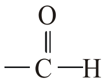
CARBONYL COMPOUNDS

INTRODUCTION

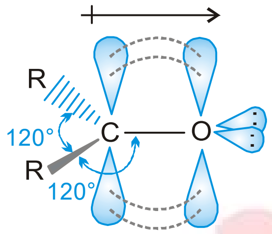
Organic Compounds having $>C=O$ group are called carbonyl compounds and $>C=O$ group is known as carbonyl or oxo group. It's general formula is $C_n H_{2n}O$ (n = 1, 2, 3......) Carbonyl compounds are grouped into two categories.

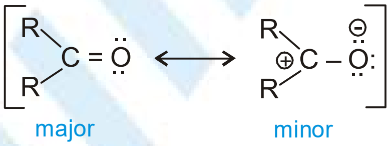
(a) Aldehydes : Aldehyde group is  $-\overset{\overset{\large O}{\|}}{C}-H$ (also known as formyl group). It is a monovalent group

(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.

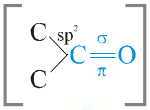
STRUCTURE AND BONDING IN ALDEHYDES AND KETONES

The carbonyl carbon atom is sp^2 hybridized. The unhybridized p-orbital overlaps with a p-orbital of oxygen to form a pi bond. The double bond between carbon and oxygen is shorter, stronger, and polarized.
Orbital diagram for the formation of carbonyl group is as follows:





This polarity confirms that there is nucleophilic addition reaction takes place in carbonyl compound.
The double bond of the carbonyl group has a large dipole moment because oxygen is more electronegative than carbon.
Carbonyl carbon act as an electrophile **(Lewis acid)**
Carbonyl oxygen act as a nucleophile **(Lewis base)**

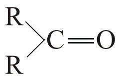


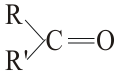
The C—C—O and H—C—O bond angles are of 120°.

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 dipole moment.

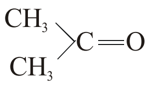
Ketones are further classified as :

(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.  $\begin{matrix}R\\R'\end{matrix}\!>C=O$

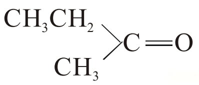
Ex : **(Ketones) :**

Symmetrical



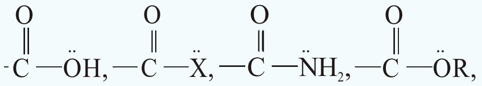
(Acetone or Dimethyl ketone)
2–Propanone

Unsymmetrical



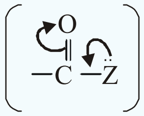
(Ethyl methyl ketone)
2–Butanone

EDUBULL KEY POINTS



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

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



so resonance occurs. These compounds have $\overset{\overset{O}{\|}}{-C-}$ group still they are not carbonyl compounds because carbonyl group takes parts in resonance with the lone pair of electrons.

GENERAL METHODS OF PREPARATION

(A) FOR BOTH ALDEHYDES AND KETONES

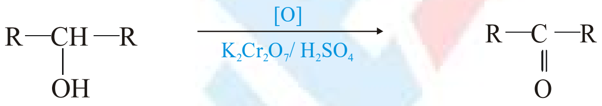
By Oxidation of Alcohols :

Primary alcohols $\xrightarrow{[O]}$ Aldehydes
Secondary alcohols $\xrightarrow{[O]}$ Ketones

By $K_2Cr_2O_7$ / H_2SO_4 :

Oxidation of primary alcohols gives aldehyde and oxidation of secondary alcohols gives Ketones. Here, ($K_2Cr_2O_7$ / H_2SO_4) is a strong oxidising agent.

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



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

Aldehydes are quite susceptible to further oxidation to acids -

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

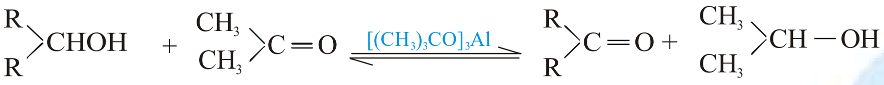
Thus oxidation of primary alcohols is made at the temperature much above the boiling point of aldehyde and thus aldehydes are vapourised out and prevented from being oxidised.

ETOOS KEY POINTS

Aldehydes can be prepared from 1° alcohol, secondary alcohols can be oxidized to ketones, by oxidation with pyridinium chlorochromate (PCC) in CH_2Cl_2 solvent, pyridinium dichromate (PDC) and with Jones reagent (CrO_3+H_2SO_4) in acetone.

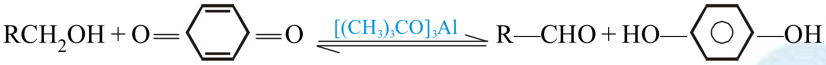
Oppenauer Oxidation :

The oxidation of secondary alcohols to ketones by heating them with specific reagent : $[(CH_3)_3CO]_3Al$ (Aluminium-t-butoxide) in presence of acetone. Primary alcohols may also be oxidized to aldehydes if ketones is replaced by a better hydrogen acceptor, e.g. p-benzoquinone. The equilibrium can be controlled by the amount of acetone, an excess of which favours the oxidation of the alcohol.



$$R_2CHOH + (CH_3)_2C{=}O \xrightleftharpoons{[(CH_3)_3CO]_3Al} R_2C{=}O + (CH_3)_2CH-OH$$

2^{O} Alcohol Acetone Ketone Isopropyl alcohol



1^{0} Alcohol Quinone Aldehyde Quinol

Note : The reaction is the reverse of **Meerwein-Ponndorf -verley reduction**.

Mild Oxidising Agent :

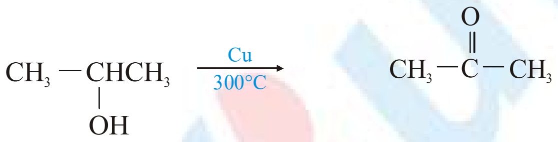
1^{o} alcohols will get oxidised with CrO_3 / Pyridine, **collin's reagent** Ag/O_2 at $250^{o}C$

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

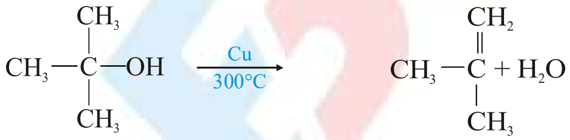
By this reaction, **good yield of aldehyde** is possible.

Dehydrogenation of alcohols :

$$CH_3CH_2OH \xrightarrow[300°C]{Cu} CH_3CHO$$ (Acetaldehyde)



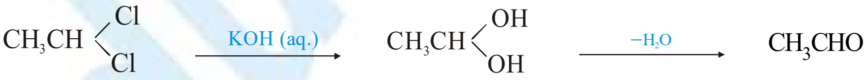
$$CH_3-\underset{OH}{\underset{|}{C}}HCH_3 \xrightarrow[300°C]{Cu} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$ (Acetone)



$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH \xrightarrow[300°C]{Cu} CH_3-\underset{CH_3}{\underset{|}{\overset{CH_2}{\overset{\|}{C}}}} + H_2O$$ (Isobutylene)

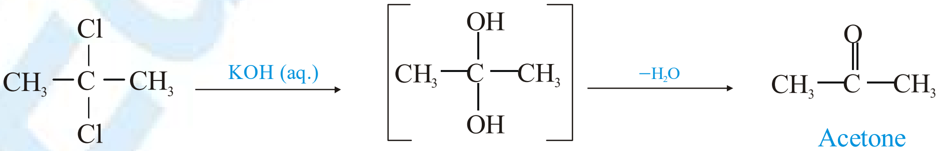
By Hydrolysis of gem dihalides :

Terminal gem-dihalides on hydrolysis give aldehydes while the non-terminal dihalides give ketone.



$$CH_3CHCl_2 \xrightarrow{KOH\ (aq.)} CH_3CH(OH)_2 \xrightarrow{-H_2O} CH_3CHO$$

Terminal gem-dihalide [unstable] Acetaldehyde



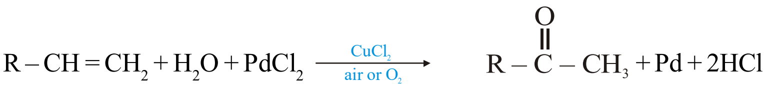
$$CH_3-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-CH_3 \xrightarrow{KOH\ (aq.)} \left[CH_3-\underset{OH}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3\right] \xrightarrow{-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

unstable Acetone

Wacker process :

Alkenes can directly be oxidised to corresponding aldehydes or ketones by treating them with a solution of $PdCl_2$ containing a catalytic amount of $CuCl_2$ in presence of air or O_2. Except ethene any higher alkene will give ketone.

$$CH_2=CH_2+H_2O+PdCl_2 \xrightarrow[\text{air or } O_2]{CuCl_2} CH_3-CH=O+Pd+2HCl$$

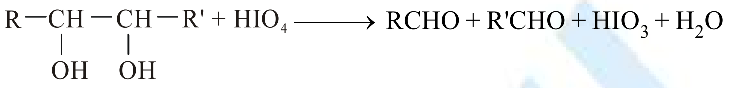


$$R-CH=CH_2+H_2O+PdCl_2 \xrightarrow[\text{air or } O_2]{CuCl_2} R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3+Pd+2HCl$$

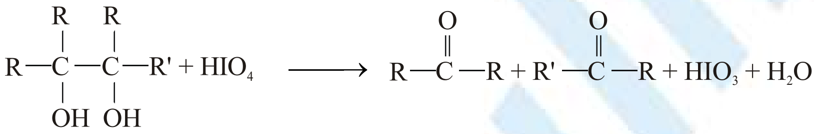
Note During the reaction $PdCl_2$ is reduced to Pd and $CuCl_2$ is reduced to Cu(I)

By Oxidation of diols :

With periodic acid (HIO_4) & lead tetra acetate $(CH_3COO)_4$ Pb vicinal diols gets oxidised to form carbonyl compounds



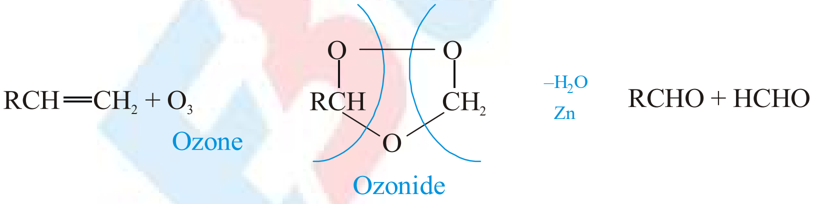
$$R-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH}-R'+HIO_4 \longrightarrow RCHO+R'CHO+HIO_3+H_2O$$

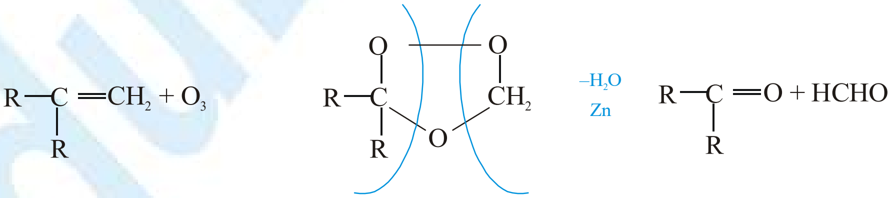


$$R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-R'+HIO_4 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-R+R'-\overset{\overset{\displaystyle O}{\|}}{C}-R+HIO_3+H_2O$$

By Ozonolysis of alkenes :

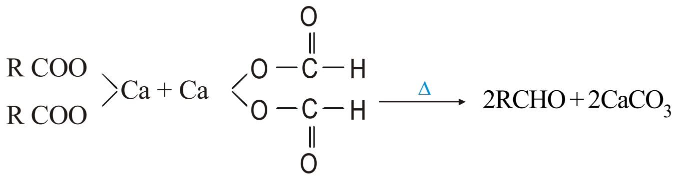
This reaction is used to determine the position of double bond in alkene.





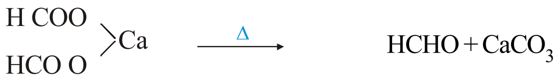
Unbranched alkene ⟶ Aldehyde
Branched alkene ⟶ Ketone

By dry distillation of Ca-salts of carboxylic acid :

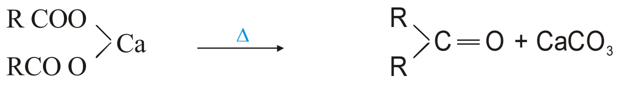


$$\begin{matrix}R\,COO\\R\,COO\end{matrix}\!\!>Ca + Ca<\begin{matrix}O-\overset{\overset{O}{\|}}{C}-H\\O-\underset{\underset{O}{\|}}{C}-H\end{matrix}\xrightarrow{\Delta}2RCHO+2CaCO_3$$

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



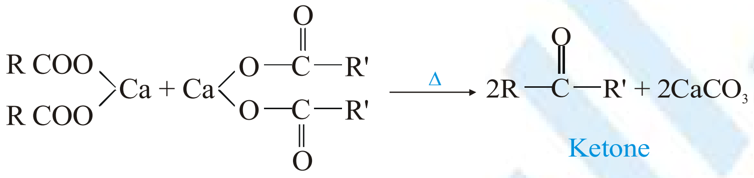
$$\begin{matrix}H\,COO\\HCO\,O\end{matrix}\!\!>Ca\xrightarrow{\Delta}HCHO+CaCO_3$$



$$\begin{matrix}R\,COO\\RCO\,O\end{matrix}\!\!>Ca\xrightarrow{\Delta}\begin{matrix}R\\R\end{matrix}\!\!>C=O+CaCO_3$$

Calcium-alkanoate Ketone

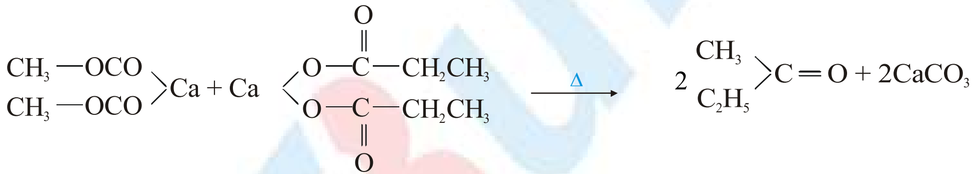
Calcium salts of acids other then formic acid on heating together gives ketone



$$\begin{matrix}R\,COO\\R\,COO\end{matrix}\!\!>Ca + Ca<\begin{matrix}O-\overset{\overset{O}{\|}}{C}-R'\\O-\underset{\underset{O}{\|}}{C}-R'\end{matrix}\xrightarrow{\Delta}2R-\overset{\overset{O}{\|}}{C}-R'+2CaCO_3$$

Ketone

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

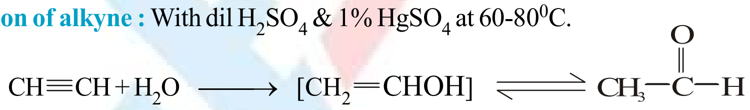


$$\begin{matrix}CH_3-OCO\\CH_3-OCO\end{matrix}\!\!>Ca + Ca<\begin{matrix}O-\overset{\overset{O}{\|}}{C}-CH_2CH_3\\O-\underset{\underset{O}{\|}}{C}-CH_2CH_3\end{matrix}\xrightarrow{\Delta}2\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>C=O+2CaCO_3$$

Calcium Acetate Calcium propionate Ethyl methyl ketone

From Alkyne :

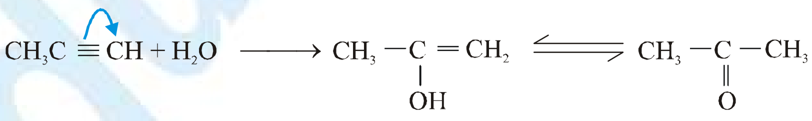
Hydration of alkyne : With dil H_2SO_4 & 1% $HgSO_4$ at 60-80^{0}C.



$$CH\equiv CH+H_2O\longrightarrow[CH_2=CHOH]\rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-H$$

(Tautomerisation)

Other alkynes give ketone :

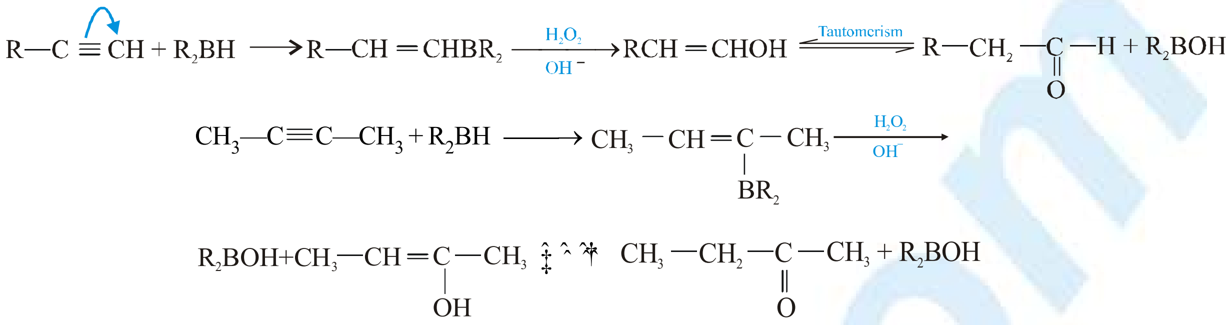


$$CH_3C\equiv CH+H_2O\longrightarrow CH_3-\underset{\underset{OH}{|}}{C}=CH_2\rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

(enol)

Hydroboration of alkynes : Reaction with B_2H_6, $2BH_3$ or R_2BH give dialkyl borane.

1 – alkyne gives ⟶ Aldehyde
other alkyne ⟶ Ketone



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

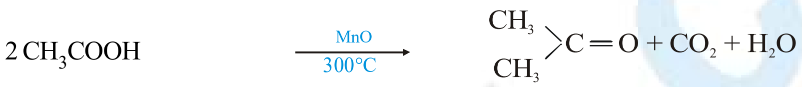
$$CH_3-C\equiv C-CH_3 + R_2BH \longrightarrow CH_3-CH=\underset{\underset{BR_2}{|}}{C}-CH_3 \xrightarrow[OH^-]{H_2O_2}$$

$$R_2BOH+CH_3-CH=\underset{\underset{OH}{|}}{C}-CH_3 \rightleftharpoons CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 + R_2BOH$$

By Thermal decomposition of carboxylic acids :

Vapour of carboxylic acids when passed over MnO/300^{0}C give carbonyl compounds

$$2\,HCOOH \xrightarrow[300°C]{MnO} HCHO + H_2O + CO_2$$



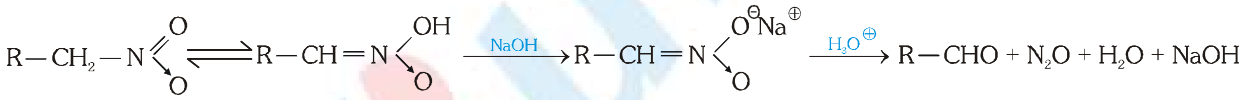
$$2\,CH_3COOH \xrightarrow[300°C]{MnO} \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle C=O + CO_2 + H_2O$$

$$RCOOH + HCOOH \xrightarrow[300°C]{MnO} RCHO + CO_2 + H_2O$$

$$RCOOH + R'COOH \xrightarrow[300°C]{MnO} RCOR' + CO_2 + H_2O$$

By Nef's reaction :

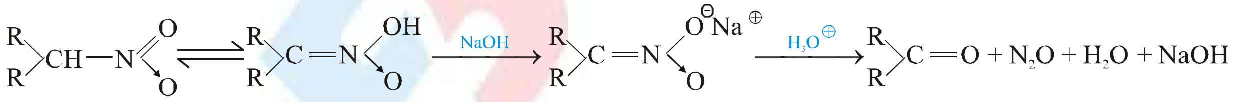
Nitro alkanes are used in this reaction. The α–H of nitro alkane shows acidic nature.



$$R-CH_2-N\left\langle\begin{matrix}O\\O\end{matrix}\right. \rightleftharpoons R-CH=N\left\langle\begin{matrix}OH\\O\end{matrix}\right. \xrightarrow{NaOH} R-CH=N\left\langle\begin{matrix}O^{\ominus}Na^{\oplus}\\O\end{matrix}\right. \xrightarrow{H_3O^{\oplus}} R-CHO + N_2O + H_2O + NaOH$$

(Nitro form) (Aci form) (Aldehyde)

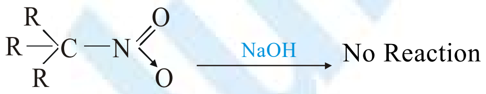
1° nitro alkane



$$\left.\begin{matrix}R\\R\end{matrix}\right\rangle CH-N\left\langle\begin{matrix}O\\O\end{matrix}\right. \rightleftharpoons \left.\begin{matrix}R\\R\end{matrix}\right\rangle C=N\left\langle\begin{matrix}OH\\O\end{matrix}\right. \xrightarrow{NaOH} \left.\begin{matrix}R\\R\end{matrix}\right\rangle C=N\left\langle\begin{matrix}O^{\ominus}Na^{\oplus}\\O\end{matrix}\right. \xrightarrow{H_3O^{\oplus}} \left.\begin{matrix}R\\R\end{matrix}\right\rangle C=O + N_2O + H_2O + NaOH$$

(Nitro form) (Aci form) (Ketone)

2° nitro alkane



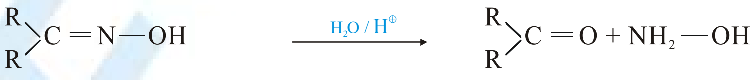
$$R-\overset{R}{\underset{R}{C}}-N\left\langle\begin{matrix}O\\O\end{matrix}\right. \xrightarrow{NaOH} \text{No Reaction}$$

(3° nitro alkane)

By hydrolysis of carbonyl derivatives :

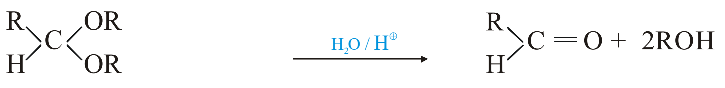
$$R-CH=N-OH \xrightarrow{H_2O/H^{\oplus}} R-CHO + NH_2-OH$$

(Aldoxime) (Aldehyde) (Hydroxyl amine)



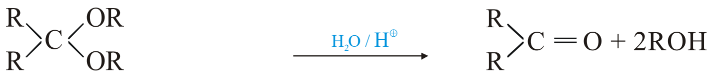
$$\left.\begin{matrix}R\\R\end{matrix}\right\rangle C=N-OH \xrightarrow{H_2O/H^{\oplus}} \left.\begin{matrix}R\\R\end{matrix}\right\rangle C=O + NH_2-OH$$

(Ketoxime) (Ketone)



$$\mathrm{R(H)C(OR)_2} \xrightarrow{H_2O / H^{\oplus}} \mathrm{R(H)C{=}O} + 2ROH$$

(Acetal) (Aldehyde) (Alcohol)



$$\mathrm{R_2C(OR)_2} \xrightarrow{H_2O / H^{\oplus}} \mathrm{R_2C{=}O} + 2ROH$$

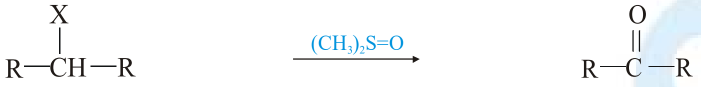
(Ketal) (Ketone) (Alcohol)

By oxidation of alkyl halides:

Oxidation takes place by $(CH_3)_2S{=}O$ dimethyl sulphoxide (DMSO).

$$R{-}CH_2{-}X + (CH_3)_2S{=}O \longrightarrow RCHO + (CH_3)_2S + HX$$

Alkyl halide (Aldehyde) (Dimethyl thio ether)

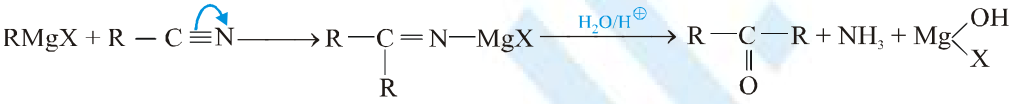


$$R{-}\overset{X}{\overset{|}{C}}H{-}R \xrightarrow{(CH_3)_2S=O} R{-}\overset{O}{\overset{\|}{C}}{-}R$$

2° halide Ketone

From Grignard reagents :

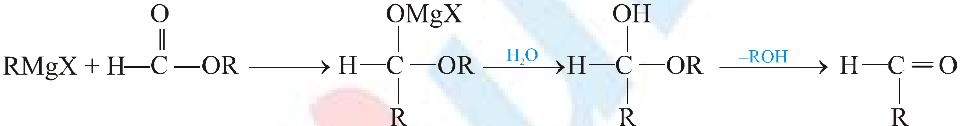
By Cyanides using RMgX :



$$RMgX + R-C\equiv N \longrightarrow R-\underset{R}{\underset{|}{C}}=N-MgX \xrightarrow{H_2O/H^{\oplus}} R-\underset{O}{\underset{\|}{C}}-R + NH_3 + Mg\langle^{OH}_{X}$$

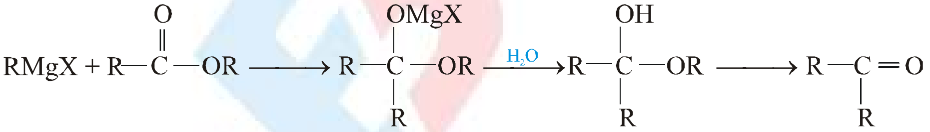
(Ketone)

By Esters using RMgX : HCHO can't be prepared by this method.



$$RMgX + H{-}\overset{O}{\overset{\|}{C}}{-}OR \longrightarrow H{-}\underset{R}{\underset{|}{\overset{OMgX}{\overset{|}{C}}}}{-}OR \xrightarrow{H_2O} H{-}\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}{-}OR \xrightarrow{-ROH} H{-}\underset{R}{\underset{|}{C}}{=}O$$

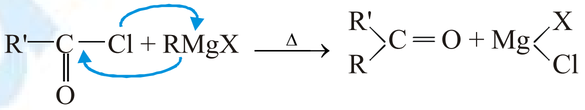
(Alkyl formate) (Hemiacetal) (Aldehyde)



$$RMgX + R{-}\overset{O}{\overset{\|}{C}}{-}OR \longrightarrow R{-}\underset{R}{\underset{|}{\overset{OMgX}{\overset{|}{C}}}}{-}OR \xrightarrow{H_2O} R{-}\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}{-}OR \longrightarrow R{-}\underset{R}{\underset{|}{C}}{=}O$$

(Alkyl Alkanoate) (Hemiacetal) (Ketone)

By acid chlorides using RMgX :

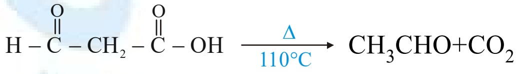


$$R'{-}\underset{O}{\underset{\|}{C}}{-}Cl + RMgX \xrightarrow{\Delta} \mathrm{R'(R)C{=}O} + Mg\langle^{X}_{Cl}$$

From β-keto acids :

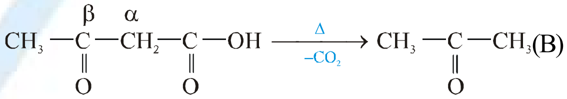
The decarboxylation reaction takes place via formation of six membered ring transition state.

(a)



$$H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[110°C]{\Delta} CH_3CHO+CO_2$$

(b)

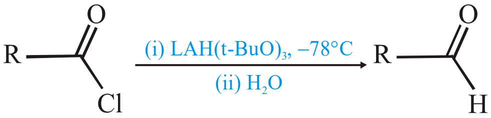


$$CH_3-\underset{O}{\underset{\|}{\overset{\beta}{C}}}-\overset{\alpha}{C}H_2-\underset{O}{\underset{\|}{C}}-OH \xrightarrow[-CO_2]{\Delta} CH_3-\underset{O}{\underset{\|}{C}}-CH_3 (B)$$

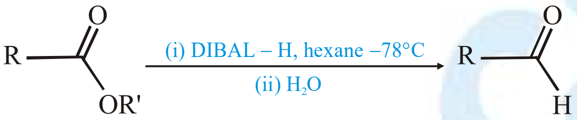
(B) FOR ALDEHYDES ONLY

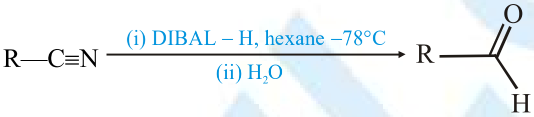
Reduction of acyl halides, esters and nitriles :

Acyl chlorides can be reduced to aldehydes by treating them with lithium-tri-tert-butoxyaluminium hydride, LiAlH[OC(CH_3)$_3$], at – 78°C.



Both esters and nitriles can be reduced to aldehydes by DIBAL-H. Reduction must be carried out at low temperatures. Hydrolysis of the intermediates gives the aldehyde.





Rosenmund's reduction :

Quinoline or sulphur act as a poisoned catalyst, controls the further reduction of aldehyde to alcohols.

$$RCOCl + H_2 \xrightarrow[\text{Quinoline or sulphur}]{\text{Pd/ BaSO}_4} RCHO + HCl$$

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

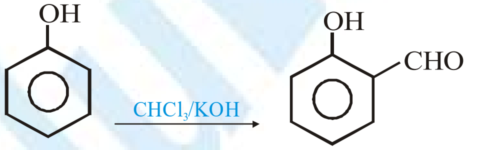
Formaldehyde can not be prepared by this method.

Ex. $C_2H_5COCl + H_2 \xrightarrow[\text{Quinoline or sulphur}]{\text{Pd/ BaSO}_4} C_2H_5CHO + HCl$

Propionyl Chloride Propanal

Reimer-Tiemann Reaction :

By this method phenolic aldehyde is prepared



Phenol Salicylic aldehyde

Stephen's reduction :

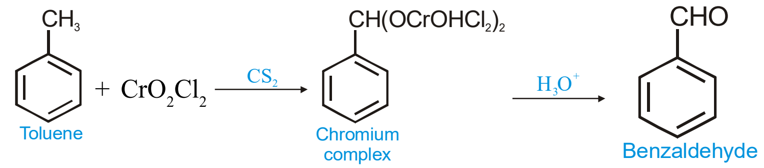
Alkyl cyanides are reduced by $SnCl_2$ and HCl.

$$R{-}C{\equiv}N \xrightarrow{SnCl_2/HCl} R{-}CH{=}NH \xrightarrow{H_3O^+} RCHO + NH_3$$

$$C_2H_5{-}C{\equiv}N \xrightarrow{SnCl_2/HCl} C_2H_5CH{=}NH \xrightarrow{H_3O^+} C_2H_5CHO + NH_3$$

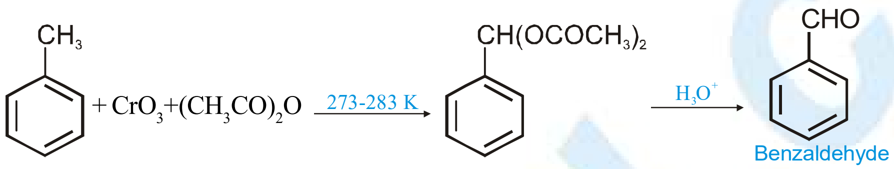
From hydrocarbons :

By oxidation of methyl benzene and its derivative using chromyl chloride (CrO_2Cl_2)



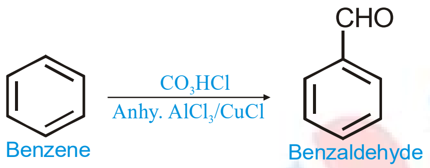
This reaction is called **Etard reaction.**

By oxidation of methyl benzene and its derivative using chromic oxide (CrO_3) in acetic anhydride:



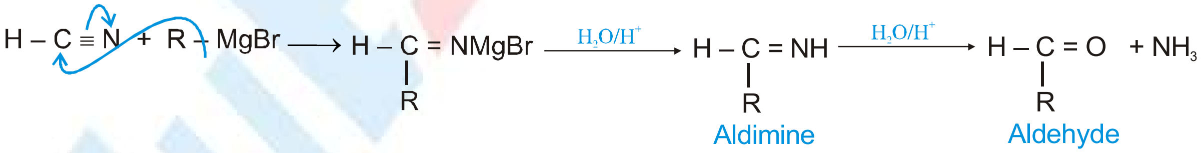
By Gattermann-Koch reaction :

$$\text{Benzene or its derivative} \xrightarrow[\text{Anhy. AlCl}_3\text{/CuCl}]{\text{CO,HCl}} \text{Benzaldehyde or substituted benzaldehyde}$$



By hydrogen cyanide :

Hydrogen cyanide on treating with Grignard reagent followed by double decomposition with water gives aldehyde via aldimine.

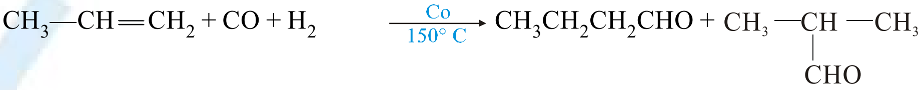


$$H-C\equiv N + R-MgBr \longrightarrow \underset{\displaystyle R}{\underset{|}{H-C}}=NMgBr \xrightarrow{H_2O/H^+} \underset{\text{Aldimine}}{\underset{\displaystyle R}{\underset{|}{H-C}}=NH} \xrightarrow{H_2O/H^+} \underset{\text{Aldehyde}}{\underset{\displaystyle R}{\underset{|}{H-C}}=O} + NH_3$$

Oxo reaction or hydroformylation :

In this reaction symmetrical alkene gives 1^0 aldehyde while unsymmetrical alkene gives isomeric aldehyde (Chain isomers).

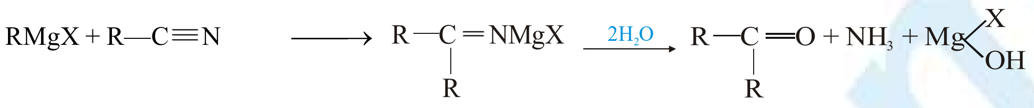
$$CH_2{=}CH_2 + \underbrace{CO + H_2}_{\text{Water gas}} \xrightarrow[150^\circ\ C]{Co} CH_3CH_2CHO$$



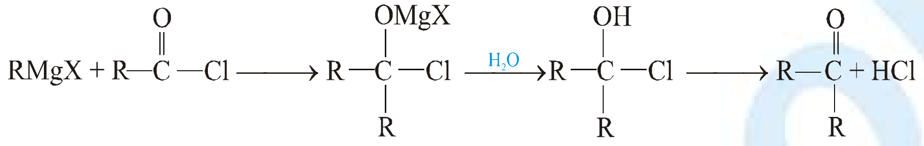
$$CH_3{-}CH{=}CH_2 + CO + H_2 \xrightarrow[150^\circ\ C]{Co} CH_3CH_2CH_2CHO + CH_3-\underset{\displaystyle CHO}{\underset{|}{CH}}-CH_3$$

For Ketones only :

From Grignard's reagent :

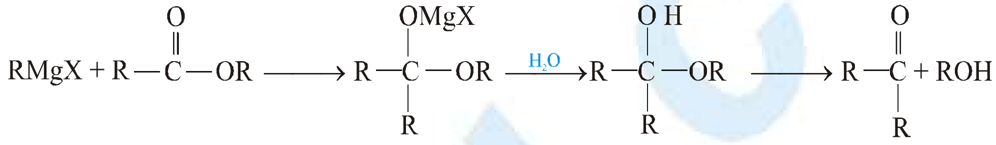


$$RMgX + R-C\equiv N \longrightarrow R-\underset{R}{\underset{|}{C}}=NMgX \xrightarrow{2H_2O} R-\underset{R}{\underset{|}{C}}=O + NH_3 + Mg\Big\langle{}^{X}_{OH}$$



$$RMgX + R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow R-\overset{OMgX}{\overset{|}{\underset{R}{\underset{|}{C}}}}-Cl \xrightarrow{H_2O} R-\overset{OH}{\overset{|}{\underset{R}{\underset{|}{C}}}}-Cl \longrightarrow R-\overset{O}{\overset{\|}{\underset{R}{\underset{|}{C}}}} + HCl$$

$$RMgX + R-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow RH + (RCONH)Mg(X)\ ;\ \text{Ketone does not forms.}$$



$$RMgX + R-\overset{O}{\overset{\|}{C}}-OR \longrightarrow R-\overset{OMgX}{\overset{|}{\underset{R}{\underset{|}{C}}}}-OR \xrightarrow{H_2O} R-\overset{OH}{\overset{|}{\underset{R}{\underset{|}{C}}}}-OR \longrightarrow R-\overset{O}{\overset{\|}{\underset{R}{\underset{|}{C}}}} + ROH$$

By acylation or benzoylation of aromatic hydrocarbon (Friedel-Crafts Reaction)

$$C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Dry} C_6H_5COCH_3 + HCL$$

Acetophenone

$$C_6H_6 + C_6H_5COCl \xrightarrow[AlCl_3]{Dry} C_6H_5COC_6H_5 + HCL$$

Benzophenone

$$C_6H_6 + COCl_2 \xrightarrow[AlCl_3]{Dry} C_6H_5COC_6H_5 + HCL$$

excess Benzophenone

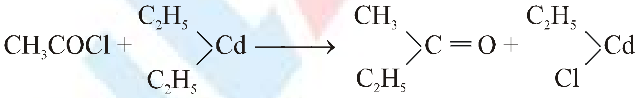
From dialkyl Cadmium :

RCdR' (dialkyl Cadmium) is a organometallic compound.

$$RCOCl + RCdR' \longrightarrow RCOR' + RCdCl$$

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

Example :

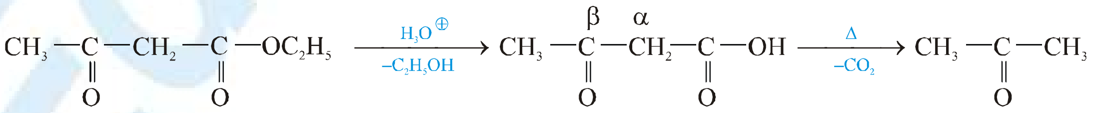


$$CH_3COCl + \begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\Big\rangle Cd \longrightarrow \begin{matrix}CH_3\\ C_2H_5\end{matrix}\Big\rangle C=O + \begin{matrix}C_2H_5\\ Cl\end{matrix}\Big\rangle Cd$$

From R_2CuLi :

$$R_2CuLi + R'COCl \longrightarrow R'COR + RCu + LiCl$$

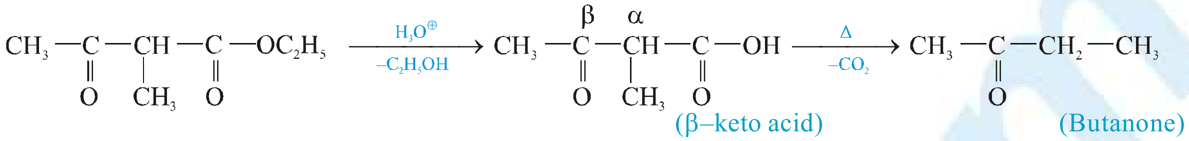
By hydrolysis of Aceto Acetic Ester (AAE) :



$$CH_3-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-OC_2H_5 \xrightarrow[-C_2H_5OH]{H_3O^{\oplus}} CH_3-\underset{O}{\underset{\|}{\overset{\beta}{C}}}-\overset{\alpha}{CH_2}-\underset{O}{\underset{\|}{C}}-OH \xrightarrow[-CO_2]{\Delta} CH_3-\underset{O}{\underset{\|}{C}}-CH_3$$

(β - keto acid) (Acetone)

Ex.



$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow[-C_2H_5OH]{H_3O^{\oplus}} CH_3-\overset{\beta}{\underset{\underset{O}{\|}}{C}}-\overset{\alpha}{\underset{\underset{CH_3}{|}}{CH}}-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[-CO_2]{\Delta} CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$$

(β–keto acid) (Butanone)

PHYSICAL PROPERTIES

State :

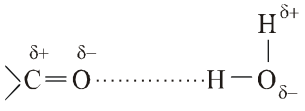
Only formaldehyde is gas, all other carbonyl compounds upto C_{11} are liquids and C_{12} & onwards solid.

Odour :

Lower aldehydes give unpleasant smell, higher aldehydes and all ketones have pleasant smell.

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

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

Boiling point : Boiling point ∝ Molecular weight

Boiling point order is - **Alcohol** > **Carbonyl compounds** > **Alkane**

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

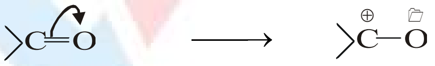
$$>\overset{\delta+}{C}=\overset{\delta-}{O}\cdots\cdots\cdots\cdots>\overset{\delta+}{C}=\overset{\delta-}{O}$$

Density : Density of carbonyl compounds is lower than water.

CHEMICAL PROPERTIES :

Reactions of both aldehydes and ketones :

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 $\ddot{N}u$. The negatively charged oxygen is attacked by electron deficient (electrophile) E^+.

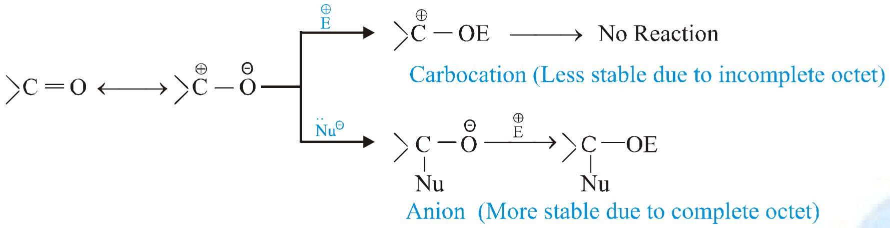
$>C=O$ bond in carbonyl group is stronger than C=C bond in alkanes.

$C-O$	Bond energy is	84.0 K Cals	$C-C$	Bond energy is	83.1 K Cals
$C=O$	Bond energy is	178 K Cals	$C=C$	Bond energy is	146 K Cals

Reactivity of carbonyl group ∝ **Magnitude of +ve charge** ∝ **– I group** ∝ $\dfrac{1}{\textbf{+I group}}$

Ex. Why carbonyl compound gives nucleophilic addition reaction (NAR) ?

Sol.

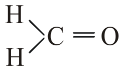


Carbocation (Less stable due to incomplete octet)

Anion (More stable due to complete octet)

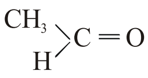
Ex. Arrange the following for reactivity in decreasing order

(I) **(i)**



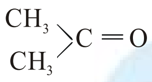
$\begin{matrix}H\\H\end{matrix}\!>C=O$

(ii)



$\begin{matrix}CH_3\\H\end{matrix}\!>C=O$

(iii)

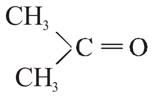


$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C=O$

(II) **(i)** $ClCH_2CHO$ **(ii)** NO_2CH_2CHO **(iii)** CH_3CHO **(iv)** CH_3CH_2CHO

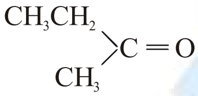
(III) **(i)** CH_3CHO **(ii)** $ClCH_2CHO$ **(iii)** $HCCl_2CHO$ **(iv)** CCl_3CHO

(IV) **(i)**



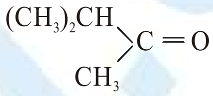
$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C=O$

(ii)



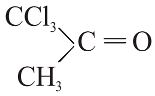
$\begin{matrix}CH_3CH_2\\CH_3\end{matrix}\!>C=O$

(iii)



$\begin{matrix}(CH_3)_2CH\\CH_3\end{matrix}\!>C=O$

(iv)



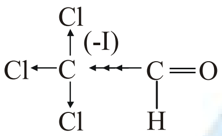
$\begin{matrix}CCl_3\\CH_3\end{matrix}\!>C=O$

Sol. **(A)** I > II > III **(B)** II > I > III > IV **(C)** IV > III > II > I **(D)** IV > I > II > III

[Hint : CH_3— is +I group, decreases the intensity of +ve charge on C-atom of $>C=O$ group.

Cl – is –I group increases the intensity of +ve charge on C-atom of $>C=O$ group.]

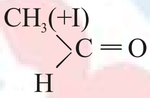
Ex. In



$Cl\leftarrow\underset{\underset{Cl}{\downarrow}}{\overset{\overset{Cl}{\uparrow}\,(-I)}{C}}\leftarrow\!\!\leftarrow\!\!\leftarrow\underset{\underset{H}{|}}{C}=O$

Chloral

and



$\begin{matrix}CH_3(+I)\\H\end{matrix}\!>C=O$

, which one is more reactive ?

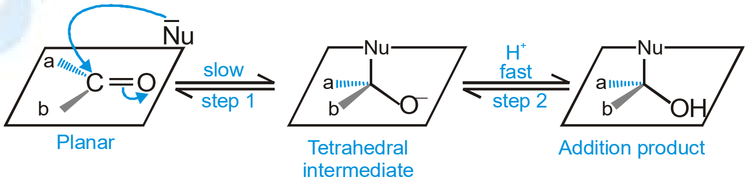
Sol. I is more reactive than II.

CHEMICAL REACTIONS

Carbonyl compounds in general under goes nucleophilic addition reaction :

Addition of a nucleophile and a proton across the (C = O) double bond. The reactivity of the carbonyl group arises from the electronegativity of the oxygen atom and the resulting polarization of the carbon-oxygen double bond. The electrophilic carbonyl carbon atom is sp^2 hybridized and flat, leaving it relatively unhindered and open to attack from either face of the double bond.

Mechanism

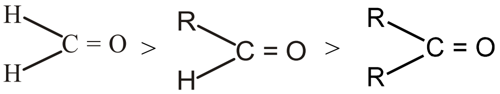


Nucleophile (Nu^-) attacks the carbonyl group perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon.

In the process, hybridisation of carbon changes from sp^2 to sp^3.

A tetrahedral alkoxide is formed as intermediate.

Reactivity : Aldehydes are more reactive than ketones in nucleophilic addition reactions.



There are two factors which influence the reactivity of ketone and aldehyde.

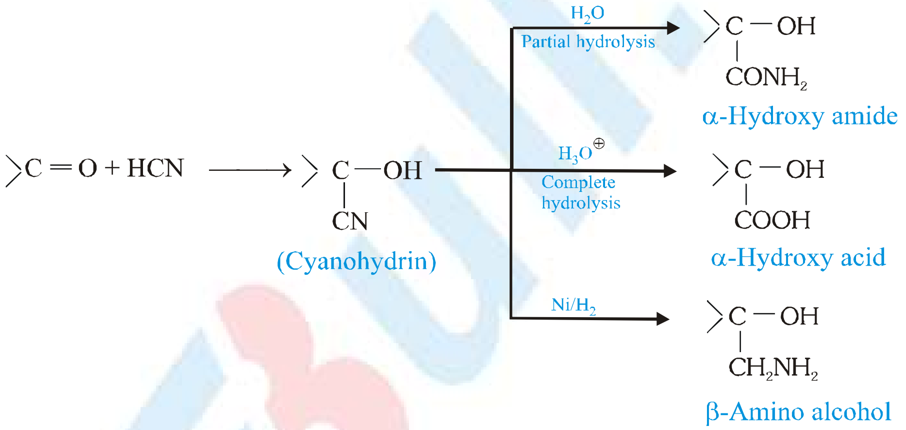
(i) Inductive effect **(ii)** steric factor

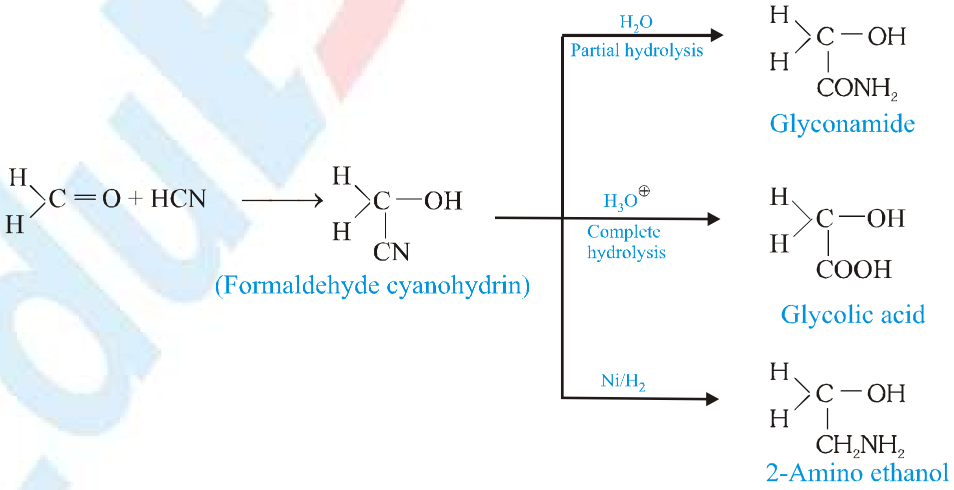
(i) + I effect of alkyl group decrease the amount of charge on C^+ ($C^+ - O^-$). in ketones.

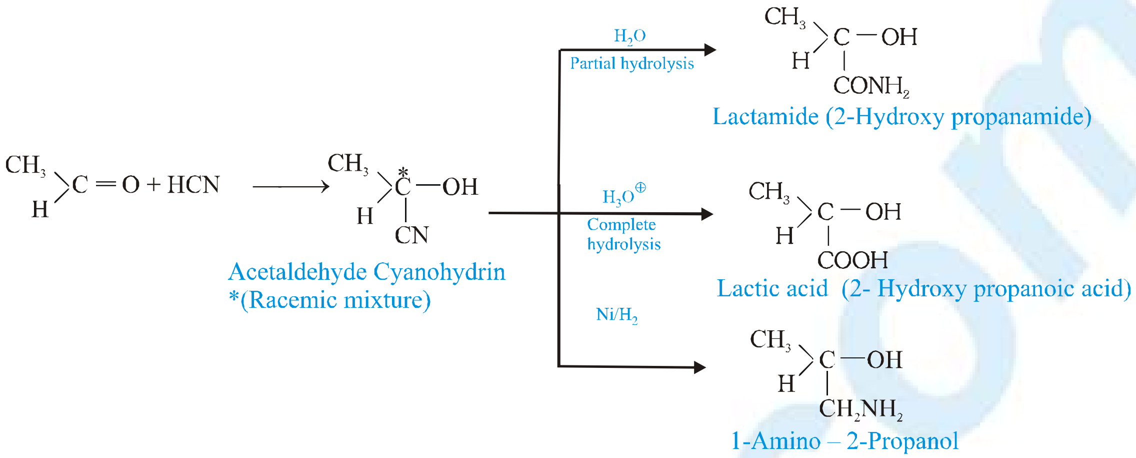
(ii) Steric effect also causes the less reactivity of carbonyl group.

Nucleophilic addition reactions :

(1) Addition of HCN :







Acetaldehyde Cyanohydrin
*(Racemic mixture)

Lactamide (2-Hydroxy propanamide)

Lactic acid (2- Hydroxy propanoic acid)

1-Amino – 2-Propanol

(2) Addition of $NaHSO_3$:

This reaction is utilized for the separation of carbonyl compounds from non - carbonyl compounds.

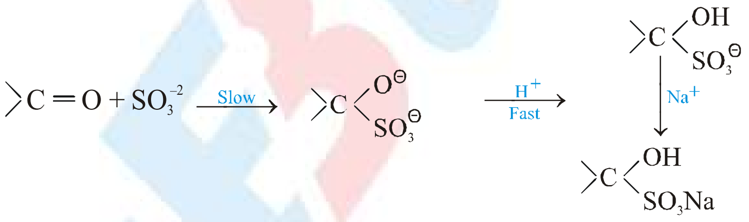
Sodium bi sulphite

Bisulphite compound
(Crystalline)

Mechanism :

$NaHSO_3 \rightleftharpoons Na^+ + HS\bar{O}_3$

$HS\bar{O}_3 \rightleftharpoons H^+ + SO_3^{-2}$



(3) Reaction with ammonia derivatives :

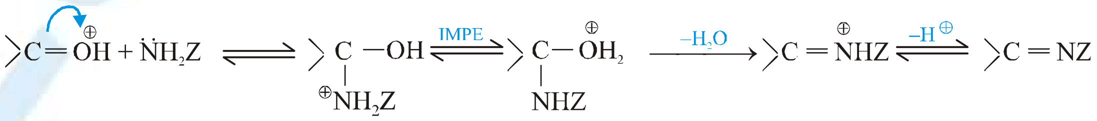
These are condensation or addition elimination reaction. These proceeds well in weakly acidic medium.

$NH_3 \longrightarrow NH_2Z$ (Ammonia derivative)

$>C=O + H_2N-Z \xrightarrow[+Z]{-H} >C=N-Z + H_2O$

Addition - elimination (Condensation)

Mechanism :



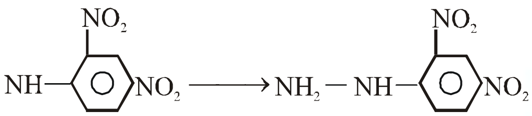
Ammonia derivatives (NH_2Z) :

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)

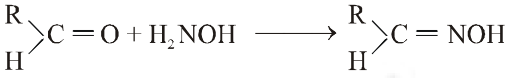
Z =



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

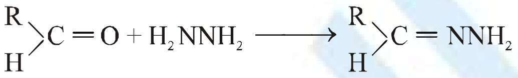
Z = $NHCONH_2$ $\longrightarrow$ $NH_2NHCONH_2$

Semi Carbazide.



$$\begin{matrix}R\\H\end{matrix}\!\!>C=O+H_2NOH\longrightarrow\begin{matrix}R\\H\end{matrix}\!\!>C=NOH$$

(Aldoxime)

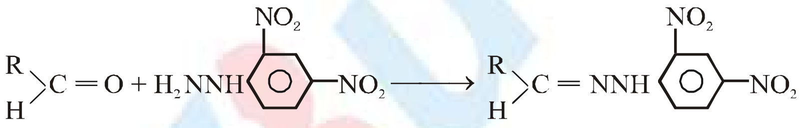


$$\begin{matrix}R\\H\end{matrix}\!\!>C=O+H_2NNH_2\longrightarrow\begin{matrix}R\\H\end{matrix}\!\!>C=NNH_2$$

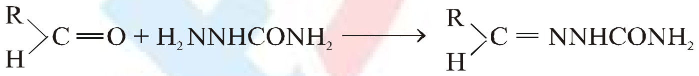
(Hydrazone)

$$\begin{matrix}R\\H\end{matrix}\!\!>C=O+H_2NNHC_6H_5\longrightarrow\begin{matrix}R\\H\end{matrix}\!\!>C=NNHC_6H_5$$

(Phenyl hydrazone)



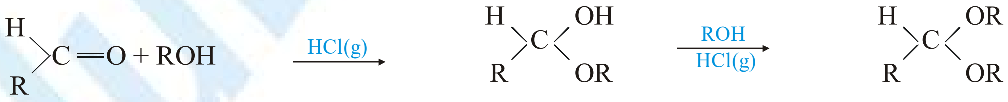
2,4-DNP (Brady's reagent) (2, 4 - dinitro phenyl hydrazone)



$$\begin{matrix}R\\H\end{matrix}\!\!>C=O+H_2NNHCONH_2\longrightarrow\begin{matrix}R\\H\end{matrix}\!\!>C=NNHCONH_2$$

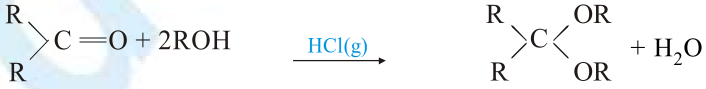
(Semi Carbazone)

(4) With alcohol and thioalcohol :



$$\begin{matrix}H\\R\end{matrix}\!\!>C=O+ROH\xrightarrow{HCl(g)}\begin{matrix}H\\R\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\OR\end{matrix}\xrightarrow[HCl(g)]{ROH}\begin{matrix}H\\R\end{matrix}\!\!>C<\!\!\begin{matrix}OR\\OR\end{matrix}$$

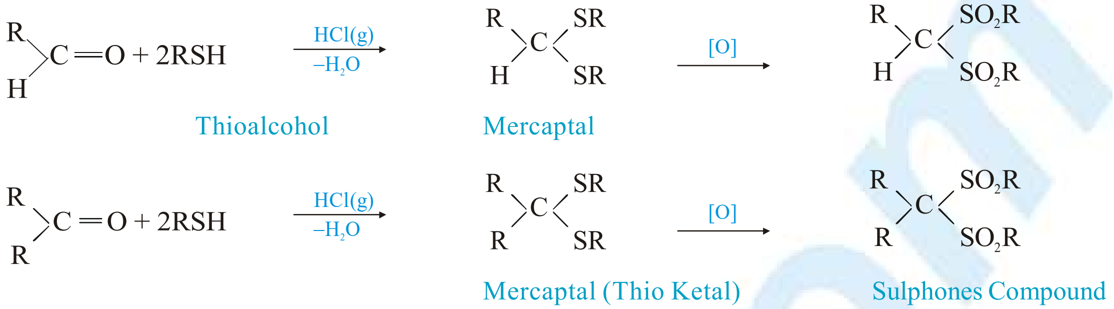
Hemi-acetal Acetal



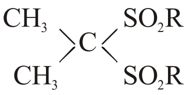
$$\begin{matrix}R\\R\end{matrix}\!\!>C=O+2ROH\xrightarrow{HCl(g)}\begin{matrix}R\\R\end{matrix}\!\!>C<\!\!\begin{matrix}OR\\OR\end{matrix}+H_2O$$

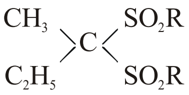
Ketal

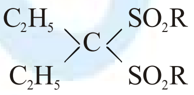
Tri ethoxy methane [$HC(OC_2H_5)_3$] remove the water formed during the reaction and so the reaction proceeds in forward direction.



All sulphones compounds are hypnotic compounds.


Sulphonal

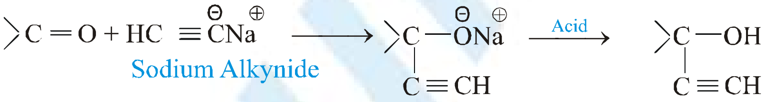

Trional


Tetronal

(5) Reaction with glycol (group protection) :

(neutral) Cyclic acetal / ketal

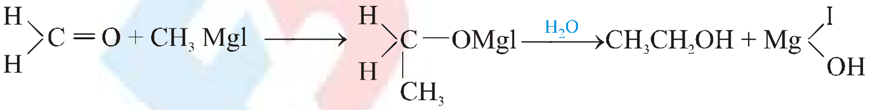
(6) Reaction with sodium alkynide :



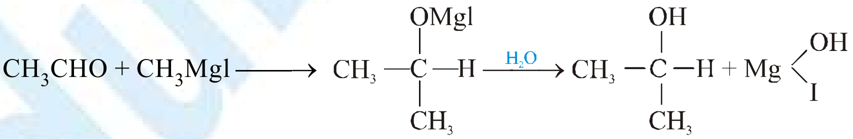
Sodium Alkynide

Acetylinic alcohol

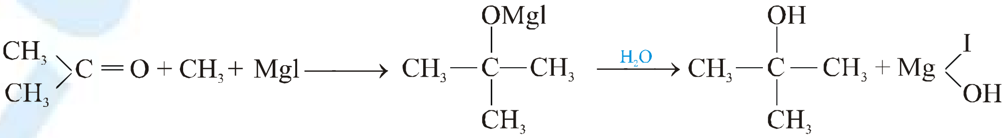
(7) Reaction with Grignard reagent :



Ethanol (1° alcohol)

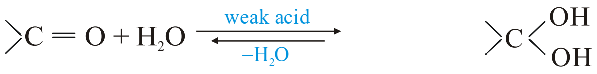


2–Propanol (2° alcohol)



2–Methyl–2–propanol (3° alcohol)

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



(neutral) unstable hydrate

Ex. Which compound form more stable hydrate with H_2O?

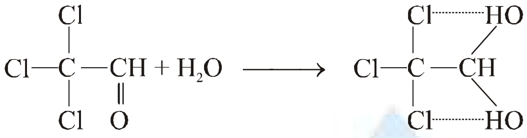
(A) HCHO **(B)** CH_3CHO **(C)** CH_3COCH_3 **(D)** $CH_3COC_2H_5$

[Hint : HCHO since it is more reactive towards this reaction.]

Ans. (A)

Ex. Which carbonyl compound not gives reversible reaction with water ?

Sol. Chloral hydrate.

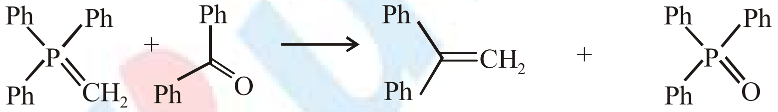


(Chloral) (Chloral hydrate)

Stable by intra molecular hydrogen bonding.

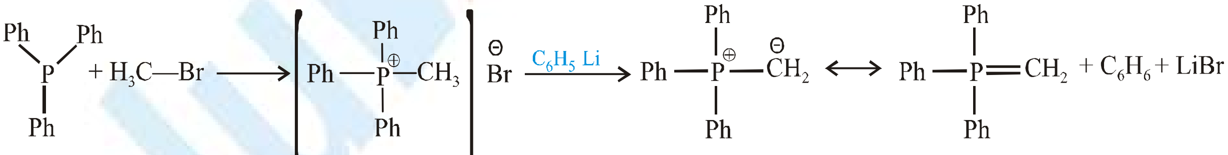
Wittig Reaction :

Wittig reaction affords an important and useful method for the synthesis of alkenes by the treatment of aldehydes or ketones with alkylidenetriphenylphosphorane ($Ph_3P = CR_2$) or simply known as phosphorane



(1-phenylvinyl) benzene triphenylphosphine oxide

The wittig reagent, alkylidenetriphenylphosphorane (ylide), is prepared by treating trialkyl or triarylphosphine usually the latter with an alkyl halide in either solution. The resulting phosphonium salt is treated with strong base (such as C_6H_5Li, BuLi, $NaNH_2$, NaH, C_2H_5ONa, etc.)



(I) (II)

Cannizaro's reaction :

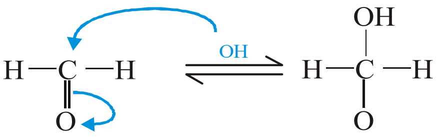
Those aldehydes which do not contain α -H atom give this reaction, with conc. NaOH or KOH; Products are Salt of carboxylic acid + alcohol.

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

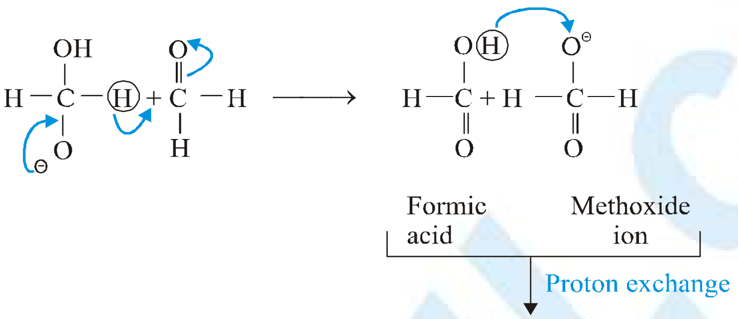
$$HCHO + HCHO \xrightarrow[\text{NaOH}]{\text{conc.}} HCOONa + CH_3OH$$

Mechanism : (Cannizaro reaction)

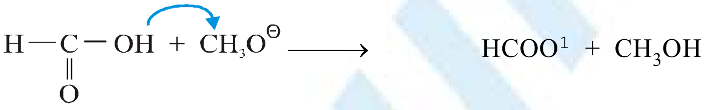
(a) Rapid reversible addition of $\bar{O}H$ to one molecule of HCHO.



(b) Transfer of hydride ion $\overset{1}{H}$ to second molecule of HCHO



(c) Proton exchange



$$H-\underset{\underset{O}{\|}}{C}-OH + CH_3O^{\ominus} \longrightarrow HCOO^{1} + CH_3OH$$

$$HCOO^{1} + Na^{\oplus} \longrightarrow HCOONa$$

When molecules are same ⟶ **Simple cannizaro reaction**
Two different molecules ⟶ **Mixed cannizaro reaction**

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

$$HCHO + C_6H_5CHO \xrightarrow{NaOH} HCOONa + C_6H_5CH_2OH$$

HCOONa	$C_6H_5CH_2OH$
Oxidized	Reduced
(Sodium formate)	(Benzyl alcohol)

Ex : $CH_3CHO + HCHO \xrightarrow{Ca(OH)_2} C(CH_2OH)_4 + (HCOO)_2Ca$, explain mechanism ?

2, 2-Dihydroxy methyl –1, 3–propane diol.(Penta erythritol)

Tishchenko reaction :

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

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

Ester

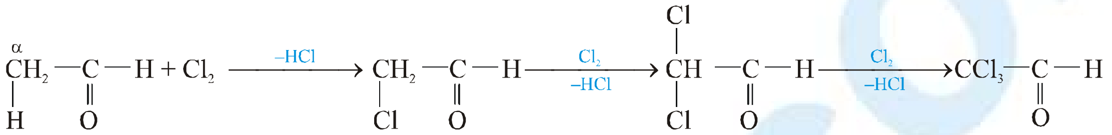
Ex. $$CH_3CHO + CH_3CHO \xrightarrow{(C_2H_5O)_3Al} \underbrace{CH_3COOH + CH_3CH_2OH}_{\text{Esterification}\downarrow}$$

$$CH_3—COOCH_2CH_3$$ (Ethyl acetate)

Reaction With Halogen :

Replacement of α-H atoms :

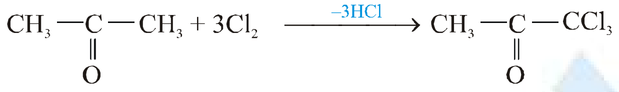
This reaction is not shown by formaldehyde (HCHO), since α -H atoms are absent, as enolisation does not takes place in HCHO.



$$\underset{\underset{H}{|}}{\overset{\alpha}{CH_2}}-\underset{\underset{O}{\|}}{C}-H + Cl_2 \xrightarrow{-HCl} \underset{\underset{Cl}{|}}{CH_2}-\underset{\underset{O}{\|}}{C}-H \xrightarrow[-HCl]{Cl_2} \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{CH}}-\underset{\underset{O}{\|}}{C}-H \xrightarrow[-HCl]{Cl_2} CCl_3-\underset{\underset{O}{\|}}{C}-H$$

Chloral

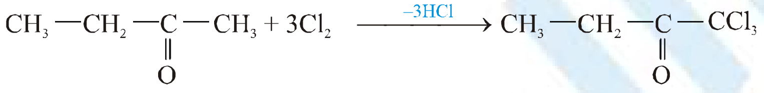
Ex.



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + 3Cl_2 \xrightarrow{-3HCl} CH_3-\underset{\underset{O}{\|}}{C}-CCl_3$$

Tri chloro acetone

Ex.

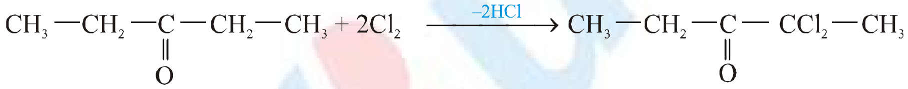


$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 + 3Cl_2 \xrightarrow{-3HCl} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CCl_3$$

Ex.

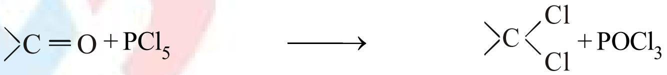
$$CCl_3-\underset{\underset{O}{\|}}{C}-R + NaOH \longrightarrow CHCl_3 + NaO-\underset{\underset{O}{\|}}{C}-R$$

Ex.



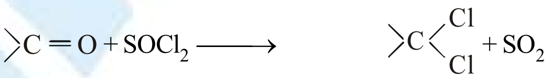
$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_3 + 2Cl_2 \xrightarrow{-2HCl} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CCl_2-CH_3$$

Replacement of O-atom of $\rangle C=O$ group : It takes place by PCl_5 or $SOCl_2$.



$$\rangle C=O + PCl_5 \longrightarrow \rangle C\langle^{Cl}_{Cl} + POCl_3$$

Phosphorus penta chloride



$$\rangle C=O + SOCl_2 \longrightarrow \rangle C\langle^{Cl}_{Cl} + SO_2$$

Thionyl chloride

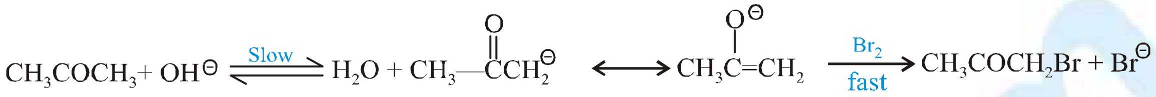
Haloform reactions :

Chlorine or bromine replaces one or more α-hydrogen atoms in aldehydes and ketones, e.g., acetone may be brominated in glacial acetic acid to give mono bromoacetone :

$$CH_3COCH_3 + Br_2 \longrightarrow CH_3COCH_2Br + HBr\ (43–44\%)$$

The halogenation of carbonyl compounds is catalysed by acids and bases. Let us consider the case of acetone. In alkaline solution, tribromo acetone and bromoform are isolated. Thus, the introduction of a second and a third bromine atom is more rapid than the first. In aqueous sodium hydroxide, the rate has been shown to be independent of the bromine concentration, but first order with respect to both acetone and base i.e.,

$$Rate = k\,[acetone]\,[OH^1]$$



$$CH_3COCH_3 + OH^{\ominus} \xrightleftharpoons{Slow} H_2O + CH_3-\overset{O}{\overset{\|}{C}}CH_2^{\ominus} \longleftrightarrow CH_3\overset{O^{\ominus}}{\overset{|}{C}}=CH_2 \xrightarrow[fast]{Br_2} CH_3COCH_2Br + Br^{\ominus}$$

Aldol Condensation :

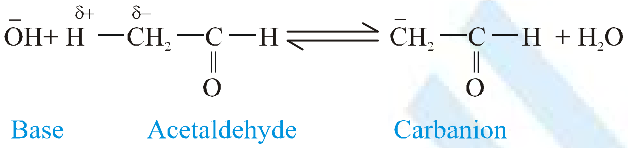
Two molecules of an aldehyde or a ketone undergo condensation in the presence of a base to yield a β-hydroxyaldehyde or a β-hydroxyketone. This reaction is called the aldol condensation. In general Carbonyl compounds which contain α-H atoms undergo aldol condensation with dil. NaOH. Aldol contains both alcoholic and carbonyl group.

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

- Formation of Carbanion
- Combination of carbanion with other aldehyde molecule.

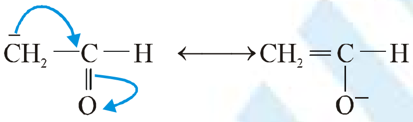
Formation of Carbanion :

α-H atom of $>C=O$ group are quite acidic which can be removed easily as proton, by a base.



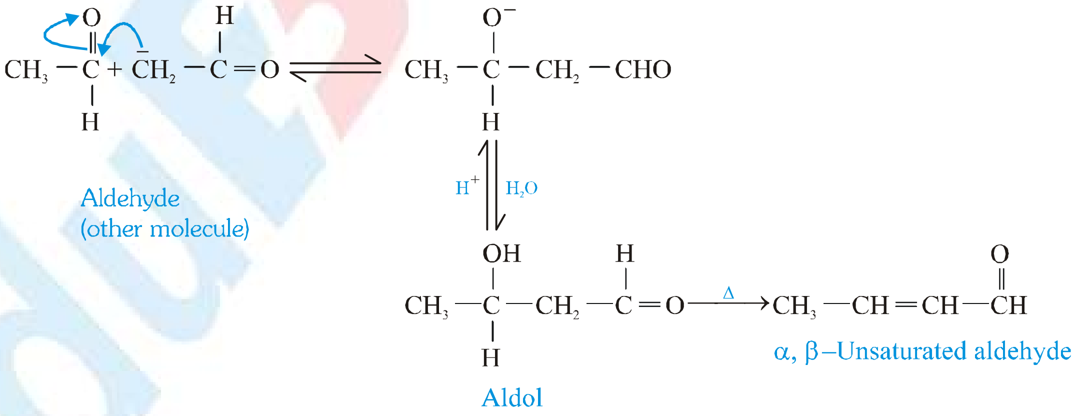
$$\overset{-}{O}H + \overset{\delta+}{H}-\overset{\delta-}{CH_2}-\underset{\underset{O}{\|}}{C}-H \rightleftharpoons \overset{-}{C}H_2-\underset{\underset{O}{\|}}{C}-H + H_2O$$

Carbanion thus formed is stable because of resonance -



$$\overset{-}{C}H_2-\underset{\underset{O}{\|}}{C}-H \longleftrightarrow CH_2=\underset{\underset{O^-}{|}}{C}-H$$

Combination of carbanion with other aldehyde molecule :

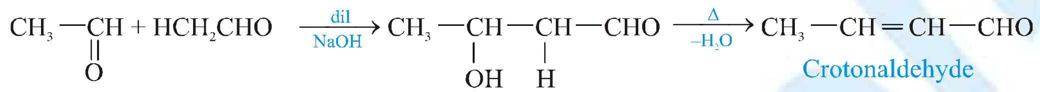


Aldol condensation is possible between :

1. Two aldehyde (Same or different)
2. Two ketones (Same or different)
3. One aldehyde and one ketone

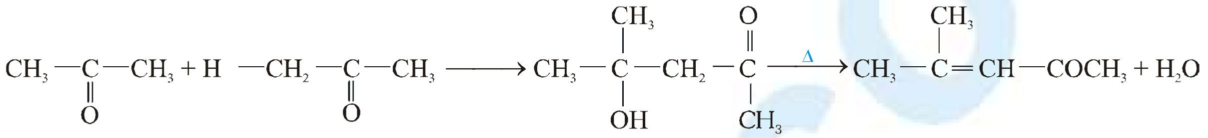
Identical carbonyl compounds ⟶ **Simple or self aldol condensation**
Different carbonyl compounds ⟶ **Mixed or crossed aldol condensation**

Simple or Self condensation :



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

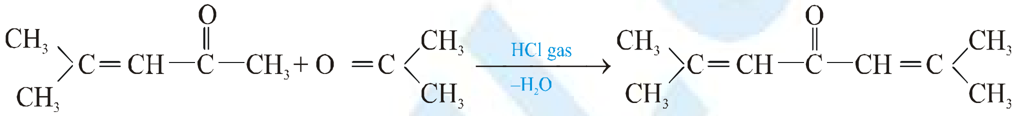
Crotonaldehyde



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + H-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{C}} \xrightarrow{\Delta} CH_3-\overset{\overset{CH_3}{|}}{C}=CH-COCH_3 + H_2O$$

diacetone alcohol

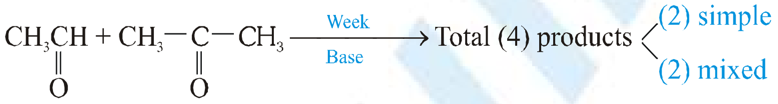
Mesityl oxide or
4–Methyl– 3–pentene– 2–one



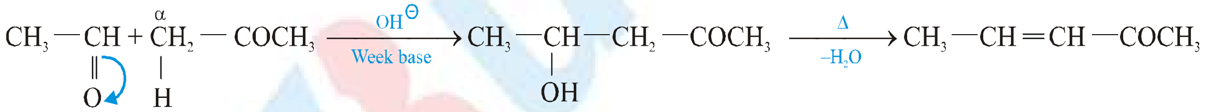
$${}^{CH_3}_{CH_3}\!\!>C=CH-\overset{\overset{O}{\|}}{C}-CH_3 + O=C<^{CH_3}_{CH_3} \xrightarrow[-H_2O]{HCl\ gas} {}^{CH_3}_{CH_3}\!\!>C=CH-\overset{\overset{O}{\|}}{C}-CH=C<^{CH_3}_{CH_3}$$

Phorone

Mixed or Crossed aldol Condensation :

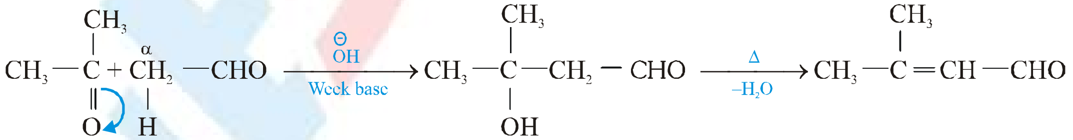


$$CH_3\underset{\underset{O}{\|}}{C}H + CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[Base]{Week} \text{Total (4) products} \begin{cases}\text{(2) simple}\\ \text{(2) mixed}\end{cases}$$



$$CH_3-\underset{\underset{O}{\|}}{C}H + \underset{\underset{H}{|}}{\overset{\alpha}{C}H_2}-COCH_3 \xrightarrow[\text{Week base}]{OH^{\ominus}} CH_3-\underset{\underset{OH}{|}}{C}H-CH_2-COCH_3 \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-COCH_3$$

(Aldol)

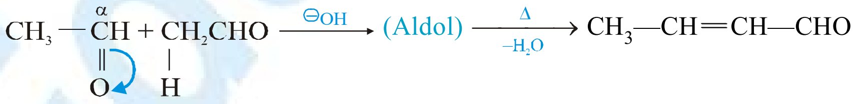


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\|}}{C}} + \underset{\underset{H}{|}}{\overset{\alpha}{C}H_2}-CHO \xrightarrow[\text{Week base}]{\overset{\ominus}{OH}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CHO$$

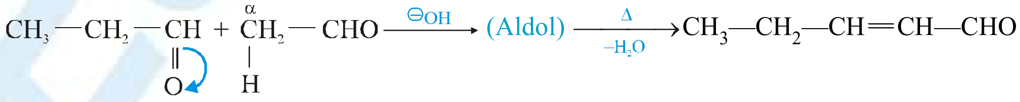
(Aldol)

Ex : $CH_3CHO + CH_3CH_2CHO \xrightarrow[(WB)]{\ominus OH}$ Total 4 products. Write structure of products ?

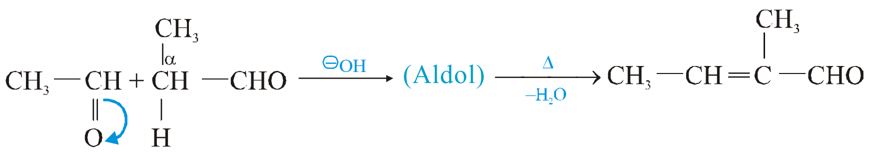
Sol.



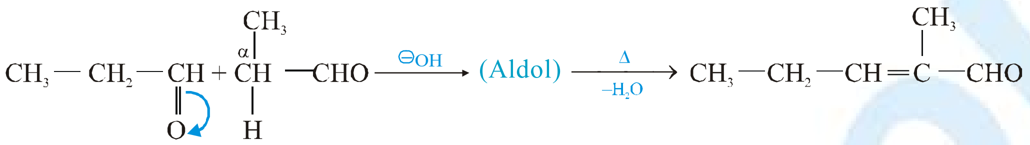
$$CH_3-\underset{\underset{O}{\|}}{\overset{\alpha}{C}H} + \underset{\underset{H}{|}}{C}H_2CHO \xrightarrow{\ominus OH} \text{(Aldol)} \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$



$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}H + \underset{\underset{H}{|}}{\overset{\alpha}{C}H_2}-CHO \xrightarrow{\ominus OH} \text{(Aldol)} \xrightarrow[-H_2O]{\Delta} CH_3-CH_2-CH=CH-CHO$$

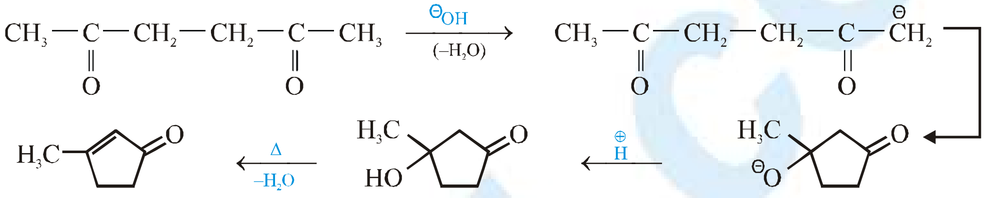


$$CH_3-\underset{\underset{O}{\|}}{C}H + \overset{\overset{CH_3}{|\alpha}}{\underset{\underset{H}{|}}{CH}}-CHO \xrightarrow{\ominus OH} (\text{Aldol}) \xrightarrow[-H_2O]{\Delta} CH_3-CH=\overset{\overset{CH_3}{|}}{C}-CHO$$



$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}H + \overset{\overset{CH_3}{\alpha|}}{\underset{\underset{H}{|}}{CH}}-CHO \xrightarrow{\ominus OH} (\text{Aldol}) \xrightarrow[-H_2O]{\Delta} CH_3-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CHO$$

Intramolecular aldol condensation :



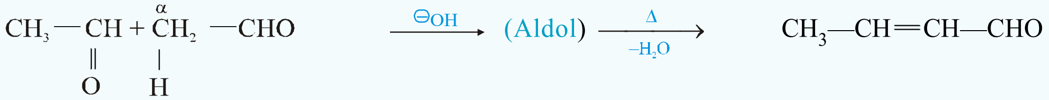
(α,β – Unsaturated Ketone) (Aldol)

Here 5 membered ring is more stable than 3 membered ring so above product is formed as a major product.

EDUBULL KEY POINTS

If in crossed aldol condensation reaction , only one carbonyl compound have α–H than total two product formed.

$$CH_3CHO + C_6H_5CHO \xrightarrow[(WB)]{\ominus OH} \text{Total 2 product.}$$



$$CH_3-\underset{\underset{O}{\|}}{C}H + \overset{\alpha}{\underset{\underset{H}{|}}{CH_2}}-CHO \xrightarrow{\ominus OH} (\text{Aldol}) \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

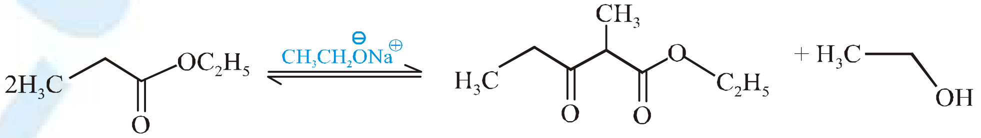
(Crotonaldehyde)

$$C_6H_5-\underset{\underset{O}{\|}}{C}H + \overset{\alpha}{\underset{\underset{H}{\|}}{CH_2}}-CHO \xrightarrow{\ominus OH} (\text{Aldol}) \xrightarrow[-H_2O]{\Delta} C_6H_5-CH=CH-CHO$$

(Cinnamaldehyde)

Claisen Condensation :

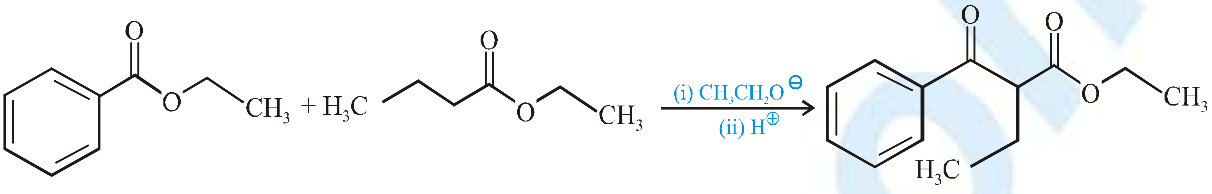
When two molecules of ester undergo a condensation reaction, the reaction is called Claisen condensation. The product of the claisen condensation is a β-keto ester.



β-keto ester

After nucleophilic attack, the aldol addition and the Claisen condensation differ. In the claisen condensation, the negatively charged oxygen reforms the carbon oxygen π-bond and eliminates the OR group.

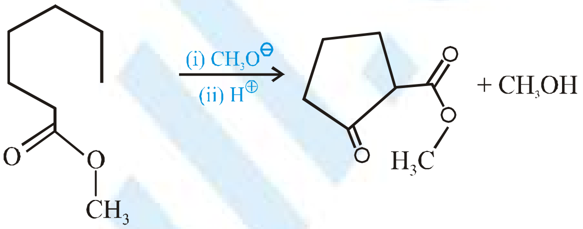
Mixed Claisen Condensation :

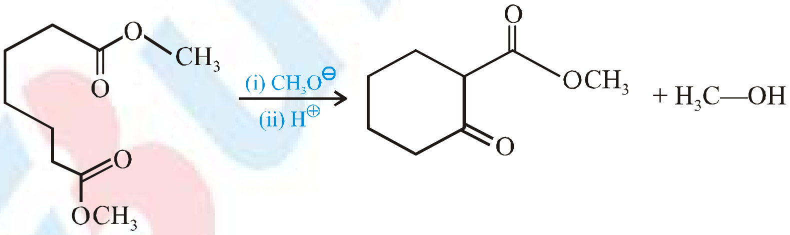


b-keto ester

Intramolecular Claisen Condensation :

Dieckmann condensation : The addition of base to a 1,6-diester causes the diester to undergo intramolecular claisen condensation, thereby forming a five membered ring β-keto ester. An intramolecular claisen condensation is called a Dieckmann condensation.



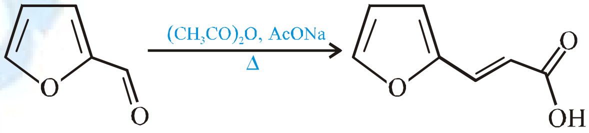


Perkin Reaction :

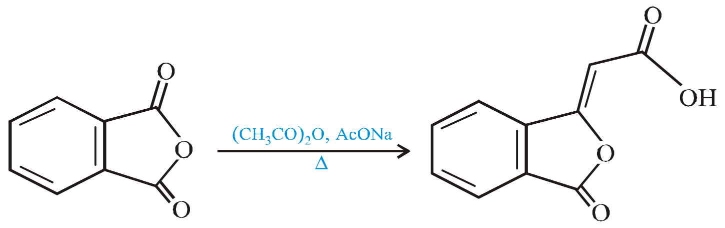
In perkin reaction, condensation has been effected between aromatic aldehydes and aliphatic acid anhydride in the presence of sodium or potassium salt of the acid corresponding to the anhydride, to yield α, β-unsaturated aromatic acids.

The acid anhydride should have at least two α-H.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow[170-180°C]{AcONa} C_6H_5—CH{=}CH—COOH$$



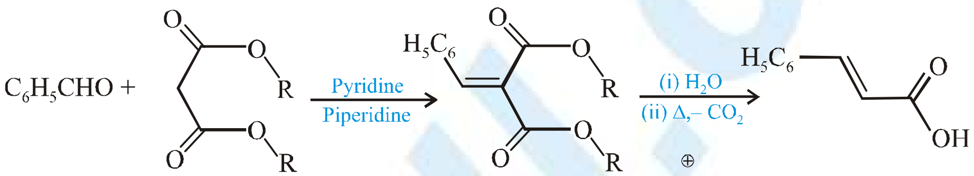
3-(α-furyl) acrylic acid



phthalic anhydride phthalyl acetic acid

Knoevenagel Reaction :

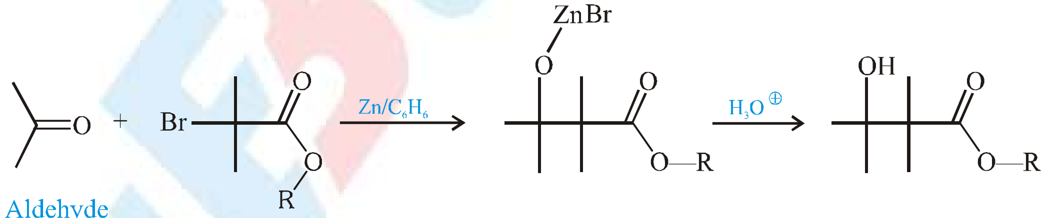
Condensation of aldehydes and ketones with compounds having active methylene group in the presence of basic catalyst to form a, b-unsaturated compounds is called Knoevenagel Reaction. The basic catalyst may be ammonia or its derivative. Thus 1°, 2°, 3° amines i.e., aniline, di-or tri - alkyl amines, pyridine or piperidine are used.



Malonic Ester Cinnamic acid

Reformatsky Reaction :

A similar reaction like the addition of organometallic compounds on carbonyl compounds that involves the addition of an organozinc reagent to the carbonyl group of an aldehyde or ketone. This reaction, called Reformatsky reaction, extends the carbon skeleton of an aldehyde or ketone and yields b-hydroxy esters. It involves treating an aldehyde or ketone with an α-bromo ester in the presence of zinc metal; the solvent most often used is benzene. The initial product is a zinc alkoxide, which must be hydrolysed to yield the β-hydroxy ester.



Aldehyde or ketone a-bromoester β-hydroxy ester

Schmidt Reaction :

This is the reaction between a carbonyl compound and hydrazoic acid in the presence of a strong acid concentrated sulphuric acid. Aldehydes give a mixture of cyanide and formyl derivatives of primary amines, whereas ketones give amides :

$$\mathrm{RCHO} + \mathrm{HN_3} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{RCN} + \mathrm{RNHCHO} + \mathrm{N_2}$$

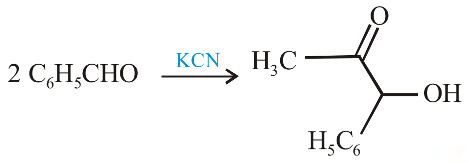
$$\mathrm{RCOR} + \mathrm{HN_3} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{RCONHR} + \mathrm{N_2}$$

Reaction with primary amine : $\rangle \mathrm{C=O} + \mathrm{H_2NR} \longrightarrow \rangle \mathrm{C=NR} + \mathrm{H_2O}$

Schiff's Base

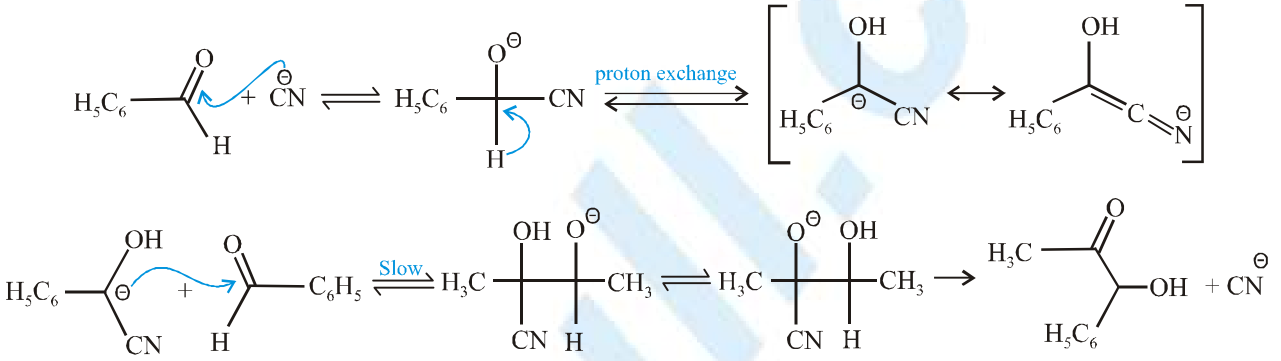
Benzoin condensation :

The benzoin condensation is essentially a dimerisation of two aromatic aldehydes under the catalytic influence of cyanide ions to give benzoin (I).



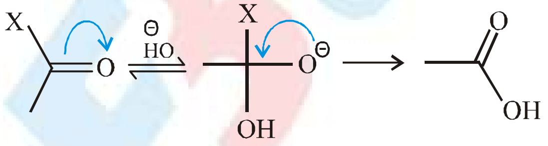
(I)

The hydrogen atom attached to the carbonyl group of aldehyde is not active enough to be removed easily but the addition of the cyanide ion to the carbonyl carbon places this hydrogen in the alpha position of the nitrile thus rendering it relatively acidic. The carbanion, thus generated, attacks the carbonyl carbon of the second aldehyde molecule in a rate-determining step forming an unstable cyanohydrin of benzoin which immediately breaks down into benzoin and hydrogen cyanide.



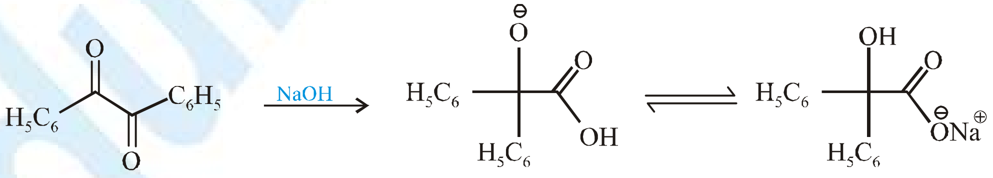
Benzilic acid rearrangement :

The addition of a strong base to a carbonyl group results in the formation of an anion. The reversal of the anionic charge may cause expulsion of the attached group X, e.g.



However, in a 1, 2-diketone the group X may migrate to the adjacent electron-deficient carbonyl carbon forming α-hydroxy acid.

Thus, benzil on treatment with a strong base forms benzilic acid (salt), hence the name benzilic acid rearrangement.



benzil

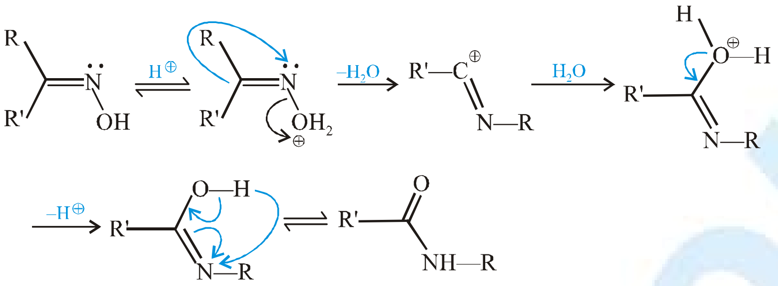
sodium salt of benzilic acid

The Beckmann rearrangement :

The acid catalysed transformation of a ketoxime to an N-substituted amide is known as the Beckmann rearrangement.

$$\rangle C=O + H_2N-OH \xrightarrow{-H_2O} \rangle C=N-OH$$

Oxime



The rearrangement is catalysed by a variety of acidic reagents such as H_3PO_2, H_2SO_4, $SOCl_2$, PCl_5, etc.

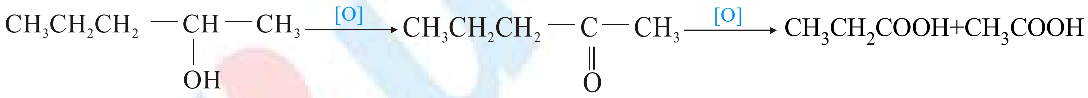
Oxidation Reactions :

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 C-atom. While, 2^0 alcohol on oxidation gives ketone which on further oxidation gives acid with less C-atom.

$$R—CH_2OH \xrightarrow{[O]} R—CH{=}O \xrightarrow{[O]} R—COOH$$

(1° alcohol)



$$CH_3CH_2CH_2—\underset{\underset{OH}{|}}{CH}—CH_3 \xrightarrow{[O]} CH_3CH_2CH_2—\underset{\underset{O}{\|}}{C}—CH_3 \xrightarrow{[O]} CH_3CH_2COOH+CH_3COOH$$

(2° alcohol)

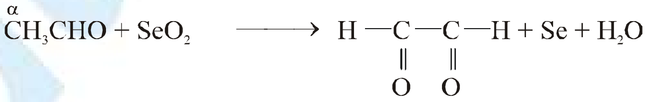
(i) 3° alcohol is not oxidised within 2 or 3 minutes.

(ii) 1° and 2° alcohol converts orange colour of $K_2Cr_2O_7$ to green in 2-3 minutes.

SeO_2 (Selenium Oxide) :

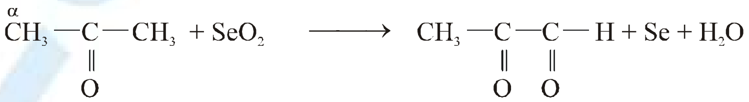
Ketones or aldehydes on oxidation with SeO_2 gives dicarbonyl compounds. This reaction is possible only in compounds containing α–carbon.

HCHO doesn't show this reaction.



$$\overset{\alpha}{C}H_3CHO + SeO_2 \longrightarrow H—\underset{\underset{O}{\|}}{C}—\underset{\underset{O}{\|}}{C}—H + Se + H_2O$$

Glyoxal

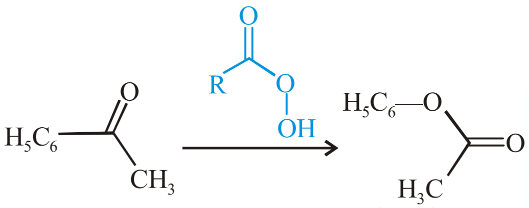


$$\overset{\alpha}{C}H_3—\underset{\underset{O}{\|}}{C}—CH_3 + SeO_2 \longrightarrow CH_3—\underset{\underset{O}{\|}}{C}—\underset{\underset{O}{\|}}{C}—H + Se + H_2O$$

Methyl glyoxal (Pyruvaldehyde)

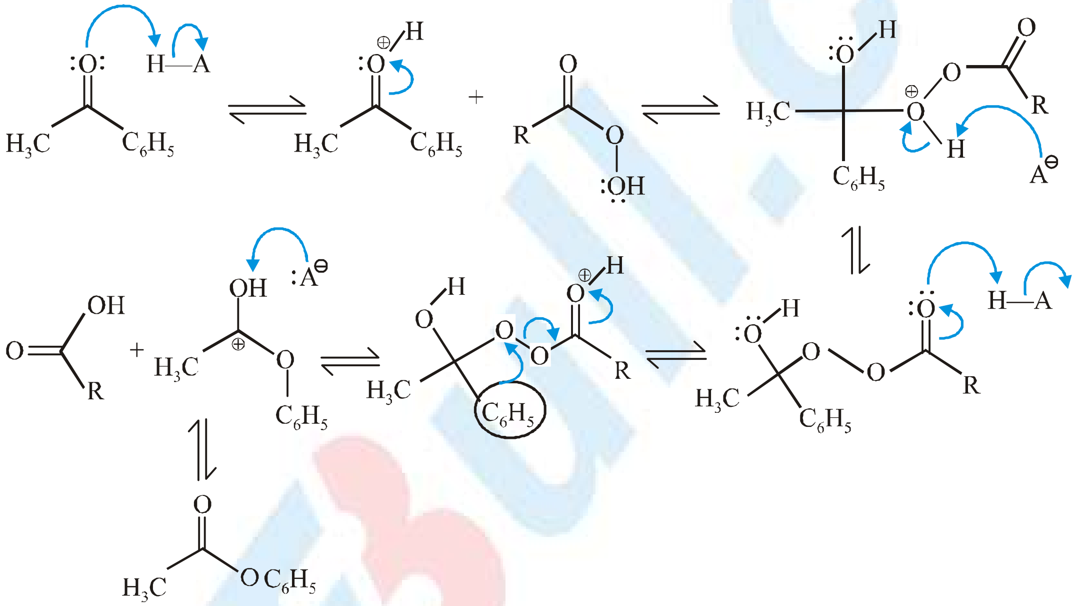
Baeyer's Villiger oxidation :

Both aldehyde and ketones are oxidized by peroxy acids. This reaction, called the Baeyer-villiger oxidation, is especially useful with Ketones, because it converts them to carboxylic esters. For example, treating acetophenone with a peroxy acid converts it to the ester phenyl acetate.



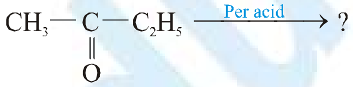
phenyl acetate

Mechanism :



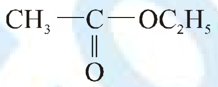
The product of this reaction show that a phenyl group has a greater tendency to migrate then a methyl group. Had this not been the case, the product would have been $C_6H_5COOCH_3$ and not $CH_3COOC_6H_5$. This tendency of a group to migrate is called is migratory aptitude. Studies of the Baeyer-villiger oxidation and other reaction have shown that the migratory aptitude of groups H > phenyl > 3° alkyl > 2° alkyl 1° alkyl > methyl. In all cases, this order is for groups migrating with their electron pairs, that is, as anions.

Ex.



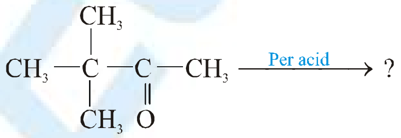
$CH_3-\underset{\underset{O}{\|}}{C}-C_2H_5 \xrightarrow{\text{Per acid}} ?$

Sol.



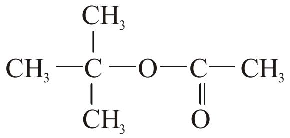
$CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5$

Ex.



$CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{\text{Per acid}} ?$

Sol.

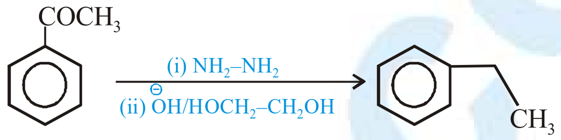


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-\underset{O}{\overset{}{C}}-CH_3$$

Reduction :

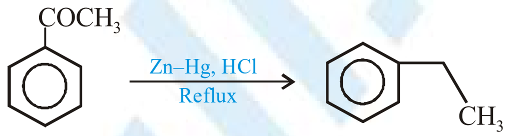
The wolf kishner reduction :

When a ketone or an aldehyde is heated in a basic solution of hydrazine, the carbonyl group is converted to a methylene group this process is called Deoxygenation because an oxygen is removed from the reactant. The reaction is known as the Wolf-kishner Reduction.



Clemmensen Reduction :

The reduction of carbonyl groups of aldehydes and ketones to methylene groups with amalgamated zinc and concentrated hydrochloric acid is known as Clemmensen reduction.



The nature of product depends upon the reducing agent used. It can be summarized as.

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

Reducing agents are

- Red P/HI at 150°C
- Zn-Hg/HCl [Clemensen's reduction]
- $NH_2—NH_2/C_2H_5OH,OH^1$ [Wolff Kishner's reduction]

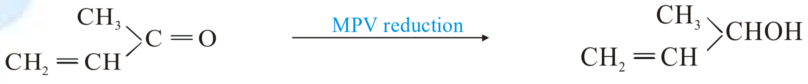
(ii) $>C=O \longrightarrow >CHOH$

Reducing agents are

- $LiAlH_4$ (Nicetron brown)
- Na/C_2H_5OH (Bouveault blank)
- NaH/Benzene (Darzen reaction)
- $[(CH_3)_2CHO]_3Al$ (Aluminium isopropoxide)
- $(CH_3)_2$ CHOH (Isopropyl alcohol)

Reduction with aluminium isopropoxide is excess of isopropanol is called MPV **(Meerwein Ponndorf Verley)** reduction. Other reducible groups are not attacked like $—NO_2$, $—CH{=}CH_2$, $—C{\equiv}C—$.

Example :



$$\begin{matrix}CH_3\\CH_2=CH\end{matrix}\!\!>C=O \xrightarrow{\text{MPV reduction}} \begin{matrix}CH_3\\CH_2=CH\end{matrix}\!\!>CHOH$$

Reactions given by only aldehydes :

Polymerisation : It is a reversible process.

Formaldehyde :

(a) $nHCHO \xrightleftharpoons[\Delta]{\text{Evaporation}} (CH_2O)_n, H_2O$

Formalin
(40% HCHO)

Paraformaldehyde
n = 6–50
Hydrated white crystal

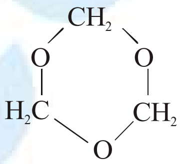
Paraformaldehyde is a linear polymer which show reducing character with Tollen's reagent, Fehling solution etc.

(b) $nHCHO \xrightleftharpoons[H_2SO_4\,\Delta]{\text{Conc.}} (CH_2O)_n, H_2O$

Poly oxy methylene
n > 100

(c) $3HCHO \xrightarrow[\text{at room temp.}]{\text{Allowed to stand}} (CH_2O)_3$

Meta formaldehyde (Trioxane)
Cyclic polymer (Trioxy methylene)
Cyclic polymer doesn't show reducing character with Tollen's reagent etc.

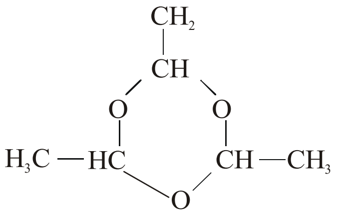


(d) $6HCHO \xrightarrow[\text{or } Ba(OH)_2]{Ca(OH)_2} C_6H_{12}O_6$

Formose sugar
A linear polymer (α -acrose)

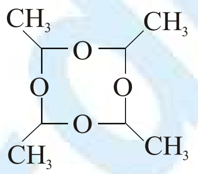
Acetaldehyde :

(a) $3CH_3CHO \xrightarrow[\text{Room temp.}]{\text{Conc. } H_2SO_4} (CH_3CHO)_3$



Para acetaldehyde
Paraldehyde (cyclic polymer)
Pleasent smelling liquid
Hypnotic compound

(b) $4CH_3CHO \xrightarrow[0°C]{\text{Conc. } HSO_4} (CH_3CHO)_4$



Meta aldehyde
White crystalline solid.
Cyclic polymer
Used as solid fuel or killing snails

Reaction with ammonia :

Except formaldehyde, all other aldehydes give addition reactions (HCHO give addition elimination i.e. condensation reaction)

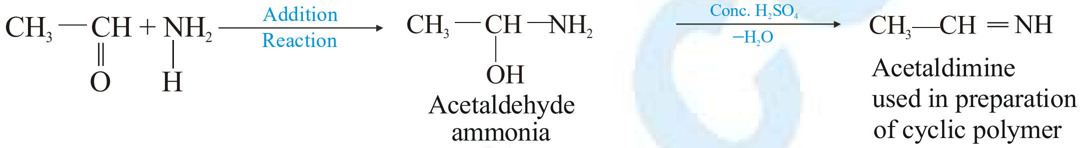
$$6CH_2O + 4NH_3 \xrightarrow[\text{Reaction}]{\text{Condensation}} (CH_2)_6N_4 + 6H_2O$$

Urotropine (Hexamine)

White crystalline solid

Used in preparation of explosive

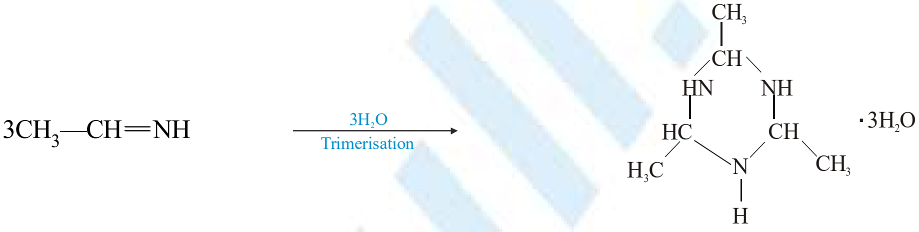
Used in treatment of urine infection diseases



$$CH_3-\underset{\underset{O}{\|}}{C}H + \underset{\underset{H}{|}}{N}H_2 \xrightarrow[\text{Reaction}]{\text{Addition}} CH_3-\underset{\underset{OH}{|}}{C}H-NH_2 \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} CH_3-CH=NH$$

Acetaldehyde ammonia

Acetaldimine used in preparation of cyclic polymer



$$3CH_3-CH=NH \xrightarrow[\text{Trimerisation}]{3H_2O}$$

Trimethyl hexahydro Triazine trihydrate

Reducing character :

Aldehydes are easily oxidised so they are strong reducing agents.

Tollen's reagent :

It oxidises aldehydes. Tollen's reagent is ammoniacal silver nitrate solution

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

$$RCHO+[Ag(NH_3)_2]OH \longrightarrow RCOOH + Ag + H_2O$$

Silver mirror

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

$$RCHO + Ag_2O \longrightarrow RCOOH + Ag\downarrow \text{ (Silver mirror)}$$

Fehling's solution :

It is a mixture of $CuSO_4$, NaOH and sodium potassium tartrate.

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

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

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

$$RCHO + Cu^{+2} + OH^{-} \longrightarrow RCOOH + Cu_2O$$

(Cuprous oxide–Red ppt.)

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

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

Benedict's solution :

It is a mixture of $CuSO_4$ + sodium citrate + Na_2CO_3. It provides Cu^{+2}. It is reduced by aldehyde to give red ppt of cuprous oxide.

$$\mathrm{RCHO + Cu^{2+} + OH^- \longrightarrow RCOOH \quad + \quad Cu_2O}$$

(Cuprous oxide–Red ppt.)

Mercuric chloride :

$HgCl_2$ is a corrosive sublimate. It is reduced by aldehyde to give white ppt of mercurous chloride (Calonal) which further react with aldehyde to give black ppt of Hg.

$$\mathrm{RCHO + HgCl_2 + H_2O \longrightarrow RCOOH + \underset{(calomal)}{Hg_2Cl_2} + HCl}$$

$$\mathrm{RCHO + Hg_2Cl_2 + H_2O \longrightarrow RCOOH + \underset{(black\ ppt)}{Hg} + HCl}$$

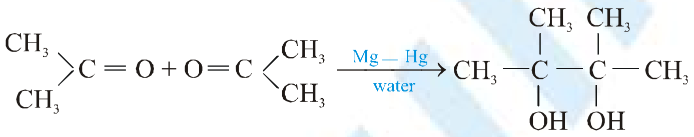
Reaction with schiff's reagent :

Schiff's reagent is dil solution of p-roseniline hydrochloride or magenta dye.

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

Reaction of only ketones :

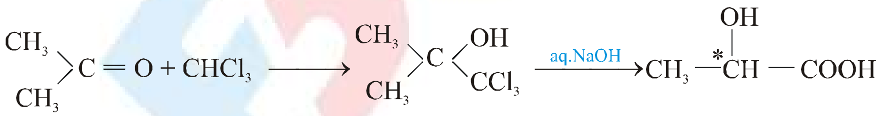
Reduction : Acetone is reduced by magnesium amalgam and water to give pinacol.



$$\mathrm{\underset{CH_3}{\overset{CH_3}{>}}C=O+O=C\underset{CH_3}{\overset{CH_3}{<}} \xrightarrow[water]{Mg-Hg} CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3}$$

Pinacol

Reaction with chloroform :

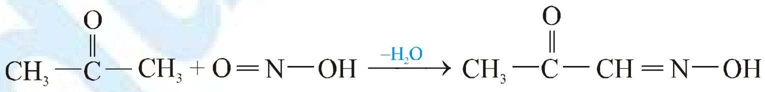


$$\mathrm{\underset{CH_3}{\overset{CH_3}{>}}C=O+CHCl_3 \longrightarrow \underset{CH_3}{\overset{CH_3}{>}}C\underset{CCl_3}{\overset{OH}{<}} \xrightarrow{aq.NaOH} CH_3-\overset{OH}{\overset{|}{\overset{*}{C}H}}-COOH}$$

(Chloretone)

(Lactic acid)
2-Hydroxy propanoic acid

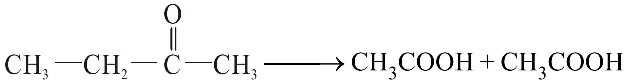
Reaction with HNO_2 :



$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-CH_3+O=N-OH \xrightarrow{-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH=N-OH}$$

Oximino acetone

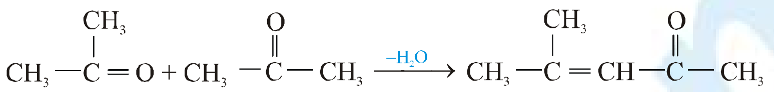
Oxidation reaction : According to popoff's rule $>C=O$ group stays with smaller alkyl group.



$$\mathrm{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3COOH+CH_3COOH}$$

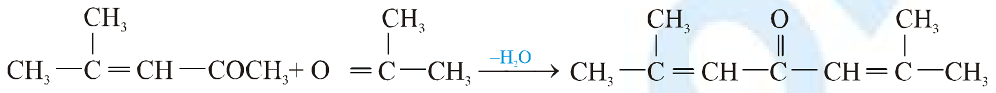
Condensation reaction :

(a) In presence of dry HCl - aldol condensation takes place



$$CH_3-\overset{CH_3}{\overset{|}{C}}=O+CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{-H_2O} CH_3-\overset{CH_3}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3$$

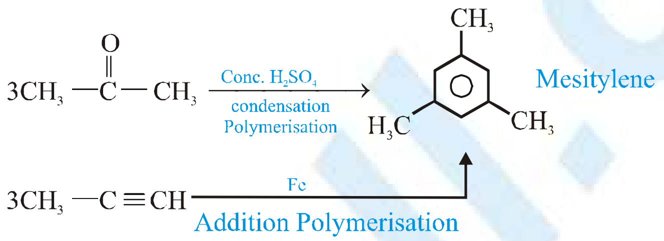
Mesityl oxide



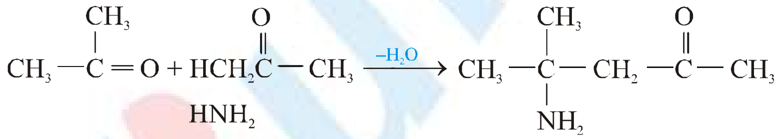
$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-COCH_3+O=\overset{CH_3}{\overset{|}{C}}-CH_3 \xrightarrow{-H_2O} CH_3-\overset{CH_3}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH=\overset{CH_3}{\overset{|}{C}}-CH_3$$

(Phorone) or 2,6–Dimethyl–2,5–hepta diene–4–one

(b) In presence of conc.H_2SO_4



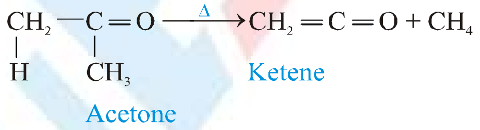
Reaction with ammonia :



$$CH_3-\overset{CH_3}{\overset{|}{C}}=O+\underset{HNH_2}{HCH_2}\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{-H_2O} CH_3-\underset{NH_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

Diacetone amine

Pyrolysis :



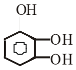
$$\underset{H}{\underset{|}{CH_2}}-\underset{CH_3}{\underset{|}{C}}=O \xrightarrow{\Delta} CH_2=C=O+CH_4$$

Acetone

Ketene

$$\left\{\begin{matrix} HCHO \xrightarrow[\text{Pyrolysis}]{\Delta} CO+H_2 \\ CH_3CHO \xrightarrow{\Delta} CH_4+CO \end{matrix}\right\}$$

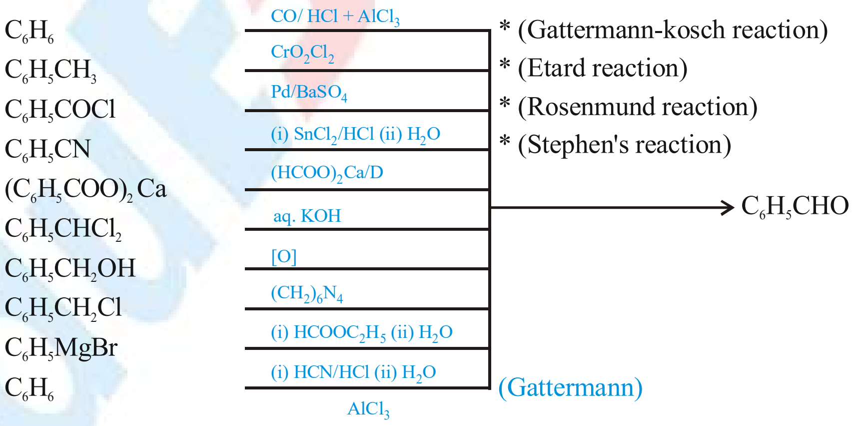
TEST FOR HCHO, CH_3CHO, CH_3COCH_3

S.No.	Test	HCHO	CH_3CHO	CH_3COCH_3
1	Legel's test :Na $[Fe(NO)(CN)_3]$ sodium nitroprusite (alk.) Only methyl >C−O	–	Red	Red
2	Compound gives this test Iodoform test (I_2 + NaOH)	– –	– yellow ppt	– yellow ppt
3	Pyragallol 	white ppt.	–	–
4	Orthonitro benzaldehyde	–	–	Blue
5	Tollen's reagent - Fehling's reagent - Mercuric chloride - Schiff's reagent -	Silver mirror Red ppt Black ppt Pink colour	Silver mirror Red ppt Black ppt Pink colour	– – – –
6	DNP	Orange colour	Orange colour	Orange colour

BENZALDEHYDE (C_6H_5CHO)

Oil of bitter almonds

General Method of Preparation :



$$C_6H_6 \xrightarrow{CO/\ HCl + AlCl_3} C_6H_5CHO$$ * (Gattermann-kosch reaction)

$$C_6H_5CH_3 \xrightarrow{CrO_2Cl_2} C_6H_5CHO$$ * (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)

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

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

$$C_6H_5CH_2OH \xrightarrow{[O]} C_6H_5CHO$$

$$C_6H_5CH_2Cl \xrightarrow{(CH_2)_6N_4} C_6H_5CHO$$

$$C_6H_5MgBr \xrightarrow{(i)\ HCOOC_2H_5\ (ii)\ H_2O} C_6H_5CHO$$

$$C_6H_6 \xrightarrow[AlCl_3]{(i)\ HCN/HCl\ (ii)\ H_2O} C_6H_5CHO$$ (Gattermann)

Chemical properties :