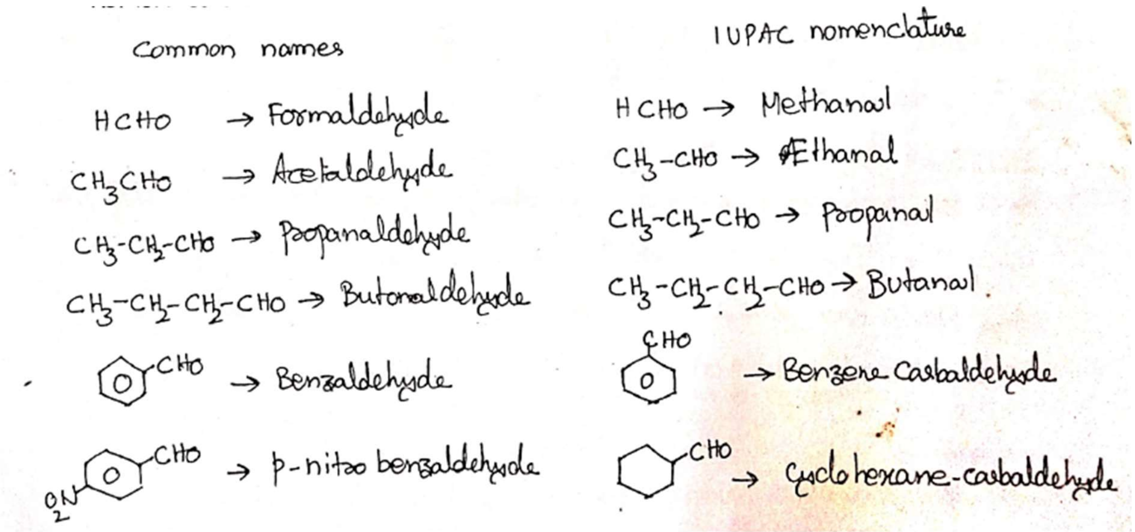
CARBONYL COMPOUNDS

Nomenclature Of Carbonyl Compounds

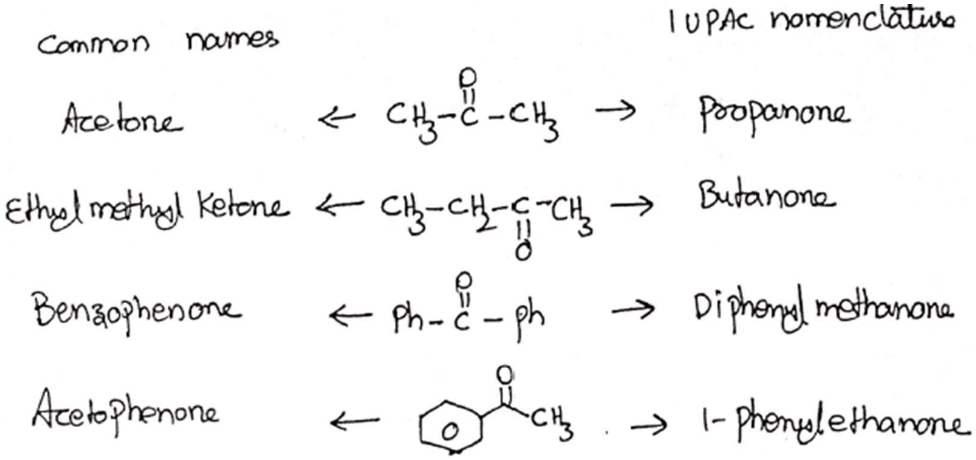
Aliphatic aldehydes are named by replacing the "-e" in the parent alkane name with "-al". The aldehyde carbon is always considered carbon 1, so a number is not needed to indicate its position.

If the aldehyde group is attached to Alicyclic or Aromatic ring, the suffix "-carbaldehyde" is used.



Common names	IUPAC nomenclature
$HCHO$ → Formaldehyde	$HCHO$ → Methanal
CH_3CHO → Acetaldehyde	CH_3-CHO → Ethanal
CH_3-CH_2-CHO → Propanaldehyde	CH_3-CH_2-CHO → Propanal
$CH_3-CH_2-CH_2-CHO$ → Butanaldehyde	$CH_3-CH_2-CH_2-CHO$ → Butanal
CHO → Benzaldehyde	CHO → Benzene Carbaldehyde
O_2N CHO → p-nitro benzaldehyde	CHO → Cyclohexane-carbaldehyde

In the IUPAC system, Ketones are named by replacing the "-e" of the parent alkane with "-one". Preceded by a number indicating the position of the carbonyl group (C=O). Start numbering from the end closest to the carbonyl group.

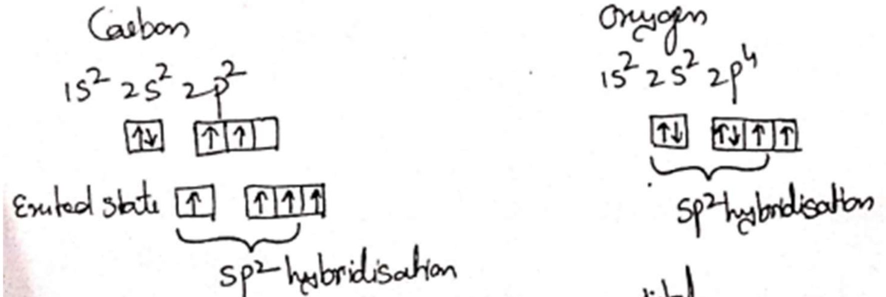


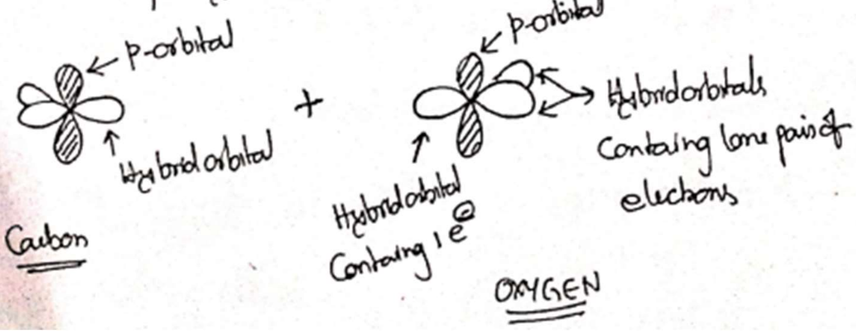
Common names		IUPAC nomenclature
Acetone	← $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ →	Propanone
Ethyl methyl Ketone	← $CH_3-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$ →	Butanone
Benzophenone	← $Ph-\overset{O}{\overset{\|}{C}}-Ph$ →	Diphenyl methanone
Acetophenone	← O, CH_3 →	1-phenylethanone

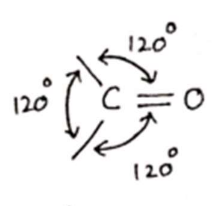
Structure of carbonyl group

Carbonyl group is Composed of one σ and one π bond ($>C=O$)

In Carbonyl group, the hybridisation of Carbon is sp^2. out of the three sp^2 hybridised orbitals one sp^2 hybridised orbitals overlaps with p-orbital of oxygen to form σ C–O σ bond. The remaining two sp^2 hybridised orbitals of Carbon forms σ bonds with s-orbital of hydrogen (or) sp^3 orbital of Alkyl group. The Three σ-bonds of the Carbonyl Carbon utilise sp^2 orbitals they lie in one plane at 120° apart. C–O π bond is formed by the sidewise overlap of p orbitals of Carbon and oxygen.







Due to electronegativity of oxygen atom the π electron cloud is attracted towards oxygen. so Oxygen attains a Partial -ve charge and Carbon attains Partial +ve charge. This polar nature of Carbonyl group Causes intermolecular attractions in aldehydes and Ketones. and hence responsible for higher boiling points.

Reactivity of carbonyl group

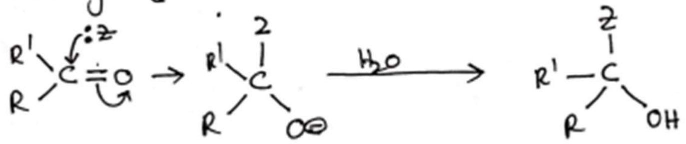
A) Carbonyl group as a site for nucleophillic addition

The π e's of C=O are pulled strongly towards oxygen which makes Carbonyl oxygen electron rich and Carbonyl Carbon electron deficient. The +ve charge on Carbon atom means that it is easily attacked by a nucleophile.

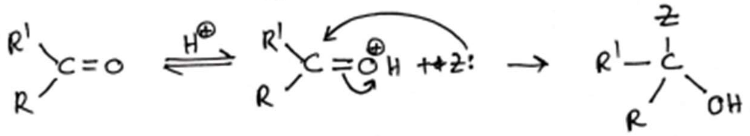
The −ve charge on oxygen atom means that nucleophillic addition is susceptible to acid catalysts.

Thus the nucleophillic addition to the C=O occurs in either of two ways

1. when the reagent is strong nucleophile, addition takes place in the following ways



2. when reaction is catalysed by acid then nucleophilic addition takes place in the following ways

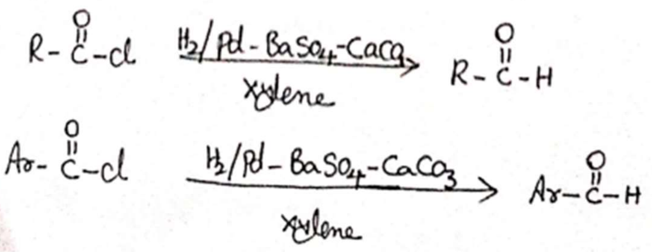


Methods of Preparation of Aldehydes

1. **Preparation from Acid chlorides**

Rosenmunds Reduction:

Acid chlorides on partial reduction give aldehydes. This reduction takes place in presence of Lindlar's Catalyst ($Pd-BaSO_4-CaCO_3$)

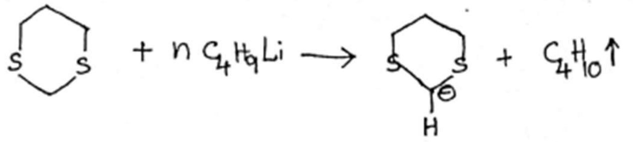


$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{Xylene}]{H_2/Pd-BaSO_4-CaCO_3} R-\overset{O}{\overset{\|}{C}}-H$$

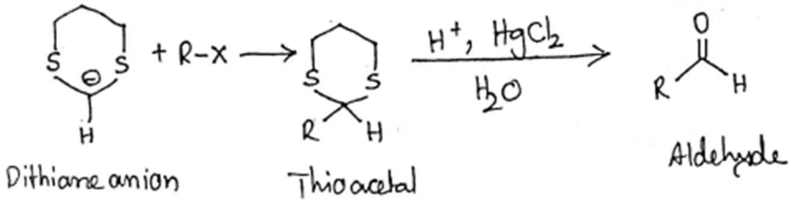
$$Ar-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{Xylene}]{H_2/Pd-BaSO_4-CaCO_3} Ar-\overset{O}{\overset{\|}{C}}-H$$

2. **Preparation from 1,3-dithiane**

1,3-dithianes reacts with strong bases such as n-butyl lithium undergo deprotonation and forms Carbanion.



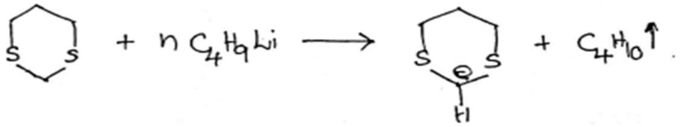
Alkylation of dithiane anion by 1° alkyl halide gives thioacetal, which can be hydrolysed in acidic solution of mercuric chloride



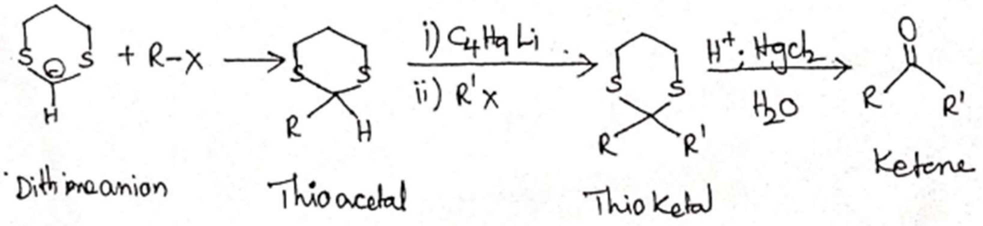
Methods of Preparation of Ketones

1. **Preparation of Ketones**

1,3 dithianes reacts with strong bases such as n-Butyl lithium undergo deprotonation and forms Carbanion.

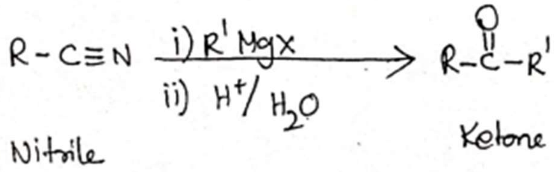


Alkylation of dithiane anion by 1° Alkyl halide gives thio acetal, Further alkylation of thioacetal followed by hydrolysis gives Ketones as final product



2. Preparation from nitriles or Cyanides

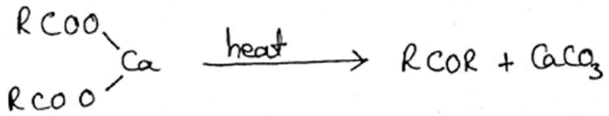
Nitriles on reaction with Grignard reagent and Acidic hydrolysis Produces Ketone as product.



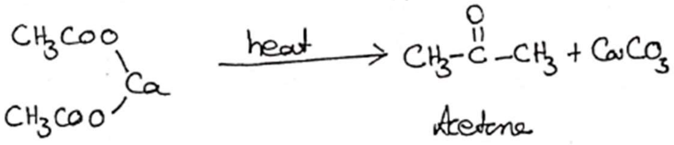
$$\underset{\text{Nitrile}}{R-C\equiv N} \xrightarrow[\text{ii) } H^+/H_2O]{\text{i) } R'MgX} \underset{\text{Ketone}}{R-\overset{\overset{O}{\|}}{C}-R'}$$

3. Preparation from carboxylic acids

Calcium salts of Carboxylic acids on distillation gives ~~alde~~Ketones



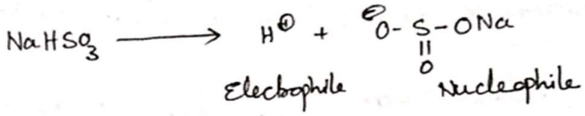
$$\begin{matrix} RCOO \\ RCOO \end{matrix}\!\!>Ca \xrightarrow{\text{heat}} RCOR + CaCO_3$$



$$\begin{matrix} CH_3COO \\ CH_3COO \end{matrix}\!\!>Ca \xrightarrow{\text{heat}} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + CaCO_3$$

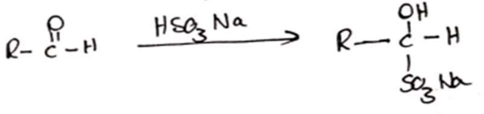
Chemical reactions

a) Addition with $NaHSO_3$

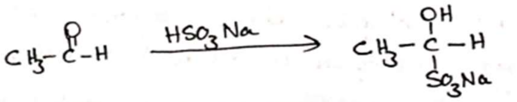


$$NaHSO_3 \longrightarrow \underset{\text{Electrophile}}{H^{\oplus}} + \underset{\text{Nucleophile}}{{}^{\ominus}O-\underset{\underset{O}{\|}}{S}-ONa}$$

i) All types of aldehydes gives addition reaction with this reagent

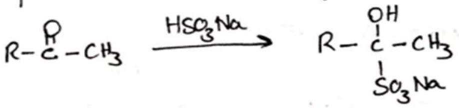


$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{HSO_3Na} R-\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}-H$$

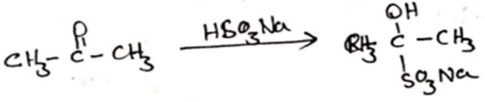


$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{HSO_3Na} CH_3-\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}-H$$

ii) only aliphatic methyl ketones gives addition reaction



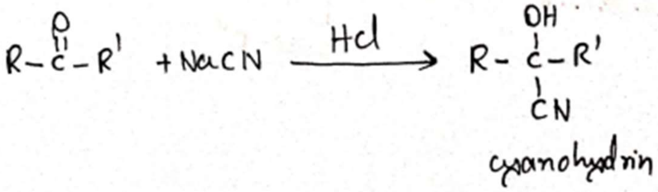
$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{HSO_3Na} R-\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{HSO_3Na} CH_3-\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

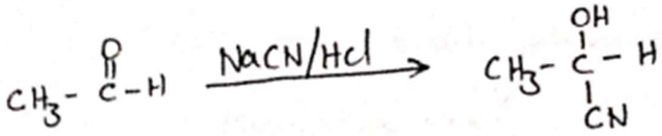
b) Addition with Hydrogen Cyanide (HCN)

Because HCN is toxic gas, the bestways to Carry out this reaction, to generate gas HCN during the reaction by adding HCl to a mixture of Carbonyl Compound and excess of NaCN



$$R-\overset{O}{\overset{\|}{C}}-R' + NaCN \xrightarrow{HCl} R-\underset{CN}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R'$$

cyanohydrin

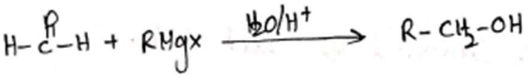


$$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaCN/HCl} CH_3-\underset{CN}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-H$$

c) Reaction with Grignard's reagent

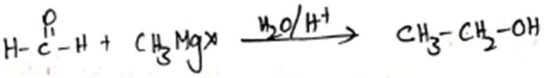
Carbonyl Compounds reacts with Grignard reagent to gives alcohols

i) Formaldehyde reacts with Grignard reagent gives 1° Alcohols



$$H-\overset{O}{\overset{\|}{C}}-H + RMgx \xrightarrow{H_2O/H^+} R-CH_2-OH$$

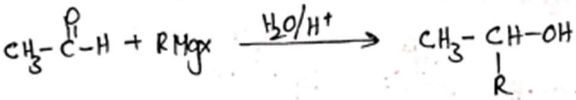
1° Alcohols



$$H-\overset{O}{\overset{\|}{C}}-H + CH_3Mgx \xrightarrow{H_2O/H^+} CH_3-CH_2-OH$$

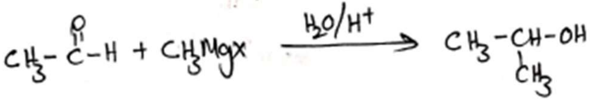
Ethyl alcohol

ii) Aldehydes (except formaldehyde) reacts with Grignard reagent gives 2° Alcohols



$$CH_3-\overset{O}{\overset{\|}{C}}-H + RMgx \xrightarrow{H_2O/H^+} CH_3-\underset{R}{\underset{|}{CH}}-OH$$

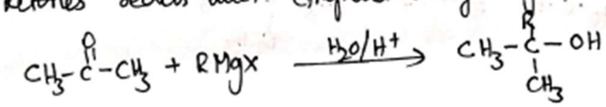
(2° Alcohol)



$$CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3Mgx \xrightarrow{H_2O/H^+} CH_3-\underset{CH_3}{CH}-OH$$

(Iso propyl Alcohol)

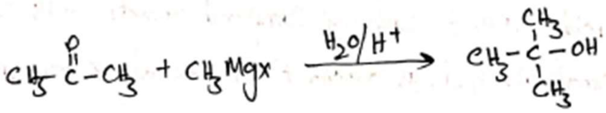
iii) Ketones reacts with Grignard reagent gives 3° Alcohols



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + RMgx \xrightarrow{H_2O/H^+} CH_3-\underset{CH_3}{\underset{|}{\overset{R}{C}}}-OH$$

(3° Alcohols)

Ketones



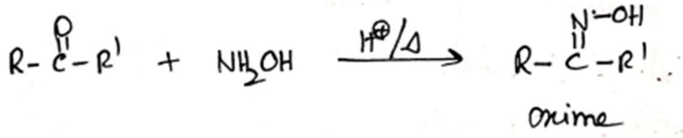
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3Mgx \xrightarrow{H_2O/H^+} CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH$$

(t-butyl alcohol)

B. Nucleophilic addition followed by elimination reactions

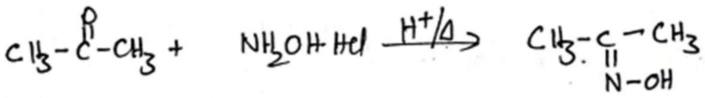
a) Reactions with hydroxylamine

Carbonyl Compounds reacts with Hydroxylamine to form oximes



$R-\overset{O}{\overset{\|}{C}}-R' + NH_2OH \xrightarrow{H^{\oplus}/\Delta} R-\overset{N-OH}{\overset{\|}{C}}-R'$

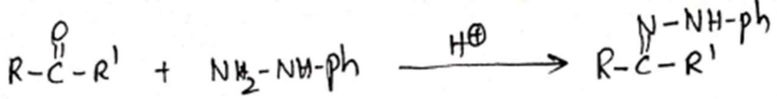
oxime



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + NH_2OH\cdot HCl \xrightarrow{H^+/\Delta} CH_3-\underset{\underset{N-OH}{\|}}{C}-CH_3$

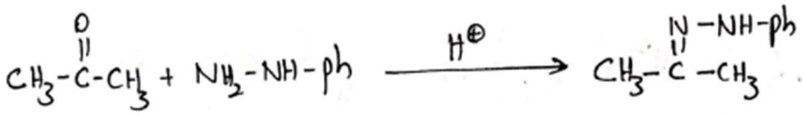
b) Reactions with phenyl hydrazine

Carbonyl compounds reacts with phenyl hydrazine to form phenyl hydra



$R-\overset{O}{\overset{\|}{C}}-R' + NH_2-NH-ph \xrightarrow{H^{\oplus}} R-\overset{N-NH-ph}{\overset{\|}{C}}-R'$

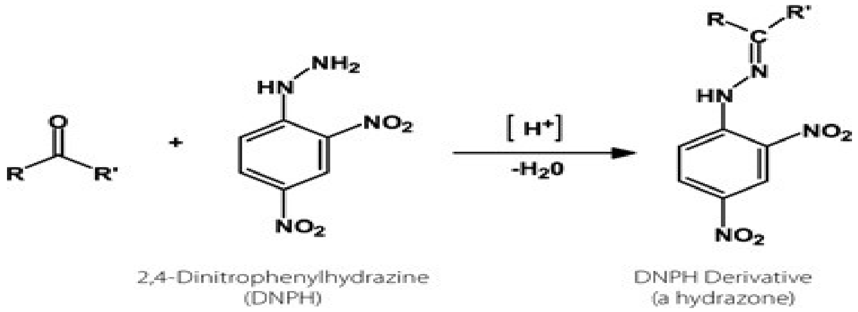
phenyl hydrazone



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + NH_2-NH-ph \xrightarrow{H^{\oplus}} CH_3-\overset{N-NH-ph}{\overset{\|}{C}}-CH_3$

c) Reactions with 2,4 DNP

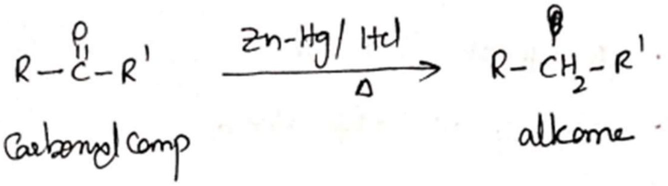
Carbonyl compounds are simply mixed with an acid solution of 2,4 DNP in methanol. yields 2,4-dinitrophenylhydrazones.



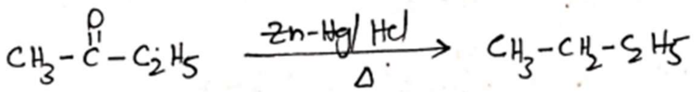
C) Reduction reactions

a) Clemmensen's reduction

Reduction of aldehydes or ketones to alkanes using Zinc amalgam and Conc Hcl.



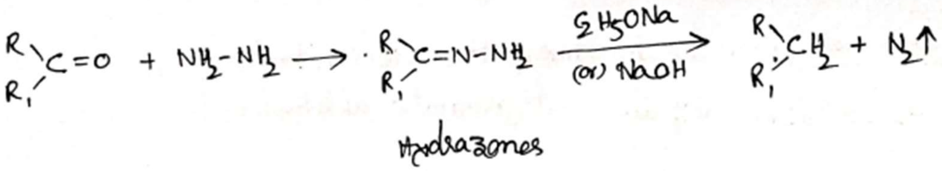
$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[\Delta]{Zn\text{-}Hg/Hcl} R-CH_2-R'$$



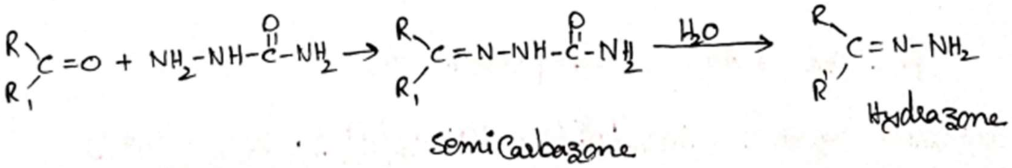
$$CH_3-\overset{O}{\overset{\|}{C}}-C_2H_5 \xrightarrow[\Delta]{Zn\text{-}Hg/Hcl} CH_3-CH_2-C_2H_5$$

b) Wolf–Kishner's reduction

Reduction of hydrazones, semicarbazones (or) azines of aldehydes (or) Ketones to hydrocarbons in basic condition is known as Wolf- Kishner reduction.



$$\begin{matrix}R\\R_1\end{matrix}\!\!>C=O + NH_2-NH_2 \longrightarrow \begin{matrix}R\\R_1\end{matrix}\!\!>C=N-NH_2 \xrightarrow[(or)\ NaOH]{C_2H_5ONa} \begin{matrix}R\\R_1\end{matrix}\!\!>CH_2 + N_2\uparrow$$



$$\begin{matrix}R\\R_1\end{matrix}\!\!>C=O + NH_2-NH-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow \begin{matrix}R\\R_1\end{matrix}\!\!>C=N-NH-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O} \begin{matrix}R\\R'\end{matrix}\!\!>C=N-NH_2$$

In reduction of semicarbazones & azines, the derivatives were first converted to hydrazone then to corresponding alkanes.

c) Reduction with $LiAlH_4$

Carbonyl compounds reduced with $LiAlH_4$ to form alcohols

Aldehydes $\xrightarrow{LiAlH_4}$ 1° Alcohols

Ketones $\xrightarrow{LiAlH_4}$ 2° Alcohols

$R-CHO \xrightarrow{LiAlH_4} R-CH_2OH$ 1° Alcohols

$CH_3-CHO \xrightarrow{LiAlH_4} CH_3-CH_2-OH$ Ethyl alcohol

$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{LiAlH_4} R-\overset{OH}{\overset{|}{C}}H-R'$ 2° Alcohols

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{LiAlH_4} CH_3-\overset{OH}{\overset{|}{C}}H-CH_3$ isopropyl alcohol

d) Reduction with $NaBH_4$

Carbonyl compounds reduced with $NaBH_4$ to form alcohols

i) Aldehydes $\xrightarrow{NaBH_4}$ 1° Alcohols

$R-CHO \xrightarrow{NaBH_4} R-CH_2-OH$ (1° Alcohol)

$CH_3-CHO \xrightarrow{NaBH_4} CH_3-CH_2-OH$ (Ethyl alcohol)

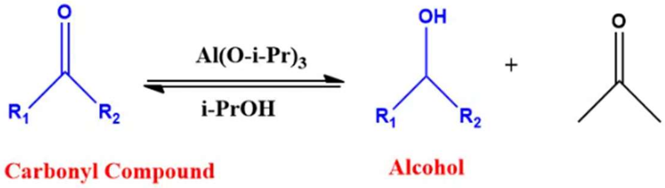
ii) Ketones $\xrightarrow{NaBH_4}$ 2° Alcohols

$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{NaBH_4} R-\overset{OH}{\overset{|}{C}}H-R'$ (2° Alcohol)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{''} CH_3-\overset{OH}{\overset{|}{C}}H-CH_3$ (iso propyl alcohol)

e) Meerwein–Ponndorf–Verley (MPV) reduction

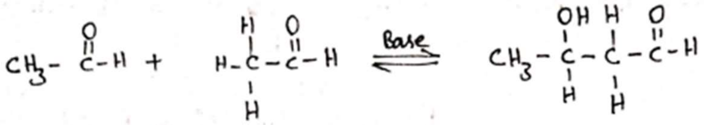
Reduction of ketones and aldehydes to their corresponding alcohols utilizing aluminium alkoxide as catalyst in the presence of a sacrificial alcohol.



NAMED REACTIONS

a) Aldol Condensation

condensation of two molecules of an aldehyde (or ketones (with atleast one α- Hydrogen atom) to form β- hydroxy aldehyde or β-hydroxy ketone is known as aldol condensation.



$$CH_3-\overset{O}{\overset{\|}{C}}-H + H-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-H \xrightleftharpoons{Base} CH_3-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-H$$

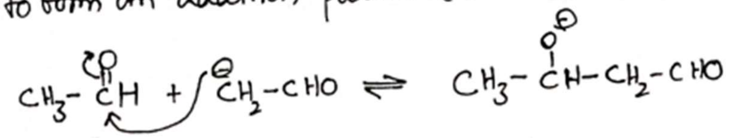
β-Hydroxy butyraldehyde

Mechanism

1. Formation of resonance stabilized Carbanion from aldehyde by the basic catalyst.

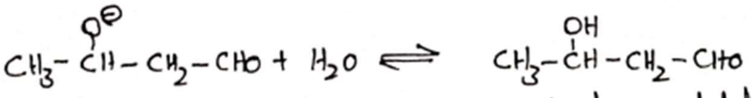
$$CH_3-CHO + OH^{\ominus} \rightleftharpoons [\overset{\ominus}{C}H_2-CHO \leftrightarrow CH_2=CH-\overset{\ominus}{O}]$$

2. The Carbanion attacks the Carbonyl Carbon of Second aldehyde molecule to form an addition product (alkoxide)



$$CH_3-\overset{O}{\overset{\|}{C}}H + \overset{\ominus}{C}H_2-CHO \rightleftharpoons CH_3-\overset{O^{\ominus}}{\overset{|}{C}}H-CH_2-CHO$$

3. Alkoxide absorbs H+ from water to form β-hydroxy aldehyde



$$CH_3-\overset{O^{\ominus}}{\overset{|}{C}}H-CH_2-CHO + H_2O \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-CHO$$

β-hydroxy aldehyde

b) Cannizzaro reaction

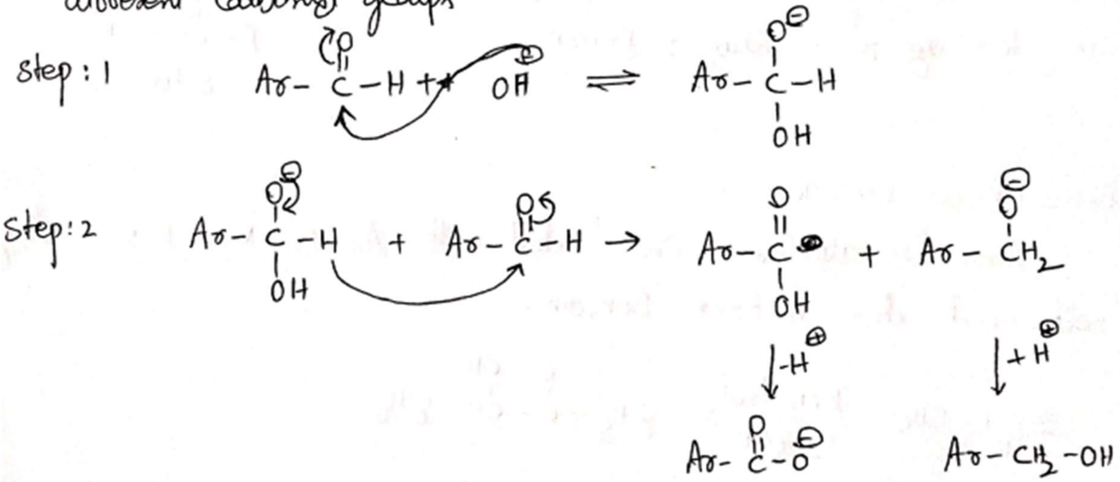
Aldehydes without α- Hydrogens, when treated with Conc alkali (Aq or Alc), undergo self oxidation -reduction to form a mixture of an alcohol and salt of carboxylic acid.

$$2C_6H_5CHO \xrightarrow{Con\ Aq\ NaOH} C_6H_5CH_2OH + C_6H_5COOH$$

Benzaldehyde — Benzyl alcohol — Benzoic acid

Mechanism

The mechanism involves two succesive nucleophilic addition, at different Carbonyl groups



c) Perkin reaction

Condensation of an aromatic aldehyde with an acid anhydride in presence of sodium salt of the same acid to form α,β unsaturated acid.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow[ii)\ H^+]{i)\ CH_3COONa} C_6H_5CH{=}CHCOOH$$

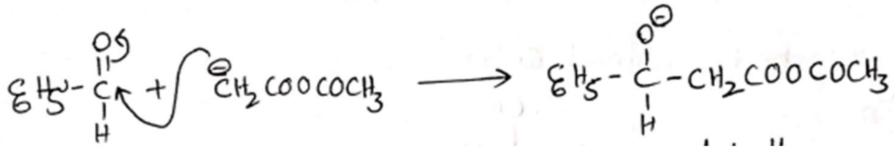
Benzaldehyde   Acetic anhydride   Cinnamic acid

Mechanism

i) Acetate ion (from sodium acetate) abstracts hydrogen atom from the α- position of the anhydride to form Carbanion

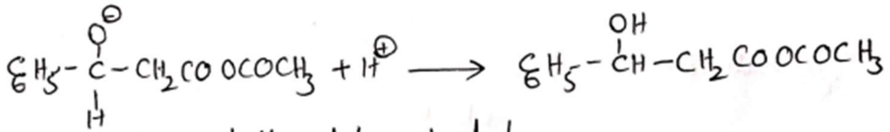
$$CH_3-CO\cdot O\cdot COCH_3 + CH_3CO\overset{\ominus}{O} \longrightarrow \overset{\ominus}{C}H_2-COOCOCH_3 + CH_3COOH$$

ii) Carbanion attacks the Carbonyl Carbon of Benzaldehyde



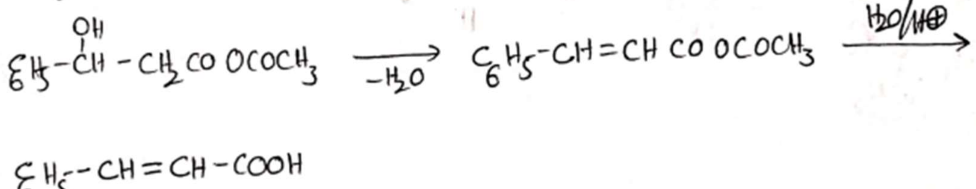
$$C_6H_5-\underset{H}{\overset{O}{\overset{\|}{C}}} + \overset{\ominus}{C}H_2COOCOCH_3 \longrightarrow C_6H_5-\underset{H}{\overset{O^{\ominus}}{\overset{|}{C}}}-CH_2COOCOCH_3$$

iii) Anionic oxygen of the carbonyl group is protonated, the required proton is furnished by CH_3COOH



$$C_6H_5-\overset{O^{\ominus}}{\underset{H}{C}}-CH_2COOCOCH_3 + H^{\oplus} \longrightarrow C_6H_5-\overset{OH}{CH}-CH_2COOCOCH_3$$

iv) Dehydration followed by hydrolysis.



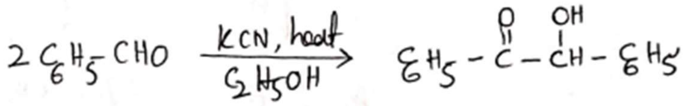
$$C_6H_5-\overset{OH}{CH}-CH_2COOCOCH_3 \xrightarrow[-H_2O]{} C_6H_5-CH=CHCOOCOCH_3 \xrightarrow{H_2O/H^{\oplus}}$$

$$C_6H_5-CH=CH-COOH$$

Cinnamic acid.

d) Benzoin condensation

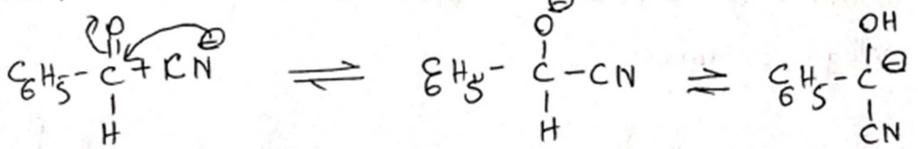
Aromatic aldehydes, when heated with Alc NaCN (or) KCN undergo self condensation to form Benzoin.



$$2C_6H_5CHO \xrightarrow[C_2H_5OH]{KCN,\ heat} C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{OH}{CH}-C_6H_5$$

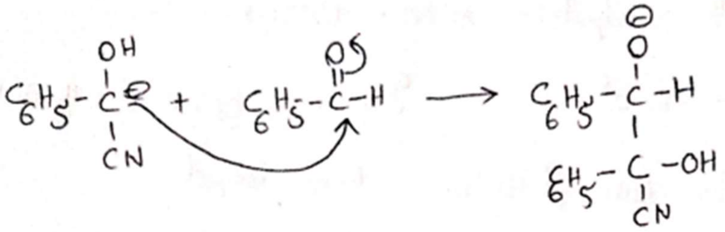
Mechanism

1. Nucleophilic addition of $CN^{\ominus}$ at the carbonyl carbon of benzaldehyde

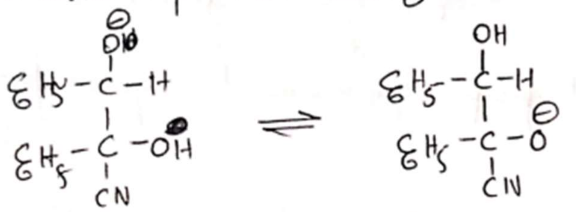


Resonance stabilized Carbanion

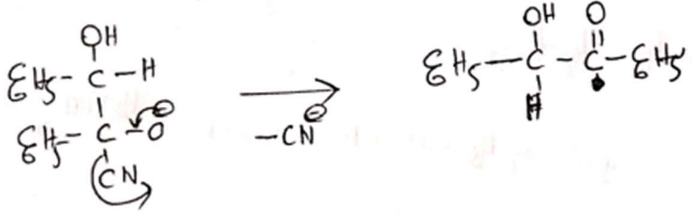
ii) attack of Resonance stabilized Carbanion on the Carbonyl Carbon of the 2nd molecule of benzaldehyde



iii) Transfer of proton to carbonyl carbon

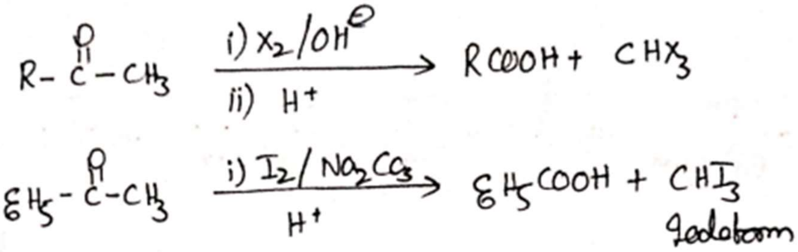


iv Removal of cyanide ion



e) Haloform reaction:

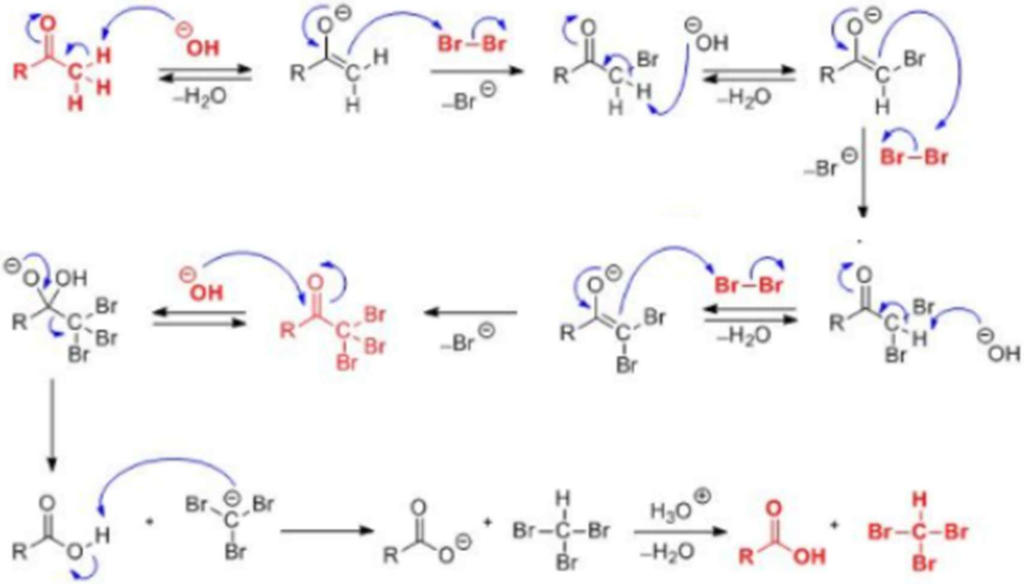
In this reaction α-methyl carbonyl compound undergo oxidation with $X_2/OH^\ominus$



$$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{ii) } H^+]{\text{i) } X_2/OH^\ominus} RCOOH + CHX_3$$

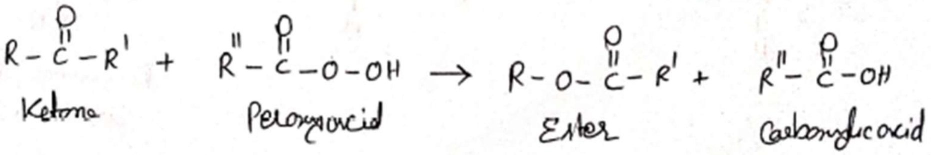
$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[H^+]{\text{i) } I_2/Na_2CO_3} C_6H_5COOH + \underset{\text{Iodoform}}{CHI_3}$$

Mechanism

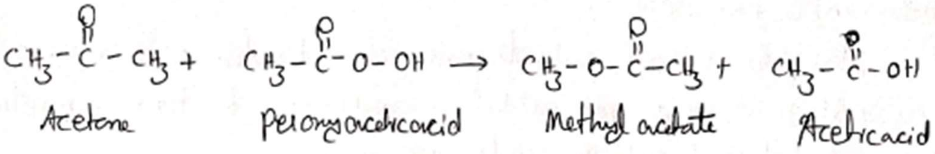


f) Baeyer-Villiger oxidation

oxidation of Ketone into ester by peroxy acids is called Bayer-villiger oxidation.



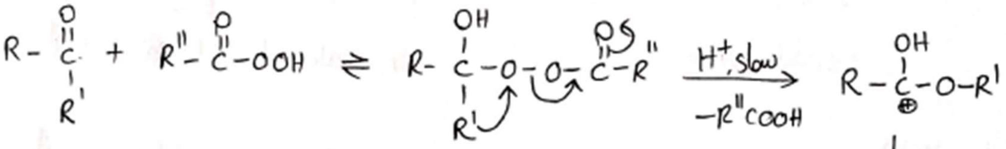
$$\underset{\text{Ketone}}{R-\overset{\overset{O}{\|}}{C}-R'} + \underset{\text{Peroxyacid}}{R''-\overset{\overset{O}{\|}}{C}-O-OH} \rightarrow \underset{\text{Ester}}{R-O-\overset{\overset{O}{\|}}{C}-R'} + \underset{\text{Carboxylic acid}}{R''-\overset{\overset{O}{\|}}{C}-OH}$$



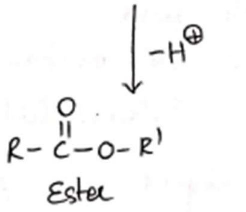
$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{\text{Peroxyaceticacid}}{CH_3-\overset{\overset{O}{\|}}{C}-O-OH} \longrightarrow \underset{\text{Methyl acetate}}{CH_3-O-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{\text{Aceticacid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH}$$

Mechanism

1. Acid catalysed addition of peroxyacid to Ketonic Carbonyl group.
2. Migration of an alkyl group to e⁻ deficient oxygen atom



$$R-\underset{R'}{\overset{\overset{O}{\|}}{C}} + R''-\overset{\overset{O}{\|}}{C}-OOH \rightleftharpoons R-\underset{R'}{\overset{OH}{C}}-O-O-\overset{\overset{O}{\|}}{C}-R'' \xrightarrow[-R''COOH]{H^+,\ slow} R-\underset{\oplus}{\overset{OH}{C}}-O-R'$$

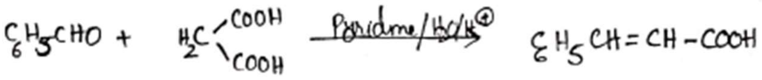


$$\xrightarrow{-H^{\oplus}} \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-O-R'}$$

The order of migration of alkyl group is teritary > secondary > primary

g) Knoevenagel reaction

Condensation of aldehydes or Ketones, with ~~not~~ α Hydrogen atom, with active methylene compound in particular malonic ester in presence of weak base like NH_3 or 1° amine. gives unsaturated compound

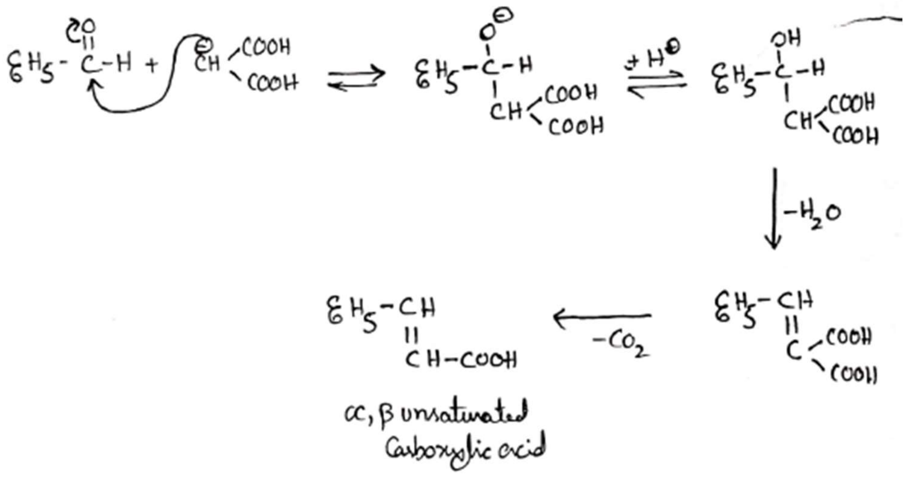


$$C_6H_5CHO + H_2C\begin{smallmatrix}COOH\\COOH\end{smallmatrix} \xrightarrow{\text{Pyridine}/H_2O/H^{\oplus}} C_6H_5CH=CH-COOH$$

Mechanism

$$\text{i)}\quad H_2C\begin{smallmatrix}COOH\\COOH\end{smallmatrix} + \text{Base} \longrightarrow \overset{\ominus}{C}H\begin{smallmatrix}COOH\\COOH\end{smallmatrix}$$

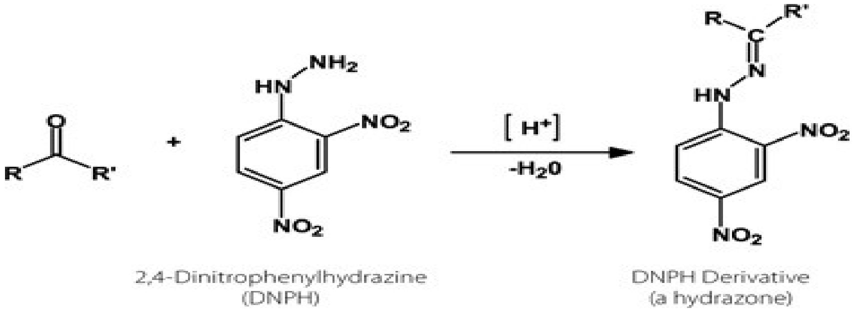
ii)



Analysis of aldehydes and ketones

a) **2,4-DNPH test**

2,4-DNPH test is a common test for identifying aldehydes and ketones. The reaction of 2,4-dinitrophenylhydrazine (2,4-DNP) with aldehydes or ketones results in the formation of a 2,4-dinitrophenylhydrazone which appears as yellow to orange coloured precipitate.



b) **Tollen's test**

Tollen's test is also known as the silver mirror test, It is used to distinguish aldehydes and ketones. The diamine silver (I) complex oxidizes the aldehyde to a carboxylate ion during the reaction silver (I) is reduced to elemental silver (0). The elemental silver deposits on the inner surface of the test tube which is called as "silver mirror".

$$2\,[\mathrm{Ag(NH_3)_2}]^+ + \mathrm{R{-}CHO} + \mathrm{H_2O} \longrightarrow 2\,\mathrm{Ag(s)} + 4\,\mathrm{NH_3} + \mathrm{R{-}COOH} + 2\,\mathrm{H^+}$$

Preparation of Tollen's reagent:

Few drops of dilute sodium hydroxide are added to some aqueous 0.1 M silver nitrate. The -OH^- ions convert the silver aquo complex form into silver (I) oxide Ag_2O which precipitates from the solution as a brown solid.

$$2\,\mathrm{AgNO_3} + 2\,\mathrm{NaOH} \longrightarrow \mathrm{Ag_2O(s)} + 2\,\mathrm{NaNO_3} + \mathrm{H_2O}$$

Sufficient aqueous ammonia is added to dissolve the brown silver (I) oxide. The resulting solution contains the $[Ag(NH_3)_2]^+$

$$Ag_2O(s) + 4\,NH_3 + 2\,NaNO_3 + H_2O \longrightarrow 2\,[Ag(NH_3)_2]NO_3 + 2\,NaOH$$

c) **Fehling test**

Fehling's test is used to identify the presence of reducing sugars and aldehydes. Fehling's solution is prepared by combining two separate solutions. They are Fehling's A and Fehling's B

Fehling's A is blue coloured aqueous solution of copper (II) sulphate

Fehling's B which is a colorless solution of aqueous potassium sodium tartrate (also known as Rochelle salt) made strongly alkaline with NaOH.

Aldehydes reacts with Fehling's solution and the mixture is heated. The bistartratocuprate (II) complex oxidizes the aldehyde to a carboxylate anion. During the reaction the copper (II) ions of the complex are reduced to copper (I) ions which are red in colour.

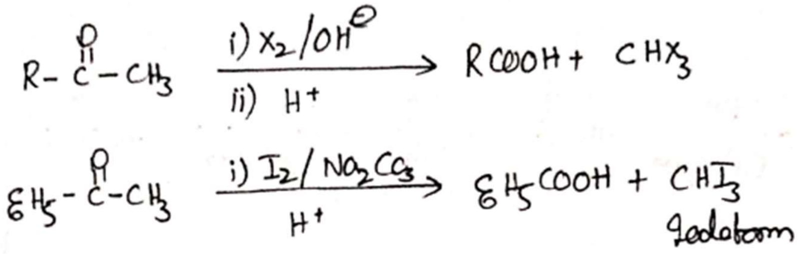
$$RCHO + 2\,Cu^{2+} + 5\,OH^- \longrightarrow RCOO^- + Cu_2O + 3\,H_2O$$

d) **Schiff's test**

This is the qualitative test used for detection of aldehyde functional group. Aldehyde when treated with decolourized Schiff's reagent turns to purple or magenta colour confirms the presence of aldehydes.

e) **Haloform test**

In this reaction α-methyl carbonyl compound undergo oxidation with $X_2/OH^\ominus$



$$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{ii) } H^+]{\text{i) } X_2/OH^\ominus} RCOOH + CHX_3$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[H^+]{\text{i) } I_2/Na_2CO_3} C_6H_5COOH + \underset{\text{Iodoform}}{CHI_3}$$