## CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT Based Notes of Chapter - 11) GANESH KUMAR DATE:- 14/10/2020

# Aldehyde, Ketones and Carboxylic Acid

### **Preparation of Aldehydes and Ketones**

**1. By oxidation of alcohols**: Primary alcohols on oxidation with mild oxidising agents like CrO<sub>3</sub> to give aldehydes while secondary alcohols give ketones.

 $\begin{array}{ccc} R-CH_2OH & \stackrel{[0]}{\longrightarrow} & R-CHO \\ Primary alcohol & Aldehyde \\ R_2CHOH & \stackrel{[0]}{\longrightarrow} & R_2CO \\ Secondary alcohol & Ketones \end{array}$ 

 By dehydrogenation of alcohols: Alcohols when heated with Cu or Silver catalyst at 573K, we get carbonyl compounds. Primary alcohols give aldehydes, while secondary alcohols give ketones.

 $\begin{array}{ccc} \text{R-CH}_2\text{OH} & \underbrace{\text{Cu/573 K}}_{\text{W}} & \text{R-CHO} \\ \text{Primary alcohol} & \text{Aldehyde} \\ \text{R}_2\text{CHOH} & \underbrace{\text{Cu/573 K}}_{\text{W}} & \text{R}_2\text{CO} \\ \text{Secondary alcohol} & \text{Ketones} \end{array}$ 

**3.** By ozonolysis of alkenes: Alkenes add ozone followed by hydrolysis with zinc dust and water, we get aldehydes or ketones.



**4.** By hydration of alkynes: Alkynes add water in the presence of H<sub>2</sub>SO<sub>4</sub> and HgSO<sub>4</sub> to give carbonyl compounds. Ethyne (acetylene) gives acetaldehyde and all other alkynes give ketones.

 $CH \equiv CH + H_2O \xrightarrow{H2SO4/HgSO4} CH_3-CHO$ 

Ethyne

Acetaldehyde

 $CH_{3}-C \equiv CH + H_{2}O \xrightarrow{H2SO4/HgSO4} CH_{3}-CO-CH_{3}$ 

Propyne

Acetone

### Preparation of Aldehydes

#### 1. From acyl chloride (Acid chloride) [Rosenmund's Reduction]:

Acid chlorides react with hydrogen in presence of Pd supported on  $BaSO_4$ , we get aldehydes. This reaction is called Rosenmund's reduction.



Benzoyl chloride

Benzaldehyde

#### 2. From nitriles and esters: (Stephen reaction)

Nitriles when reduced with stannous chloride in the presence of hydrochloric acid, we get imines, which on hydrolysis give corresponding aldehyde. This reaction is called *Stephen reaction*.

 $\begin{array}{ccc} \text{RCN} + \text{SnCl}_2 + \text{HCI} & \longrightarrow & \text{R-CH=NH} \xrightarrow{\text{H3O+}} & \text{R-CHO} \\ \text{Nitrile} & \text{Imines} & \text{Aldehyde} \end{array}$ 

Nitriles can also be selectively reduced by *diisobutylaluminium hydride* (DIBAL-H) to imines followed by hydrolysis to aldehydes. DIBAL-H does not affect other reducable groups like double bonds.

 $\begin{array}{c} \text{R-CN} & \underbrace{1.\text{AlH (i-Bu)}^2}_{2. \text{ H2O}} & \text{R-CHO} \\ \text{Nitrile} & 2. \text{ H2O} & \text{Aldehyde} \end{array}$   $\text{CH}_3\text{-CH=CH-CH}_2\text{-CN} & \underbrace{1. \text{ DIBAL-H}}_{2 \text{ H2O}} & \text{CH}_3\text{-CH=CH-CH}_2\text{-CHO} \end{array}$ 

Esters are also reduced to aldehydes with DIBAL-H.

CH<sub>3</sub>-CH<sub>2</sub>-COOCH<sub>3</sub> Methyl Propanoate 1. DIBAL-H 2 H2O CH<sub>3</sub>-CH<sub>2</sub>-CHO Propanal