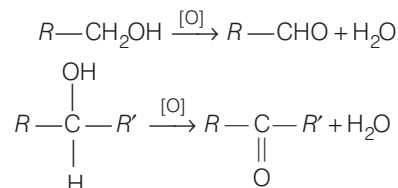


## Chapter\_12

### Aldehydes, Ketones and Carboxylic Acids

- The C=O group is known as the carbonyl group and the compounds containing C=O group are known as **carbonyl compounds**. In aldehydes, the carbonyl group is bonded with a carbon and a hydrogen, while in ketones, it is bonded with two carbon atoms. Aldehydes are named by adding suffix 'al' and ketones by adding suffix 'one'.

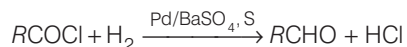
- Preparation of aldehydes and ketones** are obtained by the oxidation of 1° and 2° alcohols respectively by using PCC (Pyridine Chloro Chromate) or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> / H<sub>2</sub>SO<sub>4</sub> as reagents.



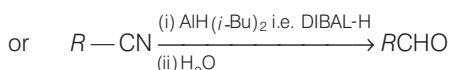
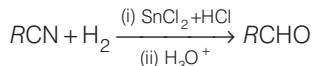
These are also obtained by dehydrogenation of alcohols, ozonolysis of alkenes, hydration of alkynes.

#### 3. Preparation of Aldehydes

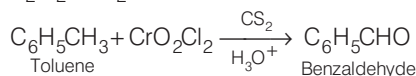
- Aldehydes are obtained by the reduction of carbonyl chloride with Pd / BaSO<sub>4</sub>, S. (Rosenmund reduction).



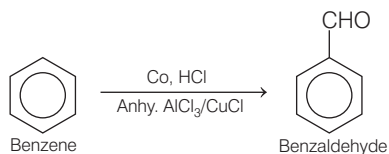
or by the reduction of —CN with SnCl<sub>2</sub> + HCl (Stephen reduction) followed by hydrolysis.



- Etard reaction** is also used to synthesise benzaldehyde from toluene by treating it with CrO<sub>2</sub>Cl<sub>2</sub> / CS<sub>2</sub> followed by hydrolysis.

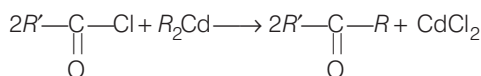


- Gattermann-Koch reaction**

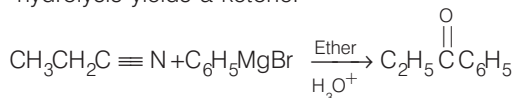


#### 4. Preparation of Ketones

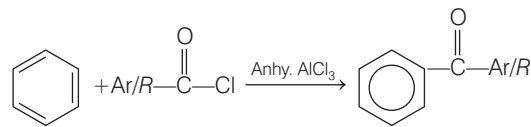
- Treatment of acyl chlorides with dialkyl cadmium give ketones.



- Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



- Treatment of benzene or substituted benzene with acid chloride in presence of anhyd. AlCl<sub>3</sub> gives ketone. This reaction is called Friedel Craft's acylation.

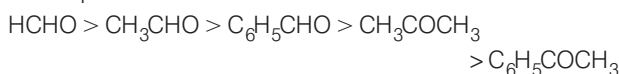


#### 5. Physical Properties

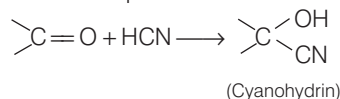
- Boiling points of aldehydes and ketones** are higher than hydrocarbons and ethers of comparable molecular masses.
- The solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.

#### 6. Chemical Properties

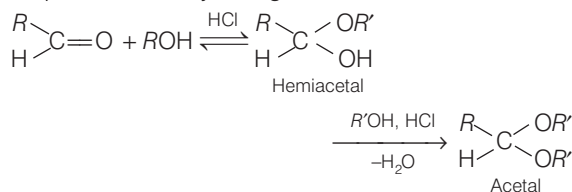
The order of reactivity of aldehydes and ketones for nucleophilic addition reactions are



- Carbonyl compound form **cyanohydrin** when treated with HCN in the presence of a base.

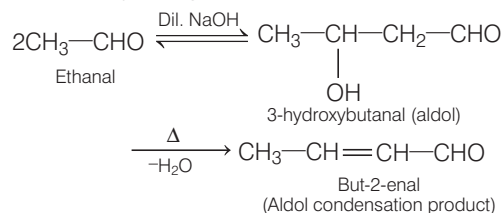


- Aldehydes form **hemiacetal** and **acetal** when treated with one or two equivalents of alcohol respectively in the presence of dry HCl gas.



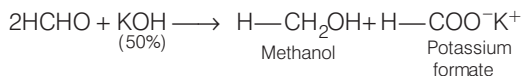
Ketones in this reaction form ketals.

- Carbonyl compounds form **2,4-DNP derivatives** (orange or yellow or red ppt.) with 2,4-DNP (2,4-dinitrophenyl hydrazine), Brady's reagent.
- Aldehydes reduce Tollen's reagent (ammoniacal silver nitrate) into silver mirror, Fehling's solution into red ppt. of Cu<sub>2</sub>O and Benedict's solution into red ppt. These reactions are not given by ketones.
- >C=O group is reduced to CH<sub>2</sub> group by using Zn-Hg/conc. HCl (Clemmensen reduction) or by using NH<sub>2</sub>—NH<sub>2</sub> + KOH (Wolff-Kishner reduction).
- Aldehydes and ketones containing α-H atoms undergo **aldol condensation** in the presence of dilute alkali as catalyst, e.g.



β-hydroxy aldehydes or ketones are collectively called **aldols** and the reaction is called **aldol condensation**.

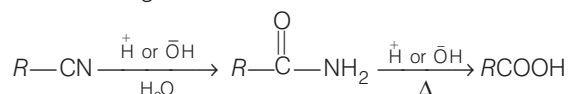
- When aldehydes having lack of  $\alpha$ -H atoms are treated with 50% alkali, it disproportionates to give reduction product, alcohol and oxidised product, salt of acid. This reaction is called **Cannizzaro reaction**.



7. Carbon compounds containing a carboxyl functional group ( $-\text{COOH}$ ) are known as **carboxylic acids**. Their names are derived by replacing the terminal 'e' from the name of corresponding straight chain alkane with suffix 'oic acid'.

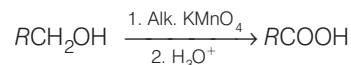
## 8. Preparation of Carboxylic Acids

- Nitriles are first hydrolysed to amides and then to acids in the presence of  $\text{H}^+$  or  $\text{OH}^-$  as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.

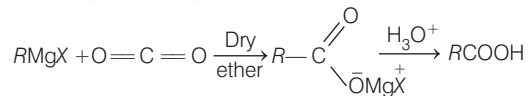


- Aromatic acids are obtained by vigorous oxidation of alkyl benzene with chromic acid or acidic or alkaline  $\text{KMnO}_4$ .

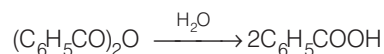
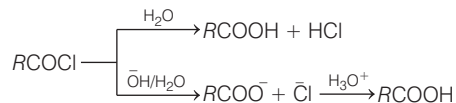
- From primary alcohols,



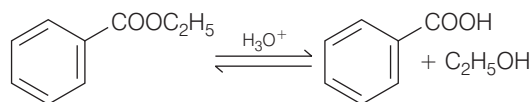
- From Grignard reagent,



- From acyl halide and anhydrides,



- From esters,

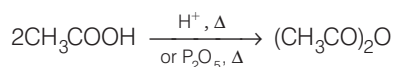


## 9. Physical Properties

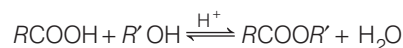
- Carboxylic acids have higher boiling points as compared to hydrocarbons, aldehydes and ketones, because they have high extent of hydrogen bonding with water due to which they exist as associated molecules.
- Melting point of an acid containing even number of carbon atoms is higher than the adjacent members containing odd number of carbon atoms.

## 10. Chemical Properties

- Carboxylic acids are stronger acids than phenols because carboxylate ion is much more resonance stabilised than phenoxide ion. Electron withdrawing groups (EWG) increase the stability of the carboxylate ion by dispersing the negative charge, while electron donating group decreases the stability of the carboxylate ion by intensifying the negative charge.
- Carboxylic acids on heating with mineral acids such as  $\text{H}_2\text{SO}_4$  or  $\text{P}_2\text{O}_5$  give anhydride.



- Carboxylic acids are esterified with alcohols or phenols in presence of a mineral acids such as conc.  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  gas.

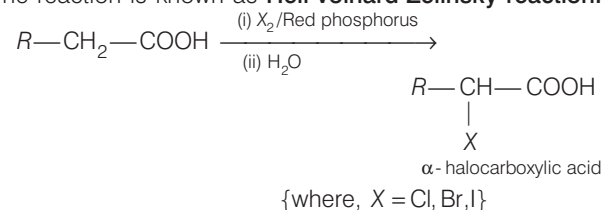


- Carboxylic acids react with  $\text{PCl}_3$ ,  $\text{PCl}_5$  and  $\text{SOCl}_2$  to give acyl chloride.
- Carboxylic acid react with ammonia to form amides.



- Carboxylic acids having an  $\alpha$ -hydrogen are halogenated at the  $\alpha$ -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give  $\alpha$ -halocarboxylic acids.

The reaction is known as **Hell-Volhard-Zelinsky reaction**.



11. **Aromatic carboxylic acids** undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and *meta*-directing group. However, they do not undergo Friedel-Crafts reaction because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.