Short Notes for CUET UG Chemistry

Unit VII: Alcohols, Phenols and Ethers

1. Classification and Nomenclature

These compounds are formed by the replacement of hydrogen atom(s) in a hydrocarbon by hydroxyl group(s) ($-OH$) or alkoxy/aryloxy groups ($-OR$/$-OAr$).

Classification

- **Alcohols & Phenols:** Classified as mono-, di-, tri-, or polyhydric based on whether they contain one, two, three, or many $-OH$ groups.
- **Monohydric Alcohols:** Sub-classified according to the hybridization of the carbon attached to the $-OH$ group:
  - sp^3 **C-OH bonds:** Primary (1°), secondary (2°), and tertiary (3°) alcohols; Allylic alcohols ($-OH$ next to $C=C$); Benzylic alcohols ($-OH$ attached to a benzylic carbon).
  - sp^2 **C-OH bonds:** Vinylic alcohols ($-OH$ directly attached to $C=C$); Phenols ($-OH$ directly attached to a benzene ring).
- **Ethers:** Classified as **symmetrical (simple)** if the alkyl/aryl groups attached to the oxygen are identical, and **unsymmetrical (mixed)** if they are different.

Nomenclature

- **Alcohols:** IUPAC name is derived by replacing the 'e' of the parent alkane with **-ol** (e.g., Ethanol, Propan-2-ol).
- **Phenols:** The simplest hydroxy derivative of benzene is phenol. It is both a common and an IUPAC accepted name.
- **Ethers:** IUPAC names are derived as alkoxy derivatives of alkanes. The larger alkyl group is chosen as the parent alkane (e.g., Methoxyethane for $CH_3-O-C_2H_5$).

2. Structures of Functional Groups

- **Alcohols:** The oxygen of the $-OH$ group is sp^3 hybridized. The $C-O-H$ bond angle is slightly less than the regular tetrahedral angle (109.28°) due to repulsion between the unshared electron pairs of oxygen.
- **Phenols:** The $-OH$ group is attached to an sp^2 hybridized carbon. The $C-O$ bond length is shorter than in alcohols due to the partial double bond character arising from the conjugation of unshared electron pairs of oxygen with the aromatic ring.
- **Ethers:** The oxygen atom is sp^3 hybridized. The $R-O-R$ bond angle is greater than the tetrahedral angle due to the repulsive interaction between the two bulky alkyl groups.

3. Methods of Preparation

A. Preparation of Alcohols

1. **From Alkenes:**
   - **Acid-catalyzed hydration:** Follows Markovnikov's rule.
   - **Hydroboration-oxidation:** Diborane (B_2H_6) reacts with alkenes followed by oxidation with H_2O_2 in an alkaline medium. Yields anti-Markovnikov alcohol addition.
2. **From Carbonyl Compounds:**
   - **Reduction of aldehydes and ketones:** Using Pd/H_2, $NaBH_4$, or $LiAlH_4$. Aldehydes yield 1° alcohols; ketones yield 2° alcohols.
   - **Reduction of carboxylic acids and esters:** Using strong reducing agents like $LiAlH_4$.
3. **From Grignard Reagents ($RMgX$):** Reacts with methanal (formaldehyde) to

yield 1° alcohols, other aldehydes yield 2° alcohols, and ketones yield 3° alcohols.

B. Preparation of Phenols

1. **From Haloarenes (Dow Process):** Chlorobenzene is fused with $NaOH$ at 623 K and 300 atm, followed by acidification.
2. **From Benzene Sulphonic Acid:** Benzene is sulphonated with oleum, then fused with molten $NaOH$, and acidified.
3. **From Diazonium Salts:** Aniline reacts with $NaNO_2 + HCl$ at 273-278 K to form benzene diazonium chloride, which is warmed with water to yield phenol.
4. **From Cumene (Commercial Method):** Cumene (isopropylbenzene) is oxidized in the air to cumene hydroperoxide, which is then treated with dilute acid to yield phenol and acetone (a valuable byproduct).

C. Preparation of Ethers

1. **By Dehydration of Alcohols:** Heating ethanol with concentrated H_2SO_4 at 413 K yields ethoxyethane (at 443 K, it yields ethene instead).
2. **Williamson Synthesis:** An alkyl halide reacts with sodium alkoxide. (Note: For best yields of unsymmetrical ethers, the alkyl halide should be primary, and the alkoxide can be bulky/tertiary).
   $R - X + R' - O^-Na^+ \rightarrow R - O - R' + Na$

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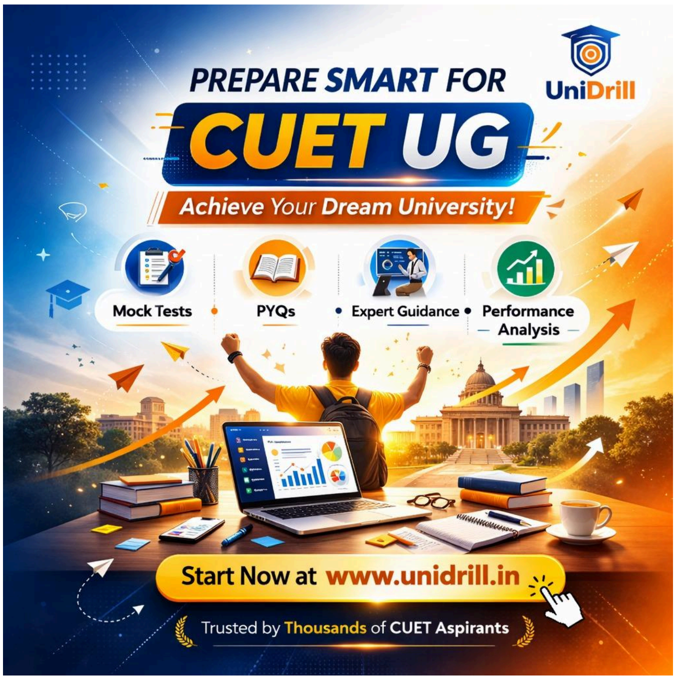
4. Physical Properties

- **Boiling Points:** Alcohols and phenols have much higher boiling points than hydrocarbons, ethers, and haloalkanes of comparable molecular masses. This is due to the presence of intermolecular hydrogen bonding.
  - Boiling points increase with an increase in the number of carbon atoms.
  - For isomeric alcohols, boiling points decrease with increased branching (decreased surface area).
- **Solubility:** Lower alcohols and ethers are soluble in water because they can form hydrogen bonds with water molecules. Solubility decreases sharply as the size of the hydrophobic alkyl/aryl group increases.



5. Chemical Properties of Alcohols

A. Reactions involving cleavage of O-H bond (Acidity)

- **Reaction with Metals:** React with active metals (Na, K, Al) to yield alkoxides and hydrogen gas.
- **Acidity:** Alcohols are weaker acids than water. The electron-releasing (+I) effect of the alkyl group decreases the polarity of the O-H bond.
- **Esterification:** React with carboxylic acids, acid chlorides, and acid anhydrides to form esters.

B. Reactions involving cleavage of C-O bond

- **Reaction with Hydrogen Halides (HX):** Form alkyl halides. The Lucas Test ($HCl + ZnCl_2$) distinguishes between 1°, 2°, and 3° alcohols based on turbidity appearance.
- **Dehydration:** Heating with concentrated H_2SO_4 or H_3PO_4 removes a molecule of water to form alkenes.
- **Oxidation:** * 1° alcohols are oxidized to aldehydes, then to carboxylic acids (using $KMnO_4$ or $K_2Cr_2O_7$). Mild oxidizing agents like PCC stop the reaction at the aldehyde stage.
    - 2° alcohols are oxidized to ketones.
    - 3° alcohols do not undergo oxidation easily.

6. Chemical Properties of Phenols

- **Acidity:** Phenols are much more acidic than alcohols because the phenoxide ion left after releasing an H^+ is stabilized by resonance. Electron-withdrawing groups (like $-NO_2$) increase acidity, while electron-donating groups (like $-CH_3$) decrease it.
- **Electrophilic Aromatic Substitution:** The $-OH$ group activates the benzene ring and directs incoming electrophiles to ortho and para positions.
    - **Nitration:** With dilute HNO_3 at low temperature, yields a mixture of ortho and para-nitrophenol. With concentrated HNO_3, it yields 2,4,6-trinitrophenol (Picric acid).
    - **Halogenation:** With bromine water, yields a white precipitate of 2,4,6-tribromophenol. With bromine in CS_2 at low temperature, yields monobromophenols.
- **Kolbe's Reaction:** Phenoxide ion reacts with CO_2 followed by acidification to yield Salicylic acid.
- **Reimer-Tiemann Reaction:** Treatment with chloroform in the presence of aqueous $NaOH$ yields Salicylaldehyde.
- **Oxidation:** Oxidation with chromic acid yields a conjugated diketone.
  $$Phenol \xrightarrow{Na_2Cr_2O_7/H_2SO_4} \text{Benzoquinone}$$
- **Reduction:** Heating with zinc dust reduces phenol to benzene.
  $$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$$

7. Chemical Properties of Ethers

- **Cleavage of C-O bond:** Ethers are relatively unreactive. The C-O bond is cleaved only under drastic conditions with excess hydrogen halides (HI or HBr).
  $$R - O - R' + HX \rightarrow R - X + R' - OH$$
    - In alkyl aryl ethers, the alkyl-oxygen bond is cleaved (yielding phenol and alkyl halide) because the aryl-oxygen bond has partial double bond character and is stronger.
- **Electrophilic Substitution:** The alkoxy group ($-OR$) is ortho-para directing and activates the aromatic ring toward halogenation, Friedel-Crafts reaction, and nitration.

8. Commercially Important Alcohols

- **Methanol (CH_3OH):** Also known as "wood spirit". Produced commercially by the catalytic oxidation of carbon monoxide at high temperature and pressure in the presence of $ZnO - Cr_2O_3$ catalyst. It is highly poisonous; ingestion causes blindness or death.
- **Ethanol (C_2H_5OH):** Obtained commercially by the fermentation of sugars (molasses or starch) using enzymes invertase and zymase present in yeast.
    - **Denatured Alcohol:** To prevent misuse of industrial ethanol for drinking, it is made unfit by adding poisonous substances like methanol, pyridine, and copper sulphate (to give it color).