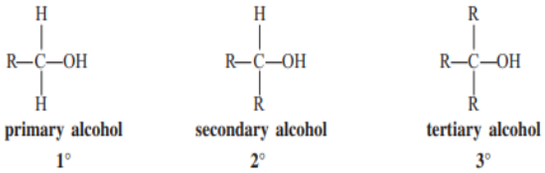
26

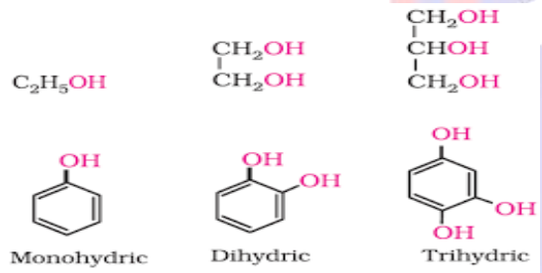
ALCOHOLS, PHENOLS AND ETHERS

ALCOHOLS

- Hydroxyl (–OH) derivatives of alkane are called alcohols.
- Alcohols are classified as 1°, 2° and 3°



- –OH group is attached to sp^3 hybridized carbon. Alcohols further may be monohydric, dihydric and polyhydric on the basis of OH group.



General Methods of Preparation

(i) Acid catalysed hydration of alkenes:

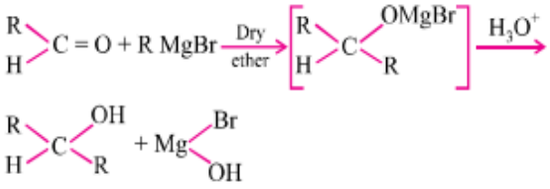
$$CH_3-CH=CH_2 + H_2O \xrightarrow{dil.H_2SO_4} CH_3-\underset{OH}{CH}-CH_3$$

(ii) Hydroboration oxidation:

$$3CH_3-CH=CH_2 + \tfrac{1}{2}B_2H_6 \xrightarrow{D.E} (CH_3-CH_2-CH_2)_3B \xrightarrow[H_2O_2]{OH^-}$$

$$CH_3-CH_2-CH_2OH + H_3BO_3$$

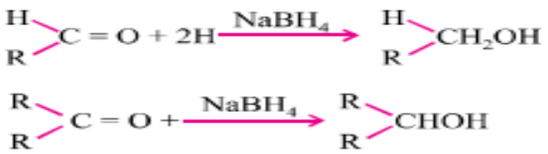
(iii) From carbonyl compounds with Grignard's reagent:



- Formaldehyde gives 1º alcohol and ketones gives tertiary alcohol.

(iv) By reduction of carbonyl compounds:

$$RCHO + 2H \xrightarrow{Pd} RCH_2OH$$



(v) By reduction of esters with $LiAlH_4$ or Na/C_2H_5OH:

$$R-\overset{O}{\overset{\|}{C}}-OR' + 4H \xrightarrow{LiAlH_4} R-CH_2OH + R'-OH$$

(vi) By hydrolysis of esters:

$$R-\overset{O}{\overset{\|}{C}}-O-R' + H_2O \underset{H_2SO_4}{\overset{conc}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-OH + R'-OH$$

(vii) From alkyl halides:

$$R-X + KOH\,(aq) \rightarrow R-OH + KX$$

(viii) By reduction of acids and their derivatives:

$$R-COOH \xrightarrow{LiAlH_4} RCH_2OH$$

$$R-COCl + 2H_2 \xrightarrow{Ni} R.CH_2OH + HCl$$

Structure and Physical Properties

- Most of the common alcohols are colourless liquids at room temperature. Methyl alcohol, ethyl alcohol, and isopropyl alcohol are free-flowing liquids with fruity odours. The boiling points of alcohols are much higher than those of alkanes with similar molecular weights.
- The structure of alcohols is similar to that of water.

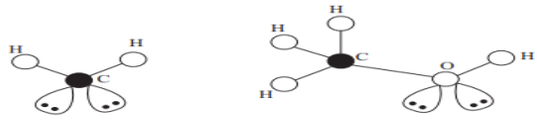
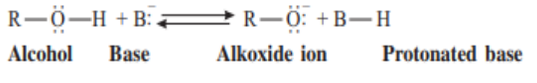


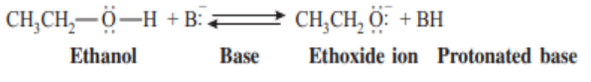
Fig. 26.1: Water and Methanol molecule

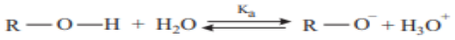
Reactions of Alcohols

1. Acidic and Basic behavior

- Alcohol behaves both as acids and bases. They are weakly acidic. A strong base such as a hydride ion (H–) in sodium hydride (NaH), can remove the proton from the alcohol molecule and an alkoxide ion results.



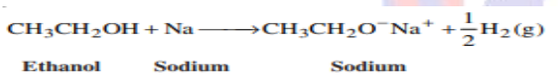


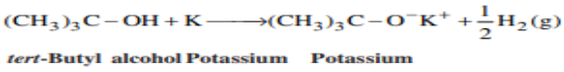


$$K_a = \frac{[H_3O^+]][RO^-]}{[ROH]}$$

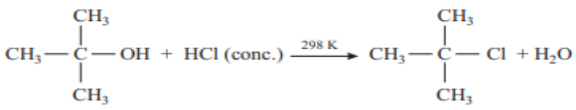
$$pK_a = -\log K_a$$

2. Formation of Alkoxides

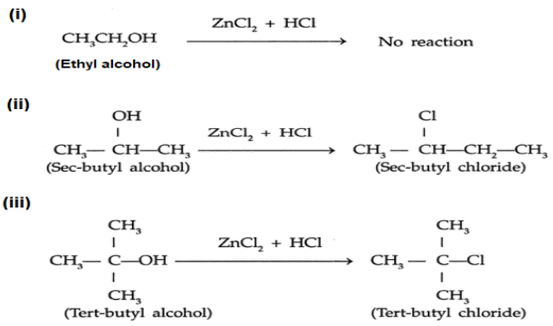




3. Conversion to Alkyl Halides



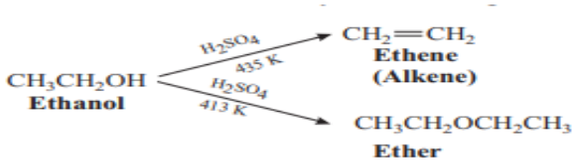
- **Lucas Test:** Lucas test is used to differentiate and categorize primary, secondary and tertiary alcohols using a solution of anhydrous zinc chloride in concentrated hydrochloric acid.



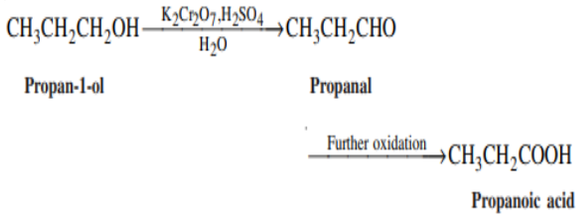
4. Formation of Alkenes

- Alcohols can be dehydrated to alkenes. This reaction requires an acidic catalyst and is favoured at higher tempratures.
- The ease of dehydration follows the followingorder amongst alcohols.
  Tertiary alcohols > secondary alcohols > primary alcohols

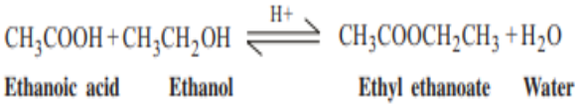
5. Dehydration to form Ethers



6. Oxidation

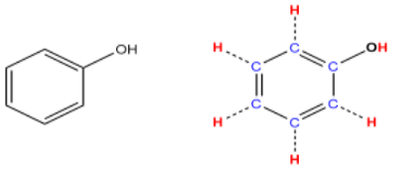


7. Formation of Esters



PHENOLS

- The name phenol is specifically used for the following compound (hydroxybenzene) in which one hydroxyl group is attached to the benzene ring.



Nomenclature of Phenols

- Some representative examples of phenolic compounds are given below:

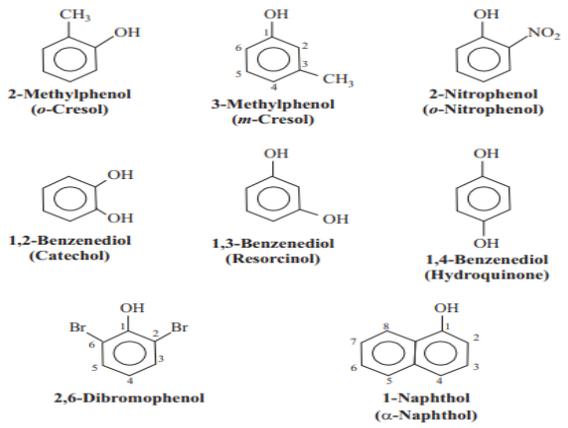
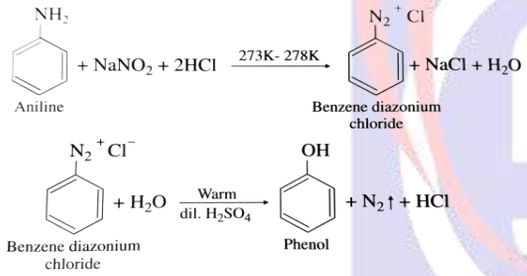


Fig: 1 Nomenclature of Phenols

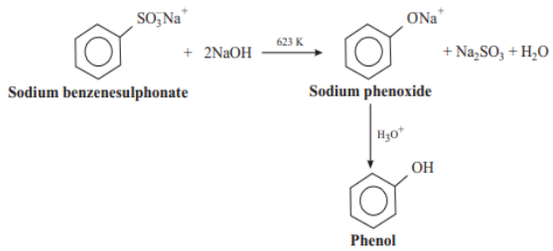
General Methods of Preparation

A. Laboratory Synthesis of Phenols

1. From Arenediazonium Salts

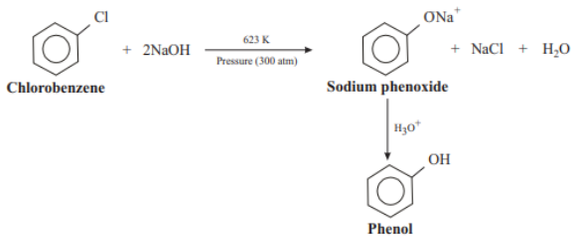


2. Alkali Fusion of Sodium Benzenesulphonate



B. Industrial Synthesis of Phenols

1. Dow Process



2. From Cumene Hydroperoxide

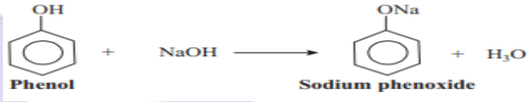
Physical Properties

- These are colourless liquids or crystalline solids but become coloured due to slow oxidation with air.
- Phenol is also called carbolic acid.
- Because of the presence of polar -OH bond, phenols form intermolecular H-bonding with other phenol molecules and with water.

Reactions of Phenols

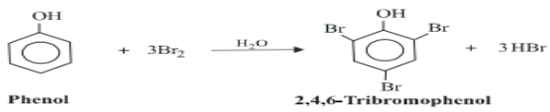
1. Acidic and Basic Nature

- Aqueous solutions of phenol are weakly acidic and turn blue litmus slightly to red. Phenol is neutralized by sodium hydroxide forming ***sodium phenate or phenolate***, but being weaker than carbonic acid, it cannot be neutralized by sodium bicarbonate or sodium carbonate to liberate carbon dioxide.

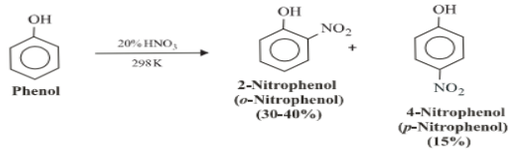


2. Electrophilic Substitution Reactions

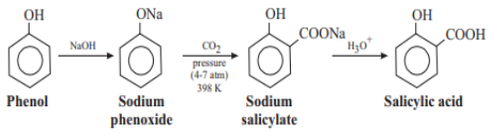
(i) Halogenation:



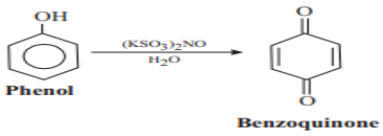
(ii) Nitration:



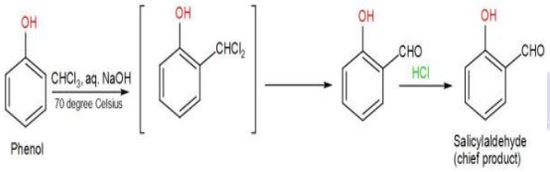
3. Kolbe Reaction:



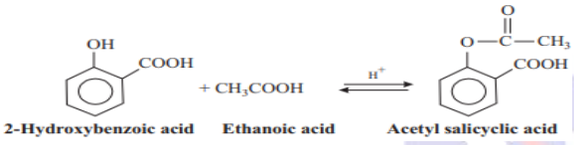
4. Oxidation



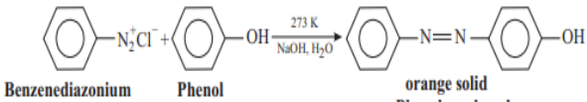
5. Reimer Tiemann Reaction



6. Esterification

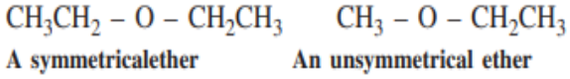


7. Coupling Reaction

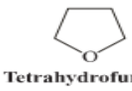


ETHERS

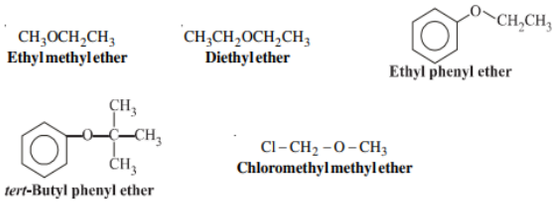
- Ethers are organic compounds in which an oxygen atom is bonded to two alkyl groups or aryl groups.



- The oxygen atom of the ether can also be part of a ring, in which case the ether is known as cyclic ether.

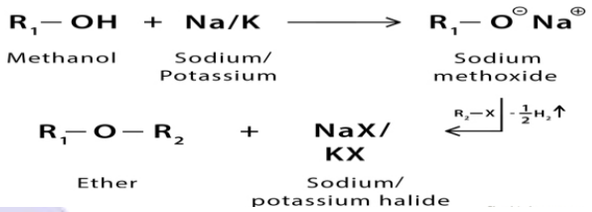


Nomenclature of Ethers



General Methods of Preparation

Williamson Synthesis:



Structure and Properties of Ethers

- Ethers have geometry similar to water and alcohols. The oxygen atom is 3 sp hybridised.

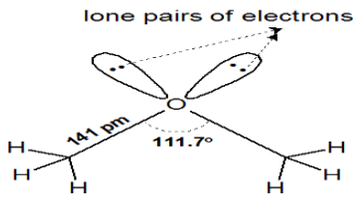
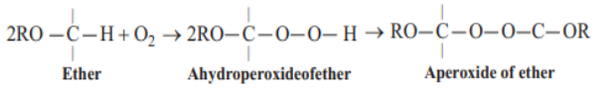


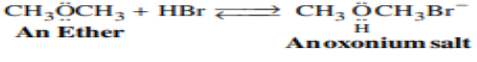
Fig. 26.7: Polar ether molecule

Reactions of Ethers

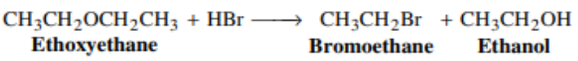
1. Reaction with Oxygen:



2. Reaction wtih Acids



3. Acidic Cleavage



Check Yourself

1. Among the following compounds, strongest acid is

(A) H-C = C-H (B) C_6H_6

(C) C_2H_6 (D) CH_3OH

2. The compound which gives the most stable carbonium ion on dehydration is

(A) $(CH_3)_2CHCH_2OH$

(B) $(CH_3)_3COH$

(C) $CH_3CH_2CH_2CH_2OH$

(D) $CH_3CHOHCH_2CH_3$

3. In CH_3CH_2OH, the bond that undergoes heterolytical change most readily is

(A) C-C (B) C-O

(C) C-H (D) O-H

4. Phenol reacts with Br_2 in CS_2 at low temperature to give

(A) o-Bromophenol

(B) o-and p-promophenols

(C) p-Bromophenol

(D) 2, 4, 6 Tribromophenol

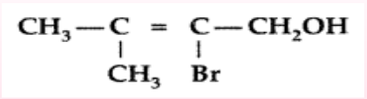
5. In the reaction of phenol with CHCl3 and aqueous NaOH at 343 K, the electrophile attacking the ring is:

(A) $CHCl_3$ (B) $CHCl_2$

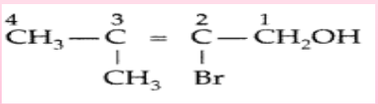
(C) CCl_2 (D) $COCl_2$

Test Yourself

Question: Give the IUPAC name of the following compound:



Answer:



IUPAC name: 2-Bromo-3-methyl-but-2-ene-1-ol

Stretch Yourself

1. Write the structure of the molecule of a compound whose IUPAC name is: 1-phenylpropan-2-ol
2. How would you convert ethanol to ethene?
3. Draw the structure of 2, 6-Dimethylphenol.
4. Ortho nitrophenol has lower boiling point than p-nitrophenol. Why?
5. The C-O bond is much shorter in phenol than in ethanol. Give reason.

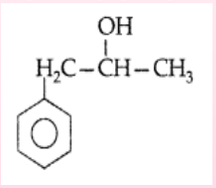
Answers

Check Yourself

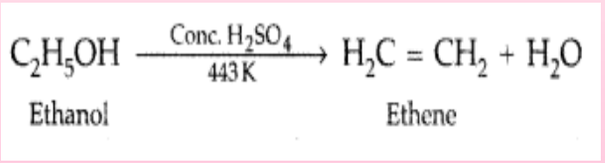
Answer: 1(D); 2(B); 3(D); 4(B); 5(C)

Stretch Yourself

1. 1-phenylpropan-2-ol



2.



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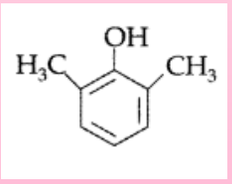

4. Ortho-nitrophenol has lower boiling point due to formation of intramolecular H-bonding whereas p-nitrophenol forms intermoleeular H-bonding.

5. Carbon of C-O bond of phenol is Sp^2 hybridised, so it acquires a partial double bond character but in ethanol it is Sp^3 hybridised and a single bond. Double bond is shorter than a single bond.