ALDEHYDES AND KETONES

❑ 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 $-\overset{\overset{\displaystyle O}{\|}}{C}-H$ (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.

◆ Ketones are further classified as :

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

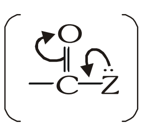
(ii) **Mixed or unsymmetrical ketones** : Having two different alkyl groups. $\begin{matrix} R \\ R' \end{matrix}\!>\!C=O$

Example : (Ketones) : Symmetrical — **Unsymmetrical**

Symmetrical	Unsymmetrical
$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!C=O$	$\begin{matrix} CH_3CH_2 \\ CH_3 \end{matrix}\!>\!C=O$
(Acetone or Dimethyl ketone)	(Ethyl methyl ketone)
2–Propanone	2–Butanone

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

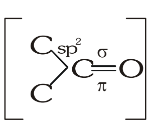
In all the compounds given above, lone pair of electrons and double bond are conjugate.



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

◆ **Structure** :

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



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.

❑ General Methods of Preparation :

(A) For both Aldehydes and Ketones :

(1) By Oxidation of Alcohols :

(a) By $K_2Cr_2O_7$ / H_2SO_4 :

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

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

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

Aldehydes are quite susceptible to further oxidation to acids -

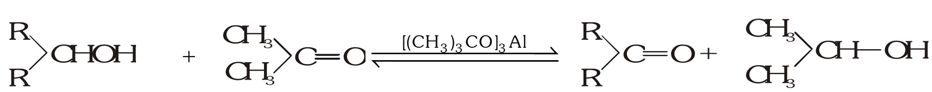
$$RCH_2OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-COOH$$

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.

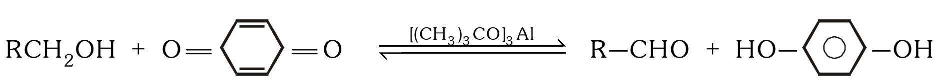
◆ **Note :** Aldehydes can be prepared from 1 alcohol,secondary alcohols can be oxidized to ketones, by oxidation with pyridinium chlorchromate (PCC) in CH_2Cl_2 solvent, pyridinium dichromate (PDC) and with Jones reagent(CrO_3+H_2SO_4) in acetone.

(b) Oppenaur 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.



2^O Alcohol   Acetone   Ketone   Isopropyl alcohol



1^0 Alcohol   Quinone   Aldehyde   Quinol

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

(c) Mild Oxidising Agent :

1° alcohols will get oxidised with CrO_3 / Pyridine, **collin's reagent** Ag/O_2 at $250^\circ C$

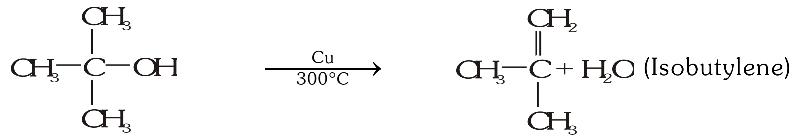
$$RCH_2OH + [O] \longrightarrow RCHO + H_2O$$

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

(2) Dehydrogenation of alcohols :

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

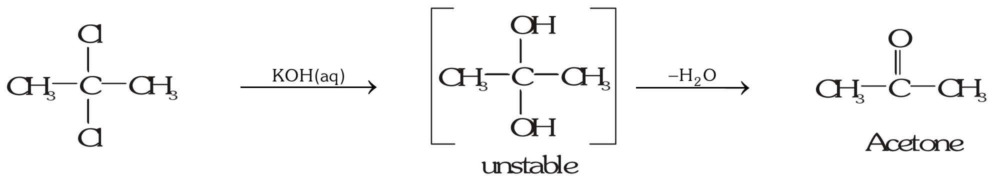
$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}CH_3 \xrightarrow[300^\circ C]{Cu} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \quad \text{(Acetone)}$$



(3) **By Hydrolysis of gem dihalides :**

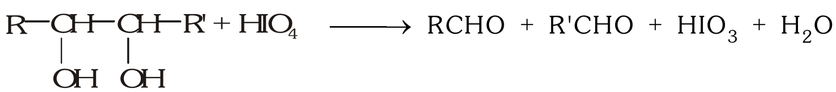
Terminal gem-dihalides on hydrolysis give aldehydes while the non-terminal dihalides give ketone.

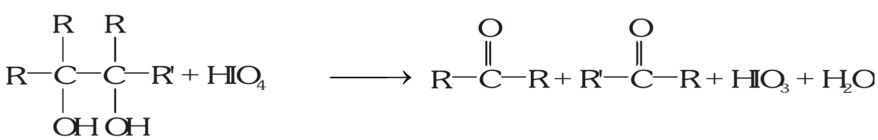
Terminal gem-dihalide [unstable] Acetaldehyde



(4) **By Oxidation of diols :**

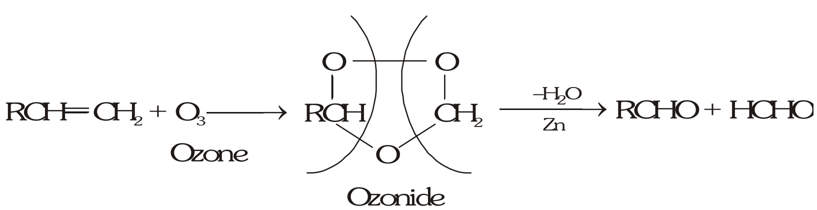
With periodic acid (HIO_4) & lead tetra acetate $(CH_3COO)_4$ Pb vicinal diols gets oxidised to form carbonyl compounds

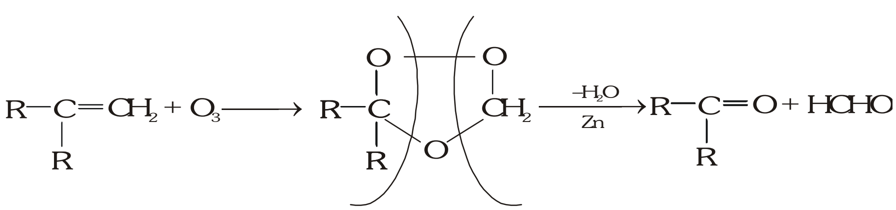




(5) **By Ozonolysis of alkenes :**

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





Unbranched alkene	⟶	aldehyde
Branched alkene	⟶	ketone

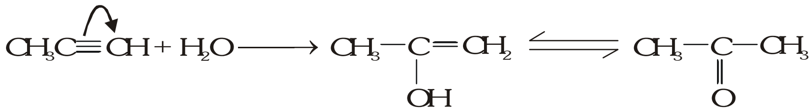
(6) **From Alkyne :**

(a) **Hydration** : With dil H_2SO_4 & 1% $HgSO_4$ at 60-80^{0}C.

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

(Tautomerisation)

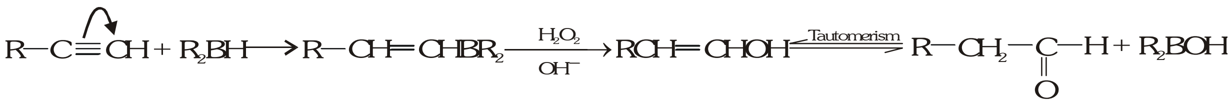
Other alkynes give ketone :

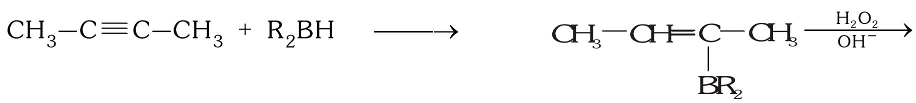


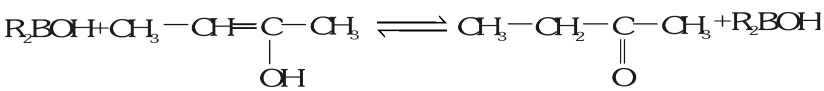
(enol)

(b) Hydroboration : Reaction with B_2H_6, $2BH_3$ or R_2BH give dialkyl borane.

1 – alkyne gives	$\longrightarrow$	aldehyde
other alkyne	$\longrightarrow$	ketone

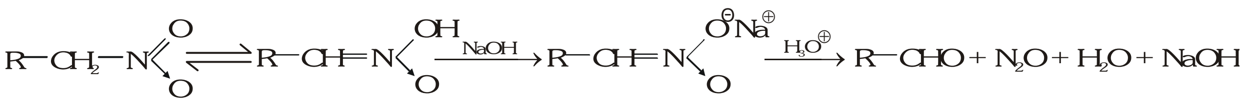






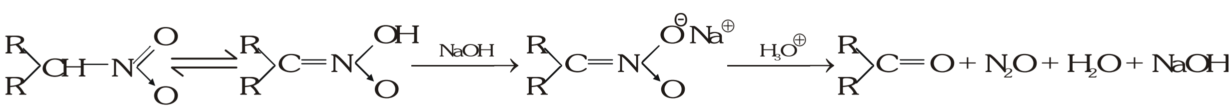
(7) By Nef's reaction :

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



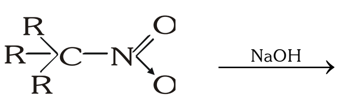
(Nitro form) (Aci form) (Aldehyde)

1 nitro alkane



(Nitro form) (Aci form) (Ketone)

2 nitro alkane



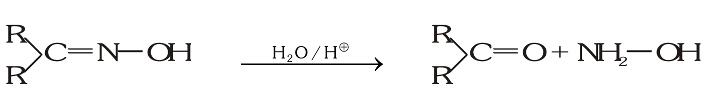
No Reaction

(3 nitro alkane)

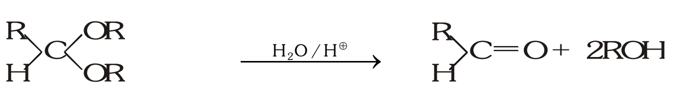
(8) By hydrolysis of carbonyl derivatives :

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

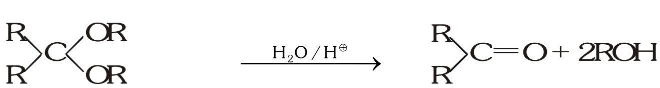
(Aldoxime) (Aldehyde) (Hydroxyl amine)



(Ketoxime) (Ketone)



(Acetal) (Aldehyde) (Alcohol)



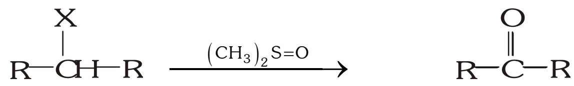
(Ketal) (Ketone) (Alcohol)

(9) **By oxidation of alkyl halides:**

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

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

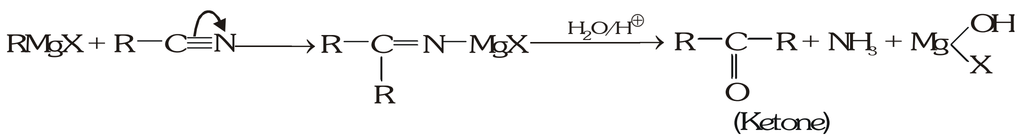
Alkyl halide (Aldehyde) (Dimethyl thio ether)



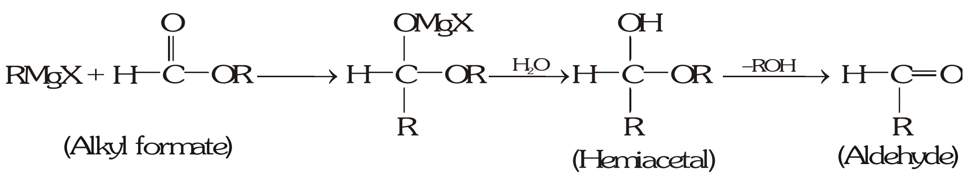
2 halide Ketone

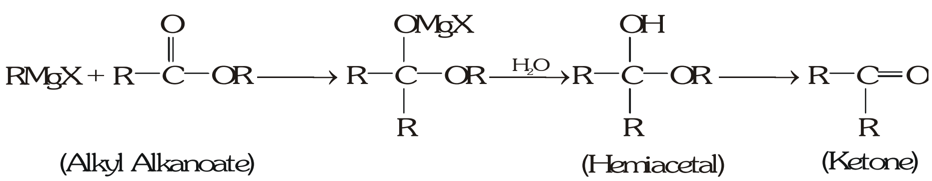
(10) **From Grignard reagents :**

(a) **By Cyanides :**

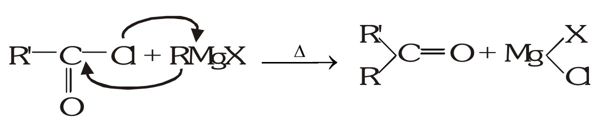


(b) **By Esters :** HCHO can't be prepared by this method.





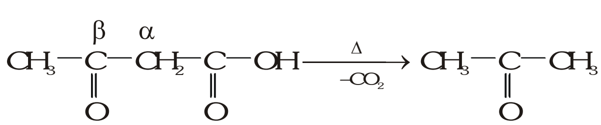
(c) **By acid chlorides :**



(11) **From β-keto acids :**

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

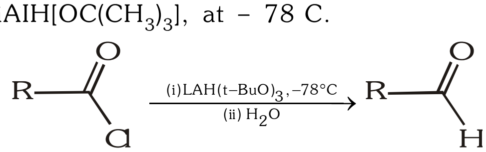
(a) $HCOCH_2COOH \xrightarrow[110°C]{\Delta} CH_3CHO + CO_2$

(b) 

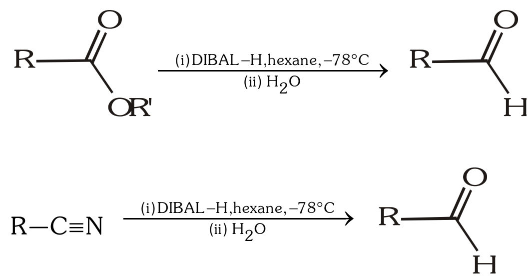
(B) **For Aldehydes only :**

(1) **Reduction of acyl halides, esters and nitriles :**

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



(b) 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.



(2) Rosenmund's reduction :

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

$$RCOCl + H_2 \xrightarrow[\text{Quinoline or sulphur}]{Pd/BaSO_4} RCHO + HCl$$

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

Formaldehyde can not be prepared by this method.

Example : $C_2H_5COCl + H_2 \xrightarrow[\text{Quinoline or sulphur}]{Pd/BaSO_4} C_2H_5CHO + HCl$

Propionyl Chloride — Propanal

(3) Stephen's reduction :

Alkyl cyanides are reduced by $SnCl_2$ and HCl.

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

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

(4) Oxo reaction or hydroformylation :

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

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

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

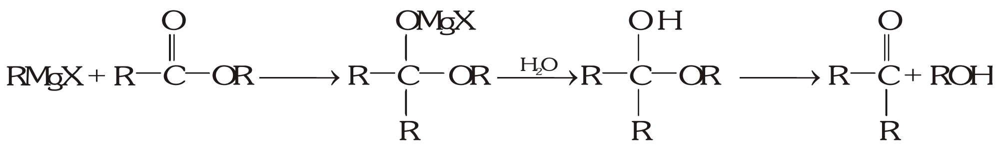
(C) For Ketones only :

(1) From Grignard's reagent :

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

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

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



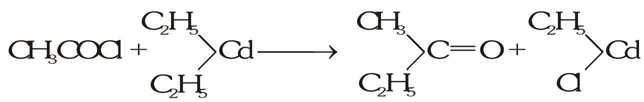
(2) From dialkyl Cadmium :

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.

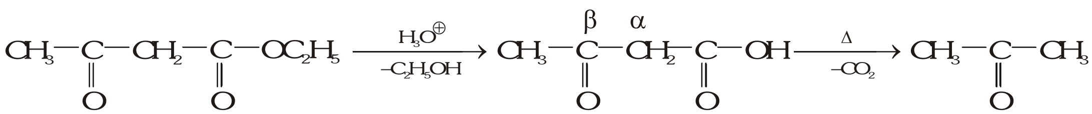
Example :



(3) From R_2CuLi :

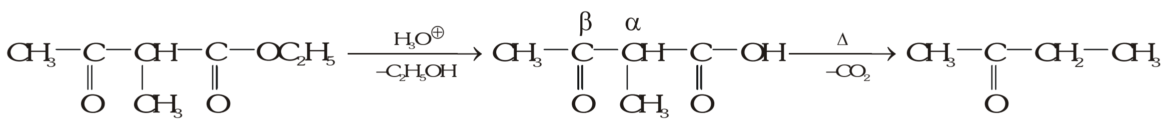
$$R_2CuLi + R'COCl \longrightarrow R'COR + RCu + LiCl$$

(4) By hydrolysis of Aceto Acetic Ester (AAE) :



(β - keto acid) (Acetone)

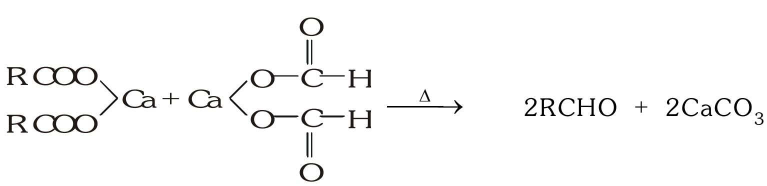
Ex :



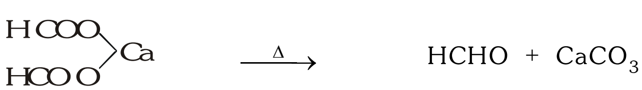
(β–keto acid) (Butanone)

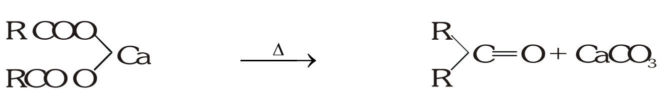
❑ **Other methods for aldehyde and ketone :**

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



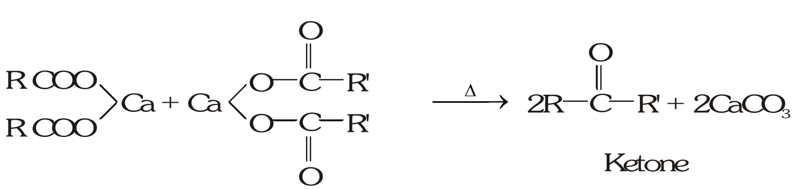
Calcium formate (Also R—C(=O)—R and HCHO formed)





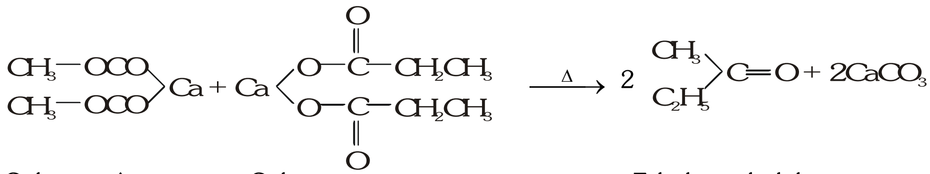
Calcium-alkanoate Ketone

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



Ketone

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



Calcium Acetate   Calcium propionate   Ethyl methyl ketone

(2) By Thermal decomposition of carboxylic acids :

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

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

$$2\ CH_3COOH \xrightarrow[300°C]{MnO} (CH_3)_2C{=}O + CO_2 + H_2O$$

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

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

(3) Wacker process :

In this reaction double bond is not cleaved so same C-atom aldehyde and ketones are formed.

$$CH_2{=}CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3CHO + Pd + HCl$$

All other alkenes gives ketone.

$$RCH{=}CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} R{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + Pd + HCl$$

❑ **Physical Properties :**

◆ **State :**

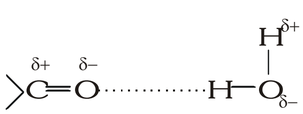
Only formaldehyde is gas, all other carbonyl compounds upto C_{11} are liquids and C_{12} & onwards solid.

◆ **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.



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

H-bonding

◆ **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 vander 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^+.

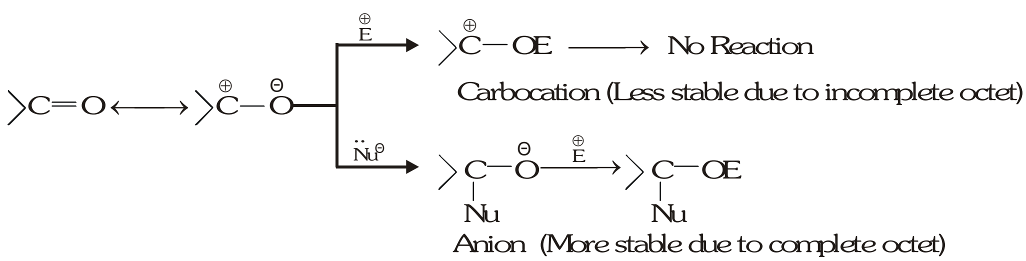
$>C=O$ bond in carbonyl group is stronger than C=C bond in alkanes.

$$\begin{cases} C-O & \text{Bond energy is } 84.0 \text{ K Cals} \\ C=O & \text{Bond energy is } 178 \text{ K Cals} \end{cases} \qquad \begin{cases} C-C & \text{Bond energy is } 83.1 \text{ K Cals} \\ C=C & \text{Bond energy is } 146 \text{ K Cals} \end{cases}$$

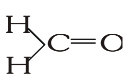
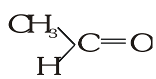
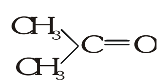
Reactivity of carbonyl group $\propto$ **Magnitude of +ve charge** $\propto$ **– I group** $\propto$ $\dfrac{1}{+\text{I group}}$

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

Sol.

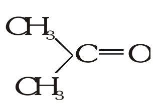
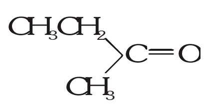
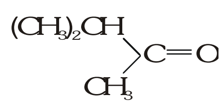
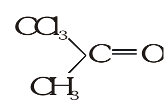


Ex. Arrange the following for reactivity in decreasing order

(I) (i)  (ii)  (iii) 

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

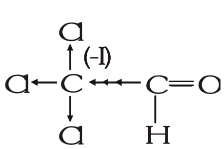
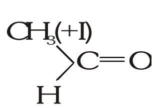
(III) (i) CH_3CHO (ii) $ClCH_2CHO$ (iii) $HCCl_2CHO$ (iv) CCl_3CHO

(IV) (i)  (ii)  (iii)  (iv) 

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  and  , which one is more reactive ?

Chloral

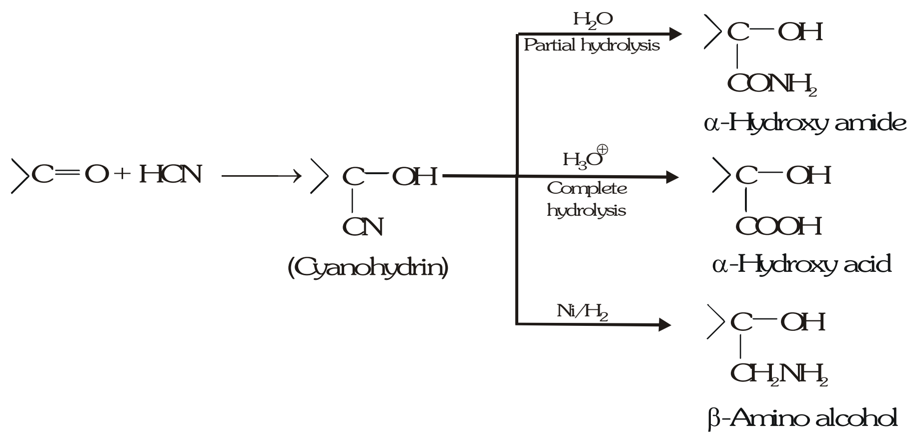
Sol. I is more reactive than II.

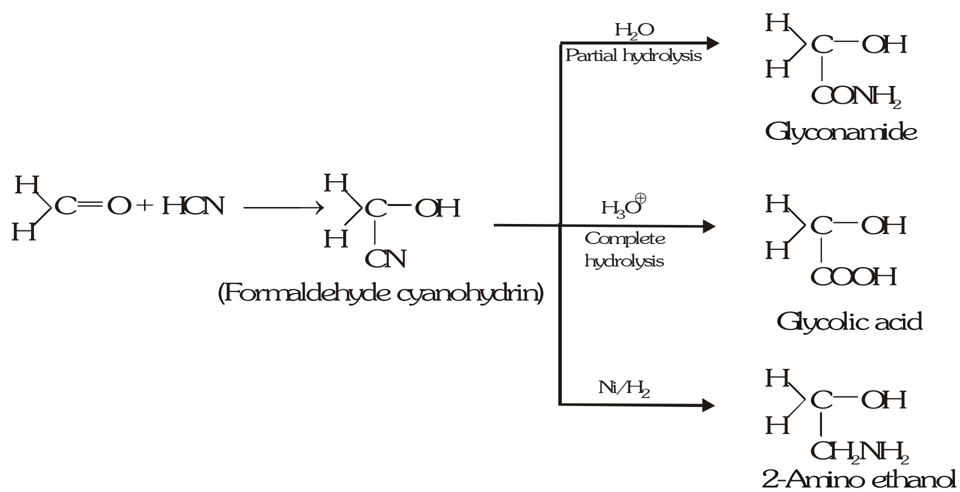
- **Chemical Reactions :**

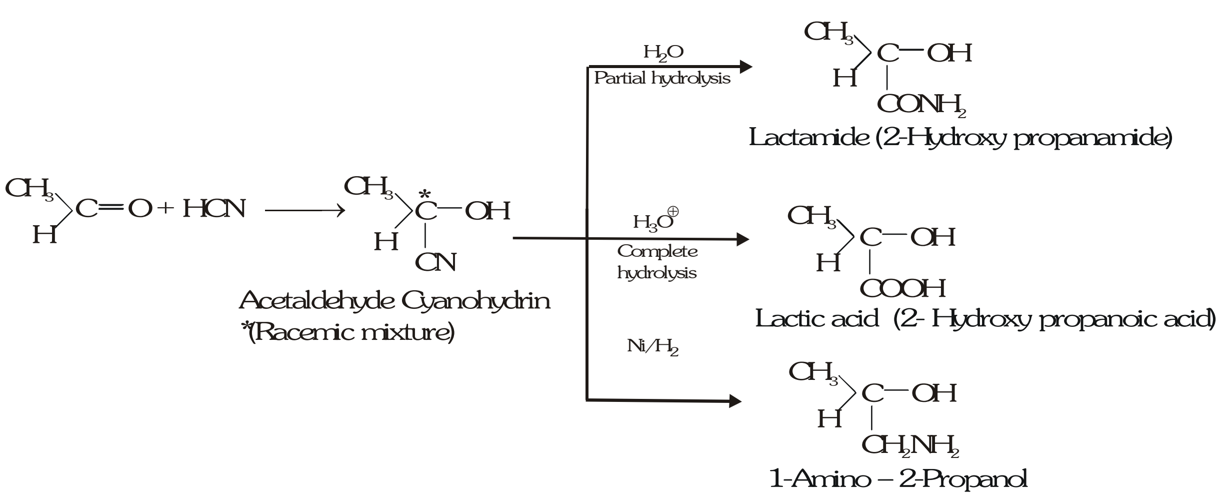
Carbonyl compounds in general under goes neucleophilic addition reaction :

(A) Nucleophilic addition reactions :

(1) Addition of HCN :







(2) **Addition of $NaHSO_3$:**

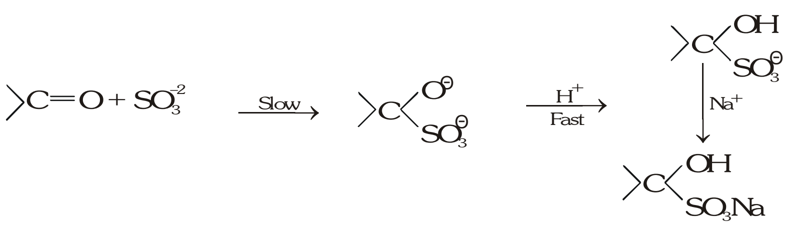
This reaction is utilized for the separation of carbonyl compounds from non - carbonyl compounds.

$$>C{=}O + NaHSO_3 \longrightarrow >C(OH)(SO_3Na) \xrightarrow{H_3O^{\oplus}}$$ Carbonyl compounds. *(Regain)

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 :**

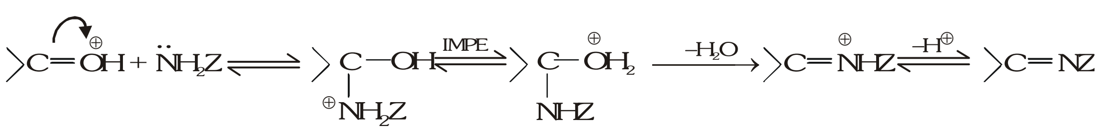
These are condensation or addition elimination reaction. These proceeds well in weakly acidic medium.

$NH_3 \longrightarrow NH_2Z$ (Ammonia derivative)

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

Addition - elimination (Condensation)

Mechanism :

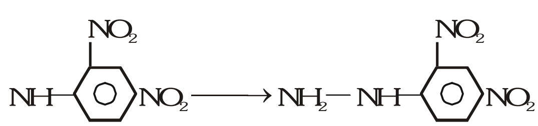


- **Ammonia derivatives (NH_2Z) :**

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)

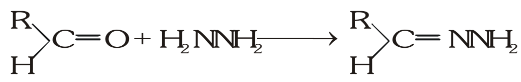
Z = 

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

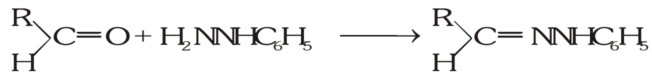
Z = $NHCONH_2$ $\longrightarrow$ $NH_2NHCONH_2$

Semi Carbazide.

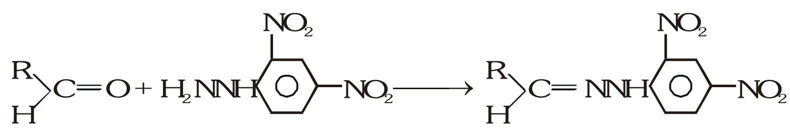
$$\begin{matrix}R\\H\end{matrix}\!\!>C{=}O + H_2NOH \longrightarrow \begin{matrix}R\\H\end{matrix}\!\!>C{=}NOH$$ (Aldoxime)



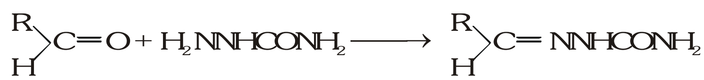
(Hydrazone)



(Phenyl hydrazone)

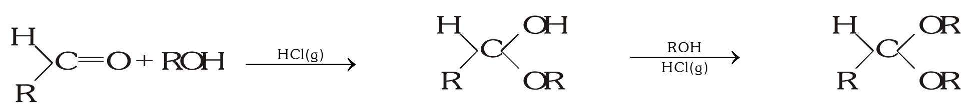


2,4-DNP (Brady's reagent) (2, 4 - dinitro phenyl hydrazone)

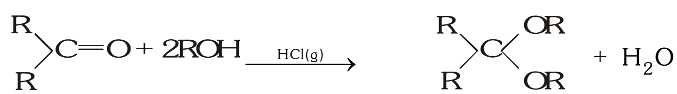


(Semi Carbazone)

(4) With alcohol and thioalcohol :

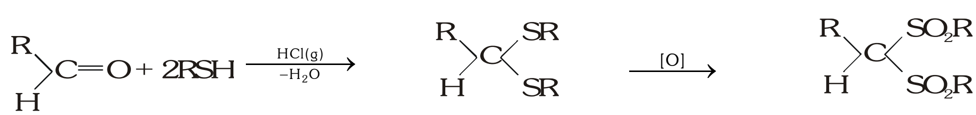


Hemi-acetal Acetal

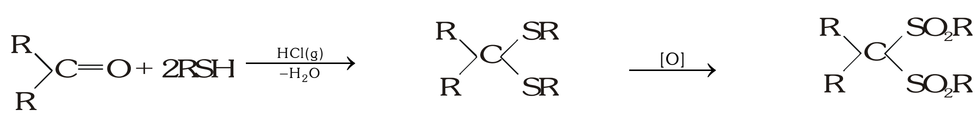


Ketal

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

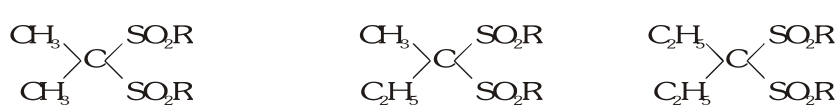


Thioalcohol Mercaptal



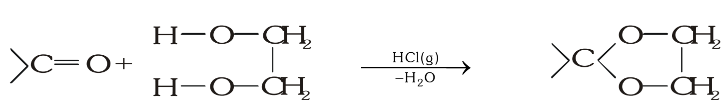
Mercaptal (Thio Ketal) Sulphones Compound

All sulphones compounds are hypnotic compounds.



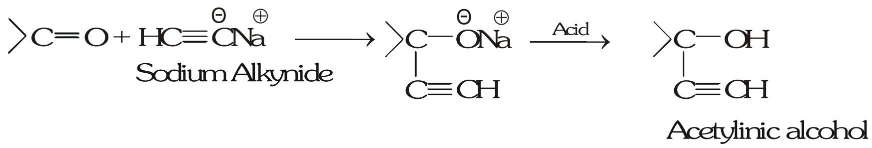
Sulphonal Trional Tetronal

(5) Reaction with glycol (group protection) :

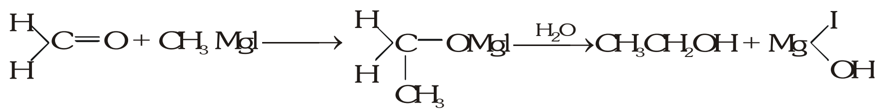


(neutral) Cyclic acetal / ketal

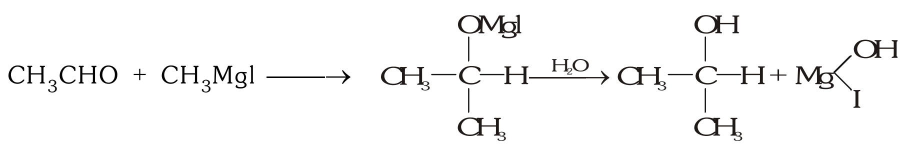
(6) Reaction with sodium alkynide :



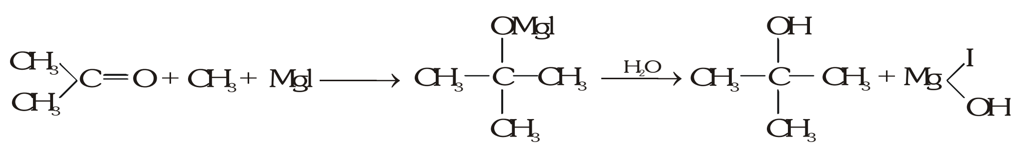
(7) Reaction with Grignard reagent :



Ethanol (1 alcohol)

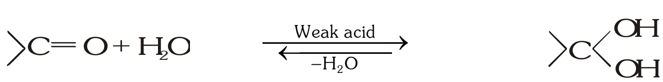


2–Propanol (2 alcohol)



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?

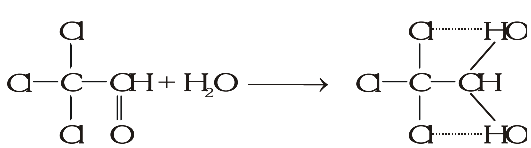
(A) HCHO (B) CH_3CHO (C) CH_3COCH_3 (D) $CH_3COC_2H_5$

[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.



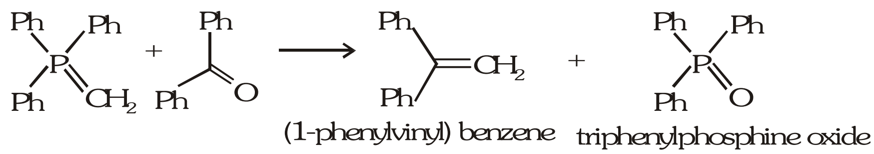
(Chloral) (Chloral hydrate)

Stable by intra molecular hydrogen bonding.

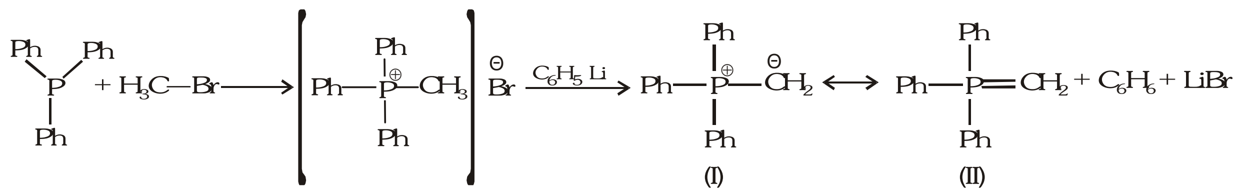
(B) Other Reactions :

(1) Wittig Reaction :

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



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



(2) Cannizaro's reaction :

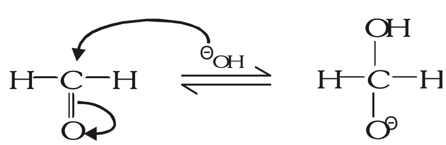
Those aldehydes which do not contain α-H atom give this reaction, with conc. NaOH or KOH; Products are Salt of carboxylic acid + alcohol.

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)

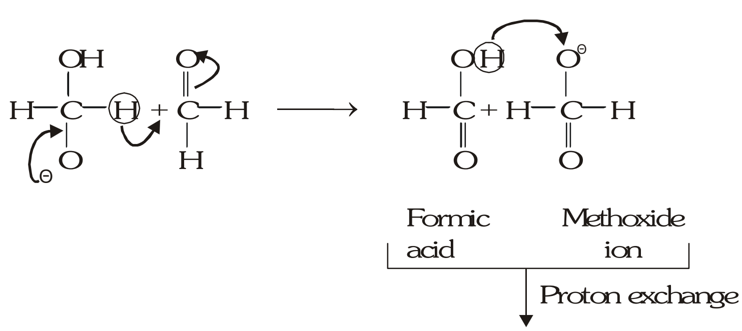
$$HCHO + HCHO \xrightarrow[NaOH]{Conc.} HCOONa + CH_3OH$$

Mechanism : (Cannizaro reaction)

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



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



(c) Proton exchange

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

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

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

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

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

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)

(3) Tischenko reaction :

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

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

Example : $CH_3CHO + CH_3CHO \xrightarrow{(C_2H_5O)_3Al} CH_3COOH + CH_3CH_2OH$

Esterification ↓

$CH_3-COOCH_2CH_3$ (Ethyl acetate)

(4) Reaction With Halogen :

(a) 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.

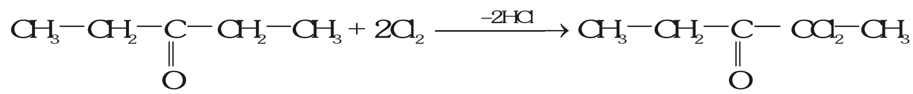
$$\overset{\alpha}{C}H_2(H)-\underset{\underset{O}{\|}}{C}-H + Cl_2 \xrightarrow{-HCl} CH_2(Cl)-\underset{\underset{O}{\|}}{C}-H \xrightarrow[-HCl]{Cl_2} CHCl_2-\underset{\underset{O}{\|}}{C}-H \xrightarrow[-HCl]{Cl_2} \underset{\text{Chloral}}{CCl_3-\underset{\underset{O}{\|}}{C}-H}$$

Example : $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + 3Cl_2 \xrightarrow{-3HCl} \underset{\text{Tri chloro acetone}}{CH_3-\underset{\underset{O}{\|}}{C}-CCl_3}$

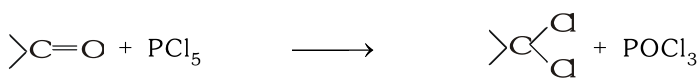
Example : $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 + 3Cl_2 \xrightarrow{-3HCl} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CCl_3$

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

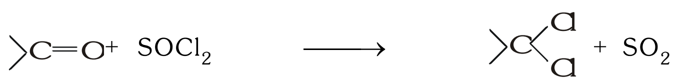
Example :



(b) Replacement of O-atom of $>C=O$ group : It takes place by PCl_5 or $SOCl_2$.



Phosphorus penta chloride



Thionyl chloride

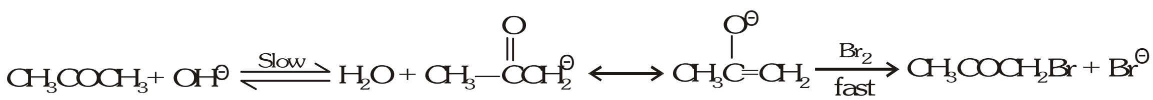
(c) Haloform reactions :

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 monobromoacetone :

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

The halogenation of carbonyl compounds is catalysed by acids and bases. Let us consider the case of acetone. In alkaline solution, tribromoacetone 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.,

$$\text{Rate} = k\ [\text{acetone}]\ [OH^{\ominus}]$$



(5) 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.

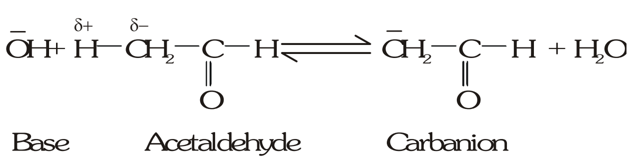
- **Mechanism of aldol condensation** : It takes place in the following two stages :

(a) Formation of Carbanion

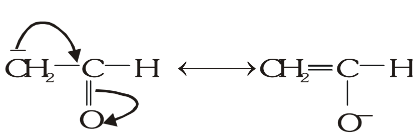
(b) Combination of carbanion with other aldehyde molecule.

(a) Formation of Carbanion :

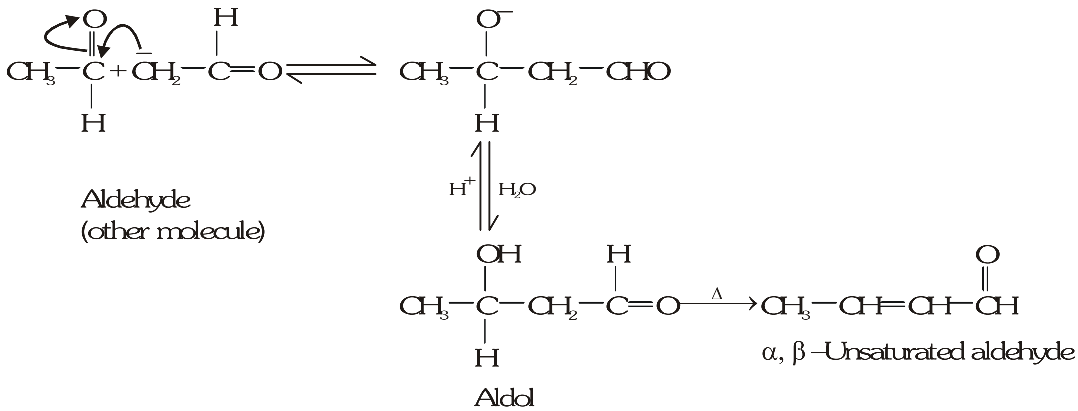
α-H atom of $>C=O$ group are quite acidic which can be removed easily as proton, by a base.



Carbanion thus formed is stable because of resonance -



(b) Combination of carbanion with other aldehyde molecule :

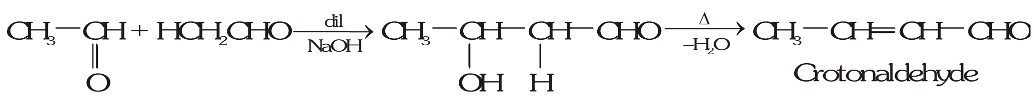


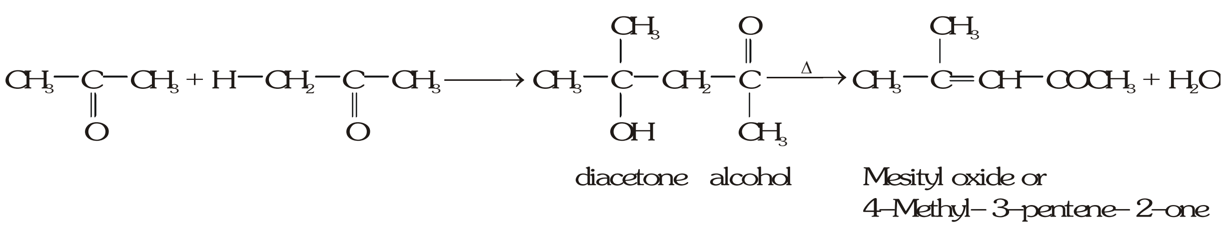
Aldol condensation is possible between :

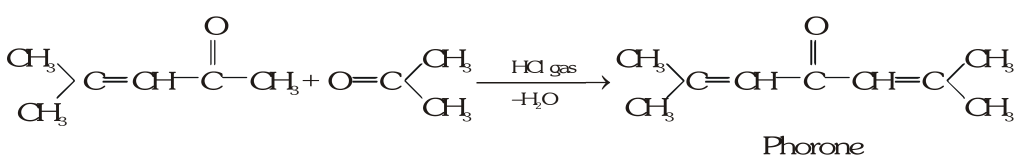
1. Two aldehyde (Same or different)
2. Two ketones (Same or different)
3. One aldehyde and one ketone

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

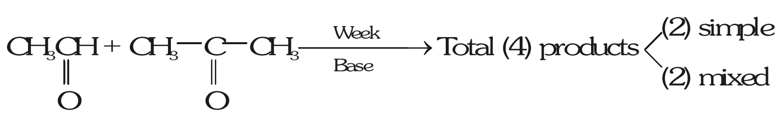
Simple or Self condensation :

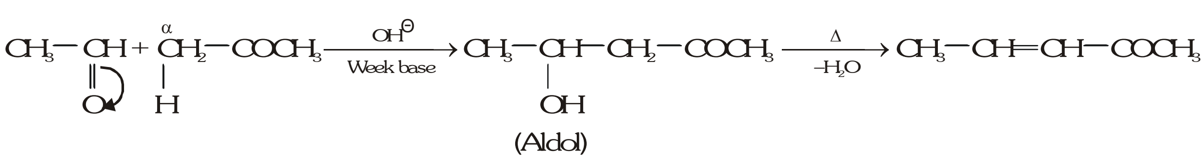


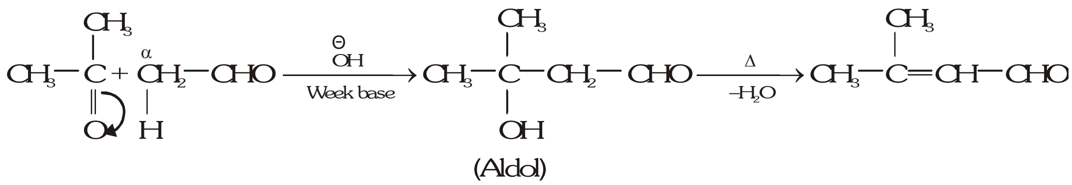




Mixed or Crossed aldol Condensation :

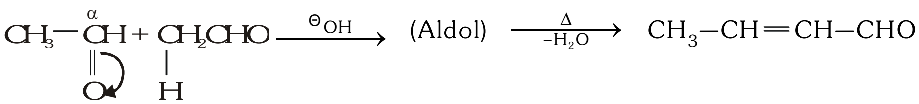


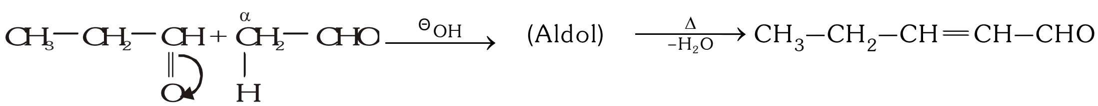


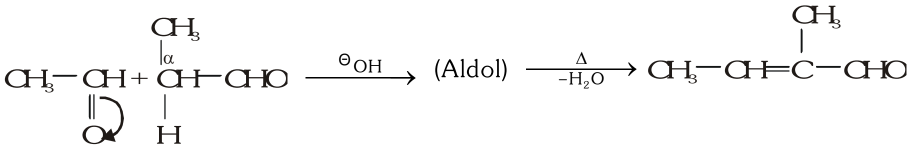


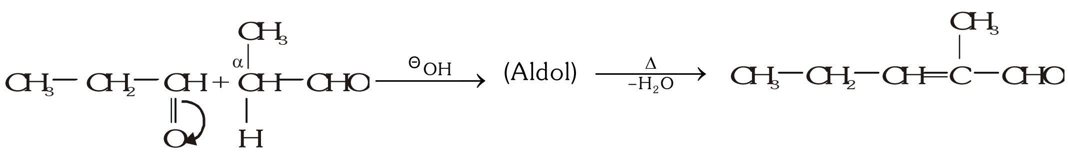
Ex : $CH_3CHO + CH_3CH_2CHO \xrightarrow[(WB)]{^{\ominus}OH}$ Total 4 products. Write structure of products ?

Sol.

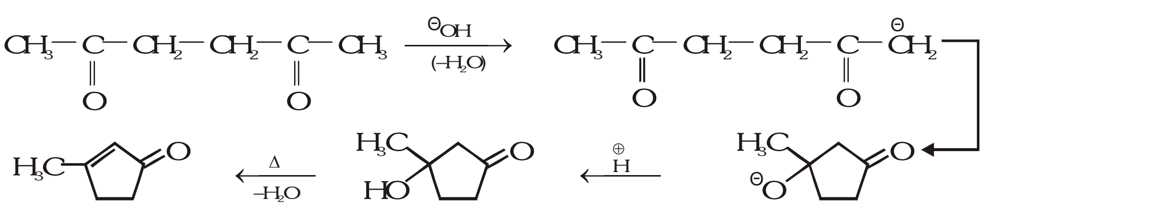








- **Intramolecular aldol condensation :**



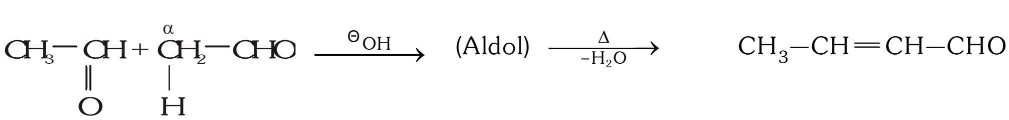
(α,β – Unsaturated Ketone) (Aldol)

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

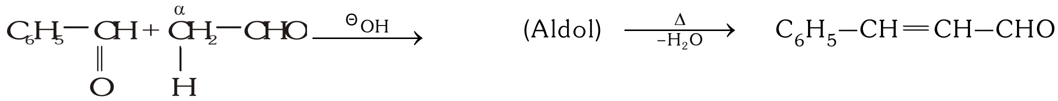
Note :

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

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



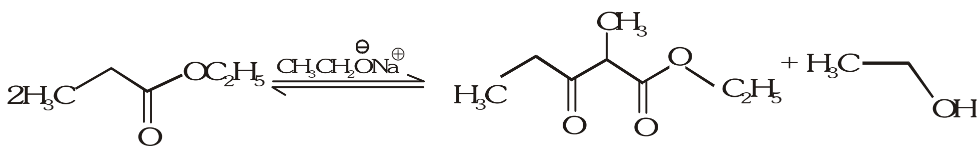
(Crotonaldehyde)



(Cinnamaldehyde)

(6) Claisen condensation :

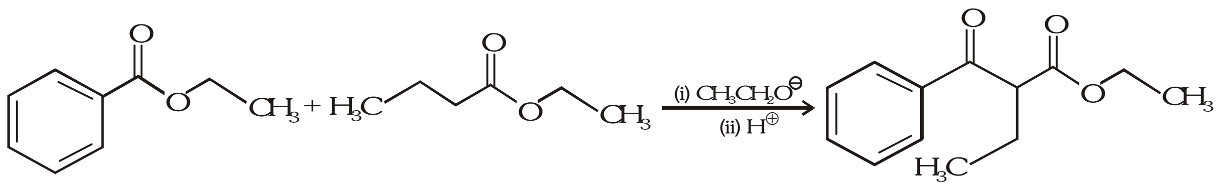
When two molecules of ester undergo a condensation reaction, the reaction is called Claisen condensation. The product of the claisen condensation is a β-keto ester.



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.

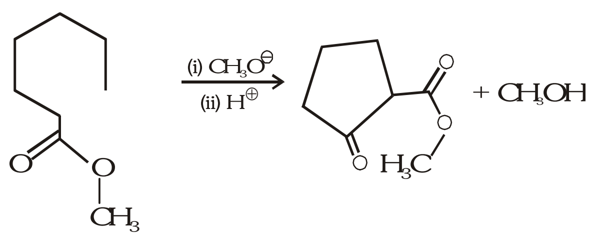
❑ **Mixed claisen condensation :**

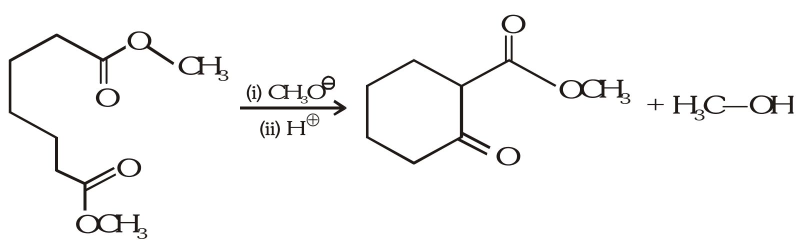


β-keto ester

(7) 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.



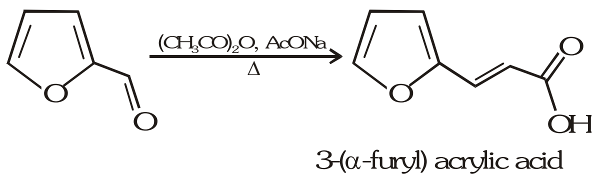


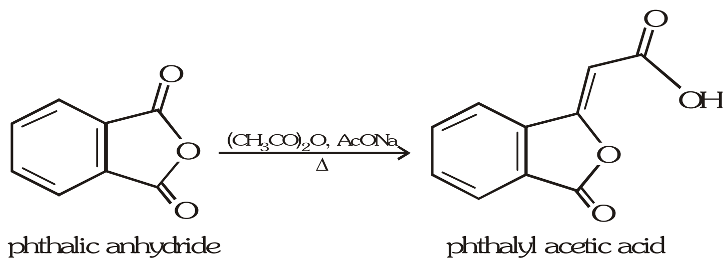
(8) Perkin reaction :

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.

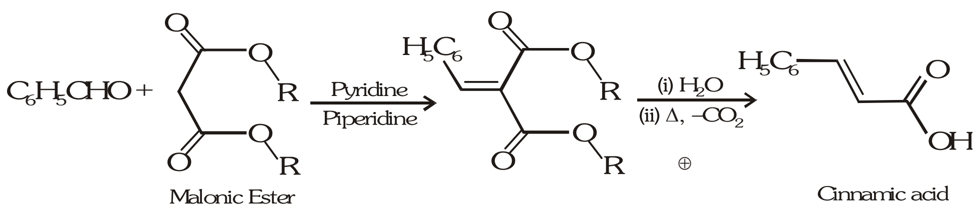
$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow[170-180°C]{AcONa} C_6H_5-CH=CH-COOH$$





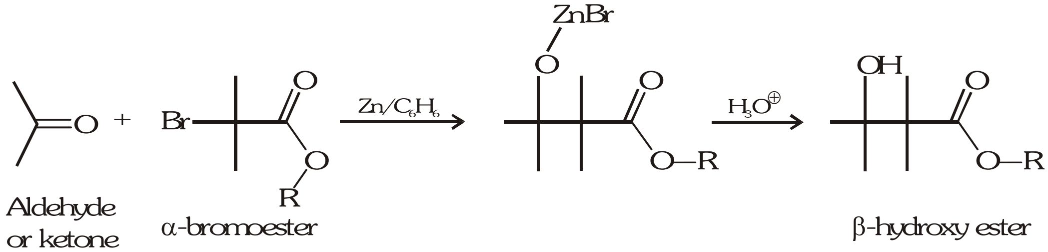
(9) Knoevenagel Reaction :

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.



(10) 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 yileds 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.



(11) 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 :

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

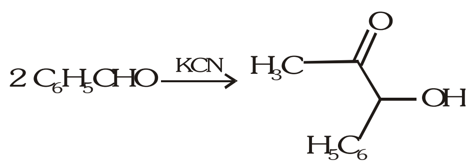
$$RCOR + HN_3 \xrightarrow{H_2SO_4} RCONHR + N_2$$

Reaction with primary amine : $>C=O + H_2NR \longrightarrow >C=NR + H_2O$

Schiff's Base

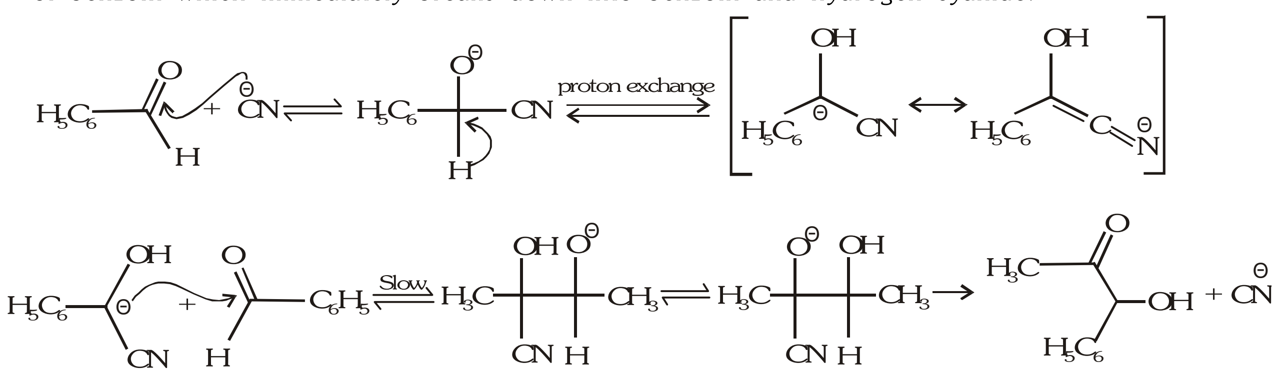
(12) Benzoin condensation :

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



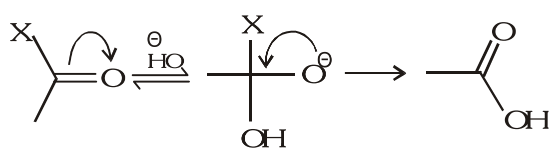
(I)

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.



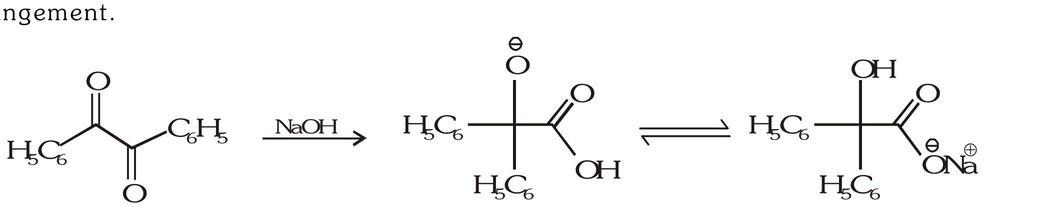
(13) Benzilic acid rearrangement :

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

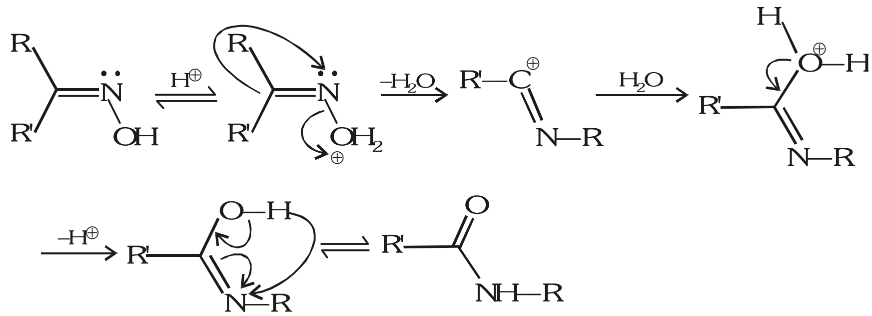
sodium salt of benzilic acid

(14) The Beckmann rearrangement :

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

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

Oxime



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

(C) Oxidation Reactions :

(a) 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.

(b) 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.

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

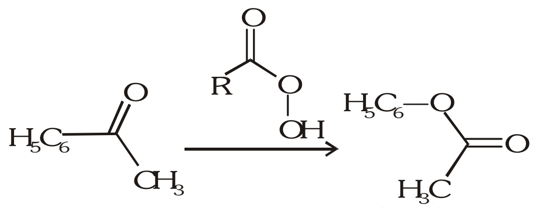
Glyoxal

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

Methyl glyoxal (Pyruvaldehyde)

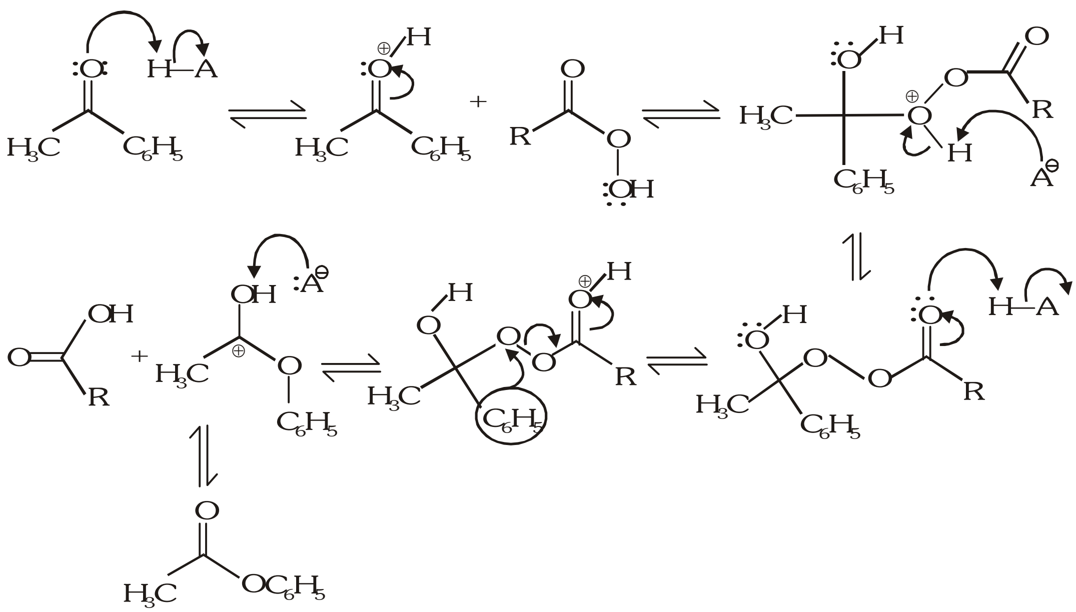
(c) Baeyer's Villiger oxidation :

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.

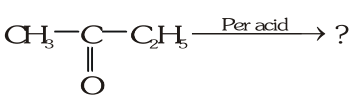


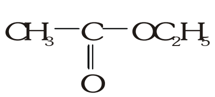
phenyl acetate

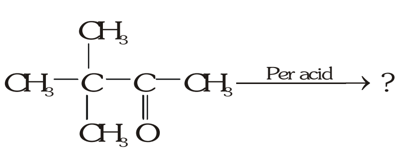
Mechanism :

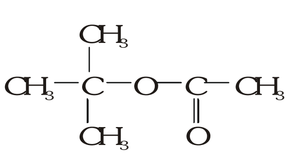


The product of this reaction show that a phenyl group has a greater tendency to migrate then a methyl group. Had this not been the case, the product would have been $C_6H_5COOCH_3$ and not $CH_3COOC_6H_5$. This tendency of a group to migrate is called is migratory aptitude. Studies of the Baeyer-villiger 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. 

Sol. 

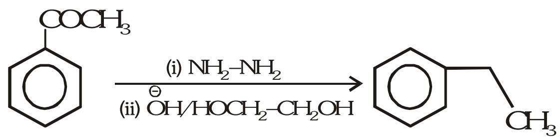
Ex. 

Sol. 

(D) Reduction :

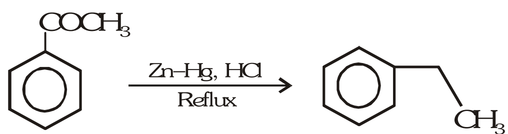
(a) The wolf kishner reduction :

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.



(b) 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) $\rangle C{=}O \longrightarrow \rangle CH_2$ Reducing agents are

- Red P/HI at 150 C
- Zn-Hg/HCl [Clemensen's reduction]
- $NH_2-NH_2/C_2H_5OH, OH^{\ominus}$ [Wolff Kischner's reduction]

(ii) $\rangle C{=}O \longrightarrow \rangle CHOH$ Reducing agents are

- $LiAlH_4$ (Nicetron brown)
- Na/C_2H_5OH (Bouvalt 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 Ponndroff Verley)** reduction. Other reducible groups are not attacked like $-NO_2$, $-CH{=}CH_2$, $-C{\equiv}C-$.

Example : $\begin{matrix} CH_3 \\ CH_2{=}CH \end{matrix}\rangle C{=}O \xrightarrow{\text{MPV Reduction}} \begin{matrix} CH_3 \\ CH_2{=}CH \end{matrix}\rangle CHOH$

(E) Reactions given by only aldehydes :

(1) Polymerisation : It is a reversible process.

Formaldehyde :

(a) $nHCHO \underset{\Delta}{\overset{\text{Evaporation}}{\rightleftharpoons}} (CH_2O)_n, H_2O$

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) $nHCHO \underset{H_2SO_4 \Delta}{\overset{Conc.}{\rightleftharpoons}} (CH_2O)_n H_2O$

Poly oxy methylene

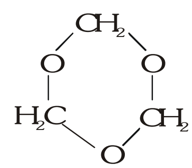
$n > 100$

(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.



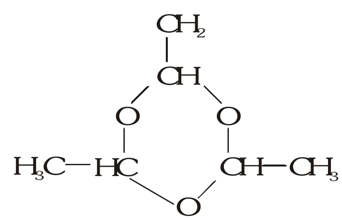
(d) $6HCHO \xrightarrow[\text{or } Ba(OH)_2]{Ca(OH)_2} C_6H_{12}O_6$

Formose sugar

A linear polymer (α-acrose)

Acetaldehyde :

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



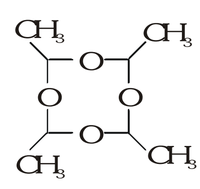
Para acetaldehyde

Paraldehyde (cyclic polymer)

Pleasent smelling liquid

Hypnotic compound

(b) $4CH_3CHO \xrightarrow[0°C]{\text{conc. } H_2SO_4} (CH_3CHO)_4$



Meta aldehyde

White crystalline solid.

Cyclic polymer

Used as solid fuel or killing snails

(4) Reaction with ammonia :

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

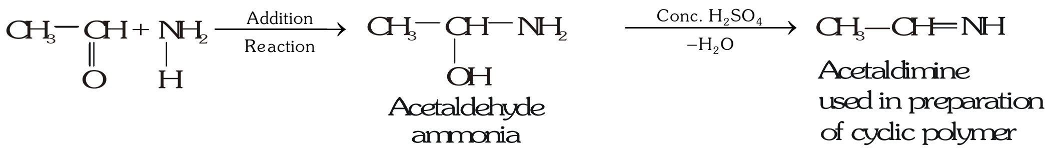
$$6CH_2O + 4NH_3 \xrightarrow[\text{Reaction}]{\text{Condensation}} (CH_2)_6N_4 + 6H_2O$$

Urotropine (Hexamine)

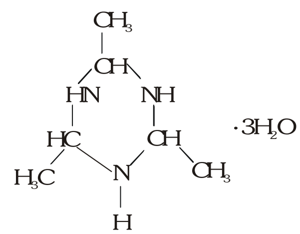
White crystalline solid

Used in preparation of explosive

Used in treatment of urine infection diseases



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



Trimethyl hexahydro Triazine trihydrate

(5) **Reducing character :**

Aldehydes are easily oxidised so they are strong reducing agents.

(a) **Tollen's reagent :**

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

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

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

Silver mirror

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

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

(b) **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.)

(c) **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.

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

(Cuprous oxide–Red ppt.)

(d) **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.

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

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

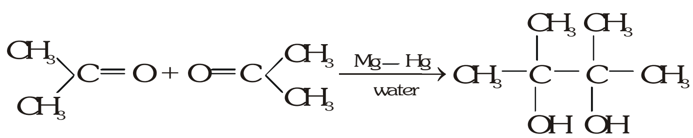
(e) **Reaction with schiff's reagent** :

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.

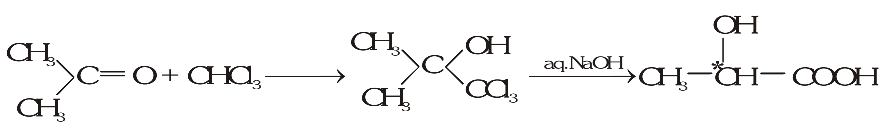
(F) Reaction of only ketones :

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



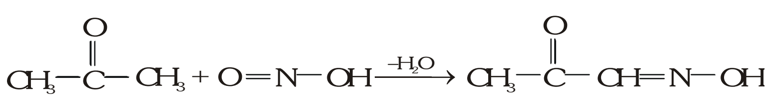
Pinacol

(2) Reaction with chloroform :



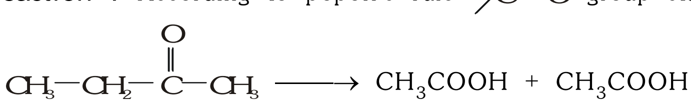
(Chloretone) (Lactic acid)
2-Hydroxy propanoic acid

(3) Reaction with HNO_2 :



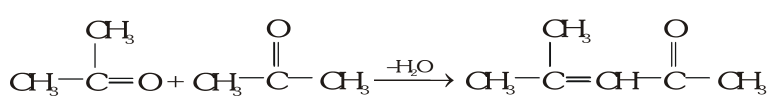
Oximino acetone

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

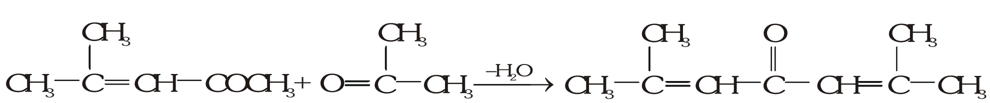


(5) Condensation reaction :

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

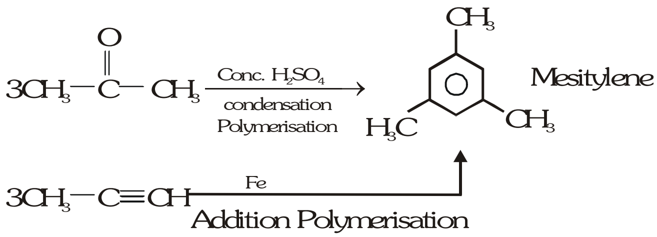


Mesityl oxide



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

(b) In presence of conc.H_2SO_4



(6) Reaction with ammonia :

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

Diacetone amine

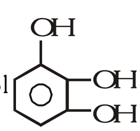
(7) Pyrolysis :

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

Acetone Ketene

$$\left\{\begin{array}{l} HCHO \xrightarrow[\text{pyrolysis}]{\Delta} CO + H_2 \\ CH_3CHO \xrightarrow{\Delta} CH_4 + CO \end{array}\right\}$$

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 $\rangle C=O$ compound gives this test	–	Red	Red
2.	Iodoform test	–	–	–
	(I_2 + NaOH)	–	yellow ppt	yellow ppt
3.	Pyragallol 	white ppt.	–	–
4.	Orthonitro benzaldehyde	–	–	Blue
5.	Tollen's reagent -	Silver mirror	Silver mirror	–
	Fehling's reagent -	Red ppt	Red ppt	–
	Mercuric chloride -	Black ppt	Black ppt	–
	Schiff's reagent -	Pink colour	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 —CO/ HCl + $AlCl_3$→ C_6H_5CHO *(Gattermann-kosch reaction)
- $C_6H_5CH_3$ —CrO_2Cl_2→ C_6H_5CHO *(Etard reaction)
- C_6H_5COCl —Pd/$BaSO_4$→ C_6H_5CHO *(Rosenmund reaction)
- C_6H_5CN —(i) $SnCl_2$/HCl (ii) H_2O→ C_6H_5CHO *(Stephen's reaction)
- $(C_6H_5COO)_2Ca$ —$(HCOO)_2Ca/\Delta$→ C_6H_5CHO
- $C_6H_5CHCl_2$ —aq. KOH→ C_6H_5CHO
- $C_6H_5CH_2OH$ —[O]→ C_6H_5CHO
- $C_6H_5CH_2Cl$ —$(CH_2)_6N_4$→ C_6H_5CHO
- C_6H_5MgBr —(i) $HCOOC_2H_5$ (ii) H_2O→ C_6H_5CHO
- C_6H_6 —(i) HCN/HCl (ii) H_2O, $AlCl_3$→ C_6H_5CHO (Gattermann)

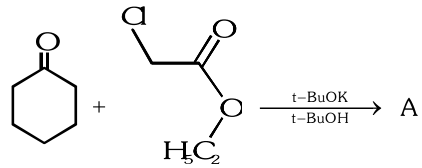
Chemical properties :

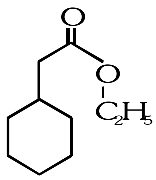
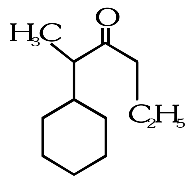
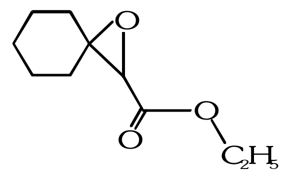
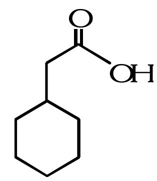
C_6H_5CHO →

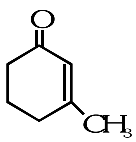
- (Similar) HCN → $C_6H_5CH(OH)CN$
- $NaHSO_3$ → $C_6H_5CH(OH)SO_3Na$
- NH_2-Z → $C_6H_5CH=N-Z$
- Red P + HI → $C_6H_5CH_3$
- Oxidation → C_6H_5COOH
- PCl_5 → $C_6H_5CHCl_2$
- Tollen reagent → Silver mirror *test*
- NaOH → $C_6H_5COONa + C_6H_5CH_2-OH$ Cannizaro reaction
- $Ar-NH_2$ → $C_6H_5CH=N-Ar$ Schiff's base
- Schiff's reagent → Pink colour
- $AlCl_3$ / $Al(OR)_3$ → $C_6H_5COOCH_2C_6H_5$ Tischenko reachion
- C_6H_5MgBr / H_2O → $C_6H_5-CH(OH)-C_6H_5$
- (different) 170 /Cl_2 → C_6H_5COCl
- $2NH_3$ / $2C_6H_5CHO$ → $(C_6H_5-CH=N)_2CH-C_6H_5$
- $2C_6H_5CHO$ / alc.KCN → $C_6H_5-CH(OH)-C(=O)-C_6H_5$ Benzoin
- $(CH_3CO)_2O, CH_3COONa$ → $C_6H_5-CH=CH-COOH$ Perkin
- H_2CH-NO_2 / HO^- → $C_6H_5-CH=CH-NO_2$ Nitrostyrene
- (i) Zn+$CH_2(Br)COOC_2H_5$ (ii) H_2O → Cinnamic acid Reformatsky reaction
- HNO_3/H_2SO_4 → m – nitrobenzaldehyde
- Fuming H_2SO_4 → m–formyl benzene sulphonic acid
- $Cl_2/FeCl_3$ → Chloro benzaldehyde
- $CH_3-C(=O)-CH_3$ / $\overset{\ominus}{O}H$ → $C_6H_5CH=CH-C(=O)-CH_3$

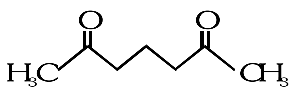
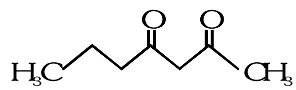
SOLVED EXAMPLES

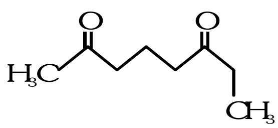
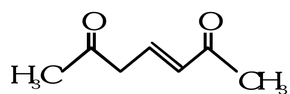
Ex 1. What is A in the following reaction ?

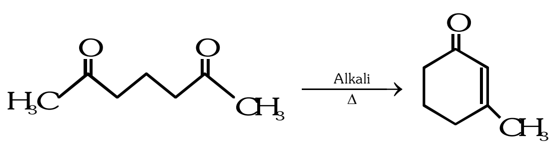


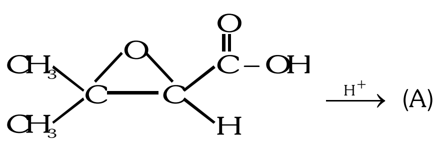
(A)  (B)  (C)  (D) 

Ex 2.  is the final product obtained when one of the following is reacted with base :

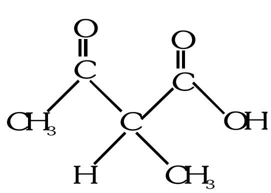
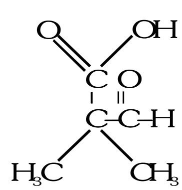
(A)  (B) 

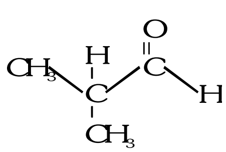
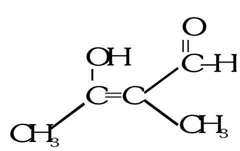
(C)  (D) 

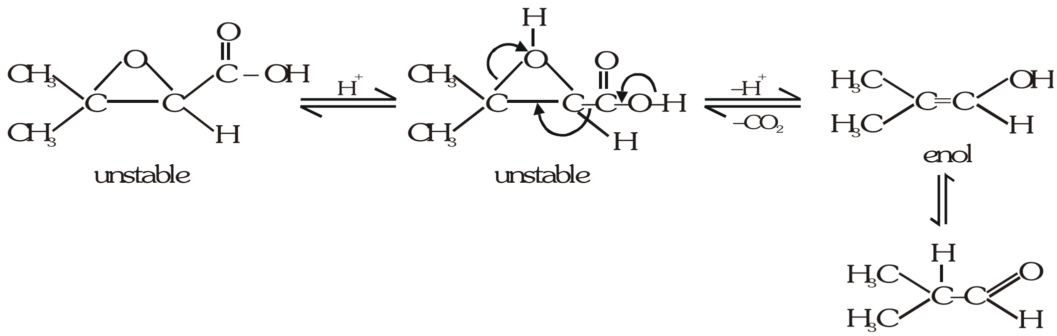
Sol. 

Ex 3. 

The product (A) in the given reaction would be :

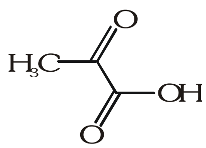
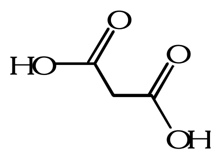
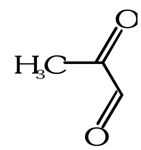
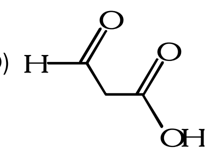
(A)  (B) 

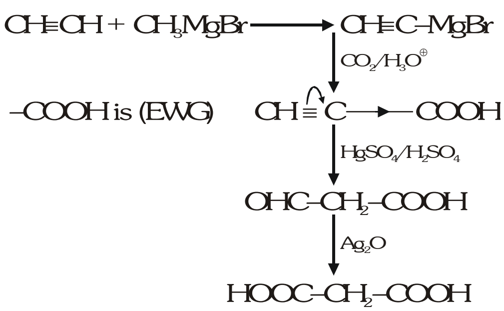
(C)  (D) 

Sol. 

Ex 4. End product of the following sequence of reactions is :

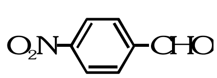
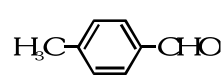
$$CH\equiv CH \xrightarrow{CH_3MgBr} \xrightarrow{CO_2/H_3O^{\oplus}} \xrightarrow{HgSO_4/H_2SO_4} \xrightarrow[\Delta]{Ag_2O}$$

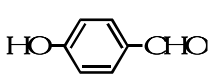
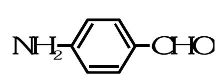
(A)  (B)  (C)  (D) 

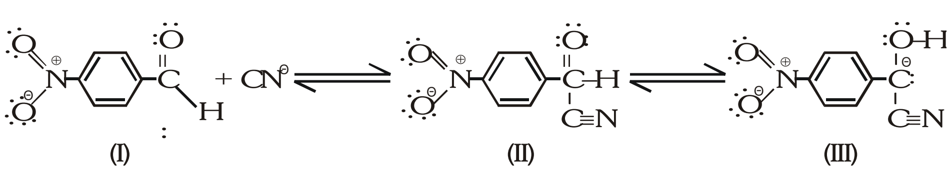
Sol. 

∴ (B)

Ex 5. In which of the following substrates, rate of Benzoin condensation will be maximum ?

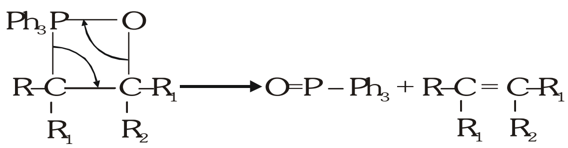
(A)  (B) 

(C)  (D) 

Sol. 

Benzoin condensation is due to stability of intermediate (III) when negative charge on C extensively delocalised in benzene ring, nitro and C≡N group. In all other cases, such dispersal is not extensively possible. On the other hand, NO_2– is also creating a positive charge center on carbonyl carbon, making it more susceptible to nucleophilic attack of CN^-.

Ex 6. This intermediate is converted into product in the wittig reaction :



Out of following which statements are correct ?

(A) C–O bond is weaker as compared to P–O bond

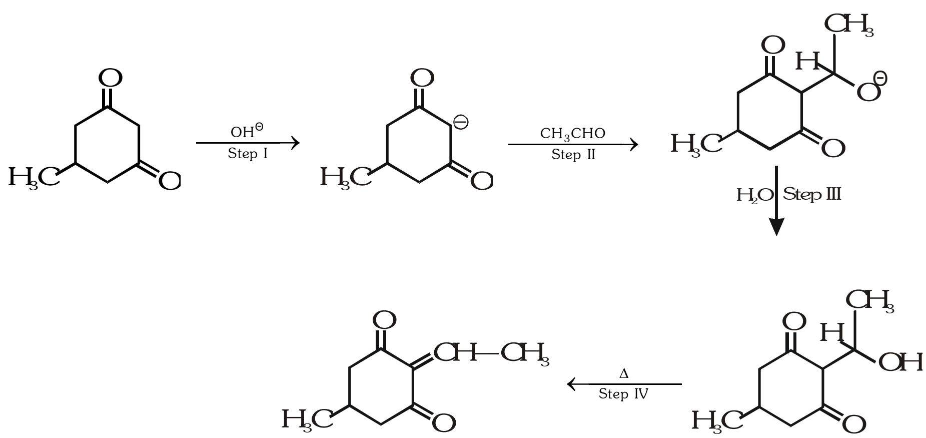
(B) Lone pair of oxygen atom participate in pπ–dπ bonding with phosphorous atom

(C) C–P bond is weaker as compare to C–C bond

(D) C–C bond is weaker as compare to C–O bond

Sol. (A), (B), (C)

Ex 7. Consider the following sequence :



Which of following statements are correct for above reaction sequence ?

(A) Step I is acid-base reaction

(B) Step II is nucleophilic addition reaction

(C) Step III is acid base reaction

(D) Step IV is elimination reaction

Sol. (A), (B), (C), (D)

Ex 8. Which of the following oxidation reaction can be carried out with chromic acid in aqueous acetone at 5–10 C.

(A) $CH_3(CH_2)_3C\equiv C-\underset{OH}{\underset{|}{C}H}-CH_3 \longrightarrow CH_3(CH_2)_3C\equiv C-\overset{O}{\overset{||}{C}}-CH_3$

(B) $CH_3(CH_2)_3CH=CH-CH_2OH \longrightarrow CH_3(CH_2)_3CH=CH-CHO$

(C) $C_6H_5CH_3 \longrightarrow C_6H_5COOH$

(D) $CH_3(CH_2)_3CH_2OH \longrightarrow CH_3(CH_2)_3CHO$

Sol. (A), (B), (C), (D)

Ex 9. $CH_3-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{SeO_2} A$; A will :

(A) Reduce Tollen's reagent

(B) Give iodoform test

(C) Form oxime

(D) Give Cannizaro reaction

Sol. SeO_2 oxidises – α – CH_2 – a w.r.t. keto group

∴ (A), (B), (C) and (D)

Ex 10. $3HCHO + CH_3CHO \xrightarrow{NaOH} A$. A found can

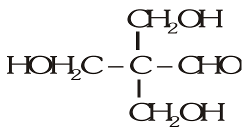
(A) Reduce Tollen's reagent

(B) Give Cannizaro reaction

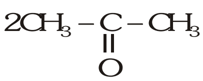
(C) React with Na

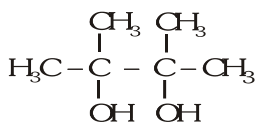
(D) Give green colour with $Cr_2O_7^{2-}/H^+$

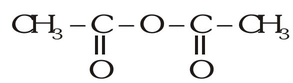
Sol. A is by aldol condensation

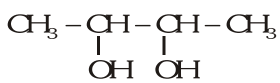


$\therefore$ (A), (B), (C) and (D)

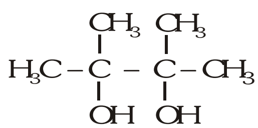
Ex 11.  $\xrightarrow[H^+]{Mg/Hg}$ Product, product in the reaction is :

(A) 

(B) 

(C) 

(D) None of these

Sol. (A) $2CH_3 - CO - CH_3 \xrightarrow[H_2O]{Mg/Hg}$ 

(Pinacol)

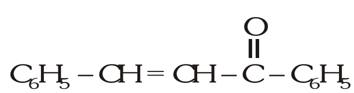
Ex 12. Benzaldehyde on reaction with acetophenone in the presence of sodium hydroxide solution gives :

(A) $C_6H_5CH = CHCOC_6H_5$

(B) $C_6H_5COCH_2C_6H_5$

(C) $C_6H_5CH = CHC_6H_5$

(D) $C_6H_5CH(OH)COC_6H_5$

Sol. (A) $C_6H_5CHO + CH_3COC_6H_5 \xrightarrow[-H_2O]{NaOH}$ 

Ex 13. Product in following reaction is :

$CH_3MgI + HCHO \rightarrow$ Product

(A) CH_3CHO

(B) CH_3OH

(C) C_2H_5OH

(D) $CH_3 - O - CH_3$

Sol. (C) $H - CHO + CH_3MgI \rightarrow CH_3 - CH_2 - OH +$