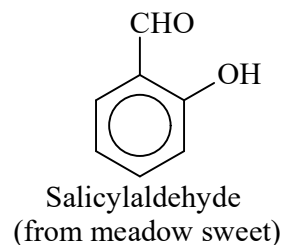
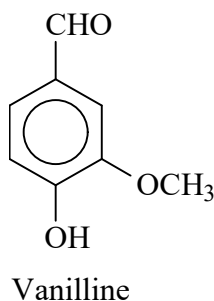
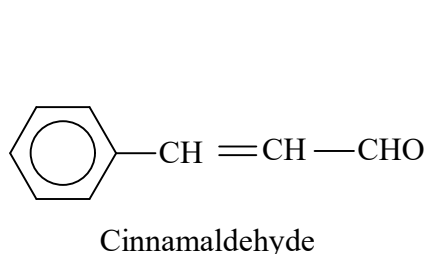


## CHAPTER - 09

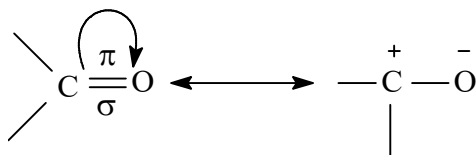
# ALDEHYDES AND KETONES

In aldehydes the functional group is  $\text{-CHO}$  while in ketones the functional group is  $\text{>C=O}$ . Therefore both aldehydes and ketones are collectively called carbonyl compounds due to the presence of common  $\text{>C=O}$  group in their functional groups. They can be represented by the general formula  $\text{C}_n\text{H}_{2n}\text{O}$ . They are functional isomers. They are widely spread in plants and animals kingdom. They are responsible for a fragrance and flavour of the naturally occurring compounds. Eg : Vanilline from vanilla beans. Cinnamaldehyde from (Cinnamon)



### Structure and Nomenclature

The carbonyl carbon is  $\text{sp}^2$  hybridised having trigonal planar structure and approximately  $120^\circ$  bond angles.



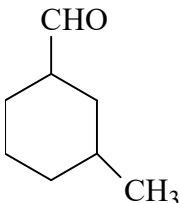
The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen and as a result of this, carbonyl carbon is an electrophile (Lewis acid) and oxygen is nucleophile (Lewis base). Hence they have high dipole moments.

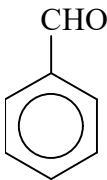
$\text{H-CHO}$  Methanal or Formaldehyde

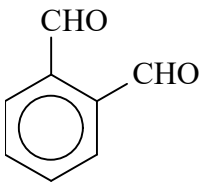
$\text{CH}_3 - \text{CHO}$  Ethanal or Acetaldehyde

$\text{CH}_3 - \text{CH}_2 - \text{CHO}$  propanal

$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CHO} \\ | \\ \text{CH}_3 \end{array}$  2-methylpropanal

 3-Methyl cyclohexane carbaldehyde

 Benzaldehyde

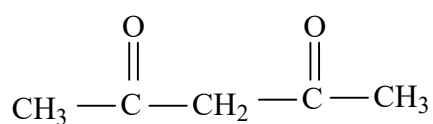
 Phthalaldehyde or Benzene 1, 2-dicarbaldehyde

$\begin{array}{c} \text{CHO} \\ | \\ \text{CHO} \end{array}$  Glyoxal or Ethane 1, 2-dial

$\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ | \quad | \quad | \\ \text{CHO} \quad \text{CHO} \quad \text{CHO} \end{array}$  Propane-1, 2, 3-tricarbaldehyde

$\begin{array}{c} \text{O} \\ || \\ \text{CH}_3 - \text{C} - \text{CH}_3 \end{array}$  Acetone or propanone

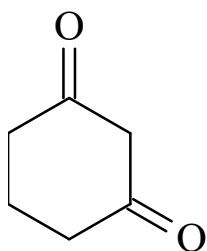
$\begin{array}{c} \text{O} \\ || \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3 \end{array}$  Butan-2-one



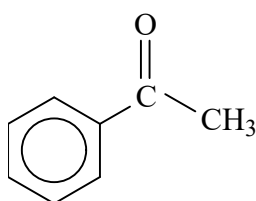
Pentane-2,4-dione



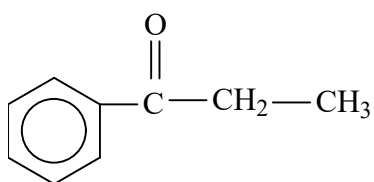
Cyclopropanone



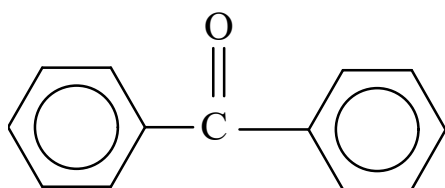
Cyclohexane-1,3-dione



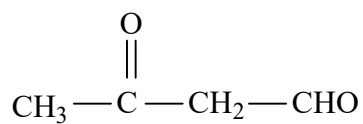
1-Phenyl ethanone or acetophenone



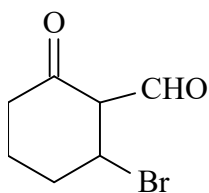
1-Phenyl propanone



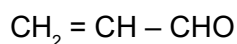
Benzophenone



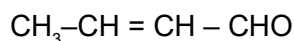
3-oxo butanal



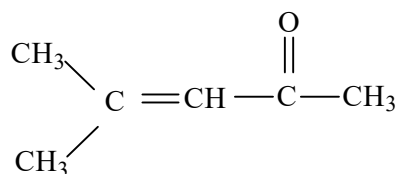
2-Bromo-6-oxo-cyclohexane carbaldehyde



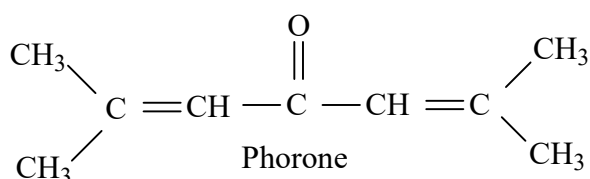
Acrolein or Acraldehyde prop-2-enal



Crotonaldehyde or but-2-enal



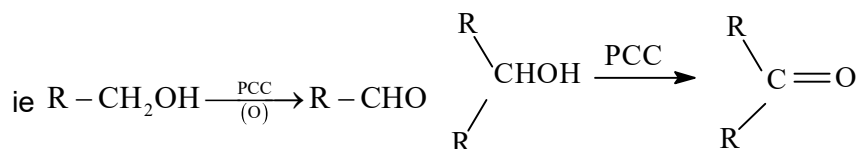
4-Methylpent-3-en-2-one



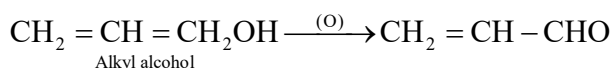
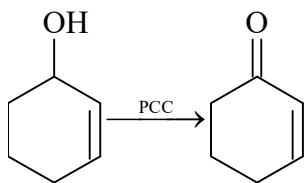
2, 6-Dimethyl-hepta-2,5-dien-4-one

### PREPARATION OF ALDEHYDES AND KETONES

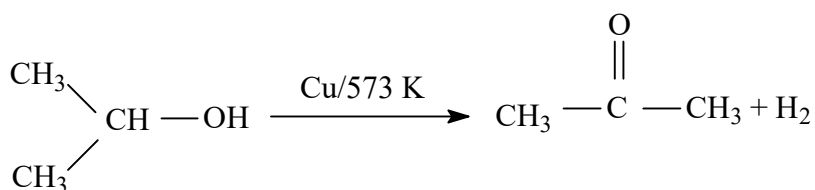
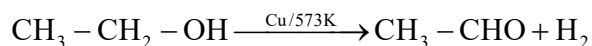
- Oxidation of alcohols :** A number of mild oxidising agents like, PCC (pyridinium chloro chromate) a mixture of pyridine, HCl and  $\text{CrO}_3$  in  $\text{CH}_2\text{Cl}_2$ . PDC (pyridiniumdichromate), Collin's reagent etc are used to oxidise  $1^\circ$  alcohols to aldehydes and  $2^\circ$  alcohols to ketones.

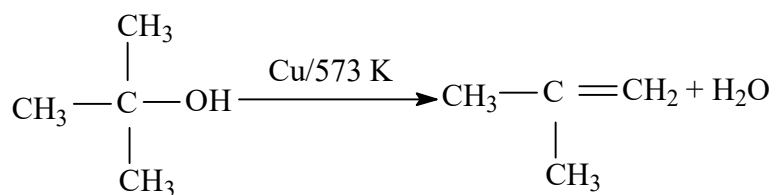


These reagents do not attack the double bonds during their oxidation.

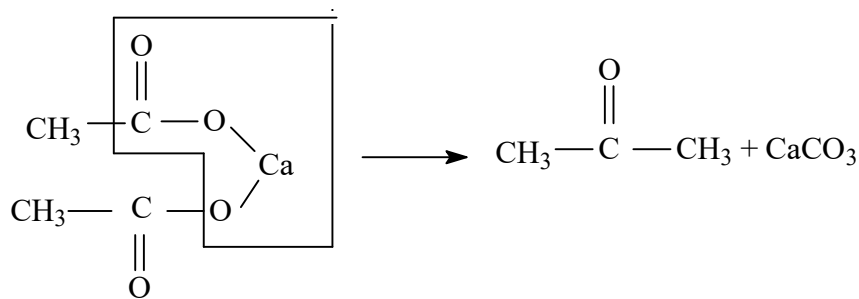
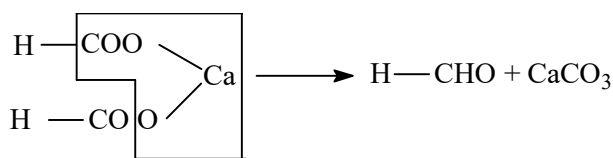


- By catalytic dehydrogenation of alcohols:**  $1^\circ$  alcohol vapours when passed over heated Cu at 573 K form an aldehyde, while  $2^\circ$  alcohol form a ketone. But  $3^\circ$  form an alkene due to elimination.

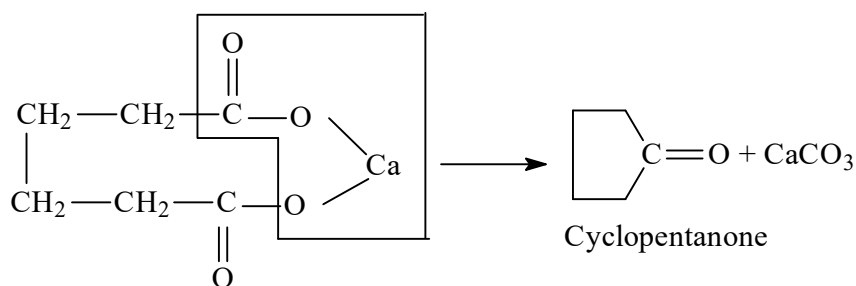




3. **By dry distillation of calcium salts of fatty acids:** Calcium formate on dry distillation form methanal while any other acid salts gives symmetrical ketones.



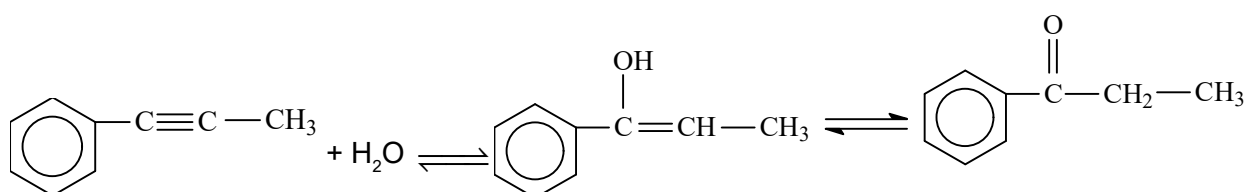
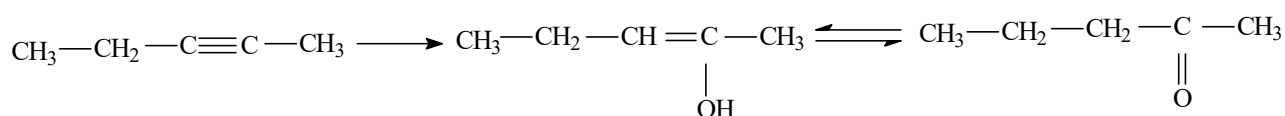
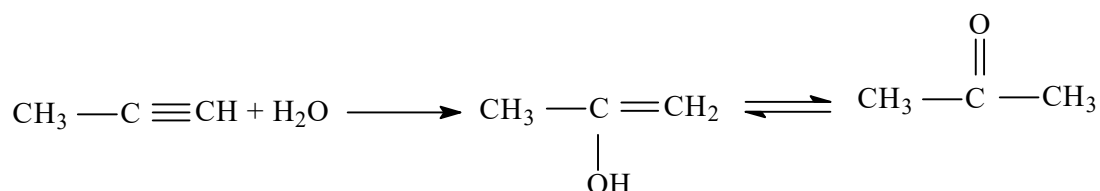
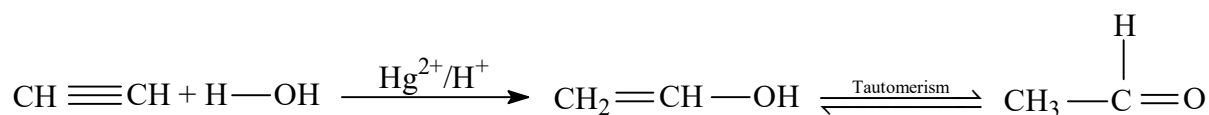
But if calcium salt of dicarboxylic acids are used, 5 or 6 membered cyclic ketones are formed having one carbon atom less than the acid.



#### 4. From hydrocarbons :

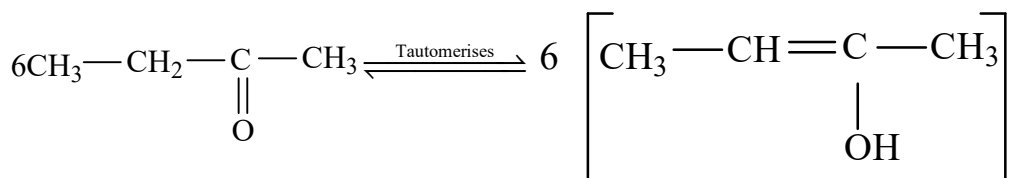
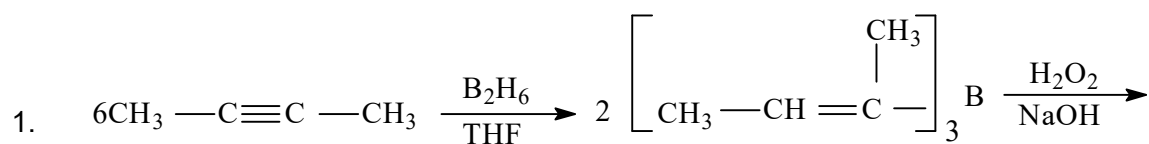
##### (a) Hydration of alkynes

In presence of 1%  $\text{HgSO}_4$  and 20% dil.  $\text{H}_2\text{SO}_4$  alkynes add a molecule of water to form aldehydes or ketones. By this method only ethyne form ethanal, but all other alkynes form ketones. Formaldehyde can not be prepared by this method. In this addition, first an intermediate compound is formed which tautomerised to form aldehydes or ketones.

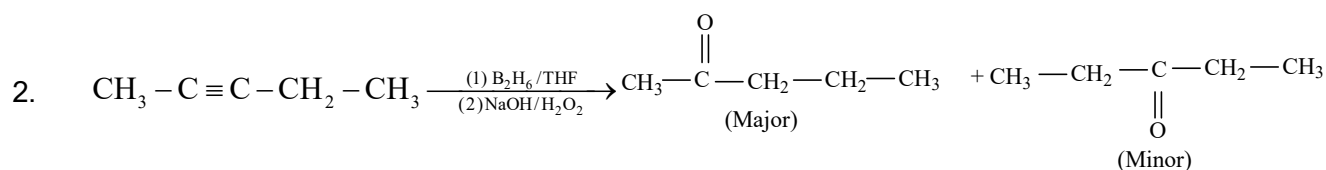


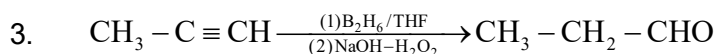
### (b) Hydroboration-oxidation of alkynes : [HBO]

Non terminal alkynes on HBO form ketones while terminal alkynes form aldehydes. But unsymmetrical non-terminal alkynes form ketones in which keto group stay with smaller alkyl group.

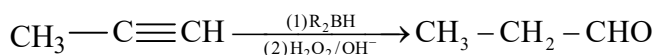


Enol



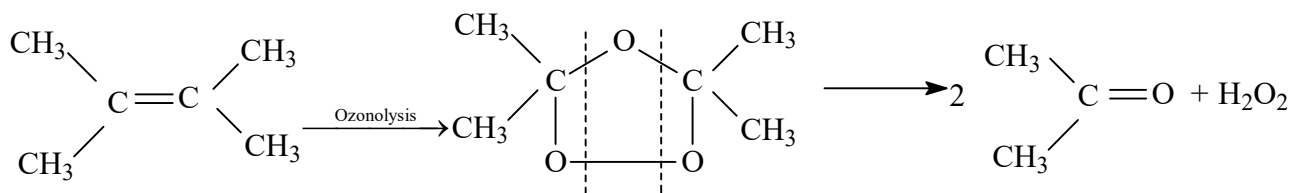
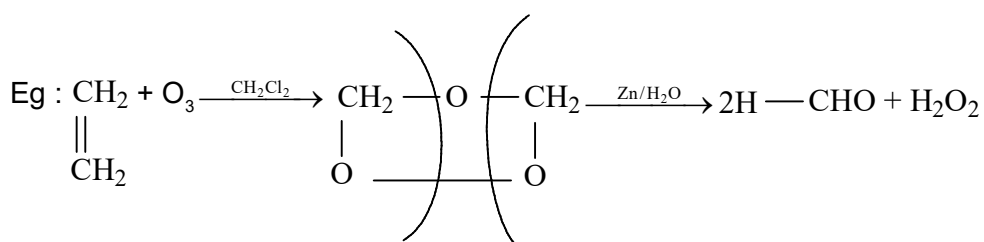


Aldehydes can also be prepared from terminal alkynes by using sterically hindered boranes like bis (1, 2 dimethyl propyl) borane known as disimyl borane in place of  $\text{B}_2\text{H}_6$ .



### (c) By ozonolysis of alkenes

Alkenes on reductive ozonolysis form aldehydes and ketones.

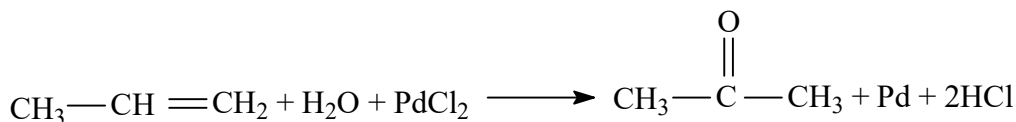
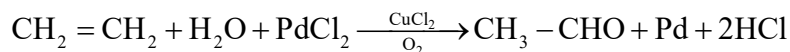


### Note:

By this method we can locate the position of double bonds, estimate the number of double bond, and elucidate the structure of hydrocarbon. If one molecule contain two carbonyl groups, then hydrocarbon will be alkadiene. If all compounds contain two carbonyl group then hydrocarbon will be cycloalkatriene. It is used for the preparation of aliphatic carbonyl compounds.

### (d) Oxidation of alkenes - Wacker process

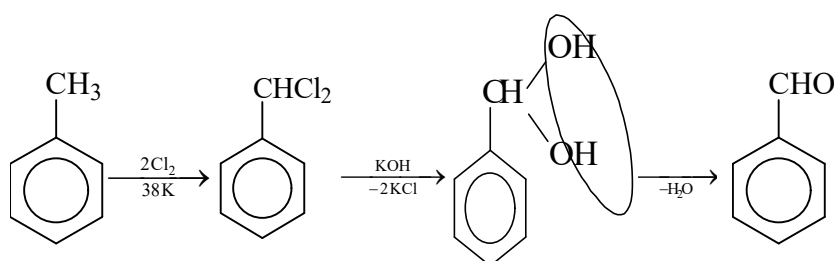
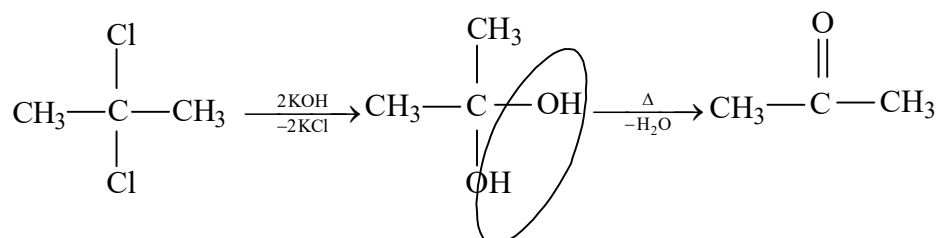
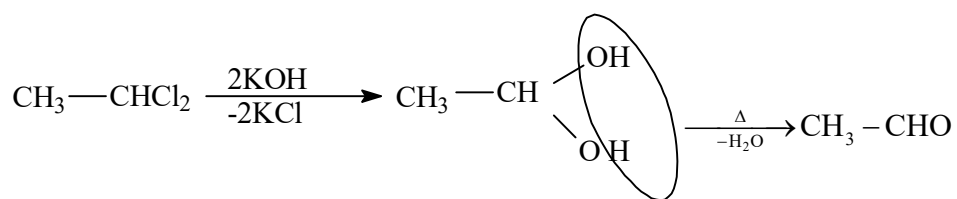
Alkenes are oxidised to aldehydes and ketones in presence of air using  $\text{PdCl}_2$  containing  $\text{CuCl}_2$ .



Only ethene form ethanal while higher alkenes will give ketones. In this reaction  $\text{PdCl}_2$  reduced to  $\text{Pd}$ . The function of  $\text{CuCl}_2$  is to oxidise  $\text{Pd}$  to  $\text{PdCl}_2$  and  $\text{CuCl}_2$  is reduced to  $\text{Cu}_2\text{Cl}_2$  which itself, reoxidised to  $\text{CuCl}_2$ .  $\text{CuCl}_2$  is called supporting catalyst in this reaction.

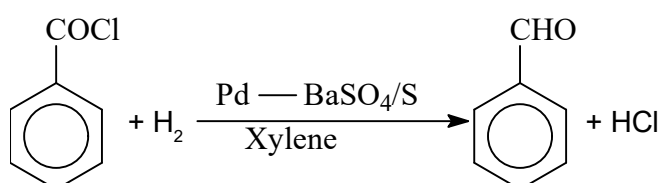
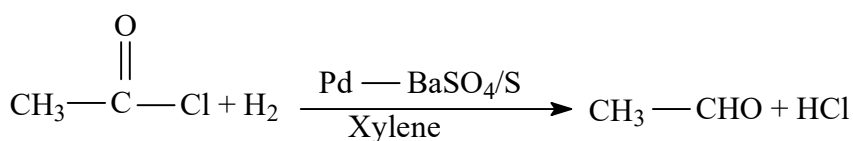
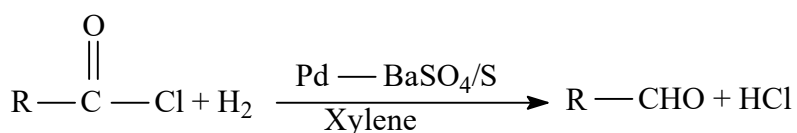
### 6. From dihalides

Terminal geminal dihalides on alkaline hydrolysis form aldehydes while non-terminal geminal dihalide form ketones.



## 7. Rosenmund reduction

Acid chlorides are easily reduced to the corresponding aldehydes by  $\text{H}_2$  in presence of Pd-supported over  $\text{BaSO}_4$  in boiling xylene.

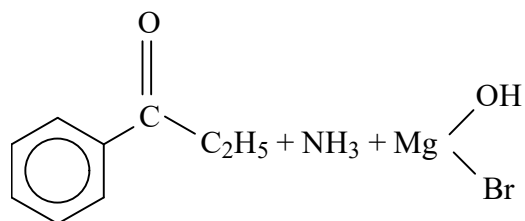
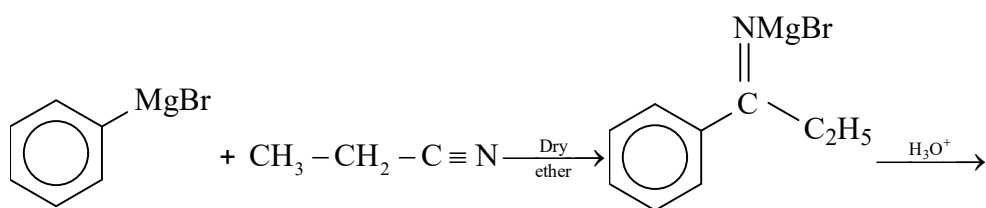
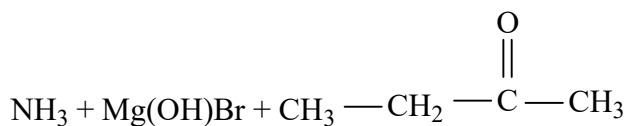
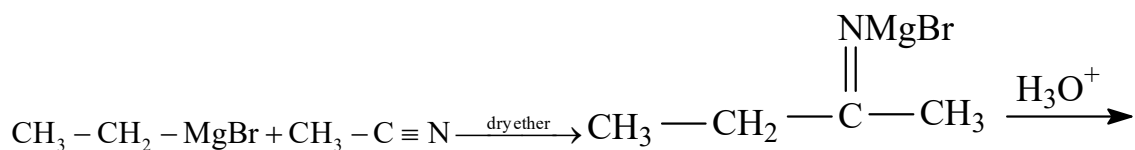
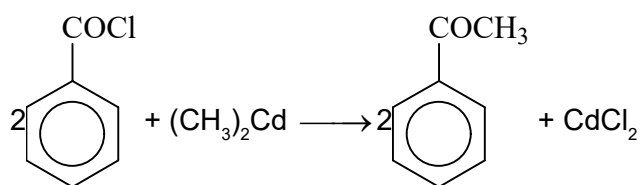
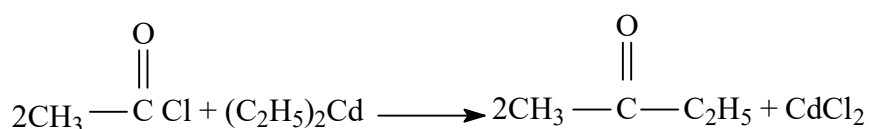
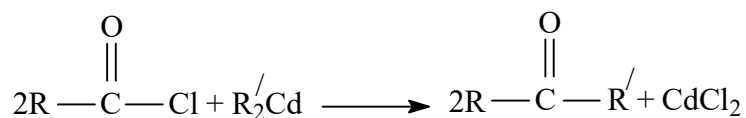


- Formaldehyde cannot be prepared by the method since  $\text{HCOCl}$  is unstable gas at room temperature.

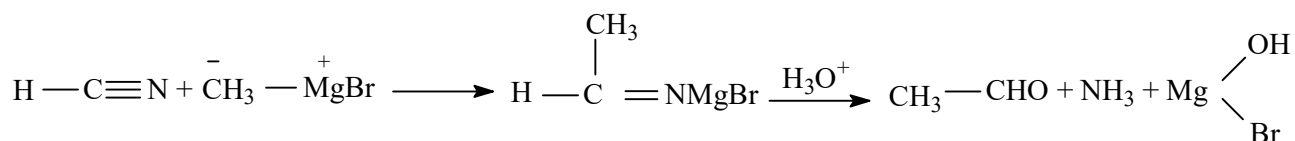


2.  $\text{BaSO}_4/\text{S}$ /quinoline acts as a catalytic poison.
3. If  $\text{Pd}/\text{Li}[\text{AlH}_4]$  or  $\text{Na}[\text{BH}_4]$  used for reduction final product will be an alcohol.

But ketones can be prepared by the action of dialkyl cadmium on an acid chloride in ether medium.

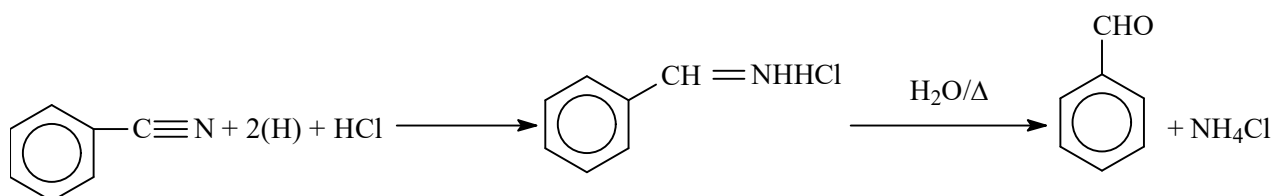
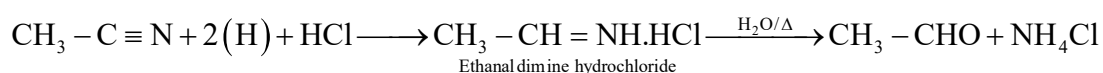
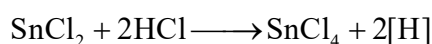


If instead of alkyl or aryl nitrites, HCN is used in the above reaction, aldehydes will be formed.



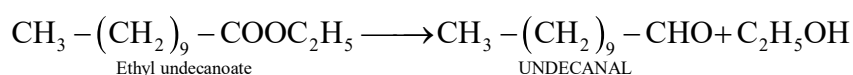
## 8. From nitriles and esters

When an ethereal solution of a nitrile is reduced with  $\text{SnCl}_2$  and  $\text{HCl}$  at room temperature, aldimine hydrochloride is precipitated which on hydrolysis with  $\text{H}_2\text{O}$  gives aldehydes.



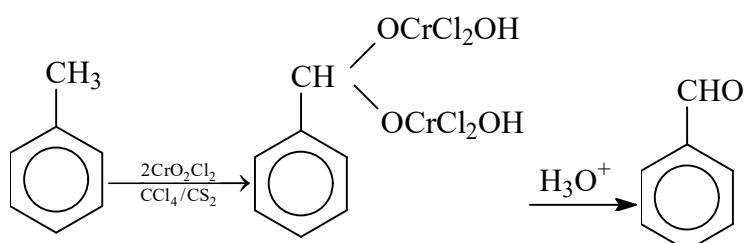
This is called Stephens reduction. But nitriles can be selectively reduced by diisobutyl aluminium hydride [DIBAL-H] to aldehydes.

$\text{R}-\text{C}\equiv\text{N} \xrightarrow[(2)\text{H}_2\text{O}/\Delta]{(1)\text{DIBAL-H}} \text{R}-\text{CHO} + \text{NH}_3$ . It is also used to reduce unsaturated nitriles to unsaturated aldehydes and esters to aldehydes and alcohol.



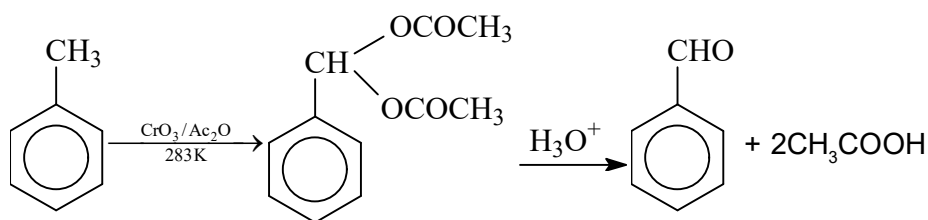
## 9. From aromatic hydrocarbon:

1. Toluene can be oxidised to Benzaldehyde in presence of  $\text{CrO}_2\text{Cl}_2$  in  $\text{CS}_2$  or  $\text{CCl}_4$ . The brown chromium complex is separated and decomposed with dil. acid form benzaldehyde.



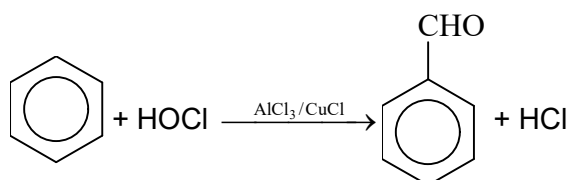
This called **Etard's** reaction. Similarly m-xylene on oxidation form m-Tolualdehyde.

Benzaldehyde is also prepared by the oxidation of toluene in presence of  $\text{CrO}_3$  in  $\text{Ac}_2\text{O}/(\text{CH}_3\text{CO})_2\text{O}$



Benzaldehyde to benzoic acid is avoided by trapping the aldehyde as gem-diacetate which cannot be further oxidised.

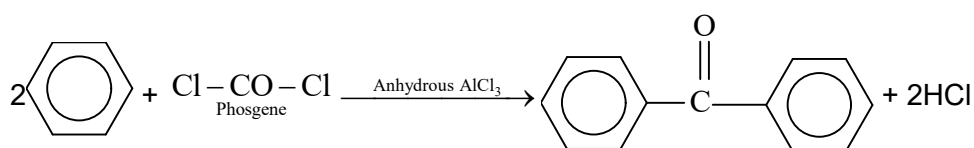
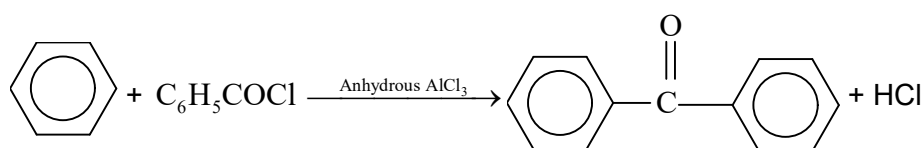
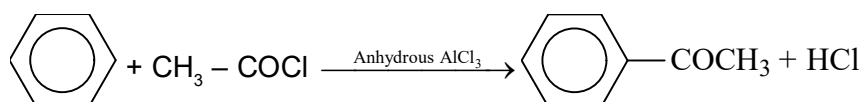
**Gattermann-Koch reaction:** When a mixture of CO and HCl gas is passed through a solution of benzene or toluene in nitrobenzene at 323 K in presence of  $\text{AlCl}_3$  and  $\text{CuCl}$ , benzaldehyde is formed.



This is also called Gattermann-Koch formylation or aldehyde synthesis reaction.

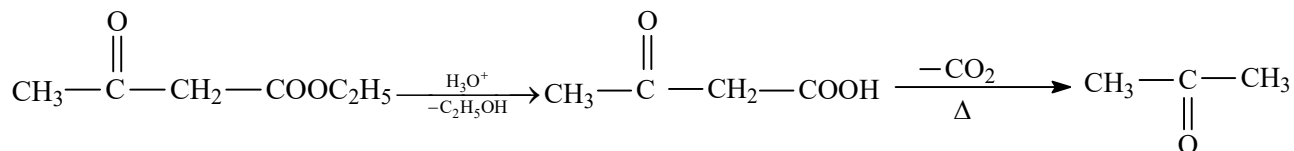
## 11. Friedel - Crafts acylation reaction

It is one of the most convenient method used for the preparation of aromatic ketone in which the keto group is attached to the aromatic ring. It involves the treatment of aromatic hydrocarbon with acid halide in presence of  $\text{AlCl}_3$ .



This is an electrophilic substitution reaction.

**13. By acid hydrolysis of  $\beta$ -keto ester:-**



**14. Physical properties of aldehydes and ketones**

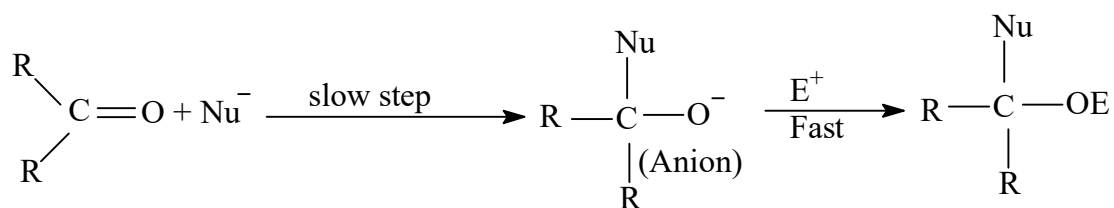
The first member of the aldehyde series, formaldehyde, is a gas at room temperature, while the next ten members are colourless volatile liquids. Ketones upto eleven carbon atoms are colourless volatile liquids. But higher members are solids. But aqueous solution of formaldehyde is called **formalin**; **Which is 40% H-CHO, 8% CH<sub>3</sub>OH and 52% H<sub>2</sub>O**, Used as a preservative for anatomical specimens. Lower aldehydes have unpleasant odour but higher members have fruity smell. Aromatic aldehydes and ketones possess pleasant smell. They are almost solids and liquids.

**Solubility** - Lower aliphatic aldehydes and ketones are soluble in H<sub>2</sub>O due to formation of H-bonding with water but it decrease with increase in molar mass. Aromatic aldehydes and ketones are insoluble in H<sub>2</sub>O but soluble in organic solvents.

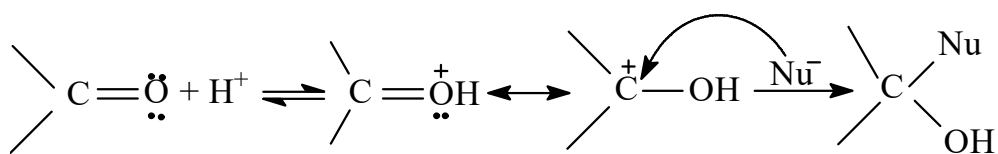
**Boiling points** : The boiling points of aldehydes and ketones are higher than those of ethers and hydrocarbons of comparable molar masses due to dipole-dipole interactions. (Vander Waals force of attraction) but lower than those of corresponding alcohols and acids due to the absence of H-bonding.

Among isomeric aldehydes and ketones, ketones have slightly higher boiling points due to slightly higher dipole moments because of the +I effect of the two alkyl groups.

**Reactivity of aldehydes and ketones:** They mainly undergoes nucleophilic addition reactions because the intermediate anion formed is more stable than cation as the less stable sp<sup>2</sup> hybridised carbonyl carbon is transformed into more stable sp<sup>3</sup> hybridised carbon, which then picks up a proton either from a solvent or from the reagent to complete the addition.



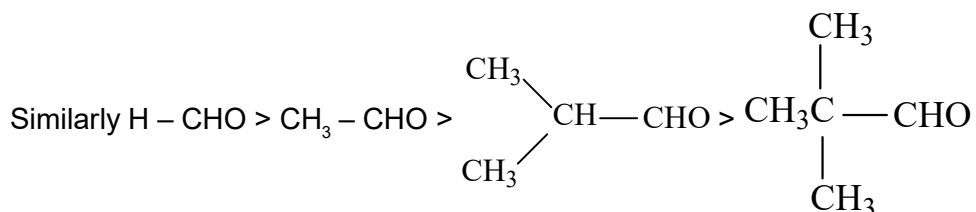
If the attacking nucleophile is weak, the nucleophilic addition reactions are usually carried out in weakly acidic medium. This is because the carbonyl group gets protonated, by resonance which increases the positive charge on the carbonyl carbon and thereby makes it more electrophilic. As a result weak nucleophiles adds to the carbonyl group easily.



In general aldehydes are more reactive than ketones due to the following reasons. The relative reactivities of aliphatic aldehydes and ketones depends upon the following factors.

1. **+I effect of alkyl groups** : Greater the number of alkyl groups attached to the carbonyl group, higher is the electron density on the carbonyl carbon and hence lower is its reactivity towards nucleophilic

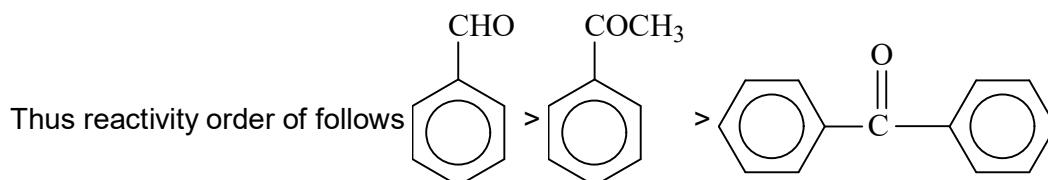
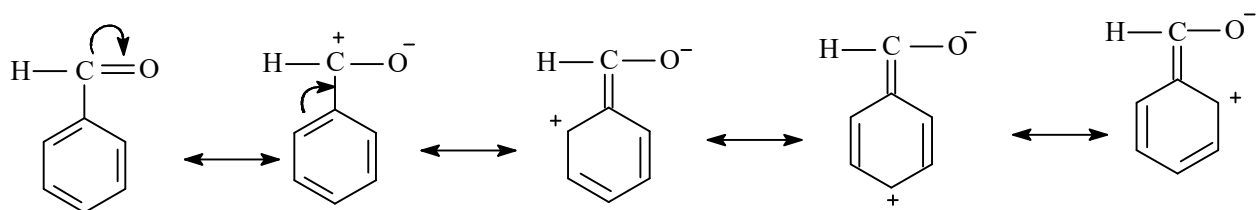
addition reactions. Thus reactivity order decreases as  $\text{H}-\text{CHO} > \text{CH}_3-\text{CHO} > \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ .



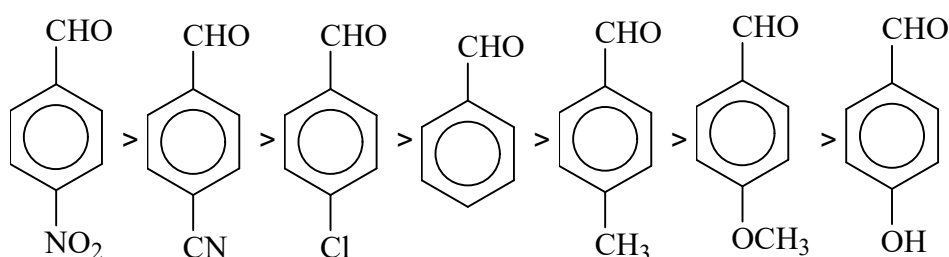
2. **Steric effects** : As the number and size of the alkyl groups attached to the carbonyl carbon increases, the attack of the nucleophile on the carbonyl group becomes more and more difficult due to steric hindrance. Hence the reactivity decreases as

$\text{H}-\text{CHO} > \text{CH}_3-\text{CHO} > \text{CH}_3\text{COCH}_3 > \text{CH}_3-\text{CO}-\text{CH}_2-\text{CH}_3 > \text{pentan-3-one} > \text{Di-isopropyl ketone}$ .

In general aromatic aldehydes and ketones are less reactive than aliphatic analogues. This is due to +R effect of the benzene ring which reduces nucleophilicity of the carbonyl carbon as below.

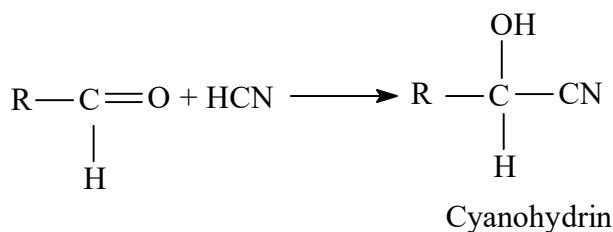
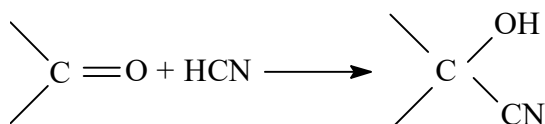
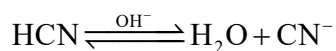


Again, the presence of electron donating groups in the benzene ring decreases the electrophilicity of the carbonyl carbon and hence decreases the reactivity of aldehydes and ketones while the presence of electron withdrawing groups increases the reactivity of aldehydes and ketones towards nucleophilic addition. Hence the order of reactivity is

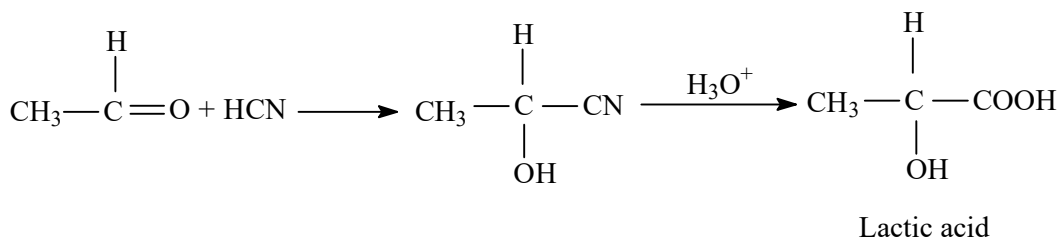


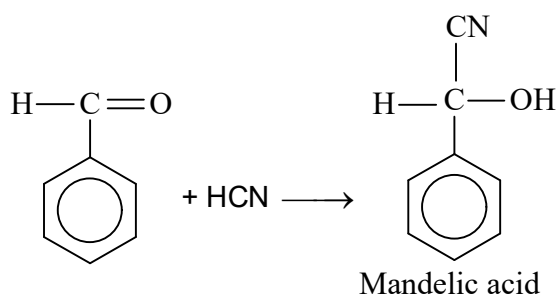
Some important nucleophilic addition reactions are:

- Addition of HCN :** - Aldehydes and ketones react with HCN to form cyanohydrins very slowly because HCN is a weak acid. Hence it is catalysed at pH = 9 - 10 in presence of a base.



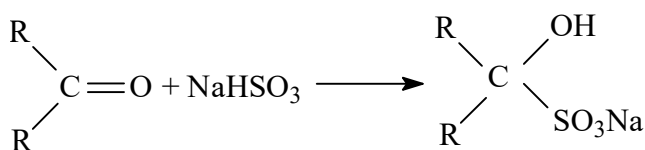
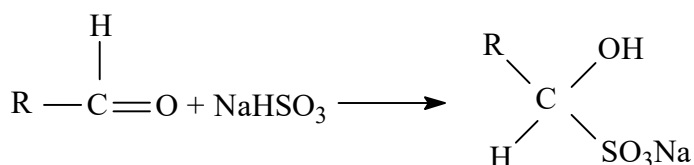
Addition of  $\text{CN}^-$  is a slow step and hence it is a nucleophilic addition. These cyanohydrins are good synthetic reagents used for the synthesis of substituted acids.



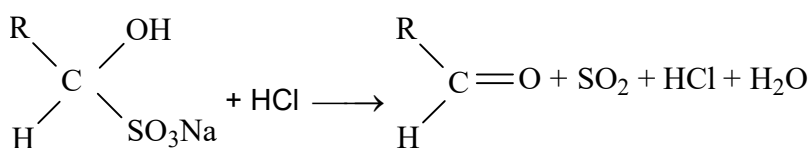


This type of synthesis of an optically active compound from an optically inactive compound without recourse to resolution is called Asymmetric synthesis.

2. **Addition of  $\text{NaHSO}_3$**  : Most of the aldehydes and aliphatic methyl ketones, aromatic aldehydes like benzaldehyde react with a saturated solution of  $\text{NaHSO}_3$  to form white crystalline products. Higher ketones and other aromatic compounds do not react due to steric effect.

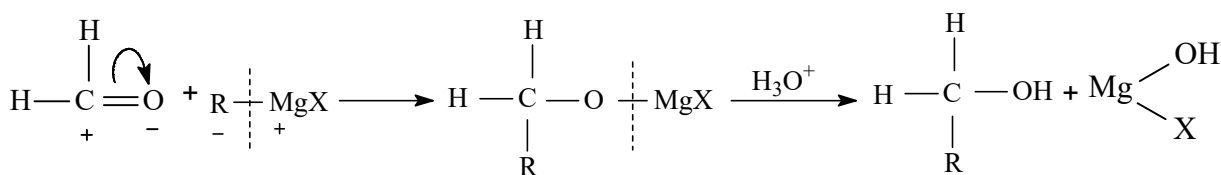


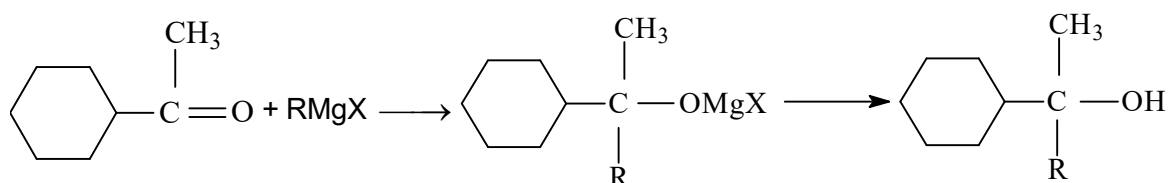
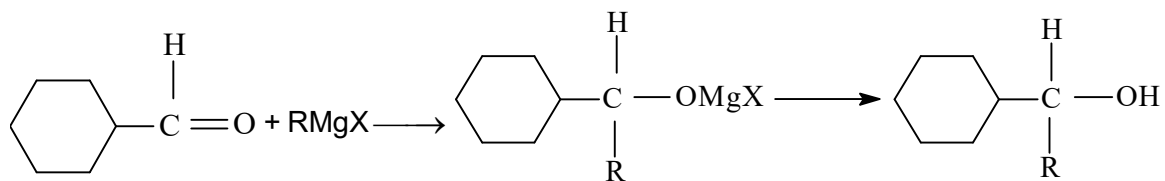
These bisulphite addition products are further hydrolysed to give back pure aldehydes and ketones.



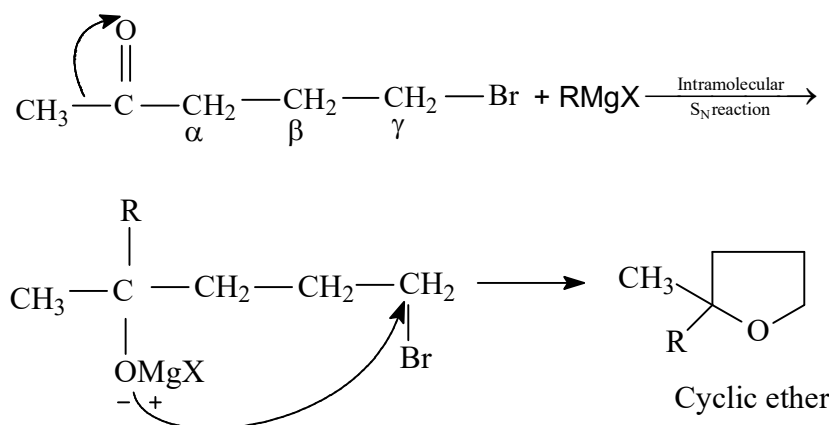
∴ This property is used in the separation and purification of aldehydes and ketones.

3. **Addition of Grignard reagents**: Formaldehyde react with  $\text{RMgX}$  form  $1^\circ$  alcohols. All other aldehydes form  $2^\circ$  alcohols but ketones under similar condition form  $3^\circ$  alcohols.

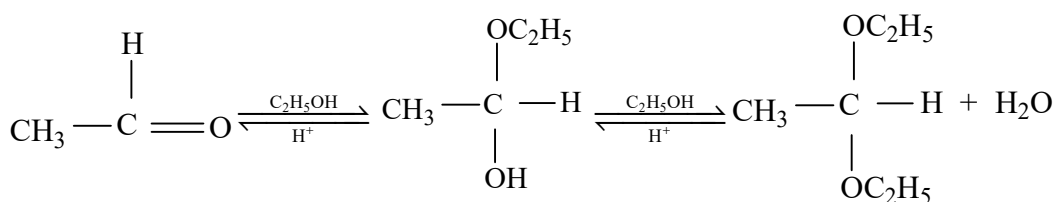
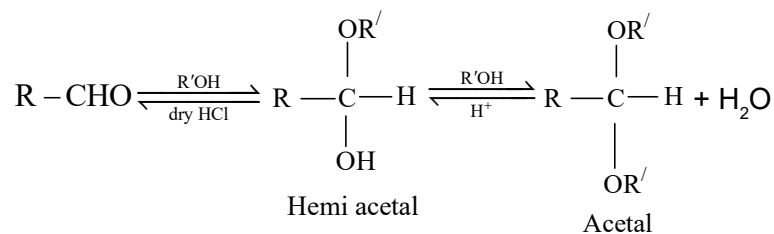




But  $\gamma$  or  $\delta$  - Halogenated carbonyl compound on treatment with RMgX form a five or six membered cyclic ether.

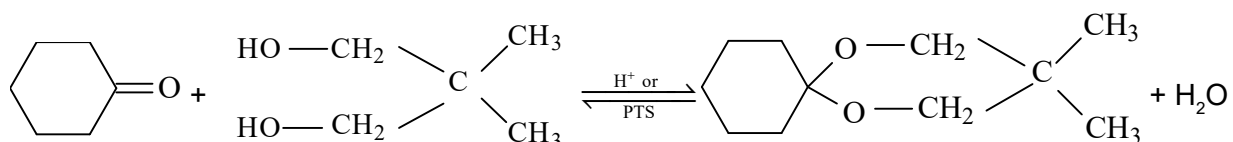
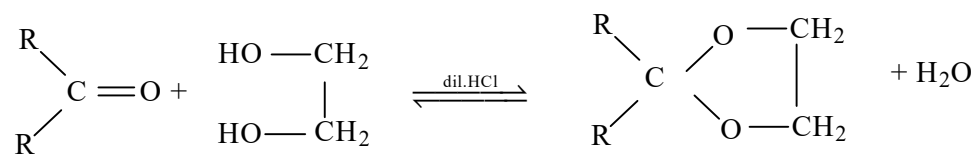


5. Aldehydes react with one equivalent of monohydric alcohols in the presence of dry HCl gas to form alkoxy alcohol intermediate called hemiacetals which further react with another molecule of alcohol to form gem-dialkoxy alkane called acetals:





Ketones do not react with monohydric alcohols but with dihydric alcohols under similar condition form cyclic ketals.

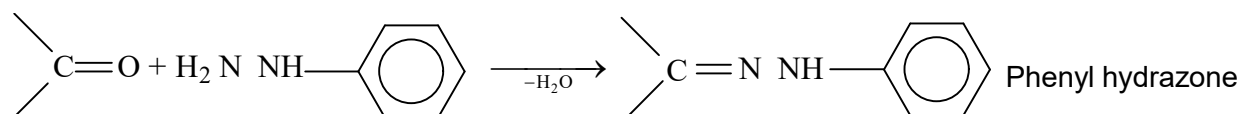
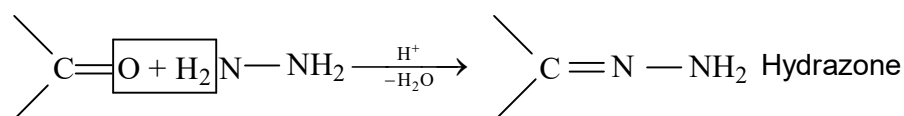
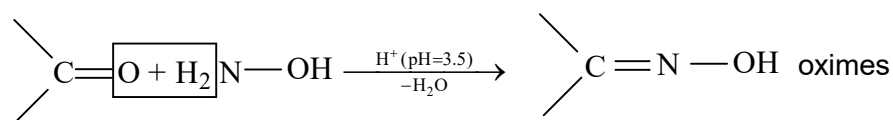
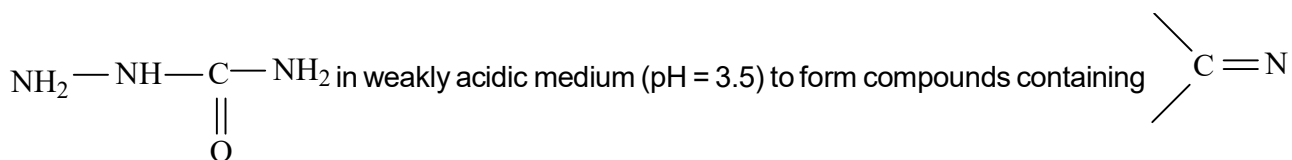


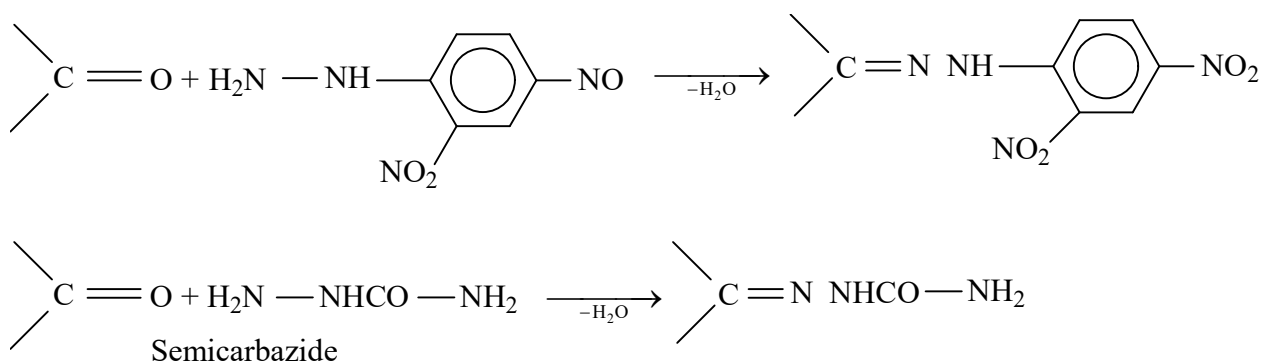
The function of dry HCl is to protonates the oxygen of the carbonyl compounds and hence increases the electrophilicity of the carbonyl carbon facilitating the nucleophilic attack. These acetals and ketals are hydrolysed to give back original aldehydes and ketones. Hence they are used to protect these groups in organic synthesis.

## 6. Reaction with Ammonia and its derivatives:

Aldehydes and ketones react with a number of ammonia derivatives like  $\text{NH}_2\text{OH}$ ,  $\text{NH}_2\text{-NH}_2$ ,

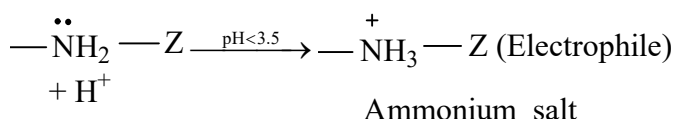
$\text{C}_6\text{H}_5\text{-NHNH}_2$ ,  $\text{O}_2\text{N}-\text{C}_6\text{H}_3(\text{NO}_2)_2\text{-NHNH}_2$  (2, 4-DNPH) (Called Brady's reagent) and





All these derivatives are crystalline solids with sharp M.P. and hence used for the identification of aldehydes and ketones. These derivatives when hydrolysed by dil. acids to regenerate original aldehydes and ketones. Hence these are used for purification of carbonyl compounds.

If pH is less than 3.5, these ammonia derivatives will be converted into ammonium salt, which is an electrophile and hence nucleophilic addition will not occur.



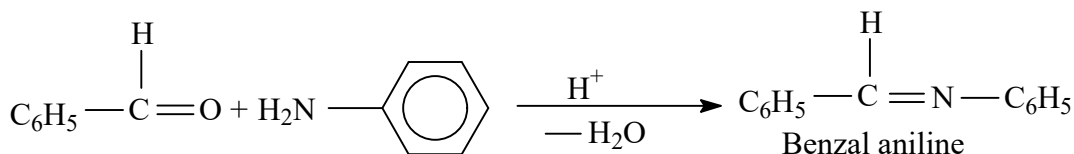
If pH > 3.5, the carbonyl group will not get protonation. i.e. the positive charge on the carbonyl carbon will not increase and hence the reaction will not occur. Hence, an optimum pH of 3.5 should be maintained.

In case of semicarbazide the  $\text{-NH}_2$  group attached to the  $\text{>C=O}$  directly is involved in resonance

and hence not available for nucleophilic attack on carbonyl group.

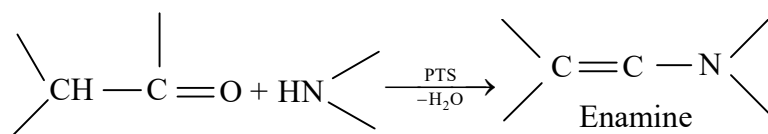
### Reaction with 1° amines :

Carbonyl compounds react with 1° amines in presence of acid form Schiff's base or azomethines. The most stable Schiff's base is obtained from aromatic aldehyde with Aromatic 1° amine.



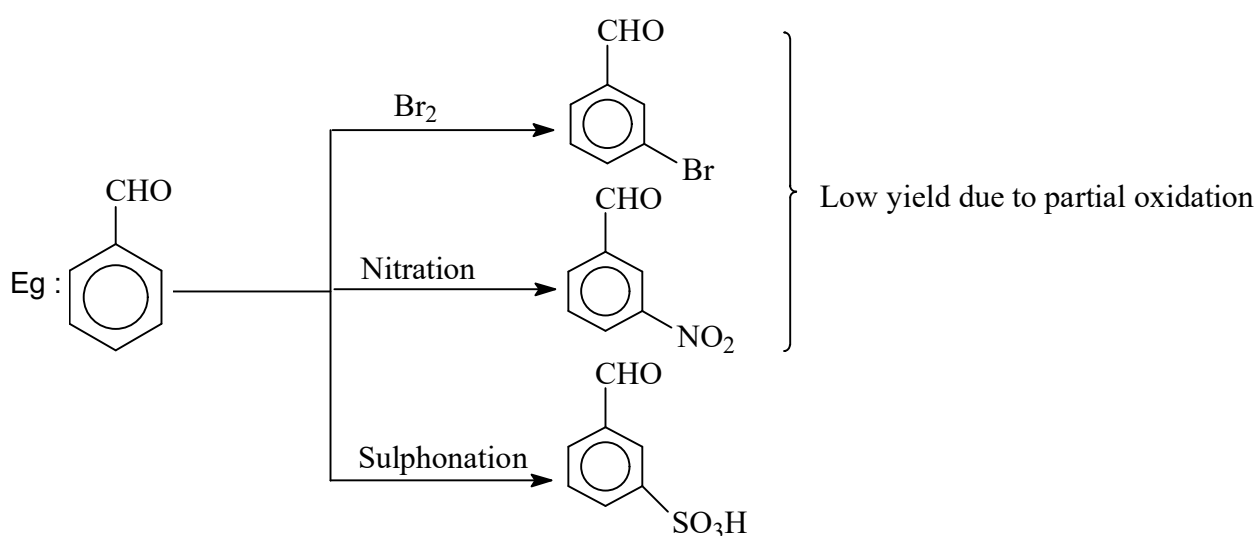
### Reaction with 2° amines :

Carbonyl compounds contain at least one  $\alpha$ -Hydrogen react with 2° amine in presence of (PTS)  $\rightarrow$  p-toluene sulphonic acid. to form  $\alpha, \beta$  **unsaturated amines called enamines**.



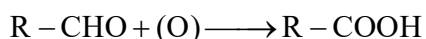
### Electrophilic substitution

Since  $-\text{CHO}$ ,  $\text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{CH}_3$  groups etc are deactivating or m-directing, during electrophilic substitution reaction, benzaldehyde gives m-substituted derivatives.

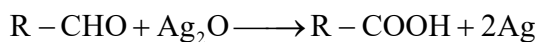


### Oxidation of aldehydes and ketones

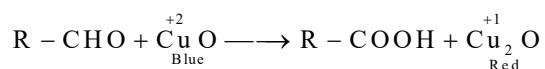
Aldehydes act as a reducing agents since they can be easily oxidised to corresponding acids.



Aldehydes reduce Tollen's reagent (Ammoniacal Silver Nitrate Solution) to metallic silver. This is also called silver mirror test.



**Fehling solution test :** A mixture of alkaline  $\text{CuSO}_4$  and sodium potassium tartarate (Rochelle salt) is called Fehling solution. Aliphatic aldehyde reduce Fehling solution while aromatic aldehydes do not due to +R effect of benzene ring, they are weak reducing agent.

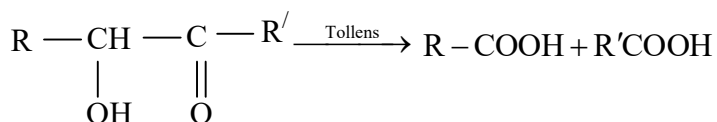


$\therefore$  This test is used to distinguish between aliphatic and aromatic aldehydes. Aldehydes can also be oxidised by  $\text{Br}_2/\text{H}_2\text{O}$  to acids.  $\text{R} - \text{CHO} \xrightarrow{\text{Br}_2/\text{H}_2\text{O}} \text{R} - \text{COOH}$

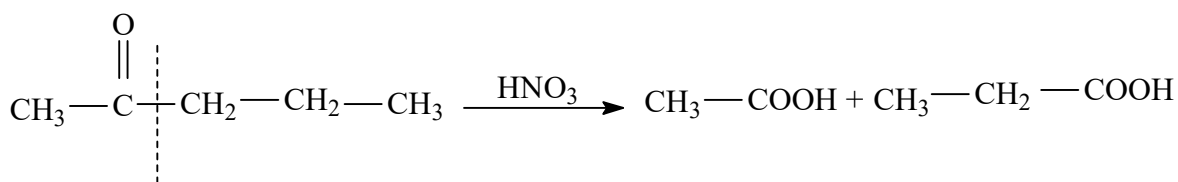
### Benedict solution test:

A mixture of alkaline  $\text{CuSO}_4$  and sodium citrate is called Benedict solution. Chemical reaction is

similar to those of Fehling test.  $\alpha$ -Hydroxy ketones  $\left( \begin{array}{c} \text{R} - \text{CH} - \text{C} \text{ R}' \\ | \quad || \\ \text{OH} \quad \text{O} \end{array} \right)$  do not contain an aldehyde group, like aldehydes they reduce Tollen's, Fehling and Benedict solutions.

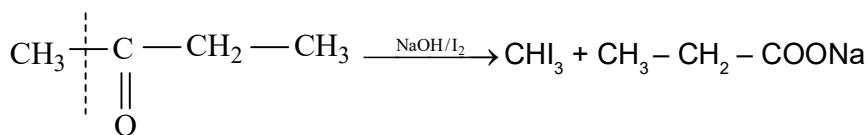
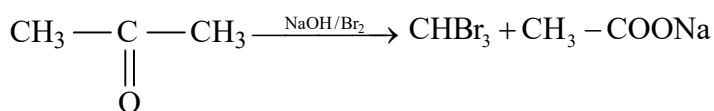
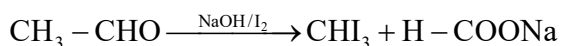


But ketones do not undergo oxidation because they are less reactive than aldehydes. Tollen's, Fehling and Benedict solutions do not react with ketones. Hence they are used to distinguish between them. Ketones on oxidation with con: $\text{HNO}_3$  form mixture acids. During this C-C bond fission occur in such a way that keto group will stay with smaller alkyl group. This is **popoff's rule**.

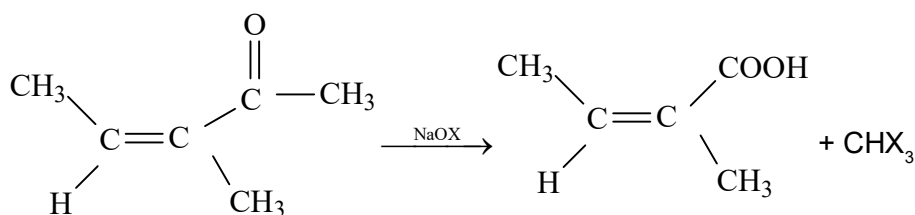


### Haloform reaction:

Acetaldehyde and all methyl ketones react with excess of  $\text{Cl}_2$ ,  $\text{Br}_2$  or  $\text{I}_2$  in presence of alkali produce haloform.

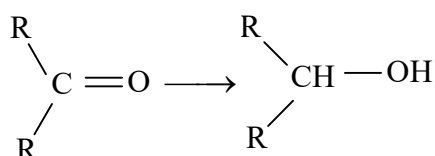
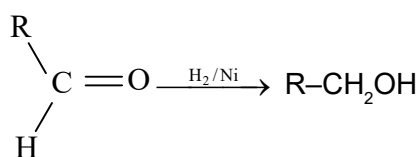


In this reaction ( $\text{OX}^- \rightarrow \text{hypohalite}$ ) is involved in the oxidation of carbonyl compounds. It is used to distinguish between methyl ketones from other ketones. It is also used to oxidise  $\alpha$ ,  $\beta$ -unsaturated methyl ketones to  $\alpha$ ,  $\beta$ -unsaturated acids without affecting the double bond.



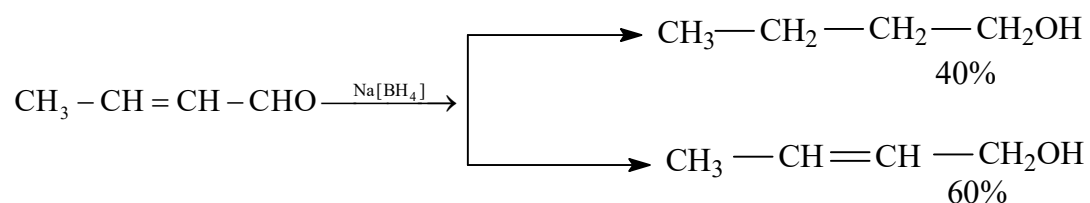
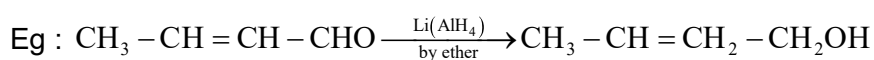
### Reduction of carbonyl compound

Aldehydes are reduced into 1° alcohols while ketones into 2° alcohols in presence of Ni, Pd, Pt, Li[AlH<sub>4</sub>], Na(BH<sub>4</sub>), Na-C<sub>2</sub>H<sub>5</sub>OH etc.

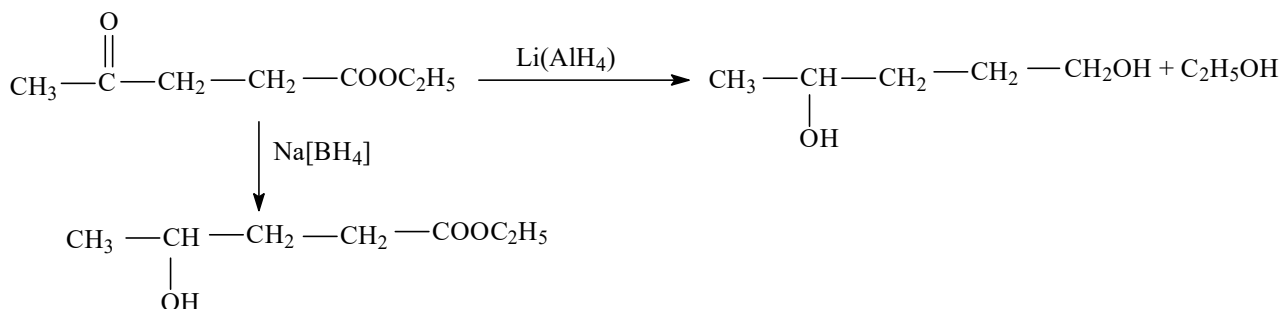
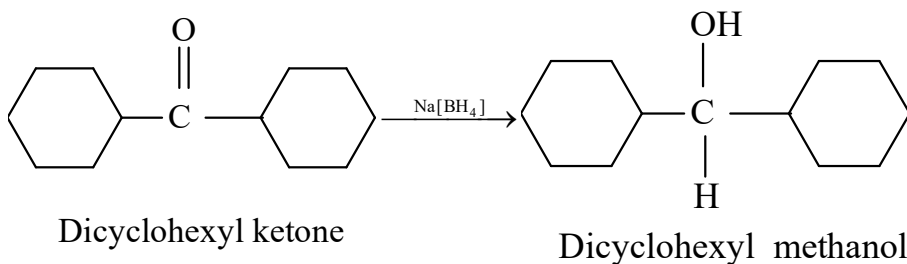
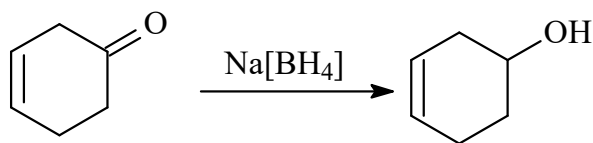
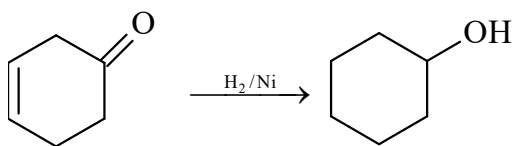
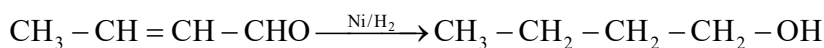


Reduction by Na-C<sub>2</sub>H<sub>5</sub>OH is called Bouveault-Blanc reduction. Neither Li[AlH<sub>4</sub>] or Na[BH<sub>4</sub>] reduces isolated double bonds. But in case of α,β-unsaturated aldehydes and ketones, Li[AlH<sub>4</sub>] reduces only

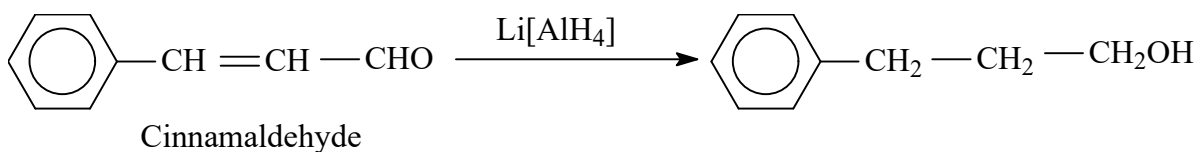
$\diagdown \text{C} = \text{O} \text{ group leaving } \diagdown \text{C} = \text{C} \diagup$  intact, while by Na[BH<sub>4</sub>] reduces both  $\diagdown \text{C} = \text{O}$  and  $\diagdown \text{C} = \text{C} \diagup$  forming a mixture of saturated and unsaturated alcohols in which one reduction group product predominates over the other.



While reduction, unsaturated alcohol by H<sub>2</sub>/Ni produce saturated alcohol.

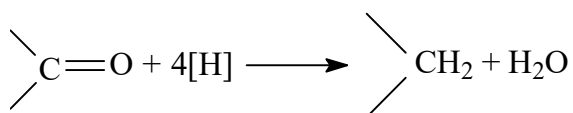


However if an  $\alpha - \beta$  unsaturated part is bonded to aromatic nucleus reduction by  $\text{Li}[\text{AlH}_4]$  produce saturated alcohol.

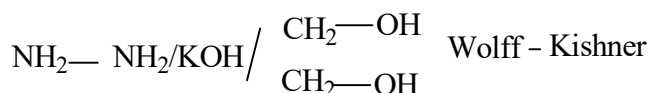
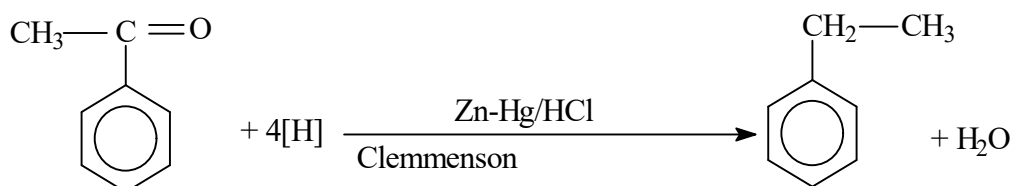
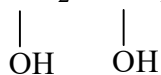


### CLEMMENSEN AND WOLFF KISHNER REDUCTION

The carbonyl group of aldehydes and ketones to methylene  $\left( \begin{array}{c} \diagup \\ \text{CH}_2 \\ \diagdown \end{array} \right)$  group to form hydrocarbon by the following methods.

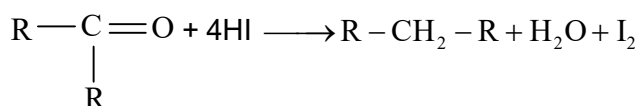
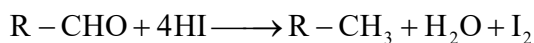


Reduction using Zn - Hg/HCl is called Clemmensen reduction while with  $\text{NH}_2 - \text{NH}_2$ , KOH and  $\text{CH}_2 - \text{CH}_2$  is called Wolff-Kishner reduction.

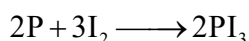


### Reduction with HI and Red P :

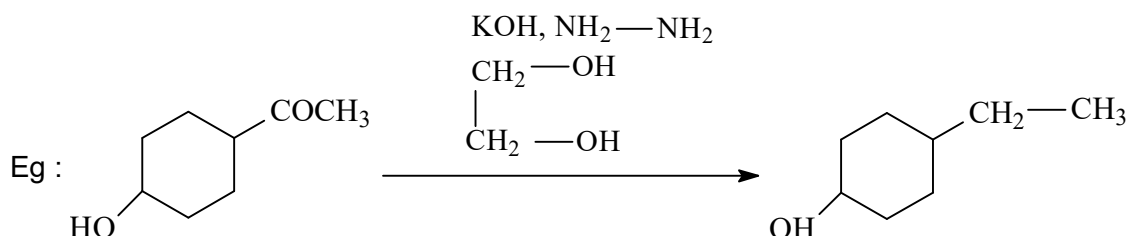
Carbonyl compounds are reduced into corresponding hydrocarbons by HI and Red P at 423 K.



The function of Red 'P' is to remove  $\text{I}_2$  as  $\text{PI}_3$ , otherwise iodination will take place.

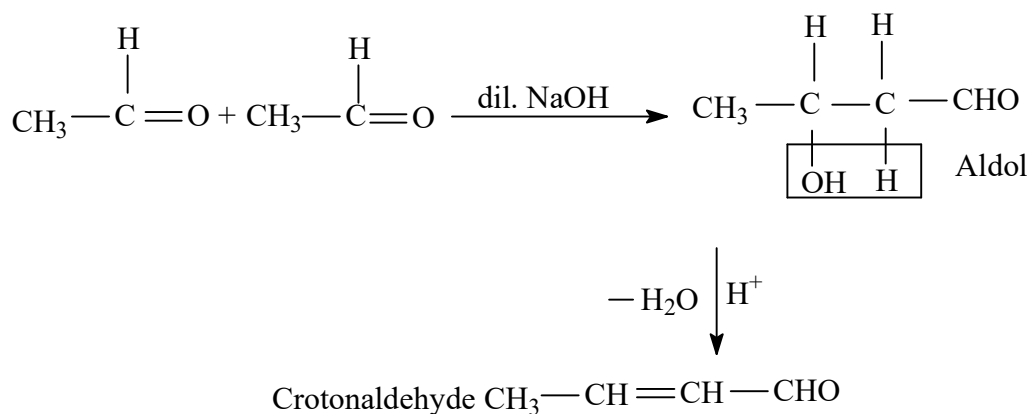


Clemmensen reduction and reduction with con : HI and Red P cannot be used for carbonyl compounds containing acid sensitive groups like  $-\text{OH}$ , Wolff-Kishner method is suitable.

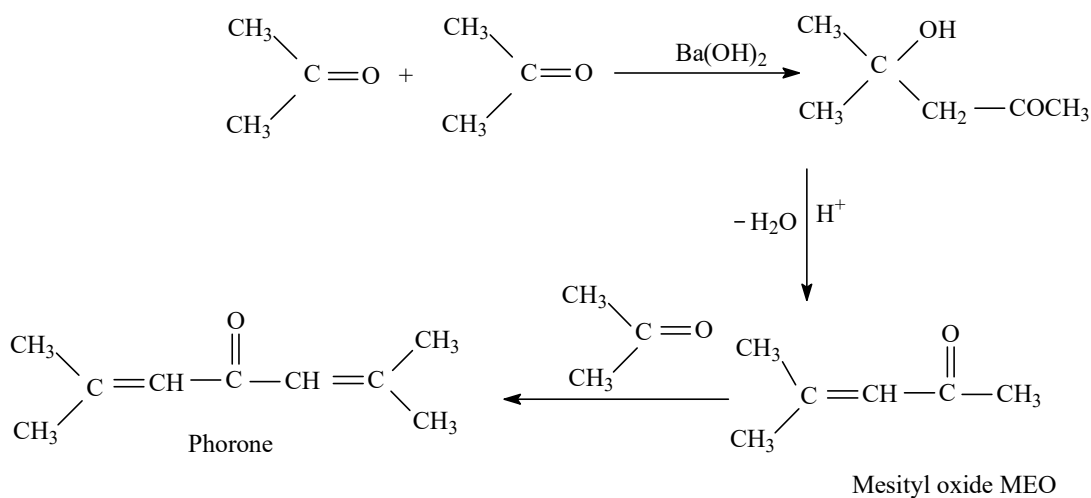


### Condensation reactions:

1. **Aldol condensation reaction :** Carbonyl compounds having one or more  $\alpha$ -Hydrogen when heated in presence of dil. NaOH, KOH,  $\text{Na}_2\text{CO}_3$ ,  $\text{Ba}(\text{OH})_2$  etc to form  $\beta$ -hydroxy aldehyde or ketones called aldol or ketol, which when heated in presence of dilute acid undergo dehydration to give  $\alpha-\beta$  unsaturated aldehydes or ketones. This is called aldol condensation.



Similarly,

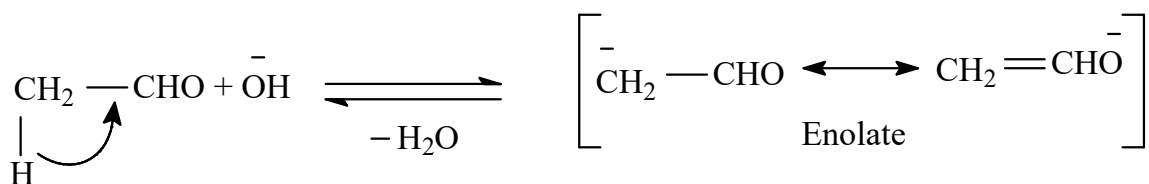


### Mechanism

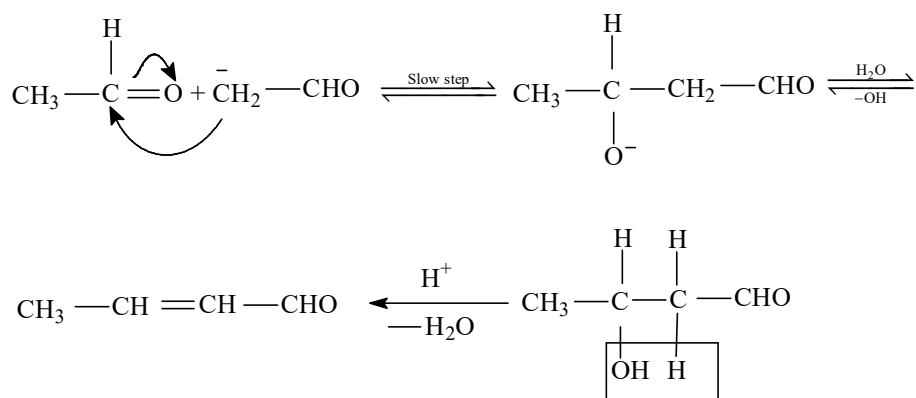
Base catalysed alcohol condensation occurs through carbanion or enolate anion formation while acid-catalysed aldol condensation through enol form of carbonyl compound. These  $\alpha-\text{H}$  atoms are weakly

acidic due to  $-\text{I}$  effect of  $\text{C}=\text{O}$  group. Reactivity increases due to electron withdrawing group while decreases by electron donating group. Thus nitro ethanol react more faster than ethanal.

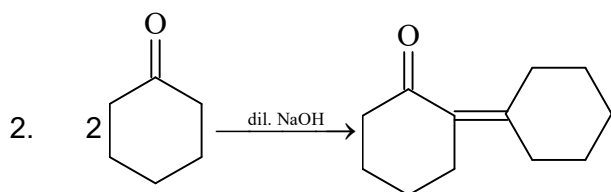
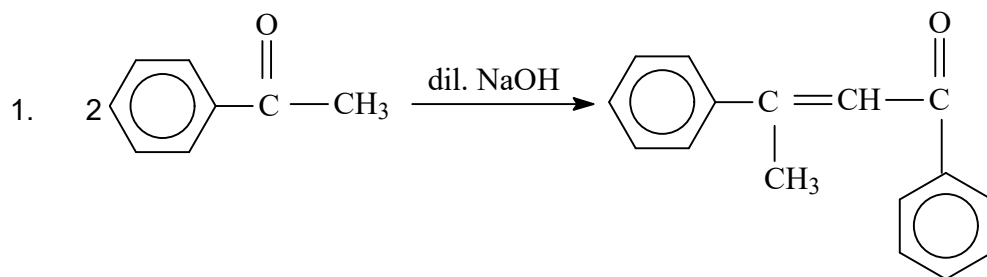




Which then induces its negative charge to the carbonyl carbon of second molecule to form anion and it exchanges a proton with  $\text{H}_2\text{O}$  form aldol.

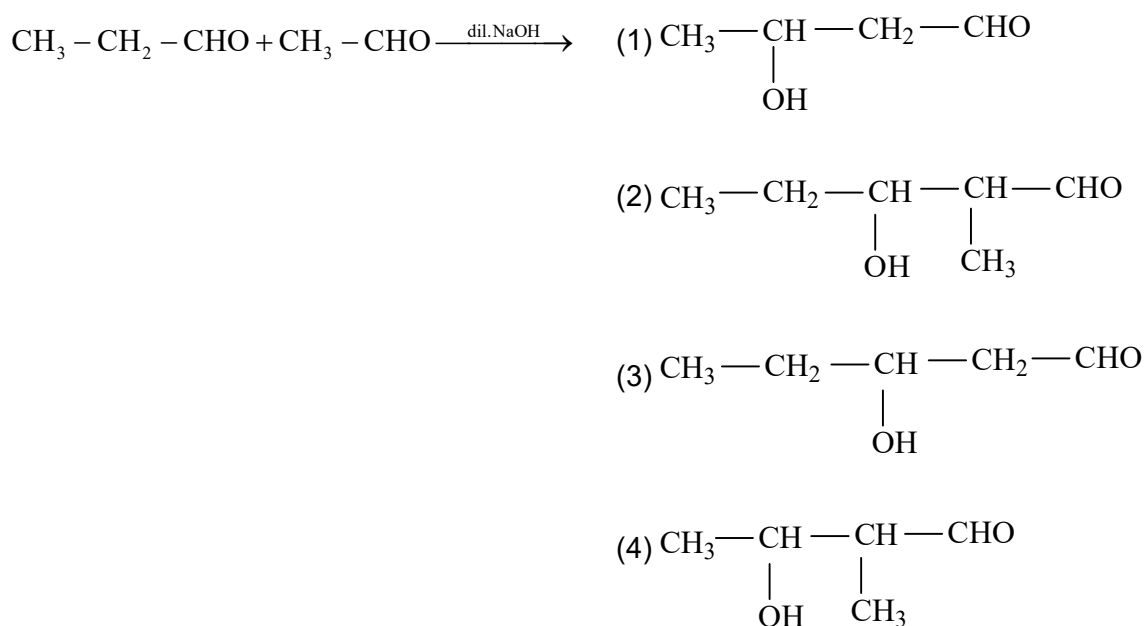


Similarly, Examples:-



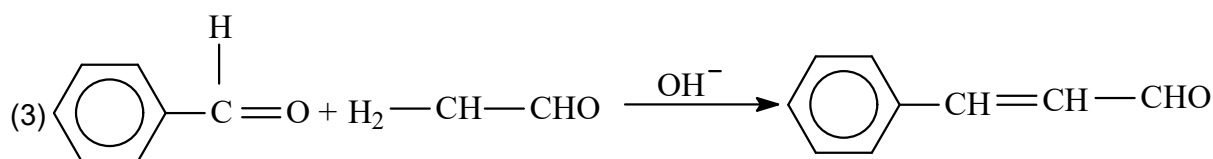
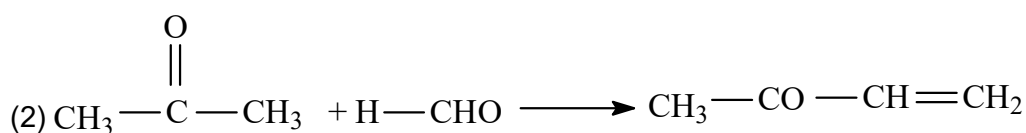
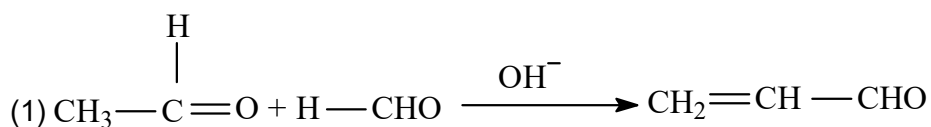
### Crossed Aldol condensation

Aldol condensation between two different aldehydes or ketones or between one aldehyde and one ketone is called crossed aldol condensation, which give four different products and are difficult to separate them.



But if one of the aldehydes or ketones does not possess  $\alpha$ -Hydrogen atoms only one product is formed.

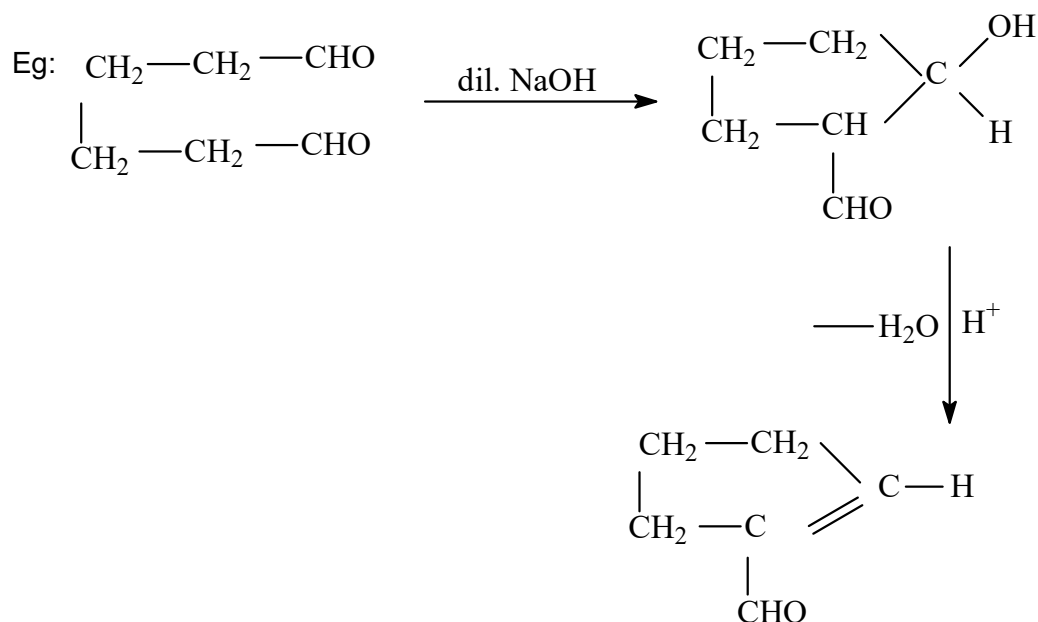
**Examples:**



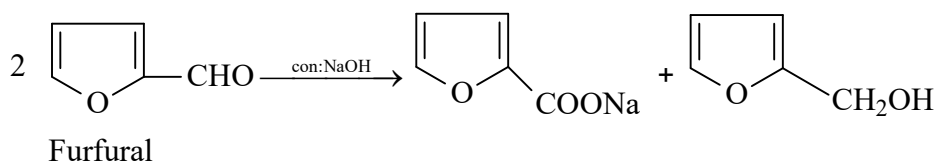
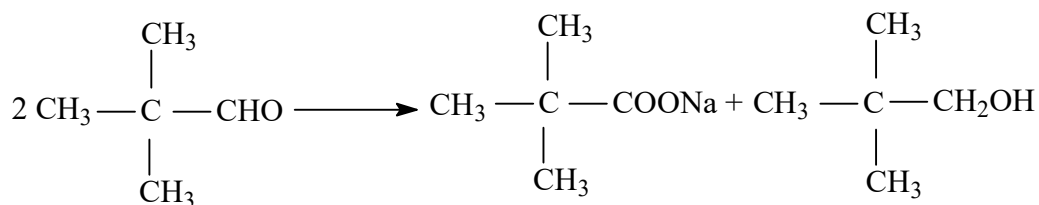
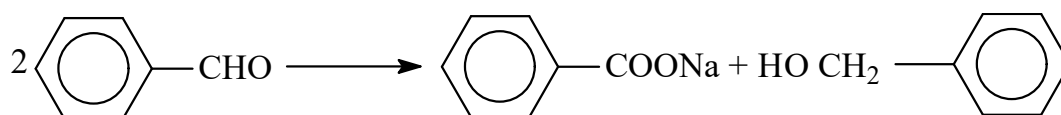
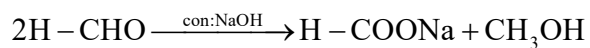
Such a base catalysed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is called Claisen-Schmidt Condensation reaction.

**Intra molecular aldol condensation**

If a compound contains two aldehyde or keto groups or one aldehyde and one keto group at 1, 6 or 1, 7 position with respect to each other, then the enolate ion of one carbonyl group can add to the carbonyl group of the other to form an aldol which loses  $\text{H}_2\text{O}$  to form  $\alpha, \beta$ -unsaturated aldehyde or ketone.

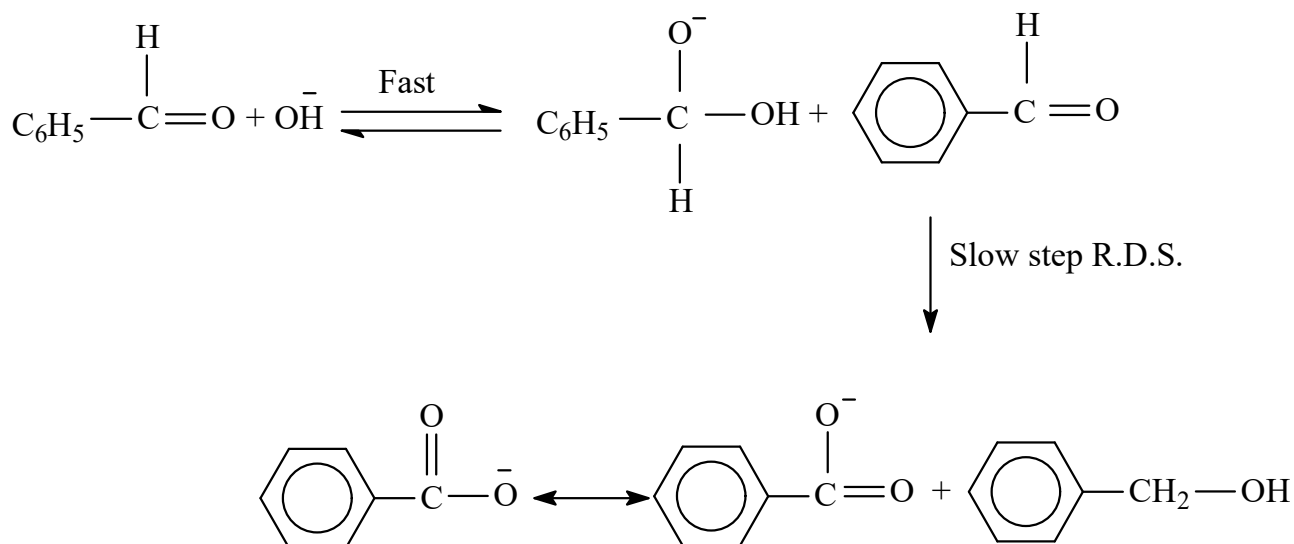
**Cannizzaro's reaction:**

Aldehydes having no  $\alpha$ -H atoms when heated in presence of strong base like NaOH or KOH undergo self oxidation reduction or disproportionation to form a mixture of acid salt and alcohol. Since in this reaction one molecule of an aldehyde is reduced at the expense of the other which is oxidised.

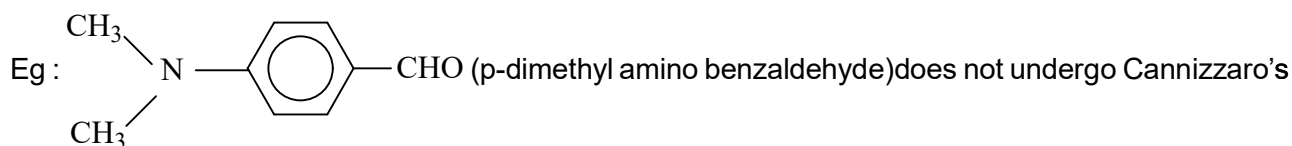


### Mechanism :

The rapid addition of  $\text{OH}^-$  to one molecule of aldehyde results in the formation of hydroxy alkoxide ion which transfer a hydride ion to the second molecule of aldehyde and since it is a slow step process it is called rate determining step. (II order w.r.to aldehyde and I order w.r.to base). In the final step, the acid and the alkoxide ion exchange a proton to acid anion and alcohol for attain stability.



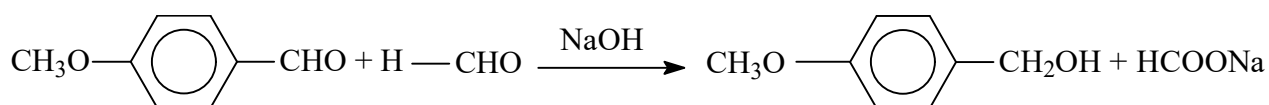
It has been seen that the rate of reaction depends on the nucleophilic attack on the carbonyl carbon.  $\therefore$  the factors which reduce the positive charge on the carbonyl carbon retard the reaction and the reaction may not occur.



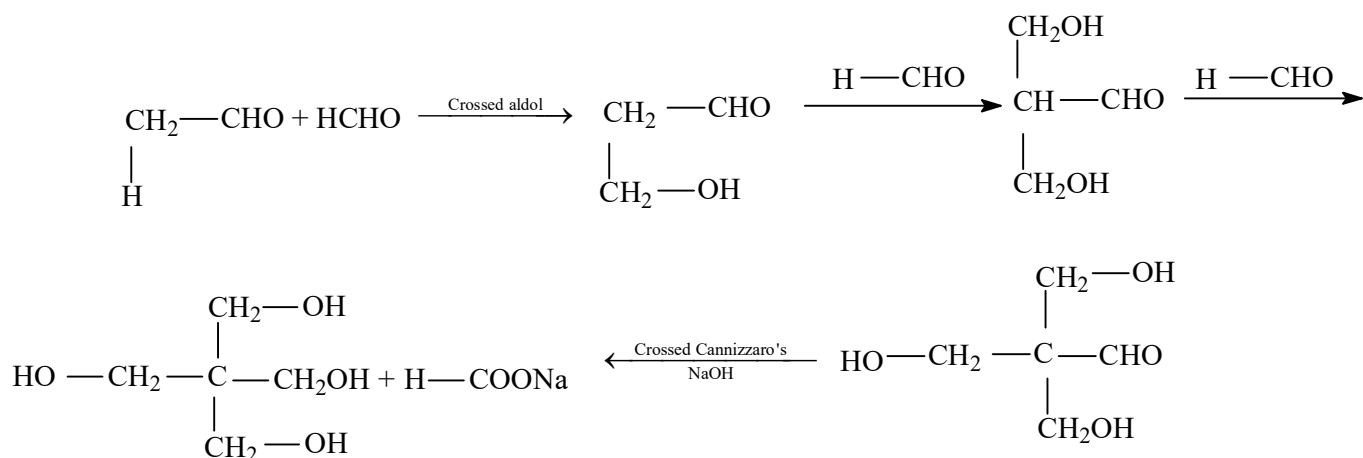
reaction and sterically hindered aldehydes also do not undergo this reaction.

### Crossed Cannizzaro's reaction

Two different aldehydes having no  $\alpha$ -H atom when heated with con: NaOH, most reactive aldehyde oxidised to form acid while the least one reduced into alcohol. This is called Crossed Cannizzaro's reaction.

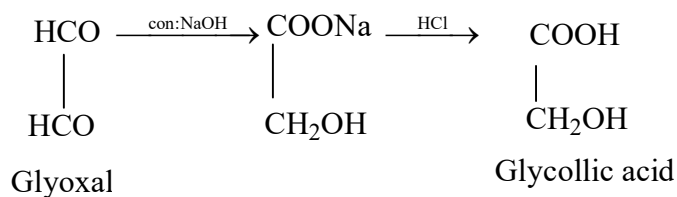


For example :  $\text{CH}_3-\text{CHO}$  with excess  $\text{H}-\text{CHO}$  form penta erythritol (Tetramethylolmethane).

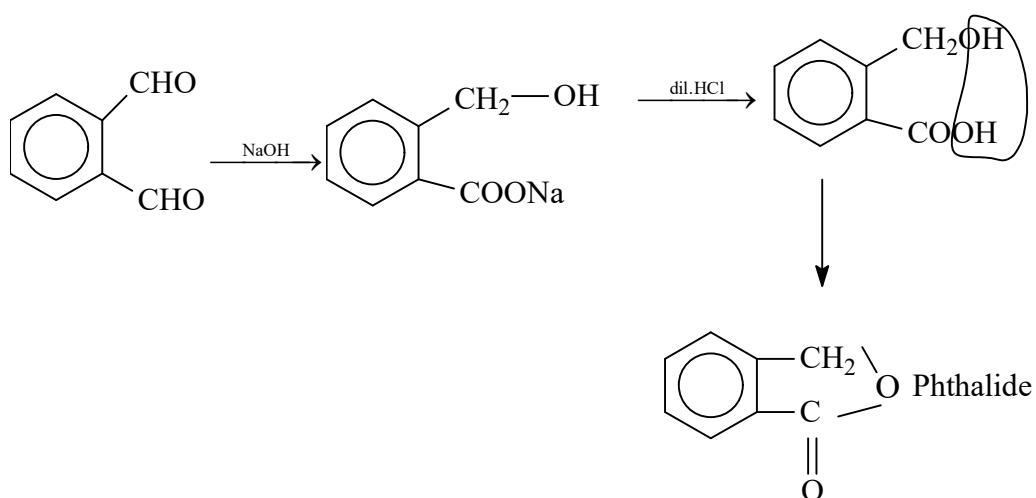


### Intramolecular Cannizzaro's reaction:

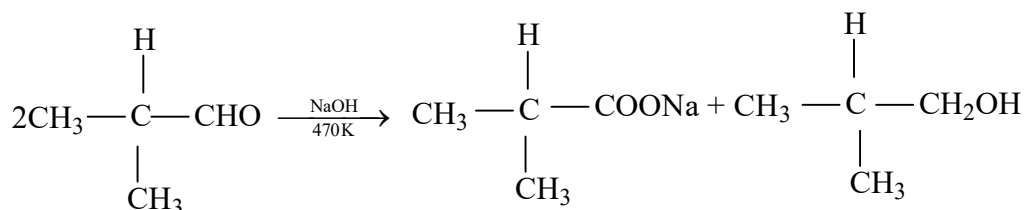
Dialdehydes which do not contain  $\alpha$ -hydrogens undergo intramolecular Cannizzaro's reaction in presence of strong alkali.



In certain cases intramolecular Cannizzaro's reaction product upon acidification followed by dehydration from lactones.

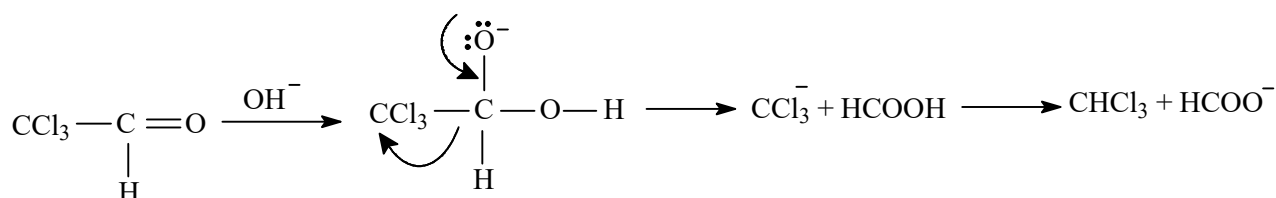


But isobutanal having one  $\alpha$  - H atom undergo Cannizzaro's reaction when heated with con: NaOH at high temperature.

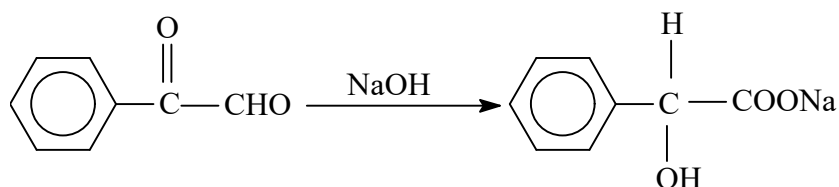


This is due to +I effect of methyl group, the carbanions of these aldehydes are not stable and hence instead of undergoing aldol condensation it will undergo Cannizzaro reaction.

Similarly  $\text{CCl}_3-\text{CHO}$  (chloral) is also not having  $\alpha$  -atom doesn't undergo Cannizzaro reaction. But it undergoes haloform reaction.



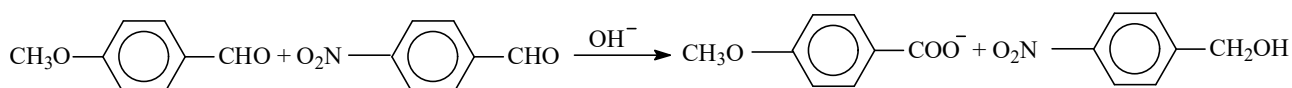
1-phenyl glyoxal when boiled with NaOH undergoes intramolecular crossed Cannizzaro reaction.



The reactivity of an aldehyde towards' Cannizzaro reaction depends upon the following two factors.

1. Ease of attach of  $\text{OH}^-$  in first fast step which requires a less sterically hindered carbonyl carbon.
2. Ease of hydride ion transfer : Electron donating group facilitate the attack of hydride ion.

### Example



The +R effect of  $-\text{OCH}_3$  through resonance facilitate the release of  $\text{H}^+$  ion and electron withdrawn by  $\text{NO}_2$  through resonance increases the electropositive character of carbonyl carbon at para position and thereby increases the affinity for  $\text{H}^+$  ion.

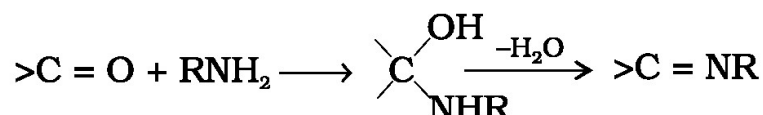
## Test for Aldehydic and Ketonic Group

### Theory

Both aldehydes and ketones contain carbonyl group ( $>\text{C} = \text{O}$ ) and are commonly known as carbonyl compounds. Identification of aldehydes and ketones is done by two important reactions of carbonyl group i.e.

- (i) addition reaction on double bond of  $>\text{C} = \text{O}$  group and
- (ii) oxidation of carbonyl group.

Addition reactions of derivatives of ammonia are important from the point of view of identification of carbonyl compounds. Addition is generally followed by elimination resulting in the formation of unsaturated compound.



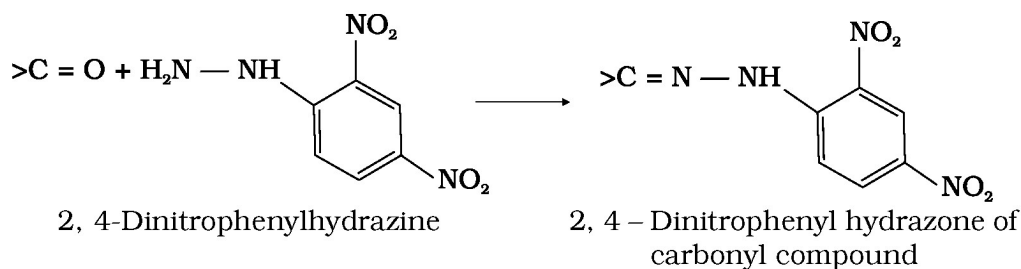
(R = alkyl, aryl or  $\text{C}_6\text{H}_5\text{NH}$  etc.)

These reactions are catalysed by an acid or a base and do not occur under strongly acidic or basic conditions. Each reaction requires an optimum pH for its occurrence. Therefore, maintenance of pH is very important while carrying out these reactions.

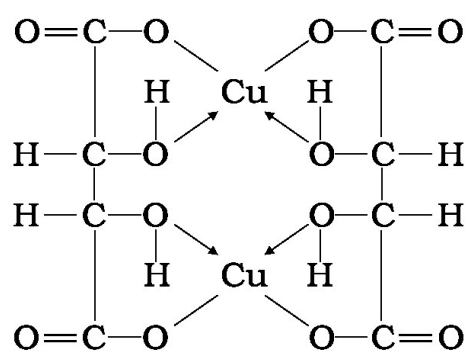
As far as oxidation is concerned, aldehydes are easily oxidised to carboxylic acids while ketones require relatively stronger oxidising agents. Distinction can be made between these two types of carbonyl compounds on the basis of difference in their reactivity.

Following tests are performed for the identification of aldehydic and ketonic groups:

(i) On reaction with 2,4-dinitrophenylhydrazine (2,4-DNP), they form the respective 2,4-dinitrophenyl hydrazones.



These two carbonyl compounds (aldehydes and ketones) are distinguished on the basis of tests using mild oxidising reagents, like Tollen's reagent and Fehling's reagent or Benedict's reagent. Tollen's reagent is an alkaline solution of silver cation complexed with ammonia, and Fehling's and Benedict's reagents are alkaline solutions containing cupric ions complexed with tartarate and citrate ions respectively. Fehling's reagent is freshly prepared by mixing equal amounts of Fehling's solution A and Fehling's solution B. Fehling's reagent deteriorates on keeping while Fehling's solutions A and B are quite stable. Fehling's solution A is an aqueous copper sulphate solution while Fehling's solution B is an alkaline solution of sodium potassium tartarate (Rochelle's salt). The reagent contains  $\text{Cu}^{2+}$  ion complexed with tartarate ions. The structure of the complex is given below :

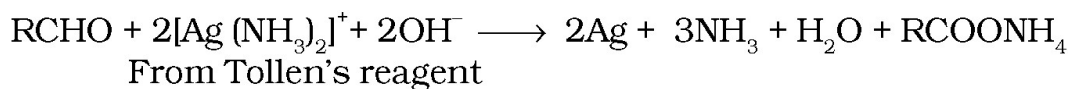


Copper tartarate complex

Benedict modified the original Fehling's test by using a single solution which is more convenient for the test. Benedict's solution is more stable than Fehling's reagent and can be stored for a long time. It is an alkaline solution containing a mixture of copper sulphate and sodium citrate ( $2\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 11\text{H}_2\text{O}$ ).

Complex formation decreases the cupric ion concentration below that necessary for precipitation of cupric hydroxide. These two reagents oxidize aldehydes while ketones remain unaffected. The chemistry of these tests is as follows:





However, aromatic aldehydes do not give positive Fehling's test. In Benedict test also,  $\text{Cu}^{2+}$  ions are reduced to  $\text{Cu}^+$  ions in the same manner as in the case of Fehling's reagent.

Aldehydes also give pink colour with Schiff's reagent (the reagent is prepared by decolourising aqueous solution of *p*-rosaniline hydrochloride dye by adding sodium sulphite or by passing  $\text{SO}_2$  gas). Ketones do not respond to this test.



- Beaker (250 mL) : One
- Test tube holder : One
- Test tubes : As per need



- Schiff's reagent : As per need
- Fehling's solutions A and B : As per need
- Silver nitrate : As per need
- Dilute ammonium hydroxide solution : As per need
- 2,4-Dinitrophenylhydrazine reagent : As per need

Silver nitrate



Ammonia solution



Ammonia gas



### A. Test given by both aldehydes and ketones

#### 2,4-Dinitrophenylhydrazine test (2,4-DNP test)

Take 2-3 drops of the liquid compound in a test tube or in case of solid compound, dissolve a few crystals of it in 2-3 mL alcohol. Add a few drops of an alcoholic solution of 2,4-dinitrophenylhydrazine. Appearance of yellow, orange or orange-red precipitate confirms the presence of carbonyl group. If precipitate does not appear at room temperature, warm the mixture in a water bath for a few minutes and cool.

### B. Tests given by aldehydes only

Following tests namely Schiff's test, Fehling's test and Tollen's test are given by aldehydes only.

#### Schiff's test

Take 3-4 drops of the liquid compound or dissolve a few crystals of organic compound in alcohol and add 2-3 drops of the Schiff's reagent. Appearance of pink colour indicates the presence of an aldehyde.

*Fehling's test*

Take nearly 1 mL of Fehling's solution A and 1 mL of Fehling's solution B in a clean dry test tube. To this add 2-3 drops of the liquid compound or about 2 mL of the solution of the solid compound in water or alcohol. Heat the content of the test tube for about 2 minutes in a water bath. Formation of brick red precipitate of copper (I) oxide indicates the presence of an aldehyde. This test is not given by aromatic aldehydes.

Add 5 drops of the liquid compound or the solution of the solid organic compound in water or alcohol to 2 mL Benedict's reagent. Place the test tube in boiling water bath for 5 minutes. An orange-red precipitate indicates the presence of an aldehyde.

*Tollen's test*

- (i) Take 1 mL of freshly prepared (~ 2 %) silver nitrate solution in a test tube. Add 1-2 drops of sodium hydroxide solution to it and shake, a dark brown precipitate of silver oxide appears. Dissolve the precipitate by adding ammonium hydroxide solution drop-wise.
- (ii) To the above solution, add an aqueous or an alcoholic solution of the organic compound.
- (iii) Heat the reaction mixture of step (ii) in a water bath for about 5 minutes. Formation of a layer of silver metal on the inner surface of the test tube which shines like a mirror, indicates the presence of an aldehyde.

**Precautions**

- (a) Always use freshly prepared reagents to perform the tests.
- (b) Do not heat the reaction mixture directly on a flame.
- (c) After performing the test, destroy the silver mirror by adding dilute nitric acid and drain off the solution with excess of water.