7.0 CARBONYL COMPOUNDS

Organic Compounds having $>C=O$ group are called carbonyl compounds and $>C=O$ group is known as carbonyl group. It's general formula is $C_n H_{2n}O$ (n = 1, 2, 3......) Carbonyl compounds are grouped into two categories.

(a) Aldehydes : Aldehyde group is $-\overset{O}{\overset{\|}{C}}-H$ (also known as formyl group). It is a monovalent group

Carbon atom of $-\overset{O}{\overset{\|}{C}}-H$ group is of 1° nature i.e. $R-\overset{1°}{\underset{H}{\underset{|}{C}}}=O$

(b) Ketones : The carbonyl group ($>C=O$) is a Ketonic group when its both the valencies are satisfied by alkyl group. It is a bivalent group.

Carbon atom of $>C=O$ group is of 2° nature i.e. $\begin{matrix}R\\R\end{matrix}\!\!>\overset{2°}{C}=O$

Ketones are further classified as :

(i) **Simple or Symmetrical ketones** : Having two similar alkyl groups. $\begin{matrix}R\\R\end{matrix}\!\!>C=O$

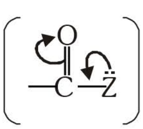
(ii) **Mixed or unsymmetrical ketones** : Having two different alkyl groups. $\begin{matrix}R\\R'\end{matrix}\!\!>C=O$

Ex. (Ketones) :

Symmetrical	Unsymmetrical
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O$	$\begin{matrix}CH_3CH_2\\CH_3\end{matrix}\!\!>C=O$
(Acetone or Dimethyl ketone) Propanone	(Ethyl methyl ketone) Butanone

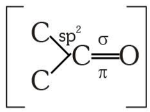
Sp. Point : $-\overset{O}{\overset{\|}{C}}-\ddot{O}H,\ -\overset{O}{\overset{\|}{C}}-\ddot{X},\ -\overset{O}{\overset{\|}{C}}-\ddot{N}H_2,\ -\overset{O}{\overset{\|}{C}}-\ddot{O}R,$

In all the compounds given above, lone pair of electrons and double bond are in conjugate system.



so resonance occurs. These compounds have $-\overset{O}{\overset{\|}{C}}-$ group still they are not carbonyl compounds because these compounds have characteristic reactions different from carbonyl compounds.

Structure : In $>C=O$ compounds C-atom is sp^2 hybridised which forms two σ bonds and one π bond. The unhybridised atomic orbital of C-atom and the parallel 2p orbital of oxygen forms the π bond in $>C=O$ group



The C—C—O / H—C—O bond angle is of 120^0

Due to electro-negativity difference in C & O atoms, the $>C=O$ group is polar.

$>\overset{\delta+}{C}=\overset{\delta-}{O}$ Hence aldehydes and Ketones posses considerable dipole moment.

7.1 General Methods of Preparation

(A) For both Aldehydes and Ketones

(1) By Oxidation of Alcohols :

(a) By $K_2Cr_2O_7$ / H_2SO_4 : Oxidation of primary alcohols gives aldehyde and oxidation of secondary alcohols gives Ketones.

$$RCH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4(\text{dil.})]{[O]} RCHO \text{ (Aldehyde)}$$

$$R-\underset{\underset{OH}{|}}{CH}-R \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} R-\underset{\underset{O}{||}}{C}-R \text{ (Ketone)}$$

Aldehydes are quite susceptible to further oxidation to acids -

$$RCH_2OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-COOH$$

Thus oxidation of primary alcohols is made at the temperature much above the boiling point of aldehyde and thus aldehydes are vapourised out and prevented from being oxidised.

(b) Mild Oxidising Agent : 1° alcohols will get oxidised with CrO_3 / Pyridine, **(collin's reagent) or** P.C.C (Pyridinium chloro chromate $CrO_3 + C_5H_5N + HCl$) to aldehyde and 2° alcohols to ketone.

$$RCH_2OH + [O] \longrightarrow RCHO + H_2O$$

By this reaction, **good yield of aldehyde** is possible.

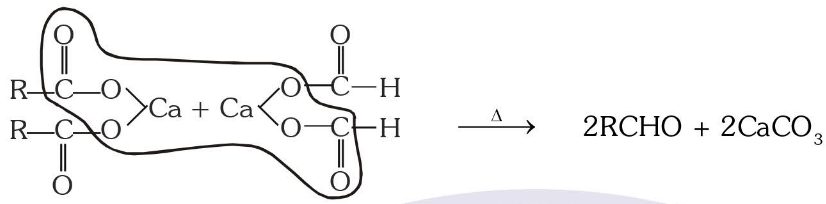
(2) Dehydrogenation of alcohols :

$$CH_3CH_2OH \xrightarrow[300^\circ C]{Cu} CH_3CHO \text{ (Acetaldehyde)}$$

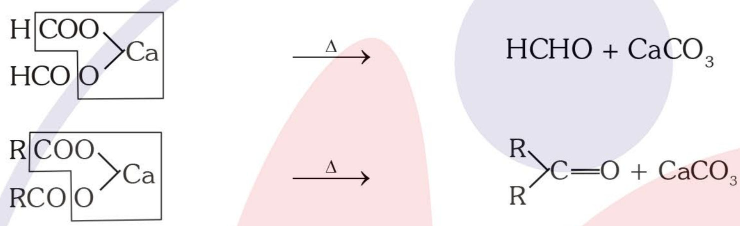
$$CH_3-\underset{\underset{OH}{|}}{CH}CH_3 \xrightarrow[300^\circ C]{Cu} CH_3-\overset{\overset{O}{||}}{C}-CH_3 \text{ (Acetone)}$$

$$(CH_3)_3C{-}OH \xrightarrow[300^\circ C]{Cu} CH_3{-}\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}} + H_2O \quad \text{(Isobutylene)}$$

(3) By dry distillation of Ca-salts of carboxylic acid :

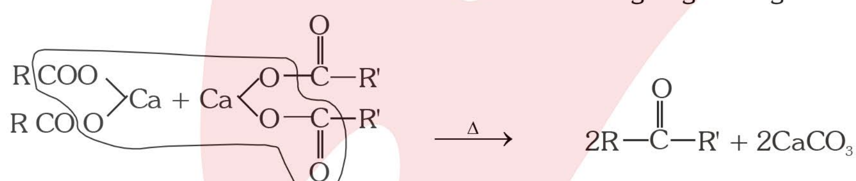


Calcium alkanoate Calcium formate ($R{-}\underset{O}{\underset{\|}{C}}{-}R$ and HCHO are also formed)



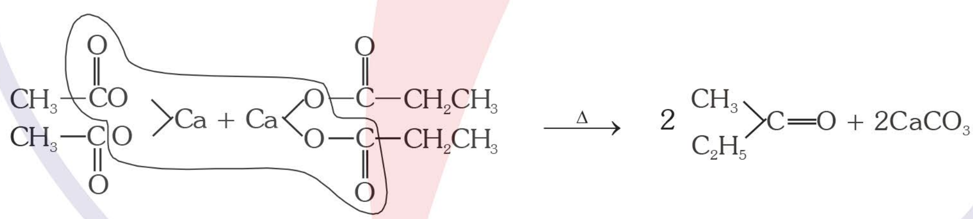
Calcium-alkanoate Ketone

Calcium salts of acids other than formic acid on heating together give unsymmetrical ketone



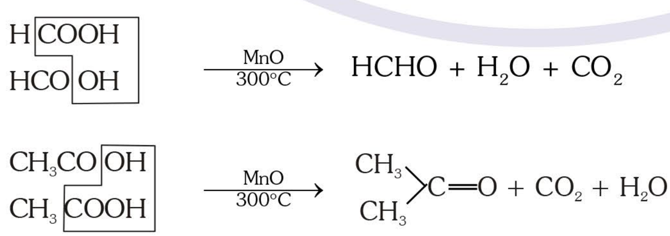
Ketone

To prepare ethyl methyl ketone Calcium acetate and Calcium propionate are used :



Calcium Acetate Calcium propionate Ethyl methyl ketone

(4) By Thermal decomposition of carboxylic acids : Vapour of carboxylic acids when passed over MnO/300°C give carbonyl compounds



$$\begin{matrix} RCO\boxed{OH} \\ H\boxed{COOH} \end{matrix} \xrightarrow[300^\circ C]{MnO} RCHO + CO_2 + H_2O$$

$$\begin{matrix} RCO\boxed{OH} \\ R'\boxed{COOH} \end{matrix} \xrightarrow[300^\circ C]{MnO} RCOR' + CO_2 + H_2O$$

(5) By Hydrolysis of gem dihalides : Terminal gem-dihalides on hydrolysis give aldehydes while the non-terminal gem-dihalides give ketones.

$$CH_3CH\begin{matrix} Cl \\ Cl \end{matrix} \xrightarrow{KOH(aq)} \left[CH_3CH\begin{matrix} OH \\ OH \end{matrix}\right] \xrightarrow{-H_2O} CH_3CHO$$

Terminal gem-dihalide [unstable] Acetaldehyde

$$CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_3 \xrightarrow{KOH(aq)} \left[CH_3-\overset{OH}{\underset{OH}{C}}-CH_3\right] \xrightarrow{-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

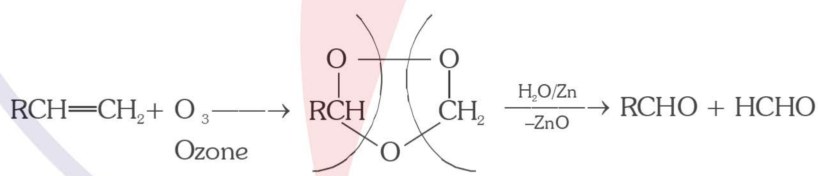
Non terminal gem-dihalide unstable Acetone

(6) By Oxidation of diols : With periodic acid (HIO_4) or lead tetra acetate $(CH_3COO)_4$ Pb vicinal diols get oxidised to form carbonyl compounds

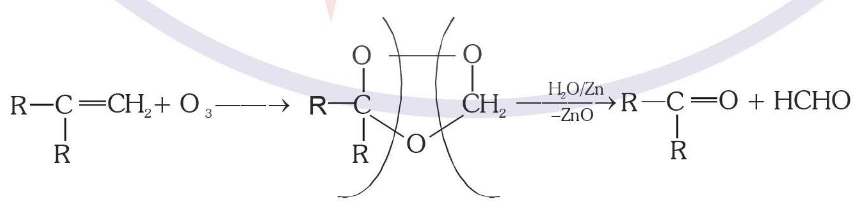
$$R-\underset{OH}{CH}-\underset{OH}{CH}-R' + HIO_4 \longrightarrow RCHO + R'CHO + HIO_3 + H_2O$$

$$R-\overset{R}{\underset{OH}{C}}-\overset{R}{\underset{OH}{C}}-R' + HIO_4 \longrightarrow R-\overset{O}{\overset{\|}{C}}-R + R'-\overset{O}{\overset{\|}{C}}-R + HIO_3 + H_2O$$

(7) By Ozonolysis of alkenes : This reaction is used to determine the position of double bond in alkene. Zn is used to decompose H_2O_2 formed during hydrolysis.



Ozonide



(8) From Alkyne :

(a) Hydration : With dil H_2SO_4 & 1% $HgSO_4$ at 60-80°C.

$$CH\equiv CH + H_2O \xrightarrow[Hg^{+2}]{H_2SO_4} [CH_2=CHOH] \xrightleftharpoons{Tautomerisation} CH_3-\overset{O}{\overset{\|}{C}}-H$$

Other alkynes mainly give ketone :

$$CH_3C\equiv CH + H_2O \xrightarrow[Hg^{+2}]{H_2SO_4} \underset{\text{(enol)}}{CH_3-\underset{OH}{\underset{|}{C}}=CH_2} \xrightleftharpoons{\text{Tautomerism}} CH_3-\underset{O}{\underset{\|}{C}}-CH_3$$

(b) Hydroboration : Reaction with B_2H_6 or R_2BH give alkenyl dialkyl borane.

1 – alkyne gives ⟶ aldehyde
other alkynes ⟶ ketone

$$R-C\equiv CH + \overset{+\delta-\delta}{R_2BH} \longrightarrow R-CH=CHBR_2 \xrightarrow[OH^-]{H_2O_2} RCH=CHOH \xrightleftharpoons{\text{Tautomerism}} R-CH_2-\underset{O}{\underset{\|}{C}}-H + R_2BOH$$

$$CH_3-C\equiv C-CH_3 + R_2BH \longrightarrow CH_3-CH=\underset{BR_2}{\underset{|}{C}}-CH_3 \xrightarrow[OH^-]{H_2O_2}$$

$$CH_3-CH=\underset{OH}{\underset{|}{C}}-CH_3 \rightleftharpoons CH_3-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$$

(B) For Aldehydes only

(1) Rosenmund's reduction :

$$RCOCl + H_2 \xrightarrow{Pd} RCHO \longrightarrow RCH_2OH$$

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

$BaSO_4$ controls the further reduction of aldehyde to alcohols. Formaldehyde can not be prepared by this method.

Ex. $$\underset{\text{Propionyl Chloride}}{C_2H_5COCl} + H_2 \xrightarrow{Pd/BaSO_4} \underset{\text{Propanal}}{C_2H_5CHO} + HCl$$

(2) Stephen's reduction :

$$R-C\equiv N+2H \xrightarrow{SnCl_2/HCl} R-CH=NH \xrightarrow{H_2O} RCHO+NH_3$$

$$C_2H_5-C\equiv N + 2[H] \xrightarrow{SnCl_2/HCl} C_2H_5CH=NH \xrightarrow{H_2O} C_2H_5CHO + NH_3$$

(C) For Ketones only

(1) From Grignard's reagent :

$$RMgX + R-C\equiv N \longrightarrow R-\underset{R}{\underset{|}{C}}=NMgX \xrightarrow{2H_2O} R-\underset{R}{\underset{|}{C}}=O + NH_3 + Mg\begin{smallmatrix}X\\OH\end{smallmatrix}$$

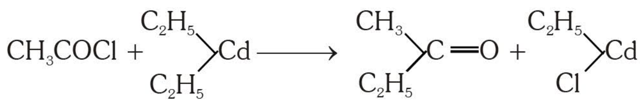
$$\underset{\text{(Limited)}}{RMgX} + R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow R-\overset{O}{\overset{\|}{C}}-R$$

$$\underset{\text{(Limited)}}{RMgX} + R-\overset{O}{\overset{\|}{C}}-OR \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-R + ROMgX$$

(2) From dialkyl Cadmium : R'CdR' (dialkyl Cadmium) is an organometallic compound.

$$RCOCl + R'CdR' \longrightarrow RCOR' + R'CdCl$$

This reaction is superior than Grignard Reaction because the ketones formed, further reacts with Grignard reagent to form 3° alcohols.

Ex. 

7.2 Physical Properties

State : Only formaldehyde is gas, all other carbonyl compounds upto C_{11} are liquids and C_{12} & onwards solid.

Solubility : C_1 to C_3 (formaldehyde, acetaldehyde and propionaldehyde) and acetone are freely soluble in water due to polarity of $>\overset{\delta+}{C}=\overset{\delta-}{O}$ bond and can form H—bond with water molecule. C_5 onwards are insoluble in water.

H-bonding

$$\boxed{\text{Solubility} \propto \frac{1}{\text{Molecular weight}}}$$

Boiling point : $\boxed{\text{Boiling point} \propto \text{Molecular weight}}$

Boiling point order is - **Alcohol > Ketone > Aldehydes > Alkane** (of comparable molecular mass)

This is because in alcohols intermolecular H-bonding is present but in carbonyl compounds H-bonding doesn't exist, instead dipole-dipole & vander waal force of attraction is present. Alkanes are non polar.

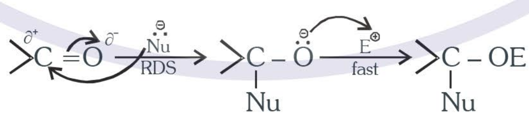
Density : Density of carbonyl compounds is lower than water.

7.3 Chemical Properties

Carbonyl compounds undergo following reactions :

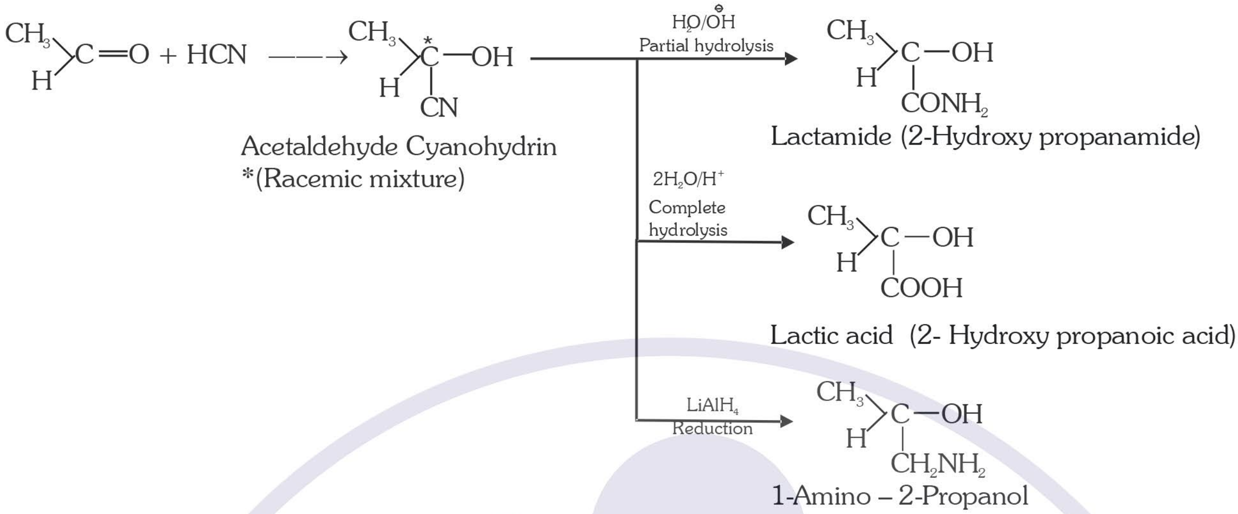
7.3.1 NAR in Aldehyde & Ketone :

Due to strong electronegativity of oxygen, the mobile π electrons pulled strongly towards oxygen, leaving the carbon atom deficient of electrons. Carbon is thus readily attacked by Nu. The negatively charged oxygen is attacked by electron deficient (electrophile) E^+.

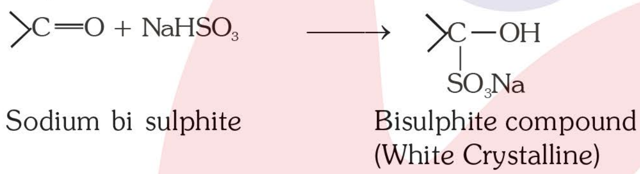


Reactivity	$\propto$	Magnitude of ∂+ve charge
of carbonyl group	$\propto$	$-I$ effect
	$\propto$	$\frac{1}{+I \text{ effect}}$

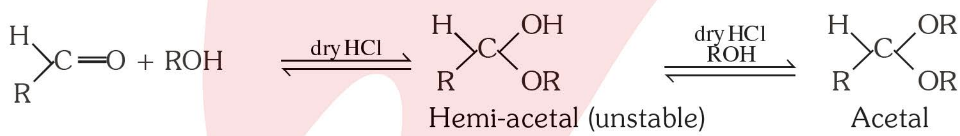
(1) Addition of HCN :



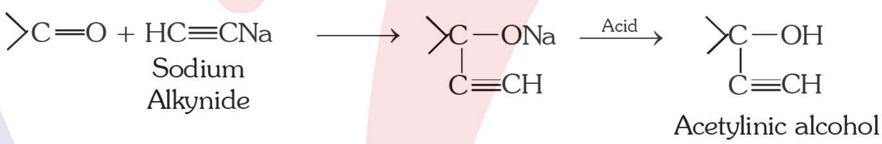
(2) Addition of $NaHSO_3$: This reaction is utilized for the separation of carbonyl compounds from non-carbonyl compounds.



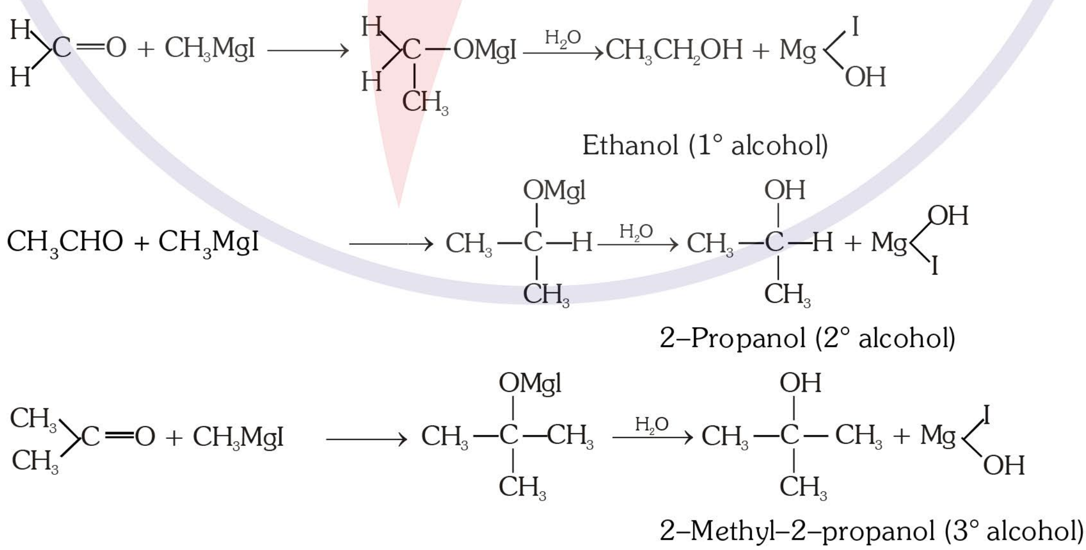
(3) With Alcohol :



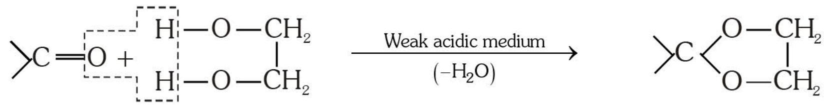
(4) Reaction with sodium alkynide :



(5) Reaction with Grignard reagent :

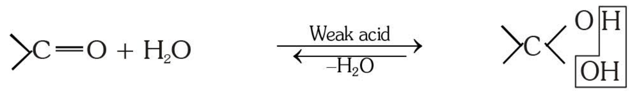


(6) Reaction with glycol :



(neutral) Cyclic acetal / ketal

(7) Reaction with H_2O : It is a reversible reaction.



(neutral) unstable hydrate

Note : Chloral ($Cl_3C–CH=O$) forms stable hydrate [$CCl_3 – CH(OH)_2$ (chloral hydrate)]

(8) Reaction with ammonia derivatives : These are condensation or addition elimination reaction. These proceeds well in weakly acidic medium.

$NH_3 \longrightarrow NH_2Z$ (Ammonia derivative)

$$>C=O + H_2N–Z \xrightarrow{H^{\oplus}} >C=N–Z + H_2O$$

Addition - elimination (Condensation)

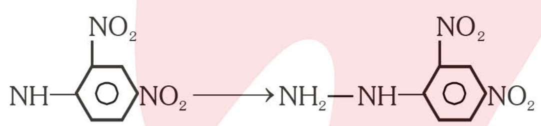
Ammonia derivatives (NH_2Z) :

Z = OH $\longrightarrow$ NH_2OH (Hydroxyl amine)

Z = NH_2 $\longrightarrow$ NH_2NH_2 (hydrazine)

Z = NHC_6H_5 $\longrightarrow$ $NH_2NHC_6H_5$ (Phenyl hydrazine)

Z =



2, 4–Dinitro phenyl hydrazine (2,4-DNP) Brady's reagent.

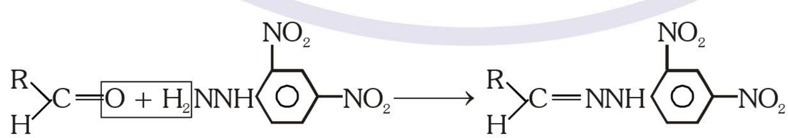
Z = $NHCONH_2$ $\longrightarrow$ $NH_2NHCONH_2$

Semi Carbazide.

$$R(H)C=O + H_2NOH \longrightarrow R(H)C=NOH$$ (Aldoxime)

$$R(H)C=O + H_2NNH_2 \longrightarrow R(H)C=NNH_2$$ (Hydrazone)

$$R(H)C=O + H_2NNHC_6H_5 \longrightarrow R(H)C=NNHC_6H_5$$ (Phenyl hydrazone)



(2, 4 - dinitro phenyl hydrazone) (Red organge ppt.)

$$R(H)C=O + H_2NNHCONH_2 \longrightarrow R(H)C=NNHCONH_2$$ (Semi Carbazone)

7.3.2 Other reactions

(a) Reduction : The nature of product depends upon the reducing agent used.

(i) $>C{=}O \longrightarrow >CH_2$

Reducing agents are

- Red P/HI at 150°C
- Zn-Hg/HCl [Clemensen's reduction]
- (i) N_2H_4 (ii) $\overset{\ominus}{O}H/\Delta$ [Wolf Kishner reduction]

(ii) $>C{=}O \longrightarrow >CHOH$

Reducing agents are

- Metal + H_2
- $LiAlH_4$
- $NaBH_4$
- Na + C_2H_5OH

(b) Reaction with PCl_5 & $SOCl_2$:

$$>C{=}O + PCl_5 \longrightarrow >CCl_2 + POCl_3$$

Phosphorus penta chloride

$$>C{=}O + SOCl_2 \longrightarrow >CCl_2 + SO_2$$

Thionyl chloride

(c) Aldol Condensation : Carbonyl compounds which contain α-H atoms undergo condensation with dil. NaOH to give aldol. Aldol contains both alcoholic and carbonyl group, which on heating in alkaline medium gets converted into α, β-unsaturated carbonyl compound.

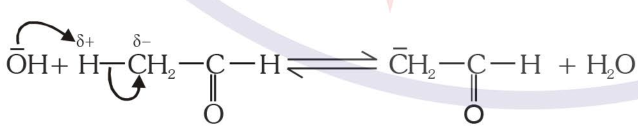
$$CH_3-\underset{\underset{O}{\|}}{C}H + HCH_2CHO \xrightarrow[NaOH]{dil} CH_3-\underset{\boxed{OH}}{CH}-\underset{\boxed{H}}{CH}-CHO \xrightarrow[-H_2O]{\overset{\ominus}{O}H/\Delta} \underset{\text{Crotonaldehyde}}{CH_3-CH{=}CH-CHO}$$

Mechanism of aldol condensation : It takes place in the following two stages :

(i) Formation of Carbanion

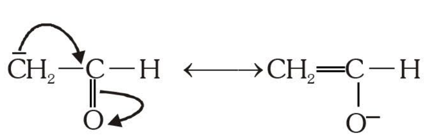
(ii) Combination of carbanion with other carbonyl molecule.

(i) Formation of Carbanion : α-H atom of $>C{=}O$ group are quite acidic which can be removed easily as proton, by a base

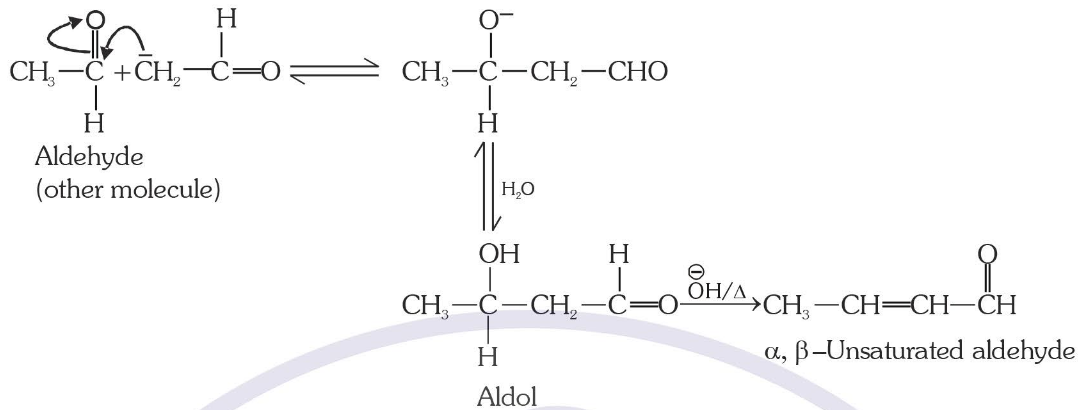


Base Acetaldehyde Carbanion

Carbanion thus formed is stable because of resonance -

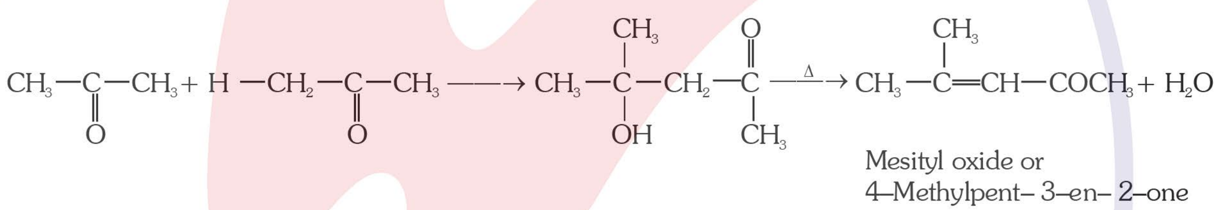


(ii) Combination of carbanion with other carbonyl molecule :

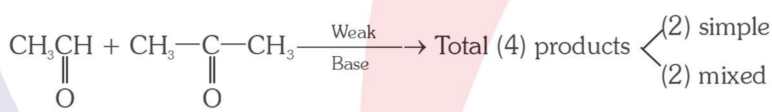


Identical carbonyl compounds ⟶	Simple or self aldol condensation.
Different carbonyl compounds ⟶	Mixed or crossed aldol condensation.

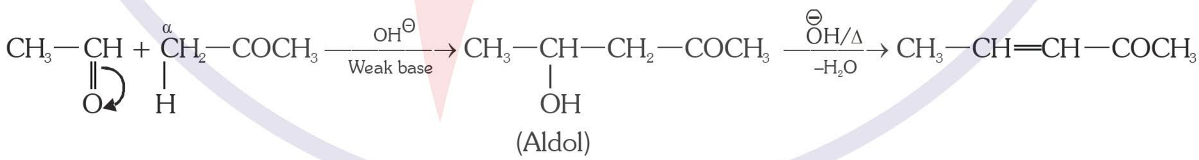
Simple or Self condensation :

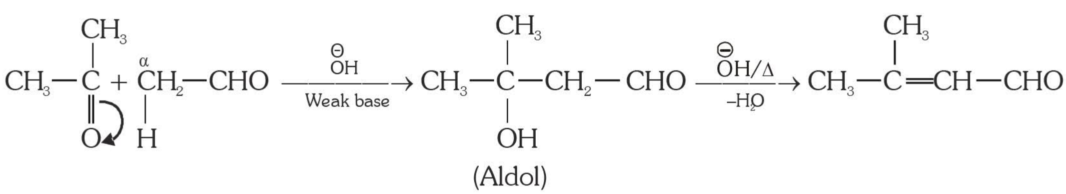


Mixed or Crossed aldol Condensation :



Mixed aldol condensation products of the above reaction are :





(d) Oxidation reactions :

(i) By $K_2Cr_2O_7/H_2SO_4$: On oxidation with $K_2Cr_2O_7/H_2SO_4$ 1° alc. gives aldehyde, which on further oxidation gives acid with same number of carbons. If 2° alcohol is oxidised at elevated temperature using $KMnO_4/H^{\oplus}$, it gets oxidised to give acids with less number of C-atom.

$$\underset{(1^\circ \text{ alcohol, 2C})}{H_3C\text{–}CH_2OH} \xrightarrow{[O]} H_3C\text{—}CH\text{=}O \xrightarrow{[O]} \underset{(\text{Acid with 2C-atoms})}{H_3C\text{—}COOH}$$

$$\underset{(2^\circ \text{ alcohol with 5C})}{CH_3CH_2CH_2\text{—}CH(OH)\text{—}CH_3} \xrightarrow{[O]} CH_3CH_2CH_2\text{—}C(=O)\text{—}CH_3 \xrightarrow{[O]} \underset{(\text{Acids having less number of C})}{CH_3CH_2COOH + CH_3COOH}$$

(ii) SeO_2 (Selenium dioxide) : Ketones or aldehydes on oxidation with SeO_2 give dicarbonyl compounds. This reaction is possible only in compounds containing α–CH_2– unit.

HCHO doesn't show this reaction.

$$\overset{\alpha}{C}H_3CHO + SeO_2 \xrightarrow{\Delta} H\text{—}C(=O)\text{—}C(=O)\text{—}H + Se + H_2O$$

Glyoxal

$$CH_3\text{—}C(=O)\text{—}\overset{\alpha}{C}H_3 + SeO_2 \xrightarrow{\Delta} CH_3\text{—}C(=O)\text{—}C(=O)\text{—}H + Se + H_2O$$

Methyl glyoxal (Pyruvaldehyde)

7.3.3 Reactions of only aldehydes :

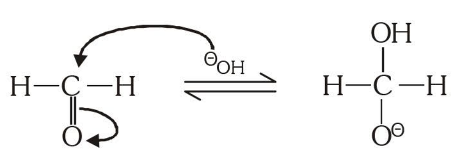
(a) Cannizaro's reaction : Those aldehydes which do not contain α - H atom give this reaction, with conc. NaOH or KOH; Products are Salt of carboxylic acid + alcohol

In this reaction one molecule of carbonyl compounds is oxidised to acid, while other is reduced to alcohol, such type of reactions are called redox reaction.

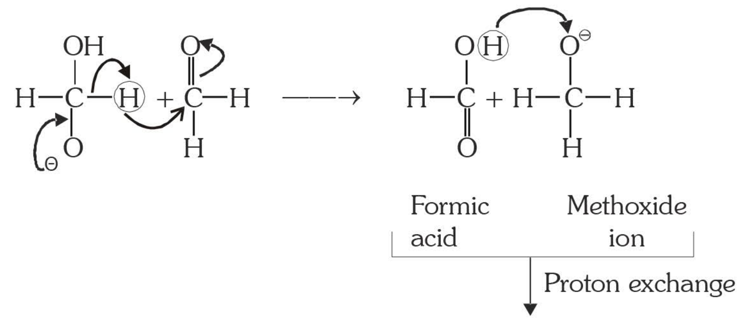
$$HCHO + HCHO \xrightarrow[\text{NaOH},\Delta]{\text{Conc.}} HCOONa + CH_3OH$$

Mechanism involved in cannizaro's reaction :

(a) Rapid reversible addition of $\bar{O}H$ to one molecule of HCHO.



(b) Transfer of hydride ion $\overset{\ominus}{H}$ to second molecule of HCHO



(c) Proton exchange

$$H-\underset{\underset{O}{\|}}{C}-OH + CH_3O^{\ominus} \longrightarrow HCOO^{\ominus} + CH_3OH$$

$$HCOO^{\ominus} + Na^{\oplus} \longrightarrow HCOONa$$

When molecules are same $\longrightarrow$	Simple cannizaro reaction (disproportionation reaction)
Two different molecules $\longrightarrow$	Mixed cannizaro reaction (Redox reaction)

In mixed or crossed cannizaro reaction more reactive aldehyde is oxidised and less reactive aldelyde is reduced.

$$HCHO + C_6H_5CHO \xrightarrow[\Delta]{NaOH} \underset{\substack{\text{Oxidized} \\ \text{(Sodium formate)}}}{HCOONa} + \underset{\substack{\text{Reduced} \\ \text{(Benzyl alcohol)}}}{C_6H_5CH_2OH}$$

(b) Tischenko reaction : It is a modified cannizaro reaction. All aldehydes undergo this reaction in presence of $(C_2H_5O)_3Al$, to form ester.

$$2RCHO \xrightarrow[\Delta]{(C_2H_5O)_3Al} \underset{\text{Ester}}{RCH_2-O-\overset{\overset{O}{\|}}{C}-R}$$

Ex. $CH_3CHO + CH_3CHO \xrightarrow{(C_2H_5O)_3Al} CH_3COOH + CH_3CH_2OH$

Esterification ↓

$CH_3-COOCH_2CH_3$ (Ethyl acetate)

(c) Reducing character : Aldehydes are easily oxidised so they are strong reducing agents.

(i) Tollen's reagent : It oxidises aldehydes. Tollen's reagent is ammonical silver nitrate solution

$$(AgNO_3 + NH_4OH) \longrightarrow [Ag(NH_3)_2]OH$$

$$RCHO + [Ag(NH_3)_2]OH \longrightarrow RCO\overset{\ominus}{O} + \underset{\text{Silver mirror}}{Ag} + H_2O$$

$$AgNO_3 + NH_4OH \longrightarrow AgOH \longrightarrow Ag_2O$$

$$RCHO + Ag_2O \longrightarrow RCO\overset{\ominus}{O} + Ag\downarrow \text{(Silver mirror)}$$

(ii) Fehling's solution : It is a mixture of aqueous $CuSO_4$, NaOH and sodium potassium tartarate.

Fehling solution A– (aq.) solution of $CuSO_4$

Fehling solution B– Roschelle salt (Sodium potassium tartarate + NaOH)

Fehling solution A + Fehlings solution B(Dark blue colour of cupric tartarate)

$$RCHO + Cu^{+2} + OH^- \longrightarrow RCO\overset{\ominus}{O} + Cu_2O$$

(Cuprous oxide–Red ppt.)

$$Cu^{2+} \longrightarrow Cu^{+}$$

(Cupric - Blue) (Cuprous - Red ppt.)

(iii) Benedict's solution : It is a mixture of $CuSO_4$ + sodium citrate + NaOH. It provides Cu^{+2}. It is reduced by aldehyde to give red ppt of cuprous oxide.

$$RCHO + Cu^{2+} + OH^- \longrightarrow RCO\overset{\ominus}{O} + Cu_2O$$

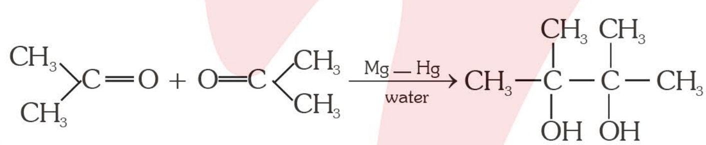
(Cuprous oxide–Red ppt.)

(iv) Schiff's reagent : Dilute solution of p-rosaniline hydrochloride or magenta dye, is a pink coloured dye and is known as schiff' dye.

Its pink colour is discharged by passing SO_2 gas and the colourless solution obtained is called schiff's reagent, Aldehyde reacts with this reagent to restore the pink colour.

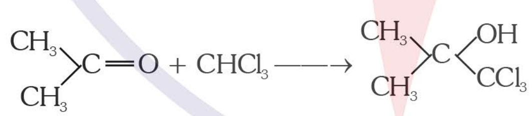
7.3.4 Reaction of Only Ketones

(1) Reduction : Acetone is reduced by magnesium amalgam and water to give pinacol.



Pinacol

(2) Reaction with chloroform :



(Chloretone)
(Hypnotic compound)

(3) Oxidation reaction : According to popoff's rule $>C=O$ group stays with smaller alkyl group.

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{[O]} CH_3COOH + CH_3COOH$$

7.4 BENZALDEHYDE (C_6H_5CHO) [OIL OF BITTER ALMONDS (COMPONENT OF BITTER ALMOND)]

7.4.1 General Methods of Preparation

$C_6H_6 \xrightarrow{CO/\,HCl\ +\ ZnCl_2} C_6H_5CHO$ (Gattermann-koch aldehyde synthesis)

$C_6H_5CH_3 \xrightarrow{(1)\ CrO_2Cl_2\ \ (2)\ H_2O} C_6H_5CHO$ (Etard reaction)

$C_6H_5COCl \xrightarrow{Pd/BaSO_4} C_6H_5CHO$ (Rosenmund reaction)

$C_6H_5CN \xrightarrow{(i)\ SnCl_2/HCl\ (ii)\ H_2O} C_6H_5CHO$ (Stephen's reaction)

$(C_6H_5COO)_2Ca \xrightarrow{(HCOO)_2Ca/\,\Delta} C_6H_5CHO$

$C_6H_5CHCl_2 \xrightarrow{aq.\ KOH} C_6H_5CHO$

$C_6H_5CH_2OH \xrightarrow{[O]\ (controlled\ oxidation)} C_6H_5CHO$

$C_6H_5MgBr \xrightarrow{HCOOC_2H_5} C_6H_5CHO$

$C_6H_6 \xrightarrow[(2)\ H_2O]{(1)\ HCN/HCl\ +\ ZnCl_2} C_6H_5CHO$ (Gattermann aldehyde synthesis)

7.4.2 Chemical Properties

$C_6H_5CHO \xrightarrow{HCN} C_6H_5CH(OH)CN$

$C_6H_5CHO \xrightarrow{NaHSO_3} C_6H_5CH(OH)SO_3Na$

$C_6H_5CHO \xrightarrow{NH_2-Z} C_6H_5CH{=}N-Z$

$C_6H_5CHO \xrightarrow{Red\ P\ +\ HI} C_6H_5CH_3$

$C_6H_5CHO \xrightarrow{Oxidation} C_6H_5COOH$

$C_6H_5CHO \xrightarrow{PCl_5} C_6H_5CHCl_2$

$C_6H_5CHO \xrightarrow{Tollen\ reagent}$ Silver mirror test

$C_6H_5CHO \xrightarrow{NaOH} C_6H_5COONa + C_6H_5CH_2-OH$ Cannizaro reaction

$C_6H_5CHO \xrightarrow{Ar-NH_2} C_6H_5CH{=}N-Ar$ Schiff's base

$C_6H_5CHO \xrightarrow{Schiff's\ reagent}$ Pink colour

$C_6H_5CHO \xrightarrow[(2)\ H_2O]{(1)\ C_6H_5MgBr} C_6H_5-CH(OH)-C_6H_5$

$C_6H_5CHO \xrightarrow[alc.KCN]{C_6H_5CHO} C_6H_5-CH(OH)-C(=O)-C_6H_5$ (Benzoin condensation) (Benzoin)

$C_6H_5CHO \xrightarrow{(CH_3CO)_2O,\ CH_3COONa} C_6H_5-CH{=}CH-COOH$ (Perkin's reaction) (Cinnamic acid)

$C_6H_5CHO \xrightarrow{HNO_3/H_2SO_4}$ m – nitrobenzaldehyde

$C_6H_5CHO \xrightarrow{Fuming\ H_2SO_4}$ m–formyl benzene sulphonic acid

$C_6H_5CHO \xrightarrow{Cl_2/FeCl_3}$ m-Chloro benzaldehyde

$C_6H_5CHO \xrightarrow[\overset{\ominus}{O}H/\Delta]{CH_3-C(=O)-CH_3} C_6H_5CH{=}CH-C(=O)-CH_3$ (Aldol condensation)

7.5 CARBOXYLIC ACID

Organic compounds having –COOH group are called Carboxylic acids. This functional group is composed of Carbonyl ($-\overset{O}{\overset{\|}{C}}-$) and hydroxyl (—OH) group.

$$-\overset{O}{\overset{\|}{C}}- \quad + \quad -OH \longrightarrow -\overset{O}{\overset{\|}{C}}-OH$$

Carbonyl group Hydroxyl group Carboxylic group

The properties of the carboxylic group are not simply the combined properties of these two groups, but it has its own distinctive properties. The acidic nature of carboxylic acids is due to the presence of replaceable H-atom in the Carboxylic group. The general formula is $C_nH_{2n}O_2$.

Classification :

Monocarboxylic acid (RCOOH) : Having one carboxylic group, also called monobasic acid.

General formula - $C_nH_{2n}O_2$ (n = 1, 2, 3, ...). Higher mono carboxylic acids are called **fatty acids**.

Ex. CH_3COOH acetic acid

Dicarboxylic acid : Having two carboxylic groups, also called dibasic acid.

Ex. $\begin{array}{c} COOH \\ | \\ COOH \end{array}$ Oxalic acid

Tricarboxylic acid : Having three carboxylic groups also called tribasic acid.

Ex. $\begin{array}{c} CH_2COOH \\ | \\ HO-C-COOH \\ | \\ CH_2COOH \end{array}$ Citric acid

Structure : The carbon atom of –COOH group is sp^2 hybridised, this C- atom is in centre and thus bond angle around C-atom is 120°.

7.5.1 General Methods of Preparation

(1) By Oxidation of alcohols & carbonyl compounds : Oxidation is carried out by acidified $K_2Cr_2O_7$ or $KMnO_4$.

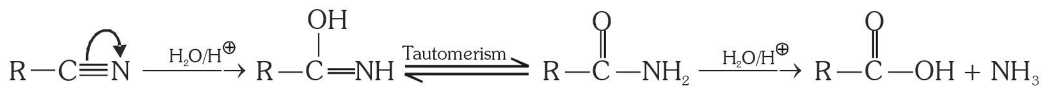
$$RCH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} RCHO \xrightarrow{[O]} RCOOH$$

Acids are third oxidation products of alkane.

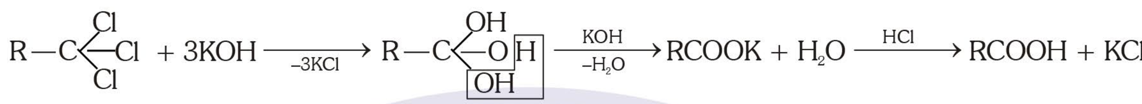
$$R-H \xrightarrow{[O]} R-OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-COOH$$

(2) By hydrolysis of alkane nitriles or cyanides : Complete hydrolysis takes place in acidic medium (dil. HCl).

In alkaline medium there is partial hydrolysis.



(3) By alkaline hydrolysis of 1, 1, 1-trihaloalkane :



(4) By hydrolysis of acid derivatives :

Z= —Cl, —OCOR, —OR, —NH_2

Reactivity order of acid derivatives : **$RCOCl > (RCO)_2O > RCOOR > RCONH_2$**

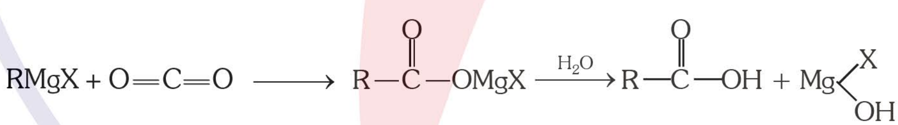
$$RCOCl \xrightarrow[\text{dil. acid}]{\text{HOH}} RCOOH + HCl$$

$$(RCO)_2O \xrightarrow[\text{dil. acid}]{\text{HOH}} 2RCOOH$$

$$RCOOR' \xrightarrow[\text{dil. acid}]{\text{HOH}} RCOOH + R'OH$$

$$R\text{—}CONH_2 \xrightarrow[\text{dil. acid}]{\text{HOH}} RCOOH + NH_3$$

(5) From Grignard's reagent :



Carbon dioxide

Solid CO_2(dry ice) is used

7.6 Physical Properties

Carboxylic acids from C_1—C_4 are completely soluble in water.

$$\text{Solubility} \propto \frac{1}{\text{molecular weight}}$$

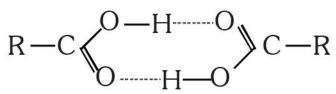
Solubility is due to intermolecular H - bonding with water molecules.

Boiling point : B. P. & M. P. $\propto$ Molecular weight,

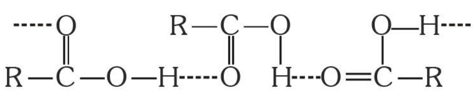
Acids > alcohol

This is because in acids two oxygen atoms take part in H - bonding (while in alcohol only one O - atom takes part).

In vapour or soluble state lower acids occur in the form of dimers.



But in liquid state it exists in polymer form.

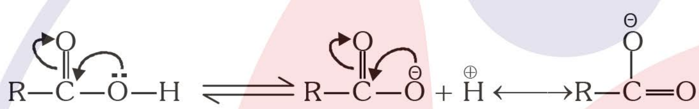


Melting point : Acids having even number of C-atoms have higher melting point as compared to having odd number of C - atoms.The carboxyl group and terminal methyl group in even member acids lie on opposite side to provide more close packing in crystal lattice which results in high melting point.

7.7 Chemical Properties

(1) Reaction due to – H atom of – COOH group

(a) Acidic character :



(Carboxylate ion, Conjugate base)

Carboxylate ion is stabilised by resonance so carboxylic acids show considerable acidic character.

In case of alcohol alkoxide ion is not stabilised so they are neutral.

$$R{-}OH \rightleftharpoons \underset{\text{alkoxide ion}}{R{-}O^- + H^+}$$

(a) Carboxylic acids turn blue litmus to red.

(b) Addition of carboxylic acid to $NaHCO_3$ in water gives out effervescence of CO_2.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$$

(c) Form salts with alkalies.

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

$$RCOOH + Ca(OH)_2 \longrightarrow (RCOO)_2Ca + H_2O$$

(d) Action of metals.

$$RCOOH + Na \longrightarrow RCOONa + \tfrac{1}{2}H_2$$

The acidic character order is :

$HCOOH > CH_3COOH > C_2H_5COOH$

$CCl_3COOH > HCCl_2COOH > CH_2Cl\,COOH > CH_3COOH$

Acidic character may be explained on the basis of I effect and resonance.

(b) Reaction with CH_2N_2 : Methyl ester can be prepared by this method.

$$RCOOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2$$

Methyl ester

(2) Reaction due to – OH group

(a) Esterification :

$$CH_3CO\,OH + H\,O\,C_2H_5 \xrightarrow{Conc.H_2SO_4} CH_3COOC_2H_5 + H_2O$$

(b) Reaction with NH_3 :

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 \xrightarrow{P_2O_5/\Delta} CH_3CN$$

(c) Reaction with thionyl chloride :

$$CH_3COOH + SOCl_2 \xrightarrow{Pyridine} CH_3COCl + SO_2\uparrow + HCl$$

(d) Reaction with PCl_5 :

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

(e) Reaction with P_2O_5 (dehydrating agent) :

$$\begin{matrix} CH_3CO\boxed{OH} \\ CH_3COO\boxed{H} \end{matrix} \xrightarrow[conc.\ H_2SO_4\ \Delta]{P_2O_5\ or} \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>O + H_2O$$

HCOOH is dehydrated by Conc. H_2SO_4

$$HCOOH \xrightarrow{Conc.H_2SO_4} CO + [H_2O.H_2SO_4]$$

(3) Reaction due to $-\overset{O}{\overset{\|}{C}}-$ group of COOH :

(a) $CH_3{-}COOH + 4H \xrightarrow{LiAlH_4} CH_3CH_2OH + H_2O$

(b) $R{-}COOH + 3H_2 \xrightarrow{Ni/\Delta} R{-}CH_2{-}OH + H_2O$

(c) $R{-}\overset{O}{\overset{\|}{C}}{-}OH + 6HI \xrightarrow[\&\ high\ Pr]{Red\ P} R{-}CH_3 + 2H_2O + 3I_2$

(4) Reaction due to – COOH group :

(a) Decarboxylation :

$$\underset{(soda\ lime)}{CH_3COONa + NaOH / CaO} \xrightarrow{\Delta} CH_4 + Na_2CO_3$$

(b) Kolbe's electrolysis :

$$\begin{matrix} CH_3COONa \\ CH_3COONa\ (aq.) \end{matrix} \xrightarrow{Electrolysis} \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + CO_2 + NaOH + H_2$$

(c) Hunsdiecker reaction :

$$CH_3COOAg + Br_2 \xrightarrow[h\nu]{CCl_4} CH_3Br + AgBr + CO_2$$

or Cl_2 — or $CH_3Cl + AgCl + CO_2$

(d) Formation of carbonyl compounds :

$(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3COCH_3$

$(HCOO)_2Ca \xrightarrow{\Delta} HCHO$

→ Dry distillation

$2HCOOH \xrightarrow{MnO} HCHO$

$2CH_3COOH \xrightarrow{MnO} CH_3COCH_3$

→ Catalytic reduction

(e) Schmidt reaction : The amine formed has one C - atom less than the reactant acid.

$$RCOOH + N_3H \xrightarrow[(2) H_2O]{(1) H_2SO_4} RNH_2 + CO_2 + N_2$$

Hydrazoic acid

(5) Reaction due to alkyl (R) group :

(a) Halogenation [HVZ reaction] : Hell volhard Zelinsky reaction**] :** In this reaction α - H atoms are replaced by halogen atoms.

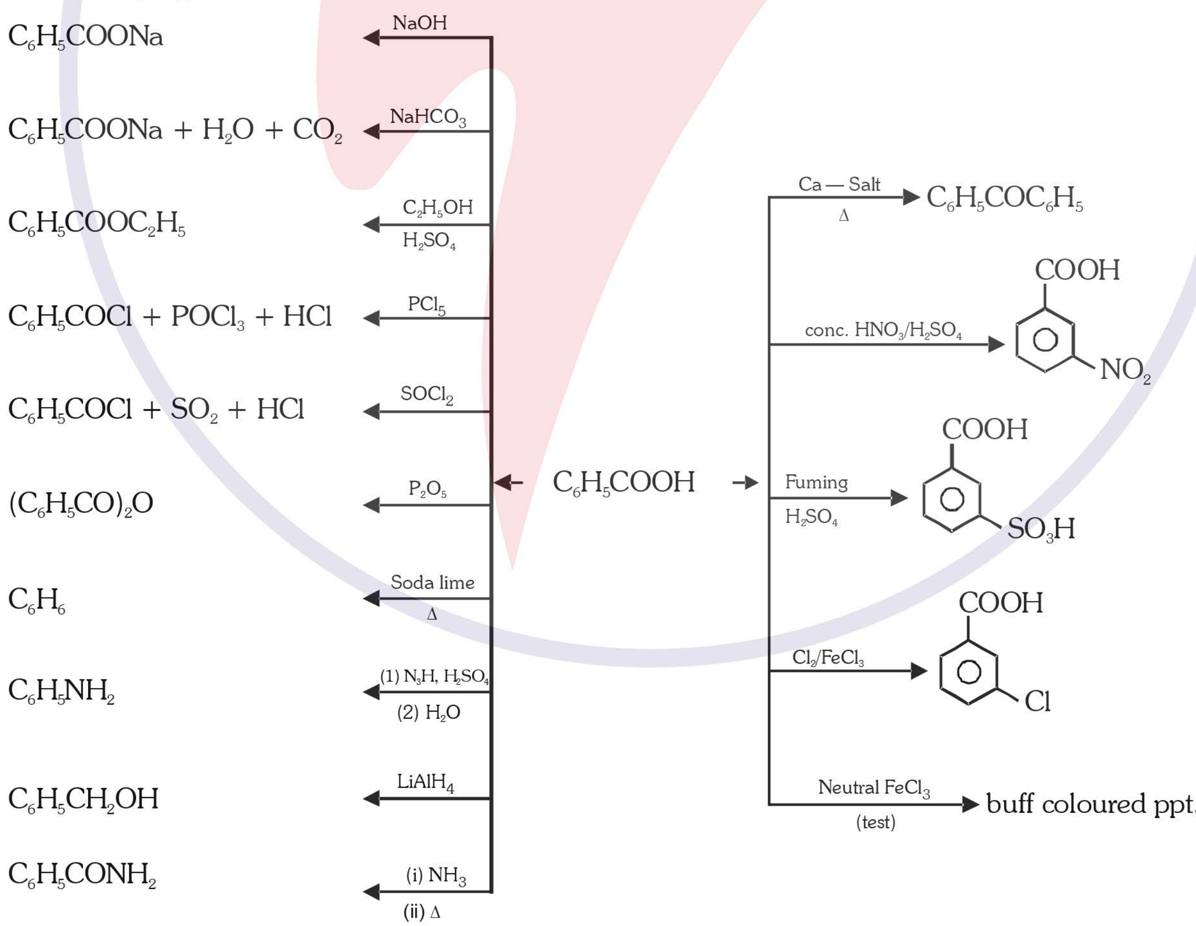
$$CH_3COOH + Cl_2 \xrightarrow{P} ClCH_2COOH \xrightarrow{P/Cl_2} Cl_2CHCOOH \xrightarrow{P/Cl_2} Cl_3CCOOH$$

7.8 BENZOIC ACID (C_6H_5COOH)

(1) General Method of Preparation :

C_6H_5CHO	[O]	C_6H_5COOH
$C_6H_5CH_3$	$H^+/KMnO_4$	C_6H_5COOH
C_6H_5CN	H_3O^+	C_6H_5COOH
$C_6H_5CCl_3$	(i) aq. KOH (ii) $\overset{\oplus}{H}$	C_6H_5COOH
C_6H_5MgBr	(i) CO_2 (ii) H_2O	C_6H_5COOH
$H-O-C_6H_4COOH$ (o, m, p)	Zn, Δ	C_6H_5COOH
C_6H_5COCl	H_2O	C_6H_5COOH
C_6H_5COOR	H_2O	C_6H_5COOH

(2) Chemical properties



7.9 ACID DERIVATIVES

Replacement of –OH group from a carboxylic group (– COOH) by a nucleophile like Cl^-, CH_3COO^-, $C_2H_5O^-$, NH_2^-, forms acid derivatives.

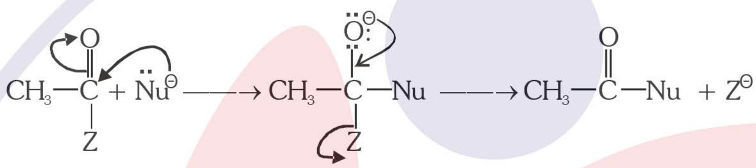
$$\underset{\text{Acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightarrow[+Z]{-OH} \underset{\text{Acid derivative}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-Z}$$

$R-\overset{\overset{O}{\|}}{C}-$ is Acyl group and Z is nucleophile $Cl^{\ominus}$, $CH_3COO^{\ominus}$, $C_2H_5O^{\ominus}$, $NH_2^{\ominus}$

Ex. $CH_3-\overset{\overset{O}{\|}}{C}-$ Acetyl group

Characteristic reaction for acid derivatives is nucleophilic substitution reaction :

Mechanism :



In this reaction Z is leaving group. Weak bases are good leaving groups.

Reactivilty order : $\boxed{CH_3COCl > CH_3COOCOCH_3 > CH_3COOC_2H_5 > CH_3CONH_2}$

Acetyl Chloride

Replacement of —OH group from a —COOH group by Cl— atom gives acid chloride.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[+Cl]{-OH} R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl$$

(1) General Method of Preparation :

(a) By heating CH_3COOH with PCl_3, PCl_5 & $SOCl_2$:

(i) $CH_3COOH + PCl_3 \longrightarrow CH_3COCl + H_3PO_3$

(ii) $CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$

(iii) $CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2\uparrow + HCl\uparrow$

(b) By heating the salt of acids with PCl_3, PCl_5 or $SOCl_2$:

(i) $CH_3COONa + PCl_3 \longrightarrow CH_3COCl + Na_3PO_3$

(ii) $CH_3COONa + PCl_5 \longrightarrow CH_3COCl + POCl_3 + NaCl$

(iii) $CH_3COONa + SOCl_2 \longrightarrow CH_3COCl + SO_2 + NaCl$

(2) Physical properties :

(i) Pungent smelling liquid.

(ii) Boiling point 52°C.

(iii) Soluble in organic solvent, slowly soluble in water.

(iv) It produces fumes in moist air due to the formation of HCl.

(3) Chemical properties :

(a) Hydrolysis : $CH_3CO\boxed{Cl + H}OH \longrightarrow CH_3COOH + HCl$

(b) Reaction with active H - contaning compounds (Acetylation) :

(i) $CH_3CO\boxed{Cl + H}NH_2 \longrightarrow CH_3CONH_2 + HCl$

(ii) $CH_3CO\boxed{Cl + H}NH{-}R \longrightarrow CH_3CONHR + HCl$

1° Amine — N– alkyl acetamide

(iii) $CH_3CO\boxed{Cl + H}NR_2 \longrightarrow CH_3CONR_2 + HCl$

2° amine — N, N– dialkyl acetamide

(iv) $CH_3CO\boxed{Cl + H}OR \longrightarrow CH_3COOR + HCl$

Alcohol — Alkyl acetate

(v) 

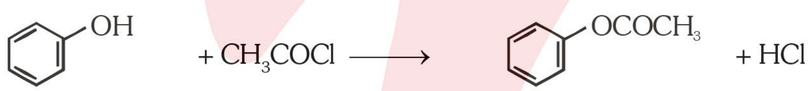
Salicylic acid — Aspirin (Acetyl salicylic acid)

(vi) $CH_3{-}\overset{O}{\overset{\|}{C}}{-}\boxed{Cl + H}{-}NH{-}NH_2 \longrightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}NHNH_2 + HCl$

Acetyl hydrazide

$$\left[R{-}\overset{O}{\overset{\|}{C}}{-}R + NH_2NH_2 \longrightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!C{=}NNH_2 \right]$$

Ketone — hydrazone

(vii) 

(Phenyl acetate)

(c) Reduction :

(i) $CH_3COCl + H_2 \xrightarrow{Pd/BaSO_4} CH_3CHO$ (Rosenmund's reduction)

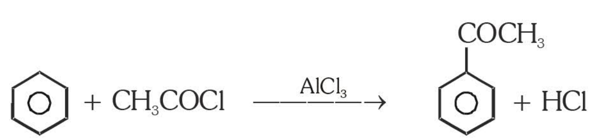
(ii) $CH_3COCl + 4H \xrightarrow[(2)H_2O]{(1)LiAlH_4} CH_3CH_2OH + HCl$

(d) With Sodium acetate : $CH_3CO\boxed{Cl + Na}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \longrightarrow CH_3CO{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + NaCl$

Acetic anhydride

(e) With Sodium ethoxide : $CH_3CO\boxed{Cl + Na}OC_2H_5 \longrightarrow CH_3COOC_2H_5 + NaCl$

Ethyl acetate

(f) Friedel crafts reaction : 

Acetophenone

7.10 Acetic Anhydride (Ethanoic Anhydride)

(1) General Method of Preparation :

(a) By heating acetyl Chloride with anhydrous sodium acetate [Lab. Method] :

$$CH_3CO\boxed{Cl + Na}O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + NaCl$$

(b) By Dehydration of acetic acid :

$$2CH_3COOH \xrightarrow[\text{dehydration}]{P_2O_5} \begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>O + H_2O$$

Acetic acid — acetic anhydride

(2) Physical Properties :

(i) It is pungent smelling liquid.

(ii) Sparingly soluble in water, soluble in ether & alcohol.

(iii) Boiling point 139°C.

(3) Chemical Properties :

(a) Hydrolysis :

$$CH_3CO-O\overset{H\,|\,OH}{|}COCH_3 \longrightarrow CH_3COOH + CH_3COOH$$

Hydrolysis order : **Alkaline > Acidic > neutral**

$$CH_3CO\text{–}O\overset{\overset{+}{Na}\,|\,\overset{-}{O}H}{|}COCH_3 \longrightarrow CH_3COONa + CH_3COOH$$

sodium acetate — Acetic acid

(b) Reaction with active H - containing compounds (Acetylation) :

(i) $CH_3-CO-\boxed{OCOCH_3 + H}NH_2 \longrightarrow CH_3CONH_2 + CH_3COOH$

(ii) $CH_3CO-\boxed{OCOCH_3 + H}NHR \longrightarrow CH_3CONHR + CH_3COOH$

(iii) $CH_3CO-\boxed{O-COCH_3 + H}NR_2 \longrightarrow CH_3CONR_2 + CH_3COOH$

(iv) $CH_3CO-\boxed{O-COCH_3 + H}OR \longrightarrow CH_3COOR + CH_3COOH$

(v)


(Salicylic acid) — (Aspirin)

(c) Reduction : With $LiAlH_4$ in ether gives ethyl alcohol

$$CH_3CO-O-COCH_3 \xrightarrow{LiAlH_4} 2CH_3CH_2OH + H_2O$$

(d) Reaction with PCl_5 & $SOCl_2$:

$$\begin{matrix}CH_3CO & | & O & | & COCH_3\\ Cl & | & PCl_3 & | & Cl\end{matrix} \longrightarrow 2CH_3COCl + POCl_3$$

Phosphorous Oxychloride

$$\begin{matrix}CH_3CO & | & O & | & COCH_3\\ Cl & | & SO & | & Cl\end{matrix} \longrightarrow 2CH_3COCl + SO_2$$

(4) Uses

(i) As an acetylating agent

(ii) In the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, & acetophenone etc.

(iii) For detection and estimation of hydroxyl and amino group.

7.11 Ethyl acetate

(1) General Method of Preparation :

(a) Tischenko reaction : By treating acetaldehyde with aluminium ethoxide. (Modified cannizaro reaction)

$$2CH_3CHO \xrightarrow{(C_2H_5O)_3Al} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

(b) Esterification :

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-C_2H_5 \underset{\Delta}{\overset{Conc.H_2SO_4}{\rightleftharpoons}} \underset{\text{Ethylacetate}}{CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5} + H_2O$$

(2) Physical Properties

(i) Fruity smell liquid.

(ii) Boling point 77°C.

(iii) Slightly soluble in water, soluble in organic solvent.

(3) Chemical Properties :

(a) Hydrolysis : In acidic medium reaction is reversible and in alkaline medium reaction is irreversible.

$$CH_3COOC_2H_5 + HOH \overset{H^+}{\rightleftharpoons} CH_3COOH + C_2H_5OH$$

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

(b) Ammonolysis :

$$CH_3CO\boxed{OC_2H_5 + H}NH_2 \xrightarrow{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Ethanol}}{C_2H_5OH}$$

(c) Reaction with NH_2NH_2 & NH_2OH :

$$CH_3CO\boxed{OC_2H_5 + H}\underset{\text{Hydrazine}}{NHNH_2} \xrightarrow{\Delta} \underset{\text{Acetyl hydrazide}}{CH_3CONHNH_2} + C_2H_5OH$$

$$CH_3CO\boxed{OC_2H_5 + H}\underset{\text{hydroxyl amine}}{NHOH} \xrightarrow{\Delta} \underset{\text{Acetyl hydroxamic acid}}{CH_3CONHOH} + C_2H_5OH$$

(d) Reduction :

$$CH_3COOC_2H_5 \xrightarrow{LiAlH_4} CH_3CH_2OH + C_2H_5OH$$

(e) Claisen condensation :

$$CH_3CO\boxed{OC_2H_5 \ + H}CH_2COOC_2H_5 \xrightarrow{NaOC_2H_5} CH_3COCH_2COOC_2H_5 + C_2H_5OH$$

7.12 Acetamide

(1) General Method of Preparation :

(a) Ammonolysis of acid derivatives :

$$CH_3CO\boxed{Cl + H}NH_2 \longrightarrow CH_3CONH_2 + HCl$$

$$CH_3CO\boxed{-O-COCH_3 + H}NH_2 \longrightarrow CH_3CONH_2 + CH_3COOH$$

$$CH_3CO\boxed{OC_2H_5 + H}NH_2 \xrightarrow{\Delta} CH_3CONH_2 + C_2H_5OH$$

(b) Hydrolysis of alkyl cyanides : By the partial hydrolysis of alkyl cyanides.

$$R-C\equiv N + H_2O \longrightarrow R-\underset{\underset{O}{\parallel}}{C}-NH_2$$

$$CH_3-C\equiv N + H_2O \longrightarrow CH_3-\underset{\underset{O}{\parallel}}{C}-NH_2$$

(2) Physical Properties :

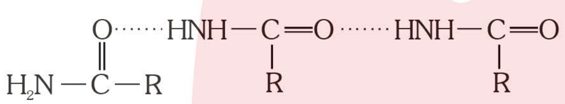
(i) Acetamide is white crystalline solid.

(ii) Pure acetamide is odourless.

(iii) Impure acetamide - Smell like mouse.

(iv) Lower amides are soluble in water, due to H–bonding.

(v) Their higher M. P. and B. P. are due to intermolecular H– bonding.



(3) Chemical Properties :

(a) Hydrolysis : Amides are hydrolysed rapidly in acidic medium. In alkaline medium hydrolysis is carried out in temperature condition.

$$R-\underset{\underset{O}{\parallel}}{C}-NH_2 + H_2O \xrightarrow{H^+} R-COOH + \overset{+}{N}H_4$$

$$CH_3-\underset{\underset{O}{\parallel}}{C}-NH_2 + NaOH \xrightarrow{\Delta} CH_3COONa + NH_3 \uparrow$$

(b) Reduction to primary amines : Amine contains same number of carbon atoms.

$$CH_3CONH_2 \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} \underset{1^\circ \text{ amine}}{CH_3CH_2NH_2} + H_2O$$

(c) Dehydration with PCl_5, $SOCl_2$ or P_2O_5 :

$$CH_3CONH_2 \xrightarrow{PCl_5} CH_3CCl_2NH_2 \xrightarrow{-2HCl} \underset{\text{Methyl cyanide}}{CH_3CN} + 2HCl$$

$$CH_3CONH_2 + P_2O_5 \xrightarrow{\Delta} \underset{\text{Methyl cyanide}}{CH_3CN} + H_2O$$

(d) Reaction with nitrous acid :

$$CH_3-CO-NH_2 + HO-N-O \xrightarrow{HNO_2} CH_3COOH + N_2 + H_2O$$

(e) Hoffmann's bromamide degradation reaction : Amides on reaction with bromine, and NaOH or KOH yield primary amines, having one C–atom less than the amides.

$$CH_3CONH_2 + Br_2 + KOH(aq.) \longrightarrow CH_3NH_2 + KBr + K_2CO_3 + H_2O$$

or (KOBr)

Mechanism :