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Alcohols, Phenols and Ethers

Introduction and Classification

Alcohols, phenols, and ethers are important classes of organic compounds containing oxygen. Alcohols have one or more hydroxyl (–OH) groups attached to saturated carbon atoms. Phenols have hydroxyl groups attached directly to aromatic rings. Ethers contain an oxygen atom connected to two alkyl or aryl groups (R–O–R').

Alcohols: Types and Structure

Alcohols are classified based on the number of hydroxyl groups: monohydric (one –OH), dihydric (two –OH, also called diols), trihydric (three –OH, triols), and polyhydric (more than three –OH groups). They are also classified by the carbon atom to which the –OH is attached: primary (1°), secondary (2°), and tertiary (3°) alcohols.

Phenols and Ethers

Phenols are aromatic compounds with hydroxyl groups attached to benzene rings, exhibiting acidic properties due to resonance stabilization of the phenoxide ion. Ethers are compounds with the general formula R–O–R', often volatile and with lower boiling points than alcohols due to lack of hydrogen bonding between molecules.

Preparation Methods

Alcohols can be prepared by hydrolysis of haloalkanes, reduction of aldehydes and ketones, hydration of alkenes, and hydroboration-oxidation. Phenols are prepared from aryl halides, benzene sulfonic acid, diazonium salts, and cumene oxidation. Ethers are synthesized by Williamson's synthesis, dehydration of alcohols, reaction of alkyl halides with silver oxide, and reaction of diazomethane with alcohols.

Physical and Chemical Properties

Alcohols and phenols exhibit hydrogen bonding, leading to higher boiling points and solubility in water. Ethers have lower boiling points and are less polar. Alcohols react with metals, acids, and undergo oxidation, dehydration, and substitution reactions. Phenols show characteristic reactions such as formation of phenoxide ions, electrophilic substitution, and complexation with ferric chloride. Ethers undergo cleavage with halogen acids and electrophilic substitution in aromatic ethers.

Acidity and Reactivity

Phenols are more acidic than alcohols due to resonance stabilization of the phenoxide ion. The acidity of alcohols decreases from primary to tertiary due to electron-donating alkyl groups. Tests such as Lucas test, iodoform test, and ferric chloride test help distinguish between types of alcohols and phenols.

Solved Examples

Example 1: Identify the type of alcohol in CH_3CH_2OH and explain its classification.

Solution: CH_3CH_2OH (ethanol) has the –OH group attached to a carbon atom bonded to only one other carbon atom, making it a primary alcohol.

Example 2: Write the reaction for the preparation of phenol from chlorobenzene.

Solution: Chlorobenzene reacts with sodium hydroxide at high temperature and pressure to form sodium phenoxide, which on acidification yields phenol.

$$\text{C}_6\text{H}_5\text{Cl} + \text{NaOH} \xrightarrow{623K, 300 atm} \text{C}_6\text{H}_5\text{ONa} + \text{NaCl} \\ \text{C}_6\text{H}_5\text{ONa} + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{NaCl}$$

Example 3: Explain the Williamson synthesis of ethers with an example.

Solution: Williamson synthesis involves the reaction of an alkyl halide with a sodium alkoxide to form an ether.

For example, bromoethane reacts with sodium ethoxide to form diethyl ether:

$$\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{ONa} \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{NaBr}$$

Practice Set

Conceptual Questions:

- **Level 1:** Define primary, secondary, and tertiary alcohols with examples.
- **Level 2:** Explain why phenols are more acidic than alcohols.

Application-based Question:

- **Level 3:** Predict the product when 2-propanol is oxidized with potassium dichromate.

Answer Key

Conceptual Questions:

- **Level 1:** Primary alcohols have the –OH group attached to a carbon bonded to one other carbon (e.g., ethanol), secondary to two carbons (e.g., isopropanol), tertiary to three carbons (e.g., tert-butanol).
- **Level 2:** Phenols are more acidic because the phenoxide ion formed after losing H^+ is resonance stabilized, whereas alkoxide ions from alcohols are not.

Application-based Question:

- **Level 3:** Oxidation of 2-propanol (secondary alcohol) with potassium dichromate yields acetone (a ketone).

Quick Reference Table

Alcohols: General formula $C_nH_{2n+1}OH$; classified as primary, secondary, tertiary; prepared by reduction of aldehydes/ketones, hydration of alkenes.

Phenols: Hydroxyl group attached to benzene ring; acidic due to resonance; prepared from aryl halides, diazonium salts.

Ethers: General formula R–O–R'; prepared by Williamson synthesis, dehydration of alcohols; lower boiling points than alcohols.

Important Reactions: Kolbe reaction (phenol to salicylic acid), Fries rearrangement (acyl phenols), Williamson synthesis (ether formation).

Common Mistakes and Misconceptions

- Confusing primary, secondary, and tertiary alcohols based on the number of hydroxyl groups instead of the carbon attachment.
- Assuming all alcohols have the same acidity; phenols are significantly more acidic.
- Believing ethers have hydrogen bonding between molecules; they do not, leading to lower boiling points.
- Mixing up Markovnikov and anti-Markovnikov rules in addition reactions.

Glossary

- **Alcohol:** Organic compound with one or more hydroxyl groups attached to saturated carbon atoms.
- **Phenol:** Aromatic compound with hydroxyl group attached directly to benzene ring.
- **Ether:** Compound with an oxygen atom connected to two alkyl or aryl groups.
- **Primary Alcohol:** –OH attached to carbon bonded to one other carbon.
- **Secondary Alcohol:** –OH attached to carbon bonded to two other carbons.
- **Tertiary Alcohol:** –OH attached to carbon bonded to three other carbons.
- **Williamson Synthesis:** Method to prepare ethers by reaction of alkyl halides with sodium alkoxides.
- **Kolbe Reaction:** Carboxylation of phenolates to form salicylic acid.
- **Fries Rearrangement:** Rearrangement of phenyl esters to hydroxy aryl ketones.