12. ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

ALDEHYDES AND KETONES

1.Nomenclature

HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
CH_3COCH_3	Acetone	Propanone

2.Preparation of Aldehydes and Ketones

- **By oxidation of alcohols:** with mild oxidising agents like CrO_3

  Primary alcohols give aldehydes $R\text{-}CH_2OH \xrightarrow{[O]} R\text{-}CHO$

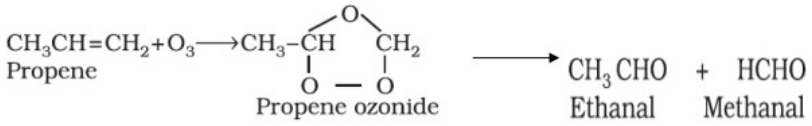
  secondary alcohols give ketones. $R_2CHOH \xrightarrow{[O]} R_2CO$

- **By dehydrogenation of alcohols:** with Cu or Silver catalyst at 573K,

  Primary alcohols give aldehydes $R\text{-}CH_2OH \xrightarrow{Cu/573\ K} R\text{-}CHO$

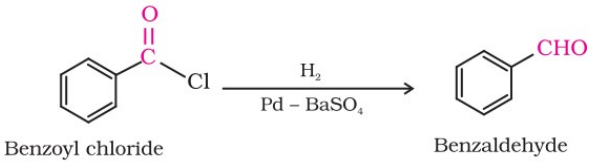
  secondary alcohols give ketones. $R_2CHOH \xrightarrow{Cu/573\ K} R_2CO$

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



3. Preparation of Aldehydes

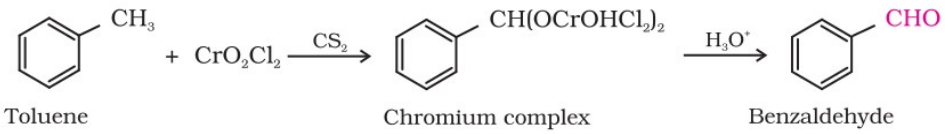
- **Rosenmund reduction.** Acid chlorides react with hydrogen in presence of Pd supported on $BaSO_4$, we get aldehydes.



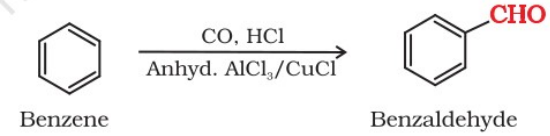
- **Stephen reaction.**:-Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3O^+} RCHO$$

- **Etard reaction.** Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde

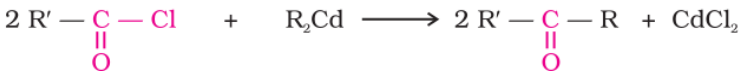


- **By Gatterman – Koch reaction:-**When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde
- or substituted benzaldehyde.

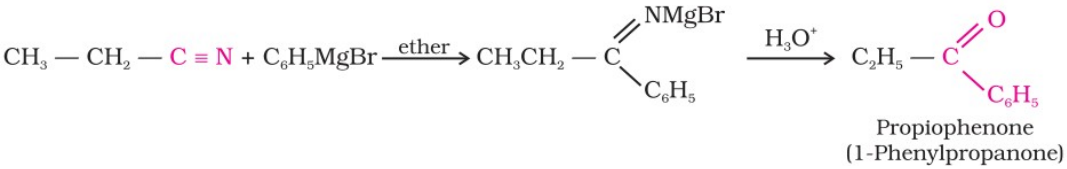


4. Preparation of Ketones

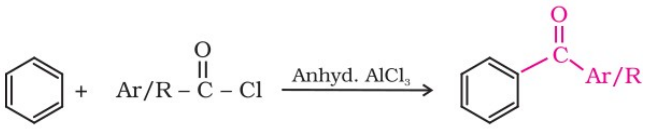
- **From acyl chlorides:**-Treatment of acyl chlorides with dialkylcadmium gives ketones.



- **From nitriles :**-Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



- **Friedel-Crafts acylation reaction.:**-When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride,gives corresponding ketone.



5. Chemical Reactions of Aldehydes and Ketones

a).Reduction

(i) Reduction to alcohols: Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$) as well as by catalytic hydrogenation

$$R\text{-}CHO \xrightarrow{[H]} R\text{-}CH_2OH$$

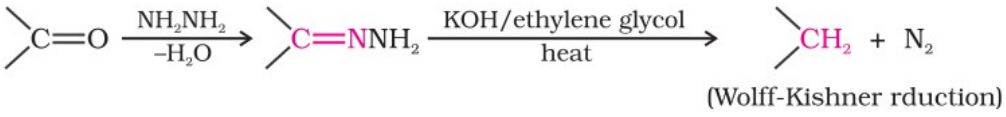
$$R_2CO \xrightarrow{[H]} R_2CHOH$$

b)Reduction to hydrocarbons:

i) Clemmensen reduction The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc- amalgam and concentrated hydrochloric acid

ii).Wolff-Kishner reduction

with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol .

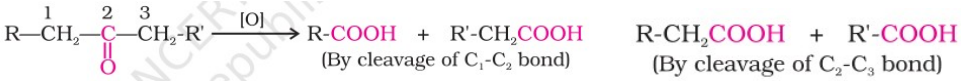


c)Oxidation

Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes.

$$R\text{-}CHO \xrightarrow{[O]} R\text{-}COOH \qquad CH_3\text{-}CHO \xrightarrow{[O]} CH_3\text{-}COOH$$

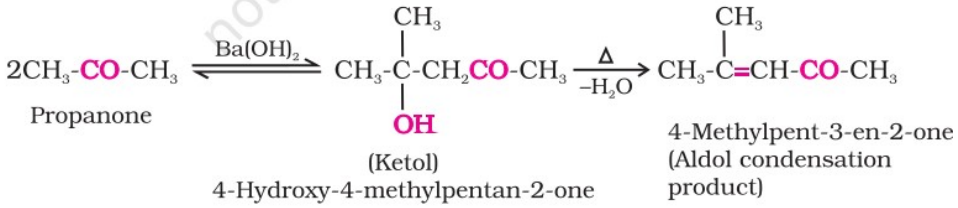
Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures.

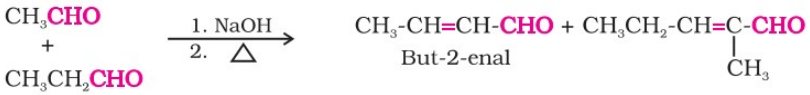


d) Aldol condensation Reaction: Aldehydes and ketones having at least one α-hydrogen atom when treated with dilute alkali, we get β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol) respectively. The aldol or ketol thus produced on heaing undergo dehydration to give α,β-unsaturated aldehyde or ketone. This reaction is called Aldol condensation.

$2CH_3\text{-}CHO \xrightarrow{\text{dil. NaOH}} CH_3\text{-}CH(OH)\text{-}CH_2\text{-}CHO \longrightarrow CH_3\text{-}CH{=}CH\text{-}CHO$

Ethanal — 3-Hydroxybutanal (aldol) — But-2-enal (Crotanaldehyde)

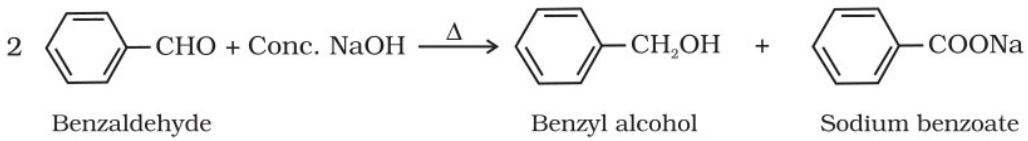




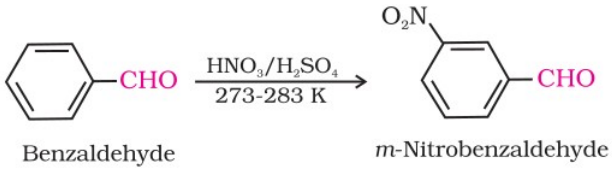
e)Cannizzaro Reaction: Aldehydes having no α-hydrogen atom (e.g. HCHO, C_6H_5-CHO, CCl_3-CHO etc), when treated with Conc. alkali (NaOH or KOH) undergo self oxidation and reduction (disproportionation) to form one molecule of the alcohol and one molecule of carboxylic acid salt. This reaction is called Cannizzaro reaction.

$2\ HCHO \xrightarrow{\text{Conc. KOH}} CH_3\text{-}OH + H\text{-}COOK$

Formaldehyde — methanol — potassium formate



e)Electrophilic substitution reaction: Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group.



6. Tests to distinguish Aldehydes and Ketones

- **Tollens' test:** On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3\,\bar{O}H \longrightarrow RCO\bar{O} + 2Ag + 2H_2O + 4NH_3$$

- **Fehling's test:** Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.

$$R\text{-}CHO + 2Cu^{2+} + 5\bar{O}H \longrightarrow RCO\bar{O} + Cu_2O + 3H_2O$$

Red-brown ppt

CARBOXYLIC ACIDS

1.Nomenclature

HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
C_6H_5COOH	Benzoic acid	Benzenecarboxylic acid(Benzoic acid)

2. Preparation of Carboxylic Acids

From primary alcohols and aldehydes

Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ($KMnO_4$) in neutral, acidic or alkaline media or by potassium dichromate ($K_2Cr_2O_7$) and chromium trioxide (CrO_3) in acidic media (Jones reagent).

$$R\text{-}CH_2OH \xrightarrow{\text{alkaline KMnO4/H3O +}} R\text{-}COOH$$

$$CH_3\text{-}CH_2\text{-}OH \xrightarrow{CrO3/H2SO4} CH_3\text{-}COOH$$

Aldehydes on oxidation with mild oxidising agents like CrO3 or Tollen's reagent to give carboxylic acids.

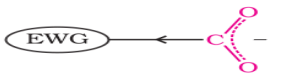
$$R\text{-}CHO \xrightarrow{[O]} R\text{-}COOH$$

$$CH_3\text{-}CHO \xrightarrow{[O]} CH_3\text{-}COOH$$

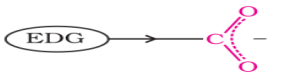
3. Chemical Reactions

Effect of substituents on the acidity of carboxylic acids:

Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.



Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid



Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

4. Esterification Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral acid such as concentrated H_2SO_4 or HCl gas as a catalyst.

$$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$$

4. Reactions with PCl_5, PCl_3 and $SOCl_2$

$$R\text{-}COOH + PCl_3 \longrightarrow R\text{-}COCl + H_3PO_3$$
$$R\text{-}COOH + PCl_5 \longrightarrow R\text{-}COCl + POCl_3 + HCl$$
$$R\text{-}COOH + SOCl_2 \longrightarrow R\text{-}COCl + SO_2 + HCl$$

5. Reduction:

Carboxylic acids when reduced with lithium aluminium hydride or with diborane, primary alcohols are formed.

$$R\text{-}COOH \xrightarrow{\text{i) LiAlH4/ether or B2H6 ii) H3O +}} R\text{-}CH_2OH$$
$$CH_3\text{-}COOH \xrightarrow{\text{i) LiAlH4/ether or B2H6 ii) H3O +}} CH_3\text{-}CH_2OH$$

6.Decarboxylation:

i) When sodium salts of carboxylic acid are heated with sodalime (a mixture of NaOH and CaO), they undergo decarboxylation (elimination of CO_2) to form alkanes.

$$R\text{-}COONa + NaOH \xrightarrow{CaO/\Delta} R\text{-}H + Na_2CO_3$$
$$CH_3\text{-}COONa + NaOH \xrightarrow{CaO/\Delta} CH_4 + Na_2CO_3$$

ii) Kolbe's electrolysis: When an aqueous solution of sodium or potassium salt of carboxylic acid is electrolysed, we get alkanes having twice the number of carbon atoms that present in the alkyl group of the acid. This reaction is known as Kolbe electrolysis.

$$2\ R\text{-}COOK + 2H_2O \xrightarrow{\text{electrolysis}} R\text{-}R + 2KOH + H_2 + 2CO_2$$
$$2\ CH_3\text{-}COOH + 2\ H_2O \xrightarrow{\text{electrolysis}} CH_3\text{-}CH_3 + 2KOH + H_2 + 2CO_2$$

7.HVZ Reaction- Halogenation

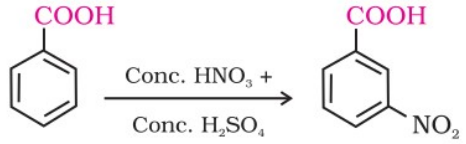
Carboxylic acids having an α-hydrogen atom, when treated with halogen (chlorine or bromine) in the presence of red phosphorus, we get α-halocarboxylic acids. This reaction is synthetically important since the halogen atom can be replaced by other groups.

$$R\text{-}CH_2\text{-}COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\text{Red phosphorus}} R\text{-}\underset{\displaystyle X}{\underset{|}{CH}}\text{-}COOH$$

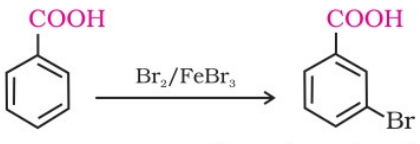
X = Cl, Br

α – Halocarboxylic acid

8.Electrophilic substitution reactions: The –COOH group is a deactivating group and meta-directing. So on electrophilic substitution reactions, we get meta derivatives.



m-Nitrobenzoic acid



m-Bromobenzoic acid