



Knowledge... Everywhere

Chemistry

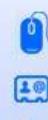
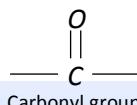
Aldehydes and ketones

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I. *Introduction.*

Carbonyl compounds are of two types, aldehydes and ketones. Both have a carbon-oxygen double bond often called as carbonyl group.



Both aldehydes and ketones possess the same general formula $C_nH_{2n}O$.

Aldehyde	<p>Aldehydes may be considered as derivatives of hydrocarbons in which two hydrogen atoms of the end carbon atom have been replaced by a bivalent oxygen atom.</p> $\begin{array}{c} H & & H \\ & & \\ H - C - H & \xrightarrow[-2H]{+ [O]} & H - C = O \\ & & \\ H & & \end{array}$ <p style="text-align: center;">Formaldehyde</p> <p>Methane</p> <p>Aldehydes contain the monovalent group $\begin{array}{c} H \\ \\ -C=O \end{array}$ (aldehydic group) linked to a hydrogen atom or an alkyl group. Hence, the general formula of the aldehydes is represented as, $R - C = O$ (R may be H or alkyl group).</p> <p>Aldehydes can also be regarded as the first oxidation products of primary alcohols.</p> $RCH_2OH \xrightarrow{[O]} RCHO + H_2O$ <p style="text-align: left;">Primary alcohol Aldehyde</p>
Ketone	<p>Ketones may be considered as derivatives of hydrocarbons in which the two hydrogen atoms of a carbon atom present in the middle of carbon chain have been replaced by a bivalent oxygen atom.</p> $\begin{array}{c} H & & O \\ & & \\ CH_3 - C - CH_3 & \xrightarrow[-2H]{+ [O]} & CH_3 - C - CH_3 \\ & & \\ H & & \end{array}$ <p style="text-align: center;">Acetone</p> <p>Propane</p> <p>Ketones contain the divalent group (<i>ketonic group</i>) linked to two alkyl groups, same or different. Hence, the general formula of the ketones is represented as,</p> $\begin{array}{c} R & & R \\ & C = O & & C = O \\ & & & \\ R & & R' & \end{array}$ <p>Ketones can also be regarded as the first oxidation products of secondary alcohols.</p> $\begin{array}{c} CH_3 & & CH_3 & & C = O + H_2O \\ & CHOH & \xrightarrow{[O]} & & \\ & & & CH_3 & \\ & & & & \end{array}$ <p style="text-align: left;">Isopropyl alcohol Acetone</p>

2. Classification, Structure, Nomenclature and Isomerism.

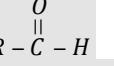
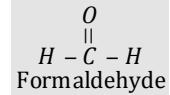
(I) Classification



Aldehydic group is always terminal. Aldehydes can be classified into three categories,

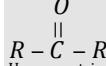


(iii) **Unsymmetrical aldehydes :** All aldehydes except formaldehyde are unsymmetrical.



Both substituents are different

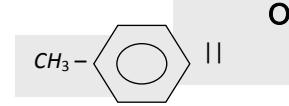
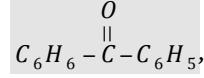
Ketonic group is never terminal. Ketones can be classified into three categories,



Symmetrical

Unsymmetrical

(ii) **Aromatic ketones :** In aromatic ketones both substituents are aryl



Alkyl group

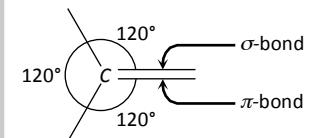
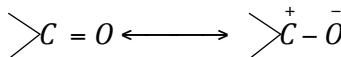
(iii) **Mixed ketones :** In mixed ketones one substituent is aryl and other is alkyl. $C_6H_5 - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - CH_3$

(2) **Structure:** Carbonyl carbon atom is joined to three atoms by sigma bonds. Since these bonds utilise sp^2 -orbitals, they lie in the same plane and are 120° apart. The carbon-oxygen double bond is different than carbon-carbon double bond. Since,

Oxygen is more electronegative, the electrons of the bond are attracted towards oxygen. Consequently, oxygen attains a partial negative charge and carbon a partial positive charge

making the bond polar. The high values of dipole moment, $\delta^+ \text{C} = \delta^- \text{O}$

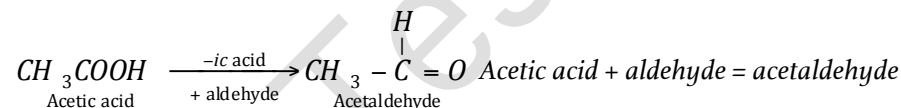
($2.3 - 2.8D$) cannot be explained only on the basis of inductive effect and thus, it is proposed that carbonyl group is a resonance hybrid of the following two structures.



(3) Nomenclature

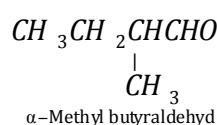
(i) **Aldehyde:** There are two systems of naming aldehydes,

(a) **Common system:** In the common system, aldehydes are named according to the name of the corresponding acid which they form on oxidation. The suffix **-ic acid** the name of the acid is replaced by aldehyde. For example, CH_3CHO derived from acetic acid (CH_3COOH) is named as **acetaldehyde**.



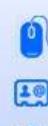
Branching in the aldehyde chain, if any, is indicated by the Greek letters α , β , γ , δ etc. The carbon attached to the $-\text{CHO}$ group is α as:

For example, $\begin{array}{ccccccc} \gamma & \beta & \alpha \\ -\text{C} - & \text{C} - & \text{C} - & \text{C} - & \text{CHO} \end{array}$



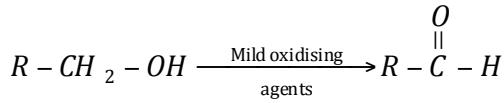
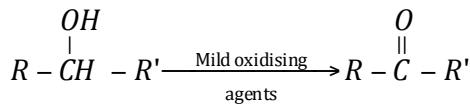
(b) **IUPAC system:** In the IUPAC system, the aldehydes are known as **alkanals**. The name of aldehyde is derived by replacing the terminal **-e** of the name of corresponding alkane by **al**.

For example, HCHO CH_3CHO $\text{C}_2\text{H}_5\text{CHO}$ Alkane **-e** + **al** = Alkanal



(1) From alcohols

(i) Primary and secondary alcohols on oxidation give aldehydes and ketones respectively.



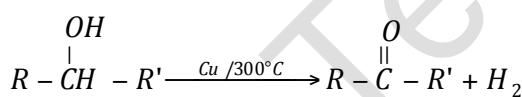
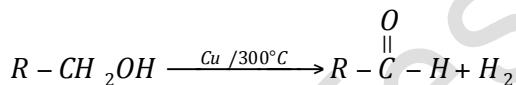
Mild oxidising agents are:

- | | | | |
|--------------------|--------------------|---------------------------------|-------------------|
| (a) X_2 | (b) Fenton reagent | (c) $K_2Cr_2O_7 / H^+$ | (d) Jones reagent |
| (e) Sarret reagent | (f) MnO_2 | (g) Aluminium tertiary butoxide | |

Note: When the secondary alcohols can be oxidised to ketones by aluminium tert-butoxide, $[(CH_3)_3CO]_3Al$ the reaction is known as oppenauer oxidation. Unsaturated secondary alcohols can also be oxidised to unsaturated ketones (without affecting double bond) by this reagent.

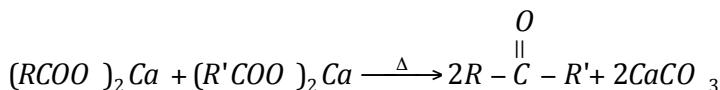
The yield of aldehydes is usually low by this methods. The alcohols can be converted to aldehydes stage by treating with oxidizing agent pyridinium chloro-chromate ($C_5H_5NH^+CrO_3Cl^-$). It is abbreviated as PCC and is called Collin's reagent. This reagent is used in non-aqueous solvents like CH_2Cl_2 (dichloro methane). It is prepared by mixing pyridine, CrO_3 and HCl in dichloromethane. This is a very good reagent because it checks the further oxidation of aldehydes to carboxylic acids.

(ii) Dehydrogenation of 1° and 2° alcohols by Cu/300°C or Ag/300°C.

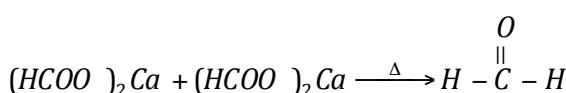


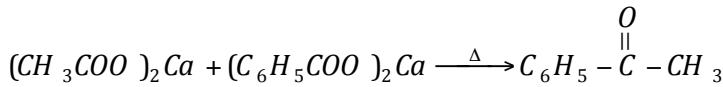
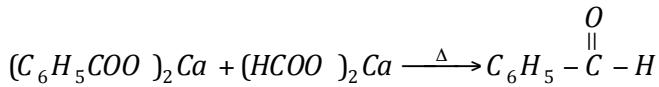
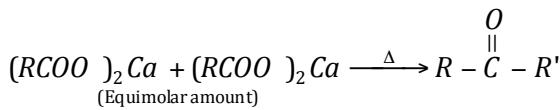
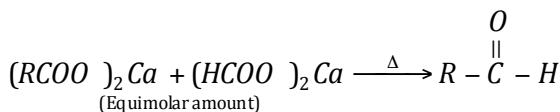
(2) From carboxylic acids

(i) Distillation of Ca, Ba, Sr or Th salts of monobasic acids: Salt of monobasic acids on distillation give carbonyl compounds. Reaction takes place as follows,

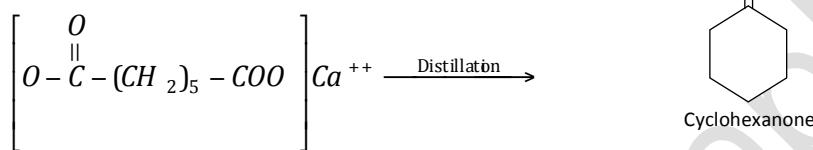


Thus in the product, one alkyl group comes from one carboxylic acid and other alkyl group from other carboxylic acid.





Calcium salts of dibasic acid (1, 4 and higher) on distillation give cyclic ketones.

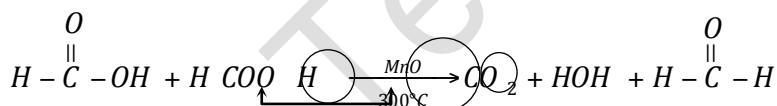


(ii) Catalytic decomposition of carboxylic acids or Decarboxylation and Dehydration of acids by $MnO / 300^\circ C$.

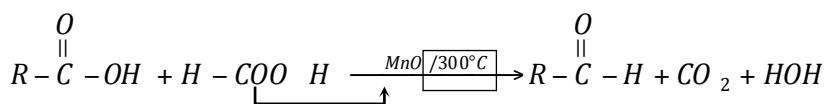
(a) This reaction takes place between two molecules of carboxylic acids. Both may be the same or different.

(b) If one of the carboxylic acids is $HCOOH$ then this acid undergoes decarboxylation because this acid is the only monobasic acid which undergoes decarboxylation even in the absence of catalyst.

Case I: When both are $HCOOH$



Case II: When only one is formic acid.

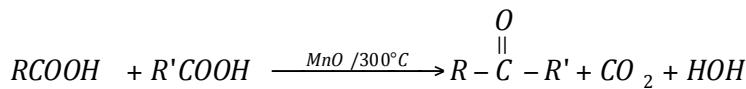


Case III: When none is formic acid.

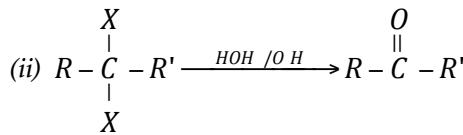
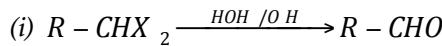


Or





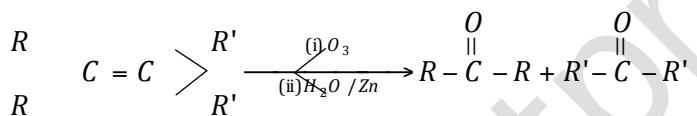
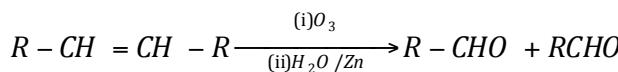
(3) **From gem dihalides:** Gem dihalides on hydrolysis give carbonyl compounds



Note: This method is not used much since aldehydes are affected by alkali and dihalides are usually prepared from the carbonyl compounds.

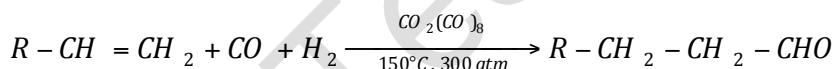
(4) **From alkenes**

(i) **Ozonolysis:** Alkenes on reductive ozonolysis give carbonyl compounds



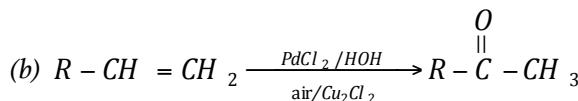
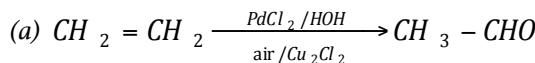
Note: This method is used only for aliphatic carbonyl compounds.

(ii) **Oxo process:** This method converts terminal alkenes into aldehydes.

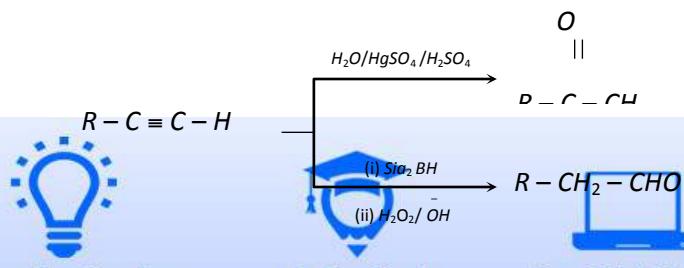


Note: Oxo process is used only for the preparation of aldehydes.

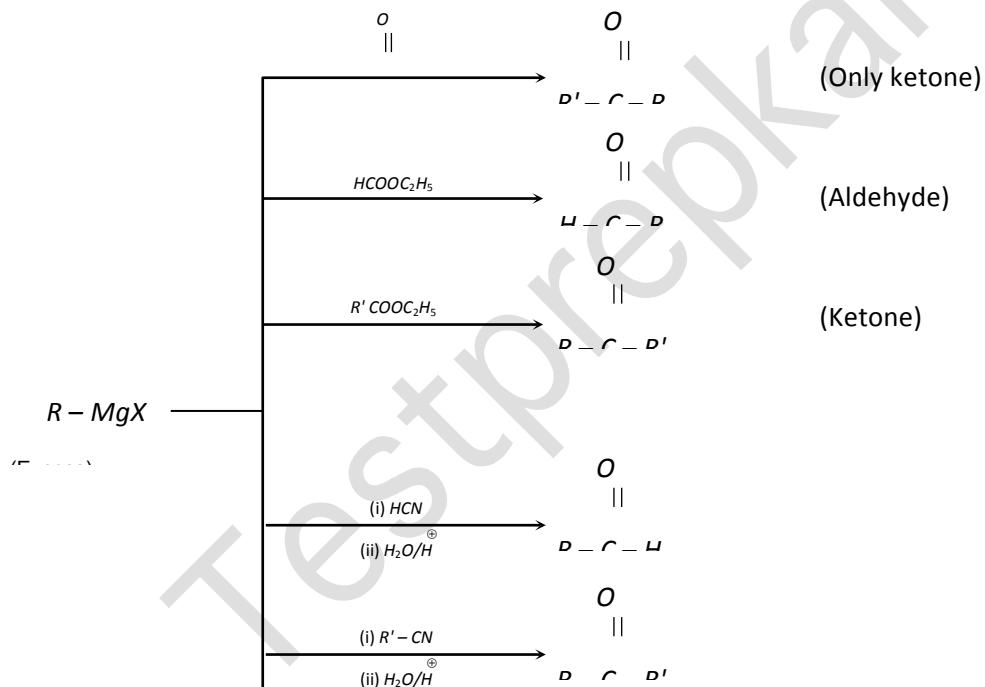
(iii) **Wacker process:** This reaction converts alkenes in carbonyl compounds.



(5) **From alkynes:** Alkynes on hydration and on boration – oxidation give carbonyl compounds.

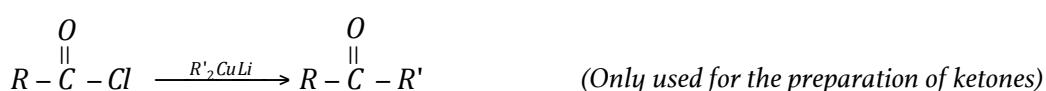
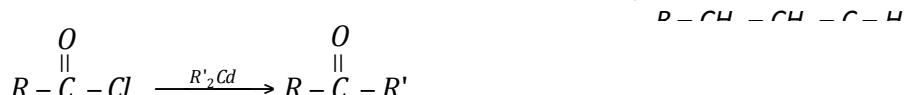


(6) **From Grignard reagents:** Carbonyl compounds can be prepared from Grignard reagents by following reactions:



(7) From acid chloride

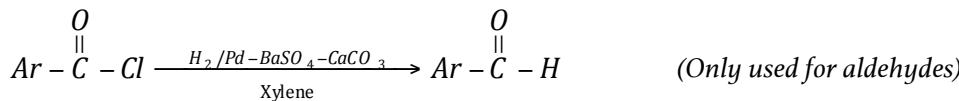
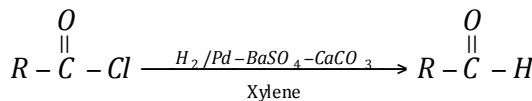
(i) Acid chlorides give nucleophilic substitution reaction with dialkyl cadmium and dialkyl lithium cuprate to give ketones. This is one of the most important method for the preparation of ketones from acid chlorides.



In this method product is always ketone because $R \neq H$ and also $R' \neq H$.

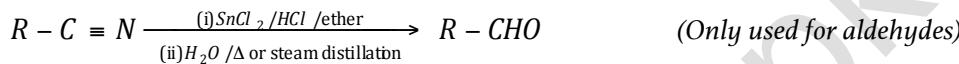


(ii) **Rosenmunds reduction:** Acid chlorides on partial reduction give aldehydes. This reduction takes place in the presence of Lindlars catalyst.

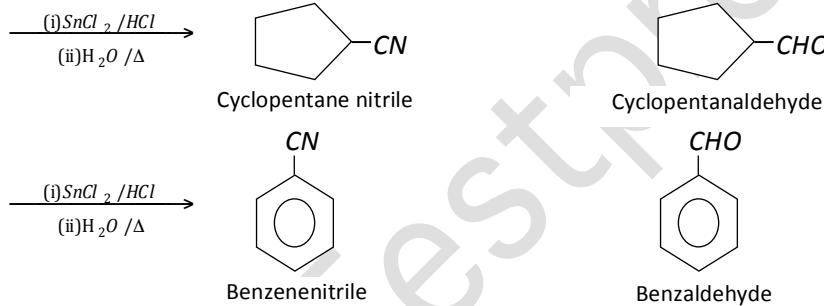


(8) **From cyanides**

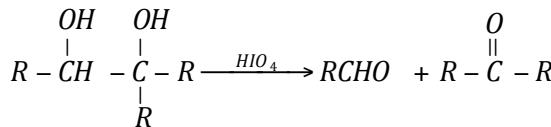
(i) **Stephen aldehyde synthesis:** Conversion of cyanides into aldehydes by partial reduction with $SnCl_2 / HCl$, followed by hydrolysis, is known as Stephens's aldehyde synthesis.



Example:



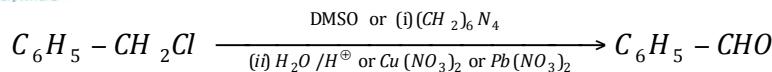
(9) **From vic diols:** Vic diols on periodate oxidation give carbonyl compounds.



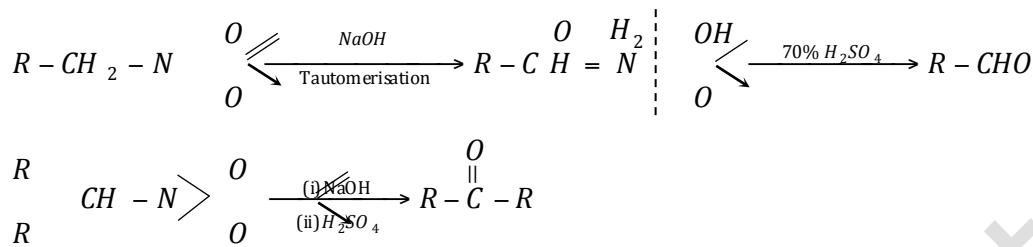
Note: $Pb(OCOCH_3)_4$ also gives similar oxidation products.

(10) **From Alkyl halides and benzyl halides:** These compounds on oxidation give carbonyl compounds.

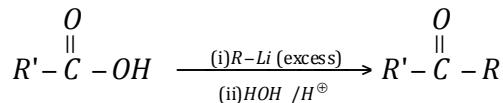




(ii) **From nitro alkanes:** Nitro alkanes having at least one α -hydrogen atom give carbonyl compounds on treatment with conc NaOH followed by 70% H_2SO_4 . The reaction is known as Nef carbonyl synthesis.

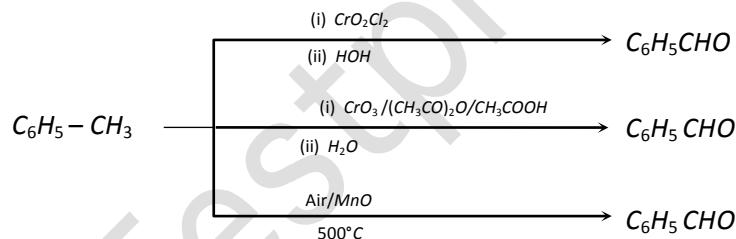


(12) **Reaction with excess alkyl lithium:** Carboxylic acids react with excess of organo lithium to give lithium salt of gem diols which on hydrolysis give ketones.

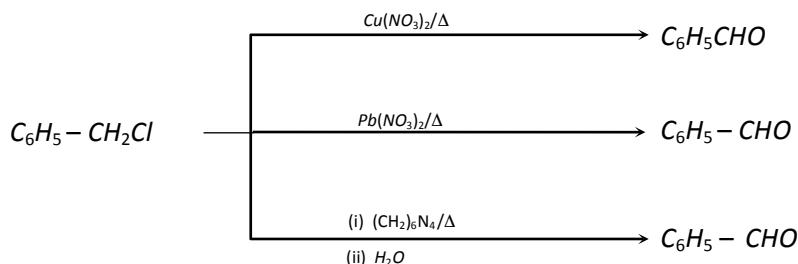


Preparation of only aromatic carbonyl compounds

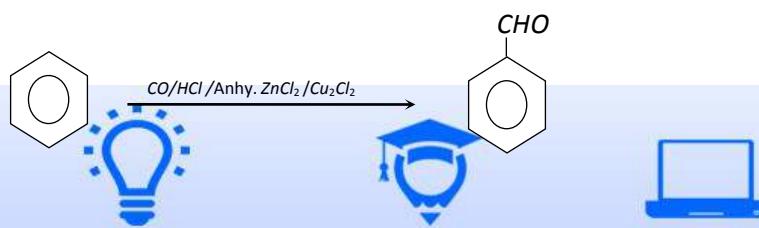
(1) **From methyl arenes:** Methyl arenes can be converted into aldehydes by the following reagents

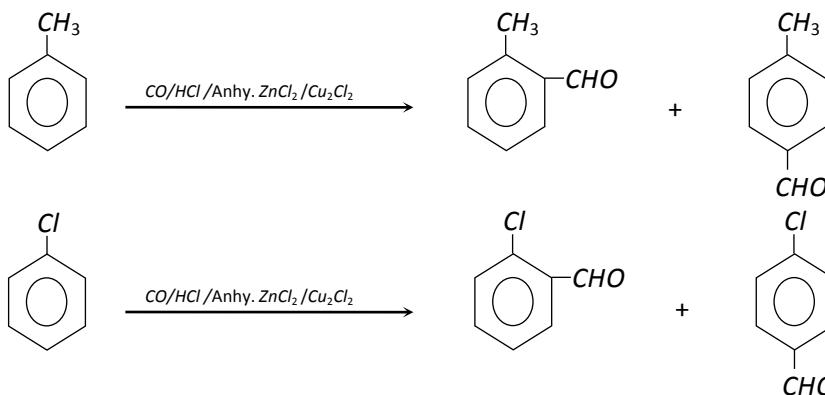


(2) **From chloro methyl arenes:** Chloromethyl arenes on oxidation give aromatic aldehydes.

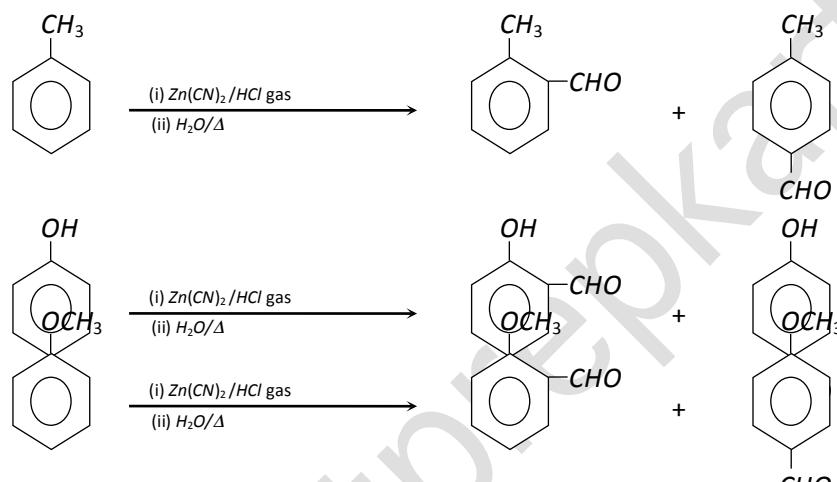


(3) **Gattermann – Koch formylation:** This reaction is mainly given by aromatic hydrocarbons and halobenzenes.

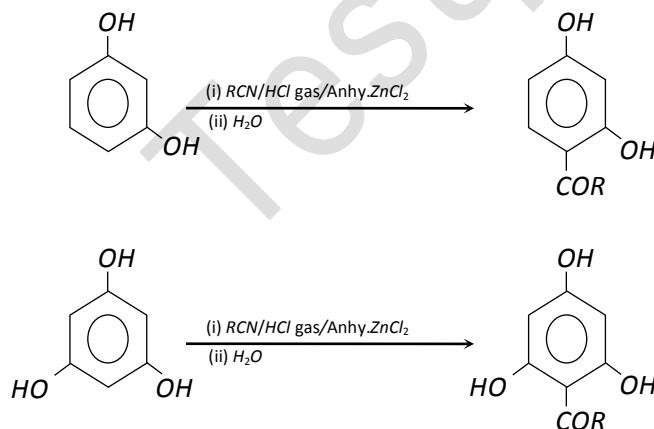




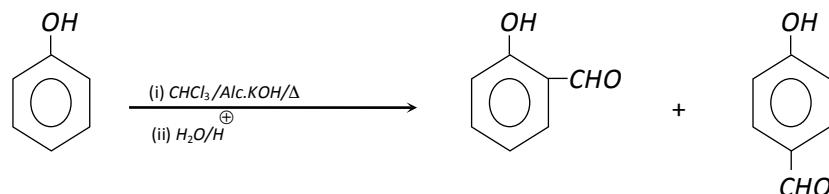
(4) **Gattermann formulation:** This reaction is mainly given by alkyl benzenes, phenols and phenolic ethers.



(5) **Houben – Hoesch reaction:** This reaction is given by di and polyhydric benzenes.



(6) **Reimer – Tiemann reaction:** Phenol gives o- and p- hydroxy benzaldehyde in this reaction.



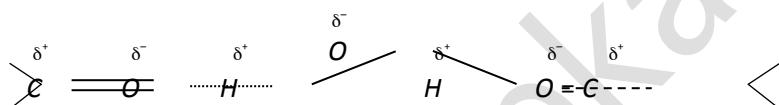
4. Physical properties of carbonyl compounds.

The important physical properties of aldehydes and ketones are given below,

(1) **Physical state:** Methanal is a pungent smell gas. Ethanal is a volatile liquid, b.p. 294 K. Other aldehydes and ketones containing up to eleven carbon atoms are colourless liquids while still higher members are solids.

(2) **Smell:** With the exception of lower aldehydes which have unpleasant odours, aldehydes and ketones have generally pleasant smell. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones have been used in blending of perfumes and flavouring agents.

(3) **Solubility:** Aldehydes and ketones upto four carbon atoms are miscible with water. This is due to the presence of hydrogen bonding between the polar carbonyl group and water molecules as shown below :



With the increase in the size of alkyl group, the solubility decreases and the compounds with more than four carbon atom are practically insoluble in water. All aldehydes and ketones are, however, soluble in organic solvents such as ether, alcohol, etc. The ketones are good solvents themselves.

(4) **Boiling points:** The boiling points of aldehydes and ketones are higher than those of non polar compounds (hydrocarbons) or weakly polar compounds (such as ethers) of comparable molecular masses. However, their boiling points are lower than those of corresponding alcohols or carboxylic acids. This is because aldehydes and ketones are polar compounds having sufficient intermolecular dipole-dipole interactions between the opposite ends of C = O dipoles.

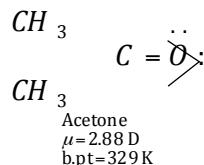
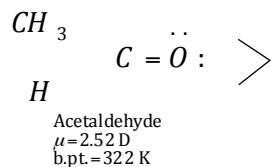


However, these dipole-dipole interactions are weaker than the intermolecular hydrogen bonding in alcohols and carboxylic acids. Therefore, boiling points of aldehydes and ketones are relatively lower than the alcohols and carboxylic acids of comparable molecular masses.

Compounds	$CH_3CH_2CH_2CH_2CH_3$ Pentane	$CH_3CH_2OCH_2CH_3$ Ethoxyethane	$CH_3CH_2CH_2CH_2OH$ Butan - 1-ol	$CH_3CH_2CH_2CHO$ Butanal	$CH_3COCH_2CH_3$ Butan-2-one
Molecular mass	72	74	74	72	72
Boiling point (K)	309	308	391	349	353

Among the carbonyl compounds, ketones have slightly higher boiling points than the isomeric aldehydes. This is due to the presence of two electrons releasing groups around the carbonyl carbon, which makes them more polar.





(5) **Density:** Density of aldehydes and ketones is less than that of water.

5. Chemical properties of carbonyl compounds.

Carbonyl compounds give chemical reactions due to carbonyl compounds group and α -hydrogens.

Chemical reactions of carbonyl compounds can be classified into following categories.

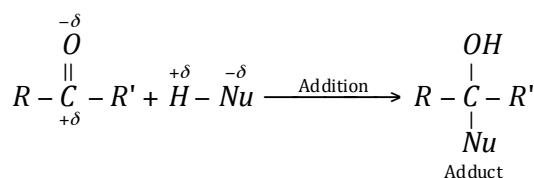
- (1) Nucleophilic addition reactions
- (2) Addition followed by elimination reactions
- (3) Oxidation
- (4) Reduction
- (5) Reactions due to α -hydrogen
- (6) Condensation reactions and
- (7) Miscellaneous reactions

(i) Nucleophilic addition reactions

(i) Carbonyl compounds give nucleophilic addition reaction with those reagents which on dissociation give electrophile as well as nucleophile.

(ii) If nucleophile is weak then addition reaction is carried out in the presence of acid as catalyst.

(iii) Product of addition reactions can be written as follows,

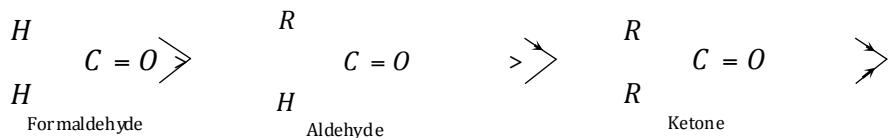


In addition reactions nucleophile adds on carbonyl carbon and electrophile on carbonyl oxygen to give adduct.

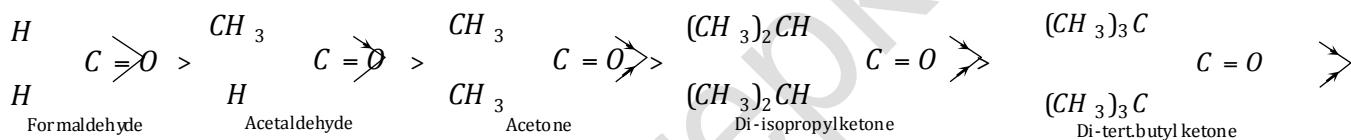
(iv) **Relative reactivity of aldehydes and ketones:** Aldehydes and ketones readily undergo nucleophilic addition reactions. However, ketones are less reactive than aldehydes. This is due to electronic and steric effects as explained below:



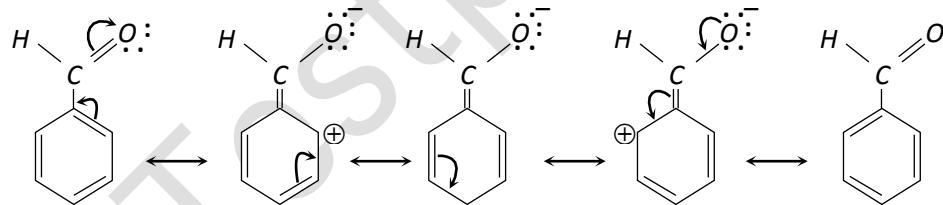
(a) **Inductive effect:** The relative reactivities of aldehydes and ketones in nucleophilic addition reactions may be attributed to the amount of positive charge on the carbon. A greater positive charge means a higher reactivity. If the positive charge is dispersed throughout the molecule, the carbonyl compound becomes more stable and its reactivity decreases. Now, alkyl group is an electron releasing group (+I inductive effect). Therefore, electron releasing power of two alkyl groups in ketones is more than that of one in aldehyde. As a result, the electron deficiency of carbon atom in the carbonyl group is satisfied more in ketones than in aldehydes. Therefore, the reduced positive charge on carbon in case of ketones discourages the attack of nucleophiles. Hence ketones are less reactive than aldehydes. Formaldehyde with no alkyl groups is the most reactive of the aldehydes and ketones. Thus, the order of reactivity is:



(b) **Stearic effect:** The size of the alkyl group is more than that of hydrogen. In aldehydes, there is one alkyl group but in ketones, there are two alkyl groups attached to the carbonyl group. The alkyl groups are larger than a hydrogen atom and these cause hindrance to the attacking group. This is called **stearic hindrance**. As the number and size of the alkyl groups increase, the hindrance to the attack of nucleophile also increases and reactivity decreases. The lack of hindrance in nucleophilic attack is another reason for the greater reactivity of formaldehyde. Thus, the reactivity follows the order:



In general, **aromatic aldehydes and ketones are less reactive than the corresponding aliphatic analogues**. For example, benzaldehyde is less reactive than aliphatic aldehydes. This can be easily understood from the resonating structures of benzaldehyde as shown below:



It is clear from the resonating structures that due to electron releasing (+I effect) of the benzene ring, the magnitude of the positive charge on the carbonyl group decreases and consequently it becomes less susceptible to the nucleophilic attack. Thus, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones. The order of reactivity of aromatic aldehydes and ketones is,

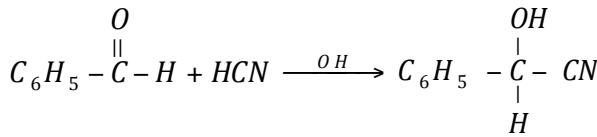
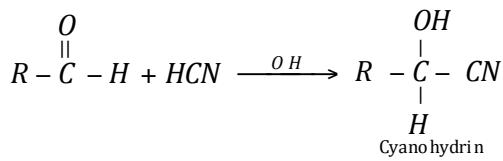


Some important examples of nucleophilic addition reactions

Some important nucleophilic addition reactions of aldehydes and ketones are given below,

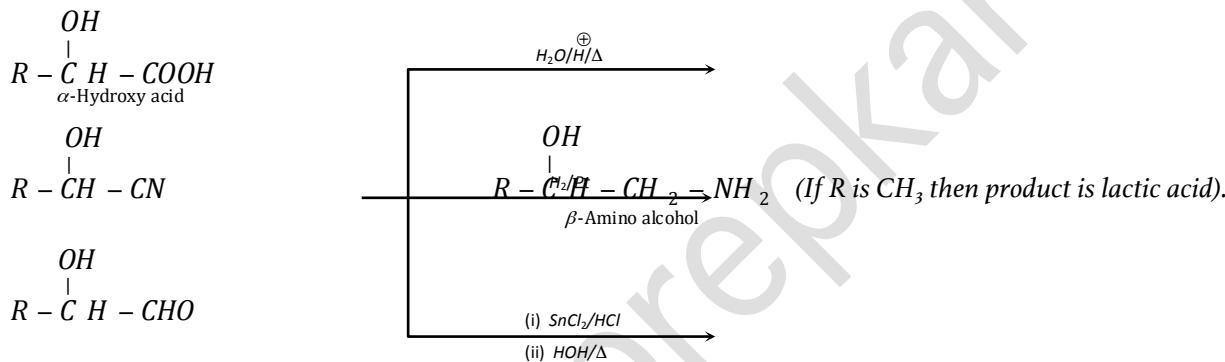
Addition of HCN: Carbonyl compounds react with HCN to form cyanohydrins. This reaction is catalysed by base.



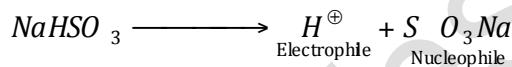


Note: Because HCN is a toxic gas, the best way to carry out this reaction, to generate hydrogen cyanide during the reaction by adding HCl to a mixture of the carbonyl compound and excess of NaCN.

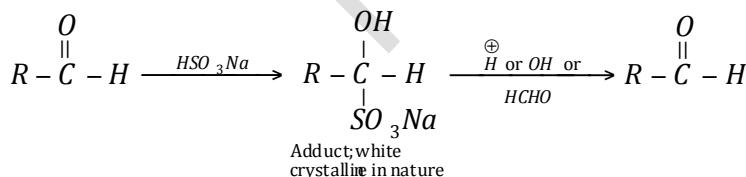
- Benzophenone does not react with HCN.
- Except formaldehyde, all other aldehydes gives optically active cyanohydrin (racemic mixture).
- This reaction is synthetically useful reaction for the preparation of α -hydroxy acids, β -amino alcohols and α -hydroxy aldehydes.



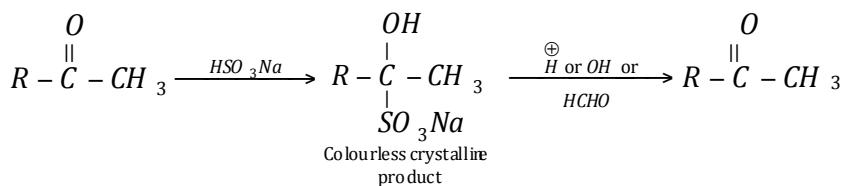
Addition of sodium bisulphite: Sodium bisulphite dissociates as follows:



(i) All types of aldehydes give addition reaction with this reagent. The adduct of aldehyde is white crystalline compound which again converts into aldehyde on treatment with acid, base or HCHO.

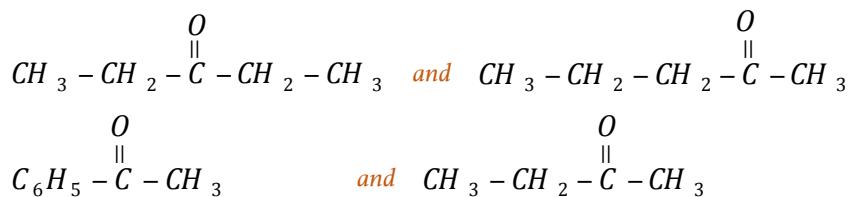


(ii) Only aliphatic methyl ketones give addition reaction with sodium bisulphite.



Note: This reagent can be used for differentiation between ketones and aliphatic methyl ketones, e.g.





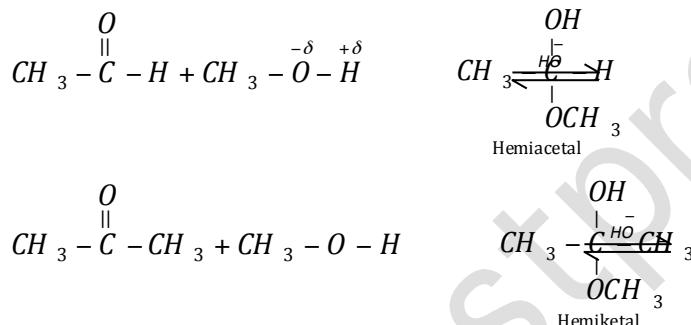
This reagent can be used for the separation of aldehydes and aliphatic methyl ketones from the mixture, e.g.



These two compounds can be separated from their mixture by the use of $NaHSO_3$. Higher aliphatic ketones and aromatic ketones do not react with $NaHSO_3$.

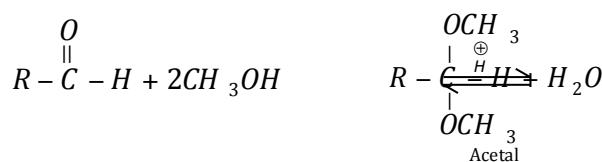
Addition of alcohols: Carbonyl compounds give addition reaction with alcohols. This reaction is catalysed by acid and base. Nature of product depends on the catalyst.

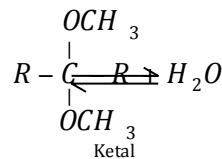
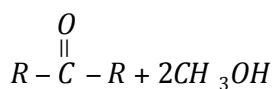
Case I: Addition catalysed by base: In the presence of base one equivalent of an alcohol reacts with only one equivalent of the carbonyl compound. The product is called hemiacetal (in case of aldehyde) and hemiketal (in case of ketone). The reaction is reversible. There is always equilibrium between reactants and product.



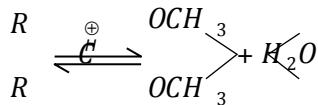
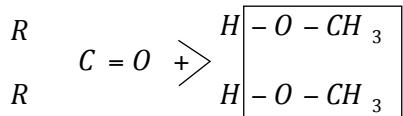
Hemiacetals and hemiketals are α -alkoxy alcohols.

Case II: Addition catalysed by acid: In the presence of acid one equivalent of carbonyl compound reacts with two equivalents of alcohol. Product of the reaction is acetal (in case of aldehyde) or ketal (in case of ketone).





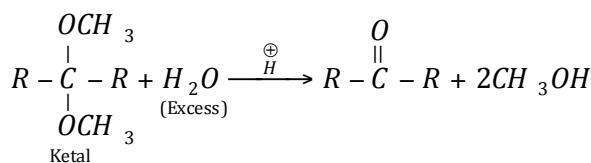
(i) Formation of acetals and ketals can be shown as follows:



(ii) Acetals and ketals are gem dialkoxy compounds.

(iii) High yield of acetals or ketals are obtained if the water eliminated from the reaction is removed as it formed because the reaction is reversible.

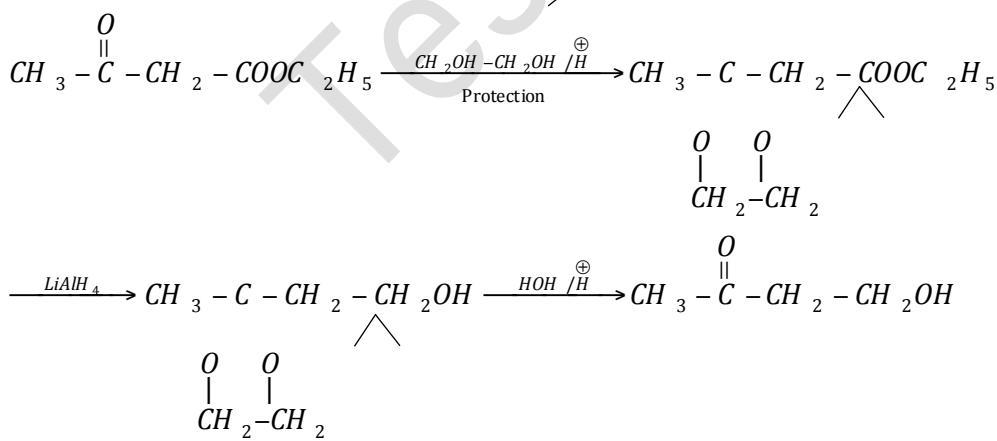
(iv) Acetals and ketals can be transformed back to corresponding aldehyde or ketone in the presence of excess of water.



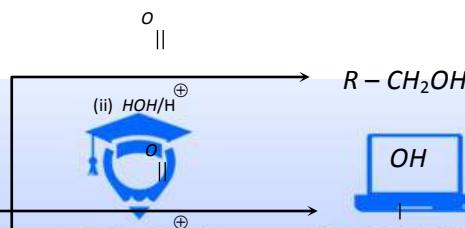
This reaction is very useful reaction for the protection of carbonyl group which can be deprotected by hydrolysis. Glycol is used for this purpose. Suppose we want to carry out the given conversion by $LiAlH_4$.



This can be achieved by protection of $C = O$ group and then by deprotection



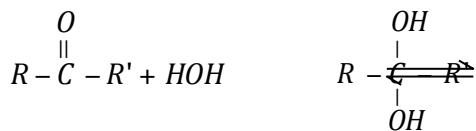
Addition of Grignard reagents: Grignard reagents react with carbonyl compounds to give alcohols. Nature of alcohol depends on the nature of carbonyl compound.



1°-alcohol

2°-alcohol

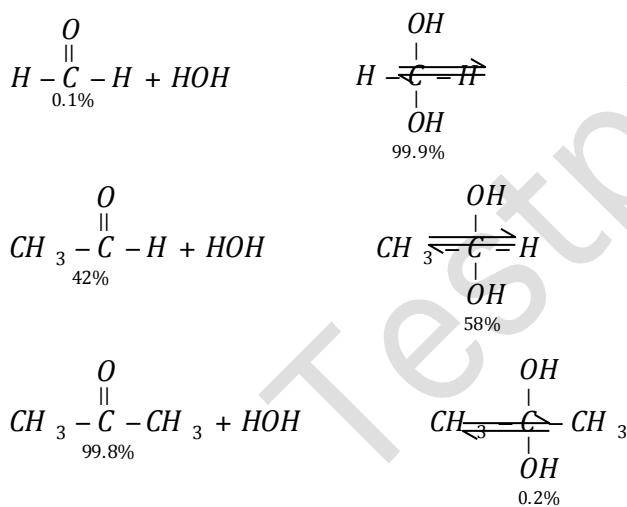
Addition of water: Carbonyl compounds react with water to give gem diols. This reaction is catalysed by acid. The reaction is reversible reaction.



Gem diols are highly unstable compounds hence equilibrium favours the backward direction. The extent to which an aldehyde or ketone is hydrated depends on the stability of gem diol.

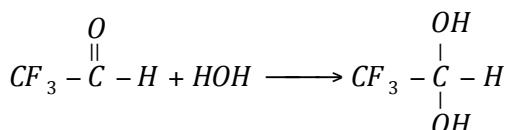
Stability of gem diols depend on the following factors:

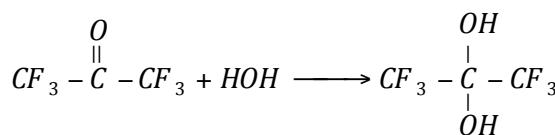
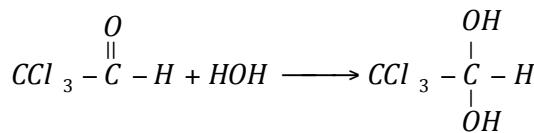
(i) Steric hindrance by +I group around α -carbon decreases the stability of gem diols. +I group decreases stability of gem diol and hence decreases extent of hydration.



(i) +I power of +I group is in increasing order

(ii) Stability of gem diols mainly depends on the presence of -I group on α -carbon. More is the -I power of the group more will be stability of gem diols.





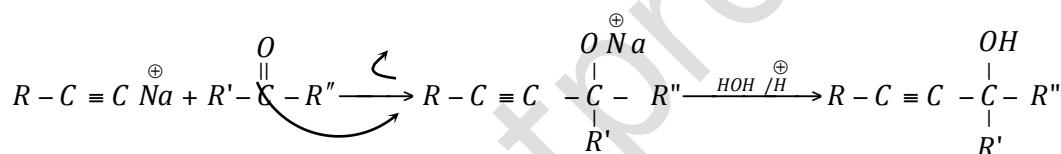
These gem diols are highly stable due to the presence of $-I$ group on α -carbon.

(iii) Intramolecular hydrogen bonding increases stability of gem diols. $-I$ groups present on carbon having gem diol group increases strength of hydrogen bond.

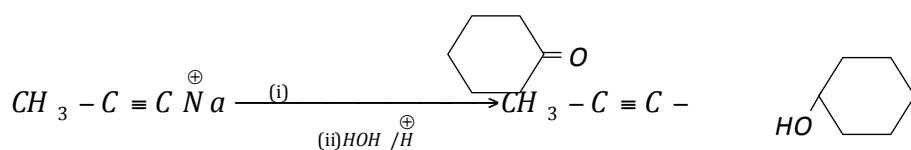
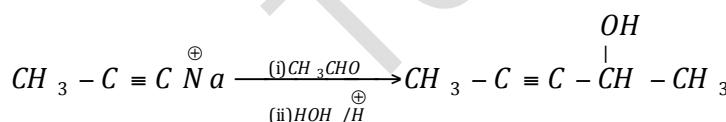
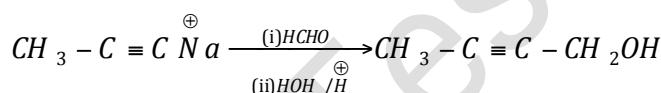
Strength of hydrogen bond α -I power of the group.

More is the strength of hydrogen bond more will be the stability of gem diol.

Addition of terminal alkynes: Sodium salt of terminal alkynes react with carbonyl compounds to give alkynol. This reaction is known as ethinylation.



Some examples are,



(2) **Addition followed by elimination reactions:** This reaction is given by ammonia derivatives ($NH_2 - Z$).

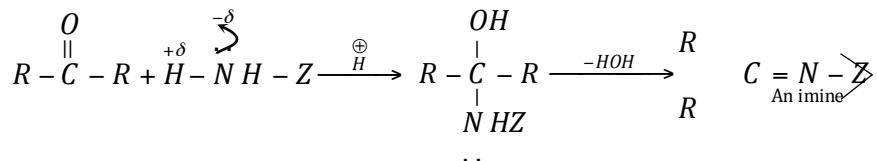
(i) In nucleophilic addition reactions poor nucleophile such as ammonia and ammonia derivatives requires acid as catalyst.



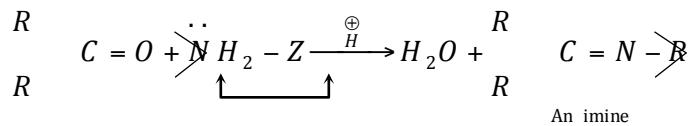
(ii) If the attacking atom of the nucleophile has a lone pair of electrons in the addition product, water will be eliminated from the addition product. This is called a nucleophilic addition elimination.

Primary amines and derivatives of ammonia react with carbonyl compounds to give adduct.

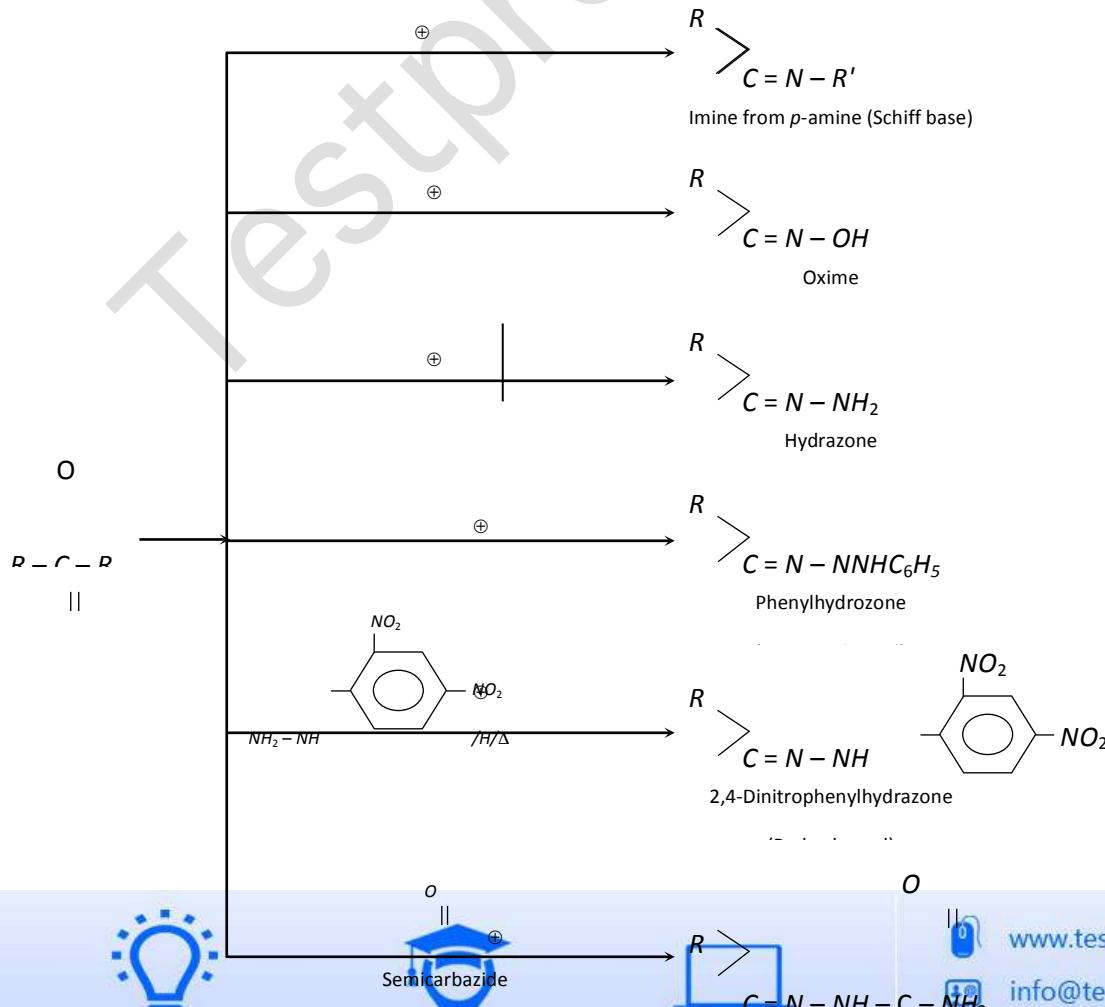
In adduct nucleophilic group has lone pair of electrons. It undergoes elimination to give product known as imine. An imine is a compound with a carbon-nitrogen double bond.



The overall reaction can be shown as follows:

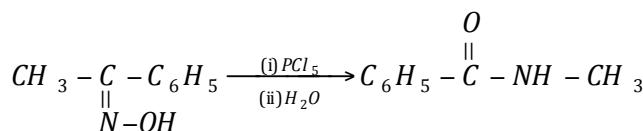
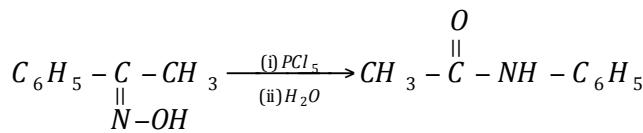


Different imine formation with $NH_2 - Z$ is given below

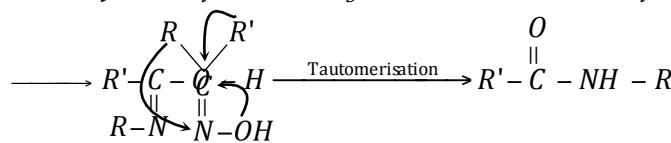


Ketoxime when treated with acid at 0°C it undergoes rearrangement known as **Beckmann rearrangement**.

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.)



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



(3) Oxidation of carbonyl compounds

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

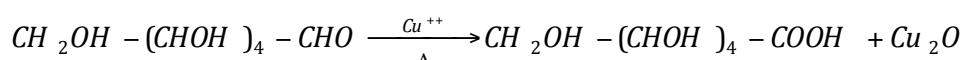
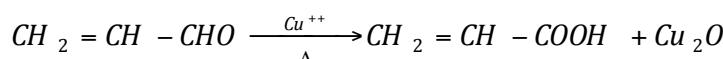
(a) **Fehling solution:** It is a mixture of two Fehling solution: Fehling solution No.1: It contains $CuSO_4$ solution and $NaOH$.

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:



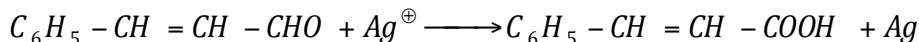
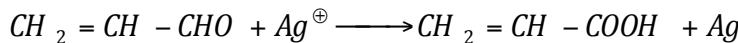
Benedict's solution and Fehling solutions are used as a reagent for the test of sugar (glucose) in blood sample.

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

☐ It oxidises aliphatic as well as aromatic aldehydes.

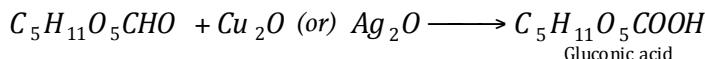


This reagent has no effect on carbon-carbon multiple bond.



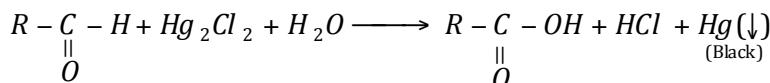
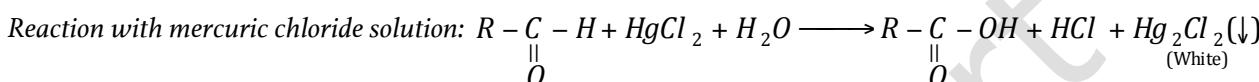
In this reaction the oxidation no. of Ag varies from +I to 0.

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



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 $HCOOH$.



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

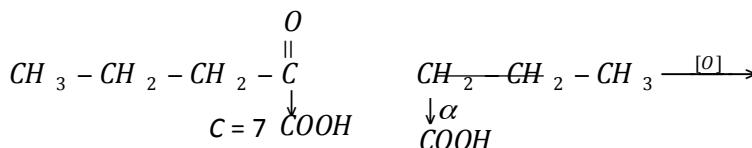
$KMnO_4 / OH^- / \Delta$, $KMnO_4 / H^+ / \Delta$, $K_2Cr_2O_7 / H^+ / \Delta$ and conc HNO_3 / Δ . These agents oxidise aldehydes as well as ketones.

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

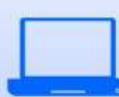


(b) **Oxidation of ketones:** Ketones undergo oxidation only in drastic conditions. During the oxidation of ketones there is breaking of carbon-carbon bond between α -carbon and carbonyl carbon. In this process both carbons convert into carboxylic groups. This leads to the formation of two moles of monocarboxylic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

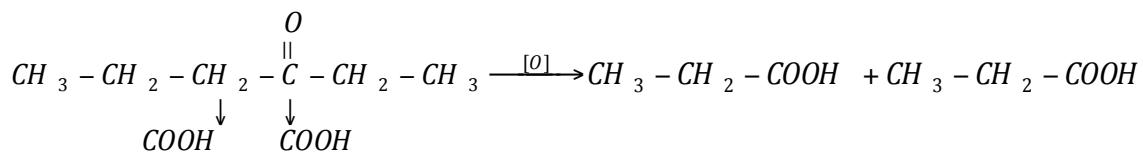
Case I: Oxidation of symmetrical ketones



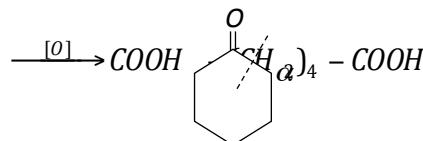
Thus number of carbons in any product is less than the number of carbons in ketone.



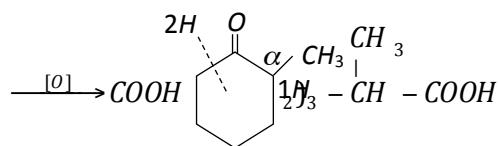
Case II: Oxidation of unsymmetrical ketones: In case of unsymmetrical ketones α -carbon whose bond breaks always belongs to the alkyl group which has more number of carbons. This rule is known as Poff's rule.



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.

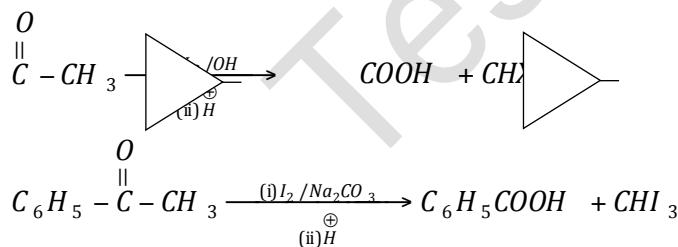
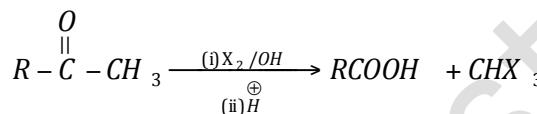


Note: If both α -carbons are not identical then bond breaking takes place between carbonyl carbon and α -carbon which has maximum number of hydrogens.



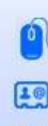
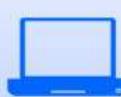
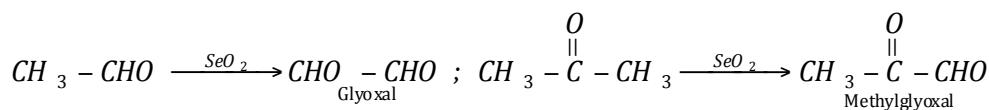
(iii) Miscellaneous oxidation

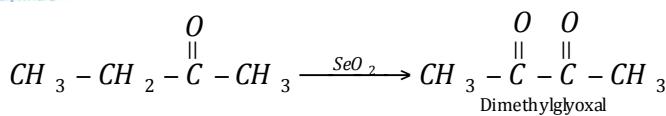
(a) **Haloform Reaction:** In this reaction α -methyl carbonyl compounds undergo oxidation with X_2 / H .



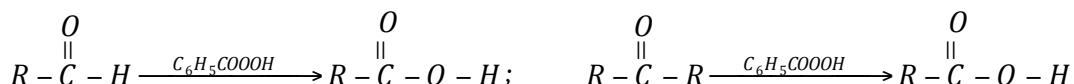
(b) **Oxidation at α -CH₂ or CH₃ by SeO₂:** SeO₂ oxidises α -CH₂-group into keto group and α -CH₃-group into aldehydic group.

In this oxidation reactivity of CH₂ is more than the CH₃ group and Oxidation is regio selective in nature.





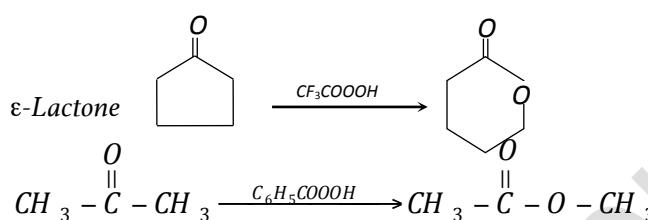
(c) **Oxidation by organic peracids:** Organic peracids oxidise aldehydes into carboxylic acids and ketones into esters. This oxidation is known as **Baeyer – Villiger oxidation.**



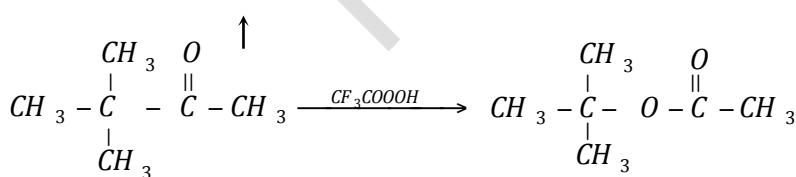
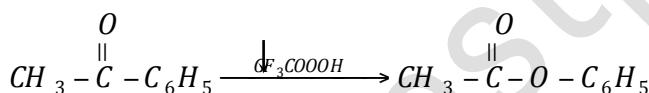
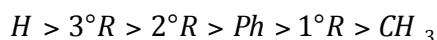
In case of aldehyde there is insertion of atomic oxygen (obtained from peracid) between carbonyl carbon and hydrogen of carbonyl carbon.

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.

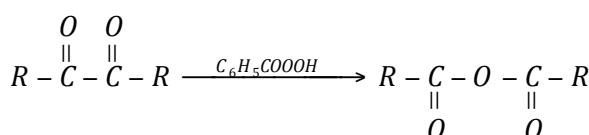
Symmetrical ketones:



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

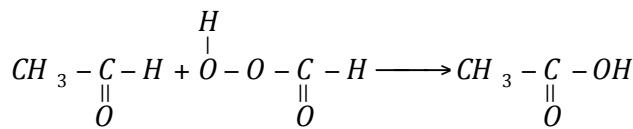
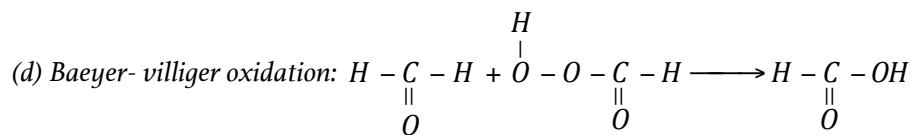
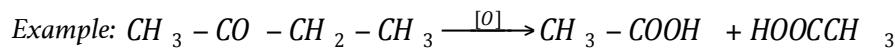


Note: Vic dicarbonyl compound also undergo oxidation & product is anhydride.



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





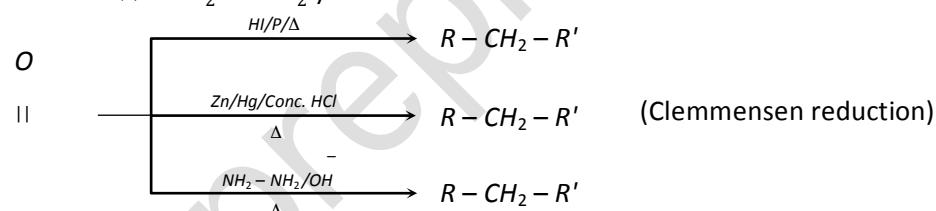
Note: Reaction will be held if the oxidation agent is performic acid.

(4) Reaction of carbonyl compounds

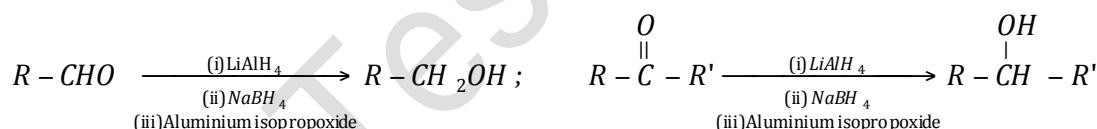
O

(i) Reduction of group into $-\text{CH}_2-$ group: Following three reagents reduce carbonyl group into $-\text{CH}_2-$ groups: (a)

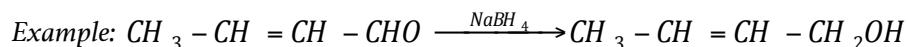
$\text{HI}/\text{P}/\Delta$ (b) $\text{Zn}/\text{Hg}/\text{Conc. HCl}$ and (c) $\text{NH}_2 - \text{NH}_2/\text{OH}$.



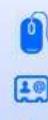
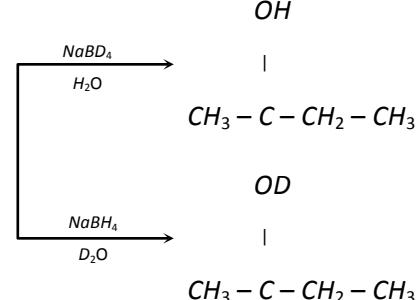
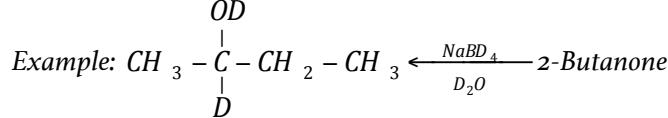
(ii) Reduction of carbonyl compounds into hydroxy compounds: Carbonyl group converts into $-\text{CHOH}-$ group by LiAlH_4 , NaBH_4 , $\text{Na/C}_2\text{H}_5\text{OH}$ and aluminium isopropoxide.



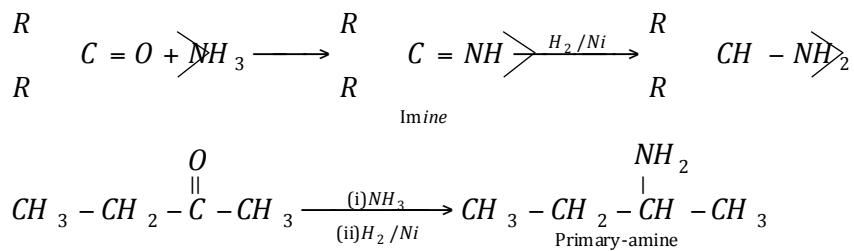
NaBH_4 is regioselective reducing agent because it reduced only. CHO in the presence of other reducible group.



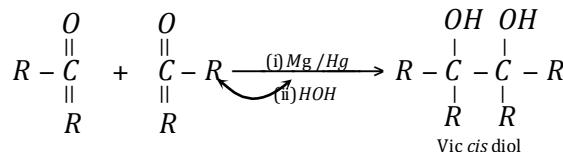
Hydride ion of NaBH_4 attack on carbonyl carbon during reduction.



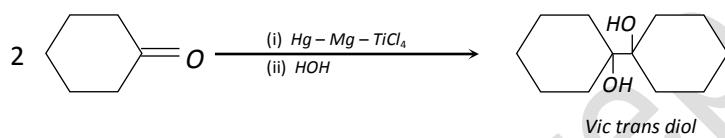
(iii) **Reductive amination:** In this reduction $-CO-$ group converts into $-CH-NH_2$ group as follows:



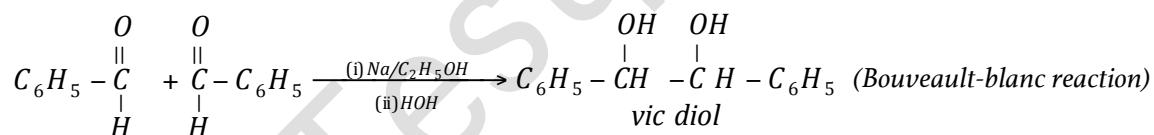
(iv) **Reduction of ketones by Mg or Mg/Hg:** In this case ketones undergo reduction via coupling reaction and product is vic cis diol.



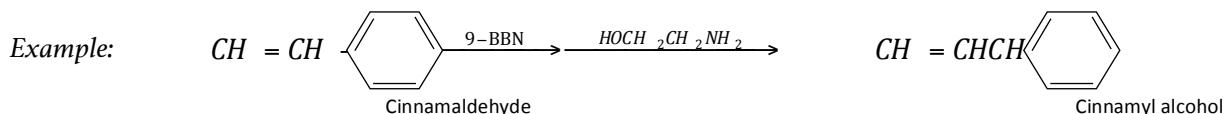
When this reaction is carried out in the presence of $Mg / Hg / TiCl_4$, the product is vic trans diol.



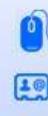
(v) **Reduction of benzaldehyde by Na/C_2H_5OH :** Benzaldehyde undergoes reduction via coupling reaction and product is vic diol.



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 along with. However, the use of the reagent 9-BBN (9-borabicyclo (3, 3, 1) nonane) prevents this and thus only the carbonyl group is reduced

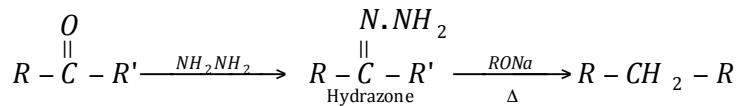


- If reducing agent is NaH , reaction is called Darzen's reaction, we can also use $LiAlH_4$ in this reaction.
- If reducing agent is aluminium iso propoxide $(CH_3-\underset{CH_3}{C}H-O-)_3Al$. Product will be alcohol. This reaction is called Meerwein – pondorff verley reduction (MPV reduction).

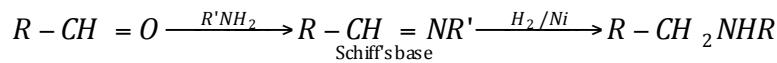


- The percentage yield of alkanes can be increased by using diethylene glycol in Wolf Kishner reduction. Then reaction is called Huang – Millan conversion.

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



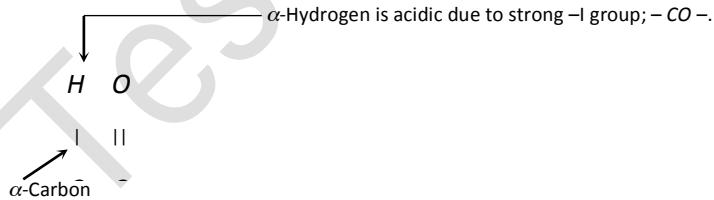
(vii) Schiff's base on reduction gives secondary amines.



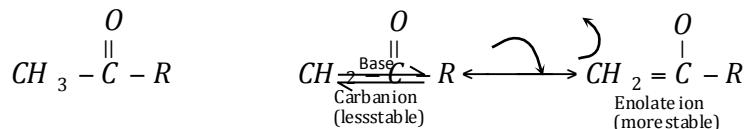
(5) Reactions due to α -hydrogen

(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.



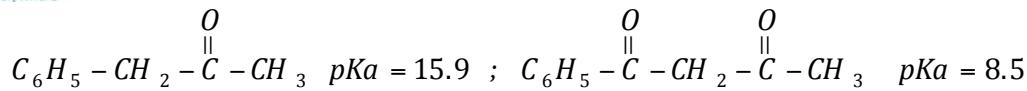
(b) Thus carbonyl compounds having α -hydrogen convert into carbanions in the presence of base. This carbanion is stabilised by delocalisation of negative charge.



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

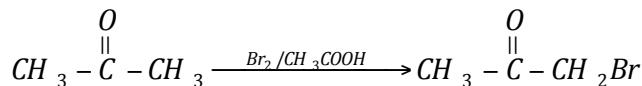
(d) Compounds having active methylene or methyne group are even more acidic than simple aldehydes and ketones.



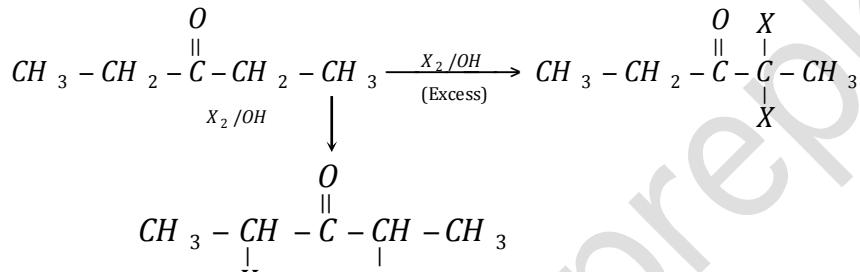


(ii) **Halogenation:** Carbonyl compounds having α -hydrogens undergo halogenation reactions. This reaction is catalysed by acid as well as base.

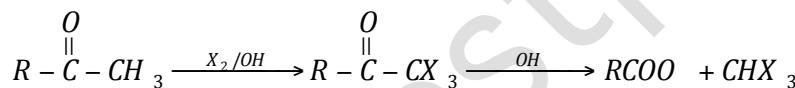
(a) Acid catalysed halogenation: This gives only monohalo derivative.



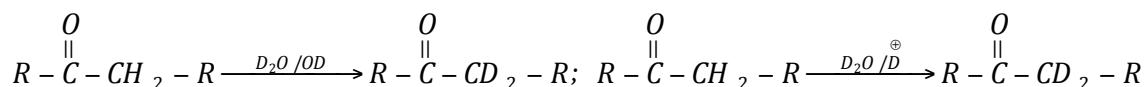
(b) Base catalysed halogenation: In the presence of base all α -hydrogens of the same carbon is replaced by halogens.



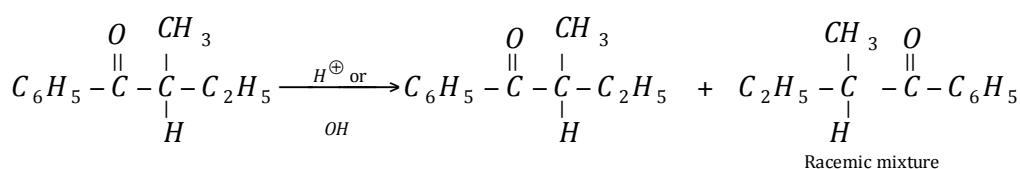
Carbonyl compounds having three α -hydrogens give **haloform** reaction.



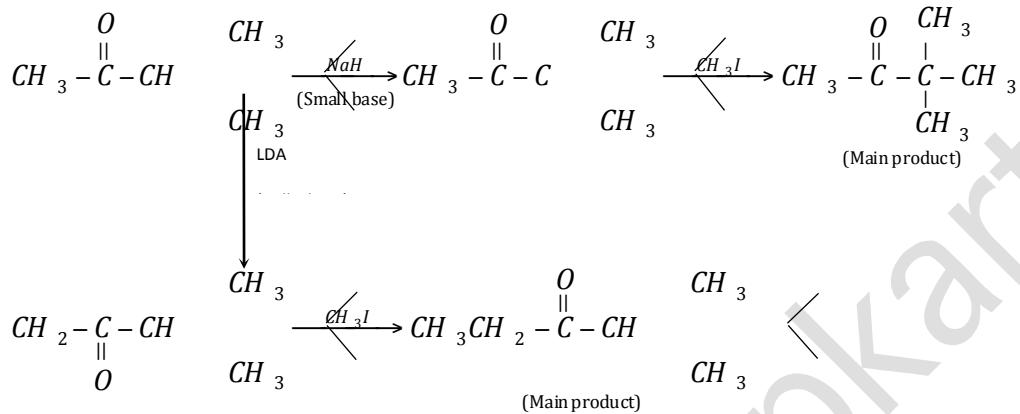
(iii) **Deuterium exchange reaction:** Deuterium exchange reaction is catalysed by acid (D^+) as well as base (OD^-). In both the cases all the hydrogens on only one α -carbon is replaced by D.



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



(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.

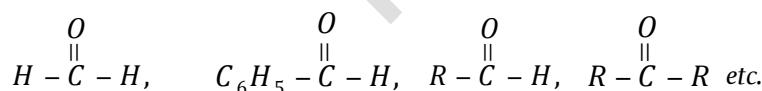


(vi) **Wittig reaction:** Aldehydes and ketones undergo the Wittig reaction to form alkenes.



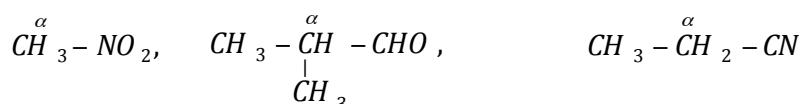
(6) **Condensation reaction of carbonyl compounds:** Nucleophilic addition reaction of compounds having carbonyl group with those compounds which have at least one acidic hydrogen at α -carbon is known as condensation reaction. In this addition reaction:

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



Addition always takes place on the carbonyl group.

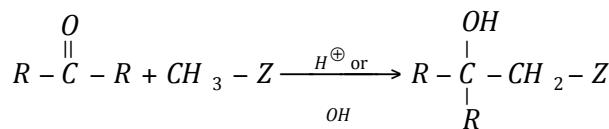
Reagents of the condensation reaction are also organic compounds having at least one hydrogen on α -carbon and α -carbon should have $-I$ group, e.g.



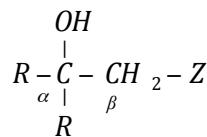
Note: If substrate and reagent both are carbonyl compounds then one should have at least one α -hydrogen and other may or may not have α -hydrogen.



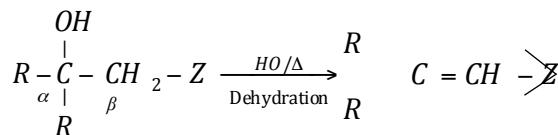
Condensation reaction always takes place in the presence of acid or base as catalyst. Best result is obtained with base at lower temp.



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



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



(i) Aldol condensation

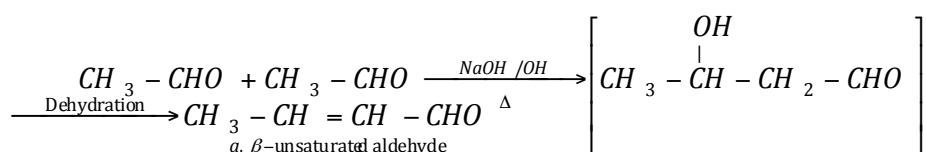
(a) This reaction takes place between two molecules of carbonyl compounds; one molecule should have at least two α -hydrogen atoms. In this reaction best result is obtained when

Both molecule are the same or

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

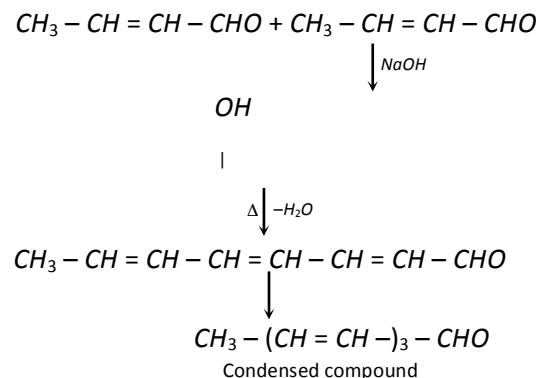
(b) These reactions are practical when base is NaOH and reaction temperature is high ($\geq 100^\circ$).

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

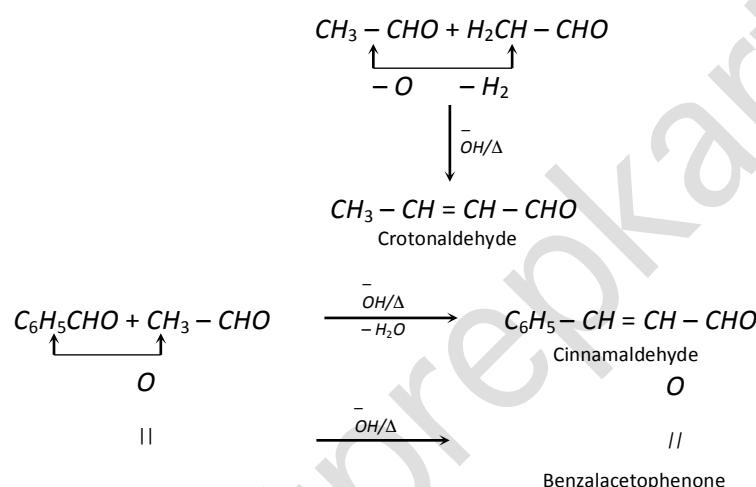


Due to hyper conjugation in crotonaldehyde further condensed give conjugated alkene carbonyl compound.





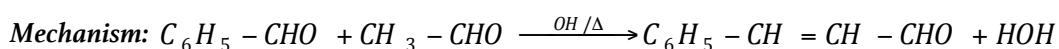
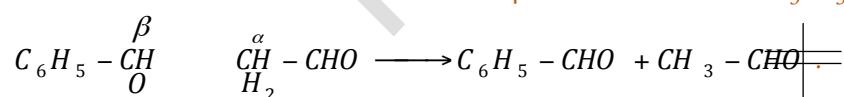
The net result can be written as follows]

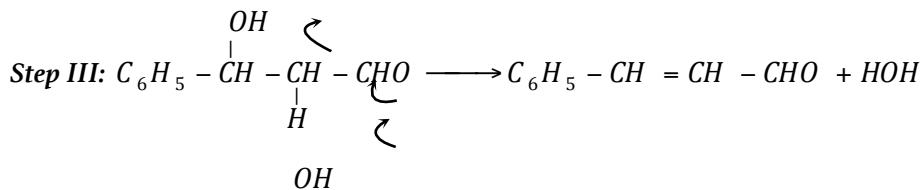
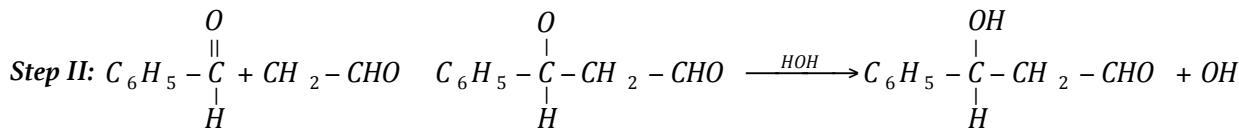
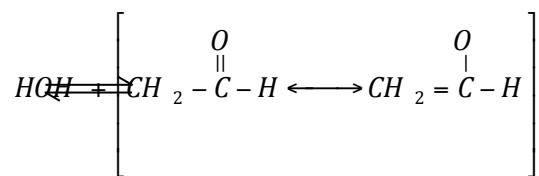
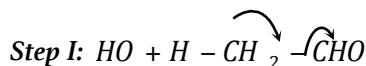


Note: If product is given then reactants can be known as follows:



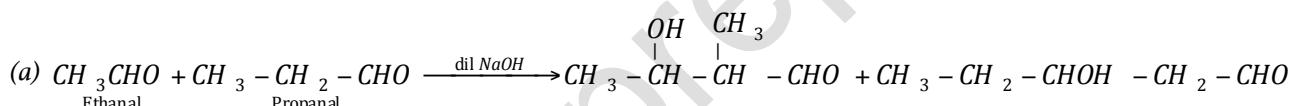
Break carbon-carbon double bond between α and β carbons and attach two hydrogens on α -carbon and an oxygen on β -carbon, i.e.



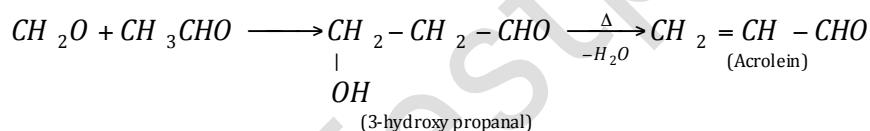


In aldol condensation, dehydration occurs readily because the double bond that forms is conjugated, both with the carbonyl group and with the benzene ring. The conjugation system is thereby extended.

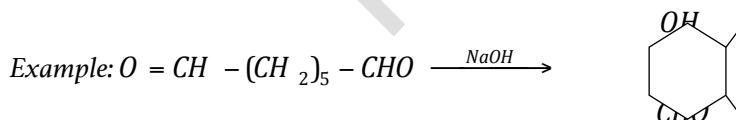
Crossed aldol condensation: Aldol condensation between two different aldehydes or two different ketones or one aldehyde and another ketone provided at least one of the components have α -hydrogen atom gives different possible product



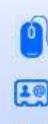
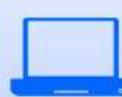
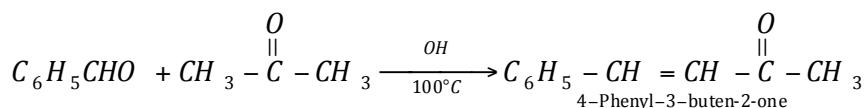
However crossed aldol condensation is important when only it the components has α -hydrogen atom.

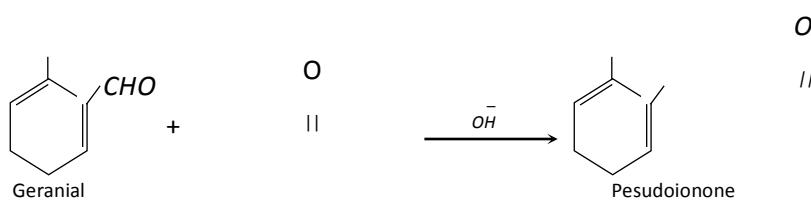
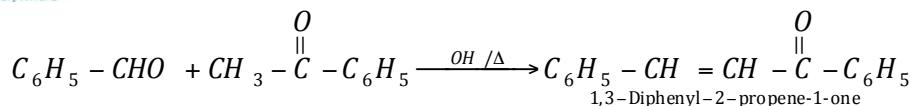


Intra molecular aldol condensation: One molecule Intramolecular condensed give aldol compounds



(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 these conditions ketones do not undergo self-condensation. Some examples of this reaction are:





6. 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.

7. 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.

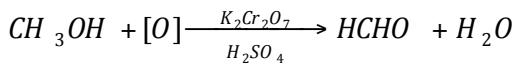


Traces of formaldehyde are formed when incomplete combustion of wood, sugar, coal, etc., occurs.

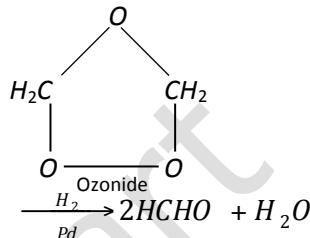


(I) Preparation

$$(i) \text{By oxidation of methyl alcohol } 2\text{CH}_3\text{OH} + \text{O}_2 \xrightarrow[\text{300--400}^\circ\text{C}]{\text{Platinised asbestos}} 2\text{HCHO} + 2\text{H}_2\text{O}$$



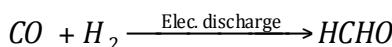
(ii) By dehydrogenation of methyl alcohol $\text{CH}_3\text{OH} \xrightarrow[300-400^\circ\text{C}]{\text{Cu or Ag}} \text{HCHO} + \text{H}_2$



(iv) By ozonolysis of ethylene: $\text{CH}_2 = \text{CH}_2 + \text{O}_3 \longrightarrow$

$$(v) \text{ Manufacture: } \text{CH}_4 + \text{O}_2 \xrightarrow[\text{Methane}]{\substack{\text{Mo-oxide} \\ \text{Catalyst}}} \text{HCHO} + \text{H}_2\text{O} \quad \text{For formaldehyde}$$

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



(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.

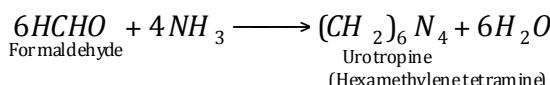
(iii) It can easily be condensed into liquid. The liquid formaldehyde boils at -21°C .

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

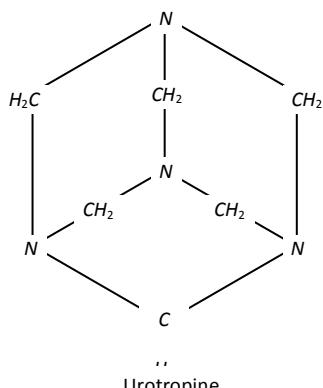
(v) Its solution acts as antiseptic and disinfectant.

(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

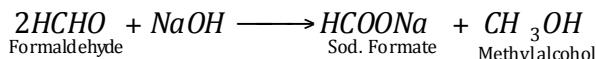
(i) **Reaction with ammonia:** Like other aldehydes, formaldehyde does not form addition product but a crystalline compound, hexamethylene tetramine, with ammonia.



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

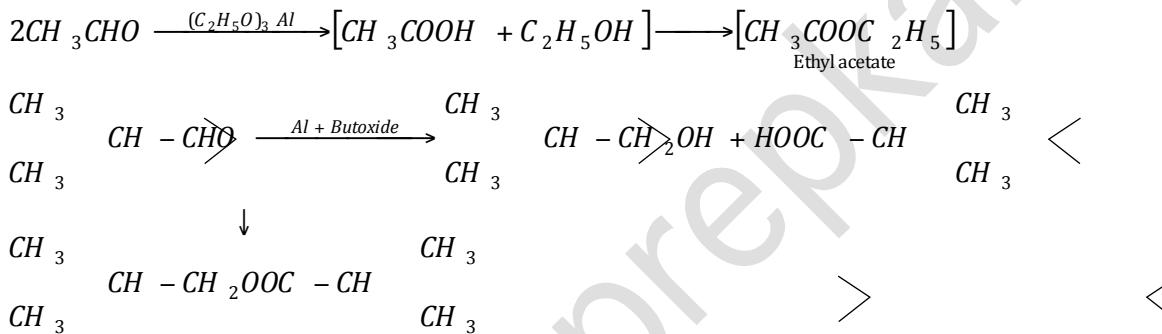


(ii) **Reaction with sodium hydroxide (Cannizzaro's reaction)**: It does not form resin with sodium hydroxide like acetaldehyde but when treated with a concentrated solution of sodium hydroxide, two molecules of formaldehyde undergo mutual oxidation and reduction forming formic acid salt and methyl alcohol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

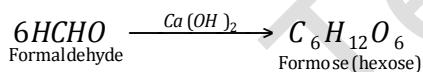


This transformation is known as Cannizzaro's reaction.

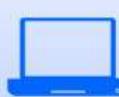
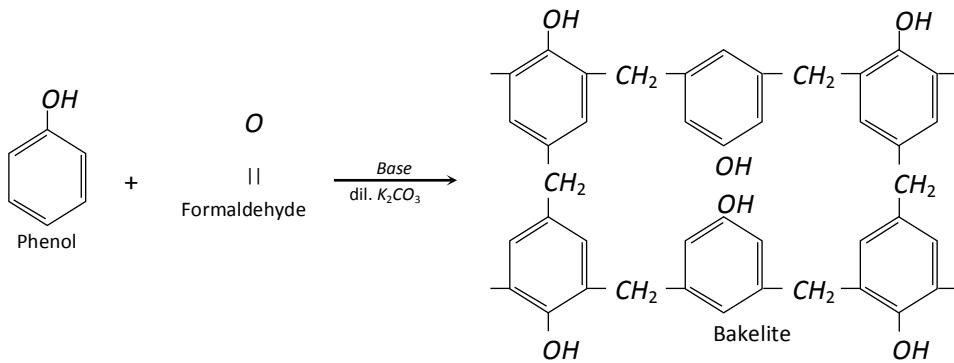
Tischenko's reaction: This is a modified form of cannizzaro's reaction. All aldehydes undergo cannizzaro's reaction in presence of aluminium ethoxide. The acid and alcohol formed react together to give the ester.



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

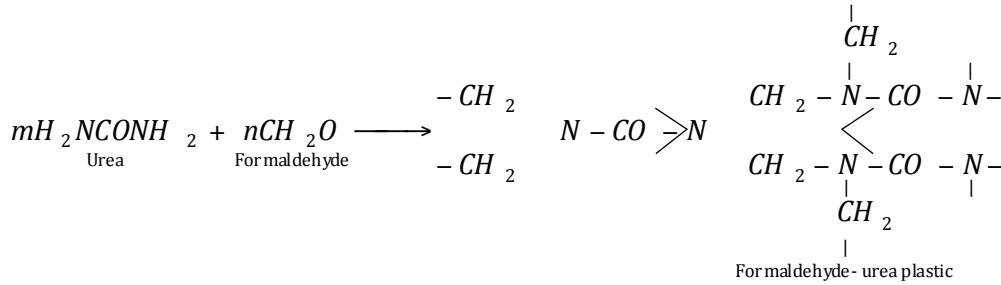


(iv) **Condensation with phenol:** Formaldehyde condenses with phenol to give a synthetic plastic, bakelite. The condensation occurs in presence of dilute sodium hydroxide or ammonia at 80 – 90°C. Bakelite is used for preparing electrical insulators, electric switches, toys, etc.

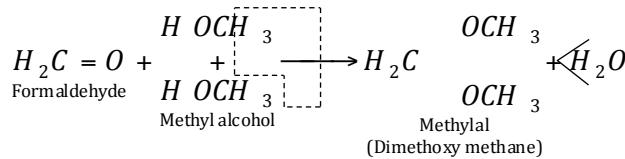


Bakelite is electrical and thermal resistant so it is used in formation of electrical appliances. This reaction is called Lederer-Manasse reaction.

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



(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.



(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.



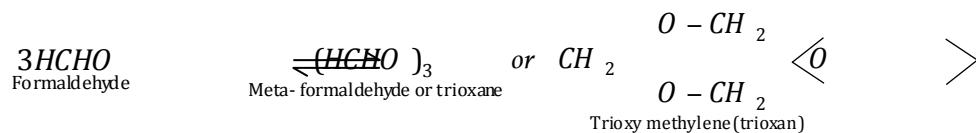
On rapid heating it gives back gaseous formaldehyde.

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

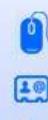
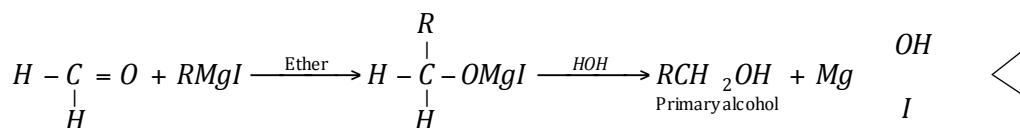


This on heating gives back formaldehyde.

(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. $61 - 62^\circ C$). This on heating gives back gaseous formaldehyde.



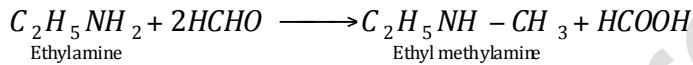
(viii) **Reaction with grignard reagent:** Formaldehyde forms primary alcohols with Grignard reagent.



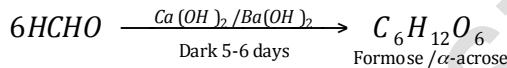
Formaldehyde does not react with chlorine and phosphorus pentachloride. It does not give iodoform test.

(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.,



- (ix) If aqueous 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.



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.

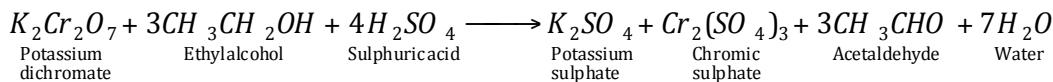
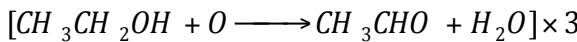
- (i) **Preparation:** It may be prepared by any of the general methods. The summary of the methods is given below
- (i) By oxidation of ethyl alcohol with acidified potassium dichromate or with air in presence of a catalyst like silver at $300^\circ C$.
- (ii) By dehydrogenation of ethyl alcohol. The vapours of ethyl alcohol are passed over copper at $300^\circ C$.
- (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).



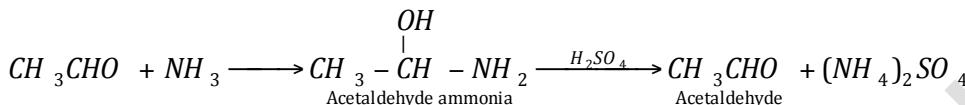
(vii) By hydration of acetylene with dil. H_2SO_4 and $HgSO_4$ at $60^\circ C$.

(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.

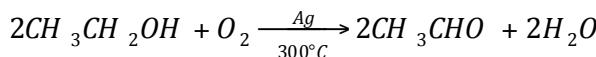


To recover acetaldehyde, the distillate is treated with dry ammonia when crystallised product, acetaldehyde ammonia, is formed. It is filtered and washed with dry ether. The dried crystals are then distilled with dilute sulphuric acid when pure acetaldehyde is collected.

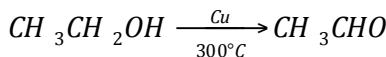


(x) **Manufacture**: Acetaldehyde can be manufactured by one of the following methods:

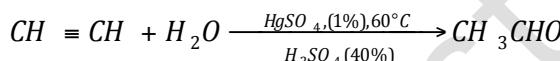
(a) By air oxidation of ethyl alcohol: Ethyl alcohol vapours and limited amount of air are passed over heated silver catalyst at 300°C .



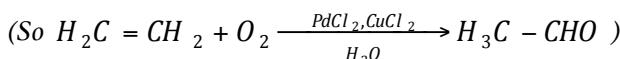
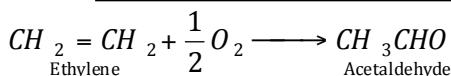
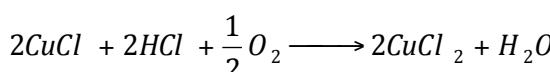
(b) By dehydrogenation of alcohol: Vapours of ethyl alcohol are passed over heated copper at 300°C .



(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.



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



(2) *Physical properties*

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



(ii) It has a characteristic pungent smell.

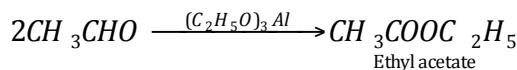
(iii) It is soluble in water, chloroform, ethyl alcohol and ether. Its aqueous solution has a pleasant odour. In water, it is hydrated to a considerable extent to form ethylidene glycol.



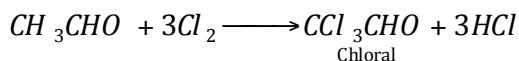
(3) **Chemical properties:** It gives all characteristic reactions of aldehydes. Besides general reactions, acetaldehyde shows the following reactions also.

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

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

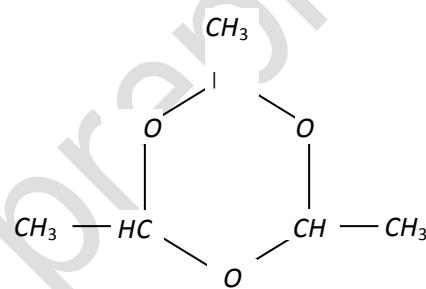


(iii) **Chlorination:** Hydrogen atoms of the methyl group are substituted by chlorine atoms when acetaldehyde is treated with chlorine.

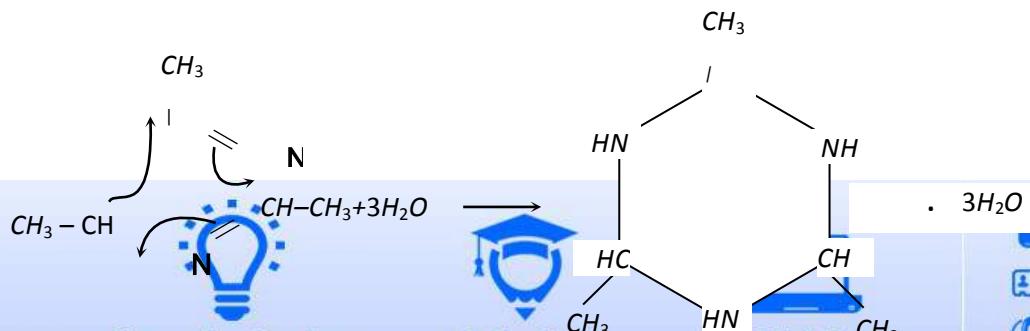
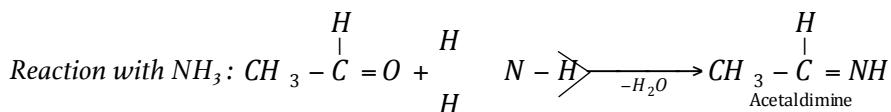


(iv) **Polymerisation:** Acetaldehyde undergoes polymerisation forming different products under different conditions.

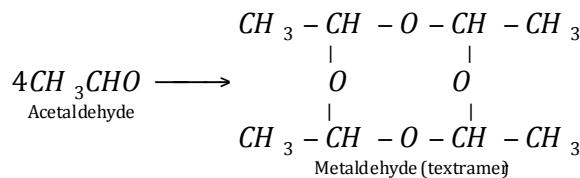
(a) **Paraldehyde:** It is formed, when anhydrous acetaldehyde is treated with conc. sulphuric acid.



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).



(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.



It is used for killing slugs and snails.

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

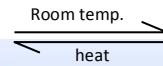
- (i) In the preparation of acetic acid, acetic anhydride, ethyl acetate, chloral, 1,3-butadiene (used in rubbers), dyes and drugs.
- (ii) As an antiseptic inhalent in nose troubles.
- (iii) In the preparation of paraldehyde (hypnotic and sporofic) and metaldehyde (solid fuel).
- (iv) In the preparation of acetaldehyde ammonia (a rubber accelerator).

Comparative study of formaldehyde and acetaldehyde

S.No.	Reaction	Formaldehyde HCHO	Acetaldehyde CH_3CHO
1.	Similarity 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 $\text{HCHO} + \text{H}_2 \longrightarrow \text{CH}_3\text{OH}$ Forms methane $\text{HCHO} + 4\text{H} \longrightarrow \text{CH}_4 + \text{H}_2\text{O}$	Forms ethyl alcohol $\text{CH}_3\text{CHO} + \text{H}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{OH}$ Forms ethyl alcohol Forms ethane $\text{CH}_3\text{CHO} + 4\text{H} \longrightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}$
2.	Addition of NaHSO_3 solution	Forms bisulphite addition product $\text{HCHO} + \text{NaHSO}_3 \longrightarrow \text{CH}_2(\text{OH})\text{SO}_3\text{Na}$	Forms bisulphite addition product $\text{CH}_3\text{CHO} + \text{NaHSO}_3 \longrightarrow$ $\text{CH}_3\text{CH}(\text{OH})\text{SO}_3\text{Na}$
3.	Addition of HCN	Forms formaldehyde cyanohydrin $\text{HCHO} + \text{HCN} \longrightarrow \text{CH}_2(\text{OH})\text{CN}$	Forms acetaldehyde cyanohydrin $\text{CH}_3\text{CHO} + \text{HCN} \longrightarrow$ $\text{CH}_3\text{CH}(\text{OH})\text{CN}$



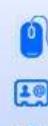
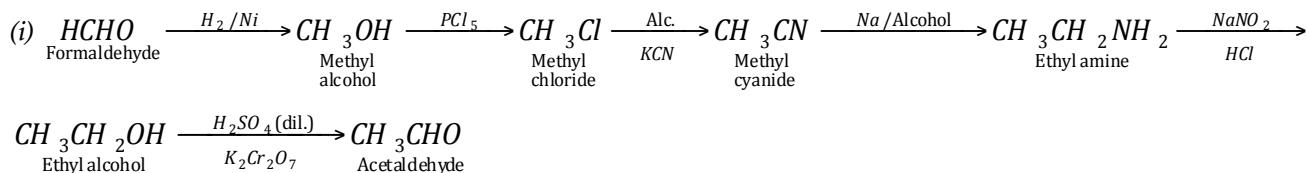
4.	Addition of Grignard reagent followed by hydrolysis	Forms ethyl alcohol $\text{HCHO} + \text{CH}_3\text{MgI} \longrightarrow \text{CH}_2 \begin{array}{c} \diagup \\ \text{OMgI} \\ \diagdown \end{array}$ $\xrightarrow[-\text{Mg(OH)}\text{I}]{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{OH}$	Forms isopropyl alcohol $\text{CH}_3\text{CHO} + \text{CH}_3\text{MgI} \longrightarrow$ $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} \text{HOMgI} \xrightarrow[-\text{Mg(OH)}\text{I}]{-\text{H}_2\text{O}}$ $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} - \text{OH}$
5.	With hydroxylamine NH_2OH	Forms formaldoxime $\text{CH}_2 = \text{O} + \text{H}_2\text{NOH} \xrightarrow{-\text{H}_2\text{O}}$ $\text{CH}_2 = \text{NOH}$	Forms acetaldoxime $\text{CH}_3\text{CH} = \text{O} + \text{H}_2\text{NOH} \xrightarrow{-\text{H}_2\text{O}}$ $\text{CH}_3\text{CH} = \text{NOH}$
6.	With hydrazine (NH_2NH_2)	Forms formaldehyde hydrazone $\text{CH}_2 = \text{O} + \text{H}_2\text{NHNH}_2 \xrightarrow{-\text{H}_2\text{O}}$ $\text{CH}_2 = \text{NNH}_2$	Forms acetaldehyde hydrazone $\text{CH}_3\text{CH} = \text{O} + \text{H}_2\text{NNH}_2 \xrightarrow{-\text{H}_2\text{O}}$ $\text{CH}_3\text{CH} = \text{NNH}_2$
7.	With phenylhydrazine $(\text{C}_6\text{H}_5\text{NNH}_2)$	Forms formaldehyde phenyl hydrazone $\text{CH}_2 = \text{O} + \text{H}_2\text{NNHC}_6\text{H}_5 \xrightarrow{-\text{H}_2\text{O}}$ $\text{CH}_2 = \text{NNHC}_6\text{H}_5$	Forms acetaldehyde phenyl hydrazone $\text{CH}_3\text{CH} = \text{O} + \text{H}_2\text{NNHC}_6\text{H}_5 \xrightarrow{-\text{H}_2\text{O}}$ $\text{CH}_3\text{CH} = \text{NNHC}_6\text{H}_5$
8.	With semicarbazide $(\text{H}_2\text{NNHCONH}_2)$	Forms formaldehyde semicarbazone $\text{CH}_2 = \text{O} + \text{H}_2\text{NNHCONH}_2 \xrightarrow{-\text{H}_2\text{O}}$ $\text{CH}_2 = \text{NNHCONH}_2$	Forms acetaldehyde semicarbazone $\text{CH}_3\text{CH} = \text{O} + \text{H}_2\text{NNHCONH}_2 \xrightarrow{-\text{H}_2\text{O}}$ $\text{CH}_3\text{CH} = \text{NNHCONH}_2$
9.	With alcohol $(\text{C}_2\text{H}_5\text{OH})$ in presence of acid	Forms ethylal $\text{H}_2\text{C} = \text{O} + 2\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{HA}}$ OC_2H_5 CH_2 OC_2H_5	Forms acetaldehyde diethyl acetal $\text{CH}_3\text{CHO} + 2\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{HA}}$ OC_2H_5 CH_3CH OC_2H_5
10.	With thioalcohols $(\text{C}_2\text{H}_5\text{SH})$ in presence of acid	Forms thio ethylal $\text{H}_2\text{C} = \text{O} + 2\text{C}_2\text{H}_5\text{SH} \longrightarrow$ SC_2H_5 CH_2 SC_2H_5	Forms acetaldehyde diethyl thioacetal $\text{CH}_3\text{CH} = \text{O} + 2\text{C}_2\text{H}_5\text{SH} \longrightarrow$ SC_2H_5 CH_3CH SC_2H_5
11.	Oxidation with acidified $\text{K}_2\text{Cr}_2\text{O}_7$	Forms formic acid $\text{HCHO} + \text{O} \longrightarrow \text{HCOOH}$	Forms acetic acid $\text{CH}_3\text{CHO} + \text{O} \longrightarrow \text{CH}_3\text{COOH}$
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 $\text{Ag}_2\text{O} + \text{HCHO} \longrightarrow 2\text{Ag} + \text{HCOOH}$	Gives black precipitate of Ag or silver mirror $\text{Ag}_2\text{O} + \text{CH}_3\text{CHO} \longrightarrow$ $2\text{Ag} + \text{CH}_3\text{COOH}$
14.	With Fehling's solution or Benedict's solution	Gives red precipitate of cuprous oxide $2\text{CuO} + \text{HCHO} \longrightarrow \text{Cu}_2\text{O} + \text{HCOOH}$	Gives red precipitate of cuprous oxide $2\text{CuO} + \text{CH}_3\text{CHO} \longrightarrow$ $\text{Cu}_2\text{O} + \text{CH}_3\text{COOH}$
15.	Polymerisation	Undergoes polymerisation $\xrightleftharpoons[\text{heat}]{\text{Room temp.}}$	Undergoes polymerisation $3\text{CH}_3\text{CHO} \xrightleftharpoons[\text{dil. H}_2\text{SO}_4, \text{ distill}]{\text{H}_2\text{SO}_4, \text{Conc.}}$

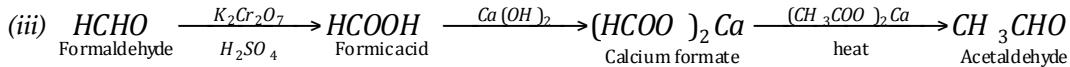
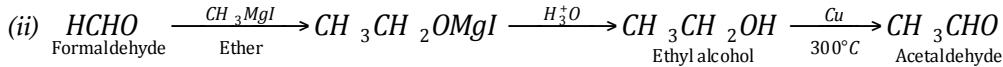


		$nHCHO$ $3HCHO$	$(HCHO)_n$ Paraformaldehyde $(HCHO)_3$ Metaformaldehyde	$(CH_3CHO)_3$ Paraldehyde $4CH_3CHO$ $(CH_3CHO)_4$ Metaldehyde
16.	Difference With PCl_5	No reaction		Forms ethyldene chloride $CH_3CHO + PCl_5 \longrightarrow \begin{matrix} CH_2CH \\ +POCl_3 \\ Cl \end{matrix}$
17.	With chlorine	No reaction		Forms chloral $CH_3CHO + 3Cl_2 \longrightarrow \begin{matrix} CCl_3CHO \\ +3HCl \end{matrix}$
18.	With SeO_2	No reaction		Forms glyoxal $CH_3CHO + SeO_2 \longrightarrow \begin{matrix} CHO .CHO \\ +Se + H_2O \end{matrix}$
19.	Iodoform reaction ($I_2 + NaOH$)	No reaction		Forms iodoform $CH_3CHO + 3I_2 + 4NaOH \longrightarrow \begin{matrix} CHI_3 + HCOONa + 3NaI + 3H_2O \end{matrix}$
20.	With dil. alkali (Aldol condensation)	No reaction		Forms aldol $CH_3CHO + HCH_2CHO \longrightarrow \begin{matrix} CH_3CH(OH)CH_2CHO \end{matrix}$
21.	With conc. $NaOH$ (Cannizzaro's reaction)	Forms sodium formate and methyl alcohol $2HCHO + NaOH \longrightarrow \begin{matrix} HCOONa \\ +CH_3OH \end{matrix}$		Forms a brown resinous mass
22.	With ammonia	Forms hexamethylene tetramine (urotropine) $6HCHO + 4NH_3 \longrightarrow \begin{matrix} (CH_2)_6N_4 + 6H_2O \end{matrix}$		Forms addition product, acetaldehyde ammonia $CH_3CHO + NH_3 \longrightarrow \begin{matrix} OH \\ CH_3CH \\ NH_2 \end{matrix}$
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 mixture of sugars)		No reaction

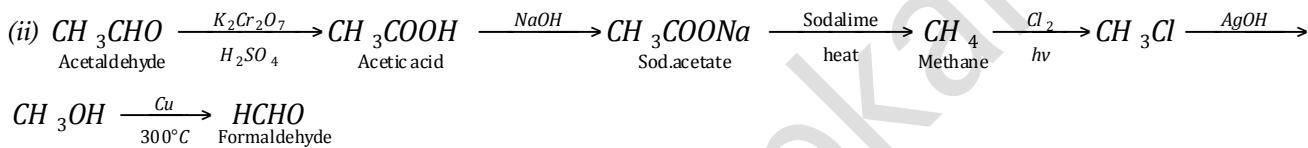
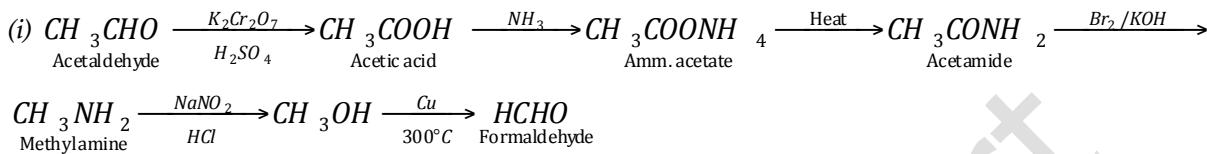
Inter conversion of formaldehyde and acetaldehyde

(i) Ascent of series: Conversion of formaldehyde into acetaldehyde





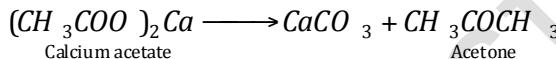
(2) Descent of series: Conversion of acetaldehyde into formaldehyde



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.

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



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°C (b.pt. pure acetone 56°C).

