12. ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

These are compounds containing carbon-oxygen double bond (>C=O) called carbonyl group. In aldehydes, the functional group is –CHO; in ketones, the functional group is > C =O and in carboxylic acid, the functional group is –COOH.

Preparation of Aldehydes and Ketones

1. **By oxidation of alcohols**: Primary alcohols on oxidation with mild oxidising agents like CrO_3 to give aldehydes while secondary alcohols give ketones.

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

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

2. **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.

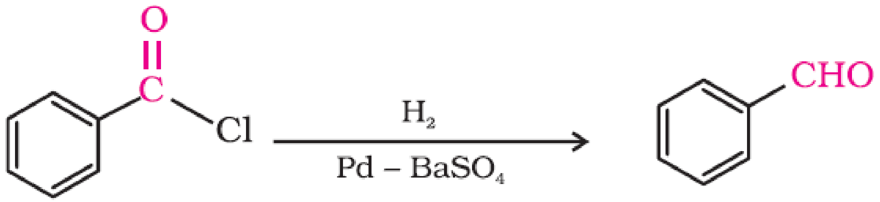
$$R\text{-}CH_2OH \xrightarrow{Cu/573\ K} R\text{-}CHO$$

$$R_2CHOH \xrightarrow{Cu/573\ K} R_2CO$$

3. **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.

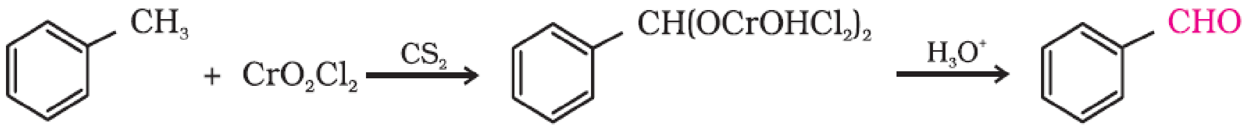
$$R\text{-}COCl + H_2 \xrightarrow{Pd/BaSO_4} R\text{-}CHO + HCl$$



Benzoyl chloride Benzaldehyde

4. **Etard reaction**:

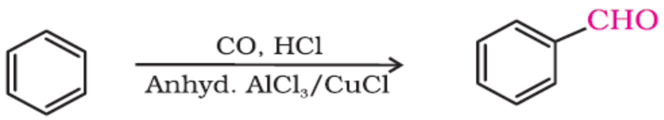
Toluene when oxidised by using chromyl chloride (CrO_2Cl_2) in CS_2 followed by acidification, we get benzaldehyde. This reaction is called ***Etard reaction***.



Toluene Chromium complex Benzaldehyde

5. **By Gatterman – Koch reaction**:

When benzene is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, we get benzaldehyde. This reaction is known as Gatterman-Koch reaction.

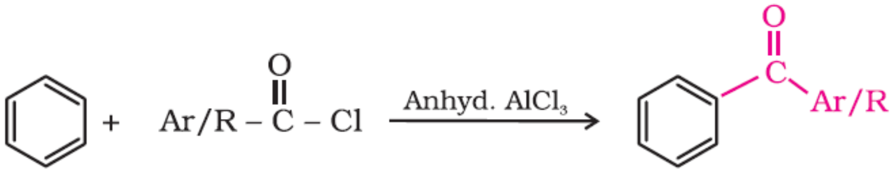


Benzene Benzaldehyde

Preparation of Ketones

From benzene or substituted benzenes [*Friedel – Crafts acylation reaction*]

When benzene or substituted benzene is treated with acid chloride (R-COCl) in the presence of anhydrous aluminium chloride, we get a ketone. This reaction is known as ***Friedel-Crafts acylation reaction***.



Chemical Reactions of Aldehydes and Ketones

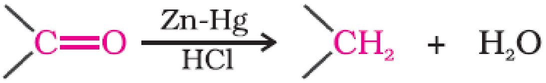
1. **Reduction:**

i) *Reduction to alcohols*: When reduced using sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$) or H_2 in presence of Ni, Pd or Pt catalyst (Catalytic hydrogenation), aldehydes give primary alcohols, while ketones give secondary alcohols.

$$R\text{-}CHO \xrightarrow{[H]} R\text{-}CH_2OH$$
$$R_2CO \xrightarrow{[H]} R_2CHOH$$

ii) Reduction to Hydrocarbons:

Clemmensen reduction: Aldehydes and ketones on treatment with zinc amalgam and concentrated hydrochloric acid, we get alkanes. During this reaction, the carbonyl group is reduced to CH_2 (methylene) group.



$$CH_3\text{-}CHO + [H] \xrightarrow{Zn/Hg} CH_3\text{-}CH_3$$

$$CH_3\text{-}CO\text{-}CH_3 + [H] \xrightarrow{Zn/Hg} CH_3\text{-}CH_2\text{-}CH_3$$

Wolff-Kishner reduction: Carbonyl group can also be reduced to methylene group, by treating with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol.

$$CH_3\text{-}CHO \xrightarrow{1)\ NH_2\text{-}NH_2\ \ 2)\ KOH/Ethylene\ glycol/\Delta} CH_3\text{-}CH_3$$

$$CH_3\text{-}CO\text{-}CH_3 \xrightarrow{1)\ NH_2\text{-}NH_2\ \ 2)\ KOH/Ethylene\ glycol/\Delta} CH_3\text{-}CH_2\text{-}CH_3$$

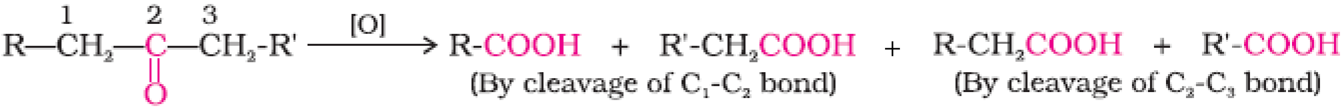
2. **Oxidation**:

Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate etc. Mild oxidising agents like CrO_3, Tollens' reagent and Fehlings' reagent can also oxidise aldehydes.

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

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

Ketones when oxidised using strong oxidising agents and at high temperatures, we get a mixture of carboxylic acids having lesser number of carbon atoms. During this reaction carbon-carbon bond cleavage occurs.



$$R\text{—}\overset{1}{C}H_2\text{—}\underset{\displaystyle O}{\overset{2}{C}}\text{—}\overset{3}{C}H_2\text{-}R' \xrightarrow{[O]} R\text{-}COOH + R'\text{-}CH_2COOH + R\text{-}CH_2COOH + R'\text{-}COOH$$

(By cleavage of C_1-C_2 bond) (By cleavage of C_2-C_3 bond)

E.g. $CH_3\text{-}CH_2\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow{[O]} 2\ CH_3\text{-}CH_2\text{-}COOH + CH_3\text{-}COOH + CH_3\text{-}CH_2\text{-}CH_2\text{-}COOH$

Tests to distinguish Aldehydes and Ketones

i) Tollens' test: Tollen's reagent is freshly prepared *ammoniacal Silver nitrate*.

Aldehydes on warming with Tollens' reagent, we get a bright silver mirror. During this reaction, the aldehyde is oxidised to corresponding carboxylate ion and silver nitrate is reduced to silver metal.

$$R\text{-}CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow R\text{-}COO^- + 2\ Ag + 2\ H_2O + 4\ NH_3$$

ii) Fehling's test: Fehling reagent is a mixture 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).*

On heating with Fehling's reagent, aldehyde gives a reddish brown precipitate of cuprous oxide (Cu_2O). Aromatic aldehydes do not give this test.

$$R\text{-}CHO + 2Cu^{2+} + 5OH^- \longrightarrow R\text{-}COO^- + \underset{\text{(Cuprous oxide)}}{Cu_2O} + 3H_2O$$

3. **Haloform Reaction**:

Aldehydes or ketones having CH_3-CO- group or CH_3-CHOH- group, when treated with sodium hypohalite or halogen in presence of NaOH, we get a haloform (CHX_3). This reaction is called haloform reaction. During this reaction, the methyl group is converted to haloform.

$$R\text{-}CO\text{-}CH_3 \xrightarrow{NaOX} R\text{-}COONa + CHX_3 \text{ (where X = Cl, Br or I)}$$

E.g. When acetone is treated with sodium hypoiodite (I_2 and NaOH), we get iodoform.

$$CH_3\text{-}CO\text{-}CH_3 \xrightarrow{NaOI} CH_3\text{-}COONa + CHI_3$$

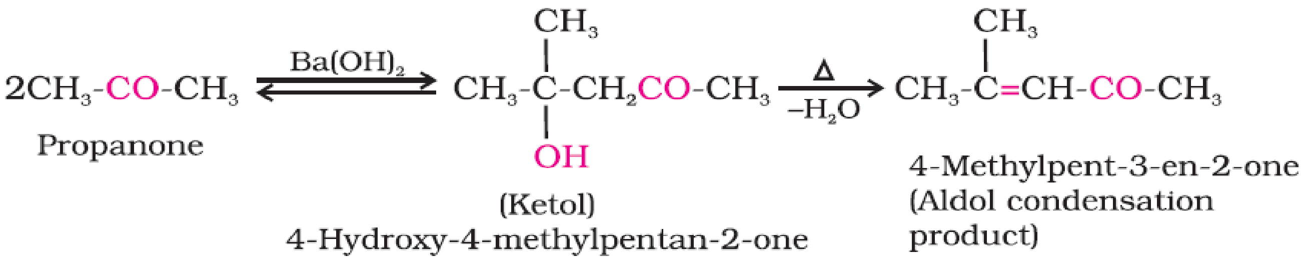
The reaction with sodium hypoiodite gives an yellow precipitate of iodoform and this reaction is used for the detection of CH_3-CO- group or CH_3-CHOH- group in a compound. For example 2-pentanone and 3-pentanone can be distinguished by iodoform reaction. 2-pentanone gives this reaction.

4. **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. This on heating undergoes dehydration to give α,β-unsaturated aldehyde or ketone. This reaction is called Aldol condensation.

$2CH_3\text{-}CHO \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} CH_3\text{-}CH(OH)\text{-}CH_2\text{-}CHO \xrightarrow{\Delta} CH_3\text{-}CH{=}CH\text{-}CHO$

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



$$2CH_3\text{-}CO\text{-}CH_3 \overset{Ba(OH)_2}{\rightleftharpoons} CH_3\text{-}\overset{CH_3}{\underset{OH}{C}}\text{-}CH_2CO\text{-}CH_3 \xrightarrow[-H_2O]{\Delta} CH_3\text{-}\overset{CH_3}{C}{=}CH\text{-}CO\text{-}CH_3$$

Propanone

(Ketol)
4-Hydroxy-4-methylpentan-2-one

4-Methylpent-3-en-2-one
(Aldol condensation
product)

5. **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

$2\ C_6H_5\text{-}CHO \xrightarrow{\text{Conc. KOH}} C_6H_5\text{-}CH_2OH + C_6H_5\text{-}COOK$

Benzaldehyde — benzyl alcohol — potassium benzoate

Preparation of Carboxylic acids

1. **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.

$R\text{-}CH_2OH \xrightarrow{\text{alkaline } KMnO_4/H_3O^+} R\text{-}COOH$

$CH_3\text{-}CH_2\text{-}OH \xrightarrow{CrO_3/H_2SO_4} CH_3\text{-}COOH$

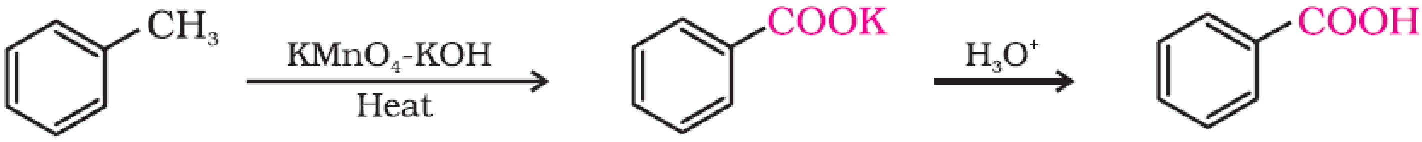
Aldehydes on oxidation with mild oxidising agents like CrO_3 or Tollen's reagent to give carboxylic acids.

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

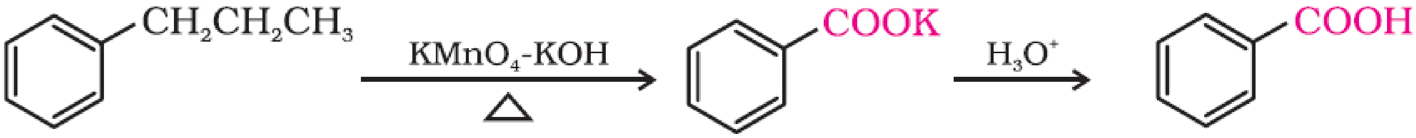
$CH_3\text{-}CHO \xrightarrow{[O]} CH_3\text{-}COOH$

2. **From alkylbenzenes:**

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected.



Toluene — Potassium Benzoate — Benzoic acid



1-phenylpropane — potassium benzoate — Benzoic acid

Chemical Reactions

1. **Acidity**:

   Reactions with metals and alkalies: Like alcohols and phenols, carboxylic acids react with electropositive metals and liberate hydrogen gas.

   $$2\ R\text{-}COOH + 2\ Na \longrightarrow 2\ R\text{-}COONa + H_2$$

   $$R\text{-}COOH + NaOH \longrightarrow R\text{-}COONa + H_2O$$

   Unlike alcohols and phenols, carboxylic acids react with sodium carbonates and bicarbonates and give brisk effervescence of carbon dioxide.

$$R\text{-}COOH + NaHCO_3 \longrightarrow R\text{-}COONa + H_2O + CO_2$$

Carboxylic acids dissociate in water to give resonance stabilized carboxylate anions and hydronium ion.

$$R\text{-}COOH + H_2O \rightleftharpoons R\text{-}COO^- + H_3O^+$$

Due to the formation of hydronium ion in water, carboxylic acids are acidic in nature.

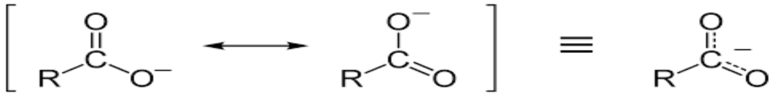
The acidity of a substance is expressed in terms of pKa value, which is the negative logarithm of Ka

i.e. $pKa = -\log Ka$

Greater the value of Ka, smaller will be pKa and stronger will be the acid.

Comparison of acidic character

Carboxylic acids are weaker than mineral acids, but they are stronger acids than other organic compounds like alcohols and simple phenols. The higher acidity of carboxylic acids as compared to phenols is due to the higher stability of the carboxylate ion formed from the ionization of carboxylic acid. The carboxylate ion is more stable than the phenoxide ion due to the following two equivalent resonance structures:



Effect of substituents on the acidity of carboxylic acids:

Presence of electron withdrawing groups increase the acidity of carboxylic acids by stabilising the carboxylate ion through delocalisation of the negative charge by inductive and resonance effects. But electron donating groups decrease the acidity by destabilising the carboxylate ion.

Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid. This is because of the greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.

Thus the acidic character of formic acid, acetic acid and benzoic acid decreases in the order:

$$C_6H_5\text{-}COOH > H\text{-}COOH > CH_3\text{-}COOH$$

The acidity of the following acids decreases in the order:

$$CCl_3\text{-}COOH > CHCl_2\text{-}COOH > CH_2Cl\text{-}COOH > CH_3\text{-}COOH$$

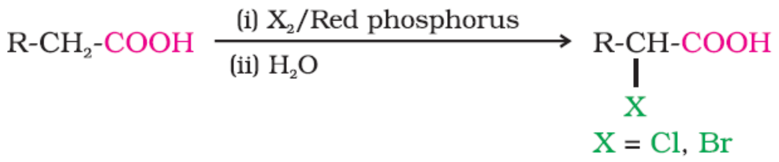
2. ***Reduction:*** Carboxylic acids when reduced with lithium aluminium hydride or with diborane, primary alcohols are formed. Diborane does not reduce functional groups like ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

   $$R\text{-}COOH \xrightarrow{\text{i) } LiAlH_4\text{/ether or } B_2H_6 \text{ ii) } H_3O^+} R\text{-}CH_2OH$$

   $$CH_3\text{-}COOH \xrightarrow{\text{i) } LiAlH_4\text{/ether or } B_2H_6 \text{ ii) } H_3O^+} CH_3\text{-}CH_2OH$$

3. ***Halogenation [HVZ Reaction]***

   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 known as Hell-Volhard-Zelinsky (HVZ) reaction.



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

X = Cl, Br

α-halocarboxylic acid

$$CH_3\text{-}CH_2\text{-}COOH \xrightarrow{\text{i) } Cl_2\text{/ Red P ii) } H_2O} CH_3\text{-}CHCl\text{-}COOH + HCl$$

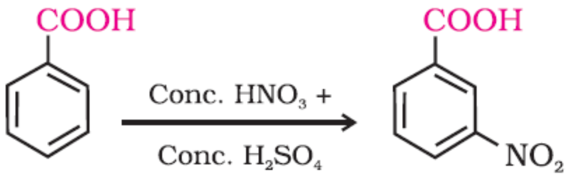
` Propanoic acid 2-chloropropanoic acid

This reaction is synthetically important since the halogen atom can be replaced by other groups.

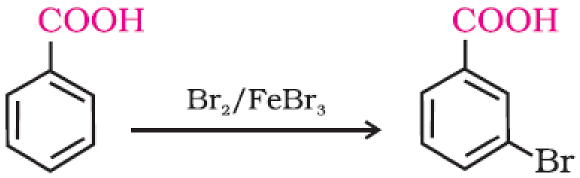
4. ***Electrophilic substitution reactions:***

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

e.g. 1. **Nitration**



2. **Bromination**



But *carboxylic acids do not undergo Friedel-Crafts reactions because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group to form salts.*