIC SUBSTITUTION STRUCTURES (20 MARKS)

(a) Draw the structures of products formed when phenol reacts with dilute nitric acid. *(6 marks)*

(b) Draw the structure of the product when phenol reacts with bromine water. *(4 marks)*

(c) Draw the major products of sulfonation of phenol. *(4 marks)*

(d) Explain, using structures, why substitution occurs mainly at ortho and para positions. *(6 marks)*

QUESTION 4: MECHANISM-BASED STRUCTURES (20 MARKS)

(a) Draw the step-by-step mechanism for nitration of phenol, including:

- Electrophile formation
- Sigma complex
- Final product
  (10 marks)

(b) Draw the intermediate (arenium ion) structures formed during electrophilic substitution. *(6 marks)*

(c) Indicate the position of charge delocalization in the intermediate. *(4 marks)*

QUESTION 5: ACIDITY AND PHENOXIDE ION (20 MARKS)

(a) Draw the structure of phenoxide ion. *(4 marks)*

(b) Show resonance stabilization of phenoxide ion with all contributing structures. *(8 marks)*

(c) Draw and compare the structure of ethoxide ion. *(4 marks)*

(d) Use structures to explain the difference in acidity between phenol and ethanol. *(4 marks)*

QUESTION 6: NAMED REACTIONS STRUCTURES (20 MARKS)

(a) Draw the structure of sodium phenoxide. *(3 marks)*

(b) Illustrate the Kolbe reaction showing structures of:

- Reactant
- Intermediate
- Product (salicylic acid)
  (8 marks)

(c) Draw the reaction pathway for the Reimer–Tiemann reaction leading to salicylaldehyde. *(6 marks)*

(d) Identify functional groups in the final products. *(3 marks)*

QUESTION 7: PREPARATION STRUCTURES (20 MARKS)

(a) Draw the structure of chlorobenzene and its conversion to phenol (Dow process). *(6 marks)*

(b) Draw the structure of benzene diazonium salt and its hydrolysis to phenol. *(6 marks)*

(c) Illustrate the cumene process with structures of intermediates. *(8 marks)*

QUESTION 8: IDENTIFICATION TESTS STRUCTURES (20 MARKS)

(a) Draw the structure of phenol reacting with $FeCl_3$ and indicate the complex formed. *(6 marks)*

(b) Draw the structure of the white precipitate formed with bromine water. *(4 marks)*

(c) Compare structures of phenol before and after reaction with NaOH. *(4 marks)*

(d) Explain structural changes during these tests. *(6 marks)*

QUESTION 9: SUBSTITUENT EFFECTS (20 MARKS)

(a) Draw structures of:

- p-nitrophenol
- p-methylphenol
  (6 marks)

(b) Show resonance in p-nitrophenol and explain electron-withdrawing effect. *(6 marks)*

(c) Compare acidity using structures. *(4 marks)*

(d) Predict and draw products of nitration for substituted phenols. *(4 marks)*

QUESTION 10: INTEGRATED STRUCTURE QUESTION (20 MARKS)

(a) Draw the structure of phenol. *(2 marks)*

(b) Show its resonance structures. *(6 marks)*

(c) Draw products of bromination and nitration. *(6 marks)*

(d) Draw phenoxide ion and explain acidity using structures. *(6 marks)*