MIND MAP-11

ALCOHOLS, PHENOLS AND ETHERS **Alcohols**

Preparation:

• By acid catalysed hydration: Alkanes reacts with H₂O in presence of acid (as catalyst).

$$CH_3CH = CH_2 + H_2O \xrightarrow{\text{H}^+} CH_3CH(OH)CH_3$$
(markovnikov's addition)

By Hydroboration-Oxidation:

Diborane with alkene gives trialkyl boride which gives alcohol with H₂O₂/OH

CH₃CH = CH₂
$$\xrightarrow{\text{(i) B}_2\text{H}_6/\text{THF}}$$
 CH₃CH₂CH₂OH
$$\xrightarrow{\text{(ii) H}_2\text{O}_2, \text{OH}^-}$$
anti-markovnikov's addition

Reduction of Aldehydes and Ketones

$$Aldehyde \xrightarrow{\quad H_2/Pd \quad} 1^{\circ}Alcohol$$

Reduction of carboxylic acids:

$$RCOOH \xrightarrow{(i) LiAlH_4} RCH_2OH$$

• From Grignard Reagent:

$$R \longrightarrow O + R'MgX \longrightarrow \begin{bmatrix} R & -+ \\ R & OMgX \end{bmatrix}$$

$$\xrightarrow{H_2O} R \longrightarrow R \longrightarrow OH + Mg(OH)X$$

- Physical Properties of Alcohols:
- Alcohols are colourless with characteristic smell (alcoholic).
- They are soluble in water due to H-bonding.
- These are partially soluble in organic solvents.
- They are liquid in nature up to 12-carbon.
- Melting point and boiling point ∞ molecular mass ∝ 1/No. of branches

 • Boiling point of alcohols are higher than the
- corresponding ether due to H-bonding.
- Chemical Properties:
- $2ROH + 2M \longrightarrow 2R \overrightarrow{OM} + H_2 (M = Na, K, Cl)$
- $RCOOH + H OR' \longrightarrow RCOOR' + H_2O$
- $RCOCl+H-OR' \longrightarrow RCOOR' + HCl$
- $ROH + R'MgX \longrightarrow R' H + ROMgX$

Commercially important alcohols:

- Methanol: Methanol, CH₃OH, also known as 'wood spirit', was produced by destructive distillation of wood. Methanol is used as a solvent in paints, varnishes and for making formaldehyde.
- Ethanol: Ethanol is a colourless liquid with boiling point 351 K. It is used as a solvent in paint industry and in the preparation of a number of carbon compounds. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

Preparation:

Physical Properties of Ethers

- Dimethyl ether and ethyl methyl ether are gases. All other are colourless liquids with pleasant
- They are sparingly soluble in water but readily soluble in organic solvents. Solubility of ether in water is due to hydrogen bonding between ether and water molecule.

$$\begin{smallmatrix}R-O---H-O-H\\|\\R\end{smallmatrix}$$

- Boiling points of ether show a gradual increase with increase in molecular weight. Ethers have low boiling points than isomeric alcohols as there is no association with hydrogen bonding between ether molecules. The boiling points of ethers are close to the boiling points of alkanes.
- They are lighter than water.
- Lower ethers are highly volatile and
- $R-OH+HCI \xrightarrow{anh. ZnCl_2} R-Cl+H_2O$
- $CH_3CH_2OH \xrightarrow{conc. H_2SO_4} CH_2 = CH_2 + H_2O$
- $RCH_2OH \xrightarrow{[O]} R C = O \xrightarrow{[O]} R C OH$

Ethers

Preparation: • Dehydration of alcohol:

$$2CH_3CH_2OH \xrightarrow{H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

Phenols

• Williamson's synthesis:

 $R-X+R'-ONa \longrightarrow ROR'+NaX$ Here, alkyl halide should be primary because secondary and tertiary alkyl halides give elimination reaction rather than substitution.

Thus, the reactivity order is $1^{\circ} > 2^{\circ} > 3^{\circ}$

Chemical Properties:

• Cleavage of C-O bond:

$$\begin{array}{l} ROR + HX \longrightarrow RX + ROH \\ ROH + HX \longrightarrow RX + H_2O \\ PhOR + HX \longrightarrow PhOH + RX \end{array}$$

• Reactivity with HX: Reactivity order of HX is HI > HBr >> HCl.

$$\begin{array}{c} \text{HI} \longrightarrow \text{CH}_3\text{I} + \text{CH}_3\text{CH}_2\text{OH} \\ & \text{HI (excess)} \longrightarrow \text{CH}_3\text{I} + \text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{CH}_3\text{CH}_2\text{I} + \text{H}_2\text{O} \\ \\ \text{C(CH}_3)_3\text{OCH}_3 + \text{HI} \longrightarrow \begin{array}{c} \text{S}_N\text{I} \longrightarrow \text{C(CH}_3)_3\text{I} \end{array}$$

• Electrophilic substitution:

$$\begin{array}{c} \text{Br}_2 \\ \text{OCH}_3 \\ \text{CH}_3\text{CI} \\ \text{anhyd. AlCl}_3 \\ \text{HNO}_3 \\ \end{array} \\ \begin{array}{c} \text{H}_2\text{SO}_4 \\ \text{HNO}_3 \\ \end{array} \\ \begin{array}{c} \text{H}_3\text{CO} \\ \text{(major)} \\ \end{array} \\ \begin{array}{c} \text{OCH}_3 \\ \text{(major)} \\ \text{NO}_2 \\ \text{(major)} \\ \end{array}$$

Preparation:

- Chlorobenzene + NaOH (i) 623 K, 300 atm. → Phenol
- Benzene $\xrightarrow{\text{(i) Oleum}}$ Phenol
 - Aniline $\xrightarrow{\text{NaNO}_2 + \text{HCl}}$ Diazonium salt $\xrightarrow{\text{H}_2\text{O}}$ Phenol
- Cumene $\xrightarrow{\text{(i) O}_2}$ Phenol

Physical properties:

- Phenols are colorless crystalline solid or liquid having characteristic odour.
- Due to hydrogen bonding phenols has higher boiling point and more solubility compared to arene compounds which contains approximately same molecular mass.

Chemical Properties:

$$\begin{array}{c} \text{dil HNO}_3 \\ \text{298 K} \\ \text{HO} \\ \text{NO}_2 \\ \text{OH} \\ \text{NO}_2 \\ \text{OH} \\ \text{(Picric acid)} \\ \text{NO}_2 \\ \text{OH} \\ \text{(Picric acid)} \\ \text{NO}_2 \\ \text{Br} \\ \text{OH} \\ \text{Br} \\ \text{OH} \\ \text{Sa}_{12} \text{ (aq)} \\ \text{Br} \\ \text{OH} \\ \text{ONa} \\ \text{(ii) H}^{+} \\ \text{OH} \\ \text{(Kolbe's reaction)} \\ \text{CHO} \\ \text{CHO}_3 \\ \text{NaOH (aq)} \\ \text{ONa} \\ \text{H}_2 \\ \text{OH} \\ \text{OH} \\ \text{(Reimer-tiemann reaction)} \\ \text{OH} \\ \text{CHO} \\ \text{OH} \\ \text{(Reimer-tiemann reaction)} \\ \text{OH} \\ \text{(Reimer-tiemann reaction)} \\ \text{OH} \\ \text{(Reimer-tiemann reaction)} \\ \text{(Reimer-tiemann react$$