Alcohols

Preparation of Alcohols:

- By hydrolysis of haloalkanes : R-X + aq. $KOH \rightarrow ROH + KX$
- By reduction of Carbonyl compounds

 By the action of Grignard's Reagent on aldehydes, ketones and esters

$$C = O + R - Mg - X \xrightarrow{\text{Dry}} C \xrightarrow{\text{OMgX}} R \xrightarrow{\text{H}_2O} C \xrightarrow{\text{OH}} R + Mg \xrightarrow{\text{N}_2O} X$$

- By Aliphatic Primary Amines: RCH₂NH₂ + HNO₂ → RCH₂OH + N₂ + H₂O
- Hydration of alkenes:

$$CH_2 = CHR + H_2SO_4 \xrightarrow{Boil} CH_3 - CH(R)OH$$

• Oxymercuration-demercuration:

$$H_3C$$
 H_3C
 H_3C
 CH_2
 H_3C
 CH_3
 HO
Markonikov's Addition

• Hydroboration-oxidation:

$$H_3C$$
 \longrightarrow
 $B_2H_6/THF/H_2O_2$
 \longrightarrow
 H_3C
 \longrightarrow
 OH

Anti Markonikov's Addition

• Hydroxylation of alkenes:

$$\begin{array}{c}
Dil.KMnO_4 \text{ or OsO}_4
\end{array}$$

$$\begin{array}{c}
OH\\
\text{OH}\\
\text{syn-Hydroxylation}
\end{array}$$

$$\begin{array}{c}
OH\\
\text{OH}\\
\text{anti-Hydroxylation}
\end{array}$$

Physical Properties of Alcohol:

- Lower alcohols are liquid at room temperature while higher ones are solid.
- High boiling point due to presence of intermolecular hydrogen bonding. Order of Boiling Point: primary > secondary > tertiary
- Solubility in water decreases with increase in molecular mass due to decrease in extent of intermolecular hydrogen bonding.

Chemical Properties of Alcohol:

- Alcohol's reaction with metal: ROH + Na→2RO⁺Na⁻ + H₂
- Formation of Halides:

$$\circ$$
 3ROH + P+I2 \rightarrow 3RI + H₃PO₃

∘ ROH +
$$SOCl_2/PCl_3/PCl_5 \rightarrow RCl$$

$$\circ$$
 ROH+HX \rightarrow RX

○ ROH+ NaBr,
$$H_2SO_4 \rightarrow R$$
-Br

- ∘ R_2 C-OH alcohol + HCl→ R_2 CCl
- Reaction with HNO₃: R-OH + HO-NO₂→ R-O-NO₂
- Reaction with carboxylic acid (Esterification): R-OH +R'-COOH +H⁺ ↔ R'-COOR
- Reaction with Grignard reagent: $R'OH + RMgX \rightarrow RH + R'OMgX$
- Reduction of alcohol : ROH + 2HI + Red P→ RH +I₂+H₂O
- **Dehydration of Alcohol:** Dehydration of alcohols takes place in acidic medium. Intra-molecular dehydration leads to the formation of alkene while inter molecular dehydration which forms ether. Ease of dehydration: $3^{\circ} > 2^{\circ} > 1$
- Satyzeff's Rule: Elimination through b carbon containing minimum b hydrogen

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} - \overset{\bullet}{\text{C}} - \text{CH}_{2} - \overset{\bullet}{\text{O}} - \text{H} + \text{H}^{+} \xrightarrow{\text{conc. H}_{2} \text{SO}_{4}} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} - \overset{\bullet}{\text{C}} - \text{CH}_{2} - \text{CH}_{3} \\ \text{CH}_{3} - \overset{\bullet}{\text{C}} - \text{CH}_{2} - \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} - \overset{\bullet}{\text{C}} - \text{CH}_{2} - \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} - \overset{\bullet}{\text{C}} = \text{CH}_{2} - \text{CH}_{3} \\ \end{array}$$

• Oxidation of Alcohol:

$$RCH_2$$
-OH + [O] \rightarrow RCHO \rightarrow RCOOH
RCH₂-OH + [O] +PCC \rightarrow RCHO

Haloform Reaction: Compound containing CH₃CO- group (or compound on oxidation gives CH₃CO – group) which is attached with a C or H, in presence of halogen and mild alkali gives haloform.CH₃-CH₂-COCH₂-CH₃, CH₃-CO-Cl, CH₃COOH will not respond to haloform reaction wile CH₃CH₂OH will respond to haloform Reaction.

$$\begin{array}{c} H & O \\ | CH_3 - C - OH \xrightarrow{Cl_2} CH_3 - C - H \\ | H \end{array}$$

$$\begin{array}{c} CH_3 - CH_3$$

Test for Alcohols:

1. Lucas Test:

 $Alcohols + ZnCl_2 + HCl$

• 1° Alcohol: $RCH_2OH + ZnCl_2 + HCl \rightarrow No$ reaction at room temperature

- 2⁰ Alcohol: $R_2CHOH + ZnCl_2 + HCl \rightarrow R_2CHCl$ White turbidity after 5-10 min.
- 30 Alcohol: $R_3CHOH + ZnCl_2 + HCl \rightarrow R_3CHCl$ white turbidity instantaneously.

2. Victor Meyer Test

$$1^{\circ} \text{ alcohol:} \qquad \text{RCH}_2\text{OH} \xrightarrow{\text{P/I}_2} \text{RCH}_2\text{I} \xrightarrow{\text{AgNO}_2} \text{RCH}_2\text{NO}_2 \xrightarrow{\text{HNO}_2} \text{R} - \text{C} - \text{NO}_2 \\ \text{NOH} \qquad \qquad \qquad \text{(nitrolic acid)} \\ \text{NaOH} \qquad \qquad \text{CH}_3\text{CNO}_2 \\ \text{Sodium salt of nitrolic acid} \qquad \text{NONa}_2 \\ \text{Red solver} \qquad \qquad \text{Red solver} \qquad$$

Nitrolic acid on treatment with alkali gives colouration

2° alcohol:

$$\begin{array}{c} R \\ R \end{array} \xrightarrow{P/I_2} \begin{array}{c} R \\ R \end{array} \xrightarrow{AgNO_2} \begin{array}{c} R \\ R \end{array} \xrightarrow{HNO_2} \\ R \xrightarrow{HNO_2} \begin{array}{c} R \\ R \end{array} \xrightarrow{HNO_2} \\ R \xrightarrow{I} \begin{array}{c} R \\ R \end{array} \xrightarrow{R} \begin{array}{c} R$$

3° alcohol:
$$R_3C - OH \xrightarrow{P/I_2} R_3C - I \xrightarrow{AgNO_2} R_3C - NO_2$$

No reaction

(colour less)