

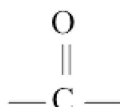
Chapter 12

ALDEHYDES AND KETONES

INTRODUCTION

Carbonyl Group:

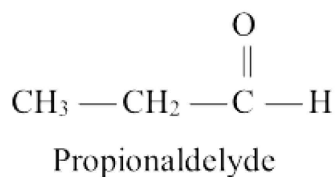
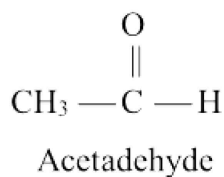
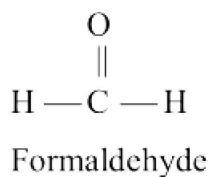
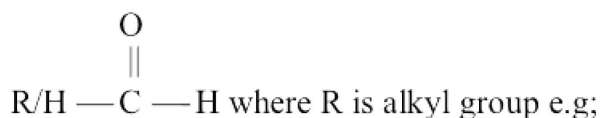
In carbonyl group, carbon atom is bonded with oxygen.



This carbonyl group $> \text{C} = \text{O}$ is present in aldehydes, ketones, carboxylic acid, esters, anhydrides, acid halides and acid amides.

Aldehydes:

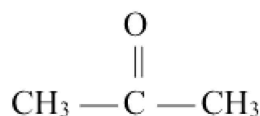
“The organic compounds in which carbonyl carbon is attached with at least one hydrogen atom, are called aldehydes.” The general formula of aldehydes is.



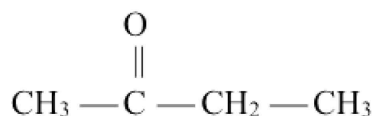
Ketone:

“The organic compounds in which carbonyl carbon is attached with two similar or dissimilar alkyl groups are called ketones.” They have general formula $\text{R} - \begin{array}{c} \text{O} \\ || \\ \text{C} \end{array} - \text{R}$.

e.g.,



Dimethyl Ketone (Acetone)



Ethyl methyl Ketone

The homologous series of both aldehydes and ketones have general formula $\text{C}_n\text{H}_{2n}\text{O}$.

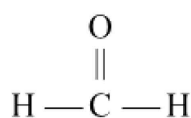
OCCURRENCE OF ALDEHYDES AND KETONES

Aldehydes and ketones are present in many naturally occurring compounds. The aldehyde group is present in most sugars. They are the principal constituents of a number of essential oils used as fragrances and flavours. Ketonic group is present in camphor and menthone.

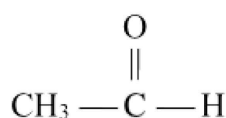
NOMENCLATURE OF ALDEHYDES

Common Names:

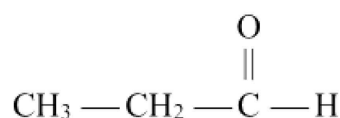
The common names of aldehydes are obtained from the common names of carboxylic acids containing the same number of carbon atoms. The ending -ic acid in the common name of the acid is replaced by the word aldehyde.



Formaldehyde

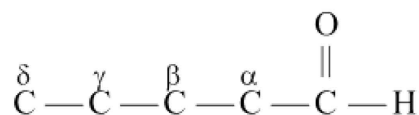


Acetaldehyde

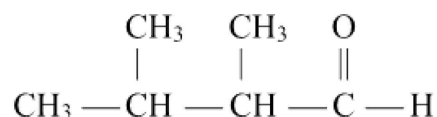


Propionaldehyde

The position of substituents on the chain are indicated by Greek letters (α , β , γ , δ). Lettering on the carbon adjacent to the carbonyl group.



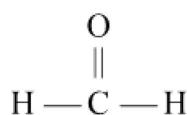
For Example:



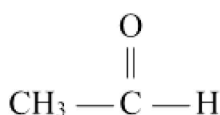
α - β -dimethyl butyraldehyde

IUPAC System:

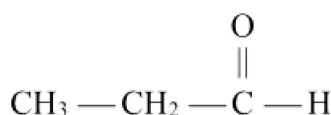
- (1) Select longest continuous chain of carbon atoms also containing carbonyl carbon atom.
- (2) Numbering is always started from carbonyl carbon atom.
- (3) The suffix “-e” of alkane is replaced “-al” in aldehydes.
- (4) The position and name of the branches are written before the name of aldehyde.
- (5) Since aldehyde group is always at one terminal of the chain, no prefix is necessary to locate the position of the aldehyde group.

Examples:

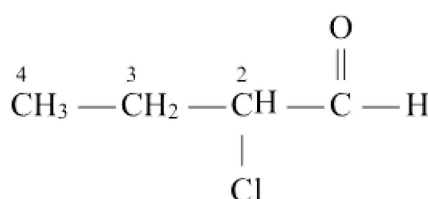
Methanal



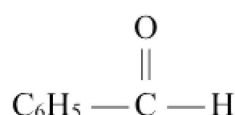
Ethanal



Propanal



2-Chlorobutanal



Benzaldehyde

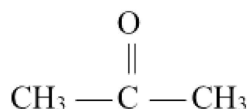
Some More Examples:

Formula	IUPAC Name	Common Name
$\text{H} - \text{CHO}$	Methanal	Formaldehyde
$\text{CH}_3 - \text{CHO}$	Ethanal	Acetaldehyde
$\text{CH}_3 - \text{CH}_2 - \text{CHO}$	Propanal	Propionaldehyde
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CHO}$	Butanal	Butyraldehyde
$\text{CH}_3 - (\text{CH}_2)_3 - \text{CHO}$	Pentanal	Valeraldehyde
$\text{CH}_3 - (\text{CH}_2)_4 - \text{CHO}$	Hexanal	Caproaldehyde
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH} - \text{CHO} \end{array}$	2-Methyl propanal	α -methyl propionaldehyde or iso-butylaldehyde
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3 - \text{CH} - \text{C} - \text{CHO} \\ \\ \text{CH}_3 \end{array}$	2, 2, 3 trimethyl butanal	α, α, β trimethyl butyraldehyde

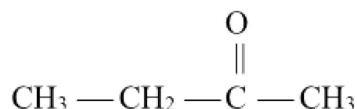
NOMENCLATURE OF KETONES

Common Names:

- (1) Common names of ketones are obtained simply naming the two-alkyl groups attached to the carbonyl group and adding the word ketones.
- (2) Prefix di is used for similar alkyl groups.
- (3) The names of alkyl group are written according to mass of group. Alkyl groups with less mass is written first.



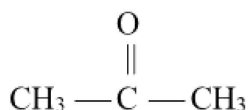
Dimethyl Ketone
(Acetone)



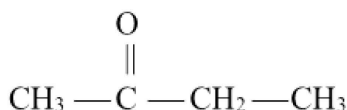
Ethyl methyl Ketone

IUPAC Names:

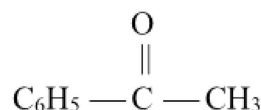
- (1) Select longest continuous carbon chain including carbonyl carbon atom.
- (2) From the name of an alkane having corresponding number of carbon atoms “-e” is replaced by “-one”.
- (3) Start numbering from that end which is nearest to carbonyl carbon atom. Mention the position of carbonyl carbon before the stem name.
- (4) The position and name of branches are written before the name of ketone.



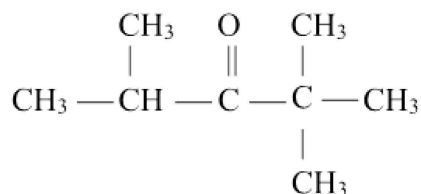
Propanone
(Dimethyl ketone)
(Acetone)



2-Butanone
(Ethyl methyl ketone)



Acetophenone
(Methyl phenyl ketone)

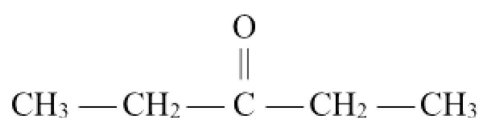


2, 2, 4-trimethyl-3-pentanone

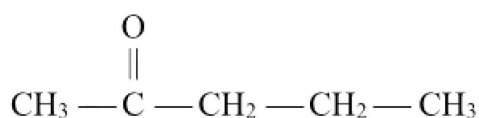
Table – Some Common Names and IUPAC Names of Ketones

Formula	IUPAC	Common Name
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \end{array}$	2-Propanone	Dimethyl ketone (Acetone)
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_3 \end{array}$	2-Butanone	Ethyl methyl ketone
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \end{array}$	2-Pentanone	Methyl-n-propyl ketone

If similarly alkyl group are present on both side of carbonyl carbon, it is called symmetrical ketone and if dissimilar groups are present on both side of carbonyl carbon, it is called unsymmetrical ketone.



Symmetrical ketone
(Diethyl ketone)



Unsymmetrical ketone
(Methyl-n-propyl ketone)

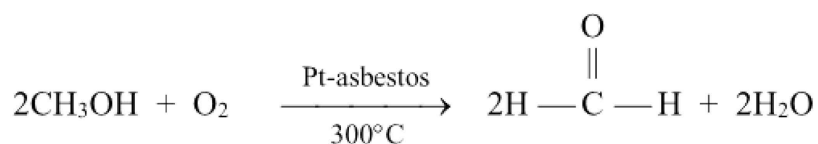
PREPARATION OF ALDEHYDES

Mostly aldehydes are prepared by the oxidation of primary alcohol.

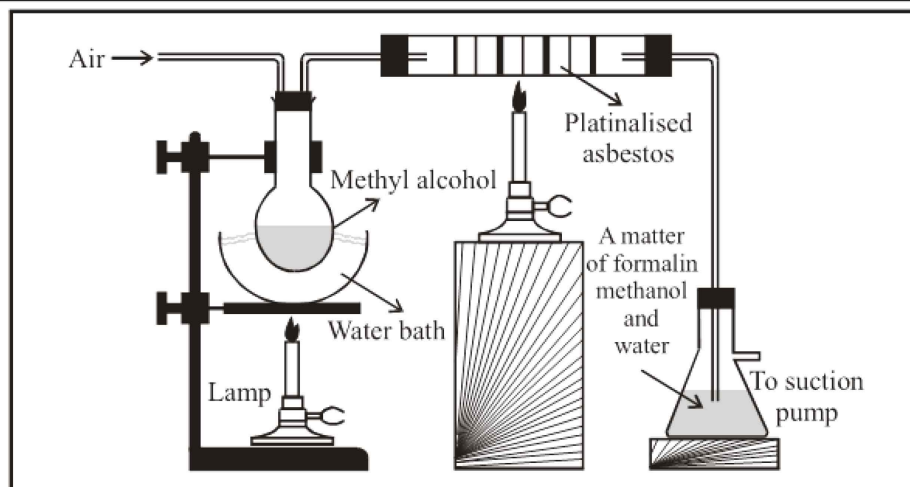
(a) Preparation of Formaldehyde or Methanal (Formalin):

(i) Laboratory Method:

Formaldehyde is prepared in the laboratory by passing a mixture of methyl alcohol vapours and air over platinized asbestos or copper or silver catalyst at 300°C.



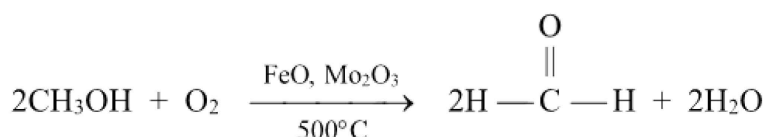
Set up the apparatus is shown in figure. Air is drawn through methyl alcohol with the help of a suction pump. Methyl alcohol is oxidised to gaseous formaldehyde which is absorbed in water. The resulting mixture is called formalin. Formalin is a mixture of 40% formaldehyde, 8% methyl alcohol and 52% water.



Preparation of Formaldehyde (formalin)

(ii) Industrial Method:

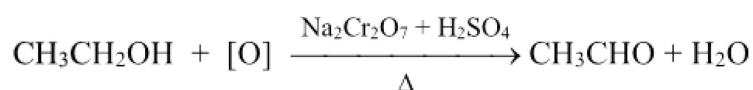
Formaldehyde is manufactured by passing a mixture of methanol vapours and air over iron oxide, molybdenum oxide or silver catalyst at 500°C.



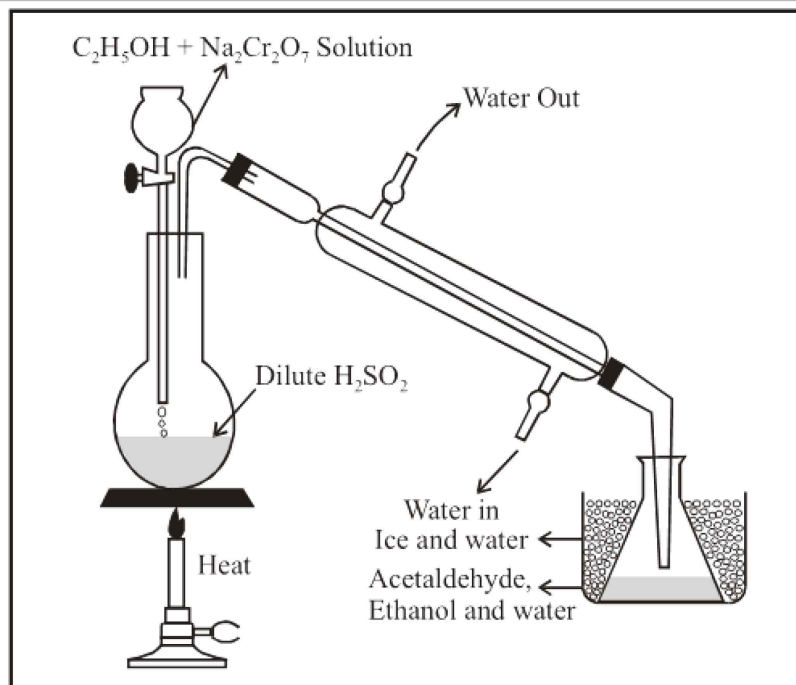
(b) Preparation of Acetaldehyde:

(i) Laboratory Method:

Acetaldehyde is prepared in the laboratory by the oxidation of ethyl alcohol with acidified sodium dichromate solution.

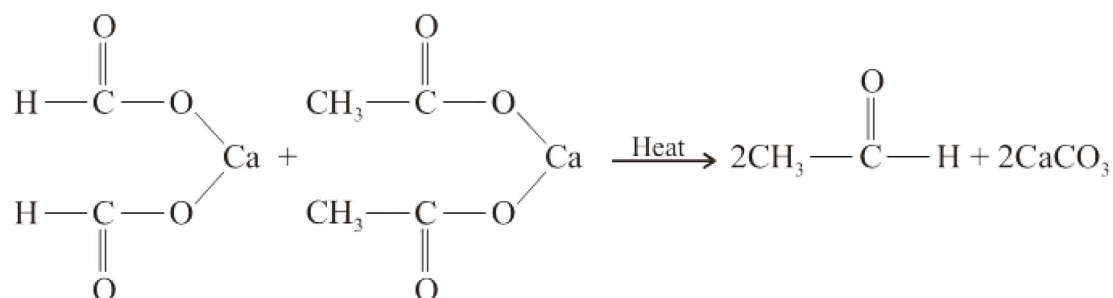


A mixture of ethyl alcohol and sodium dichromate solution is run into boiling dilute sulphuric acid. Immediately a vigorous reaction takes place and the acetaldehyde formed in liquid state is immediately distilled off. This prevents the oxidation of acetaldehyde to acetic acid. Ethyl alcohol remains in solution until it is oxidized. Pure acetaldehyde is obtained by re-distillation.



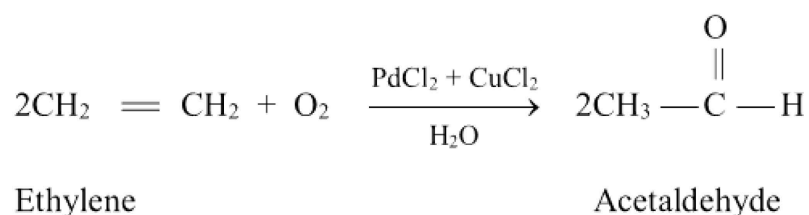
Preparation of Acetaldehyde

- (ii) Acetaldehyde can also be prepared by the dry distillation of a mixture of calcium salts of formic acid and acetic acid.



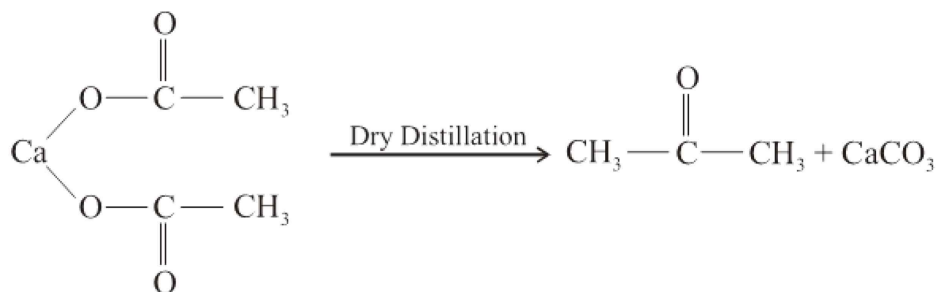
Industrial Method for Preparation of Acetaldehyde:

Acetaldehyde is prepared industrially by air oxidation of ethylene using palladium chloride catalyst with a cupric chloride promoter.



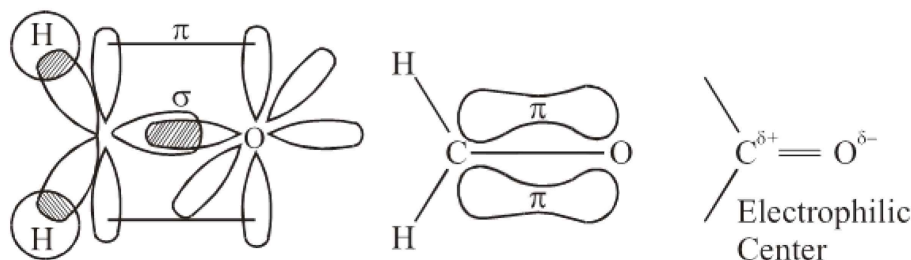
(c) **Preparation of Acetone:**

Acetone is prepared by the dry distillation of calcium acetate $\text{Ca}(\text{CH}_3\text{COO})_2$.


REACTIVITY OF CARBONYL GROUP

The carbonyl group $>\text{C}=\text{O}$, has double bond between carbon and oxygen atom, one is sigma and other is π -bond. Carbon of carbonyl is sp^2 hybridized.

Most of the reactions of aldehyde and ketones are addition reactions. Due to greater electronegativity of oxygen, the carbonyl group is polar. π electrons are attracted toward oxygen and it has partial negative charge while carbon has partial positive charge.



Due to unsymmetrical distribution of electrons, carbon of the carbonyl group behave as an electrophilic center.

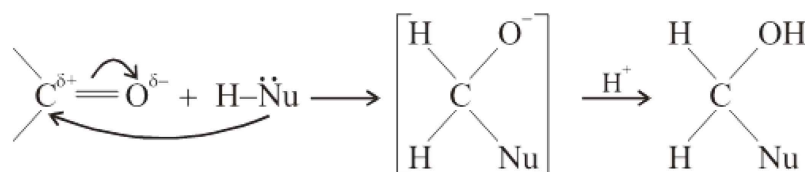
Both electrophile or nucleophile can attack on carbonyl group depending upon the reaction conditions and nature of electrophile or nucleophile.

Whatever the case may be, the **addition product or adduct** will be same. In aldehydes and ketones, however, nucleophilic addition is more common.

Nucleophilic Addition Reaction:

Suppose $\text{H}-\text{Nu}$ is a general nucleophile, Nu^- attacks at the carbon atom of the carbonyl group and donate a pair of electron to it.

Double bond between carbon and oxygen $>\text{C}=\text{O}$ changes to hydroxyl group.

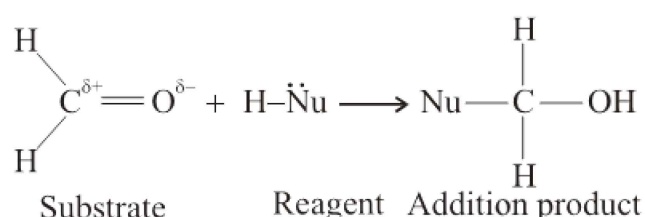


In nucleophilic addition reaction, the product will be either acid catalysed or base catalysed; A base catalyst increases the nucleophilic characters of the reagent. Acid catalyst, promotes the nucleophilic attack by increasing positive characters of carbonyl carbon atom.

REACTION OF CARBONYL COMPOUNDS

(a) Nucleophilic Addition Reactions:

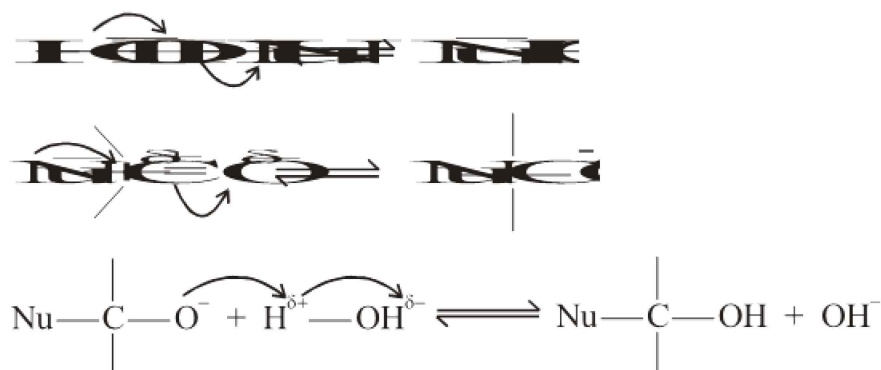
The most important reactions which takes place in aldehydes and ketones are nucleophilic addition reactions. Nucleophilic attacks at carbonyl carbon atom which has partial positive charge. A general reaction of a nucleophile is given below.



An acid or base is used as catalyst in nucleophilic addition reactions. In both cases, addition product is same. Mechanism of base catalyzed reaction is discussed below.

BASE CATALYZED NUCLEOPHILIC ADDITION REACTION

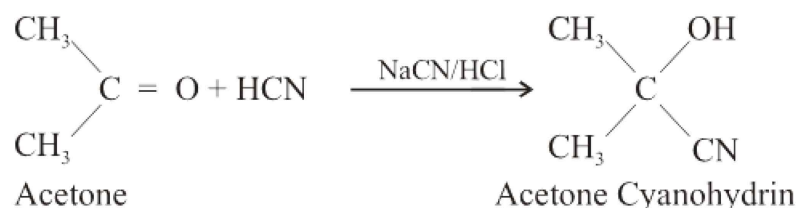
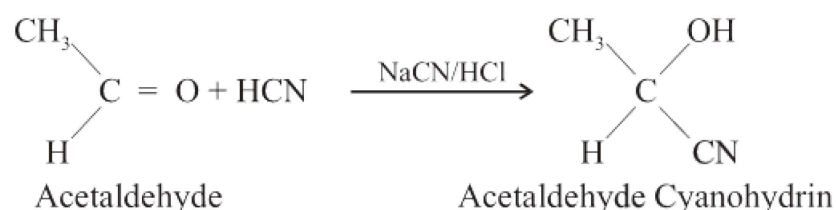
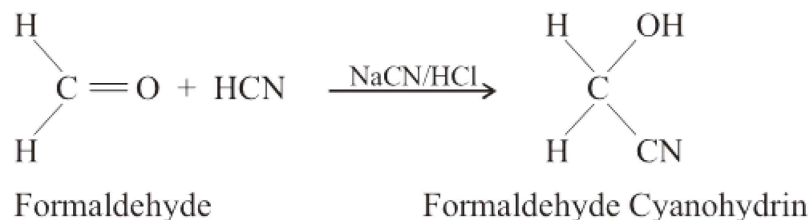
A base-catalysed nucleophilic addition reaction will take place with a strong nucleophilic reagent. The base reacts with the reagent and generates the nucleophile. The addition is initiated by the attack of a nucleophile on the electrophilic carbon of the carbonyl group. The general mechanism of the reactions is as follows.



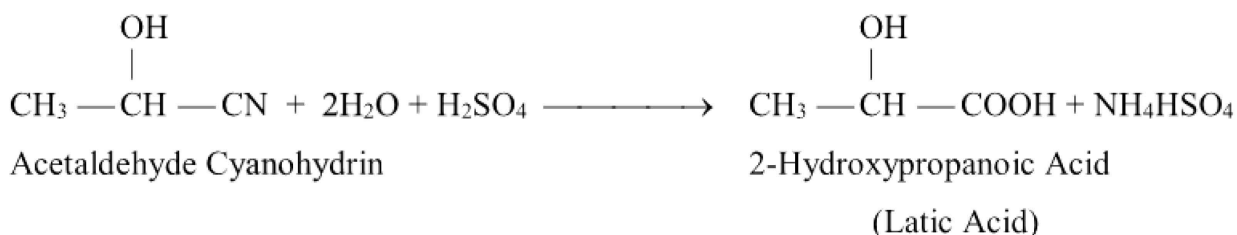
Some base catalysed nucleophilic addition reactions of aldehydes and ketones are given below:

(1) Addition of Hydrogen Cyanide:

Hydrogen cyanide adds to aldehydes or ketones to form cyanohydrins. The reaction is carried out by adding slowly a mineral acid to an aqueous solution of sodium cyanide. The acid generates HCN from sodium cyanide in situ.



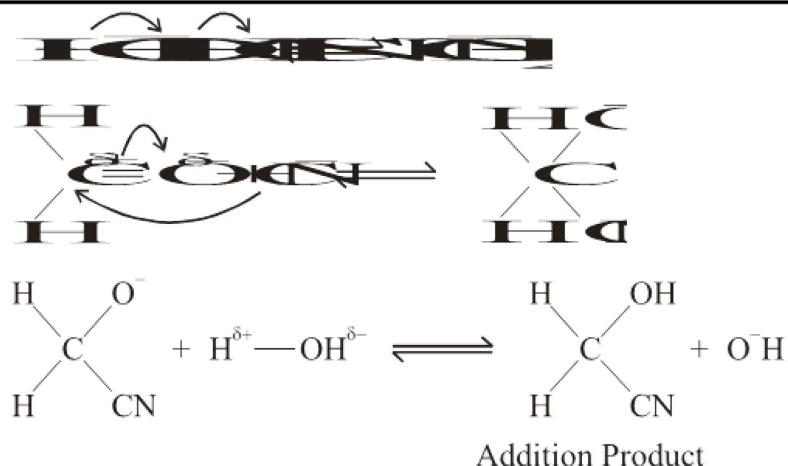
The cyano group, $-\text{C} \equiv \text{N}$ is hydrolysed by an aqueous acid into a carboxylic acid through an acid amide.



The reaction is used for the synthesis of α -hydroxy acids that contain one carbon atom more than the number of carbon atoms in the starting aldehydes or ketones.

Mechanism:

The reaction is base-catalysed because HCN has no lone pair of electrons on its carbon. the base (OH^-) generates cyanide ions which act as nucleophiles. The mechanism of the reaction is as follows.

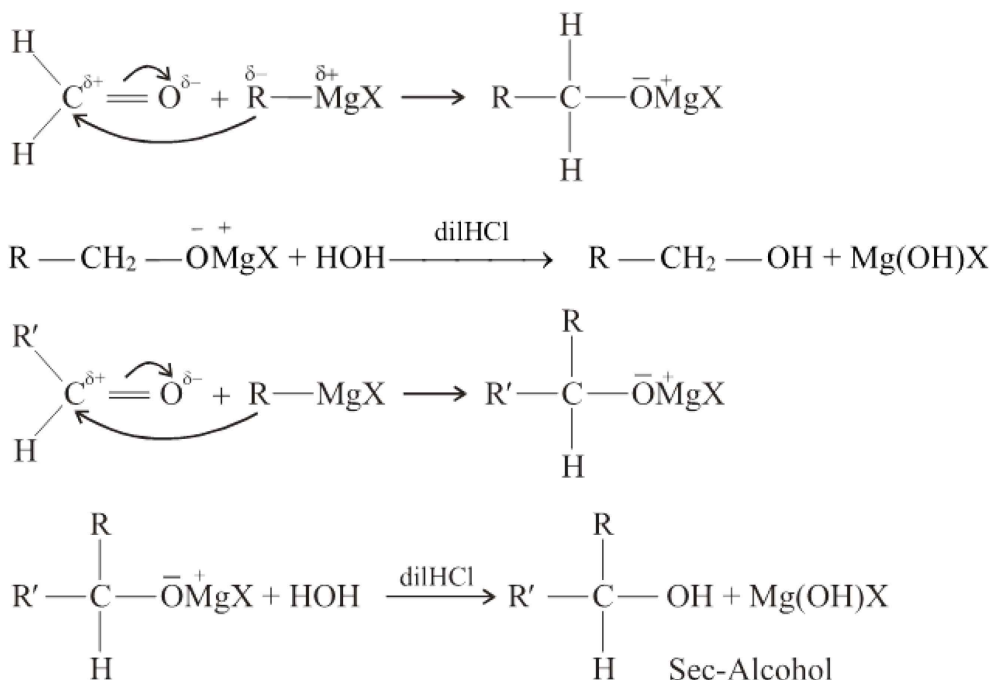


The hydroxide ion liberated in the formation of cyanohydrin reacts with undissociated hydrogen cyanide and produces more cyanide ions, which in turn react with more carbonyl compound.

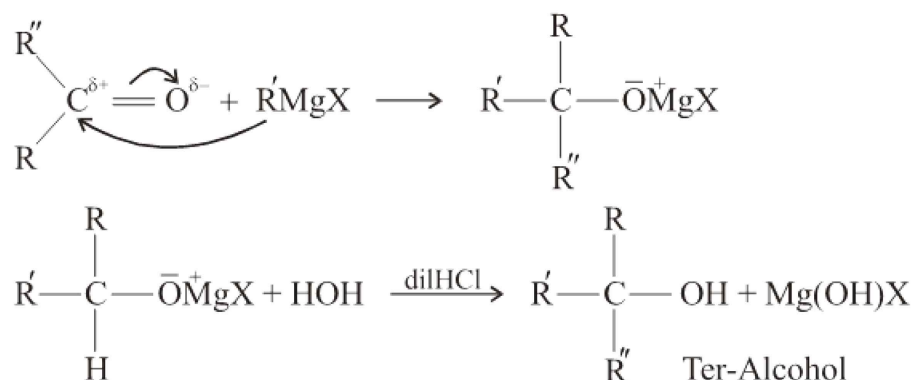


(2) Addition of Grignard's Reagent:

Aldehydes react with Grignard's Reagent to form secondary alcohol. However, formaldehyde forms primary alcohol.

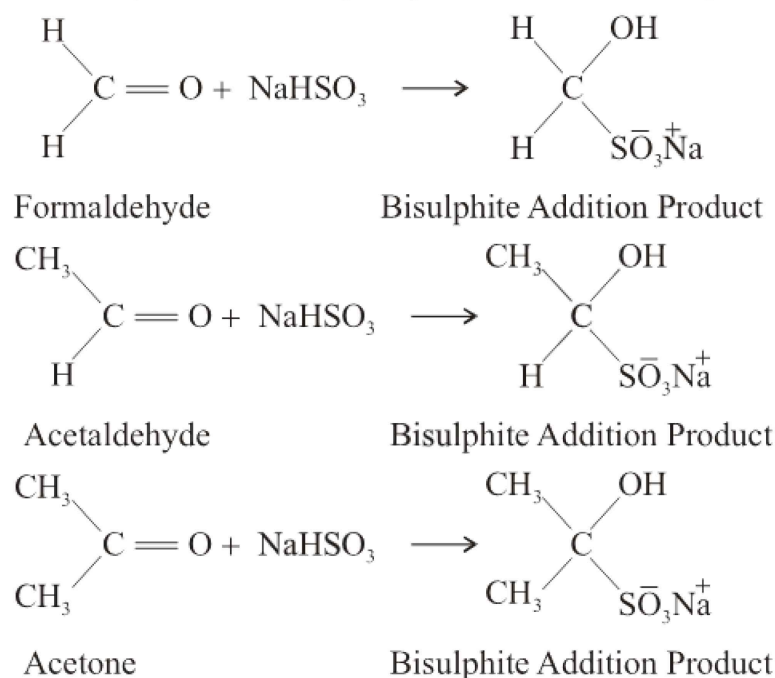


Ketones react with Grignard Reagents to form tertiary alcohols.

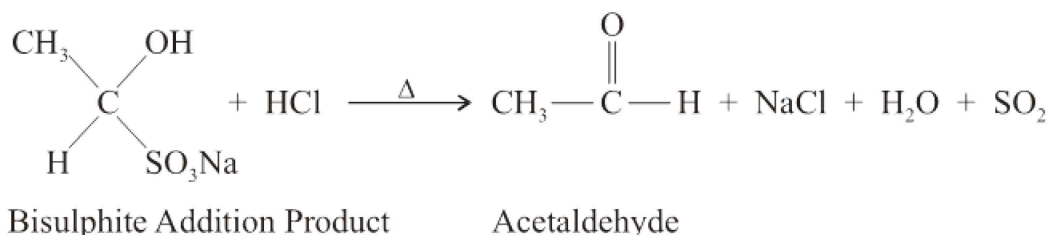


(3) Addition of Sodium Bisulphite:

Aldehydes and small ketones react with a saturated aqueous solution of sodium bisulphite to form a crystalline white precipitate of sodium bisulphite adduct.



Bisulphite on heating with a dilute mineral acid (HCl or H₂SO₄), regenerates the parent aldehyde or ketone.



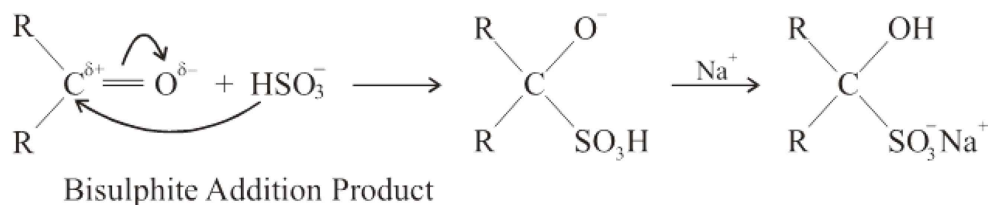
The reaction is used for the separation and purification of carbonyl compounds from non-carbonyl compounds such as alcohols.

Mechanism:

Sodium sulphite ionises to form hydrogen sulphite ion and sodium ion.



Hydrogen sulphite ion act as nucleophile.



Ketones in which both alkyl groups are larger in size do not react with sodium bisulphite NaHSO_3 .

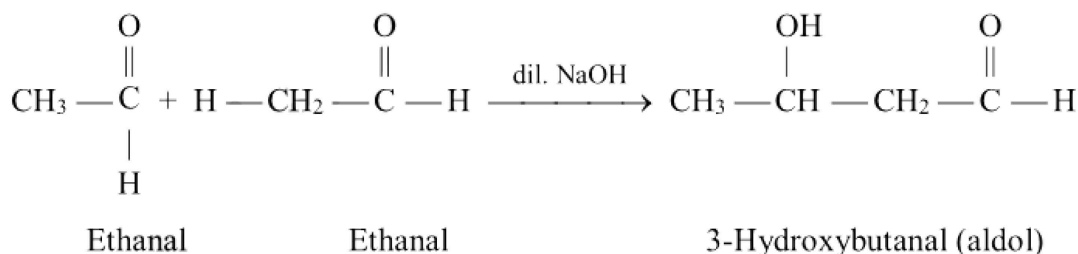
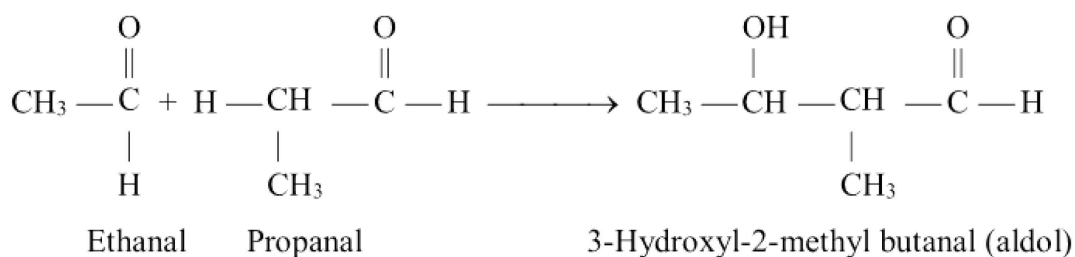
(4) Condensation Reactions:

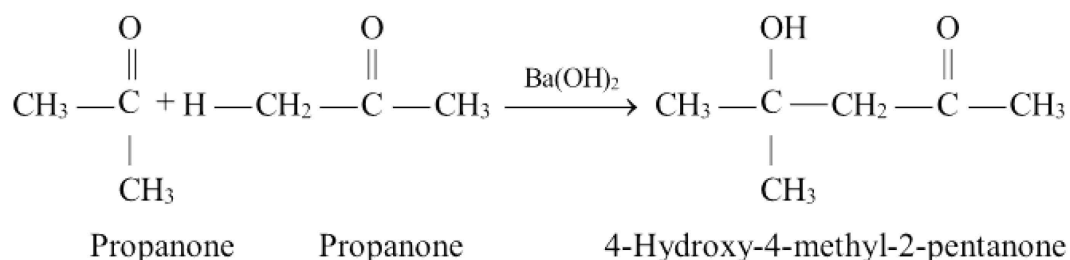
“The reactions in which two molecules of same or different compounds combine to form new compound is called condensation reaction.”

(a) Aldol Condensation:

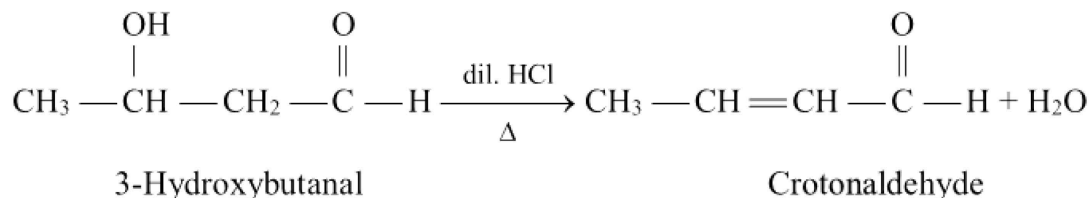
“Aldehydes and ketones possessing α -hydrogen atoms react with a cold dilute solution of an alkali to form addition products known as Aldol.”

The name ‘aldol’ is given to the product because it contains both aldehyde and alcohol functional groups. Note that the name aldol condensation is reserved for the reaction that starts with two identical carbonyl compounds.

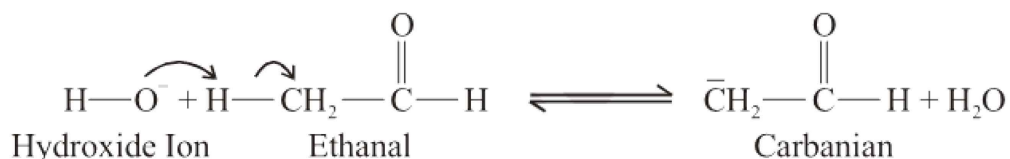
(i) Two Similar Aldehydes:**(ii) Two Dissimilar Aldehydes:**

(iii) Two Similar Ketones:

The aldol compound readily loses water on heating in the presence of dilute acid to form an unsaturated carbonyl compound. A carbon-carbon double bond is formed between the α - and β -carbon atoms.

**Mechanism of Aldol Condensation (Between Similar Aldehydes):**

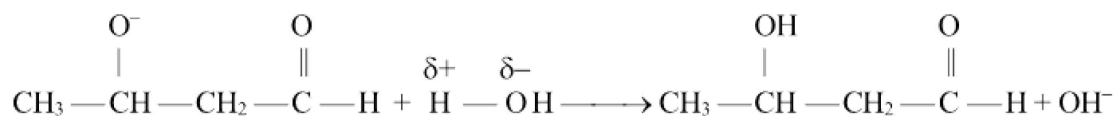
The hydroxide ion acts as a base. It removes a proton from α -carbon of one molecule of the carbonyl compound to form a carbanion.



The carbanion acts as a nucleophile. It attacks the electrophilic carbonyl carbon atom of the unchanged second molecule of ethanal to form an alkoxide ion.



The alkoxide removes a proton from water to form aldol.



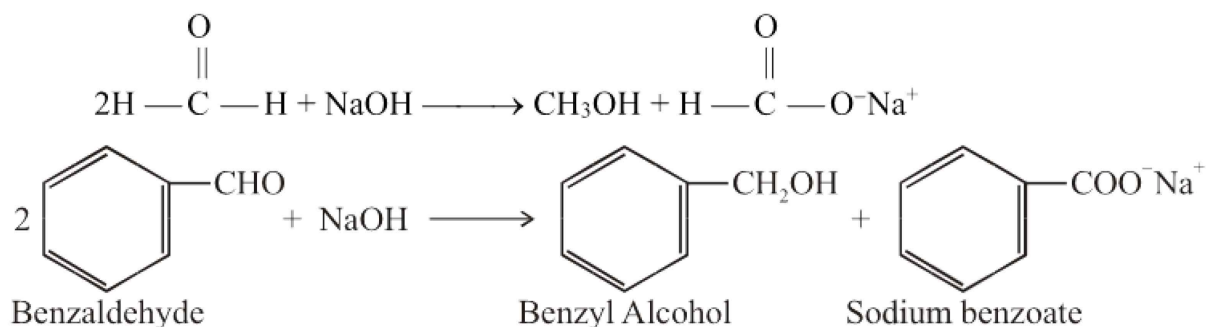
The basic catalyst hydroxide ion is regenerated.

(b) Cannizzaro's Reaction:

The aldehydes having no α -hydrogen at α -carbon atom do not undergo aldol condensation in the presence of base.

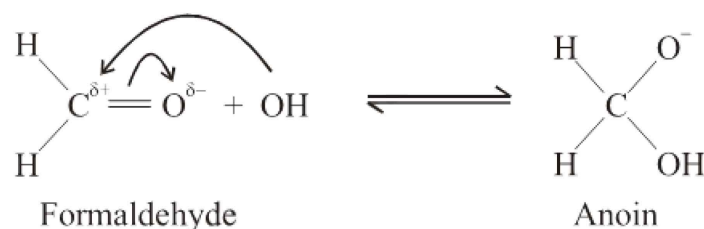
"The aldehydes having no α -hydrogen at α -carbon atom in the presence of base are converted to corresponding alcohol and carboxylic acid salt is called Cannizzaro reaction."

Cannizzaro reaction is a self oxidation-reduction reaction. In this reaction one molecule of aldehyde is oxidised to carboxylic acid while the other molecule is reduced to corresponding alcohol. This reaction is also called disproportionation reaction. For example, methanal or benzaldehyde have no α -hydrogen at α -carbon atom and undergo Cannizzaro reactions.

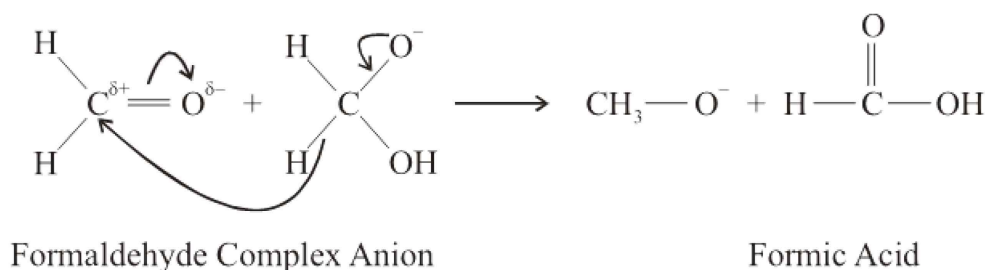


Mechanism:

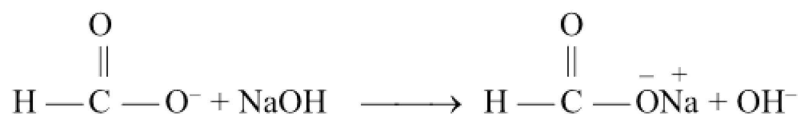
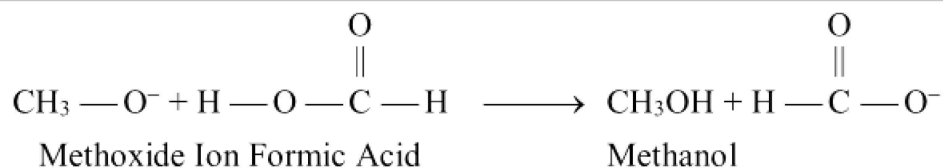
- (i) The reaction of methanal with base gives alcohol and salt of carboxylic acid. The hydroxide ion acts as a nucleophile. It attacks on the electrophilic carbonyl carbon to form a complex anion.



- (ii) The anion transfers a hydride ion to second molecule of formaldehyde. The presence of the negative charge on oxygen of the anion helps in the loss of hydride ion.

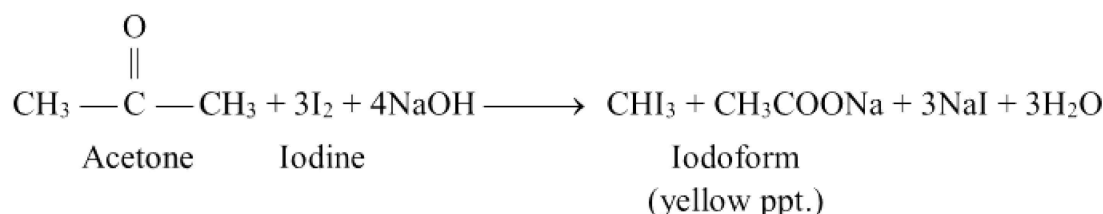
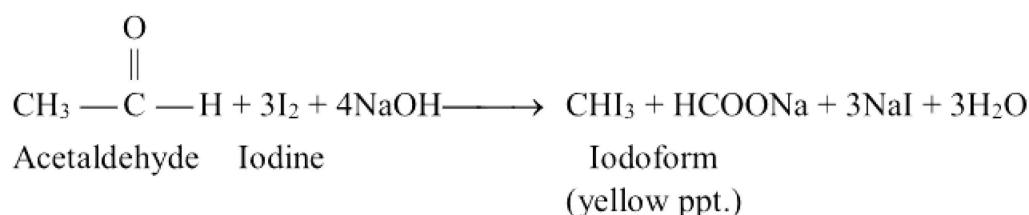
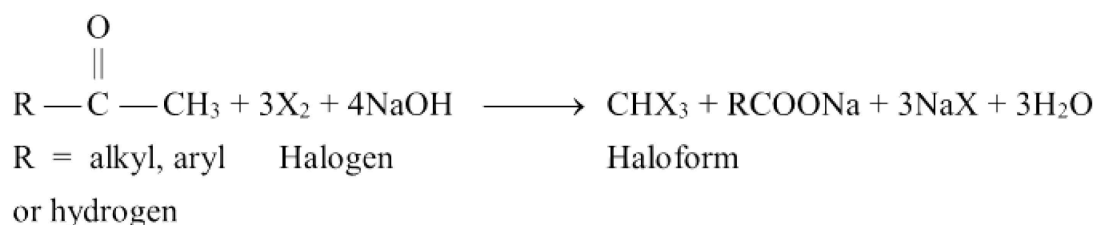


- (iii) The methoxide ion acts as a base and attracts a proton from formic acid to form methanol and formate ion. The formate ion in the presence of alkali gives a salt of the acid.

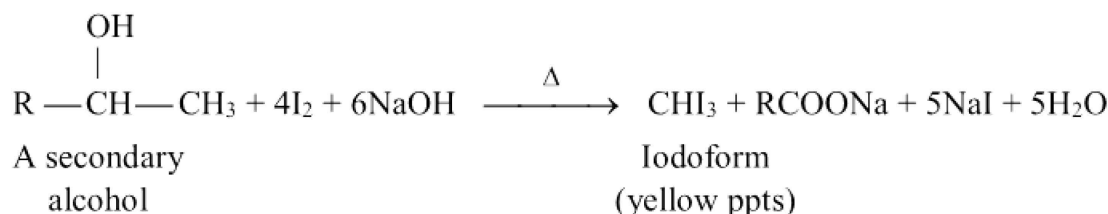


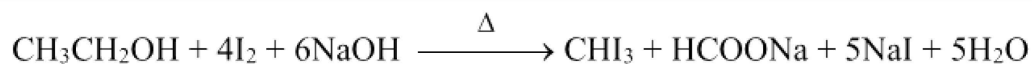
(5) Haloform Reaction:

The compounds which have methyl ketone $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} -$ group in them undergo haloform reactions. Only acetaldehyde $\text{CH}_3 - \text{CHO}$ and methyl ketones $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{R}$ reacts with halogens in the presence of base NaOH. The term haloform is derived from halogen. The products of the reactions are chloroform, bromoform or iodoform e.g;



Secondary alcohols containing the hydroxyl group on the second carbon atom also undergo this reaction. Ethanol is the only primary alcohol that gives this reaction.





Ehtanol

Yellow ppts of Iodoform

Form a synthetic point of view the haloform reaction, affords a convenient method for converting a methyl ketone to a carboxylic acid containing one carbon atom less than parent compound.

Iodoform Test:

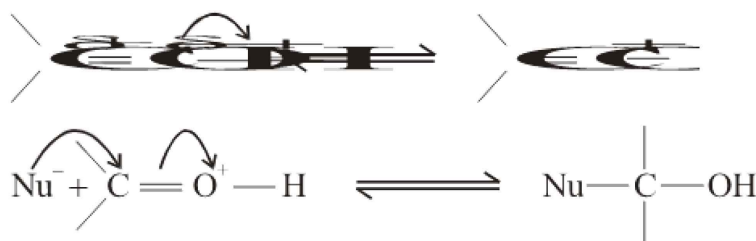
"The halogen reaction using iodine and aqueous sodium hydroxide is called iodoform test".

In this test water insoluble, yellow crystalline iodoform CHI_3 is formed. This iodoform can be used to distinguish.

- (1) Methyl ketones $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{R}$ and other higher ketones. (R. may be ethyl or higher alkyl group).
- (2) Methanol and Ethanol. Ethanol forms CHI_3 while methanol does not do so. Primary alcohols do not perform iodoform test except ethanol.

(b) Acid Catalyzed Nucleophilic Reaction:

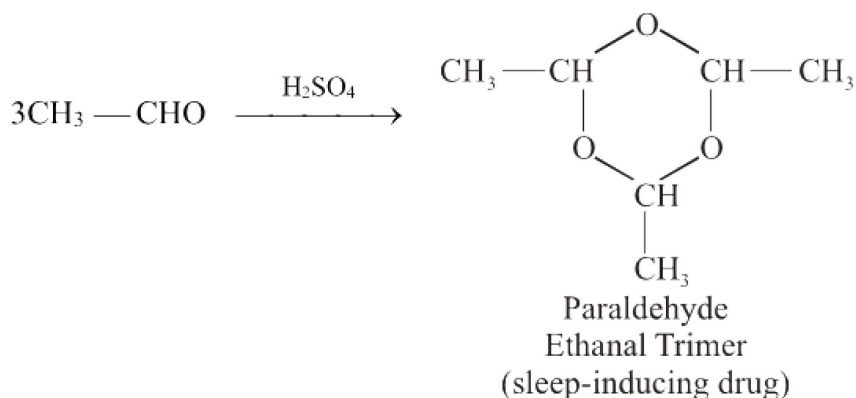
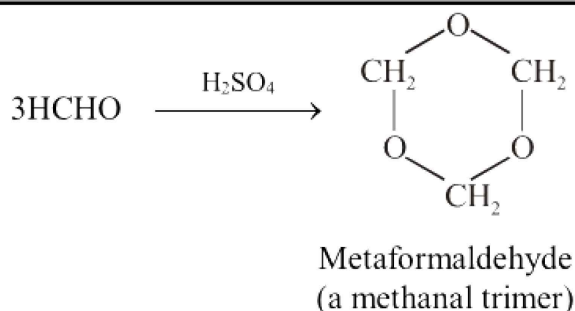
The acid catalysed nucleophilic addition reaction will take place with a weak nucleophilic reagent. The addition is initiated by the proton (H^+) liberated by the acid. The proton combines with the carbonyl oxygen atom and increases the electrophilic character on the carbonyl carbon. As a result, the attack of the weaker nucleophile on the electrophilic carbon becomes easier.



The acid-catalysed nucleophilic addition reactions of aldehydes and ketones are the following.

(1) Polymerization:

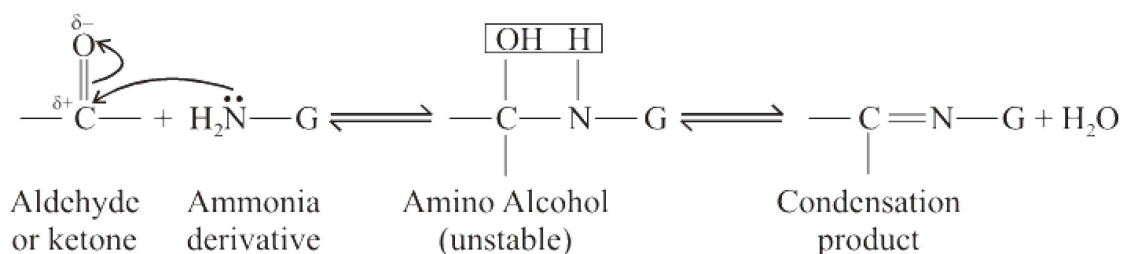
Both formaldehyde and acetaldehyde polymerize in the presence of dil. H_2SO_4 to give metaformaldehyde and paraldehyde respectively.



(2) Addition of Ammonia Derivatives:

Aldehydes and ketones react with ammonia derivatives, G—NH_2 to form compounds containing the group, $>\text{C}=\text{N—G}$ and water. The reaction is known as condensation reaction or addition-elimination reaction because water is lost during addition. The reactions are acid catalysed.

The general reaction is:



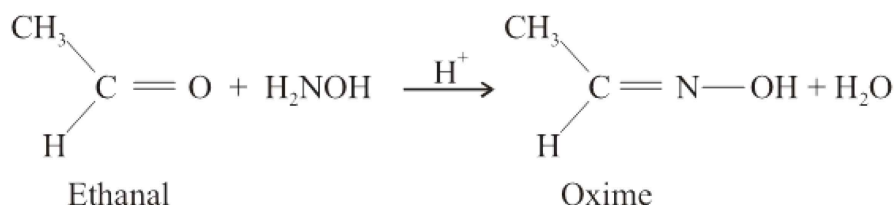
Where $\text{G} = \text{H}, \text{—H}_2, \text{—HC}_6\text{H}_5, \text{—HCONH}_2$, etc.

Some commonly used ammonia derivative are hydroxylamine, NH_2OH , hydrazine, NH_2NH_2 , phenylhydrazine, $\text{C}_6\text{H}_5\text{NHNH}_2$, semicarbazide $\text{NH}_2\text{NHCONH}_2$ and 2, 4 dinitro-phenyl-hydrazine.

The reaction of the above stated ammonia derivatives with aldehydes and ketones are as follow:

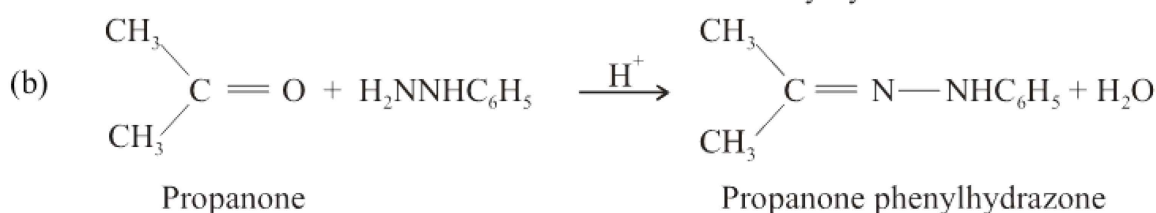
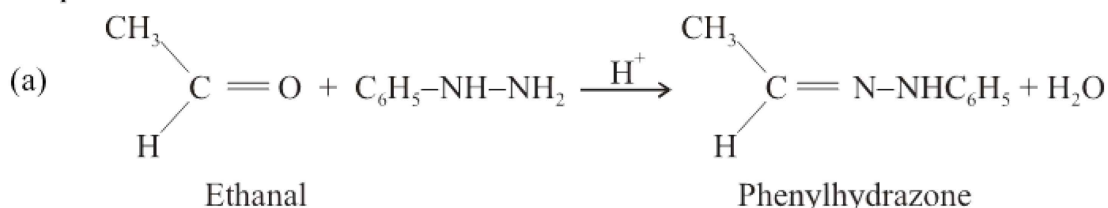
(i) Reaction with Hydroxylamine:

Aldehydes and ketones react with hydroxylamine to form oximes in the presence of an acid.



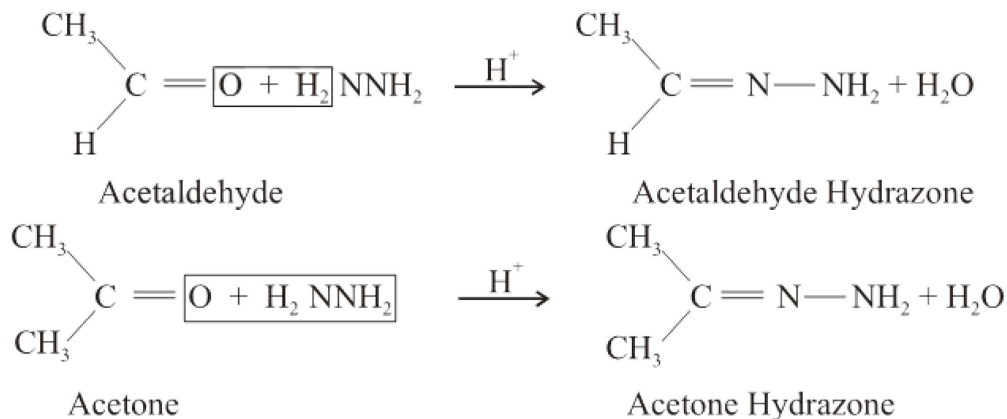
(ii) Reaction with Phenyl Hydrazine (NH₂ – NHC₆H₅):

Aldehydes and ketones react with phenylhydrazine to form phenyl hydrazones in the presence of an acid.



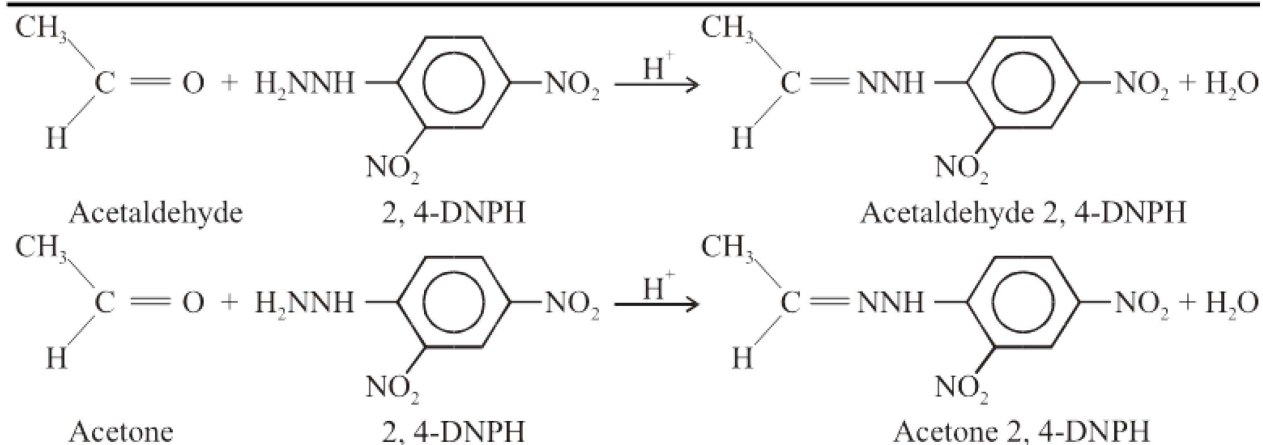
(iii) Reaction with Hydrazine (NH₂ – NH₂):

Aldehydes and ketones react with hydrazine to form hydrazones in the presence of an acid.



(iv) Reaction with 2, 4 Dinitrophenylhydrazine [2, 4, DNPH]:

Aldehydes and ketones react with 2, 4-dinitrophenylhydrazine to form 2, 4-dinitrophenylhydrazones in the presence of acid.



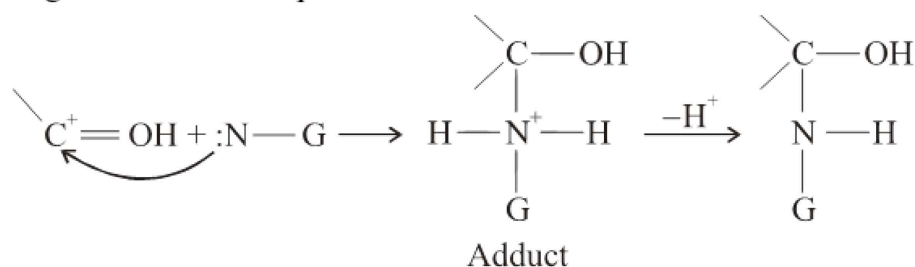
The reaction can be used for the identification of aldehydes and ketones because 2, 4-dinitrophenylhydrazones are usually yellow or orange crystalline solids.

Mechanism of the Reaction of Ammonia Derivatives:

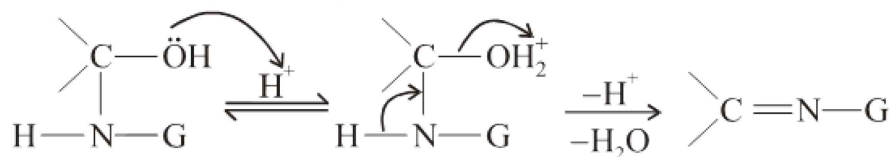
Step-I: Protonation of the carbonyl group.



Step-II: Nucleophilic attack on nitrogen of ammonia derivative on the electrophilic positively charged carbon and deprotonation of the adduct.

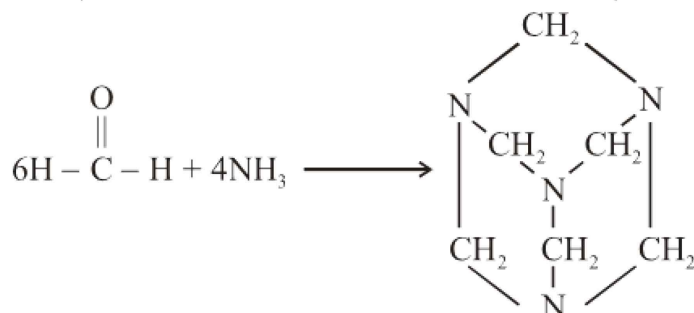


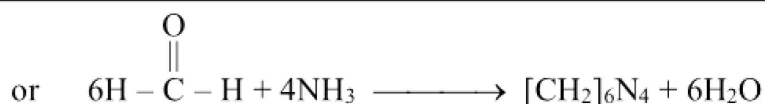
Step-III: Protonation of oxygen of hydroxyl group followed by the removal of water.



Reaction between Formaldehyde and NH_3 :

Formaldehyde reacts with NH_3 to form hexamethylene tetra-amine (urotropine).

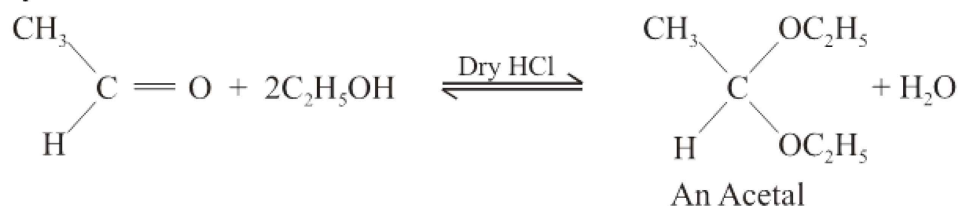




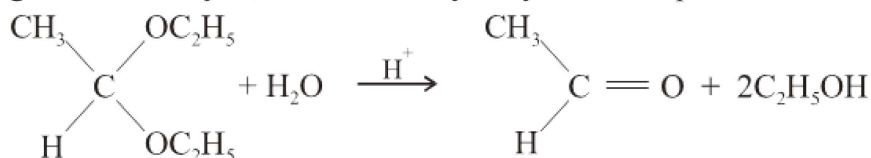
Urotropine is urinary antiseptic. It is also used to prepare antipolio vaccine.

Addition of Alcohols:

Aldehydes combine with alcohols in the presence of hydrogen chloride gas to form acetals. The hydrogen chloride acts as a catalyst. Both the alcohol and the hydrogen must be dry.



The reaction may be used to protect the aldehyde group against alkaline oxidizing agents. To regenerate aldehyde, the acetal is hydrolysed in the presence of an acid.



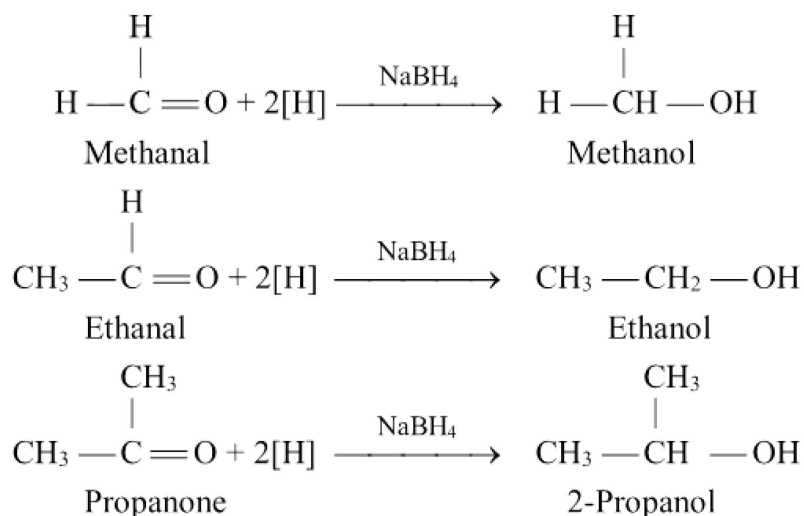
Ketones do not react under these conditions.

(3) Reduction of Carbonyl Compounds:

Aldehydes and ketones can both be reduced. Aldehydes are reduced to primary alcohols whereas ketones to secondary alcohols. The carbonyl group is converted into an alcohol.

(i) Reduction with Sodium Borohydride:

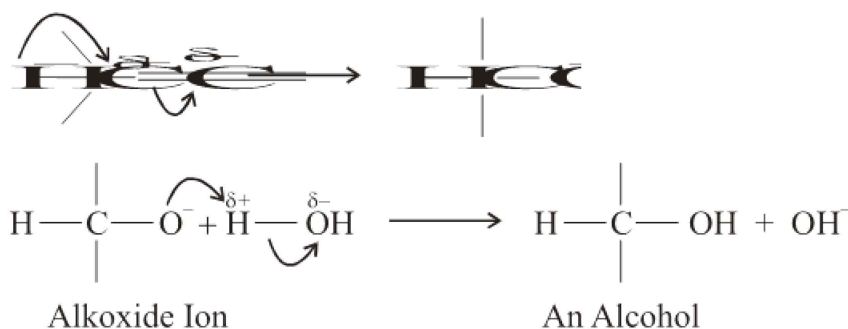
Aldehydes and ketones are reduced to alcohols with sodium borohydride, NaBH_4 . The reaction is carried out by adding sodium borohydride to an aqueous or alcoholic solution of an aldehyde or ketone.



Sodium borohydride reduces the carbon-oxygen double bond but not the carbon-carbon multiple bond.

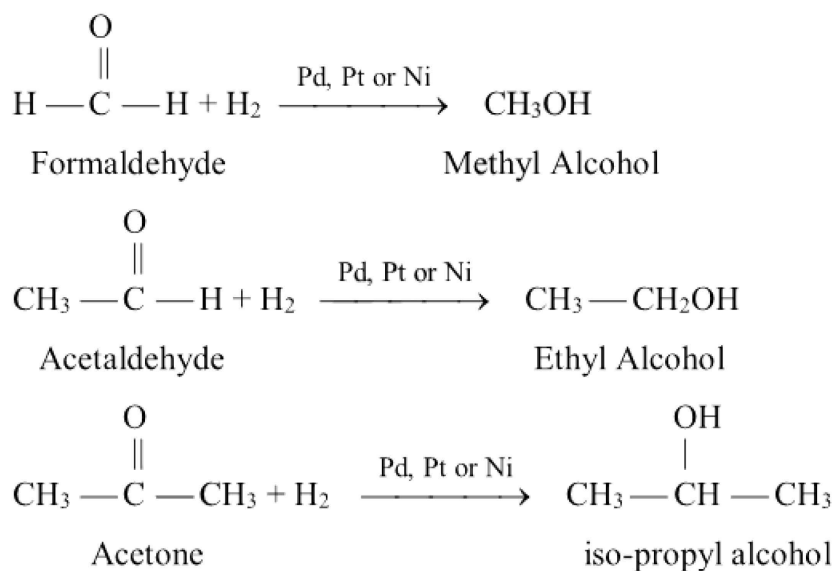
Mechanism:

The tetrahydriborate (III) ion, BH_4^- is source of hydride ion, H^- . The hydride ion acts as a nucleophile. It attacks on the electrophilic carbon of the carbonyl group to give an alkoxide ion.



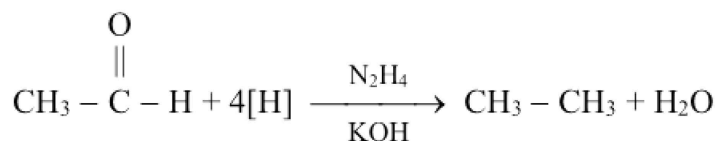
(ii) Catalytic Reduction:

Aldehydes and ketones on reduction with hydrogen in the presence of a metal catalyst like Pd, Pt or Ni form primary alcohols and secondary alcohols respectively. Hydrogen is added across the carbonyl group.



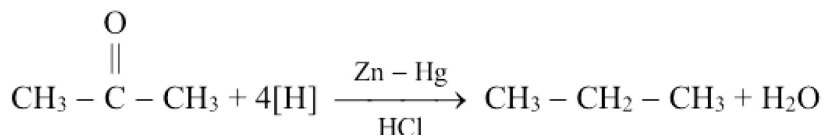
(iii) Wolf-Kishner's Reduction:

Aldehydes are reduced in the presence of N_2H_4 and KOH to form alkanes.

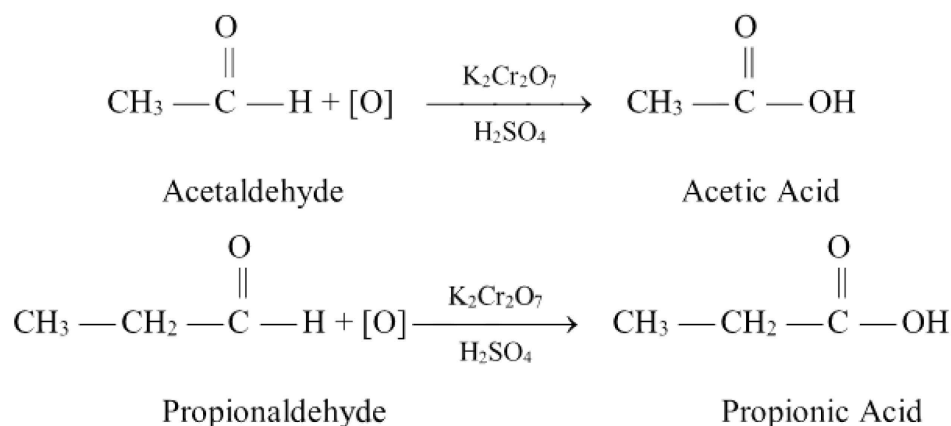


(iv) Clemenson's Reduction:

Ketones react with zinc amalgam and HCl ketones react with zinc amalgam and HCl to form alkanes.

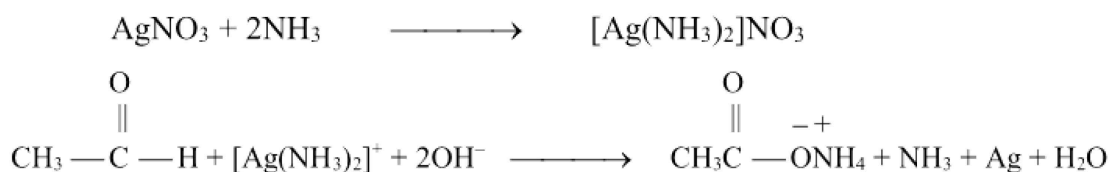
**(4) Oxidation of Carbonyl Compounds:****(a) Oxidation of Aldehydes:**

- (i) Strong oxidizing agents like $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{KMnO}_4/\text{H}_2\text{SO}_4$, or dilute HNO_3 can oxidize aldehydes as well as ketones. In aldehydes, hydrogen atom of aldehyde changes to $-\text{OH}$ and carboxylic acid is formed. Carboxylic acid has same carbon atoms in aldehydes.



- (ii) Mild oxidizing agents like Benedict solution Fehling solution or Tollen reagent (ammonical silver nitrate) can only oxidizes to aldehydes and not to ketones, e.g;

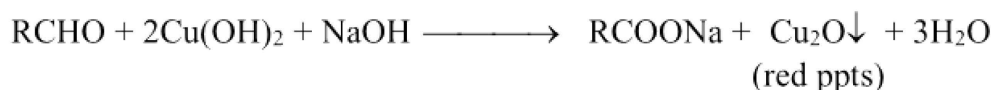
Aldehydes reacts with ammonical silver nitrate (Tollen's reagent) to form metallic silver. Silver deposit inside the test tube and seems like mirror so it also called silver mirror test.



Oxidation state of silver in AgNO_3 is +1 which changes to Ag^0 . This test is not performed by ketones.

Fehling Solution:

Fehling solution is a solution of copper (II) sulphate CuSO_4 , sodium hydroxide and tartaric acid. Fehling solution oxidizes aldehydes to carboxylic acids and cupric Cu^{++} ions are reduced to cuprous ion Cu^+ . When Fehling solution reacts with aldehydes, brick red precipitate of cuprous oxide Cu_2O , is formed.

**Benedict Solution:**

It is mixture of NaOH , CuSO_4 and citric acid. Aliphatic aldehydes react with benedict solution and brick red precipitate of Cu_2O is formed. In this peaction, Cu^{2+} ions are reduced to Cu^{1+} ions.

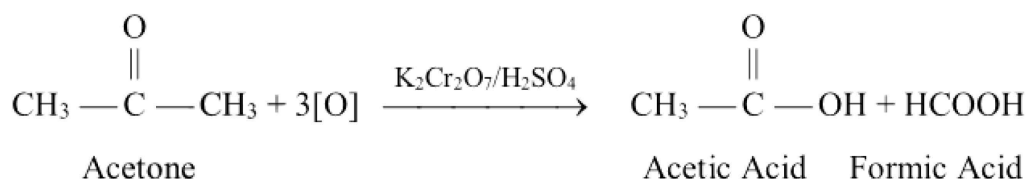


Aromatic aldehydes and ketones do not perform this test.

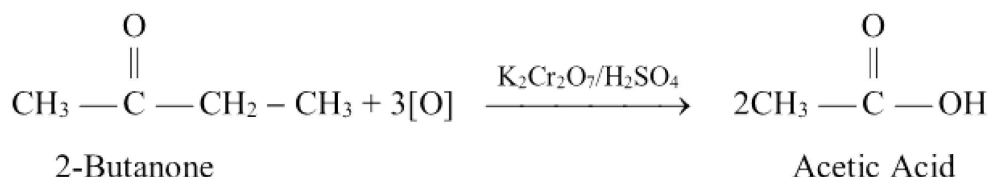
Oxidation of Ketones:

Ketones are not oxidized by mild oxidizing agents like Fehling solution, Benedict solution or Tollen reagent. Ketones are oxidizes by strong oxidizing agents like $\text{KMnO}_4/\text{H}_2\text{SO}_4$, $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, etc.

In oxidation of ketones, only the carbon atoms adjacent to the carbonyl group are attacked. The carbon atom joined to smaller number of hydrogen atoms is preferentially oxidized. In case of symmetrical ketones only one carbon atom adjacent to the carbonyl group is oxidized and a mixture of two carboxylic acids is always obtained.



However, in case of unsymmetrical ketones, the carbon atom joined to the smaller number of hydrogen atoms is preferentially oxidized and the carbonyl group remains with the smaller alkyl group.



IDENTIFICATION TESTS FOR CARBONYL COMPOUNDS

Detection Test for Aldehydes and Ketones:

Test	Aldehyde	Ketone
(1) 2, 4-DNPH test	Aldehydes give this test and yellow crystalline ppt. is formed.	Ketones also give this test and yellow crystalline ppt. is formed.
(2) NaHSO ₃ test	Aldehydes give this test and white crystalline ppt. is formed.	Small ketones only give this test and white crystalline ppt. is formed.
(3) Tollen's test	Aliphatic aldehydes give this test and silver mirror is formed.	Aromatic aldehyde and ketones do not perform this test.
(4) Benedict's solution test	Aliphatic aldehydes give this test and brick red ppt. of Cu ₂ O is formed.	Ketones do not perform this test.
(5) Fehling's solution test	Aliphatic aldehydes give this test and brick red ppt. of Cu ₂ O is formed.	Ketones do not perform this test.
(6) Sodium nitroprusside test	Aldehydes do not perform this test.	Ketones react with sodium nitroprusside and wine red or orange red colour is formed.

USES OF FORMALDEHYDE

- (i) It is used in the manufacture of resins like urea-formaldehyde and plastics such as bakelite.
- (ii) It is used in the manufacture of dyes such as indigo, para-rosaniline, etc.
- (iii) Its 40% aqueous solution called formalin is used as an antiseptic, disinfectant, a germicide, a fungicide and for preserving animal specimens and sterilizing surgical instruments.
- (iv) It is used as a decolourising agent in vat dyeing.
- (v) It is used in the silvering of mirrors.