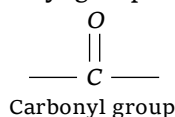


# Chapter 27

## Aldehydes and Ketones

### Introduction

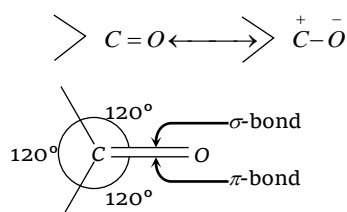
Carbonyl compounds are of two types, aldehydes and ketones. Both have a carbon-oxygen double bond often called as carbonyl group.



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

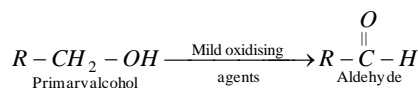
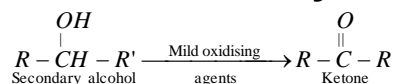
**Structure :** Carbonyl carbon atom is joined to three atoms by sigma bonds. Since these bonds utilise  $sp^2$ -orbitals, they lie in the same plane and are  $120^\circ$  apart. The carbon-oxygen double bond is different than carbon-carbon double bond. Since, oxygen is more electronegative, the electrons 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,  $\overset{\delta+}{\text{C}} = \overset{\delta-}{\text{O}}$

(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.



### Preparation of carbonyl compounds

(1) **From alcohols** (i) **By oxidation.**



Mild oxidising agents are

- (a)  $X_2$  (Halogen) (b) Fenton reagent  
( $FeSO_4 + H_2O_2$ )  
(c)  $K_2Cr_2O_7 / H^+$  (d) Jones reagent  
(e) Sarret reagent (f)  $MnO_2$   
(g) Aluminium tertiary butoxide  
[  $Al(-O-C(CH_3)_3)_3$  ]

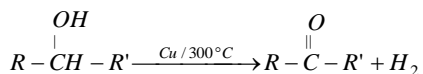
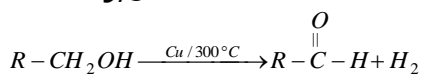
When the secondary alcohols can be oxidised to ketones by aluminium tert-butoxide,  $[(CH_3)_3CO]_3Al$  the reaction is known as *Oppenauer oxidation*. Unsaturated secondary alcohols can also be oxidised to unsaturated ketones (without affecting double bond) by this reagent.

The yield of aldehydes is usually low by this methods. The allylic alcohols can be converted to aldehydes by treating with oxidising 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

## 1256 Aldehydes and Ketones

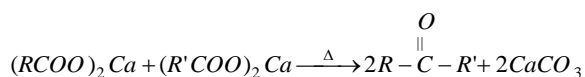
acids and is suitable method for preparing  $\alpha, \beta$ -unsaturated aldehydes.

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



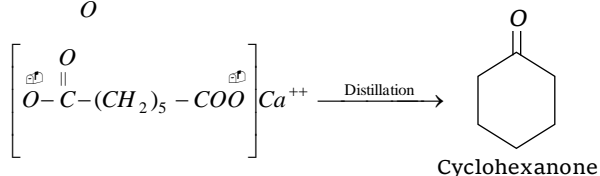
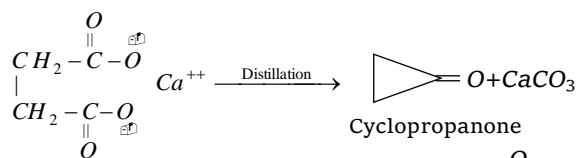
(2) **From carboxylic acids**

(i) **Distillation of Ca, Ba, Sr or Th salts of monobasic acids**



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.

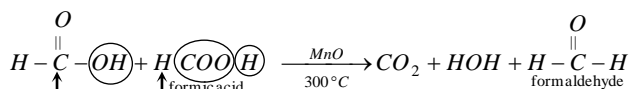


(ii) **Decarboxylation or Dehydration of acids by MnO/300°C.**

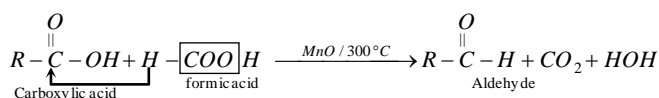
(a) This reaction takes place between two molecules of carboxylic acids. Both may be the same or different.

(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.

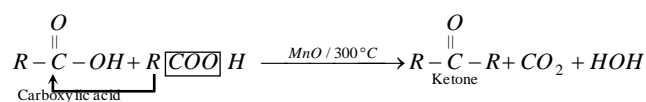
**Case I :** When both molecules are  $HCOOH$



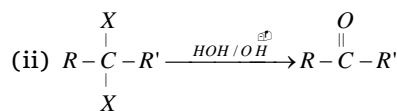
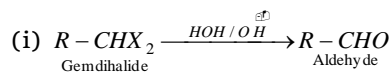
**Case II :** When only one molecule is formic acid.



**Case III :** When none of the molecule is formic acid.



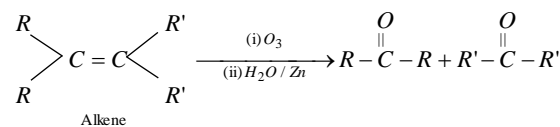
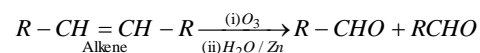
(3) **From gem dihalides :** Gem dihalides on hydrolysis give carbonyl compounds



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

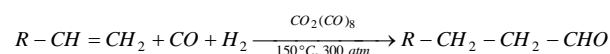
(4) **From alkenes**

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



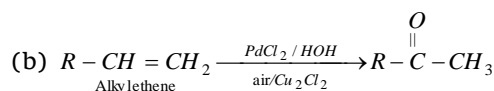
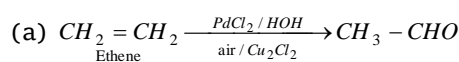
□ This method is used only for aliphatic carbonyl compounds.

(ii) **Oxo process**

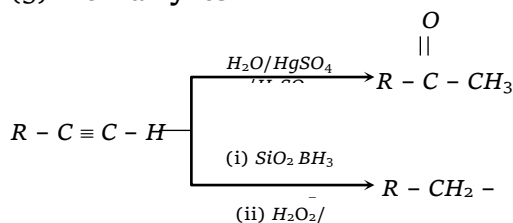


□ Oxo process is used only for the preparation of aldehydes.

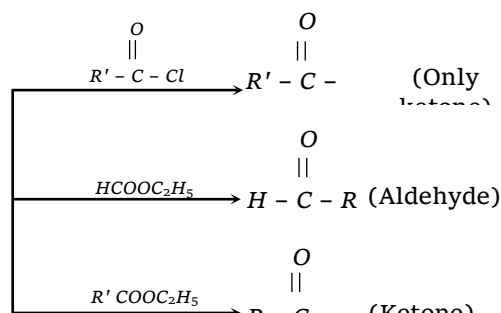
(iii) **Wacker process**

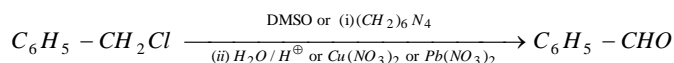


(5) **From alkynes**

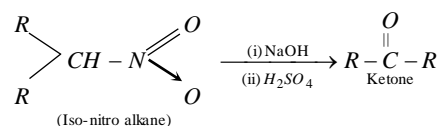
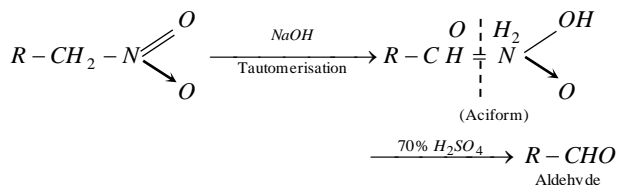


(6) **From Grignard reagents**



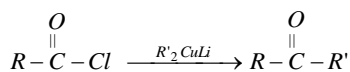
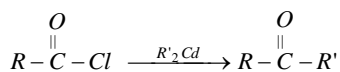


(11) **From nitro alkanes** : Nitro alkanes having at least one  $\alpha$ -hydrogen atom give carbonyl compounds on treatment with conc NaOH followed by 70%  $H_2SO_4$ . The reaction is known as **Nef carbonyl synthesis**.



### (7) From acid chloride

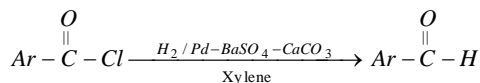
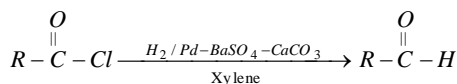
(i) Acid chlorides give nucleophilic substitution reaction with dialkyl cadmium and dialkyl lithium cuprate to give ketones. This is one of the most important method for the preparation of ketones from acid chlorides.



(Only used for the preparation of ketones)

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

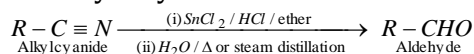
(ii) **Rosenmunds reduction** : This reduction takes place in the presence of Lindlars catalyst.



(Only used for aldehydes)

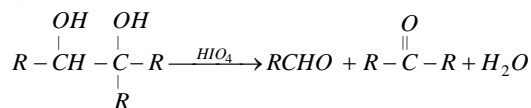
### (8) From cyanides

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



(Only used for aldehydes)

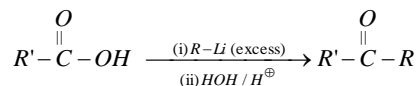
### (9) From vic diols



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

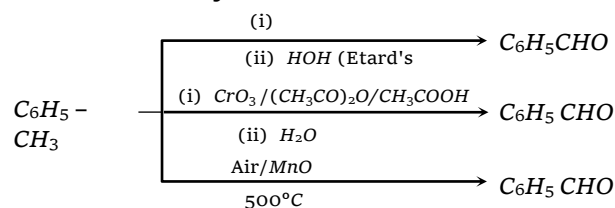
### (10) From Alkyl halides and benzyl halides

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

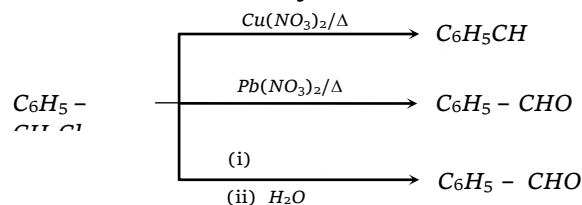


### Preparation of only aromatic carbonyl compounds

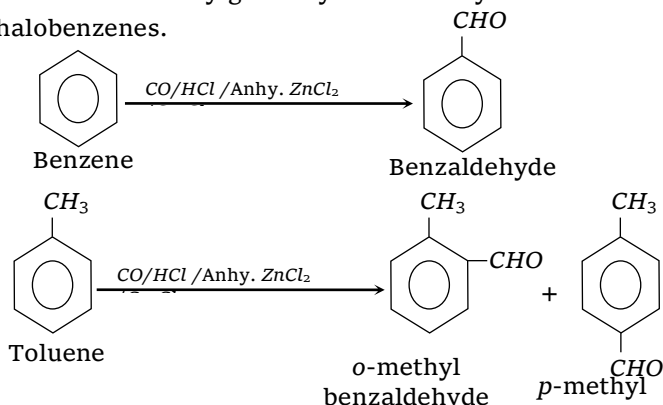
#### (1) From methyl arenes



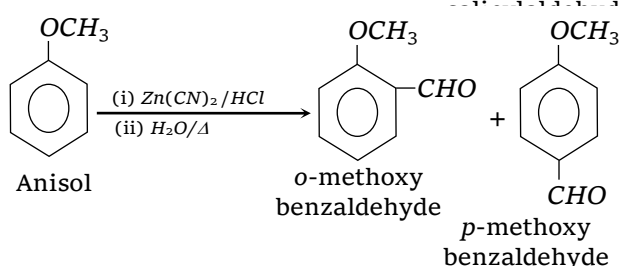
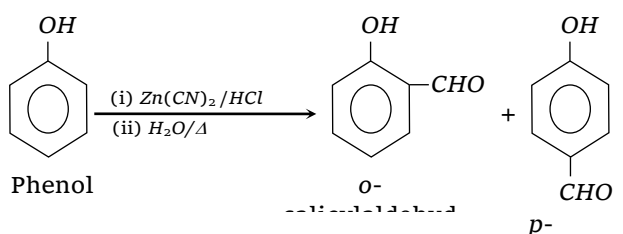
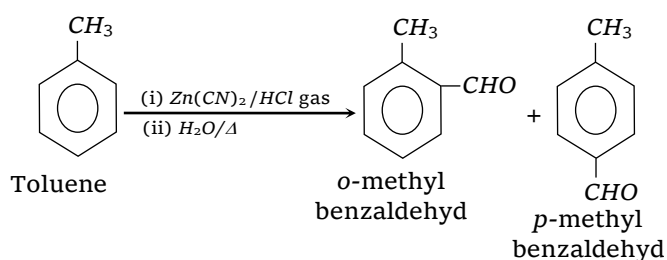
#### (2) From chloro methyl



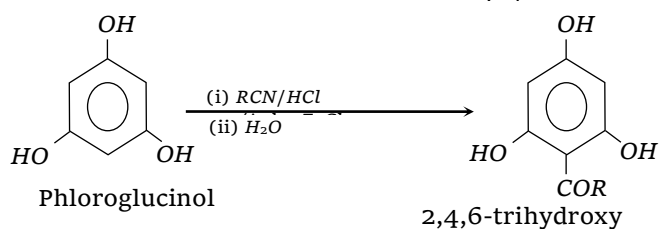
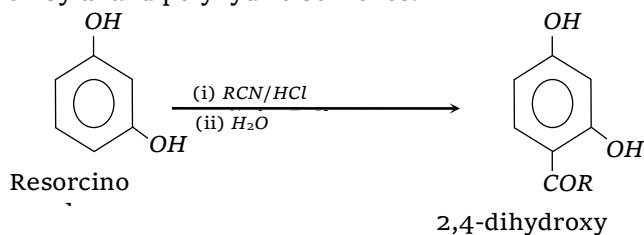
(3) **Gattermann - Koch formylation** : This reaction is mainly given by aromatic hydrocarbons and halobenzenes.



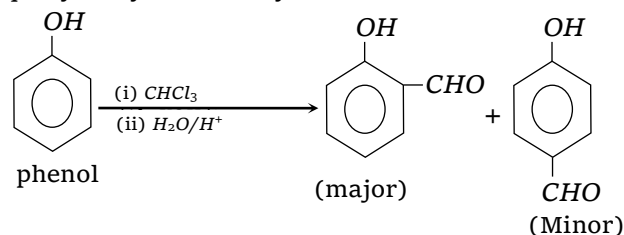
(4) **Gattermann formylation** : This reaction is mainly given by alkyl benzenes, phenols and phenolic ethers.



(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.

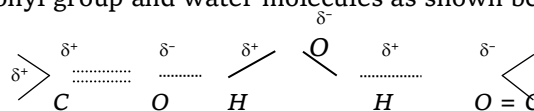


### Physical properties of carbonyl compounds

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

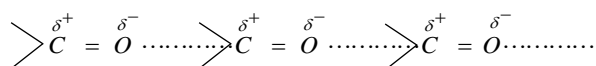
(2) **Smell** : With the exception of lower aldehydes which have unpleasant odours, aldehydes and ketones have generally pleasant smell. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones have been used in blending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

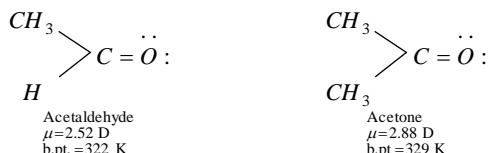
(4) **Boiling points** : The boiling points of aldehydes and ketones are higher than those of non polar compounds (hydrocarbons) or weakly polar compounds (such as ethers) of comparable molecular masses. However, their boiling points are lower than those of corresponding alcohols or carboxylic acids.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

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



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

### Chemical properties of carbonyl compounds

Carbonyl compounds give chemical reactions due to carbonyl group and  $\alpha$ -hydrogens.

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

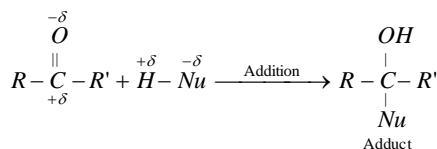
- (1) Nucleophilic addition reactions
- (2) Addition followed by elimination reactions
- (3) Oxidation
- (4) Reduction
- (5) Reactions due to  $\alpha$ -hydrogen
- (6) Condensation reactions and
- (7) Miscellaneous reactions

#### (1) 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,



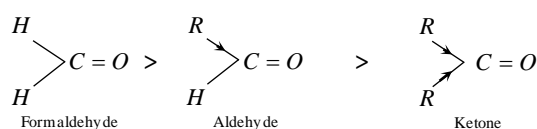
In addition reactions nucleophile adds on carbonyl carbon and electrophile on carbonyl oxygen to give adduct.

#### (iv) Relative reactivity of aldehydes and ketones

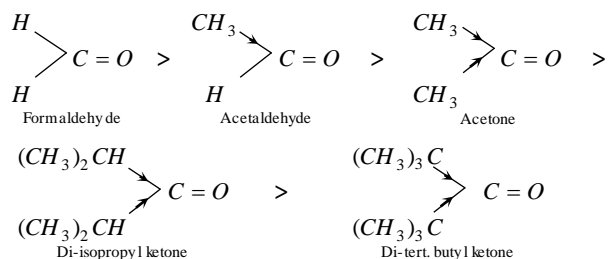
: Aldehydes and ketones readily undergo nucleophilic addition reactions. However, ketones are less reactive than aldehydes. This is due to electronic and steric effects as explained below:

(a) **Inductive effect** : The relative reactivities of aldehydes and ketones in nucleophilic addition reactions may be attributed to the amount of positive

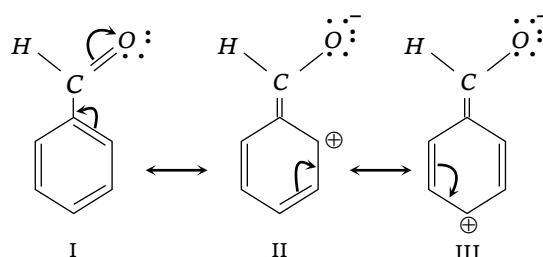
charge on the carbon. A greater positive charge means a higher reactivity. If the positive charge is dispersed throughout the molecule, the carbonyl compound becomes more stable and its reactivity decreases. Now, alkyl group is an electron releasing group (+I inductive effect). Therefore, electron releasing power of two alkyl groups in ketones is more than that of one alkyl group 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:

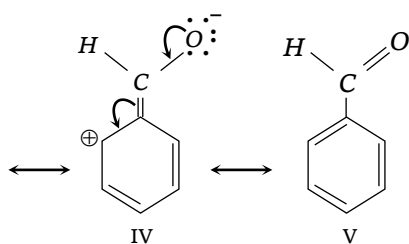


(b) **Steric effect** : The size of the alkyl group is more than that of hydrogen. In aldehydes, there is one alkyl group but in ketones, there are two alkyl groups attached to the carbonyl group. The alkyl groups are larger than a hydrogen atom and these cause hindrance to the attacking group. This is called **steric hindrance**. As the number and size of the alkyl groups increase, the hindrance to the attack of nucleophile also increases and the reactivity of a carbonyl 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:



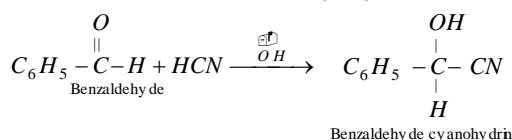
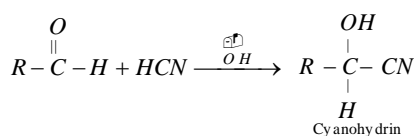


It is clear from the resonating structures that due to electron releasing resonance effect of the benzene ring, the magnitude of the positive charge on the carbonyl group decreases and consequently it becomes less susceptible to the nucleophilic attack. Thus, aromatic aldehydes and ketones are less reactive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



### Some important examples of nucleophilic addition reactions

#### Addition of HCN

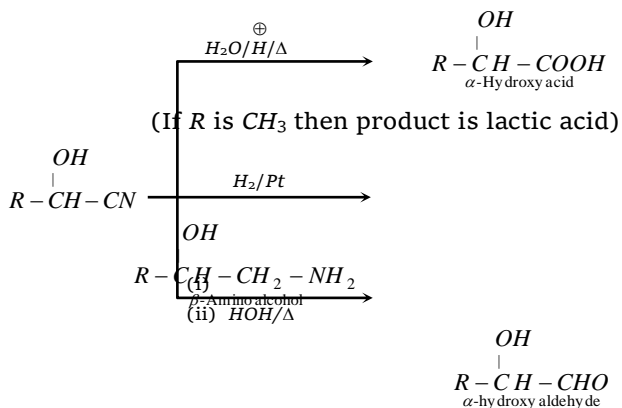


Because HCN is a toxic gas, the best way to carry out this reaction is to generate hydrogen cyanide during the reaction by adding HCl to a mixture of the carbonyl compound and excess of NaCN.

Benzophenone does not react with HCN.

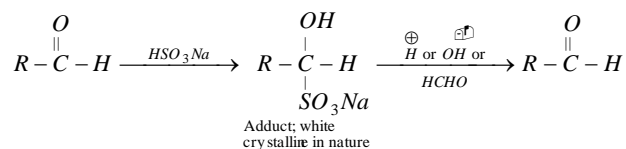
Except formaldehyde, all other aldehydes give optically active cyanohydrin (racemic mixture).

This reaction is synthetically useful reaction for the preparation of  $\alpha$ -hydroxy acids,  $\beta$ -amino alcohols and  $\alpha$ -hydroxy aldehydes.

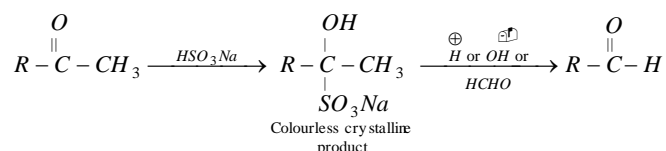


#### Addition of sodium bisulphite

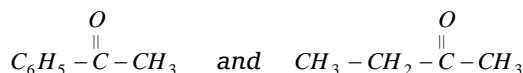
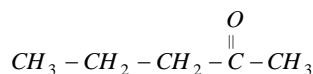
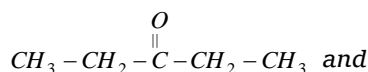
All types of aldehydes give addition reaction with this reagent.



Only aliphatic methyl ketones give addition reaction with sodium bisulphite.



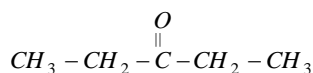
This reagent can be used for differentiation between aromatic and aliphatic methyl ketones, e.g.



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



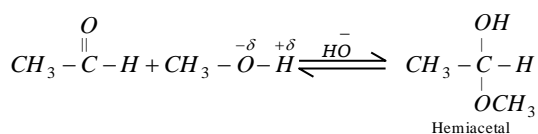
and

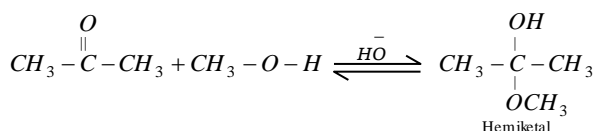


These two compounds can be separated from their mixture by the use of NaHSO<sub>3</sub>. Higher aliphatic ketones and aromatic ketones do not react with NaHSO<sub>3</sub>.

**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.

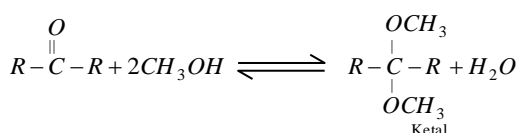
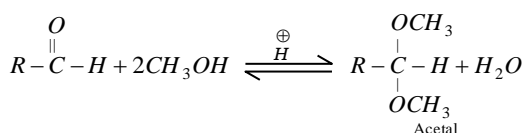
**Case I : Addition catalysed by base :** In the presence of a base one equivalent of an alcohol reacts with only one equivalent of the carbonyl compound. The product obtained is called hemiacetal (in case of aldehyde) and hemiketal (in case of ketone). The reaction is reversible. There is always equilibrium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



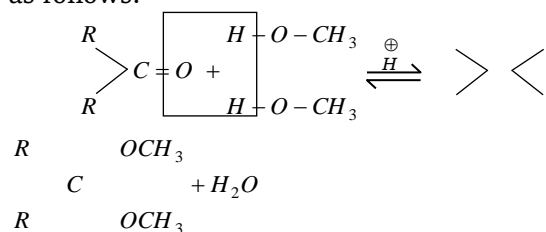


Hemiacetals and hemiketals are  $\alpha$ -alkoxy alcohols.

**Case II : Addition catalysed by acid :** In the presence of an 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).



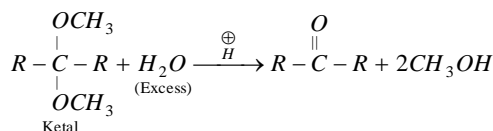
(i) Formation of acetals and ketals can be shown as follows:



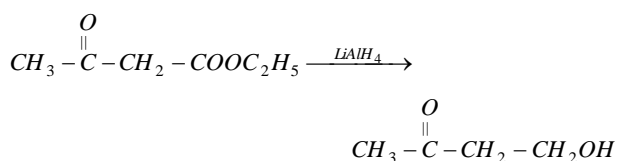
(ii) Acetals and ketals are gem dialkoxy compounds.

(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.

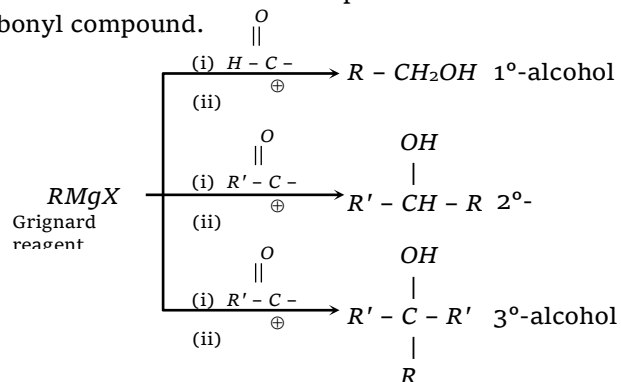


This reaction is very useful reaction for the protection of carbonyl group which can be deprotected by hydrolysis. Glycol is used for this purpose. Suppose we want to carry out the given conversion by  $\text{LiAlH}_4$ .

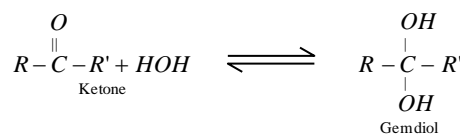


This can be achieved by protection of  $\text{C}=\text{O}$  group and then by deprotection

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



**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:

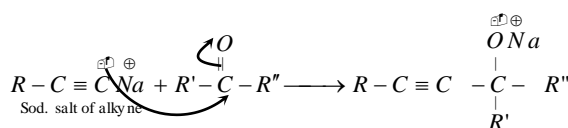
(i) Steric hindrance by +I group around  $\alpha$ -carbon decreases the stability of gem diols. +I group decreases stability of gem diol and hence decreases extent of hydration.

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

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

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

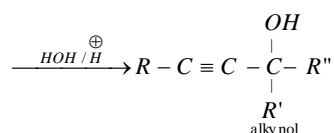
**Addition of terminal alkynes :** This reaction is known as **ethinylation**.



R-C=O

R-C=O



**(2) Addition followed by elimination reactions :**

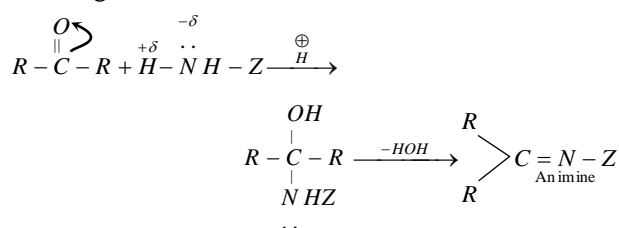
This reaction is given by ammonia derivatives ( $NH_2 - Z$ ).

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

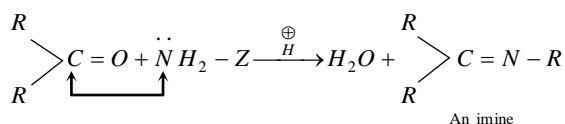
(ii) If the attacking atom of the nucleophile has a lone pair of electrons in the addition product, water will be eliminated from the addition product. This is called a nucleophilic addition elimination.

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.



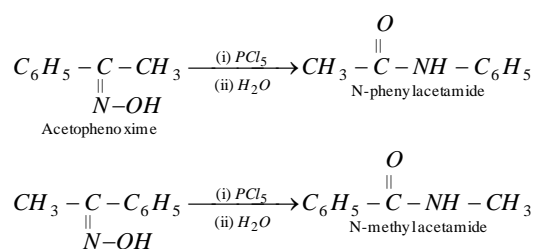
The overall reaction can be shown as follows



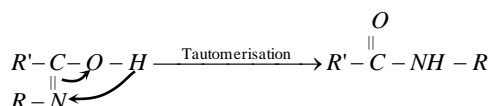
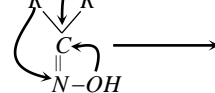
Different Imine formation with  $NH_2 - Z$  is given below

**Beckmann rearrangement :** Ketoxime when treated with acid at  $0^\circ C$  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 oxidising agents :** Mild oxidising agents oxidise only aldehydes into carboxylic acids. They do not oxidise 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. (Rochelle salt).

(b) **Benedict's solution :** This solution contains  $CuSO_4, NaOH$  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.

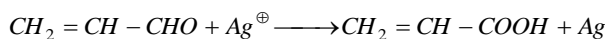


(c) **Tollens reagent** : Tollens reagent is ammoniacal silver nitrate solution. Its reacting species is  $Ag^{\oplus}$ .

□ It oxidises aliphatic as well as aromatic aldehydes.

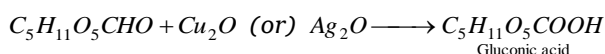
$R-CHO + Ag^{\oplus} \xrightarrow[\text{reaction}]{\text{Redox}} RCOOH + Ag$  (as silver mirror)

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



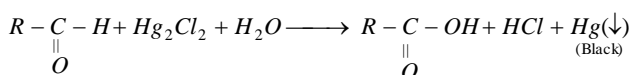
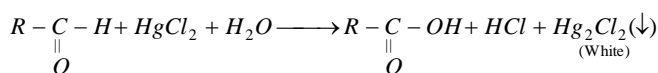
In this reaction the oxidation no. of Ag varies from +1 to 0.

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



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

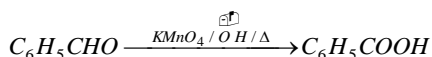
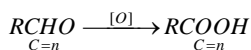
(d) Reaction with mercuric chloride solution :



(e) **Schiff's reagent** : Magenta solution  $\xrightarrow{SO_2}$  colourless solution  $\xrightarrow{CH_3CHO}$  pink colour restored (In cold).

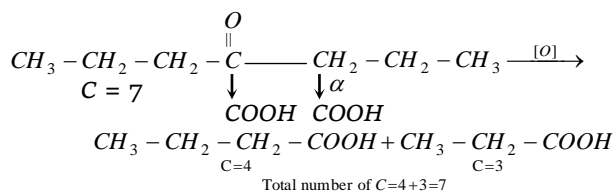
(ii) **Oxidation by strong oxidising agents** : Main strong oxidising agents are  $KMnO_4 / OH^{\ominus} / \Delta$ ,  $KMnO_4 / H^{\oplus} / \Delta$ ,  $K_2Cr_2O_7 / H^{\oplus} / \Delta$  and conc  $HNO_3 / \Delta$ . These agents oxidise aldehydes as well as ketones.

(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  $\alpha$ -carbon and carbonyl carbon. In this process both carbons convert into carboxylic groups. This leads to the formation of two moles of monocarboxylic acids.

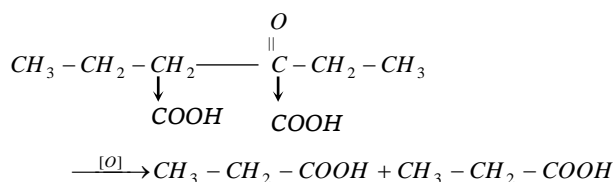
**Case I : Oxidation of symmetrical ketones**



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

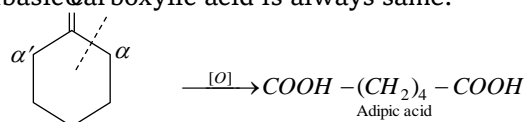
**Case II : Oxidation of unsymmetrical ketones :**

In case of unsymmetrical ketones  $\alpha$ -carbon whose bond breaks always belongs to the alkyl group which has more number of carbons. This rule is known as *Popoff's rule*.

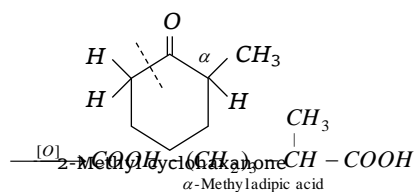


**Case III : Oxidation of cyclic ketones :**

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

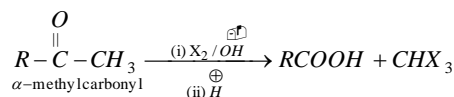


□ If both  $\alpha$ -carbons are not identical then bond breaking takes place between carbonyl carbon and the  $\alpha$ -carbon which has maximum number of hydrogens.



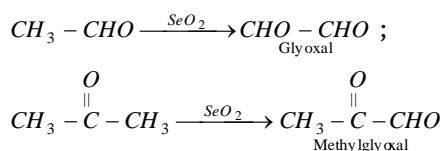
(iii) **Miscellaneous oxidation**

(a) **Haloform Reaction**



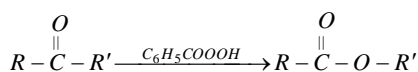
(b) **Oxidation at  $\alpha$ -CH<sub>2</sub> or CH<sub>3</sub> by SeO<sub>2</sub>** : SeO<sub>2</sub> oxidises  $\alpha$ -CH<sub>2</sub>-group into keto group and  $\alpha$ -CH<sub>3</sub>-group into aldehydic group.

In this oxidation reactivity of CH<sub>2</sub> is more than the CH<sub>3</sub> group and Oxidation is regio selective in nature.



## 1264 Aldehydes and Ketones

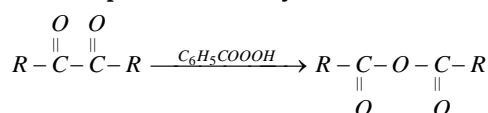
(c) **Oxidation by organic peracids** : Organic peracids oxidise aldehydes into carboxylic acids and ketones into esters. This oxidation is known as **Baeyer - Villiger oxidation**.



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

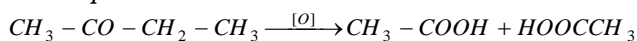
In case of ketone, insertion of oxygen takes place between carbonyl carbon and  $\alpha$ -carbon. Thus the product is ester. This is one of the most important reaction for the conversion of ketones into esters.

□ Vic dicarbonyl compound also undergo oxidation and product is anhydride.

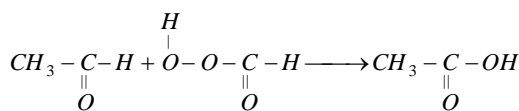
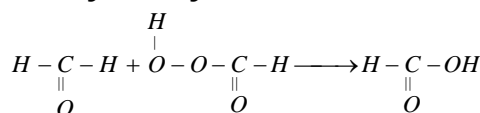


□ **Popoff's rule** : Oxidation of unsymmetrical ketones largely take place in such a way that the smaller alkyl group remains attached to the CO group during the formation of two molecules of acids. This is known as Popoff's rule

Example :



(d) **Baeyer-villiger oxidation** :



□ Reaction will be held if the oxidising agent is performic acid.

### (4) Reduction of carbonyl compounds

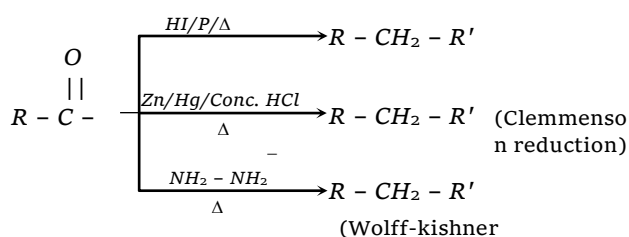
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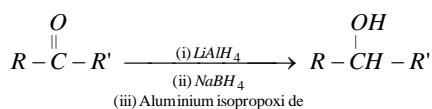
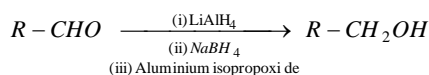
(i) **Reduction of C - group into -CH<sub>2</sub> - group** :

Following three reagents reduce carbonyl group into -CH<sub>2</sub> - groups: (a) HI/P/Δ (b) Zn/Hg/Conc. HCl and

(c) NH<sub>2</sub> - NH<sub>2</sub> / OH .

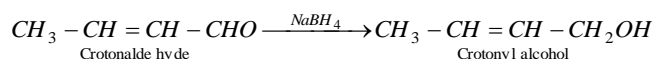


(ii) **Reduction of carbonyl compounds into hydroxy compounds** : Carbonyl group converts into -CHOH - group by LiAlH<sub>4</sub>, NaBH<sub>4</sub>, Na/C<sub>2</sub>H<sub>5</sub>OH and aluminium isopropoxide.



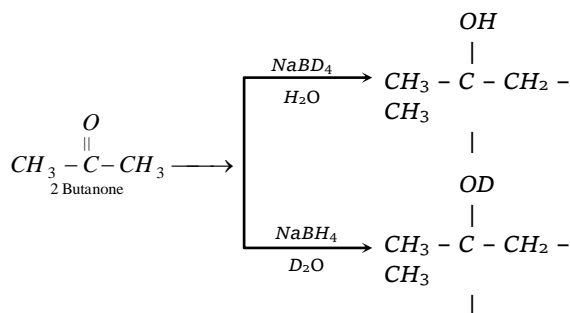
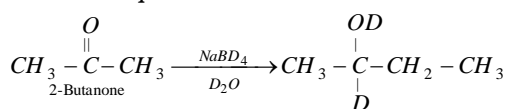
NaBH<sub>4</sub> is regioselective reducing agent because it reduced only CHO in the presence of other reducible group.

Example :

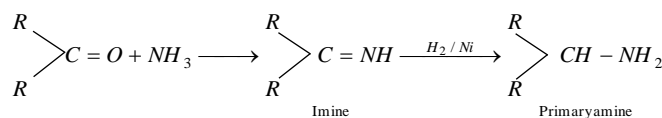


Hydride ion of NaBH<sub>4</sub> attack on carbonyl carbon during reduction.

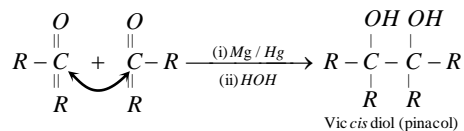
Example



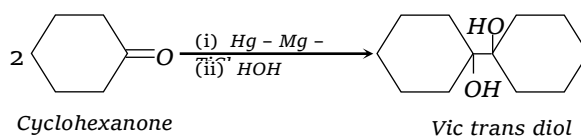
(iii) **Reductive amination** : In this reduction -CO - group converts into -CH - NH<sub>2</sub> group



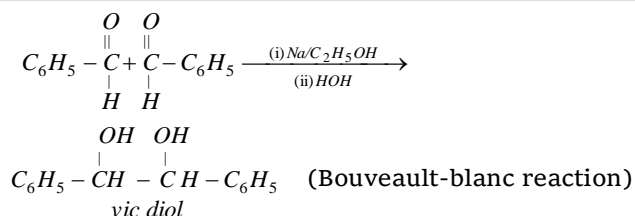
(iv) **Reduction of ketones by Mg or Mg/Hg** : In this case ketones undergo reduction via coupling reaction and product is vic cis diol.



When this reaction is carried out in the presence of Mg/Hg/TiCl<sub>4</sub>, the product is vic trans diol.

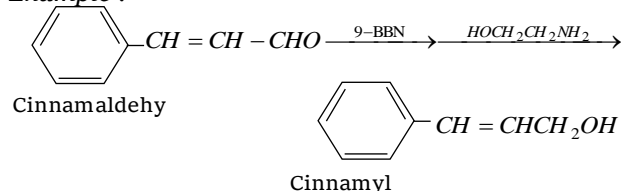


(v) **Reduction of benzaldehyde by Na/C<sub>2</sub>H<sub>5</sub>OH** : Benzaldehyde undergoes reduction via coupling reaction and product is vic diol.



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

Example :



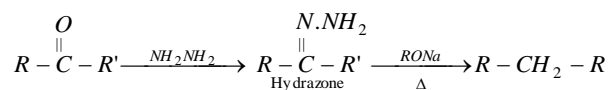
If reducing agent is NaH, reaction is called Darzen's reaction, we can also use LiAlH<sub>4</sub> in this reaction.

If reducing agent is aluminium iso propoxide (CH<sub>3</sub>-CH(O)<sub>2</sub>-Al-CH<sub>3</sub>). Product will be alcohol. This

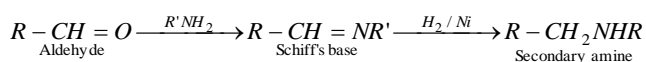
reaction is called Meerwein - pondorff verley reduction (MPV reduction).

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).



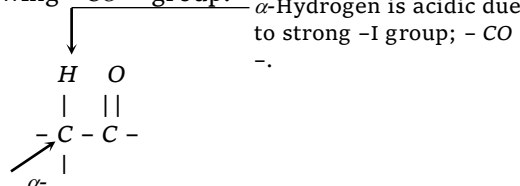
(vii) Schiff's base on reduction gives secondary amines.



### (5) Reactions due to α-hydrogen

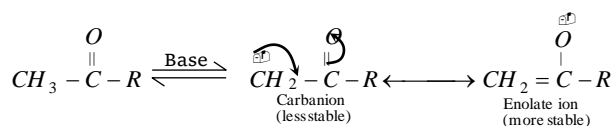
#### (i) Acidity of α-hydrogens :

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



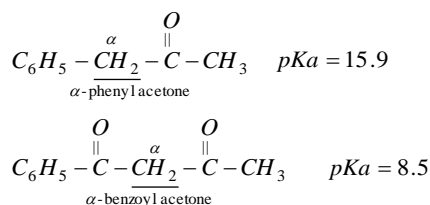
(b) Thus carbonyl compounds having α-hydrogen convert into carbanions in the presence of base. This

carbanion is stabilised by delocalisation of negative charge.



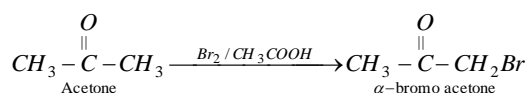
(c) The acidity of α-hydrogen is more than ethyne. pKa value of aldehydes and ketones are generally 19 - 20 where as pKa value of ethyne is 25.

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

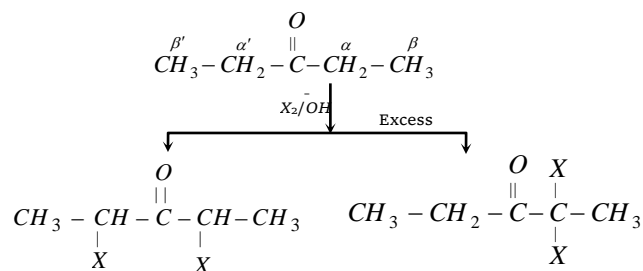


(ii) **Halogenation** : Carbonyl compounds having α-hydrogens undergo halogenation reactions. This reaction is catalysed by acid as well as base.

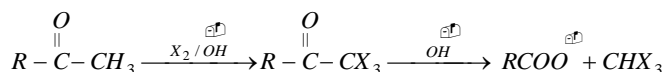
(a) **Acid catalysed halogenation** : This gives only monohalo derivative.



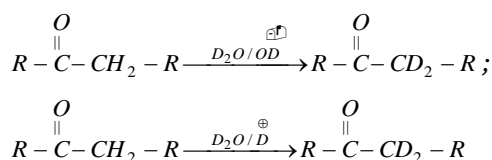
(b) **Base catalysed halogenation** : In the presence of base all α-hydrogens of the same carbon is replaced by halogens.



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

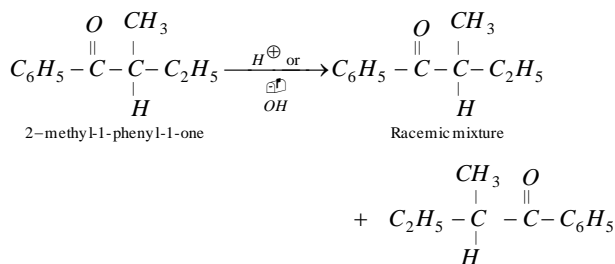


(iii) **Deuterium exchange reaction** : Deuterium exchange reaction is catalysed by acid (D<sup>+</sup>) as well as base (OD<sup>-</sup>). In both the cases all the hydrogens on only one α-carbon is replaced by D.

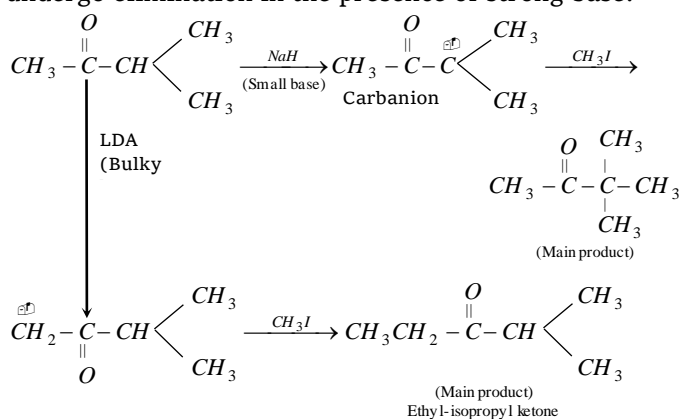


## 1266 Aldehydes and Ketones

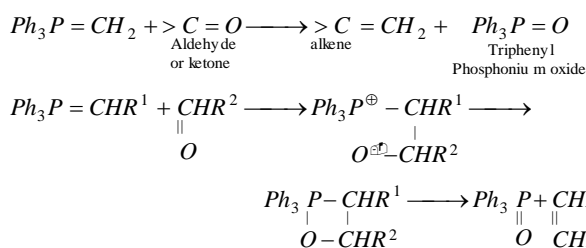
(iv) **Racemisation** : Ketones whose  $\alpha$ -carbon is chiral undergo Racemisation in the presence of acid as well as base.



(v) **Alkylation** : Carbonyl compounds having  $\alpha$ -hydrogens undergo alkylation reaction with  $\text{RX}$  in the presence of base. This reaction is  $\text{S}_{\text{N}}2$  reaction. The best result is obtained with  $\text{CH}_3\text{-X}$ . Other halides undergo elimination in the presence of strong base.

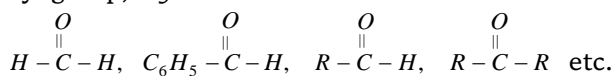


(vi) **Wittig reaction** : Aldehyde and ketones undergo the wittig reaction to form alkenes.



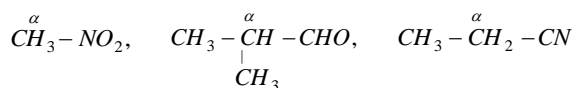
(6) **Condensation reaction of carbonyl compounds** : Nucleophilic addition reaction of compounds having carbonyl group with those compounds which have at least one acidic hydrogen at  $\alpha$ -carbon is known as condensation reaction. In this addition reaction :

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



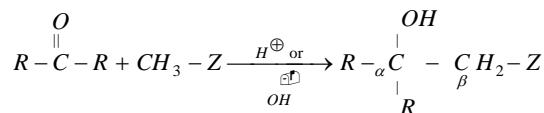
Addition always takes place on the carbonyl group.

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



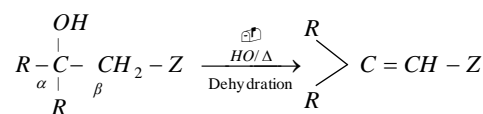
□ If substrate and reagent both are carbonyl compounds then one should have at least one  $\alpha$ -hydrogen and other may or may not have  $\alpha$ -hydrogen.

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 ( $\leq 20^\circ\text{C}$ ) because product of the reaction is alcohol which has strong -I group at  $\beta$ -carbon.

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



### (i) Aldol condensation

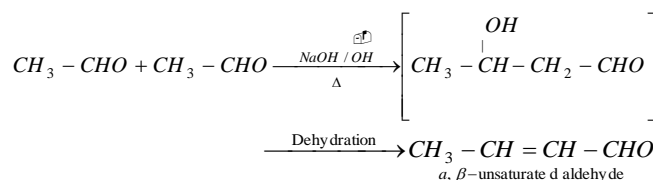
(a) This reaction takes place between two molecules of carbonyl compounds; one molecule should have at least two  $\alpha$ -hydrogen atoms. In this reaction best result is obtained when

Both molecule are the same or

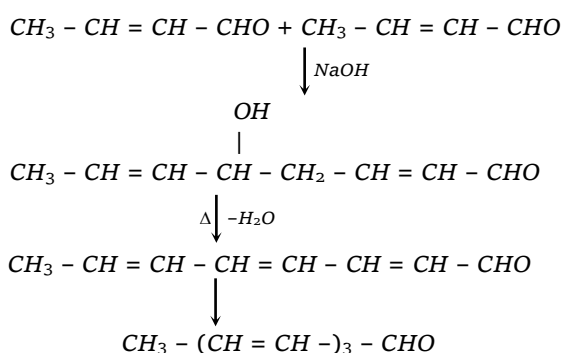
One should have no  $\alpha$ -hydrogen atom and other should have at least two  $\alpha$ -hydrogens.

(b) These reactions are practical when base is  $\text{NaOH}$  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.

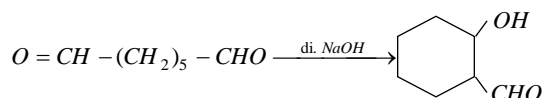


Due to hyper-conjugation in crotonaldehyde further condensation give conjugated alkene carbonyl compound.

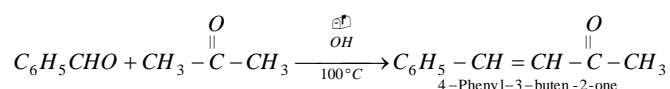


**Intra molecular aldol condensation :** One molecule Intramolecular condensation give aldol compounds

Example :



(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 :

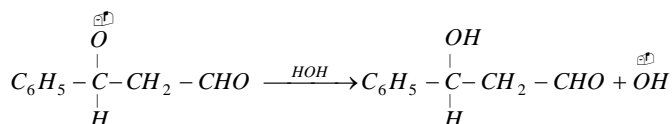
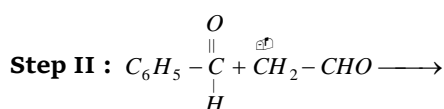
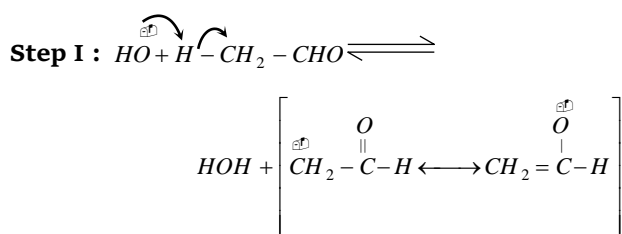
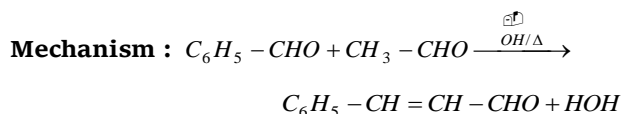


### Test of aldehydes and Ketones (Distinction)

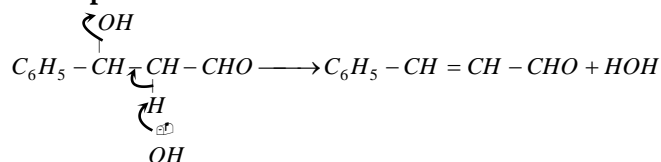
Table : 27.1

Test	Aldehydes	Ketones
With Schiff's reagent	Give pink colour.	No colour.
With Fehling's solution	Give red precipitate.	No precipitate is formed.
With Tollen's reagent	Black precipitate or silver mirror is formed.	No black precipitate or silver mirror is formed.
With saturated sodium bisulphite solution in water	Crystalline compound (colourless) is formed.	Crystalline compound (colourless) is formed.
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.
With sodium hydroxide	Give brown resinous mass (formaldehyde does not give this test).	No reaction.
With sodium nitroprusside and few drops of sodium hydroxide	A deep red colour (formaldehyde does not respond to this test).	Red colour which changes to orange.

### Some commercially important aliphatic carbonyl compounds

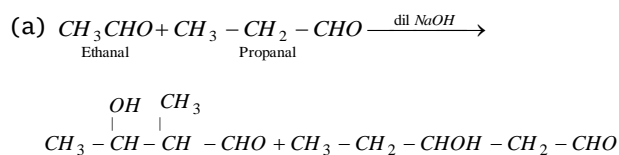


**Step III :**

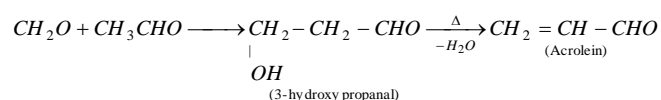


In aldol condensation, dehydration occurs readily because the double bond that forms is conjugated, both with the carbonyl group and with the benzene ring. The conjugation system is thereby extended.

**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  $\alpha$ -hydrogen atom gives different possible product



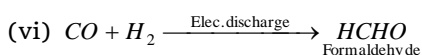
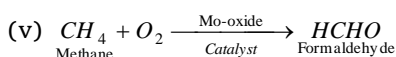
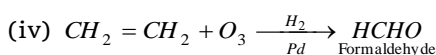
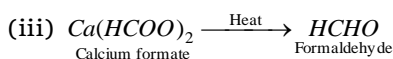
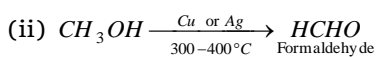
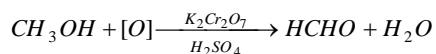
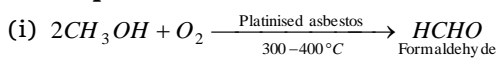
However crossed aldol condensation is important when only it the components has  $\alpha$ -hydrogen atom.



## 1268 Aldehydes and Ketones

**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.

### (1) Preparation



### (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  $-21^\circ C$ .

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

(v) Its solution acts as antiseptic and disinfectant.

### (3) 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.

## Acetaldehyde

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

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

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

(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.

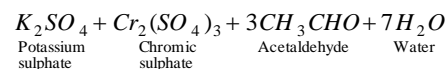
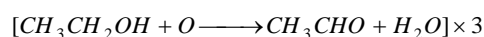
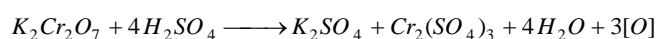
(v) By the reduction of acetyl chloride with hydrogen in presence of a catalyst palladium suspended in barium sulphate (Rosenmund's reaction).

(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  $60^\circ C$ .

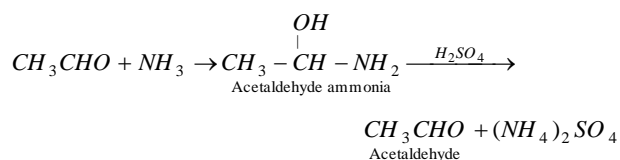
(viii) By ozonolysis of butene-2 and subsequent breaking of ozonide.

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



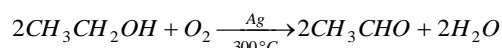
To recover acetaldehyde, the distillate is treated with dry ammonia when crystallised product, acetaldehyde ammonia, is formed. It is filtered and washed with dry ether. The dried crystals are then

distilled with dilute sulphuric acid when pure acetaldehyde is collected.

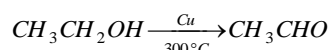


(x) **Manufacture** : Acetaldehyde can be manufactured by one of the following methods:

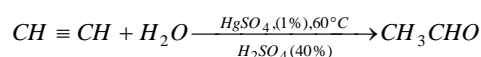
(a) *By air oxidation of ethyl alcohol*



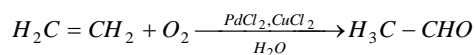
(b) *By dehydrogenation of alcohol*



(c) *By hydration of acetylene*



(d) *From ethylene (Wacker process)*

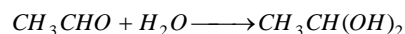


(2) **Physical properties**

(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 diol.



(3) **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 inhalant in nose troubles.

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

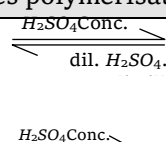
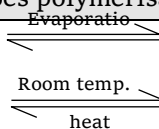
(iv) In the preparation of acetaldehyde ammonia (a rubber accelerator).

Table : 27.2 Comparative study of formaldehyde and acetaldehyde

S.No	Reaction	Formaldehyde $HCHO$	Acetaldehyde $CH_3CHO$
<b>Similarities</b>			
1.	Addition of hydrogen (a) $H_2$ in presence of catalyst, $Ni$ , $Pd$ or $Pt$ (b) $LiAlH_4$ (ether) (c) Amalgamated zinc + conc. $HCl$ (Clemmenson reduction)	Forms methyl alcohol $HCHO + H_2 \longrightarrow CH_3OH$ Forms methyl alcohol Forms methane $HCHO + 4H \longrightarrow CH_4 + H_2O$	Forms ethyl alcohol $CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$ Forms ethyl alcohol Forms ethane $CH_3CHO + 4H \longrightarrow C_2H_6 + H_2O$
2.	Addition of $NaHSO_3$ solution	Forms bisulphite addition product $HCHO + NaHSO_3 \longrightarrow CH_2(OH)SO_3Na$	Forms bisulphite addition product $CH_3CHO + NaHSO_3 \longrightarrow$ $CH_3CH(OH)SO_3Na$
3.	Addition of $HCN$	Forms formaldehyde cyanohydrin $HCHO + HCN \longrightarrow CH_2(OH)CN$	Forms acetaldehyde cyanohydrin $CH_3CHO + HCN \longrightarrow$ $CH_3CH(OH)CN$
4.	Addition of Grignard reagent followed by hydrolysis	Forms ethyl alcohol $HCHO + CH_3MgI \longrightarrow CH_2 \begin{matrix} \swarrow OMgI \\ \searrow CH_3 \end{matrix}$ $\xrightarrow[-Mg(OH)I]{H_2O} CH_3CH_2OH$	Forms isopropyl alcohol $CH_3CHO + CH_3MgI \longrightarrow$ $CH_3 - \underset{CH_3}{\overset{H}{C}} OMgI \xrightarrow[-Mg(OH)I]{H_2O}$

## 1270 Aldehydes and Ketones

			$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{OH} \\   \\ \text{CH}_3 \end{array}$
5.	With hydroxylamine $\text{NH}_2\text{OH}$	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 ( $\text{NH}_2\text{NH}_2$ )	Forms formaldehyde hydrazone $\text{CH}_2\text{O} + \text{H}_2\text{N NH}_2 \xrightarrow{-\text{H}_2\text{O}}$ $\text{CH}_2 = \text{NNH}_2$	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 phenyl hydrazine ( $\text{C}_6\text{H}_5\text{NNH}_2$ )	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 $\text{H}_2\text{C} = \text{O} + 2\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{HCl}}$ $\begin{array}{c} \text{OC}_2\text{H}_5 \\   \\ \text{CH}_2 \\   \\ \text{OC}_2\text{H}_5 \end{array} <$	Forms acetaldehyde diethyl acetal $\text{CH}_3\text{CHO} + 2\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{HCl}}$ $\begin{array}{c} \text{OC}_2\text{H}_5 \\   \\ \text{CH}_3\text{CH} \\   \\ \text{OC}_2\text{H}_5 \end{array} <$
10.	With thioalcohols ( $\text{C}_2\text{H}_5\text{SH}$ ) in presence of acid	Forms thio ethylal $\text{H}_2\text{C} = \text{O} + 2\text{C}_2\text{H}_5\text{SH} \longrightarrow$ $\begin{array}{c} \text{SC}_2\text{H}_5 \\   \\ \text{CH}_2 \\   \\ \text{SC}_2\text{H}_5 \end{array} <$	Forms acetaldehyde diethyl thioacetal $\text{CH}_3\text{CH} = \text{O} + 2\text{C}_2\text{H}_5\text{SH} \longrightarrow$ $\begin{array}{c} \text{SC}_2\text{H}_5 \\   \\ \text{CH}_3\text{CH} \\   \\ \text{SC}_2\text{H}_5 \end{array} <$
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	Undergoes polymerisation

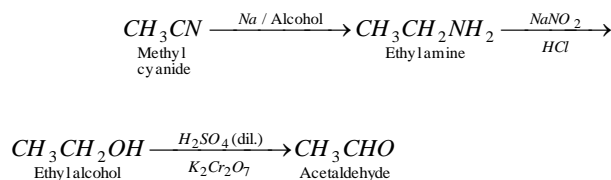
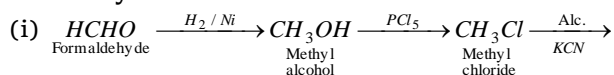


## Aldehydes and Ketones 1271

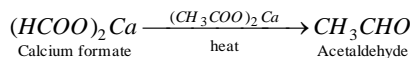
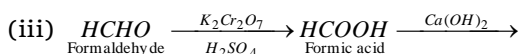
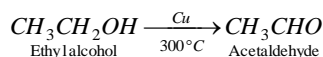
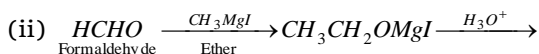
		$nHCHO$  $3HCHO$ $(HCHO)_3$ Metaformaldehyde	$(HCHO)_n$ Paraformaldehyde  $3CH_3CHO$  $(CH_3CHO)_3$ Paraldehyde  $4CH_3CHO$  $(CH_3CHO)_4$ Metaldehyde
<b>Dissimilarities</b>			
16.	With $PCl_5$	No reaction	Forms ethylidene chloride $CH_3CHO + PCl_5 \longrightarrow CH_3CH \begin{matrix} \swarrow Cl \\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

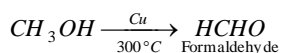
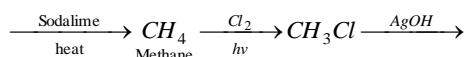
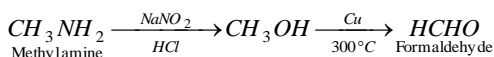
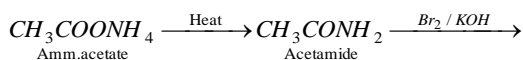
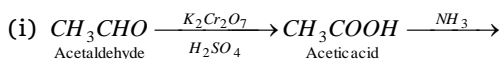
(1) **Ascent of series** : Conversion of formaldehyde into acetaldehyde



## 1272 Aldehydes and Ketones



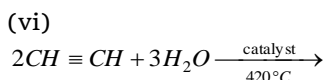
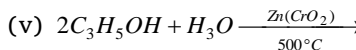
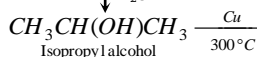
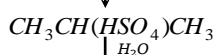
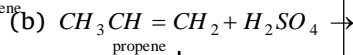
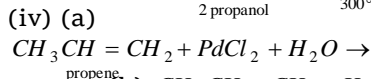
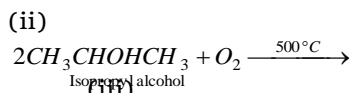
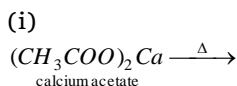
(2) **Descent of series** : Conversion of acetaldehyde into formaldehyde



### 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.

#### (1) Preparation :



(vii) **From pyroligneous acid** : Pyroligneous acid containing acetic acid, acetone and methyl alcohol is distilled in copper vessel and the vapours are passed through hot milk of lime. Acetic acid combines to form nonvolatile calcium acetate. The unabsorbed vapours of methanol and acetone are condensed and fractionally distilled. Acetone distills at  $56^\circ\text{C}$ .

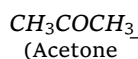
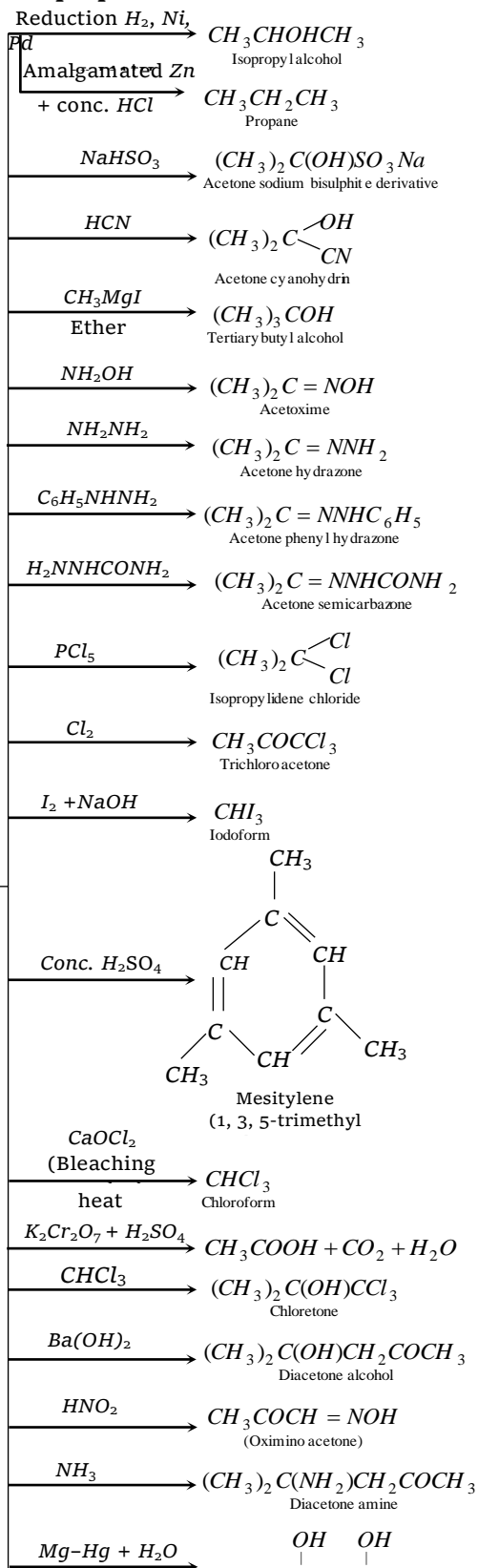
The acetone thus obtained is purified with the help of sodium bisulphite.

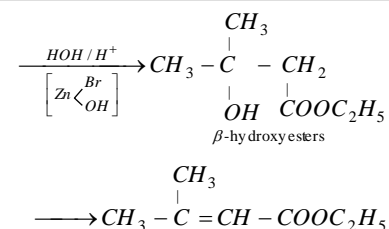
(2) **Physical properties** : (i) It is a colourless liquid with characteristic pleasant odour.

(ii) It is inflammable liquid. It boils at  $56^\circ\text{C}$ .

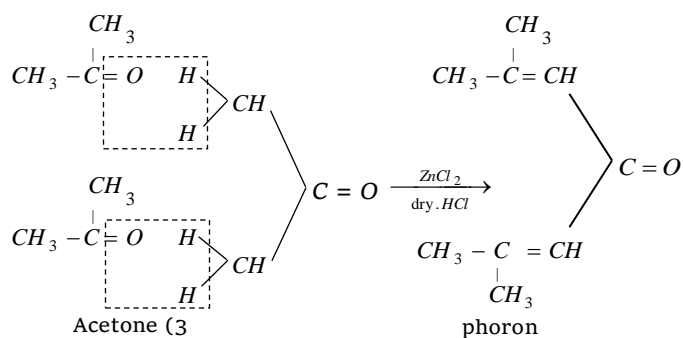
(iii) It is highly miscible with water, alcohol and ether.

#### (3) Chemical properties



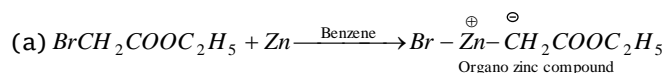


If acetone would be in excess in ketal condensation or catalyst ( $\text{ZnCl}_2$  / dry  $\text{HCl}$ ) is used then three moles of acetone undergoes condensation polymerisation and form a compound called 'Phorone'.

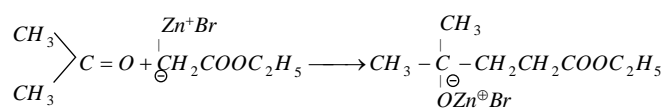


Molecular mass of phorone = 3 mole of acetone - 2 mole of  $\text{H}_2\text{O}$

**Reformatsky reaction:** This reaction involves the treatment of aldehyde and ketone with a bromo acid ester in presence of metallic zinc to form  $\beta$ -hydroxy ester, which can be easily dehydrated into  $\alpha,\beta$ -unsaturated ester.



(b) Addition to carbonyl group



#### (4) Uses

(i) As a solvent for cellulose acetate, cellulose nitrate, celluloid, lacquers, resins, etc.

(ii) For storing acetylene.

(iii) In the manufacture of cordite - a smoke less powder explosive.

(iv) In the preparation of chloroform, iodoform, sulphonal and chloretone.

(v) As a nailpolish remover.

(vi) In the preparation of an artificial scent (ionone), plexiglass (unbreakable glass) and synthetic rubber.

#### (5) Tests

(i) **Legal's test** : When a few drops of freshly prepared sodium nitroprusside and sodium hydroxide solution are added to an aqueous solution of acetone, a wine colour is obtained which changes to yellow on standing.

(ii) **Indigo test** : A small amount of orthonitrobenzaldehyde is added to about 2 ml. of acetone and it is diluted with  $\text{KOH}$  solution and stirred. A blue colour of indigotin is produced.

(iii) **Iodoform test** : Acetone gives iodoform test with iodine and sodium hydroxide or iodine and ammonium hydroxide.

Table : 27.3 Comparison between Acetaldehyde and Acetone

Reaction	Acetaldehyde	Acetone
<b>Similarities</b>		
1. Reduction with $\text{H}_2$ and $\text{Ni}$ or $\text{LiAlH}_4$	Forms ethyl alcohol $\text{CH}_3\text{CHO} + \text{H}_2 \xrightarrow{\text{Ni}} \text{CH}_3\text{CH}_2\text{OH}$	Forms isopropyl alcohol $\text{CH}_3\text{COCH}_3 + \text{H}_2 \longrightarrow \text{CH}_3\text{CHOHCH}_3$
2. Clemmensen's reduction ( $\text{Zn}/\text{Hg}$ and conc. $\text{HCl}$ )	Forms ethane (an alkane) $\text{CH}_3\text{CHO} + 4\text{H} \longrightarrow \text{CH}_3\text{CH}_3 + \text{H}_2\text{O}$	Forms propane (an alkane) $\text{CH}_3\text{COCH}_3 + 4\text{H} \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$
3. Addition of $\text{HCN}$	Forms acetaldehyde cyanohydrin	Forms acetone cyanohydrin



## 1274 Aldehydes and Ketones

	$CH_3CHO + HCN \longrightarrow \begin{matrix} OH \\   \\ CH_3CH \\   \\ CN \end{matrix}$	$(CH_3)_2CO + HCN \longrightarrow \begin{matrix} OH \\   \\ (CH_3)_2C \\   \\ CN \end{matrix}$
4. Addition of $NaHSO_3$	White crystalline derivative $CH_3CHO + NaHSO_3 \longrightarrow \begin{matrix} OH \\   \\ CH_3CH \\   \\ SO_3Na \end{matrix}$	White crystalline derivative $(CH_3)_2CO + NaHSO_3 \longrightarrow \begin{matrix} OH \\   \\ (CH_3)_2C \\   \\ SO_3Na \end{matrix}$
5. Grignard reagent followed by hydrolysis	Forms isopropyl alcohol $CH_3CHO + CH_3MgI \longrightarrow (CH_3)_2CH - OMgI$ $\xrightarrow{H_2O} CH_3CHOHCH_3$	Forms tertiary butyl alcohol $(CH_3)_2CO + CH_3MgI \longrightarrow (CH_3)_3COMgI$ $\xrightarrow{H_2O} (CH_3)_3COH$
6. With hydroxylamine ( $NH_2OH$ )	Forms acetaldoxime (an oxime) $CH_3CHO + H_2NOH \longrightarrow CH_3CH = NOH$	Forms acetoxime (an oxime) $(CH_3)_2CO + H_2NOH \longrightarrow (CH_3)_2C = NOH$
7. With hydrazine ( $NH_2NH_2$ )	Forms acetaldehyde hydrazone $CH_3CHO + H_2NNH_2 \longrightarrow CH_3CH = NNH_2$	Forms acetone hydrazone $(CH_3)_2CO + H_2NNH_2 \longrightarrow (CH_3)_2C = NNH_2$
8. With phenyl hydrazine ( $C_6H_5NHNH_2$ )	Forms acetaldehyde phenylhydrazone $CH_3CHO + H_2NNHC_6H_5 \longrightarrow$ $CH_3CH = NNHC_6H_5$	Forms acetone phenyl hydrazone $(CH_3)_2CO + H_2NNHC_6H_5 \longrightarrow$ $(CH_3)_2C = NNHC_6H_5$
9. With semicarbazide ( $H_2NNHCONH_2$ )	Forms acetaldehyde semicarbazone $CH_3CHO + H_2NNHCONH_2 \longrightarrow$ $CH_3CH = NNHCONH_2$	Forms acetone semicarbazone $(CH_3)_2CO + H_2NNHCONH_2 \longrightarrow$ $(CH_3)_2C = NNHCONH_2$
10. With $PCl_5$	Forms ethylidene chloride (Gem dihalide) $CH_3CHO + PCl_5 \longrightarrow \begin{matrix} \diagdown Cl \\   \\ CH_3CH \\   \\ Cl \end{matrix}$	Forms isopropylidene chloride (Gem dihalide) $(CH_3)_2CO + PCl_5 \longrightarrow \begin{matrix} \diagdown Cl \\   \\ (CH_3)_2C \\   \\ Cl \end{matrix}$
11. With chlorine	Forms chloral (Gem trihalide) $CH_3CHO + Cl_2 \longrightarrow CCl_3CHO$	Forms trichloro acetone (Gem trihalide) $CH_3COCH_3 + Cl_2 \longrightarrow CCl_3COCH_3$
12. With alcohols	Forms acetal (a diether) $CH_3CHO + 2C_2H_5OH \longrightarrow \begin{matrix} OC_2H_5 \\   \\ CH_3CH \\   \\ OC_2H_5 \end{matrix}$	Forms ketal (a diether) $(CH_3)_2CO + 2C_2H_5OH \longrightarrow \begin{matrix} OC_2H_5 \\   \\ (CH_3)_2C \\   \\ OC_2H_5 \end{matrix}$
13. With $SeO_2$	Forms glyoxal $CH_3CHO + SeO_2 \longrightarrow CHOCHO + Se + H_2O$	Forms methyl glyoxal $(CH_3)_2CO + SeO_2 \longrightarrow CH_3COCHO + Se + H_2O$
14. Iodoform reaction ( $I_2 + NaOH$ )	Forms iodoform	Forms iodoform
15. Bleaching powder	Forms chloroform	Forms chloroform
16. Aldol condensation with mild alkali	Forms aldol $2CH_3CHO \longrightarrow CH_3CHOHCH_2CHO$	Forms diacetone alcohol $2CH_3COCH_3 \longrightarrow (CH_3)_2C(OH)CH_2COCH_3$
17. Polymerisation	Undergoes polymerisation	Does not undergo polymerisation but gives condensation reaction
18. With $NH_3$	Forms acetaldehyde ammonia	Forms diacetone ammonia



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	$CH_3CHO + NH_3 \longrightarrow CH_3CH \begin{matrix} OH \\ NH_2 \end{matrix}$	$(CH_3)_2CO + NH_3 + OC(CH_3)_2 \longrightarrow (CH_3)_2C(NH_2)CH_2COCH_3$
19. With conc. $NaOH$	Forms brownish resinous mass	No reaction
20. With $HNO_2$	No reaction	Forms oximino acetone $CH_3COCH_3 + HNO_2 \longrightarrow CH_3COCH = NOH$
21. With chloroform	No reaction	Forms chloretone $(CH_3)_2CO + CHCl_3 \longrightarrow (CH_3)_2C \begin{matrix} OH \\ CCl_3 \end{matrix}$
22. With alk. sodium nitroprusside	Deep red colour	Red colour changes to yellow on standing
23. With sodium nitroprusside + Pyridine	Blue colour	No effect
24. Boiling point	$21^\circ C$	$56^\circ C$
<b>Dissimilarities</b>		
25. With Schiff's reagent	Pink colour	Does not give pink colour
26. With Fehling's solution	Gives red precipitate	No reaction
27. With Tollen's reagent	Gives silver mirror	No reaction
28. Oxidation with acidified $K_2Cr_2O_7$	Easily oxidised to acetic acid $CH_3CHO + O \longrightarrow CH_3COOH$	Oxidation occurs with difficulty to form acetic acid $CH_3COCH_3 + O \longrightarrow CH_3COOH + CO_2 + H_2O$

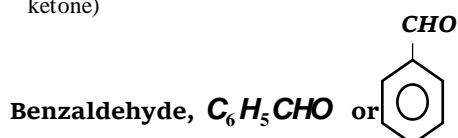
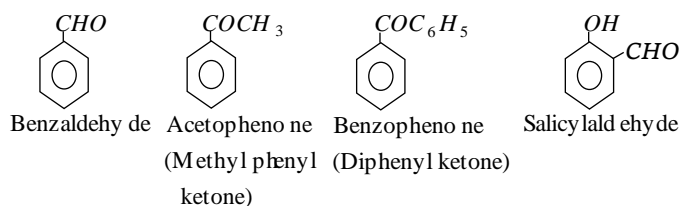
### Aromatic Carbonyl Compounds

Aromatic aldehydes are of two types :

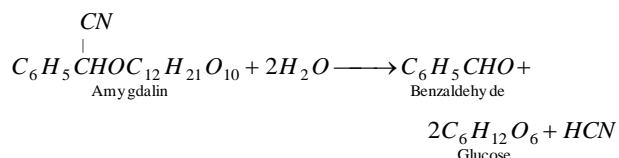
The compounds in which  $-CHO$  group is attached directly to an aromatic ring, e.g., benzaldehyde,  $C_6H_5CHO$ .

Those in which aldehyde ( $-CHO$ ) group is attached to side chain, e.g., phenyl acetaldehyde,  $C_6H_5CH_2CHO$ . They closely resemble with aliphatic aldehydes.

Aromatic ketones are compounds in which a carbonyl group ( $>C=O$ ) is attached to either two aryl groups or one aryl group and one alkyl group. Examples are :



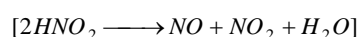
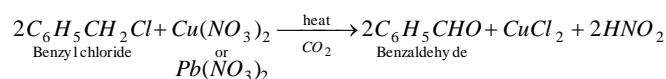
Benzaldehyde is the simplest aromatic aldehyde. It occurs in bitter almonds in the form of its glucoside, **amygdalin** ( $C_{20}H_{27}O_{11}N$ ). When amygdalin is boiled with dilute acids, it hydrolyses into benzaldehyde, glucose and  $HCN$



Benzaldehyde is also known as *oil of bitter almonds*.

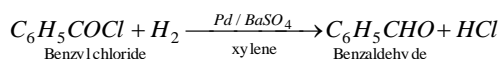
#### (1) Method of preparation

(i) **Laboratory method** : It is conveniently prepared by boiling benzyl chloride with copper nitrate or lead nitrate solution in a current of carbon dioxide.

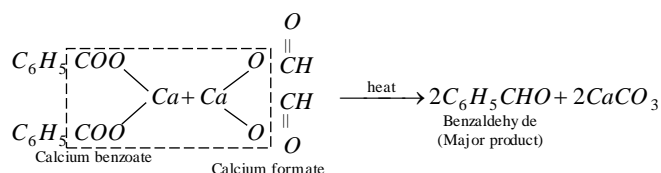


(ii) **Rosenmund reaction** :

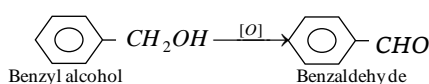
## 1276 Aldehydes and Ketones



(iii) **By dry distillation of a mixture of calcium benzoate and calcium formate**

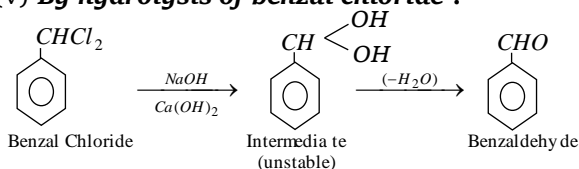


(iv) **By oxidation of benzyl alcohol** : This involves the treatment of benzyl alcohol with dil.  $HNO_3$  or acidic potassium dichromate or chromic anhydride in acetic anhydride or with copper catalyst at  $350^\circ C$ .



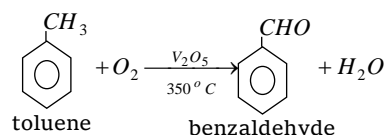
This method is used for commercial production of benzaldehyde.

(v) **By hydrolysis of benzal chloride** :



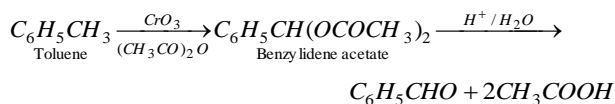
This is also an industrial method.

(vi) **By oxidation of Toluene**

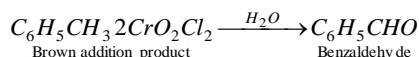


Commercially the oxidation of toluene is done with air and diluted with nitrogen (to prevent complete oxidation) at  $500^\circ C$  in the presence of oxides of  $Mn$ ,  $Mo$  or  $Zr$  as catalyst.

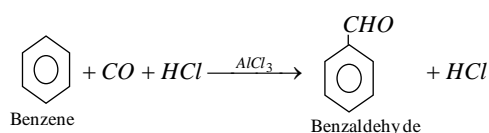
Partial oxidation of toluene with manganese dioxide and dilute sulphuric acid at  $35^\circ C$ , also forms benzaldehyde.



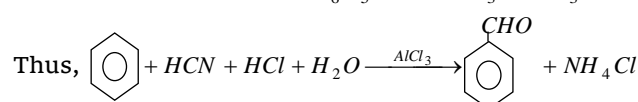
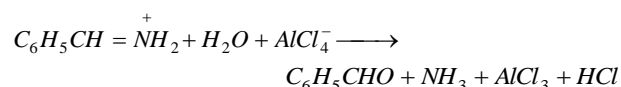
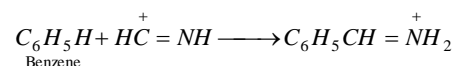
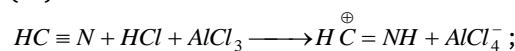
(vii) **Etard's reaction** :  $C_6H_5CH_3 + 2CrO_2Cl_2 \longrightarrow$



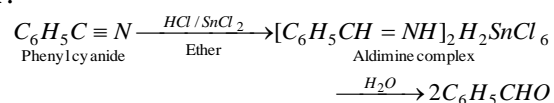
(viii) **Gattermann-koch aldehyde synthesis** : Benzene is converted into benzaldehyde by passing a mixture of carbon monoxide and  $HCl$  gas under high pressure into the ether solution of benzene in presence of anhydrous aluminium chloride and cuprous chloride.



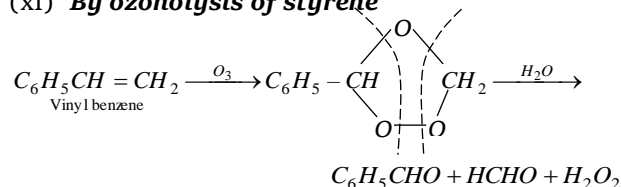
(ix) **Gattermann reaction**



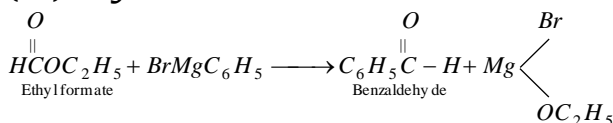
(x) **Stephen's reaction** : Benzaldehyde is obtained by partial reduction of phenyl cyanide with stannous chloride and passing dry  $HCl$  gas in ether solution followed by hydrolysis of the aldimine stannic chloride with water.



(xi) **By ozonolysis of styrene**

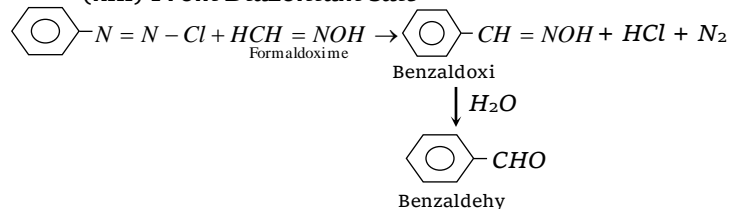


(xii) **Grignard reaction**



Other reagents like carbon monoxide or  $HCN$  can also be used in place of ethyl formate.

(xiii) **From Diazonium salt**



(2) **Physical properties**

(i) Benzaldehyde is a colourless oily liquid. Its boiling point is  $179^\circ C$ .

(ii) It has smell of bitter almonds.

(iii) It is sparingly soluble in water but highly soluble in organic solvents.

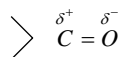
(iv) It is steam volatile.

(v) It is heavier than water (sp. gr. 1.0504 at  $15^\circ C$ ).

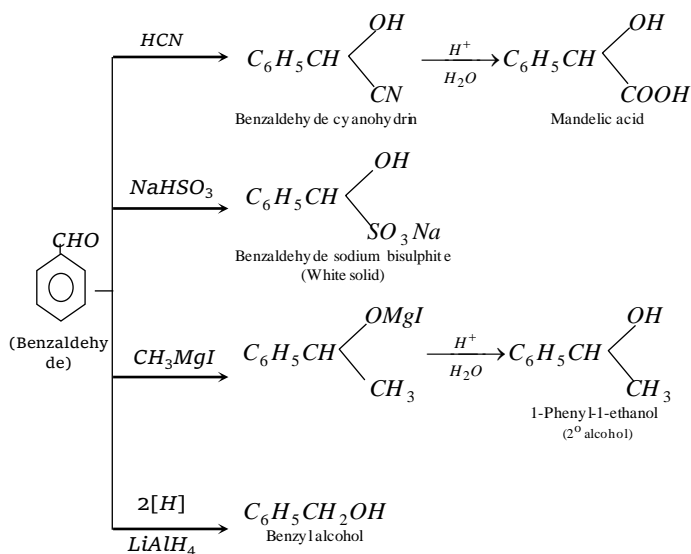
(vi) It is poisonous in nature.

(3) **Chemical properties**

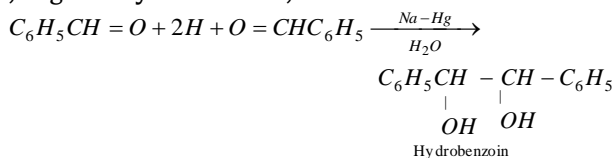
(i) **Addition reaction:** The carbonyl group is polar as oxygen is more electronegative than carbon,



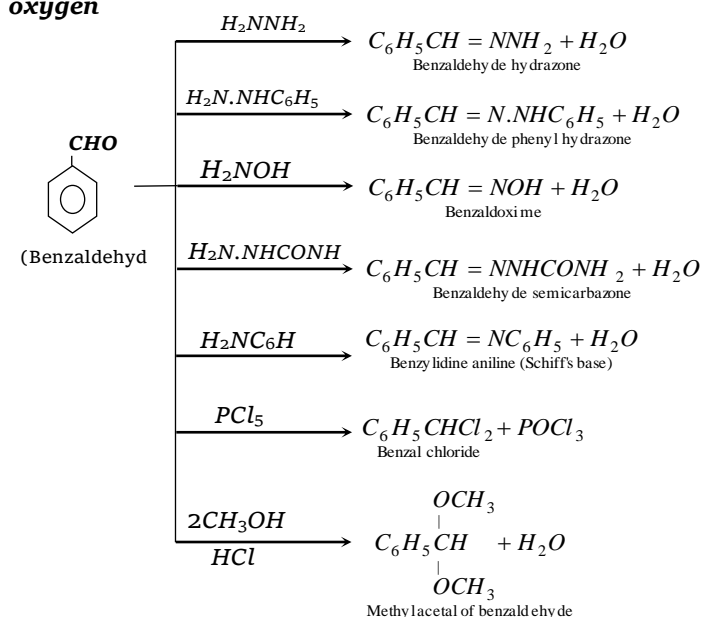
Thus, The positive part of the polar reagent always goes to the carbonyl oxygen and negative part goes to carbonyl carbon.



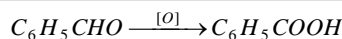
However on reduction with sodium amalgam and water, it gives hydrobenzoin,



(ii) **Reactions involving replacement of carbonyl oxygen**

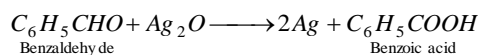


(iii) **Oxidation:** Benzaldehyde is readily oxidised to benzoic acid even on exposure to air.

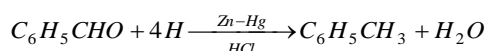


Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ , alkaline  $\text{KMnO}_4$  and dilute  $\text{HNO}_3$  can be used as oxidising agents for oxidation.

(iv) **Reducing properties:** Benzaldehyde is a weak reducing agent. It reduces ammoniacal silver nitrate solution (Tollen's reagent) to give silver mirror but does not reduce Fehling's solution.

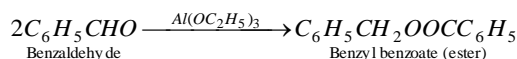


(v) **Clemmensen's reduction:** With amalgamated zinc and conc.  $\text{HCl}$ , benzaldehyde is reduced to toluene.



(vi) **Schiff's reaction:** It restores pink colour to Schiff's reagent (aqueous solution of *p*-rosaniline hydrochloride decolourised by passing sulphur dioxide).

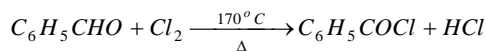
(vii) **Tischenko reaction:** On heating benzaldehyde with aluminium alkoxide (ethoxide) and a little of anhydrous  $\text{AlCl}_3$  or  $\text{ZnCl}_2$ , it undergoes an intermolecular oxidation and reduction (like aliphatic aldehydes) to form acid and alcohol respectively as such and react to produce benzyl benzoate (an ester).



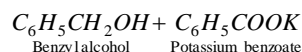
(viii) **Reactions in which benzaldehyde differs from aliphatic aldehydes**

(a) **With Fehling's solution:** No reaction

(b) **Action of chlorine:** Benzoyl chloride is formed when chlorine is passed through benzaldehyde at its boiling point in absence of halogen carrier. This is because in benzaldehyde there is no  $\alpha$ -hydrogen atom present which could be replaced by chlorine.

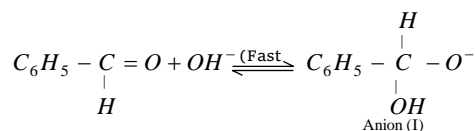


(c) **Cannizzaro's reaction:**  $2\text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{KOH}}$



The possible Mechanism is

**First step** is the reversible addition of hydroxide ion to carbonyl group.



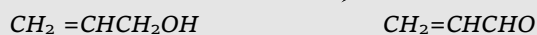
**Second step** is the transfer of hydride ion directly to the another aldehyde molecule, the latter is thus



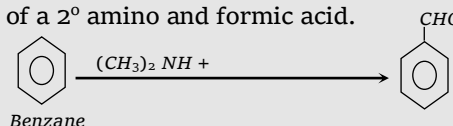


# Tips & Tricks

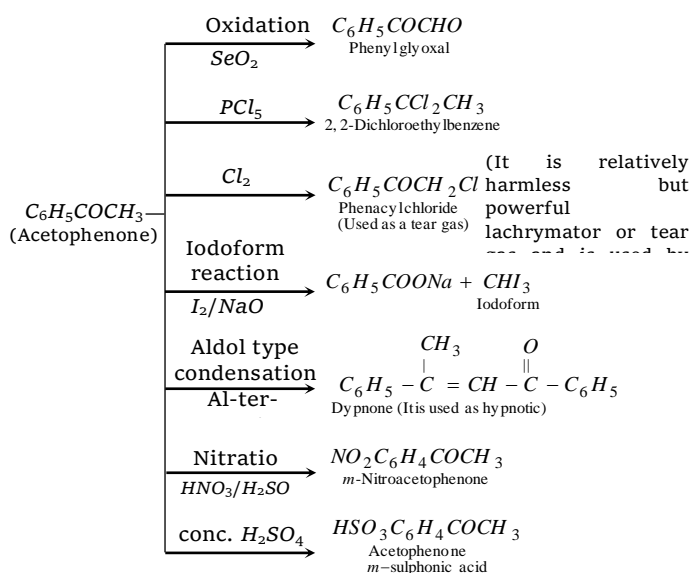
✍ Acidified  $K_2Cr_2O_7$  i.e., chromic acid sulphuric acid mixture is known as Jones's reagent. When used as an oxidising agent unlike acidified  $KMnO_4$  it does not diffect a double bond.



✍ Vilsmeier reaction : this reaction involves the conversion of aromatic compounds to aldehydes in the presence of a 2° amino and formic acid.



✍ Benzaldehyde although reduces Tollen's reagent. It does not reduce Fehling or Benedict solution.

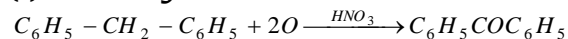


(4) **Uses** : It is used in perfumery and as a sleep producing drug.

## Benzophenone, $C_6H_5COC_6H_5$

(1) **Method of preparation**

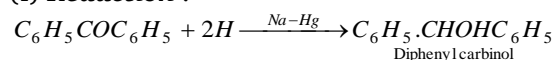
(i) **From alkyl benzenes**



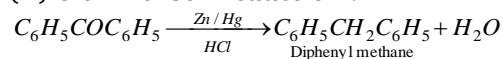
(2) **Physical properties** : It is a colourless, pleasant smelling solid.

(3) **Chemical properties** : It shows the characteristic properties of keto group but does not give bisulphite compounds.

(i) **Reduction** :



(ii) **Clemmenson reduction** :



(iii) **Fusion with KOH** :

