

Chapter_11

Alcohols, Phenols and Ethers

1. Alcohols and phenols are formed when a hydrogen atom in a hydrocarbon, (aliphatic and aromatic respectively) is replaced by —OH group. Alcohols are named by replacing 'e' of parent alkane with suffix 'ol'.

2. **Preparation methods of alcohols** are by hydration of alkenes, by hydroboration-oxidation, by reduction of aldehydes and ketones or reaction of Grignard reagent with aldehydes or ketones.

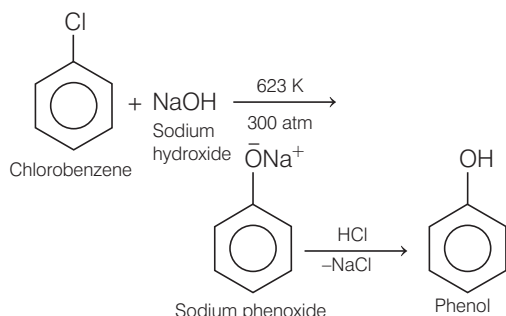
Aldehydes gives 1° alcohol and 2° alcohol on reduction while ketone gives 3° alcohol with Grignard reagent.

3. **Lucas test** Tertiary alcohol gives turbidity, immediately, secondary alcohol show turbidity in about 5 minutes while primary alcohol does give turbidity very slowly at room temperature.

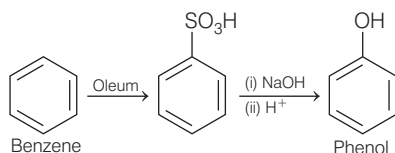
4. Preparation Methods of Phenol

These are as follows :

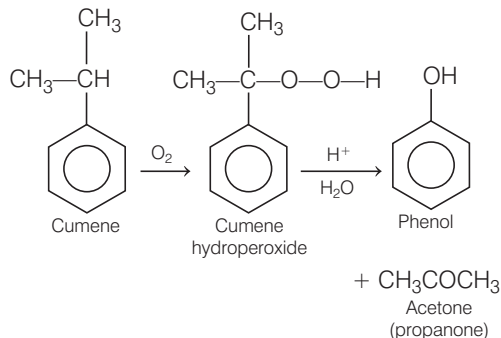
- Chlorobenzene on fusion with NaOH at 623 K and 320 atm pressure gives sodium phenoxide which on acidification yield **phenol**.



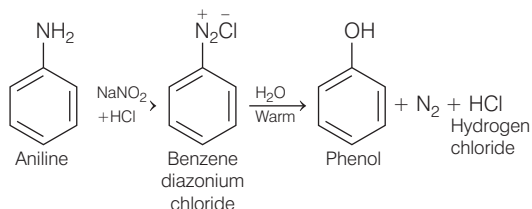
- From benzene sulphonic acid



- Cumene (isopropyl benzene) on aerial oxidation, form cumene hydroperoxide, which on subsequent hydrolysis with dilute acid gives phenol and propanone.



- From diazonium salts



5. Physical Properties

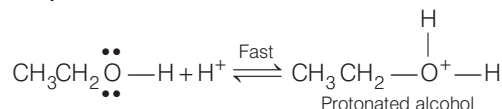
- The **boiling points of alcohols and phenols** increase with the increase in number of C-atoms (increase in van der Waals' forces). Amongst isomeric alcohols, the boiling points decreases with increase in branching in the carbon chain because of decrease in surface area (decrease in van der Waals' forces).
- Solubility of alcohols and phenols in water is due to their ability to form H-bonds with water molecules. Solubility decreases with increase in size of alkyl/aryl groups (due to steric hindrance).

6. Chemical Properties

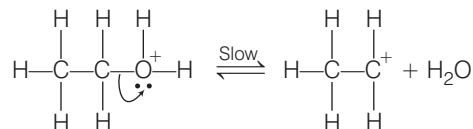
- Phenols are more acidic than alcohols**, due to more stabilisation of phenoxide ion formed by delocalisation of negative charge. Presence of electron withdrawing groups such as —NO₂, —CHO, etc. increases acidic strength of phenol by stabilising phenoxide ion whereas, electron releasing group, like —CH₃ reduces the acidic strength of phenol.
- Alcohols and phenols react with carboxylic acids, acid chlorides or acid anhydrides to form esters.
- Alcohols undergo **dehydration** when treated with conc. H₂SO₄ or H₃PO₄.

The steps involved in this process are:

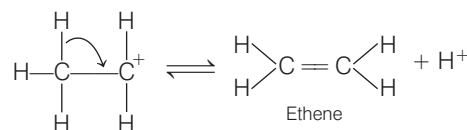
Step I Protonation of alcohol



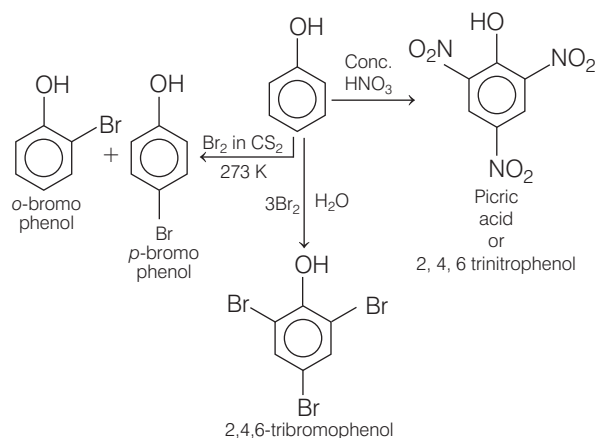
Step II Formation of carbocation [slowest step, hence is a rate determining step]



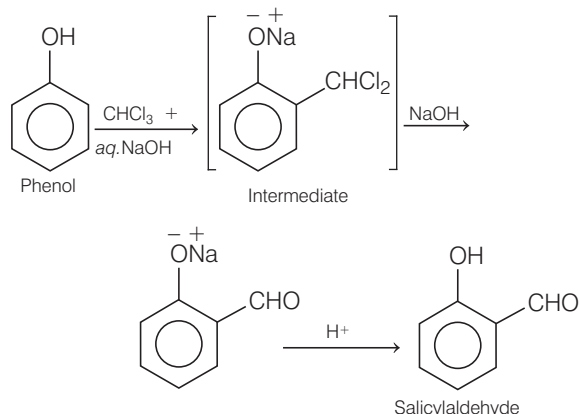
Step III Formation of ethene by elimination of a proton



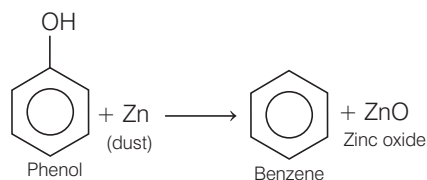
- Phenol gives 2,4,6-trinitrophenol (or picric acid) when treated with conc. HNO₃ and 2,4,6-tribromophenol when treated with Br₂/H₂O. However, when phenol is treated with Br₂ in CS₂, it gives o- and p-bromophenol.



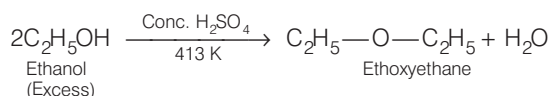
- On treating phenol with CHCl_3 (chloroform) in the presence of sodium hydroxide, a $-\text{CHO}$ group is introduced at *ortho* position of benzene ring. This reaction is called **Reimer-Tiemann reaction**. In this reaction, electrophile is dichlorocarbene ($:\text{CCl}_2$).



- Phenol can be converted to benzene on heating with zinc dust.

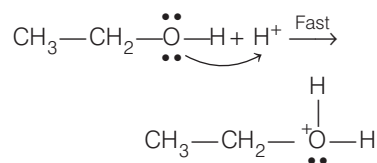


- Alcohols are made unfit for drinking by mixing some copper sulphate (CuSO_4) and pyridine in it. The process is known as **denaturation of alcohol**.
- Ethers** are named as alkoxyalkane where alkoxy is generally the smaller group attached with O-atom.
- Preparation of ethers** Ethanol is dehydrated to ethoxyethane at 413 K in the presence of sulphuric acid.

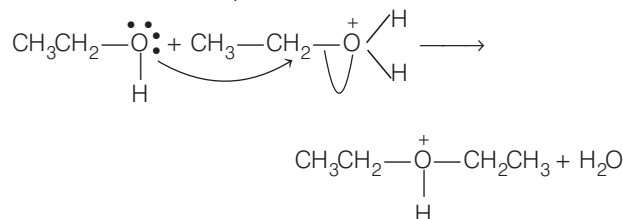


Mechanism

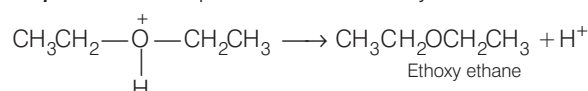
Step I Protonation of alcohol



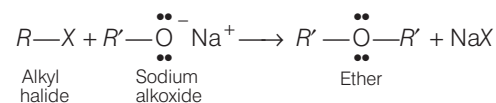
Step II Nucleophilic attack by unprotonated alcohol molecule on protonated alcohol molecule.



Step III Loss of proton to form ethoxy ethane.

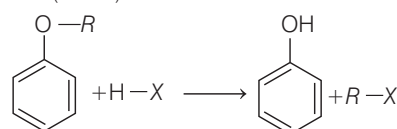
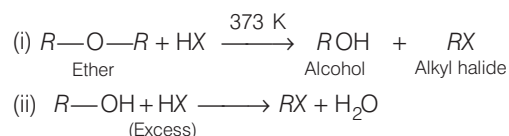


- In **Williamson's synthesis**, a primary alkyl halide is allowed to react with sodium alkoxide, to form ether.



In case of secondary or tertiary halides, elimination product is the major product.

- Chemical reactions of Ethers** The cleavage of $\text{C}-\text{O}$ bond in ethers take place under drastic conditions with HX .



Alkyl/aryl ethers are cleaved at alkyl-oxygen bond due to more stable aryl oxygen bond.

The reaction gives phenol and alkyl halide.

- Alkoxy group ($-\text{OR}$)** activates the aromatic ring towards electrophilic substitution and directs the incoming electrophile at *o*- and *p*-positions (because of the negative charges at *o*- and *p*-positions which indicates the more electron density at these positions).
- Anisole undergoes Friedel-Craft's reaction**, i.e. the alkyl and acyl groups are introduced at *o*- and *p*-positions by reaction with alkyl halide and acyl halide in the presence of anhydrous aluminium chloride (a Lewis acid) as catalyst.