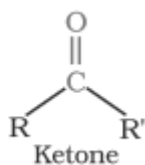
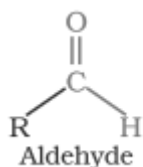


## Carbonyl Compounds: Aldehydes & Ketones, Class-XII

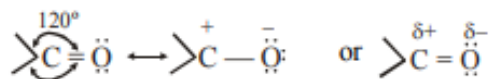
Organic compounds containing carbon-oxygen double bond ( $>C=O$ ), i.e. carbonyl group, are known as Carbonyl compounds. Carbonyl compounds are of two types: Aldehydes and Ketones. In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones, it is bonded to two carbon atoms.



### STRUCTURE AND NATURE OF CARBONYL GROUP :

The carbonyl carbon atom is  $sp^2$ -hybridised and forms three sigma ( $\sigma$ ) bonds. The fourth valence electron of carbon remains in its p-orbital and forms a  $\pi$ -bond with oxygen by overlap with p-orbital of an oxygen. In addition, the oxygen atom also has two non bonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the  $\pi$ -electron cloud is above and below this plane. The bond angles are approximately  $120^\circ$  as expected of a trigonal coplanar structure.

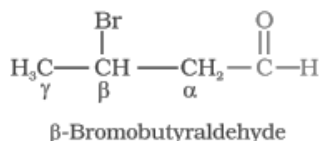
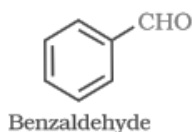
The electronegativity of oxygen is much higher than that of carbon, the p electron cloud is displaced towards the oxygen. Therefore the C–O bond is polar in nature and carbonyl compounds possess dipole moment (2.3 to 2.8 D).



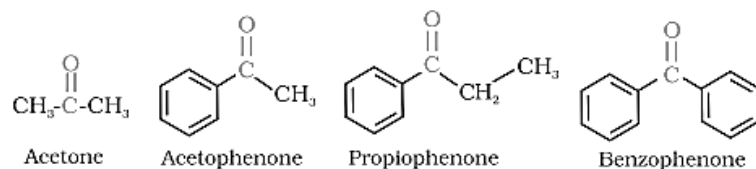
### Nomenclature of carbonyl compounds:

#### I. Common names:

(a) Aldehydes: The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending –ic of acid with aldehyde. At the same time, the names reflect the Latin or Greek term for the original source of the acid or aldehyde. The location of the substituent in the carbon chain is indicated by Greek letters  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , etc. The  $\alpha$ -carbon being the one directly linked to the aldehyde group,  $\beta$  carbon the next, and so on. For example,



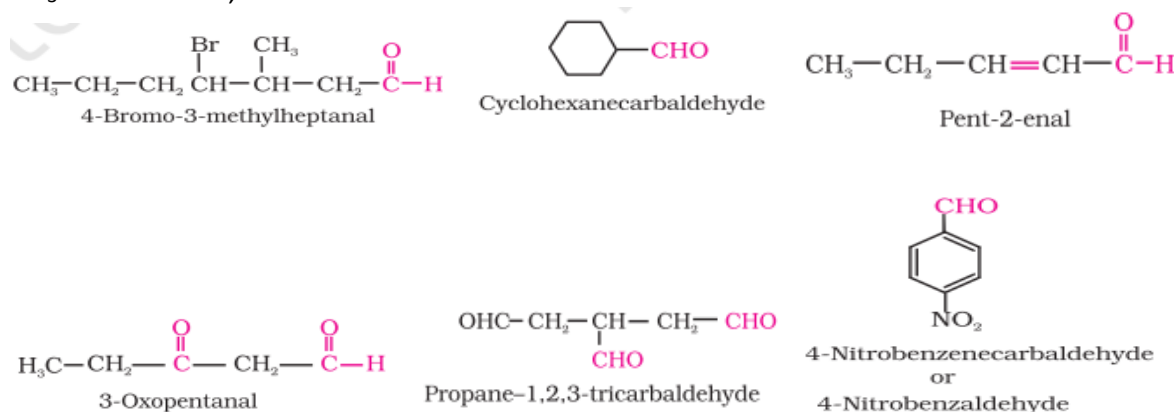
(b) **Ketones:** The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group. The locations of substituents are indicated by Greek letters,  $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\beta'$  and so on beginning with the carbon atoms next to the carbonyl group, indicated as  $\alpha$ ,  $\alpha'$ .



## II. IUPAC Name :

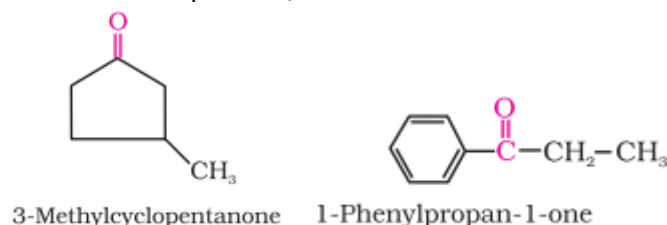
(a) **Aldehydes:** The suffix “-e” of alkane is replaced by the suffix “-al”, i.e.

HCHO Methanal;  
 CH<sub>3</sub>CHO Ethanal;



(b) **Ketones:** The suffix “-e” of corresponding alkane is replaced by “-one”, e.g.

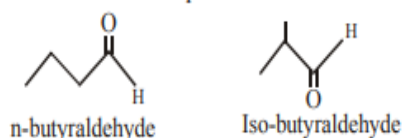
H<sub>3</sub>C.COCH<sub>3</sub> Propanone,



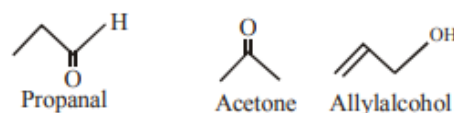
### ISOMERISM IN ALDEHYDES :

Aldehydes exhibit two types of isomerism

(i) **Chain isomerism :** Example

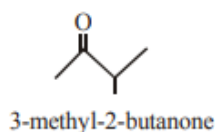
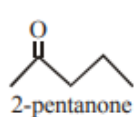


(ii) **Functional isomerism :**

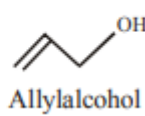
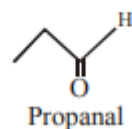
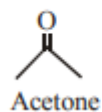


**Isomersim in ketones :** They exhibit three types of isomersim

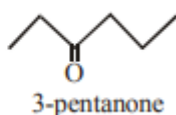
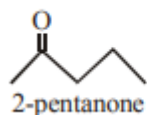
(a) **Chain isomerism :**



(b) **Functional isomersim :**



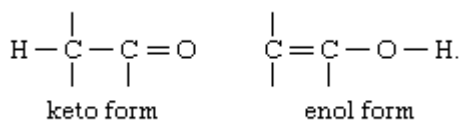
(c) **Position isomerism :**



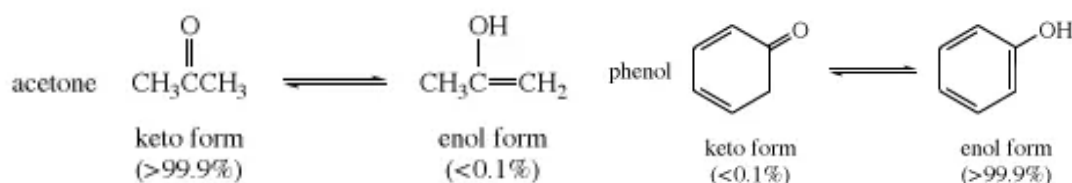
## Tautomerism:

Tautomers are structural isomers of chemical compounds that readily interconvert. The chemical reaction interconverting the two is called tautomerization. This conversion commonly results from the relocation of a hydrogen atom within the compound.

The most common type of tautomerism is that involving carbonyl, or keto, compounds and unsaturated hydroxyl compounds, or enols; the structural change is the shift of a hydrogen atom between atoms of carbon and oxygen, with the rearrangement of bonds as indicated:



In many aliphatic aldehydes and ketones, such as acetaldehyde, the keto form is the predominant one; in phenols, the enol form, which is stabilized by the aromatic character of the benzene ring, is the major component.

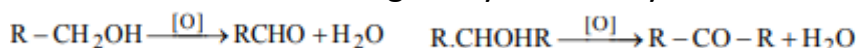


## General Methods of Preparation of Aldehydes and Ketones

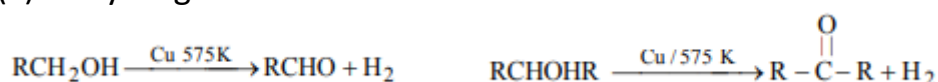
### A. Preparation of both Aldehydes and Ketones :

#### (i). Controlled oxidation of alcohols:

Oxidation of primary alcohol gives aldehydes and secondary alcohol gives a ketone. Oxidising agents such as acidified  $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$ , PCC are used for oxidation. Oxidation using PCC yield aldehydes.

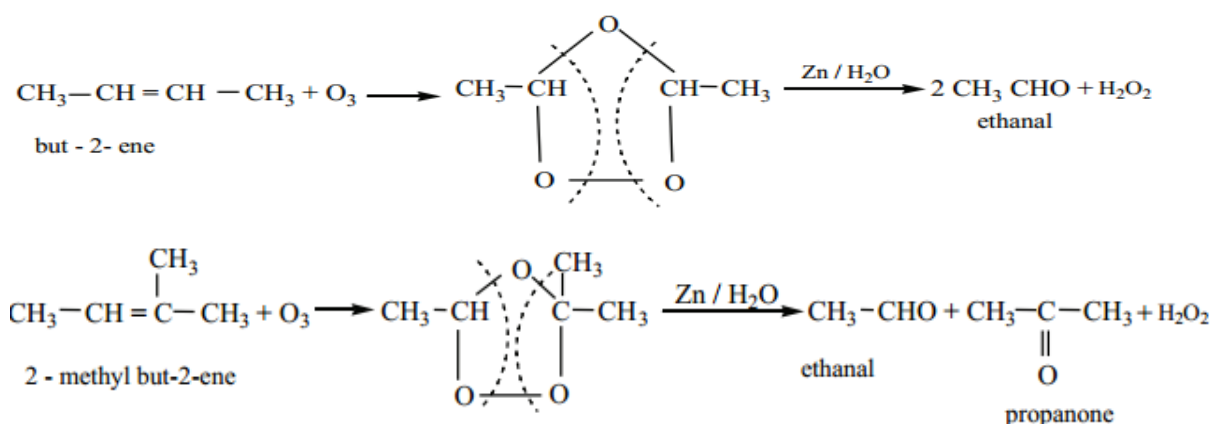


#### (ii) Dehydrogenation of alcohol :



#### (iii) Ozonolysis of Alkenes:

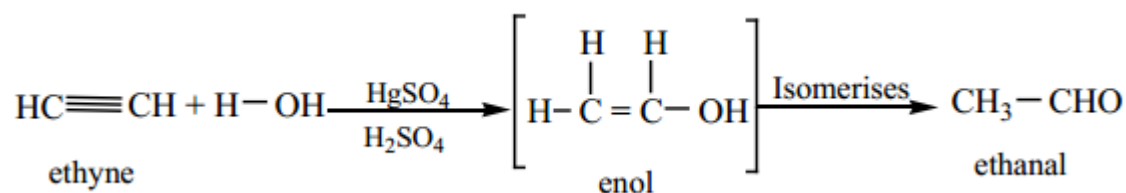
Reductive ozonolysis of alkenes gives aldehydes and ketones. Alkenes react with ozone to form ozonide which on subsequent cleavage with zinc and water gives aldehydes and ketones. Zinc dust removes  $\text{H}_2\text{O}_2$  formed, which otherwise can oxidise aldehydes/ketones.



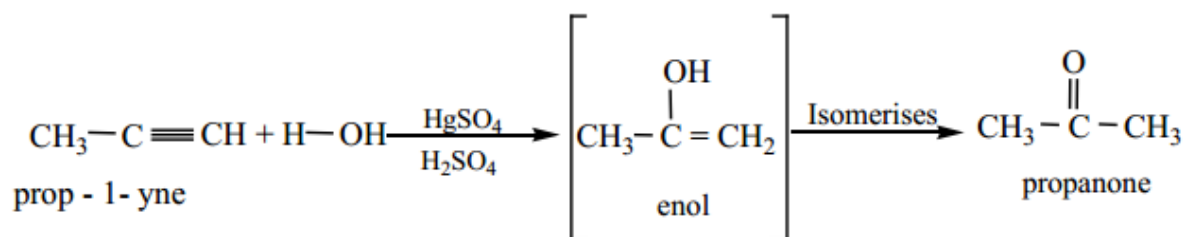
#### (iv) Hydration of Alkynes:

Hydration of alkynes in presence of 40% dilute sulphuric acid and 1%  $\text{HgSO}_4$  to give the corresponding aldehydes/ketones.

(a) Hydration of acetylene yields acetaldehyde.



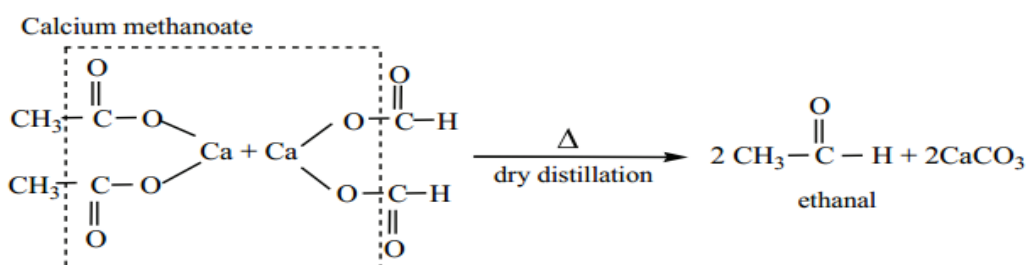
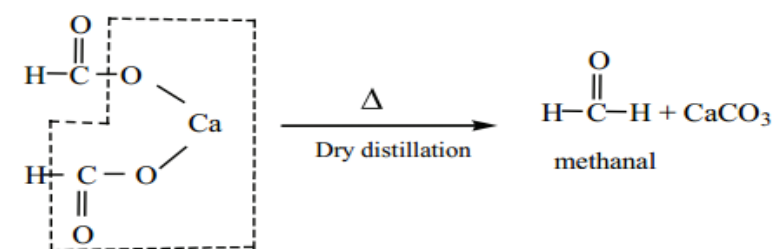
(b) Hydration of alkynes, other than acetylene gives ketones.



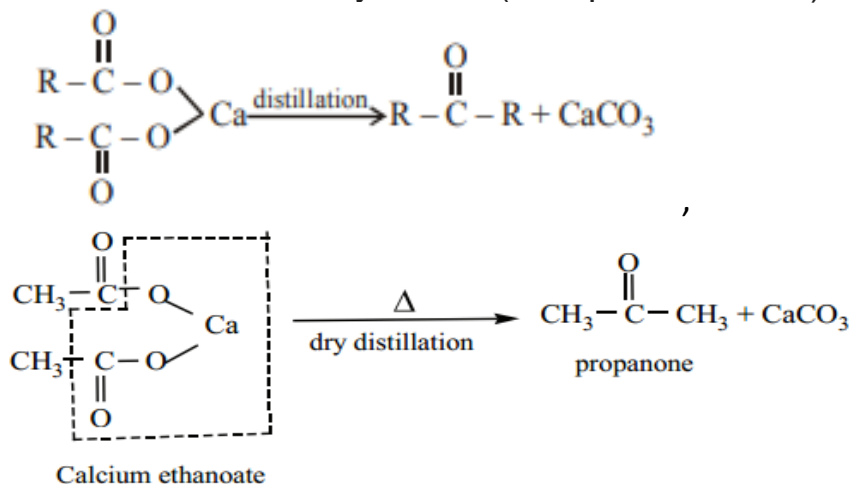
#### (v) From Calcium Salts of Carboxylic Acids

Aldehydes and ketones may be prepared by the dry distillation of calcium salts of carboxylic acids.

(a) Aldehydes are obtained when the mixture of calcium salt of carboxylic acid and calcium formate is subjected to dry distillation.

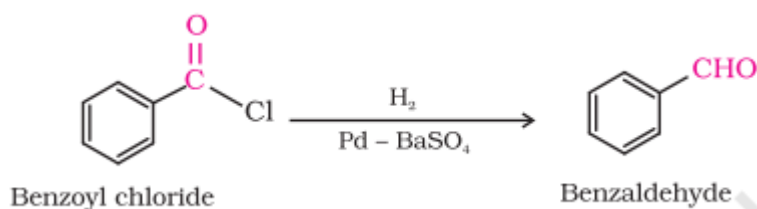
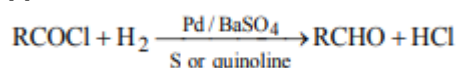


(b) Symmetrical ketones can be obtained by dry distillation of the calcium salt of carboxylic acid (except formic acid):



## B. Preparation of only Aldehydes:

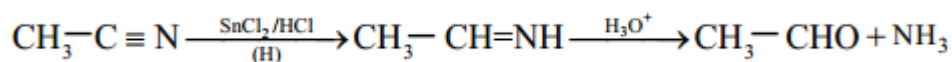
(i) By Rosenmund's reduction from acid chloride :



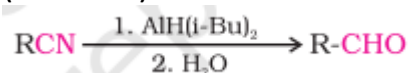
Formaldehyde cannot be prepared by this method because  $\text{HCOCl}$  is unstable.  $\text{BaSO}_4$  acts as catalytic poison to prevent further reduction of aldehyde to form primary alcohol.

(ii) Stephen's reduction of nitriles :

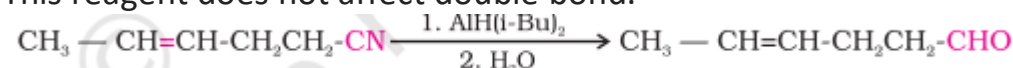
When alkyl/Aryl cyanides are reduced using  $\text{SnCl}_2/\text{HCl}$ , imines are formed, which on hydrolysis gives corresponding aldehyde.



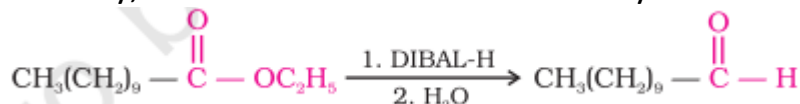
Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:



This reagent does not affect double bond.

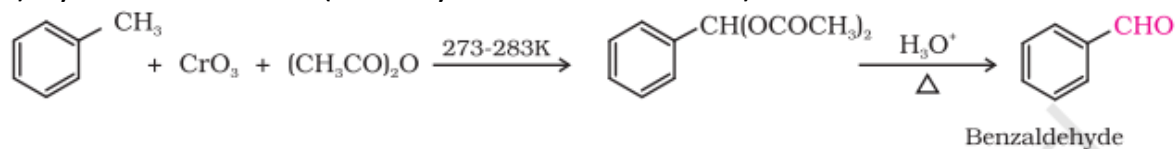


Similarly, esters are also reduced to aldehydes with DIBAL-H.

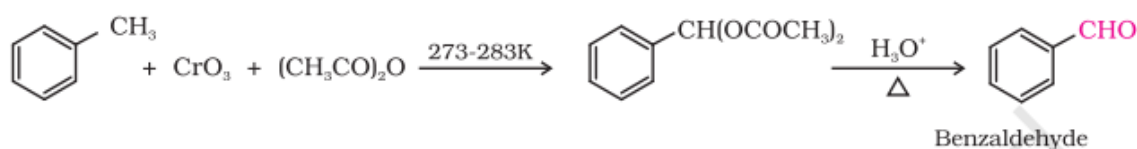


(iii) From hydrocarbons:

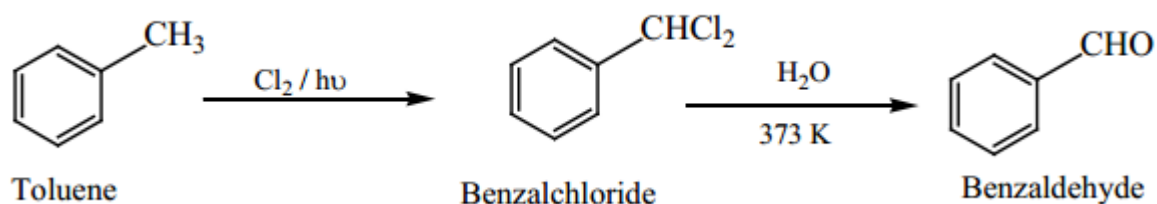
(a) By Etard oxidation (Chromyl chloride oxidation):



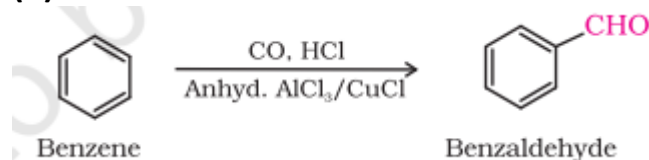
(b) Oxidation by chromic oxide ( $\text{CrO}_3$ ):



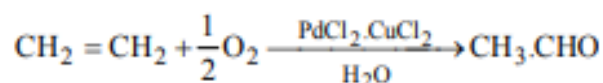
© Manufacture of Benzaldehyde from Toluene:



(d) Gattermann – Koch Reaction:



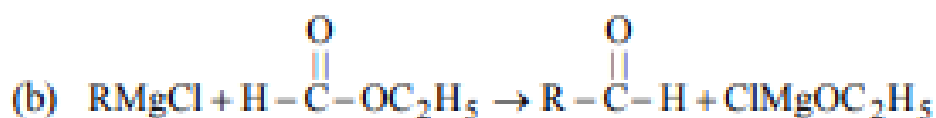
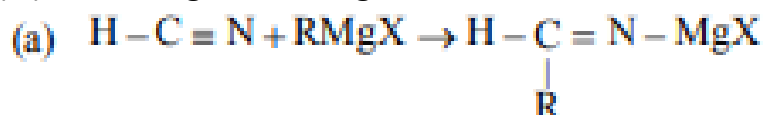
(iv) Waker's process :



(v) Oxo process :



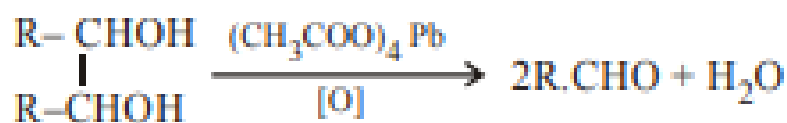
(vi) From Grignard's reagent :



(vii) Hydrolysis of Geminal halides :



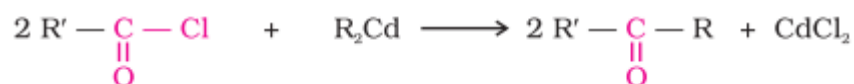
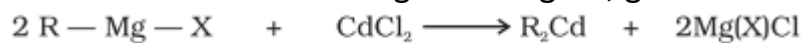
(viii) From Glycols :



### C. Preparation of Ketones:

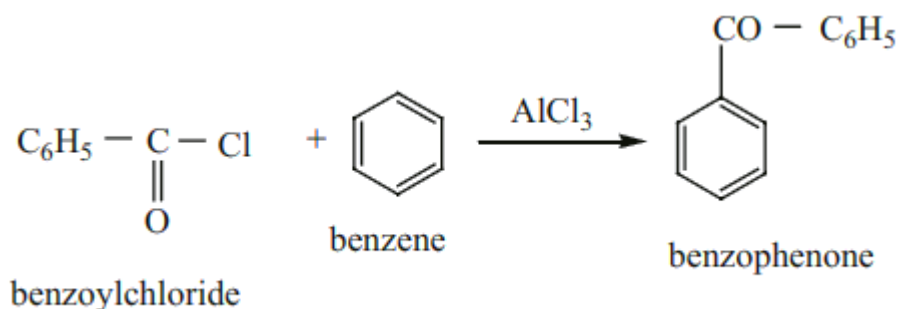
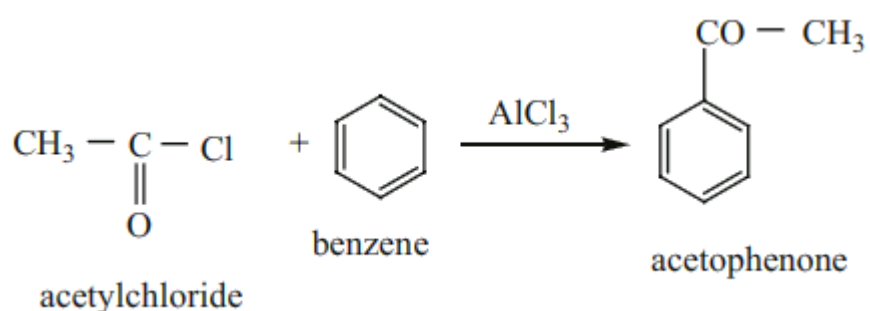
(I) From acyl chlorides :

Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.

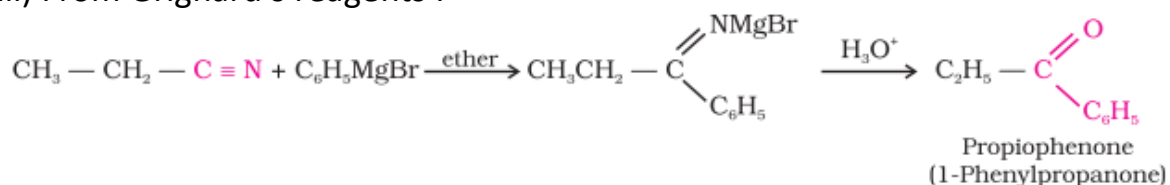


If we use R-Mg-X directly, then being more reactive, it will react with ketone to give tert. alcohol.

(ii) By Friedel – Craft Acylation:



(iii) From Grignard's reagents :





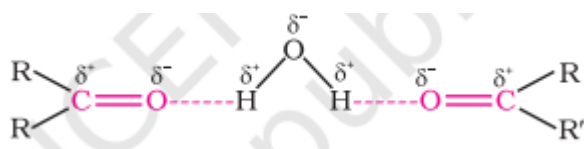
## Physical Properties of Aldehydes and Ketones:

**Boiling point:** The boiling point of aldehydes and ketones increases with an increase in molecular weight. This is because the boiling point depends upon the strength of the intermolecular forces.

- **Vander Waals dispersion forces:** As the molecules get longer and the number of electrons increases, which results in the increase in the magnitude of van der Waal forces. Therefore, for this reason, the boiling point of both aldehydes and ketones increases with the increase in the number of carbon atoms.
- **Vander Waals dipole-dipole attraction:** Because of the presence of carbon-oxygen double bond both aldehydes and ketones are polar in nature. Thus, there will be an attraction between permanent dipoles present in aldehydes and ketones as well as the molecules which are near them. This is the reason for aldehydes and ketones having boiling points higher than similar-sized hydrocarbons.
- The boiling point of aldehydes and ketones is higher than that of non-polar compounds (hydrocarbons) but lower than those of corresponding alcohols and carboxylic acids as aldehydes and ketones do not form H-bonds with themselves.

**Solubility:** Aldehydes and ketones are soluble in water but their solubility decreases with an increase in the length of the chain. Methanal, ethanal and propanone are those aldehydes and ketones which are of small size and are miscible with water in almost all proportions.

Aldehydes and ketones cannot form hydrogen bonds with themselves, but they can have hydrogen bonds with water molecules and this forms the basis for good solubility of aldehydes and ketones in water.



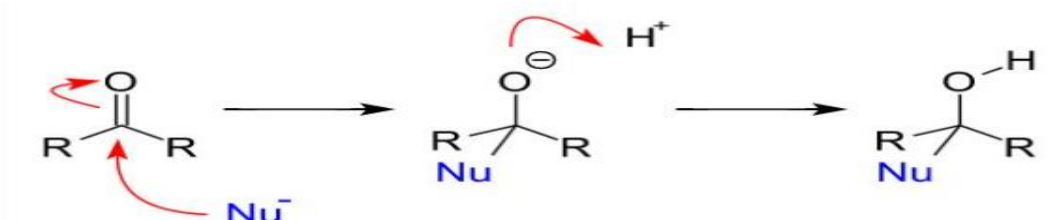
The higher members do not dissolve in water because the hydrocarbon part is larger and resists the formation of hydrogen bonds with water molecules.

## Chemical Properties:

### 1. Nucleophilic addition reactions:

Contrary to electrophilic addition reactions observed in alkenes, the aldehydes and ketones undergo nucleophilic addition reactions.

**Mechanism of nucleophilic addition reactions:** A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of  $sp^2$  hybridised orbitals of carbonyl carbon. The hybridisation of carbon changes from  $sp^2$  to  $sp^3$  in this process.



and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of  $Nu^-$  and  $H^+$  across the carbon oxygen double bond.

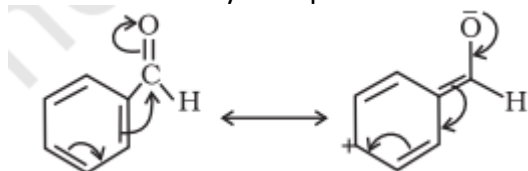
#### Relative reactivity of aldehyde and ketone towards nucleophilic addition:

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons.

Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.

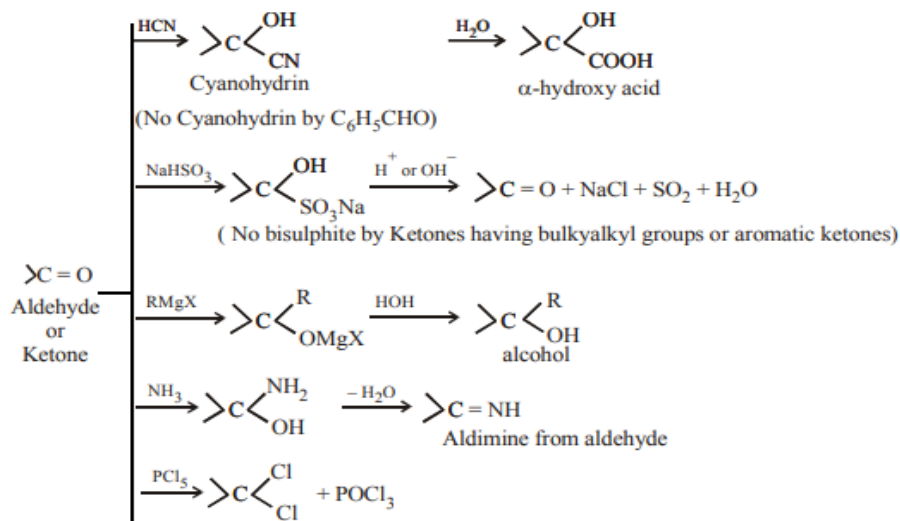
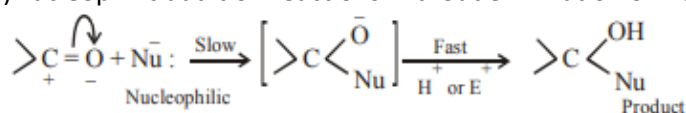
Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively than in former.

Aromatic carbonyl compounds are less reactive than aliphatic ones due to resonance.

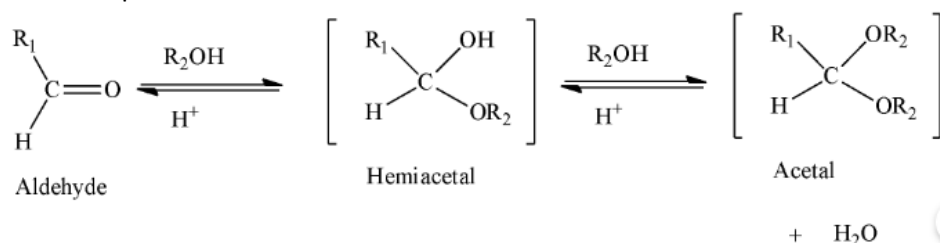


#### Examples of Nucleophilic addition:

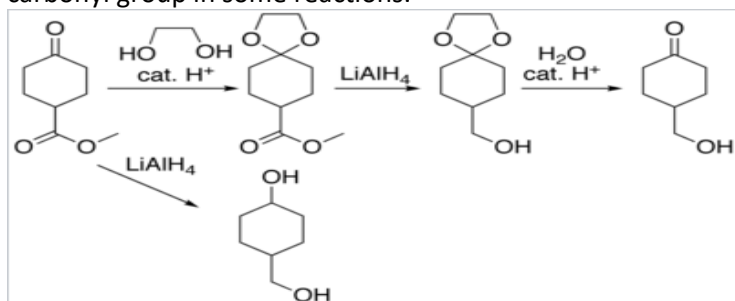
(i) Nucleophilic addition reactions without elimination of water molecule :



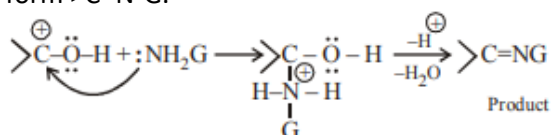
- **Addition of alcohols:** Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield alkoxyalcohol intermediate, known as hemiacetals, which further react with one more molecule of alcohol to give a gem-dialkoxo compound known as acetal.



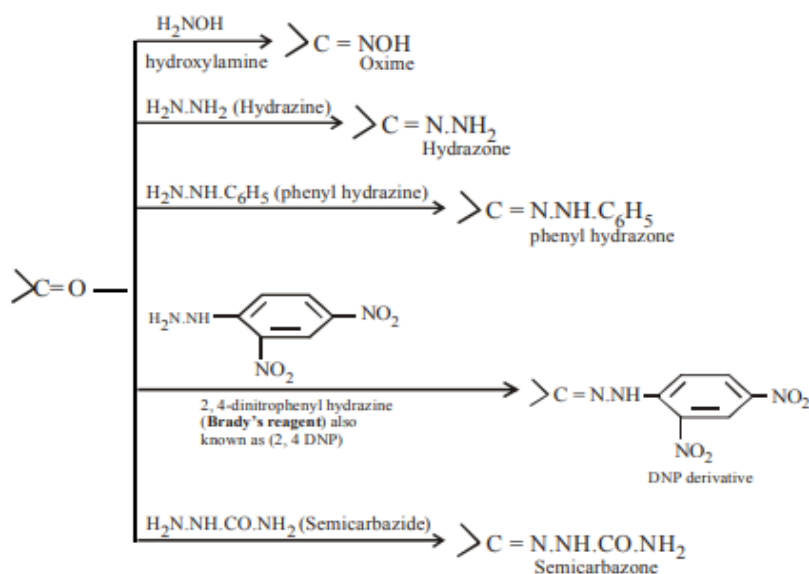
Ketones react with dihydric alcohols like ethylene glycol under similar conditions to form cyclic products known as ethylene glycol ketals. Dry hydrogen chloride protonates the oxygen of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon facilitating the nucleophilic attack of ethylene glycol. Acetals and ketals are hydrolysed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively. So, this reaction is used to protect carbonyl group in some reactions.



(ii) **Addition of ammonia and its derivatives:** Nucleophiles, such as ammonia and its derivatives  $\text{H}_2\text{N-G}$  add to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the intermediate to form  $>\text{C}=\text{N-G}$ .



Examples:



- The control of pH is must for these reactions. The optimum value is around 3.5.

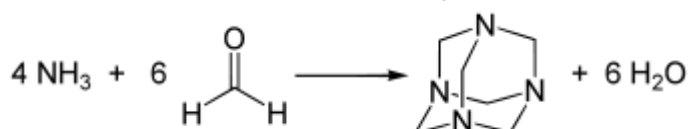
**At low pH :**  $H^+$  concentration is very high. The carbonyl compound and ammonia derivative, both protonated and latter cannot act as nucleophile ( $NH_3^{3+} G$ ).

**At high pH :**  $H^+$  concentration is too small. The protonation of carbonyl group will not occur and reaction will not occur smoothly.

Hence optimum pH of the medium is around 3.5.

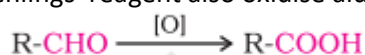
- Urotropin formation:**

It is prepared industrially by combining formaldehyde and ammonia:

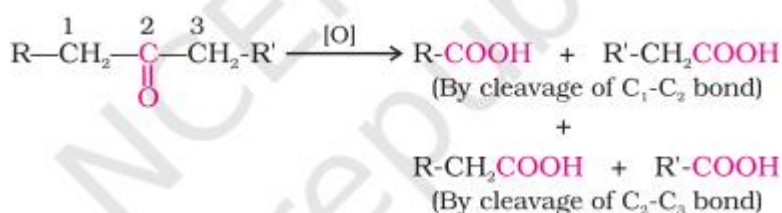


It is used for the treatment of urinary tract infection.

**Oxidation:** Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes.

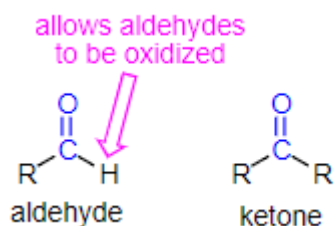


Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.

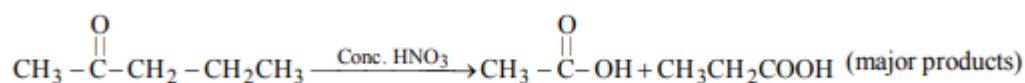


- Why do aldehydes and ketones behave differently?**

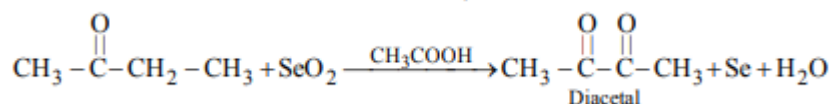
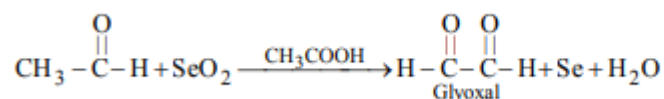
Aldehydes have a proton attached to the carbonyl carbon which can be abstracted easily due to electron withdrawing effect of carbonyl group, allowing them to be easily oxidized to form carboxylic acids. The lack of this hydrogen makes ketones generally inert to these oxidation conditions. Nevertheless, ketones can be oxidized but only under extreme conditions.



- Popoff's rule :** During oxidation of unsymmetrical ketone the carbonyl group is retained by smaller alkyl group.

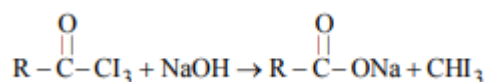
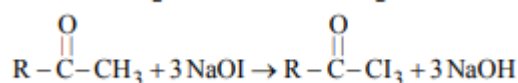
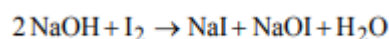


- **Oxidation with  $\text{SeO}_2$**  : The  $\text{CH}_3$  group adjacent to  $>\text{C}=\text{O}$  is oxidised to  $-\text{CHO}$  and  $>\text{CH}_2$  group is oxidised to  $>\text{C}=\text{O}$  group.



**Bayer-Villiger oxidation** : Oxidation of aliphatic Ketones by organic per acids, e.g. perbenzoic acid, peracetic acid or monoperthalic acid to form esters or their hydrolysed products :

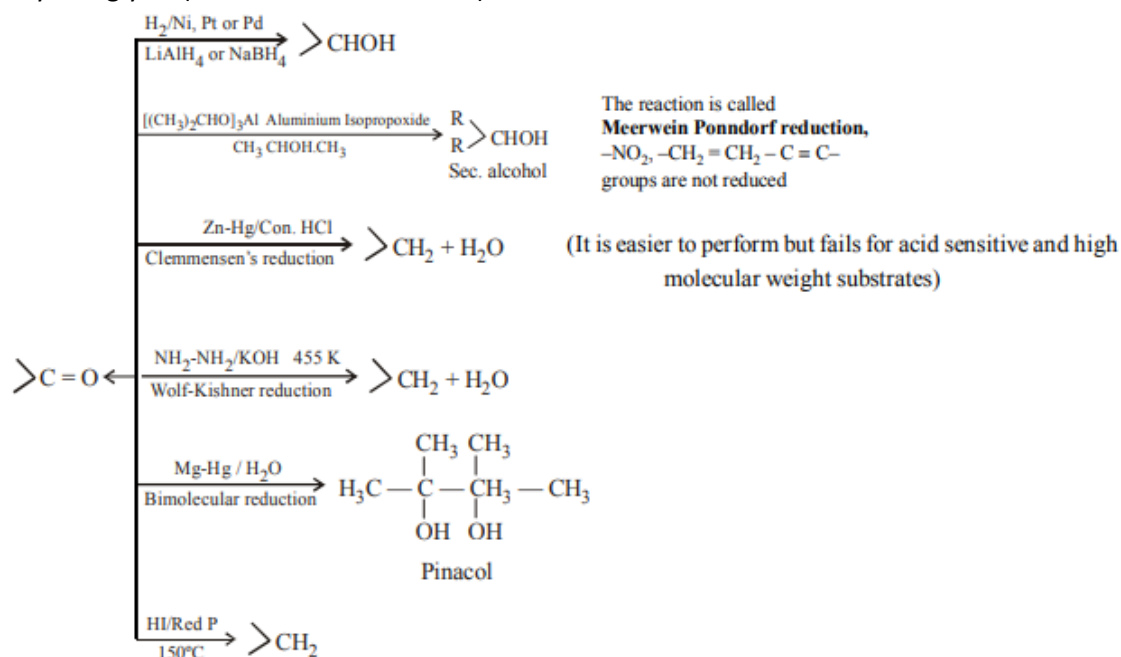
**Haloform reaction** : Oxidation of acetaldehyde or methyl ketones with Sodium Hypohalite ( $\text{NaOX}$ ) or ( $\text{X}_2 + \text{NaOH}$ ) gives haloform  $\text{CHX}_3$  . The reaction is of practical value to identify these compounds by forming  $\text{CHI}_3$  .



## Reduction:

**(i) Reduction to alcohols:** Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride ( $\text{NaBH}_4$ ) or lithium aluminium hydride ( $\text{LiAlH}_4$ ) as well as by catalytic hydrogenation .

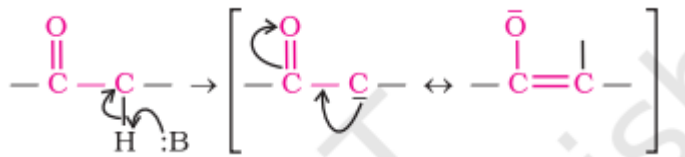
**(ii) Reduction to hydrocarbons:** The carbonyl group of aldehydes and ketones is reduced to  $\text{CH}_2$  group on treatment with zinc amalgam and concentrated hydrochloric (Clemmensen reduction) or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (Wolff-Kishner reduction).



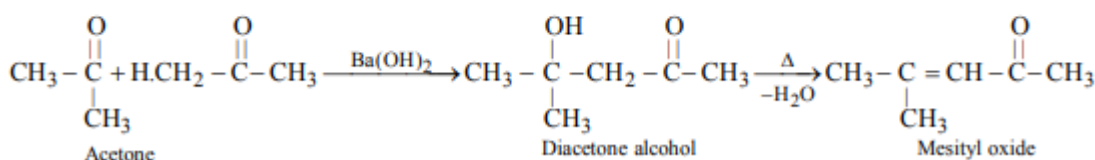
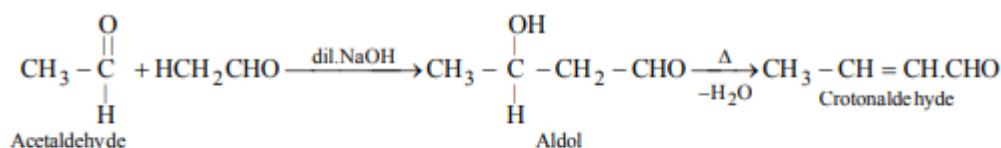
## Reactions due to $\alpha$ -hydrogen:

**Acidity of  $\alpha$ -hydrogens of aldehydes and ketones:** The aldehydes and ketones undergo a number of reactions due to the acidic nature of  $\alpha$ -hydrogen.

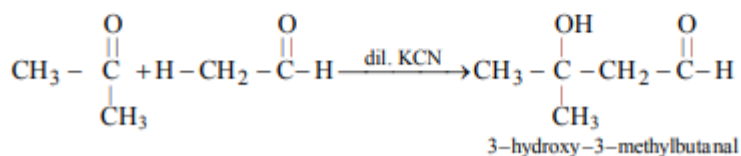
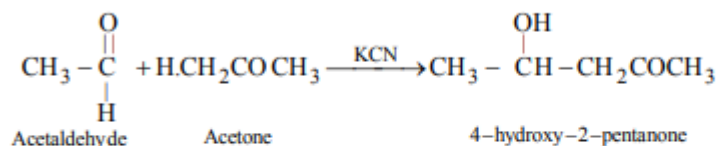
The acidity of  $\alpha$ -hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



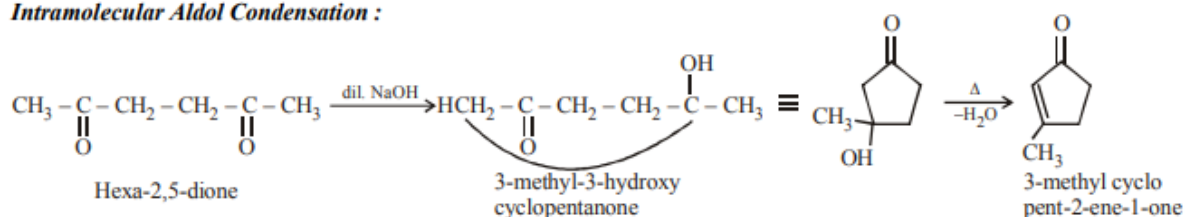
**Aldol condensation:** Aldehydes and ketones having at least one  $\alpha$ -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form  $\beta$ -hydroxy aldehydes (aldol) or  $\beta$ -hydroxy ketones (ketol), respectively. This is known as Aldol reaction.



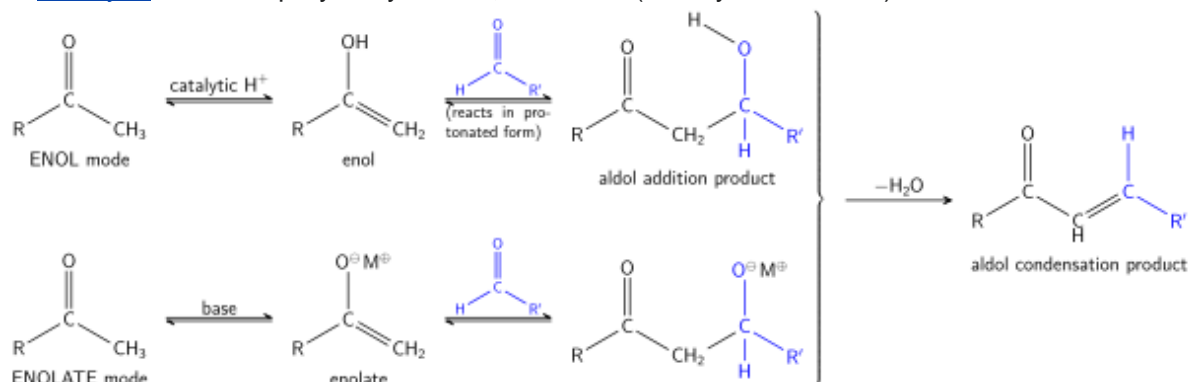
### Crossed Aldol Condensation :



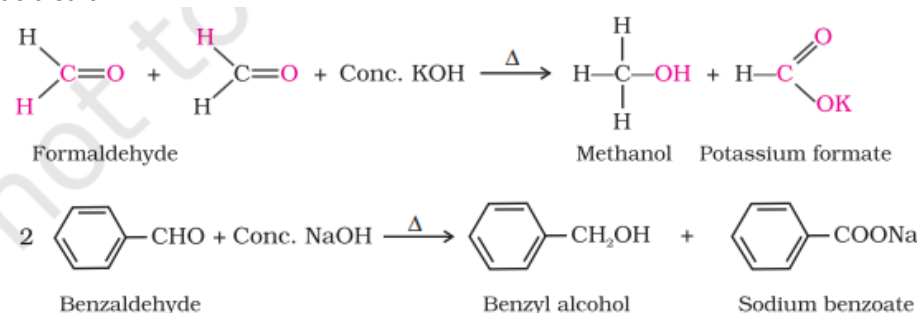
### Intramolecular Aldol Condensation :



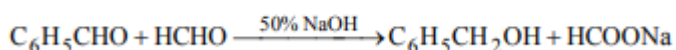
**Mechanism:** In its usual form, it involves the nucleophilic addition of a ketone enolate to an aldehyde to form a  $\beta$ -hydroxy ketone, or "**aldol**" (aldehyde + alcohol)



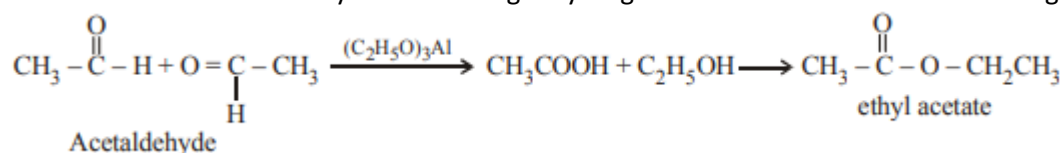
**Cannizzaro reaction:** Aldehydes which do not have an  $\alpha$ -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on heating with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.



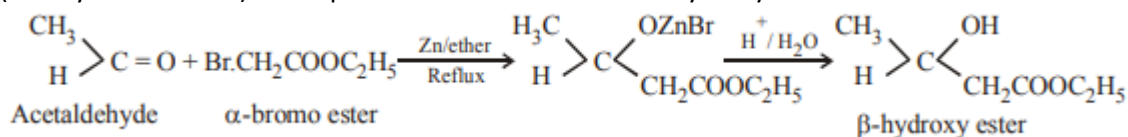
**Crossed Cannizzaro's reaction :**



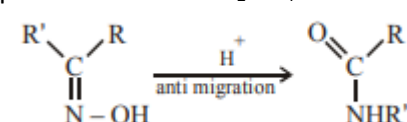
**Tischenko reaction :** Aldehydes containing  $\alpha$ -hydrogen atom with aluminium ethoxide give esters.



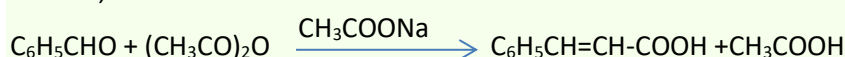
**Reformatsky reaction :** It is the reaction between an  $\alpha$ -bromoacid ester and a carbonyl compound (aldehyde or ketone) in the presence of zinc to form a  $\beta$ -hydroxy ester.



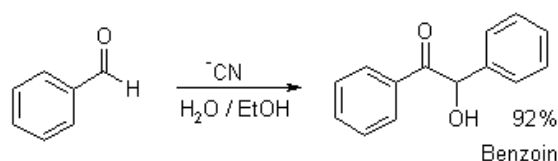
**Beckmann's rearrangement :** It is rearrangement of keto oxime to N-substituted acid amide in presence of Conc.  $H_2SO_4$ .



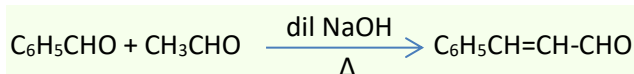
**Perkin's reaction:** When benzaldehyde is heated with acetic anhydride in the presence of sodium acetate, it forms cinnamic acid.



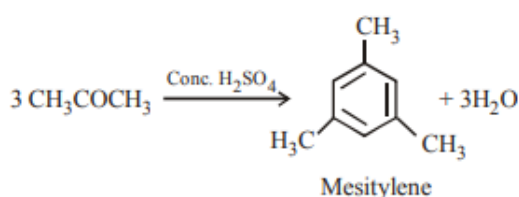
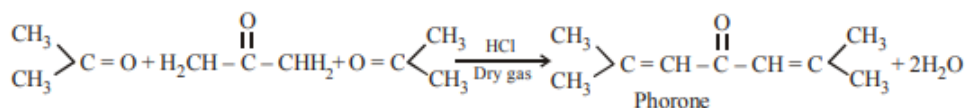
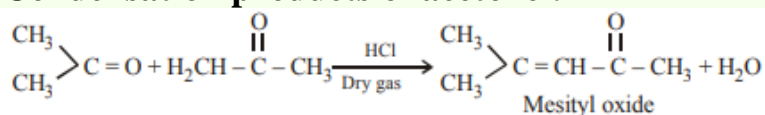
**Benzoin Condensation:** The Benzoin Condensation is a coupling reaction between two aldehydes that allows the preparation of  $\alpha$ -hydroxyketones.



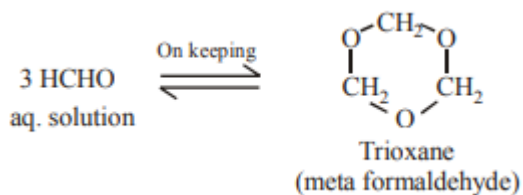
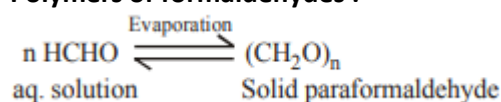
**Claisen Schmidt condensation:** When a base-catalyzed cross aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or a ketone is called Claisen Schmidt condensation or simply Claisen reaction. For example, Benzaldehyde reacts with Acetaldehyde to form 3-Phenylprop-2-en-1-al (Cinnamaldehyde).



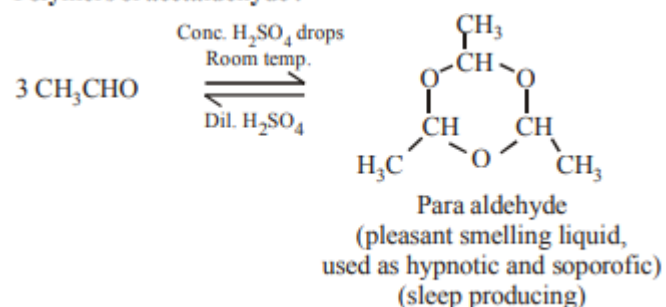
### Condensation products of acetone :



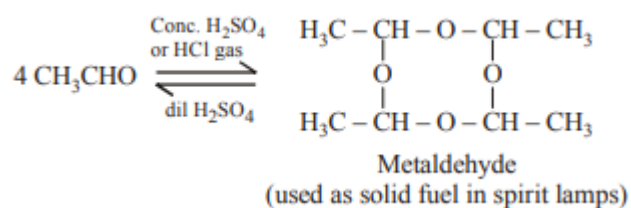
### Polymers of formaldehydes :



### Polymers of acetaldehyde :







**Electrophilic substitution reaction:**

Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group.

