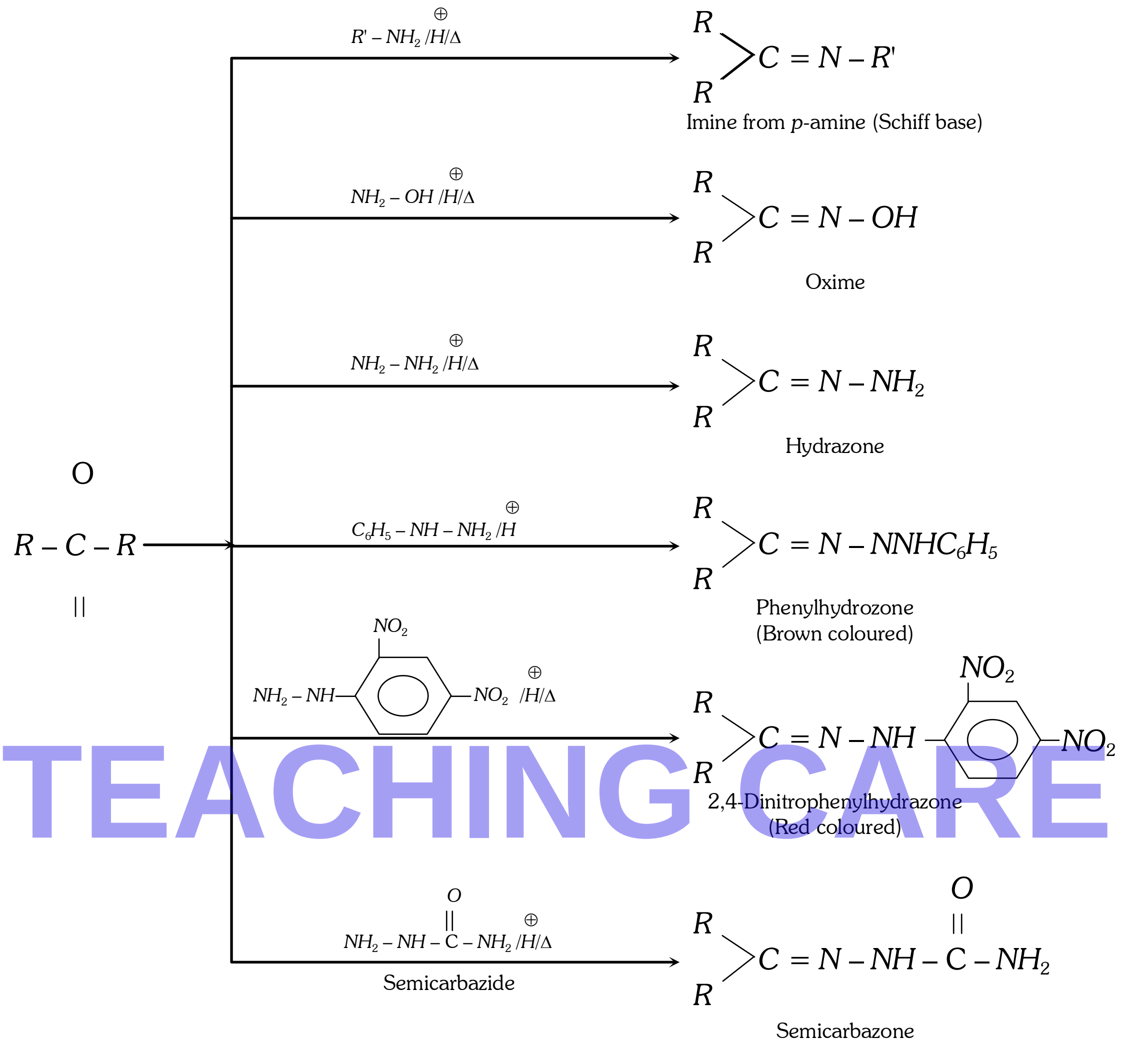
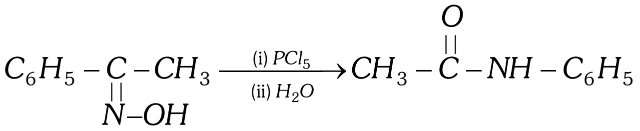
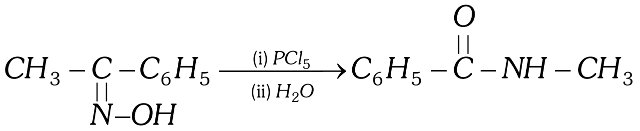
Different imine formation with NH_2-Z is given below



Ketoxime when treated with acid at 0°C it undergoes rearrangement known as **Beckmann rearrangement**. Thus acid catalysed conversion of ketoximes to N-substituted amides is called Beckmann rearrangement. Acid catalyst used are proton acids (H_2SO_4, HCl, H_3PO_4) and Lewis acids $(PCl_5, SOCl_2, PhSO_2Cl, RCOCl, SO_3, BF_3$ etc.)

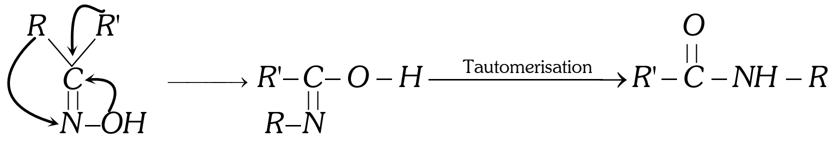


$$C_6H_5-\underset{\underset{N-OH}{||}}{C}-CH_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } PCl_5} CH_3-\overset{\overset{O}{||}}{C}-NH-C_6H_5$$



$$CH_3-\underset{\underset{N-OH}{||}}{C}-C_6H_5 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } PCl_5} C_6H_5-\overset{\overset{O}{||}}{C}-NH-CH_3$$

In short product of the rearrangement can be obtained as follows:



$$\overset{R\quad R'}{\underset{\underset{N-OH}{||}}{C}} \longrightarrow R'-\underset{\underset{R-N}{||}}{C}-O-H \xrightarrow{\text{Tautomerisation}} R'-\overset{\overset{O}{||}}{C}-NH-R$$

(3) **Oxidation of carbonyl compounds**

(i) ***Oxidation by mild oxidising agents*** **:** Mild oxidising agents oxidise only aldehydes into carboxylic acids. They do not oxidises ketones. Main oxidising agents are:

(a) *Fehling solution* : It is a mixture of two Fehling solution: Fehling solution No.1 : It contains $CuSO_4$ solution and $NaOH$.

Fehling solution No.2 **:** It contains sodium potassium tartrate. (Roschelle salt).

(b) *Benedict's solution* **:** This solution contains $CuSO_4, Na_2CO_3$ and sodium or potassium citrate.

✸ Reacting species of both solutions is Cu^{++} oxidation no. of Cu varies from 2 to 1.

✸These two oxidising agents oxidise only aliphatic aldehydes and have no effect on any other functional groups:

$$CH_3-CHO+Cu^{++}\xrightarrow[\text{reaction}]{\text{Redox}}CH_3COOH+\overset{\oplus}{Cu}\quad (\text{as } Cu_2O)\ (\text{red ppt.})$$

$$CH_2=CH-CHO\xrightarrow[\Delta]{Cu^{++}}CH_2=CH-COOH+Cu_2O$$

$$CH_2OH-(CHOH)_4-CHO\xrightarrow[\Delta]{Cu^{++}}CH_2OH-(CHOH)_4-COOH+Cu_2O$$

Benedict's solution and Fehling solutions are used as a reagent for the test of sugar (glucose) in blood sample.

(c) *Tollens reagent* : Tollens reagent is ammonical silver nitrate solution. Its reacting species is $Ag^{\oplus}$.

✸It oxidises aliphatic as well as aromatic aldehydes.

$$R-CHO+Ag^{\oplus}\xrightarrow[\text{reaction}]{\text{Redox}}RCOOH+Ag\ (\text{as silver mirror})$$

$$C_6H_5CHO+Ag^{\oplus}\longrightarrow C_6H_5COOH+Ag$$

✸This reagent has no effect on carbon-carbon multiple bond.

$$CH_2=CH-CHO+Ag^{\oplus}\longrightarrow CH_2=CH-COOH+Ag$$

$$C_6H_5-CH=CH-CHO+Ag^{\oplus}\longrightarrow C_6H_5-CH=CH-COOH+Ag$$

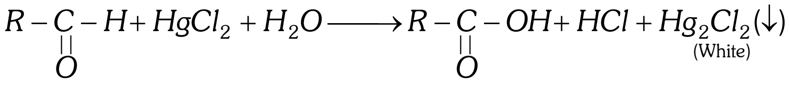
In this reaction the oxidation no. of Ag varies from $+1$ to 0.

Note : ✸ *Glucose, fructose give positive test with Tollen's reagents and Fehling solution.*

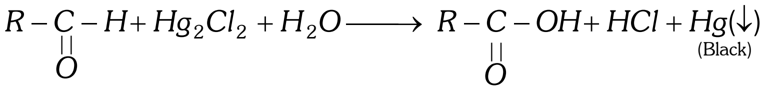
$$C_5H_{11}O_5CHO+Cu_2O\ (\text{or})\ Ag_2O\longrightarrow \underset{\text{Gluconic acid}}{C_5H_{11}O_5COOH}$$

Fructose contain $>C=O$ *(keto) group yet give positive test with Fehling solution due to presence of hydroxyl group. Tollens reagent also gives positive test with terminal alkynes and HCOOH.*

Reaction with mercuric chloride solution :



$$R-\underset{\underset{O}{||}}{C}-H+HgCl_2+H_2O\longrightarrow R-\underset{\underset{O}{||}}{C}-OH+HCl+\underset{\text{(White)}}{Hg_2Cl_2(\downarrow)}$$



$$R-\underset{\underset{O}{||}}{C}-H+Hg_2Cl_2+H_2O\longrightarrow R-\underset{\underset{O}{||}}{C}-OH+HCl+\underset{\text{(Black)}}{Hg(\downarrow)}$$

Schiff's reagent : Megenta dye $\xrightarrow{SO_2}$ colourless soln $\xrightarrow{CH_3CHO}$ pink colour restored.

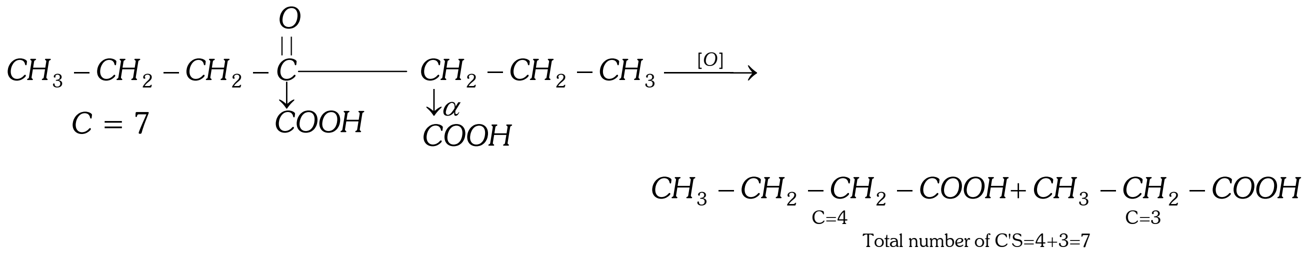
(ii) ***Oxidation by strong oxidising agents :*** Main strong oxidising agents are $KMnO_4/OH^{\ominus}/\Delta, KMnO_4/H^{\oplus}/\Delta, K_2Cr_2O_7/H^{\oplus}/\Delta$ and conc HNO_3/Δ. These agents oxidise aldehydes as well as ketones.

(a) *Oxidation of aldehydes* : Aldehydes are oxidised into corresponding acids.

$$\underset{C=n}{RCHO}\xrightarrow{[O]}\underset{C=n}{RCOOH}\,;\quad C_6H_5CHO\xrightarrow{KMnO_4/\overset{\ominus}{O}H/\Delta}C_6H_5COOH$$

(b) *Oxidation of ketones* : Ketones undergo oxidation only in drastic conditions. During the oxidation of ketones there is breaking of carbon-carbon bond between α-carbon and carbonyl carbon. In this process both carbons convert into carboxylic groups. This leads to the formation of two moles of monocarboxylic acids.

Case I : Oxidation of symmetrical ketones



$$CH_3-CH_2-CH_2-\underset{\underset{COOH}{\downarrow}}{\overset{\overset{O}{||}}{C}}\text{———}\underset{\underset{COOH}{\downarrow\alpha}}{CH_2}-CH_2-CH_3\xrightarrow{[O]}$$

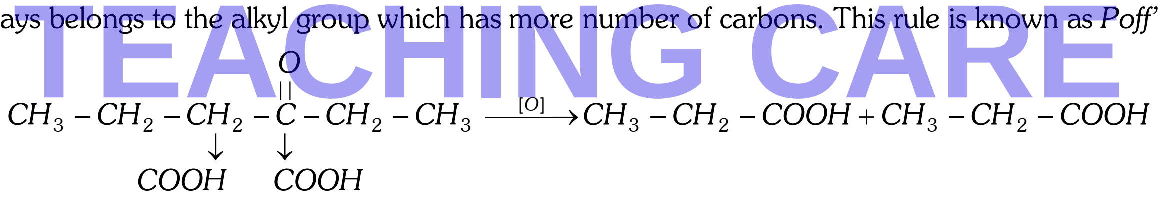
$C = 7$

$$\underset{C=4}{CH_3-CH_2-CH_2-COOH}+\underset{C=3}{CH_3-CH_2-COOH}$$

Total number of C'S=4+3=7

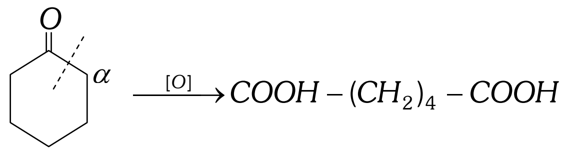
Thus number of carbons in any product is less than the number of carbons in ketone.

Case II : Oxidation of unsymmetrical ketones : In case of unsymmetrical ketones α-carbon whose bond breaks always belongs to the alkyl group which has more number of carbons. This rule is known as *Poff's rule*.



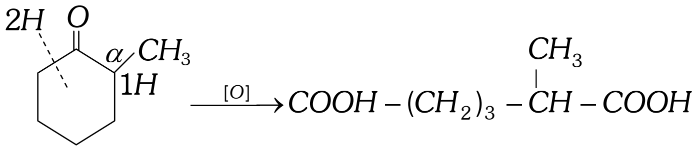
$$CH_3-CH_2-\underset{\underset{COOH}{\downarrow}}{CH_2}-\underset{\underset{COOH}{\downarrow}}{\overset{\overset{O}{||}}{C}}-CH_2-CH_3\xrightarrow{[O]}CH_3-CH_2-COOH+CH_3-CH_2-COOH$$

Case III : Oxidation of cyclic ketones : Formation of dibasic acid takes place from cyclic ketones. In this case number of carbons in ketone and dibasic carboxylic acid is always same.



$$\xrightarrow{[O]}COOH-(CH_2)_4-COOH$$

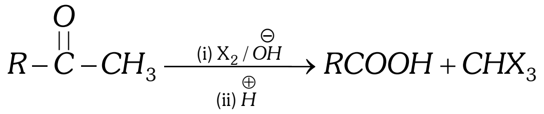
Note : ✹ *If both α-carbons are not identical then bond breaking takes place between carbonyl carbon and α-carbon which has maximum number of hydrogens.*



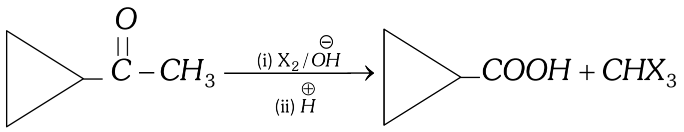
$$\xrightarrow{[O]}COOH-(CH_2)_3-\overset{\overset{CH_3}{|}}{CH}-COOH$$

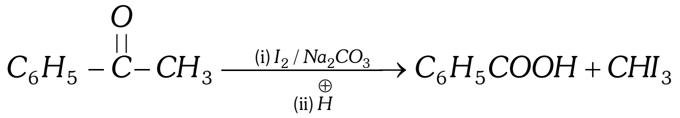
(iii) ***Miscellaneous oxidation***

(a) *Haloform Reaction* : In this reaction α-methyl carbonyl compounds undergo oxidation with $X_2/\overset{\ominus}{O}H$.



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

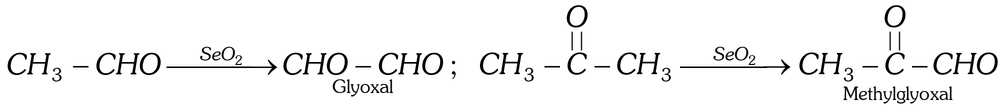




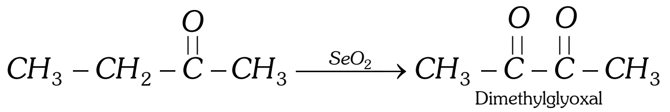
$$C_6H_5-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow[\text{(ii) } \overset{\oplus}{H}]{\text{(i) } I_2/Na_2CO_3} C_6H_5COOH+CHI_3$$

(b) *Oxidation at α-CH_2 or CH_3 by SeO_2* : SeO_2 oxidises $\alpha-CH_2-$group into keto group and $\alpha-CH_3-$group into aldehydic group.

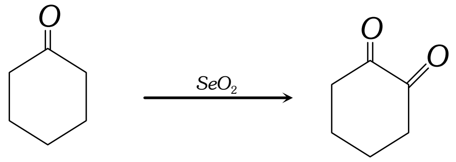
In this oxidation reactivity of CH_2 is more than the CH_3 group and Oxidation is regio selective in nature.



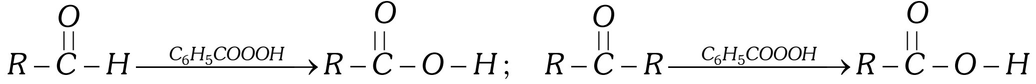
$$CH_3-CHO \xrightarrow{SeO_2} \underset{\text{Glyoxal}}{CHO-CHO};\quad CH_3-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{SeO_2} \underset{\text{Methylglyoxal}}{CH_3-\overset{\overset{O}{||}}{C}-CHO}$$



$$CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{SeO_2} \underset{\text{Dimethylglyoxal}}{CH_3-\overset{\overset{O}{||}}{C}-\overset{\overset{O}{||}}{C}-CH_3}$$



(c) *Oxidation by organic peracids* : Organic peracids oxidise aldehydes into carboxylic acids and ketones into esters. This oxidation is known as **Baeyer – Villiger oxidation**.

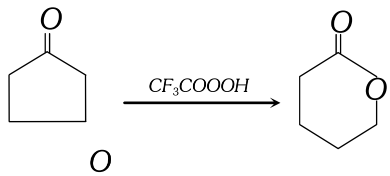


$$R-\overset{\overset{O}{||}}{C}-H \xrightarrow{C_6H_5COOOH} R-\overset{\overset{O}{||}}{C}-O-H;\quad R-\overset{\overset{O}{||}}{C}-R \xrightarrow{C_6H_5COOOH} R-\overset{\overset{O}{||}}{C}-O-H$$

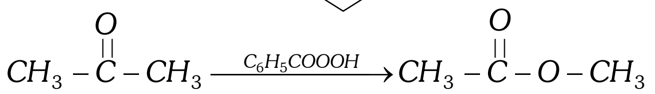
In case of aldehyde there is insertion of atomic oxygen (obtained from peracid) between carbonyl carbon and hydrogen of carbonyl carbon.

In case of ketone, insertion of oxygen takes place between carbonyl carbon and α-carbon. Thus the product is ester. This is one of the most important reaction for the conversion of ketones into esters.

Symmetrical ketones :



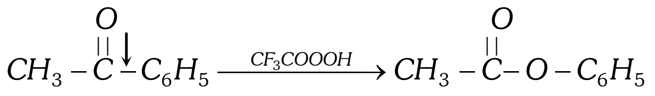
ε-Lactone



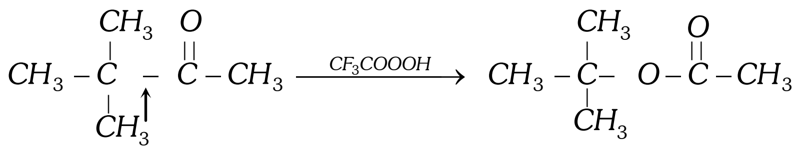
$$CH_3-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{C_6H_5COOOH} CH_3-\overset{\overset{O}{||}}{C}-O-CH_3$$

Unsymmetrical ketones : In case of unsymmetrical ketones preference of insertion in decreasing order is as

$H > 3°R > 2°R > Ph > 1°R > CH_3$

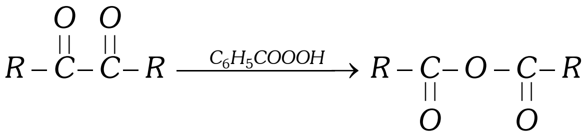


$$CH_3-\overset{\overset{O}{||}}{C}\downarrow-C_6H_5 \xrightarrow{CF_3COOOH} CH_3-\overset{\overset{O}{||}}{C}-O-C_6H_5$$



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\overset{}{\underset{\uparrow}{-}}\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{CF_3COOOH} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-\overset{\overset{O}{||}}{C}-CH_3$$

Note : ✹ Vic dicarbonyl compound also undergo oxidation & product is anhydride.

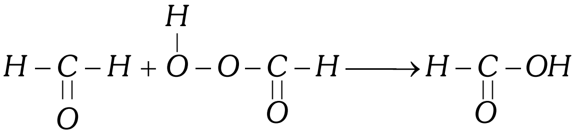


$$R-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-R \xrightarrow{C_6H_5COOOH} R-\underset{O}{\underset{||}{C}}-O-\underset{O}{\underset{||}{C}}-R$$

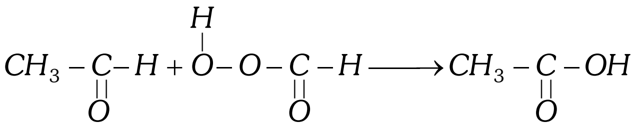
✹ *Popoff's rule : Oxidation of unsymmetrical ketones largely take place in such a way that the smaller alkyl group remains attached to the CO group during the formation of two molecules of acids. This is known as Popoff's rule*

Example : $CH_3-CO-CH_2-CH_3 \xrightarrow{[O]} CH_3-COOH+HOOCCH_3$

(d) *Baeyer- villiger oxidation :*



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

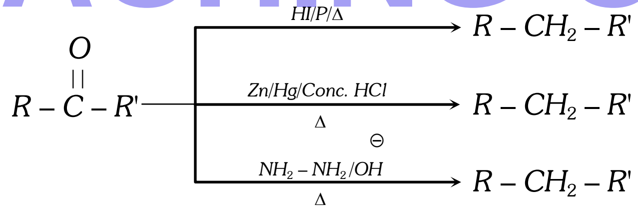


$$CH_3-\underset{O}{\underset{||}{C}}-H+\overset{H}{\overset{|}{O}}-O-\underset{O}{\underset{||}{C}}-H \longrightarrow CH_3-\underset{O}{\underset{||}{C}}-OH$$

Note : ✹ *Reaction will be held if the oxidation agent is performic acid.*

(4) Reuction of carbonyl compounds

(i) ***Reduction of*** $-\overset{O}{\overset{||}{C}}-$ ***group into*** $-CH_2-$ ***group :*** Following three reagents reduce carbonyl group into $-CH_2-$ groups: (a) $HI/P/\Delta$ (b) $Zn/Hg/Conc.\ HCl$ and (c) $NH_2-NH_2/\overset{\ominus}{O}H$.



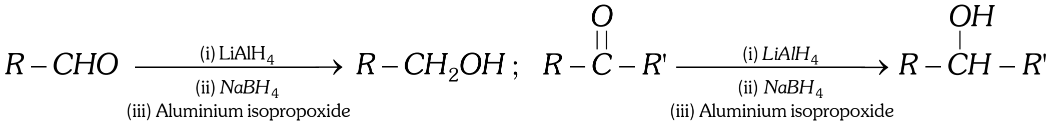
$$R-\overset{O}{\overset{||}{C}}-R' \xrightarrow{HI/P/\Delta} R-CH_2-R'$$

$$R-\overset{O}{\overset{||}{C}}-R' \xrightarrow[\Delta]{Zn/Hg/Conc.\ HCl} R-CH_2-R'$$

(Clemmensen reduction)

$$R-\overset{O}{\overset{||}{C}}-R' \xrightarrow[\Delta]{NH_2-NH_2/\overset{\ominus}{O}H} R-CH_2-R'$$

(ii) ***Reduction of carbonyl compounds into hydroxy compounds :*** Carbonyl group converts into $-CHOH-$ group by $LiAlH_4, NaBH_4, Na/C_2H_5OH$ and aluminium isopropoxide.



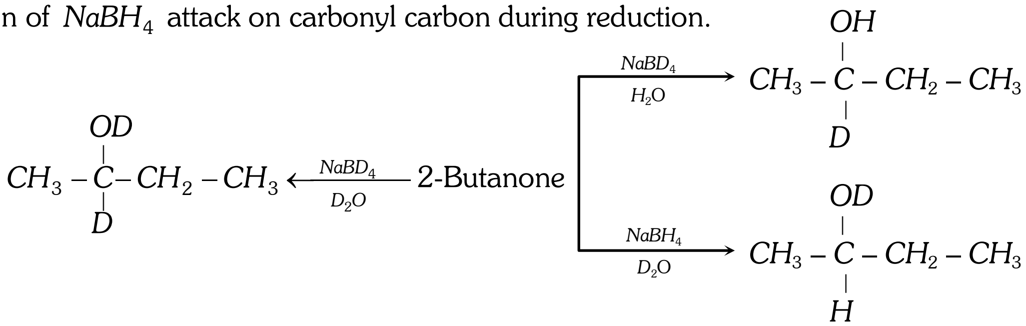
$$R-CHO \xrightarrow[\text{(ii) } NaBH_4 \text{ (iii) Aluminium isopropoxide}]{\text{(i) } LiAlH_4} R-CH_2OH;\quad R-\overset{O}{\overset{||}{C}}-R' \xrightarrow[\text{(ii) } NaBH_4 \text{ (iii) Aluminium isopropoxide}]{\text{(i) } LiAlH_4} R-\overset{OH}{\overset{|}{C}H}-R'$$

$NaBH_4$ is regioselective reducing agent because it reduced only. CHO in the presence of other reducible group.

Example : $CH_3-CH=CH-CHO \xrightarrow{NaBH_4} CH_3-CH=CH-CH_2OH$

Hydride ion of $NaBH_4$ attack on carbonyl carbon during reduction.

Example :

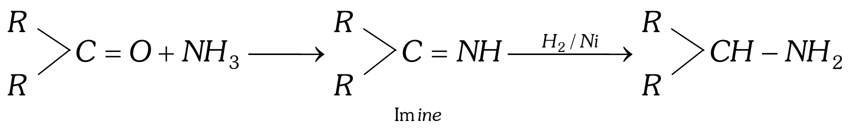


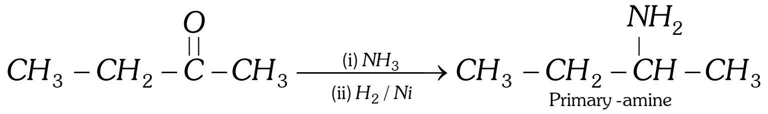
$$CH_3-\underset{D}{\underset{|}{\overset{OD}{\overset{|}{C}}}}-CH_2-CH_3 \xleftarrow[D_2O]{NaBD_4} \text{2-Butanone}$$

$$\text{2-Butanone} \xrightarrow[H_2O]{NaBD_4} CH_3-\underset{D}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-CH_3$$

$$\text{2-Butanone} \xrightarrow[D_2O]{NaBH_4} CH_3-\underset{H}{\underset{|}{\overset{OD}{\overset{|}{C}}}}-CH_2-CH_3$$

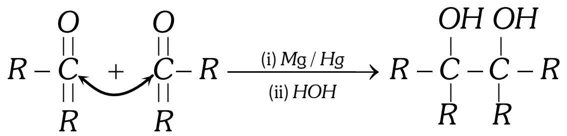
(iii) ***Reductive amination :*** In this reduction $-CO-$ group converts into $-CH-NH_2$ group as follows:





$$CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow[\text{(ii) } H_2/Ni]{\text{(i) } NH_3} \underset{\text{Primary -amine}}{CH_3-CH_2-\overset{\overset{NH_2}{|}}{CH}-CH_3}$$

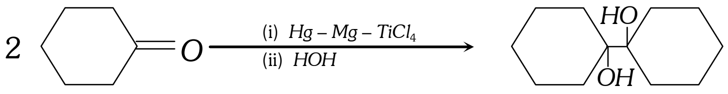
(iv) ***Reduction of ketones by Mg or Mg/Hg :*** In this case ketones undergo reduction via coupling reaction and product is vic *cis* diol.



$$R-\underset{\underset{R}{||}}{\overset{\overset{O}{||}}{C}} + \underset{\underset{R}{||}}{\overset{\overset{O}{||}}{C}}-R \xrightarrow[\text{(ii) } HOH]{\text{(i) } Mg/Hg} R-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-R$$

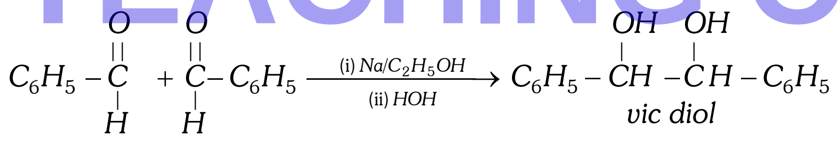
Vic *cis* diol

When this reaction is carried out in the presence of $Mg/Hg/TiCl_4$, the product is vic *trans* diol.



Vic trans diol

(v) ***Reduction of benzaldehyde by Na/C₂H₅OH :*** Benzaldehyde undergoes reduction via coupling reaction and product is vic diol.

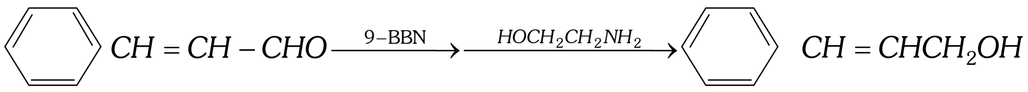


$$C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{O}{||}}{C}} + \underset{\underset{H}{|}}{\overset{\overset{O}{||}}{C}}-C_6H_5 \xrightarrow[\text{(ii) } HOH]{\text{(i) } Na/C_2H_5OH} C_6H_5-\overset{\overset{OH}{|}}{CH}-\overset{\overset{OH}{|}}{CH}-C_6H_5$$

vic diol (Bouveault-blanc reaction)

Note : ✹ *Aldehydes are reduced to 1° alcohols whereas ketones to 2° alcohols. If carbon – carbon double bond is also present in the carbonyl compound, it is also reduced alongwith. However, the use of the reagent 9-BBN (9–borabicyclo (3, 3, 1) nonane) prevents this and thus only the carbonyl group is reduced*

Example :



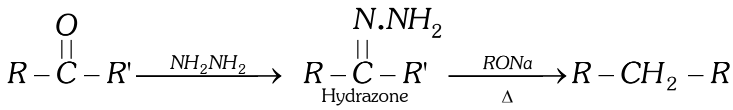
Cinnamaldehyde Cinnamyl alcohol

✹ *If reducing agent is NaH, reaction is called Darzen's reaction, we can also use* $LiAlH_4$ *in this reaction.*

✹ *If reducing agent is aluminium iso propoxide* $(CH_3-\underset{\underset{CH_3}{|}}{CH}-O-)_3Al$. *Product will be alcohol. This reaction is called Meerwein – pondorff verley reduction (MPV reduction).*

✹ *The percentage yield of alkanes can be increased by using diethylene glycol in Wolf Kishner reduction. Then reaction is called Huang – Millan conversion.*

(vi) Hydrazones when treated with base like alkoxide give hydrocarbon (Wolf – Kishner reduction).



$$R-\overset{\overset{O}{||}}{C}-R' \xrightarrow{NH_2NH_2} \underset{\text{Hydrazone}}{R-\overset{\overset{N.NH_2}{||}}{C}-R'} \xrightarrow[\Delta]{RONa} R-CH_2-R$$

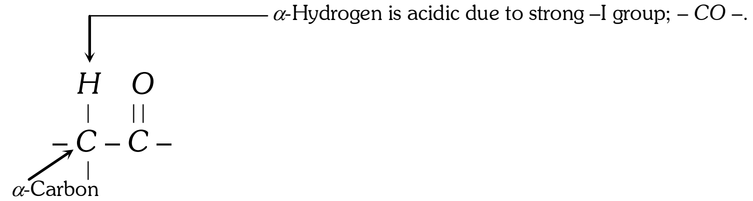
(vii) Schiff's base on reduction gives secondary amines.

$$R-CH=O\xrightarrow{R'NH_2}\underset{\text{Schiff's base}}{R-CH=NR'}\xrightarrow{H_2/Ni}R-CH_2NHR$$

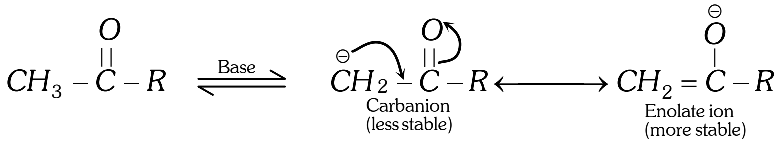
(5) Reactions due to α-hydrogen

(i) *Acidity of α-hydrogens* :

(a) α-hydrogen of carbonyl compounds are acidic in character due to the presence of the electron withdrawing $-CO-$ group.



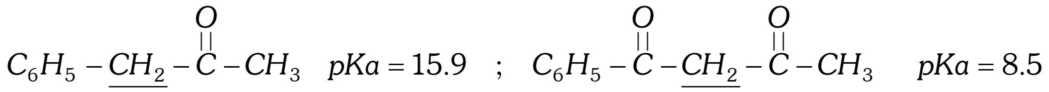
(b) Thus carbonyl compounds having α-hydrogen convert into carbanions in the presence of base. This carbanion is stabilised by delocalisation of negative charge.



$$CH_3-\overset{O}{\overset{||}{C}}-R \xrightleftharpoons{\text{Base}} \underset{\substack{\text{Carbanion}\\\text{(less stable)}}}{\overset{\ominus}{C}H_2-\overset{O}{\overset{||}{C}}-R} \longleftrightarrow \underset{\substack{\text{Enolate ion}\\\text{(more stable)}}}{CH_2=\overset{\overset{\ominus}{O}}{\overset{|}{C}}-R}$$

(c) The acidity of α-hydrogen is more than ethyne. *pKa* value of aldehydes and ketones are generally 19 – 20 where as *pKa* value of ethyne is 25.

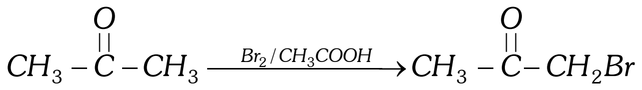
(d) Compounds having active methylene or methyne group are even more acidic than simple aldehydes and ketones.



$$C_6H_5-\underline{CH_2}-\overset{O}{\overset{||}{C}}-CH_3\quad pKa=15.9\quad;\quad C_6H_5-\overset{O}{\overset{||}{C}}-\underline{CH_2}-\overset{O}{\overset{||}{C}}-CH_3\quad pKa=8.5$$

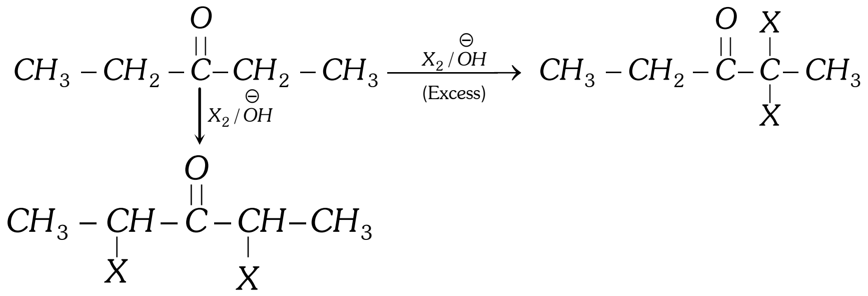
(ii) ***Halogenation*** **:** Carbonyl compounds having α-hydrogens undergo halogenation reactions. This reaction is catalysed by acid as well as base.

(a) *Acid catalysed halogenation* : This gives only monohalo derivative.



$$CH_3-\overset{O}{\overset{||}{C}}-CH_3\xrightarrow{Br_2/CH_3COOH}CH_3-\overset{O}{\overset{||}{C}}-CH_2Br$$

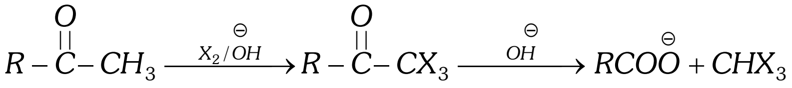
(b) *Base catalysed halogenation* : In the presence of base all α-hydrogens of the same carbon is replaced by halogens.



$$CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_2-CH_3\xrightarrow[\text{(Excess)}]{X_2/\overset{\ominus}{O}H}CH_3-CH_2-\overset{O}{\overset{||}{C}}-\underset{X}{\overset{X}{C}}-CH_3$$

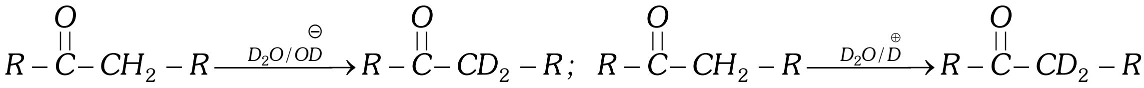
$$CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_2-CH_3\xrightarrow{X_2/\overset{\ominus}{O}H}CH_3-\underset{X}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-\underset{X}{\underset{|}{CH}}-CH_3$$

Carbonyl compounds having three α-hydrogens give **haloform** reaction.



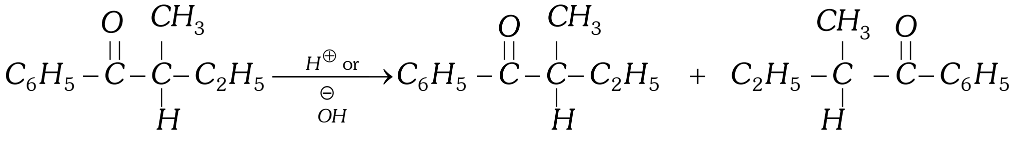
$$R-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{X_2/\overset{\ominus}{O}H} R-\overset{O}{\overset{||}{C}}-CX_3 \xrightarrow{\overset{\ominus}{O}H} RCO\overset{\ominus}{O}+CHX_3$$

(iii) ***Deuterium exchange reaction*** **:** Deuterium exchange reaction is catalysed by acid $(D^{\oplus})$ as well as base $(\overset{\ominus}{O}D)$. In both the cases all the hydrogens on only one α-carbon is replaced by D.



$$R-\overset{O}{\overset{||}{C}}-CH_2-R \xrightarrow{D_2O/\overset{\ominus}{O}D} R-\overset{O}{\overset{||}{C}}-CD_2-R;\quad R-\overset{O}{\overset{||}{C}}-CH_2-R \xrightarrow{D_2O/\overset{\oplus}{D}} R-\overset{O}{\overset{||}{C}}-CD_2-R$$

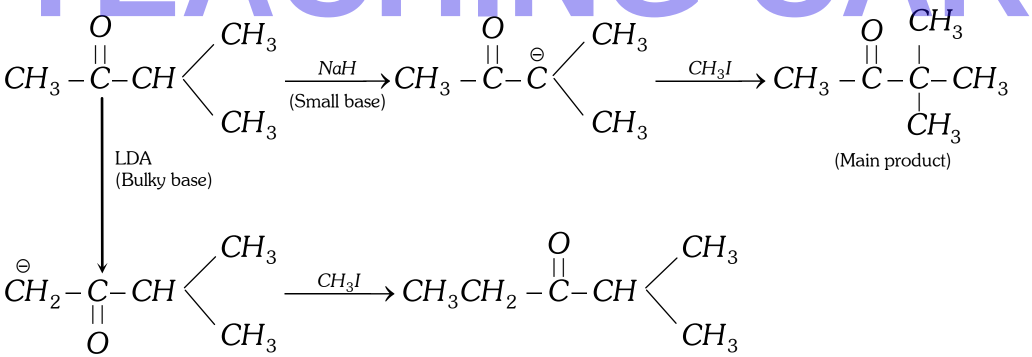
(iv) ***Racemisation*** **:** Ketones whose α-carbon is chiral undergo Racemisation in the presence of acid as well as base.



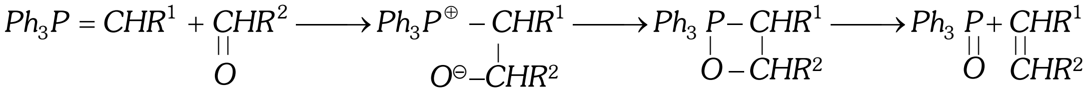
$$C_6H_5-\overset{O}{\overset{||}{C}}-\underset{H}{\overset{CH_3}{C}}-C_2H_5 \xrightarrow[\overset{\ominus}{O}H]{H^{\oplus}\text{ or}} C_6H_5-\overset{O}{\overset{||}{C}}-\underset{H}{\overset{CH_3}{C}}-C_2H_5 + C_2H_5-\underset{H}{\overset{CH_3}{C}}-\overset{O}{\overset{||}{C}}-C_6H_5$$

Racemic mixture

(v) ***Alkylation*** **:** Carbonyl compounds having α-hydrogens undergo alkylation reaction with RX in the presence of base. This reaction is SN^2 reaction. The best result is obtained with CH_3-X. Other halides undergo elimination in the presence of strong base.



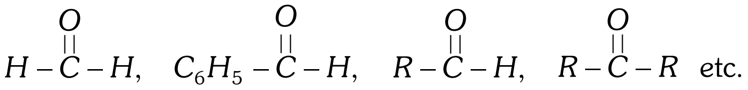
(vi) ***Wittig reaction*** **:** Aldehyde and ketones undergo the wittig reaction to form alkenes.



$$Ph_3P=CHR^1+\underset{O}{\underset{||}{C}}HR^2 \longrightarrow Ph_3P^{\oplus}-\underset{O^{\ominus}-CHR^2}{\underset{|}{CHR^1}} \longrightarrow Ph_3\,\underset{O-CHR^2}{\underset{|\quad\;\;|}{P-CHR^1}} \longrightarrow Ph_3\,\underset{O}{\underset{||}{P}}+\underset{CHR^2}{\underset{||}{CHR^1}}$$

(6) **Condensation reaction of carbonyl compounds :** Nucleophilic addition reaction of compounds having carbonyl group with those compounds which have at least one acidic hydrogen at α-carbon is known as condensation reaction. In this addition reaction :

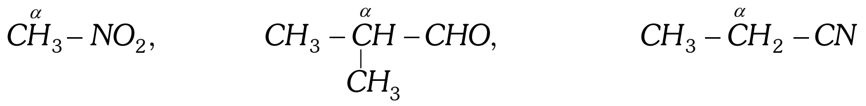
Substrate is always an organic compound having a carbonyl group, *e.g.*



$$H-\overset{O}{\overset{||}{C}}-H,\quad C_6H_5-\overset{O}{\overset{||}{C}}-H,\quad R-\overset{O}{\overset{||}{C}}-H,\quad R-\overset{O}{\overset{||}{C}}-R\ \text{ etc.}$$

Addition always takes place on the carbonyl group.

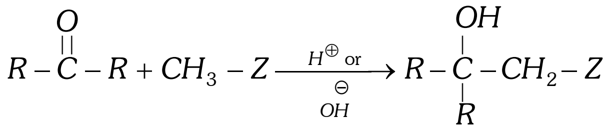
Reagents of the condensation reaction are also organic compounds having at least one hydrogen on α-carbon and α-carbon should have –I group, *e.g.*



$$\overset{\alpha}{C}H_3-NO_2,\qquad CH_3-\underset{\underset{CH_3}{|}}{\overset{\alpha}{C}H}-CHO,\qquad CH_3-\overset{\alpha}{C}H_2-CN$$

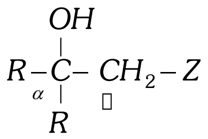
Note : ✸ *If substrate and reagent both are carbonyl compounds then one should have at least one α-hydrogen and other may or may not have α-hydrogen.*

Condensation reaction always takes place in the presence of acid or base as catalyst. Best result is obtained with base at lower temp.



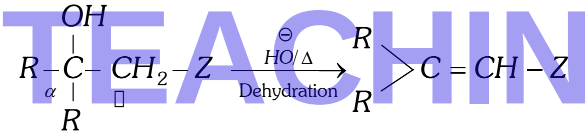
$$R-\overset{\overset{O}{||}}{C}-R+CH_3-Z\xrightarrow[\overset{\ominus}{O}H]{H^{\oplus}\text{ or}}R-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-Z$$

Condensation is carried out at lower temperature $(\le 20°C)$ because product of the reaction is alcohol which has strong –I group at β-carbon.



$$R-\underset{\alpha\ \underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\beta}{CH_2}-Z$$

Such type of alcohols are highly reactive for dehydration. They undergo dehydration in the presence of acid as well as base even at 25°C. They also undergo elimination even on strong heating.



$$R-\underset{\alpha\ \underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\beta}{CH_2}-Z\xrightarrow[\text{Dehydration}]{\overset{\ominus}{HO}/\Delta}\begin{matrix}R\\R\end{matrix}\!\!>C=CH-Z$$

(i) ***Aldol condensation***

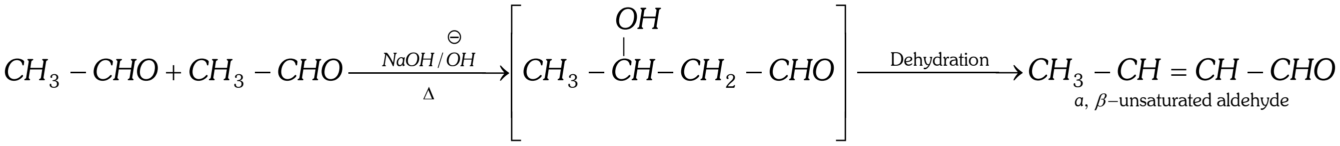
(a) This reaction takes place between two molecules of carbonyl compounds; one molecule should have at least two α-hydrogen atoms. In this reaction best result is obtained when

Both molecule are the same or

One should have no α-hydrogen atom and other should have at least two α-hydrogens.

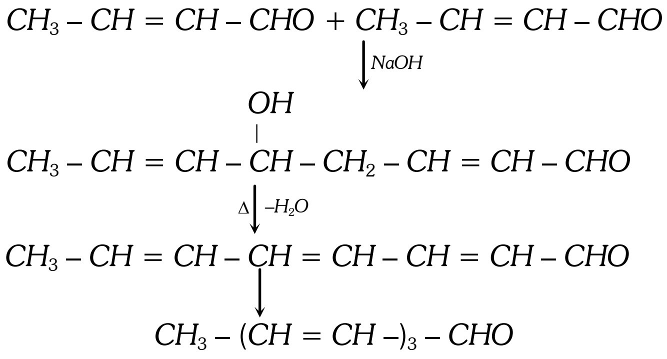
(b) These reactions are practical when base is $NaOH$ and reaction temperature is high $(\ge 100°)$.

(c) The reaction is two step reaction. First step is aldol formation and second step is dehydration of aldol.



$$CH_3-CHO+CH_3-CHO\xrightarrow[\Delta]{NaOH/\overset{\ominus}{OH}}\left[CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-CHO\right]\xrightarrow{\text{Dehydration}}\underset{\alpha,\ \beta\text{–unsaturated aldehyde}}{CH_3-CH=CH-CHO}$$

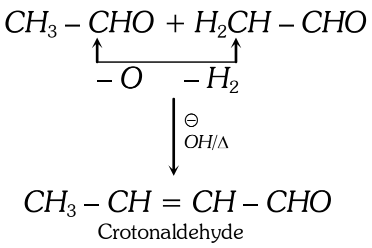
Due to hyper conjugation in crotonaldehyde further condensed give conjugated alkene carbonyl compound.



$$\begin{gathered}CH_3-CH=CH-CHO+CH_3-CH=CH-CHO\\ \Big\downarrow{\scriptstyle NaOH}\\ CH_3-CH=CH-\overset{\overset{OH}{|}}{CH}-CH_2-CH=CH-CHO\\ {\scriptstyle\Delta}\Big\downarrow{\scriptstyle -H_2O}\\ CH_3-CH=CH-CH=CH-CH=CH-CHO\\ \Big\downarrow\\ CH_3-(CH=CH-)_3-CHO\end{gathered}$$

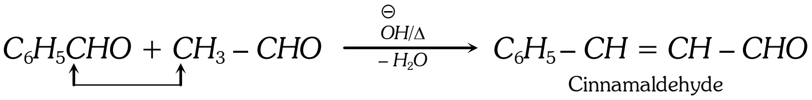
Condensed compound

The net result can be written as follows]



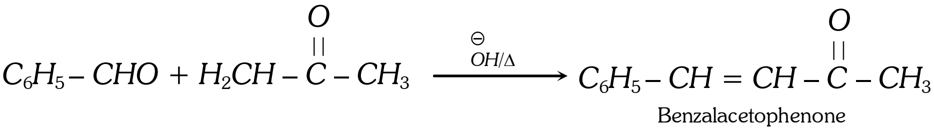
$$\underset{-O}{CH_3-CHO} + \underset{-H_2}{H_2CH-CHO} \xrightarrow{\overset{\ominus}{O}H/\Delta} CH_3-CH=CH-CHO$$

Crotonaldehyde



$$C_6H_5CHO + CH_3-CHO \xrightarrow[-H_2O]{\overset{\ominus}{O}H/\Delta} C_6H_5-CH=CH-CHO$$

Cinnamaldehyde



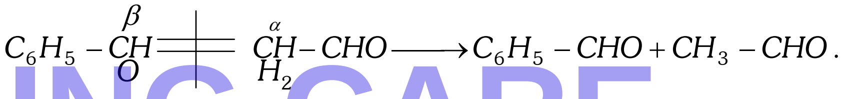
$$C_6H_5-CHO + H_2CH-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{\overset{\ominus}{O}H/\Delta} C_6H_5-CH=CH-\overset{O}{\overset{||}{C}}-CH_3$$

Benzalacetophenone

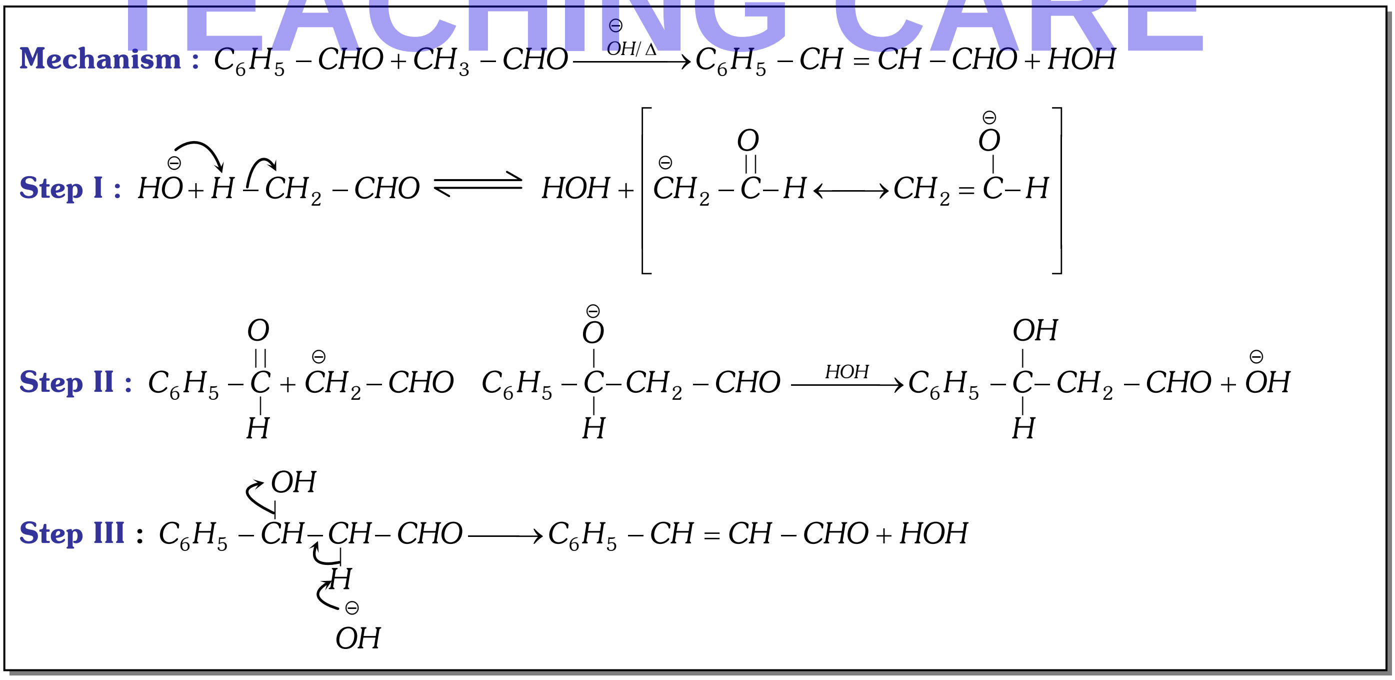
Note : ✹ *If product is given then reactants can be known as follows :*

Suppose structure of product is $C_6H_5-\overset{\beta}{C}H=\overset{\alpha}{C}H-CHO$

Break carbon-carbon double bond between α *and* β *carbons and attach two hydrogens on* α*-carbon and an oxygen on* β*-carbon, i.e.*



$$C_6H_5-\underset{O}{\overset{\beta}{CH}}\,\cancel{=}\,\underset{H_2}{\overset{\alpha}{C}}H-CHO \longrightarrow C_6H_5-CHO+CH_3-CHO.$$



Mechanism : $C_6H_5-CHO+CH_3-CHO \xrightarrow{\overset{\ominus}{O}H/\Delta} C_6H_5-CH=CH-CHO+HOH$

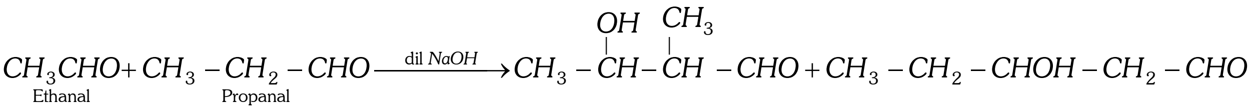
Step I : $\overset{\ominus}{HO}+H-CH_2-CHO \rightleftharpoons HOH+\left[\overset{\ominus}{C}H_2-\overset{O}{\overset{||}{C}}-H \longleftrightarrow CH_2=\overset{\overset{\ominus}{O}}{\overset{|}{C}}-H\right]$

Step II : $C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{O}{||}}{C}}+\overset{\ominus}{C}H_2-CHO \quad C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{\ominus}{O}}{\overset{|}{C}}}-CH_2-CHO \xrightarrow{HOH} C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CHO+\overset{\ominus}{O}H$

Step III : $C_6H_5-\overset{OH}{CH}-\underset{\underset{\overset{\ominus}{O}H}{H}}{\underset{|}{CH}}-CHO \longrightarrow C_6H_5-CH=CH-CHO+HOH$

In aldol condensation, dehydration occurs readily because the double bond that forms is conjugated, both with the carbonyl group and with the benzene ring. The conjugation system is thereby extended.

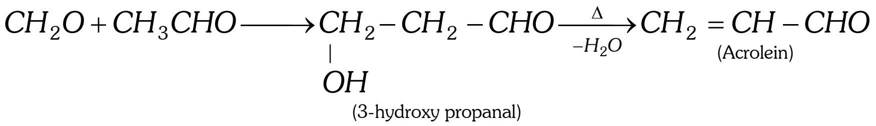
Crossed aldol condensation : Aldol condensation between two different aldehydes or two different ketones or one aldehyde and another ketone provided al teast one of the components have α-hydrogen atom gives different possible product

(a) 

$$CH_3CHO + CH_3-CH_2-CHO \xrightarrow{\text{dil } NaOH} CH_3-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CHO + CH_3-CH_2-CHOH-CH_2-CHO$$

Ethanal Propanal

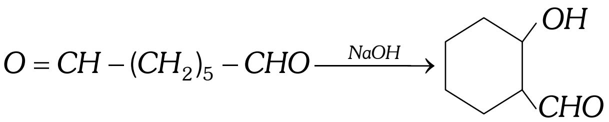
However crossed aldol condensation is important when only it the components has α-hydrogen atom.



$$CH_2O + CH_3CHO \longrightarrow \underset{\underset{OH}{|}}{CH_2}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_2=CH-CHO$$

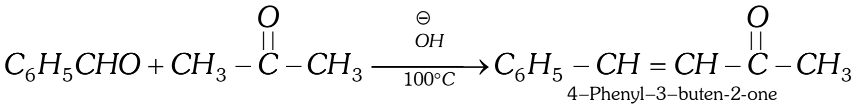
(3-hydroxy propanal) (Acrolein)

Intra molecular aldol condensation : One molecule Intramolecular condensed give aldol compounds

Example : 

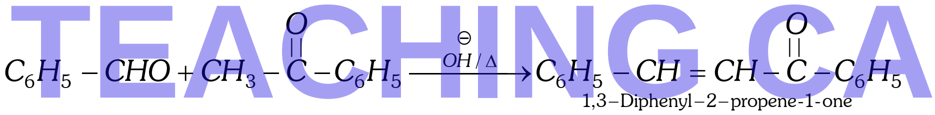
$$O=CH-(CH_2)_5-CHO \xrightarrow{NaOH}$$

(ii) ***Claisen – Schmidt reaction :*** Crossed aldol condensation between aromatic aldehyde and aliphatic ketone or mixed ketone is known as Claisen – Schmidt reaction. Claisen – Schmidt reactions are useful when bases such as sodium hydroxide are used because under there conditions ketones do not undergo self condensation. Some examples of this reaction are :



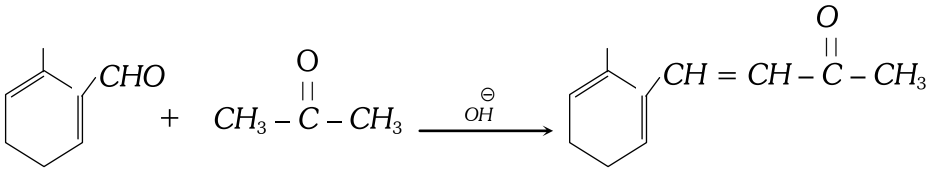
$$C_6H_5CHO + CH_3-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow[100°C]{\overset{\ominus}{OH}} C_6H_5-CH=CH-\overset{O}{\overset{||}{C}}-CH_3$$

4–Phenyl–3–buten-2-one



$$C_6H_5-CHO + CH_3-\overset{O}{\overset{||}{C}}-C_6H_5 \xrightarrow{\overset{\ominus}{OH}/\Delta} C_6H_5-CH=CH-\overset{O}{\overset{||}{C}}-C_6H_5$$

1,3–Diphenyl–2–propene-1-one



Geranial Pesudoionone

Test of aldehydes and Ketones (Distinction).

	Test	Aldehydes	Ketones
1.	With Schiff's reagent	Give pink colour.	No colour.
2.	With Fehling's solution	Give red precipitate.	No precipitate is formed.
3.	With Tollen's reagent	Black precipitate of silver mirror is formed.	No black precipitate or silver mirror is formed.
4.	With saturated sodium bisulphite solution in water	Crystalline compound (colourless) is formed.	Crystalline compound (colourless) is formed.
5.	With 2 : 4-dinitrophenyl hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.
6.	With sodium hydroxide	Give brown resinous mass (formaldehyde does not give this test).	No reaction.
7.	With sodium nitroprusside and few drops of sodium hydroxide	A deep red colour (formaldehyde does not respond to this test).	Red colour which changes to orange.

Some commercially important aliphatic carbonyl compounds.

Formaldehyde : Formaldehyde is the first member of the aldehyde series. It is present in green leaves of plants where its presence is supposed to be due to the reaction of CO_2 with water in presence of sunlight and chlorophyll.

$$CO_2 + H_2O \longrightarrow HCHO + O_2$$

Traces of formaldehyde are formed when incomplete combustion of wood, sugar, coal, etc., occurs.

(1) Preparation

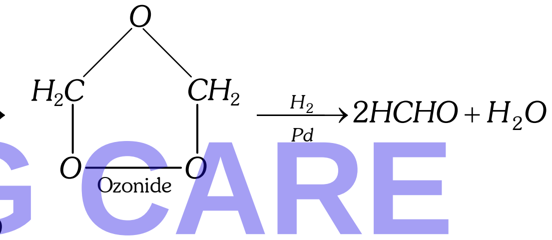
(i) ***By oxidation of methyl alcohol*** $2CH_3OH + O_2 \xrightarrow[300-400°C]{\text{Platinised asbestos}} 2HCHO + 2H_2O$

$$CH_3OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} HCHO + H_2O$$

(ii) ***By dehydrogenation of methyl alcohol*** $CH_3OH \xrightarrow[300-400°C]{Cu \text{ or } Ag} HCHO + H_2$

(iii) ***By heating calcium formate :*** $\underset{\text{Calcium formate}}{Ca(HCOO)_2} \xrightarrow{\text{Heat}} CaCO_3 + \underset{\text{Formaldehyde}}{HCHO}$

(iv) ***By ozonolysis of ethylene :*** $CH_2 = CH_2 + O_3 \longrightarrow$



(v) ***Manufacture :*** $\underset{\text{Methane}}{CH_4} + O_2 \xrightarrow[\text{Catalyst}]{\text{Mo-oxide}} \underset{\text{Formaldehyde}}{HCHO} + H_2O$

It is also prepared by passing water gas at low pressure through an electric discharge of low intensity.

$$CO + H_2 \xrightarrow{\text{Elec. discharge}} HCHO$$

(2) Physical properties

(i) It is a colourless, pungent smelling gas.

(ii) It is extremely soluble in water. Its solubility in water may be due to hydrogen bonding between water molecules and its hydrate.

(iii) It can easily be condensed into liquid. The liquid formaldehyde boils at – 21°C.

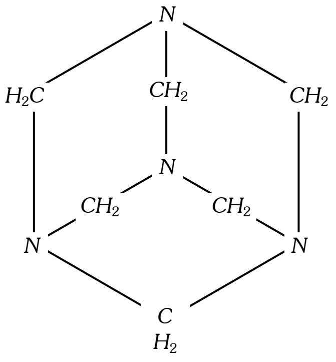
(iv) It causes irritation to skin, eyes, nose and throat.

(v) Its solution acts as antiseptic and disinfectant.

(3) Chemical properties : Formaldehyde is structurally different from other aldehydes as it contains no alkyl group in the molecule. Though it shows general properties of aldehydes, it differs in certain respects. The abnormal properties of formaldehyde are given below

(i) ***Reaction with ammonia :*** Like other aldehydes, formaldehyde does not form additon product but a crystalline compound, hexamethylene tetramine, with ammonia.

$$\underset{\text{Formaldehyde}}{6HCHO} + 4NH_3 \longrightarrow \underset{\substack{\text{Urotropine} \\ \text{(Hexamethylene tetramine)}}}{(CH_2)_6N_4} + 6H_2O$$



Urotropine

Hexamethylene tetramine has a cyclic structure. It is used as medicine in case of urinary troubles under the name of **Urotropine** or hexamine.

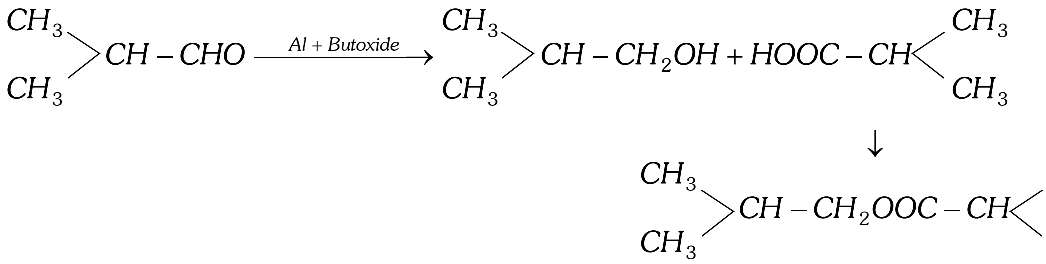
(ii) ***Reaction with sodium hydroxide (Cannizzaro's reaction) :*** It does not form resin with sodium hydroxide like acetaldehyde but when treated with a concentrated solution of sodium hydroxide, two molecules of formaldehyde undergo mutual oxidation and reduction forming formic acid salt and methyl alcohol (Disproportionation).

$$\underset{\text{Formaldehyde}}{2HCHO} + NaOH \longrightarrow \underset{\text{Sod. Formate}}{HCOONa} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

This transformation is known as Cannizzaro's reaction.

Tischenko's reaction : This is a modified form of cannizzaro's reaction. All aldehydes undergo cannizzaro's reaction in presence of aluminium ethoxide. The acid and alcohol formed react together to give the ester.

$$2CH_3CHO \xrightarrow{(C_2H_5O)_3\,Al} [CH_3COOH + C_2H_5OH] \longrightarrow \underset{\text{Ethyl acetate}}{[CH_3COOC_2H_5]}$$

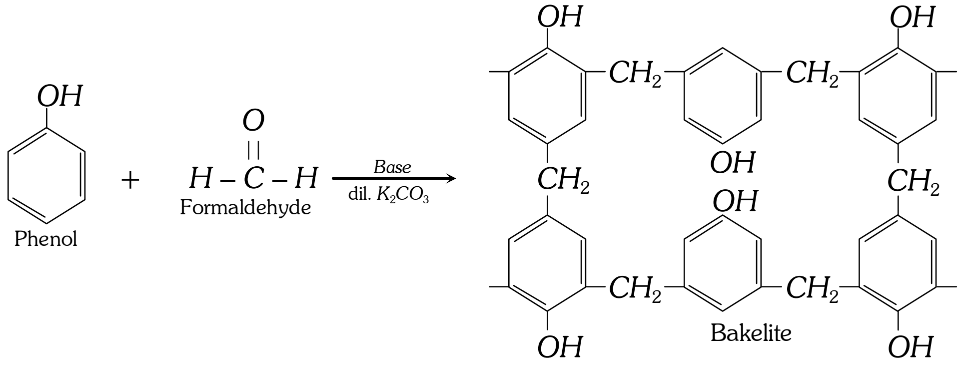


$$(CH_3)_2CH-CHO \xrightarrow{Al + Butoxide} (CH_3)_2CH-CH_2OH + HOOC-CH(CH_3)_2 \longrightarrow (CH_3)_2CH-CH_2OOC-CH(CH_3)_2$$

(iii) ***Aldol condensation :*** Formaldehyde in presence of a weak base undergo repeated aldol condensation to give formose (α- acrose).

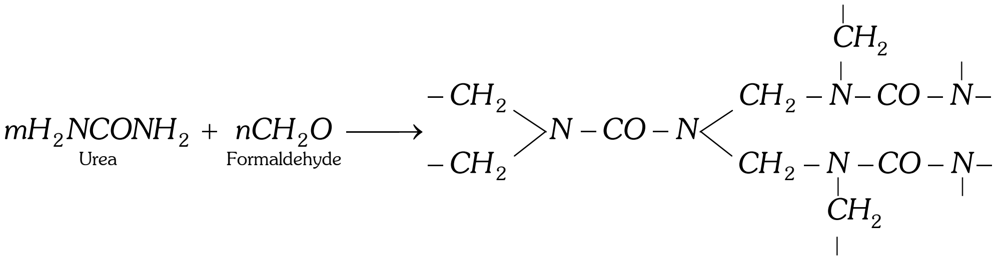
$$\underset{\text{Formaldehyde}}{6HCHO} \xrightarrow{Ca(OH)_2} \underset{\text{Formose (hexose)}}{C_6H_{12}O_6}$$

(iv) ***Condensation with phenol :*** Formaldehyde condenses with phenol to give a synthetic plastic, bakelite. The condensation occurs in presence of dilute sodium hydroxide or ammonia at 80 – 90°C. Bakelite is used for preparing electrical insulators, electric switches, toys, etc.



Bakelite is electrical and thermal resistant so it is used in formation of electrical appliances. This reaction is called Lederer- Manasse reaction.

(v) ***Condensation with urea :*** Formaldehyde also condenses with urea in acidic solution to form a plastic like product.

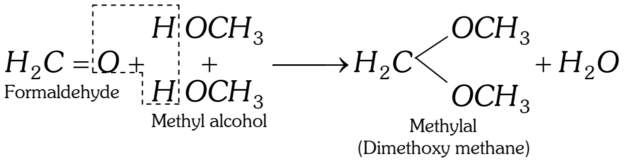


$$mH_2NCONH_2 + nCH_2O \longrightarrow \text{Formaldehyde- urea plastic}$$

Urea, Formaldehyde

Formaldehyde- urea plastic

(vi) ***Reaction with alcohol*** **:** Formaldehyde reacts with methyl alcohol in presence of dry hydrogen chloride or fused calcium chloride forming methylal which is used as soporific.



$$H_2C = O + \begin{matrix} H\,OCH_3 \\ + \\ H\,OCH_3 \end{matrix} \longrightarrow H_2C \begin{matrix} OCH_3 \\ OCH_3 \end{matrix} + H_2O$$

Formaldehyde, Methyl alcohol, Methylal (Dimethoxy methane)

(vii) ***Polymerisation*** **:** Formaldehyde readily undergoes polymerisation.

(a) *Paraformaldehyde* : When an aqueous solution of formaldehyde is evaporated to dryness, a white crystalline solid with fishy odour is obtained. It is a long chain polymer.

$$\underset{\text{Formaldehyde}}{nHCHO} \rightleftharpoons \underset{\text{Para-formaldehyde}}{(CH_2O)_n} \qquad n = 6 \text{ to } 50$$

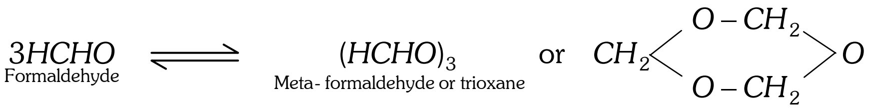
On rapid heating it gives back gaseous formaldehyde.

When a formaldehyde solution is treated with con. H_2SO_4, a white solid, polyoxy methylenes $(CH_2O)_n.H_2O$ are formed.

$$nHCHO \underset{\text{heat}}{\overset{\text{Conc. } H_2SO_4}{\rightleftharpoons}} \underset{\text{Polyoxy methylene}}{(CH_2O)_n.H_2O}\,; n > 100$$

This on heating gives back formaldehyde.

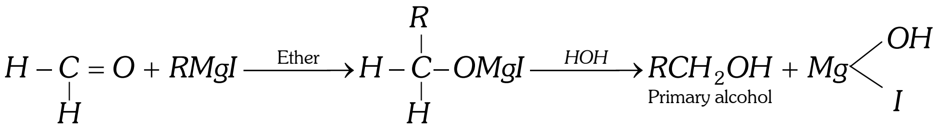
(b) *Metaformaldehyde* **:** On allowing formaldehyde gas to stand at room temperature, it slowly polymerises to metaform, $(HCHO)_3$. It is a white solid ($m.pt.$ 61 – 62°C). This on heating gives back gaseous formaldehyde.



$$\underset{\text{Formaldehyde}}{3HCHO} \rightleftharpoons \underset{\text{Meta- formaldehyde or trioxane}}{(HCHO)_3} \text{ or } CH_2 \begin{matrix} O-CH_2 \\ O-CH_2 \end{matrix} O$$

Trioxy methylene (triroxan)

(viii) ***Reaction with grignard reagent*** **:** Formaldehyde forms primary alcohols with Grignard reagent.



$$H-\underset{H}{C}=O + RMgI \xrightarrow{\text{Ether}} H-\underset{H}{\overset{R}{C}}-OMgI \xrightarrow{HOH} \underset{\text{Primary alcohol}}{RCH_2OH} + Mg \begin{matrix} OH \\ I \end{matrix}$$

Formaldehyde does not react with chlorine and phosphorus pentachloride. It does not give iodoform test.

(4) Uses

(i) The 40% solution of formaldehyde (formalin) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens.

(ii) It is used in the preparation of hexamethylene tetramine (urotropine) which is used as an antiseptic and germicide.

(iii) It is used in silvering of mirror.

(iv) It is employed in manufacture of synthetic dyes such as para-rosaniline, indigo, etc.

(v) It is used in the manufacture of **formamint** (by mixing formaldehyde with lactose) – a throat lozenges.

(vi) It is used for making synthetic plastics like bakelite, urea-formaldehyde resin, etc.

(vii) Rongalite – a product obtained by reducing formaldehyde sodium bisulphite derivative with zinc dust and ammonia and is used as a reducing agent in vat dyeing.

(viii) As a methylating agent for primary and secondary amines, e.g.,

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + 2HCHO \longrightarrow \underset{\text{Ethyl methylamine}}{C_2H_5NH-CH_3} + HCOOH$$

(ix) If aqeous solution of formaldehyde is kept with lime water in dark room for 5 – 6 days then it converts into a sweet solution called formose or α-acrose. It is an example of linear polymer.

$$6HCHO \xrightarrow[\text{Dark 5-6 days}]{Ca(OH)_2/Ba(OH)_2} \underset{\text{Formose / }\alpha\text{-acrose}}{C_6H_{12}O_6}$$

Acetaldehyde

Acetaldehyde is the second member of the aldehyde series. It occurs in certain fruits. It was first prepared by Scheele in 1774 by oxidation of ethyl alcohol.

(1) Preparation : It may be prepared by any of the general methods. The summary of the methods is given below

(i) By oxidation of ethyl alcohol with acidified potassium dichromate or with air in presence of a catalyst like silver at 300°C.

(ii) By dehydrogenation of ethyl alcohol. The vapours of ethyl alcohol are passed over copper at 300°C.

(iii) By heating the mixture of calcium acetate and calcium formate.

(iv) By heating ethylidene chloride with caustic soda or caustic potash solution.

(v) By the reduction of acetyl chloride with hydrogen in presence of a catalyst palladium suspended in barium sulphate (Rosenmund's reaction).

(vi) By the reduction of CH_3CN with stannous chloride and HCl in ether and hydrolysis (Stephen's method).

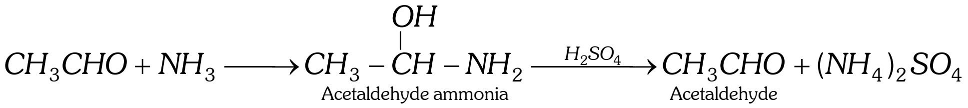
(vii) By hydration of acetylene with dil. H_2SO_4 and $HgSO_4$ at 60°C.

(viii) By ozonolysis of butene-2 and subsequent breaking of ozonide.

(ix) ***Laboratory preparation*** **:** Acetaldehyde is prepared in the laboratory by oxidation of ethyl alcohol with acidified potassium dichromate or acidified sodium dichromate.

$$\begin{array}{l}
K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O] \\
[CH_3CH_2OH + O \longrightarrow CH_3CHO + H_2O] \times 3 \\
\hline
\underset{\substack{\text{Potassium}\\\text{dichromate}}}{K_2Cr_2O_7} + \underset{\text{Ethyl alcohol}}{3CH_3CH_2OH} + \underset{\text{Sulphuric acid}}{4H_2SO_4} \longrightarrow \underset{\substack{\text{Potassium}\\\text{sulphate}}}{K_2SO_4} + \underset{\substack{\text{Chromic}\\\text{sulphate}}}{Cr_2(SO_4)_3} + \underset{\text{Acetaldehyde}}{3CH_3CHO} + \underset{\text{Water}}{7H_2O}
\end{array}$$

To recover acetaldehyde, the distillate is treated with dry ammonia when crystallised product, acetaldehyde ammonia, is formed. It is filtered and washed with dry ether. The dried crystals are then distilled with dilute sulphuric acid when pure acetaldehyde is collected.



$$CH_3CHO + NH_3 \longrightarrow \underset{\text{Acetaldehyde ammonia}}{CH_3-\overset{OH}{\overset{|}{C}}H-NH_2} \xrightarrow{H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} + (NH_4)_2SO_4$$

(x) ***Manufacture* :** Acetaldehyde can be manufactured by one of the following methods:

(a) *By air oxidation of ethyl alcohol* : Ethyl alcohol vapours and limited amount of air are passed over heated silver catalyst at 300°C.

$$2CH_3CH_2OH + O_2 \xrightarrow[300°C]{Ag} 2CH_3CHO + 2H_2O$$

(b) *By dehydrogenation of alcohol* : Vapours of ethyl alcohol are passed over heated copper at 300°C.

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

(c) *By hydration of acetylene* : Acetylene is passed through water containing 40% sulphuric acid and 1% mercuric sulphate at 60°C when acetaldehyde is formed.

$$CH \equiv CH + H_2O \xrightarrow[H_2SO_4\,(40\%)]{HgSO_4,(1\%),60°C} CH_3CHO$$

(d) *From ethylene (Wacker process)* : Ethylene is passed through an acidified aqueous solution of palladium chloride and cupric chloride, when acetaldehyde is formed.

$$CH_2 = CH_2 + PdCl_2 + H_2O \xrightarrow[H^+]{CuCl_2} CH_3CHO + Pd + 2HCl$$

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

$$\begin{array}{l} 2CuCl + 2HCl + \frac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O \\ \hline \underset{\text{Ethylene}}{CH_2 = CH_2} + \frac{1}{2}O_2 \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} \end{array}$$

(So $H_2C = CH_2 + O_2 \xrightarrow[H_2O]{PdCl_2,CuCl_2} H_3C - CHO$)

(2) Physical properties

(i) Acetaldehyde is a colourless volatile liquid. It boils at 21°C.

(ii) It has a characteristic pungent smell.

(iii) It is soluble in water, chloroform, ethyl alcohol and ether. Its aqueous solution has a pleasant odour. In water, it is hydrated to a considerable extent to form ethylidene glycol.

$$CH_3CHO + H_2O \longrightarrow CH_3CH(OH)_2$$

(3) Chemical properties : It gives all characteristic reactions of aldehydes. Besides general reactions, acetaldehyde shows the following reactions also.

(i) ***Haloform reaction* :** It responds to iodoform reaction due to the presence of CH_3CO group.

(ii) ***Tischenko's reaction* :** It forms ethyl acetate in presence of aluminium ethoxide.

$$2CH_3CHO \xrightarrow{(C_2H_5O)_3\,Al} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

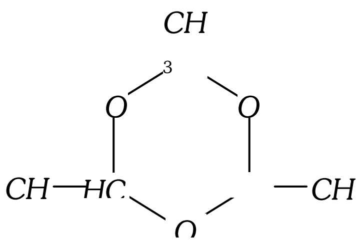
(iii) ***Chlorination*** **:** Hydrogen atoms of the methyl group are substituted by chlorine atoms when acetaldehyde is treated with chlorine.

$$CH_3CHO + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

(iv) ***Polymerisation*** **:** Acetaldehyde undergoes polymerisation forming different products under different conditions.

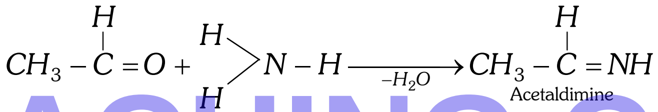
(a) *Paraldehyde* : It is formed, when anhydrous acetaldehyde is treated with conc. sulphuric acid.

$$\underset{\text{Acetaldehyde}}{3CH_3CHO} \rightleftharpoons \underset{\text{Paraldehyde, (trimer)}}{(CH_3CHO)_3}$$

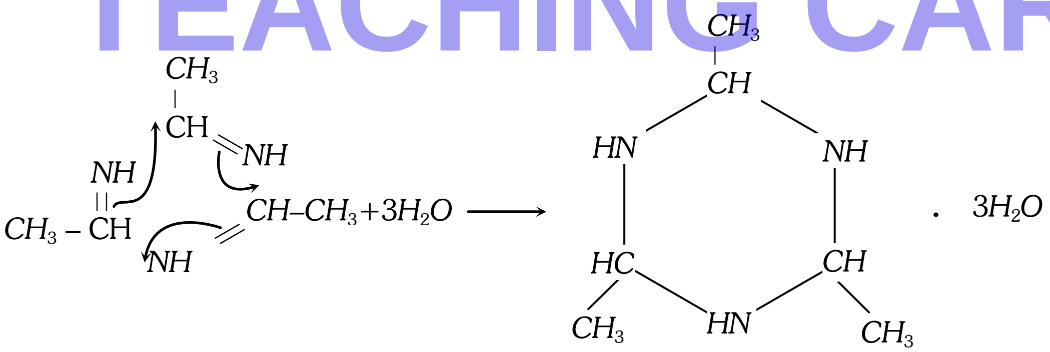


It is a pleasant smelling liquid (b.pt. 124°C). It has cyclic structure and when heated with dilute sulphuric acid it changes again into acetaldehyde. It is used as a hypnotic and soporific (sleep producing).

Reaction with NH_3 :

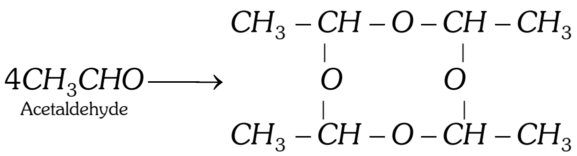


$$CH_3-\overset{H}{\overset{|}{C}}=O + \begin{matrix}H\\ H\end{matrix}\!\!>N-H \xrightarrow[-H_2O]{} \underset{\text{Acetaldimine}}{CH_3-\overset{H}{\overset{|}{C}}=NH}$$



Trimethyl hexa hydro triazine [Trihydrate]

(b) *Metaldehyde* : Acetaldehyde on treatment with hydrogen chloride or sulphur dioxide is converted into metaldehyde $(CH_3CHO)_4$. It is a white solid (m. pt. 246°C). On heating it sublimes but changes again into acetaldehyde when distilled with dilute sulphuric acid. It is used as a solid fuel.



Metaldehyde (textramer)

It is used for killing slugs and snails.

(4) **Uses :** Acetaldehyde is used :

(i) In the preparation of acetic acid, acetic anhydride, ethyl acetate, chloral, 1,3-butadiene (used in rubbers), dyes and drugs.

(ii) As an antiseptic inhalent in nose troubles.

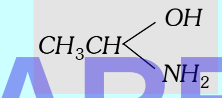
(iii) In the preparation of paraldehyde (hypnotic and sporofic) and metaldehyde (solid fuel).

(iv) In the preparation of acetaldehyde ammonia (a rubber accelerator).

Comparative study of formaldehyde and acetaldehyde

S.No.	*Reaction*	***Formaldehyde HCHO***	***Acetaldehyde CH_3CHO***
1.	**Similarty** **Addition of hydrogen** **(a) H_2 in presence of catalyst, Ni, Pd or Pt** **(b)** $LiAlH_4$ **(ether)** **(c) Amalgamated zinc + conc. HCl (Clemmensen reduction)**	**Forms methyl alcohol** $HCHO + H_2 \longrightarrow CH_3OH$ **Forms methane** $HCHO + 4H \longrightarrow CH_4 + H_2O$	**Forms ethyl alcohol** $CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$ **Forms ethyl alcohol** **Forms ethane** $CH_3CHO + 4H \longrightarrow C_2H_6 + H_2O$
2.	**Addition of** $NaHSO_3$ **solution**	**Forms bisulphite addition product** $HCHO + NaHSO_3 \longrightarrow CH_2(OH)SO_3Na$	**Forms bisulphite addition product** $CH_3CHO + NaHSO_3 \longrightarrow$ $CH_3CH(OH)SO_3Na$
3.	**Addition of HCN**	**Forms formaldehyde cyanohydrin** $HCHO + HCN \longrightarrow CH_2(OH)CN$	**Forms acetaldehyde cyanohydrin** $CH_3CHO + HCN \longrightarrow$ $CH_3CH(OH)CN$
4.	**Addition of Grignard reagent followed by hydrolysis**	**Forms ethyl alcohol** $HCHO + CH_3MgI \longrightarrow CH_2\begin{matrix} OMgI \\ CH_3 \end{matrix}$ $\xrightarrow[-Mg(OH)I]{H_2O} CH_3CH_2OH$	**Forms isopropyl alcohol** $CH_3CHO + CH_3MgI \longrightarrow$ $CH_3-\underset{\substack{\vert \\ CH_3}}{C}HOMgI \xrightarrow[-Mg(OH)I]{H_2O}$ $CH_3-\underset{\substack{\vert \\ CH_3}}{CH}-OH$
5.	**With hydroxylamine** NH_2OH	**Forms formaldoxime** $CH_2 = O + H_2NOH \xrightarrow{-H_2O}$ $CH_2 = NOH$	**Forms acetaldoxime** $CH_3CH = O + H_2NOH \xrightarrow{-H_2O}$ $CH_3CH = NOH$
6.	**With hydrazine** (NH_2NH_2)	**Forms formaldehyde hydrazone** $CH_2O + H_2N\ NH_2 \xrightarrow{-H_2O}$ $CH_2 = NNH_2$	**Forms acetaldehyde hydrazone** $CH_3CH = O + H_2NNH_2 \xrightarrow{-H_2O}$ $CH_3CH = NNH_2$
7.	**With phenyl hydrazine** $(C_6H_5NHNH_2)$	**Forms formaldehyde phenyl hydrazone** $CH_2 = O + H_2NNHC_6H_5 \xrightarrow{-H_2O}$ $CH_2 = NNHC_6H_5$	**Forms acetaldehyde phenyl hydrazone** $CH_3CH = O + H_2NNHC_6H_5$ $\xrightarrow{-H_2O} CH_3CH = NNHC_6H_5$

8.	**With semicarbazide** $(H_2NNHCONH_2)$	**Forms formaldehyde semicarbazone** $CH_2=O+H_2NNHCONH_2 \xrightarrow{-H_2O} CH_2=NNHCONH_2$	**Forms acetaldehyde semicarbazone** $CH_3CH=O+H_2NNHCONH_2 \xrightarrow{-H_2O} CH_3CH=NNHCONH_2$
9.	**With alcohol** (C_2H_5OH) **in presence of acid**	**Forms ethylal** $H_2C=O+2C_2H_5OH \xrightarrow{HCl} CH_2<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$	**Forms acetaldehyde diethyl acetal** $CH_3CHO+2C_2H_5OH \xrightarrow{HCl} CH_3CH<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$
10.	**With thioalcohols** (C_2H_5SH) **in presence of acid**	**Forms thio ethylal** $H_2C=O+2C_2H_5SH \longrightarrow CH_2<\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}$	**Forms acetaldehyde diethyl thioacetal** $CH_3CH=O+2C_2H_5SH \longrightarrow CH_3CH<\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}$
11.	**Oxidation with acidified** $K_2Cr_2O_7$	**Forms formic acid** $HCHO+O \longrightarrow HCOOH$	**Forms acetic acid** $CH_3CHO+O \longrightarrow CH_3COOH$
12.	**With Schiff's reagent**	**Restores pink colour of Schiff's reagent**	**Restores pink colour of Schiff's reagent**
13.	**With Tollen's reagent**	**Gives black precipitate of Ag or silver mirror** $Ag_2O+HCHO \longrightarrow 2Ag+HCOOH$	**Gives black precipitate of Ag or silver mirror** $Ag_2O+CH_3CHO \longrightarrow 2Ag+CH_3COOH$
14.	**With Fehling's solution or Benedict's solution**	**Gives red precipitate of cuprous oxide** $2CuO+HCHO \longrightarrow Cu_2O+HCOOH$	**Gives red precipitate of cuprous oxide** $2CuO+CH_3CHO \longrightarrow Cu_2O+CH_3COOH$
15.	**Polymerisation**	**Undergoes polymerisation** $nHCHO \xrightleftharpoons{\text{Evaporation}} \underset{\text{Paraformaldehyde}}{(HCHO)_n}$ $3HCHO \xrightleftharpoons[\text{heat}]{\text{Room temp.}} \underset{\text{Metaformaldehyde}}{(HCHO)_3}$	**Undergoes polymerisation** $3CH_3CHO \xrightleftharpoons[\text{dil. } H_2SO_4\text{. distill}]{H_2SO_4\text{Conc.}} \underset{\text{Paraldehyde}}{(CH_3CHO)_3}$ $4CH_3CHO \rightleftharpoons \underset{\text{Metaldehyde}}{(CH_3CHO)_4}$
	Difference		
16.	**With** PCl_5	**No reaction**	**Forms ethylidene chloride** $CH_3CHO+PCl_5 \longrightarrow CH_3CH<\begin{matrix}Cl\\Cl\end{matrix}+POCl_3$
17.	**With chlorine**	**No reaction**	**Forms chloral** $CH_3CHO+3Cl_2 \longrightarrow CCl_3CHO+3HCl$

18.	**With SeO_2**	**No reaction**	**Forms glyoxal** $CH_3CHO + SeO_2 \longrightarrow CHO.CHO$ $+ Se + H_2O$
19.	**Iodoform reaction (I_2+NaOH)**	**No reaction**	**Forms iodoform** $CH_3CHO + 3I_2 + 4NaOH \longrightarrow$ $CHI_3 + HCOONa + 3NaI + 3H_2O$
20.	**With dil. alkali (Aldol condensation)**	**No reaction**	**Forms aldol** $CH_3CHO + HCH_2CHO \longrightarrow$ $CH_3CH(OH)CH_2CHO$
21.	**With conc. NaOH (Cannizzaro's reaction)**	**Forms sodium formate and methyl alcohol** $2HCHO + NaOH \longrightarrow HCOONa$ $+ CH_3OH$	**Forms a brown resinous mass**
22.	**With ammonia**	**Forms hexamethylene tetramine (urotropine)** $6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$	**Forms addition product, acetaldehyde ammonia** $CH_3CHO + NH_3 \longrightarrow$  $CH_3CH\begin{matrix}OH\\NH_2\end{matrix}$
23.	**With phenol**	**Forms bakelite plastic**	**No reaction**
24.	**With urea**	**Forms urea-formaldehyde plastic**	**No reaction**
25.	**Condensation in presence of $Ca(OH)_2$**	**Form formose (a mixuture of sugars)**	**No reaction**

Inter conversion of formaldehyde and acetaldehyde

(1) **Ascent of series :** Conversion of formaldehyde into acetaldehyde

(i) $$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{H_2/Ni} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{PCl_5} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow[KCN]{\text{Alc.}} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{Na/\text{Alcohol}} \underset{\text{Ethyl amine}}{CH_3CH_2NH_2} \xrightarrow[HCl]{NaNO_2}$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7]{H_2SO_4\,(\text{dil.})} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(ii) $$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow[\text{Ether}]{CH_3MgI} CH_3CH_2OMgI \xrightarrow{H_3\overset{+}{O}} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[300°C]{Cu} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(iii) $$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Formic acid}}{HCOOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium formate}}{(HCOO)_2Ca} \xrightarrow[\text{heat}]{(CH_3COO)_2Ca} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(2) **Descent of series :** Conversion of acetaldehyde into formaldehyde

(i) $$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{Amm. acetate}}{CH_3COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2/KOH}$$

$$\underset{\text{Methyl amine}}{CH_3NH_2} \xrightarrow[HCl]{NaNO_2} CH_3OH \xrightarrow[300°C]{Cu} \underset{\text{Formaldehyde}}{HCHO}$$

(ii) $$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} \underset{\text{Sod.acetate}}{CH_3COONa} \xrightarrow[\text{heat}]{\text{Sodalime}} \underset{\text{Methane}}{CH_4} \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow{AgOH}$$

$$CH_3OH \xrightarrow[300°C]{Cu} \underset{\text{Formaldehyde}}{HCHO}$$

Acetone

It is a symmetrical (simple) ketone and is the first member of the homologous series of ketones. In traces, it is present in blood and urine.

(1) **Laboratory preparation :** Acetone is prepared in laboratory by heating anhydrous calcium acetate.

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \longrightarrow CaCO_3 + \underset{\text{Acetone}}{CH_3COCH_3}$$

The retort is heated slowly when acetone distills over and collected in the receiver.

The distillate is shaken with saturated solution of sodium bisulphite when colourless crystals are formed. These are filtered and distilled with saturated solution of sodium carbonate. The aqueous solution of acetone is dried over anhydrous calcium chloride and redistilled to obtain pure acetone. The fraction is collected between 55 to 57^oC (b.pt. pure acetone 56^oC).