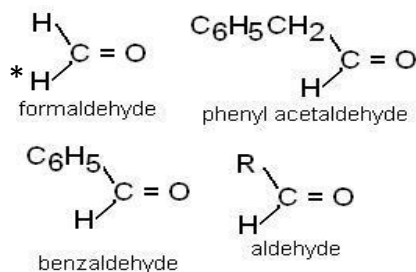
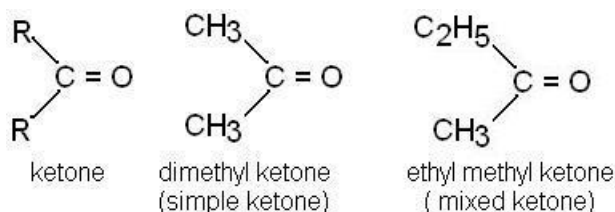


## ALDEHYDES AND KETONES

- In aldehydes, the carbonyl group is linked to either two hydrogen atom or one hydrogen atom and one carbon containing group such as alkyl, aryl or aralkyl group Examples

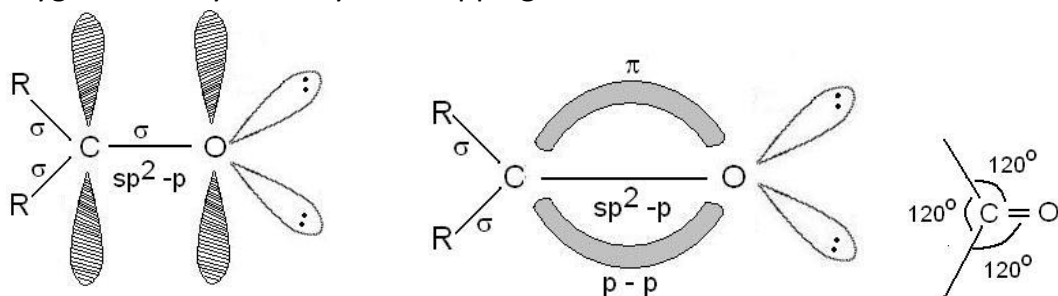


- In ketones, the carbonyl group is linked to two carbon containing groups which may be same or different alkyl, aryl group. If two R and R' groups are same, the ketone is called simple or symmetrical ketone and if R and R' are different, then ketone is known as mixed or an unsymmetrical ketone.



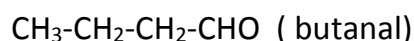
### STRUCTURE

- Carbonyl carbon of both aldehyde and ketones is  $sp^2$  – hybridised, One of the three  $sp^2$  hybridised orbital get involved in  $\sigma$ - bond formation with half –filled p-orbital of oxygen atom whereas rest of the two are consumed in  $\sigma$ -bond formation with hydrogen and carbon depending on the structure of aldehyde or ketone.
- Unhybridised p-orbital of carbonyl carbon form  $\pi$ -bond with another half-filled p-orbital of oxygen atom by sideways overlapping.

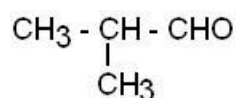


### ISOMERISM IN ALDEHYDES AND KETONES

(a) Chain isomerism: Aldehydes ( with 4 or more carbon atoms) and ketone ( with 5 or more carbon atoms) show chain isomerism. Example

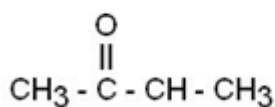
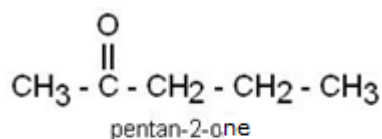


## ALDEHYDES AND KETONE



2-methylpropanal

ii)  $\text{C}_5\text{H}_{10}\text{O}$



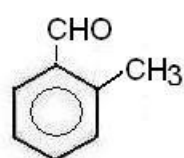
3-methylbutan-2-one

(b) Position isomerism: aliphatic aldehydes do not show position isomerism, because  $-\text{CHO}$  group is always present at the end of carbon chain.

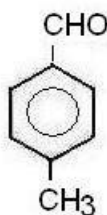
Aromatic aldehyde show position isomerism. Example

(c) Metamerism: Higher ketones show metamerism due to presence of different alkyl groups attached to the same functional group

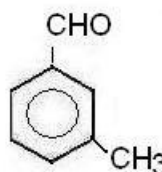
$\text{C}_5\text{H}_{10}\text{O}$



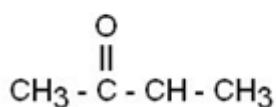
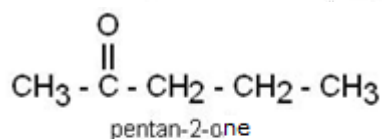
2-methylbenzaldehyde or o-tolualdehyde



4-methylbenzaldehyde or p-tolualdehyde



3-methylbenzaldehyde or m-tolualdehyde

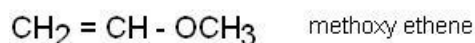
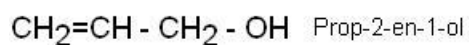
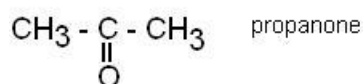
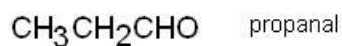


3-methylbutan-2-one

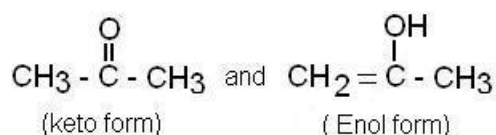
(d) Functional isomerism : Aldehydes and ketones show functional isomerism in them. In addition, they are also related to alcohols, ethers and other cyclic compounds. Example

$\text{C}_3\text{H}_6\text{O}$

## ALDEHYDES AND KETONE



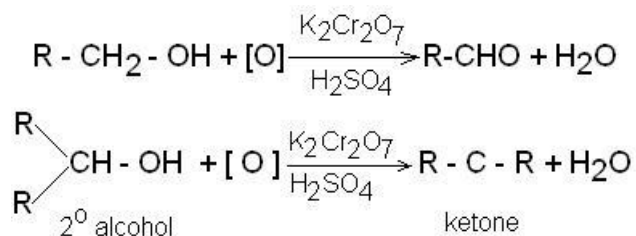
(e) Tautomerism : Aldehydes and ketones also show tautomerism



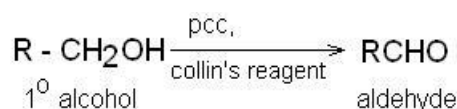
### GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

#### 1. From alcohol

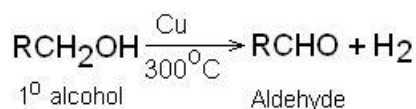
##### (i) Oxidation of alcohol



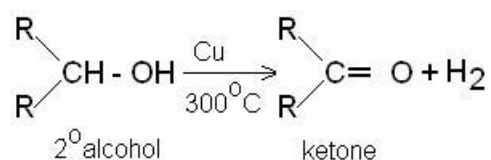
- Since the oxidizing agent used in the above reactions is a strong oxidizing agent, it oxidizes aldehydes and ketone further to carboxylic acids
- To prevent further oxidation, a mild oxidizing agent such as pyridinium chlorochromate (pcc),  $\text{CrO}_3 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$  or  $\text{CrO}_3\text{NH}^+\text{CrO}_3\text{Cl}^-$  are used Collin's reagent [  $(\text{C}_5\text{H}_5\text{N})_2 \cdot \text{CrO}_3$  ] can also used.



##### (ii) Catalytic dehydrogenation of alcohols

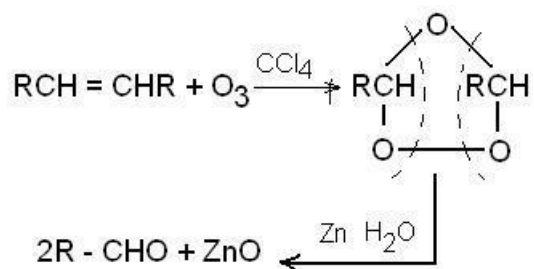


## ALDEHYDES AND KETONE

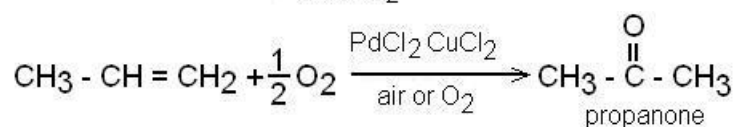
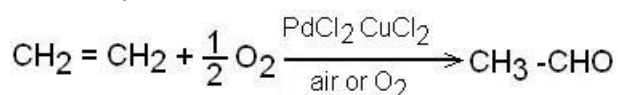


### 2. From alkenes

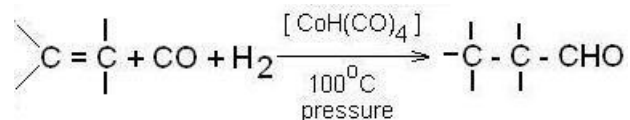
(i) Reductive ozonolysis of alkenes.



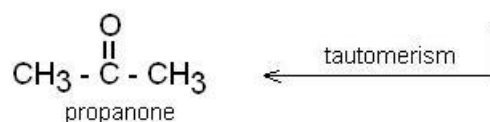
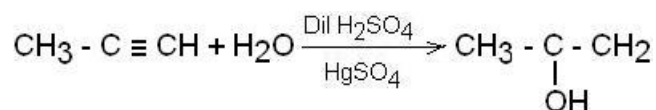
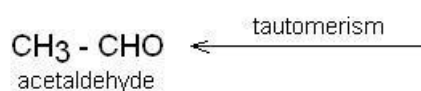
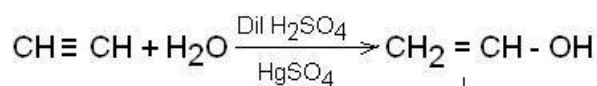
(ii) Wacker process.



(iii) OXO process [Carbonylation / Hydroformylation]



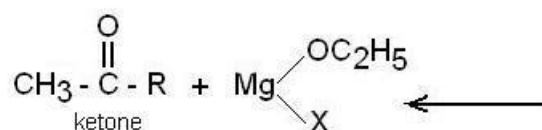
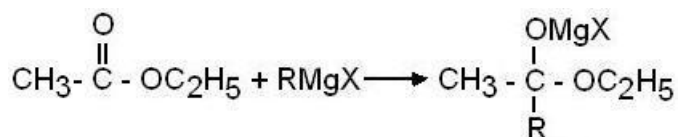
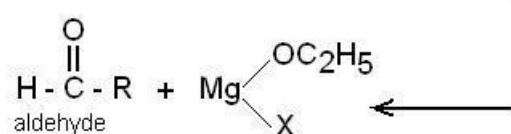
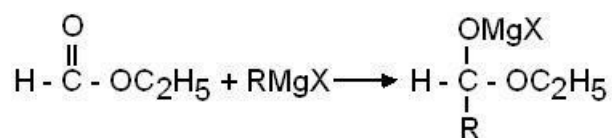
### 3. From alkynes



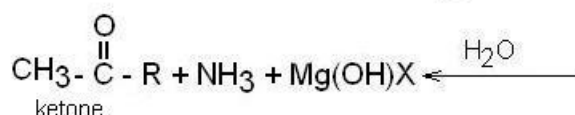
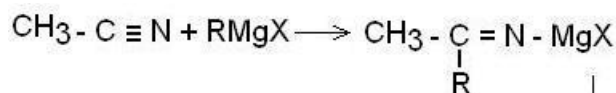
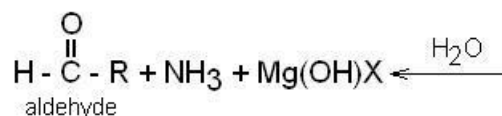
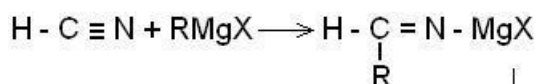
### 4. From Grignard reagent

(1) By addition to ester

## ALDEHYDES AND KETONE

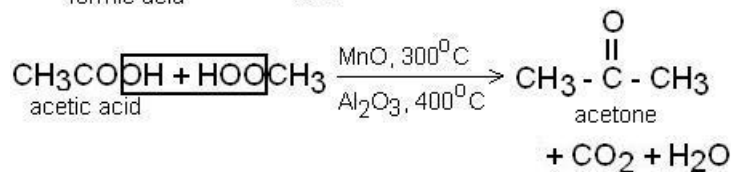
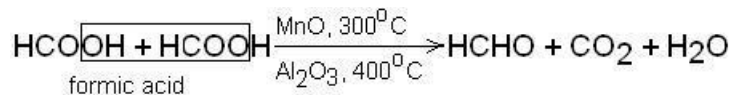


(iii) By addition to nitriles



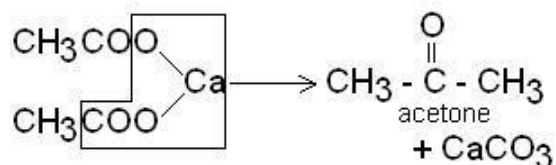
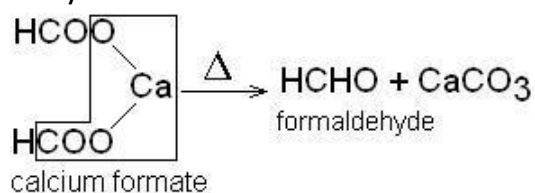
5. From carboxylic acids

(i) Catalytic decomposition of carboxylic acid.



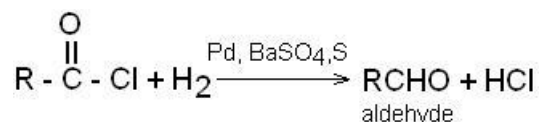
## ALDEHYDES AND KETONE

(ii) From calcium salt of carboxylic acids



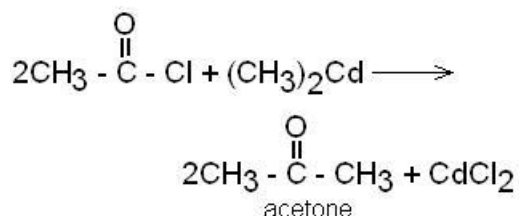
6. From derivatives of carboxylic acids

(i) Reduction of acid chlorides ( Rosenmund's reaction)

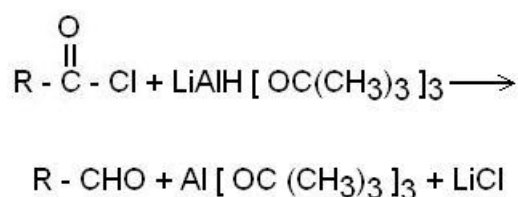


- Above reaction is known as Rosenmund's reduction and is applicable for preparation of aldehydes
- BaSO<sub>4</sub>, sulphur act as poison for Pd catalyst and prevents reduction of RCHO into RCH<sub>2</sub>OH

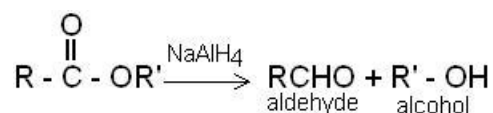
(ii) Reduction of acid chloride with dialkyl cadmium.



Reduction of acid chloride into ester can also be carried out by lithium tri-*t*-butoxy aluminium hydride, LiAlH[OC(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>

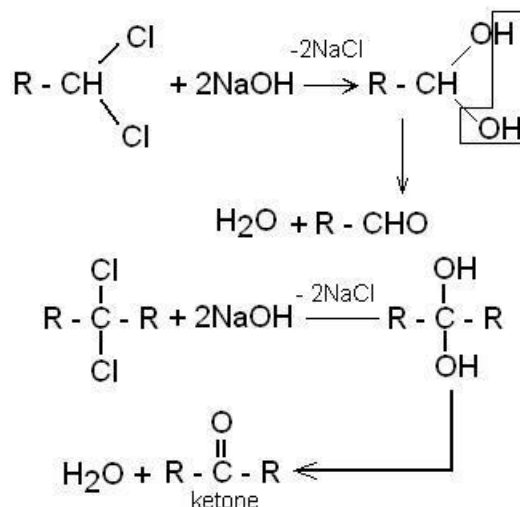


(iii) Reduction of esters



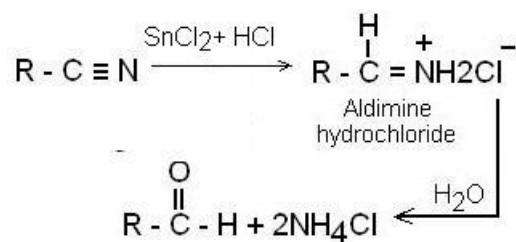
# ALDEHYDES AND KETONE

## 7. From gem-dihalides by hydrolysis

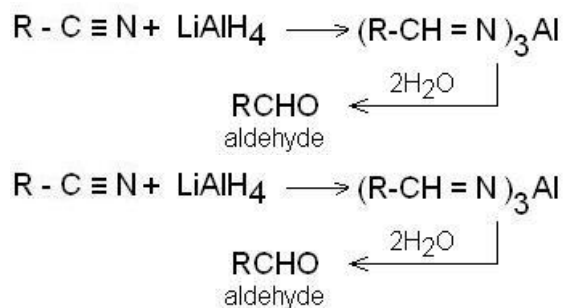


## 8. From nitriles by reduction

### (i) Stephen's reduction.

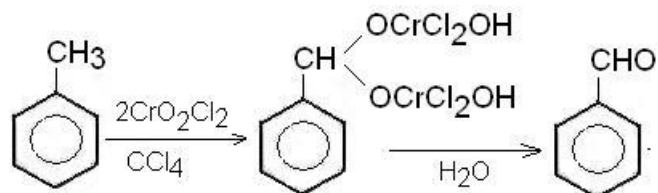


### (ii) Reduction with $\text{LiAlH}_4$



## 9. Preparation of aromatic carbonyl compounds.

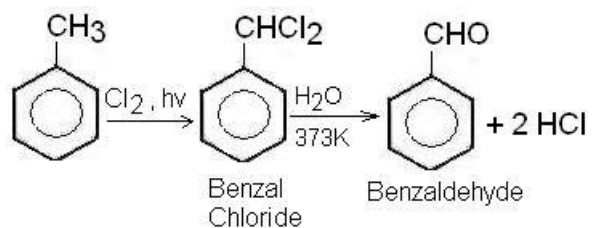
### (i)



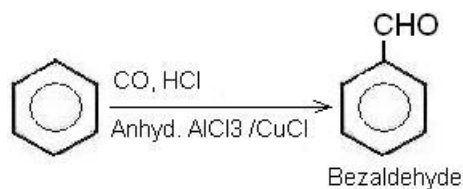
This is known as Etard reaction

## ALDEHYDES AND KETONE

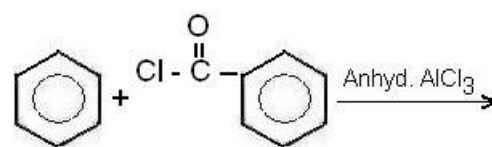
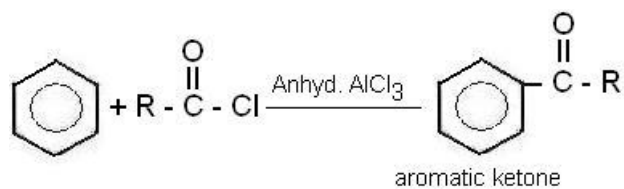
- (ii) By side chain chlorination followed by hydrolysis



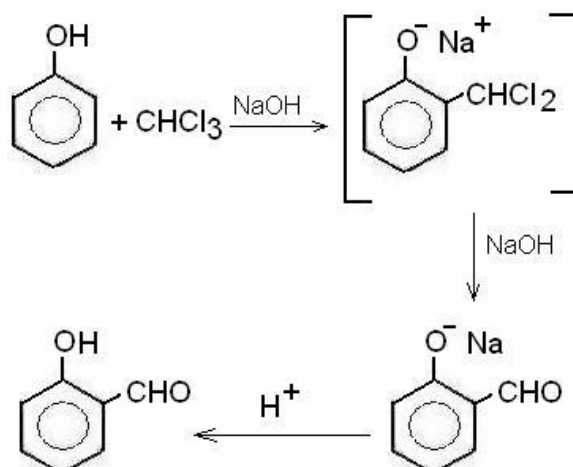
- (iii) Gatterman – Koch reaction



- (iv) Friedel Craft Acylation



- (v) Reimer – Tiemann reaction





# ALDEHYDES AND KETONE

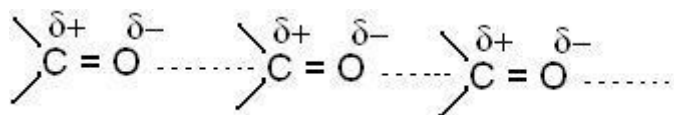
## PHYSICAL PROPERTIES OF ALDEHYDES AND KETONE

### 1. Physical state

- Lower members of aldehydes and ketones (upto  $C_{10}$ ) are colourless volatile liquids except formaldehyde which is gas at ordinary temperature
- Higher members of aldehyde and ketones are solids with fruity odour
- Lower aldehydes have unplesent odour but ketones posses pleasant smell

### 2. Boiling point

- Boiling point of aldehyde and ketones is slightly lower than corresponding alcohol due to lack of hydrogen bonding. However their boiling point is slightly higher than that of corresponding non-polar hydrocarbon or weakly polar ether. This may attributed to reason that aldehydes and ketones are polar compounds and thus possess intermolecular dipole-dipole interaction



- Among isomeric aldehydes and ketones, boiling point of ketones is slightly higher than that of aldehydes due to the presence of two electron donating alkyl groups making them more polar.

### 3. Solubility

- Lower members of aldehydes and ketones ( upto  $C_4$ ) are soluble in water due to H-bonding between polar carbonyl group and water.
- However, solubility decreases with increase in molecular weight
- Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to large benzene ring. However all carbonyl compounds are fairly soluble in organic solvents.

## RELATIVE REACTIVITY OF ALDEHYDES AND KETONES

Aldehydes are more reactive than ketones on account of the following facts:

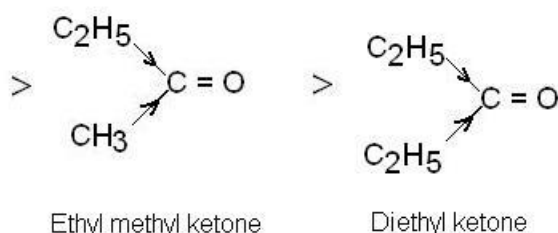
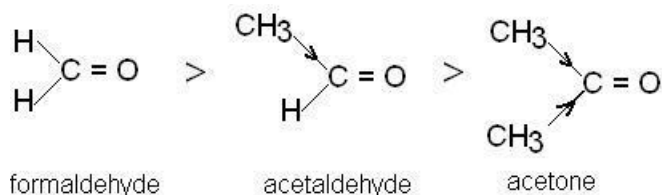
### (a) Aliphatic aldehydes and ketones

#### (i) Inductive effect:

The reactivity of the carbonyl group towards the addition reaction depends upon the magnitude of the positive charge on the carbonyl carbon atom. Hence, any substituent that increases the positive charge on the carbonyl carbon must increase its reactivity towards addition reactions. The introduction of negative group ( -I effect) increases the reactivity, while introduction of alkyl group (+I effect) decreases the reactivity, therefore, greater the number of alkyl groups attached to the carbonyl

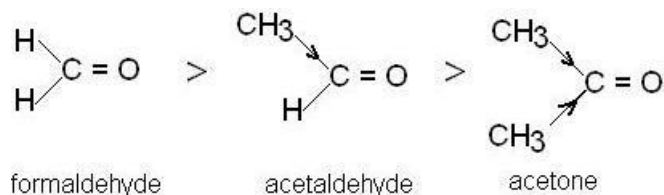
## ALDEHYDES AND KETONE

group and hence, lower is its reactivity towards nucleophilic addition reactions. Thus, the following decreasing order of reactivity is observed



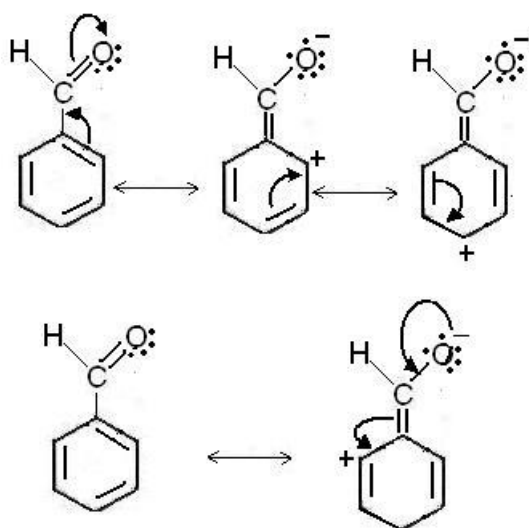
### (ii) Steric effect

- In formaldehyde there is no alkyl group while in all other aldehyde there is one alkyl group so here the nucleophile attack is relatively more easy but in ketones there are two alkyl groups attached to carbonyl group and these causes hinderance, to the attacking group. This factor is called steric hinderance (crowding). In other words the hindrance increases, the reactivity decreases accordingly. Thus order of reactivity is



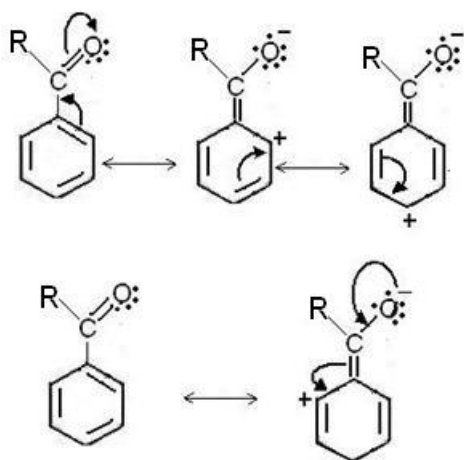
### (b) Aromatic aldehydes and ketones

- In general, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones. It is due electron releasing resonance effect of bezene ring

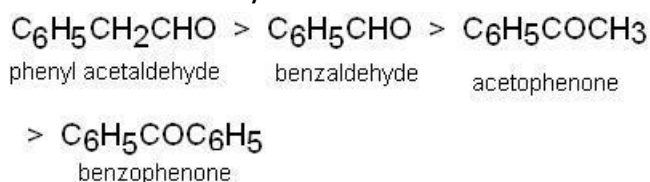


## ALDEHYDES AND KETONE

- Due to electron withdrawing resonance effect (-R effect) of benzene ring, the magnitude of positive charge on carbonyl group decreases and consequently it becomes less susceptible to nucleophilic attack.

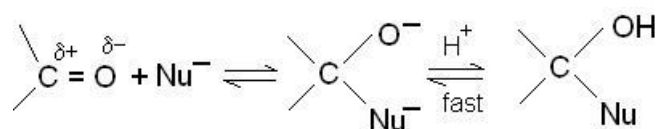


The order of reactivity of aromatic aldehydes and ketones is



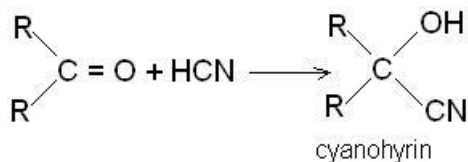
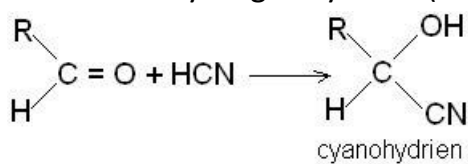
### CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

Nucleophilic addition reaction



In this reaction carbon atom of carbonyl group changes from  $sp^2$  to  $sp^3$  hybridised

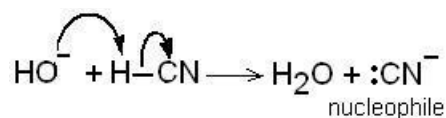
(i) Addition of hydrogen cyanide (HCN)



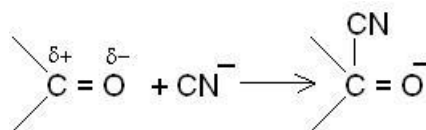
Mechanism

Step I : The hydrogen cyanide interacts with the base to form nucleophile

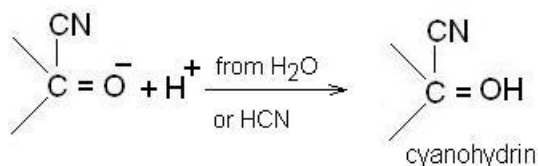
## ALDEHYDES AND KETONE



Step II : The nucleophile attacks the carbonyl carbon to form an anion

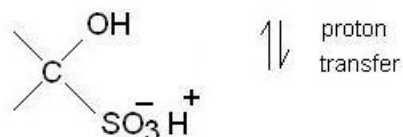
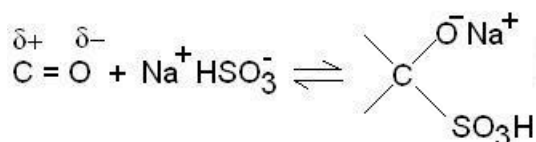


Step III: The proton from the solvent (usually water) combines with the anion to form cyanohydrin.

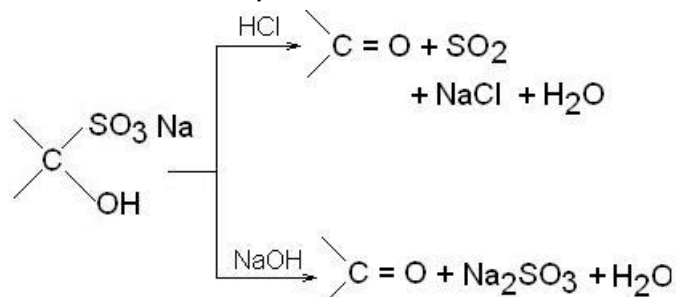


Cyanohydrins are formed by all aldehydes but in ketones, only acetone, butanone, 3-pentanone and pinacolone form cyanohydrins.

(ii) Addition of sodium bisulphate ( $\text{NaHSO}_4$ )

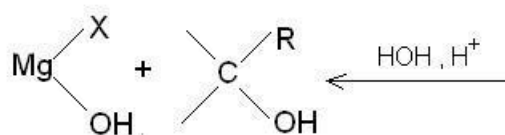
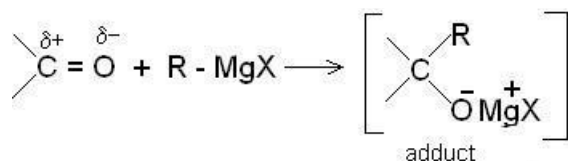


- All ketones do not undergo this reaction only methyl ketone form addition product with sodium bisulphate
- On reacting the crystalline solid bisulphate derivative with dilute HCl or alkali, these adducts decompose to regenerate the original aldehyde or ketones. Hence, this reaction is used in the separation and purification of aldehydes and ketones from non-carbonyl compounds.

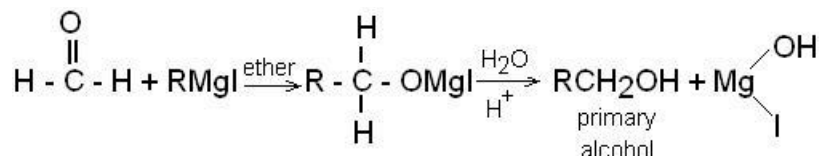


(iii) Addition of Grignard reagent

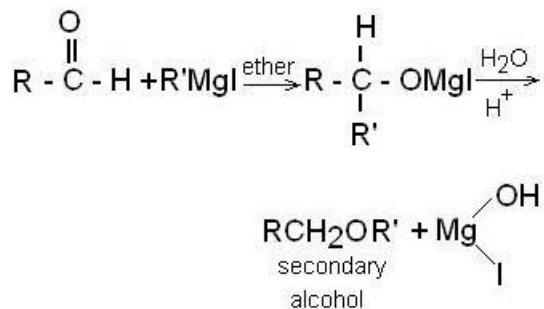
## ALDEHYDES AND KETONE



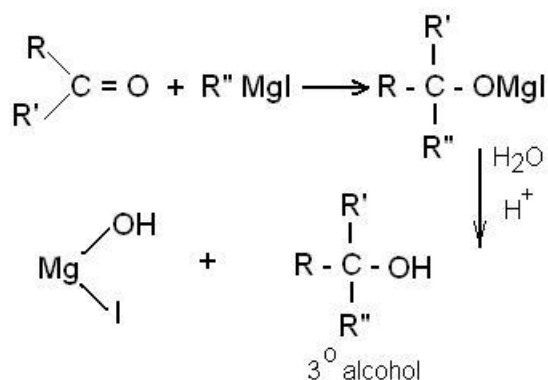
Formaldehyde form a primary alcohol



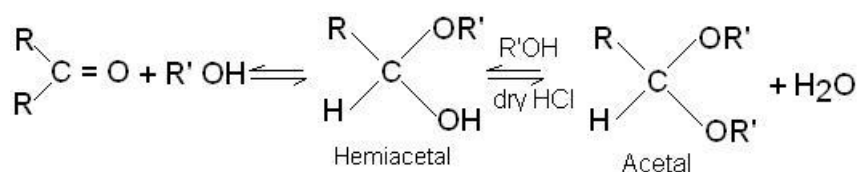
- Higher aldehydes give secondary alcohol



- Ketone give tertiary alcohols



(iv) Addition of alcohols

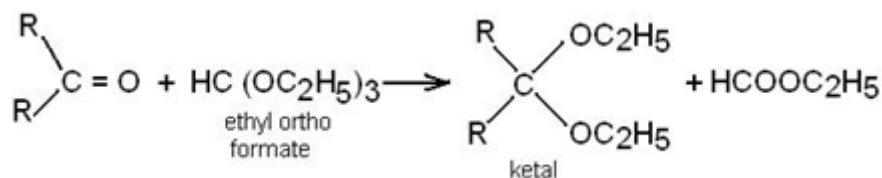


Dry HCl protonates the oxygen atom of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon and hence facilitating the nucleophilic attack by the alcohol

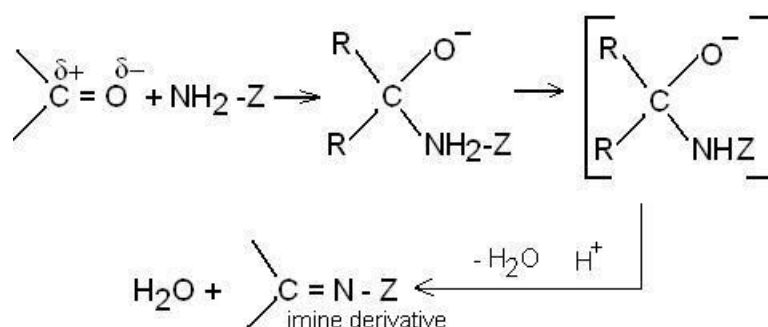
## ALDEHYDES AND KETONE

molecule. Dry HCl gas also absorbs the water produced in these reactions and thereby shifting equilibrium in forward direction.

Ketals can be prepared by treating the ketone with ethyl ortho formate



(v) Addition of ammonia derivative

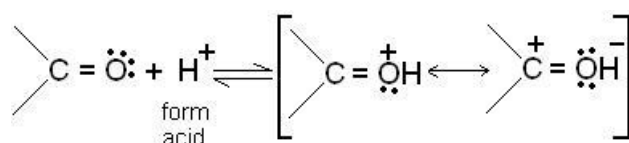


Z = OH, NH<sub>2</sub>, NHC<sub>6</sub>H<sub>5</sub>, NHCOCH<sub>2</sub> etc.

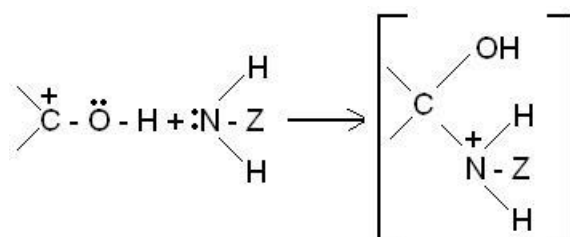
The reaction of ammonia derivatives to aldehydes and ketones is called by acids

Mechanism

Step I: In acidic medium, the carbonyl oxygen gets protonated.

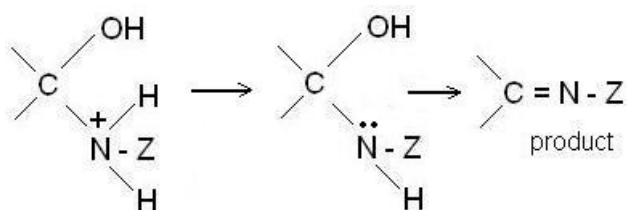


Step II : In ammonia derivatives, the nitrogen atom has a lone pair of electrons, which attack the positively charged carbonyl carbon and results in positive charge on nitrogen atom

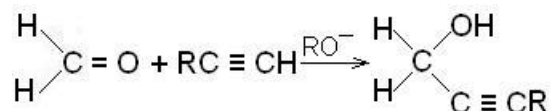


Step III : The unstable intermediate loses a proton, H<sup>+</sup> and water molecule to form stable product (imines)

## ALDEHYDES AND KETONE



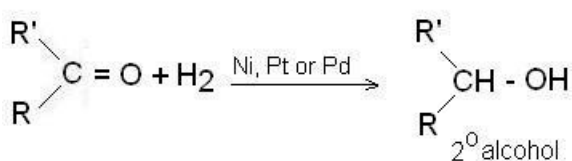
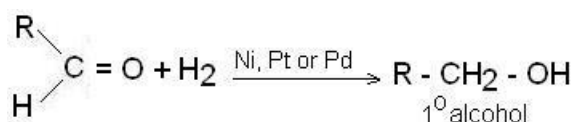
(vi) Addition of alkynes



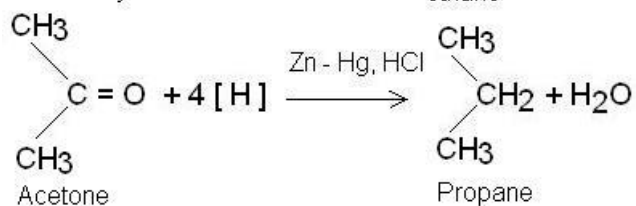
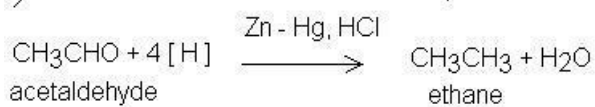
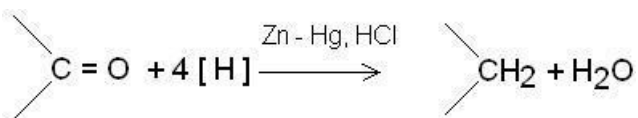
This reaction is also known as ethinylation

## 2. Reduction reactions

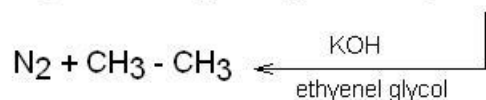
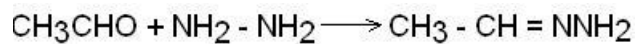
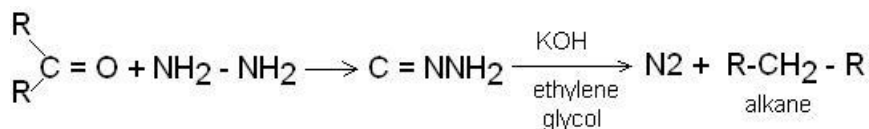
I. Catalytic reduction to alcohol



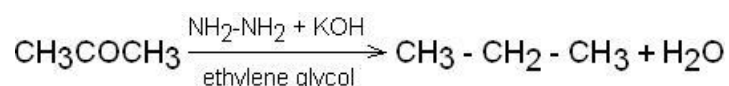
II. Clemmensen reduction



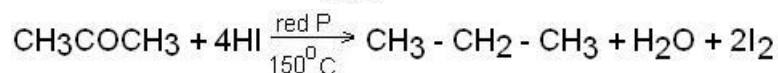
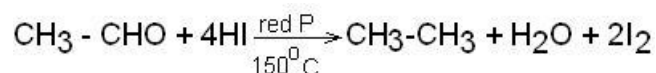
III. Wolf-Kishner reduction



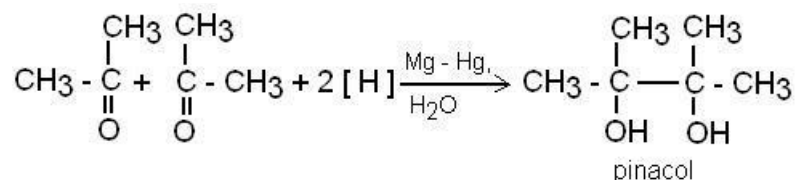
## ALDEHYDES AND KETONE



### IV. Reduction with HI + P (red)

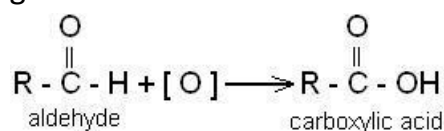


### V. Reduction to pinacols



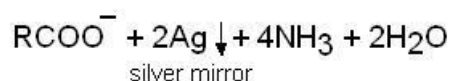
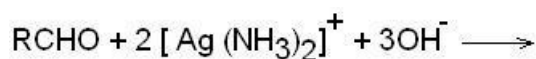
## 3. Oxidation reactions

### i. Oxidation with mild oxidizing agents



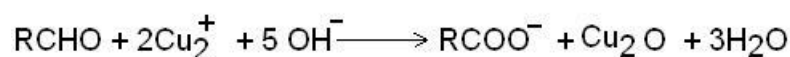
Ketones are not oxidized by mild oxidizing agents

(a) Aldehydes reduces Tollen's reagent to metallic silver which appears as a silver mirror on wall of test tube. Thus the reaction is also known as silver mirror test.



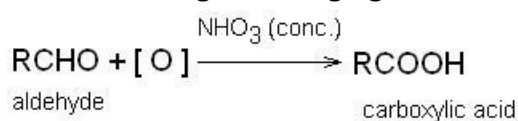
### (b) Reduction of Fehling's solution

Fehling's solution is an alkaline solution of  $\text{CuSO}_4$  mixed with Rochelle salt i.e. sodium potassium tartarate. Aldehydes reduces cupric ion ( $\text{Cu}^{2+}$ ) of Fehling's solution to cuprous ions ( $\text{Cu}^+$ ) to form red precipitate of cuprous oxide



Fehling's solution is reduced by aliphatic aldehydes only. Aromatic aldehydes and ketones so not give this reaction.

### ii. Oxidation with strong oxidizing agent



### iii. Haloform reaction

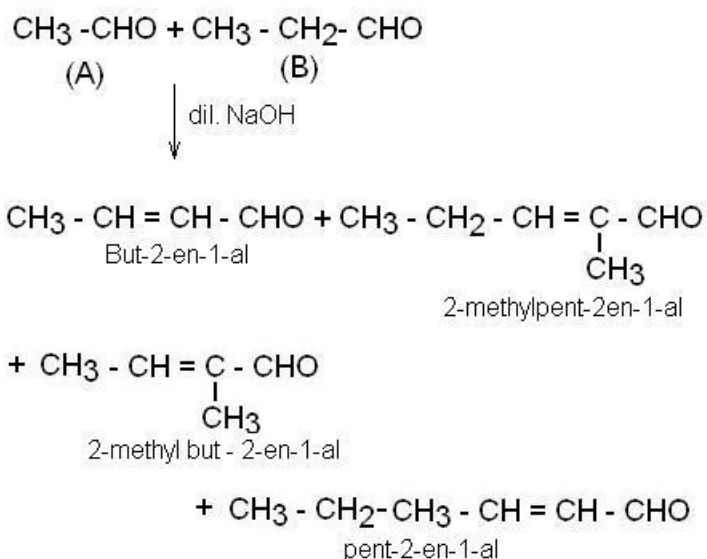




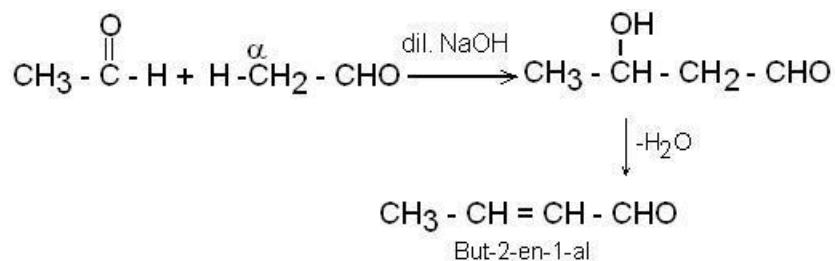
## ALDEHYDES AND KETONE

Aldehyde or ketones which do not contain  $\alpha$ -hydrogen atom like formaldehyde (HCHO), benzaldehyde ( $C_6H_5CHO$ ) and benzophenone ( $C_6H_5COC_6H_5$ ) do not undergo aldol condensation.

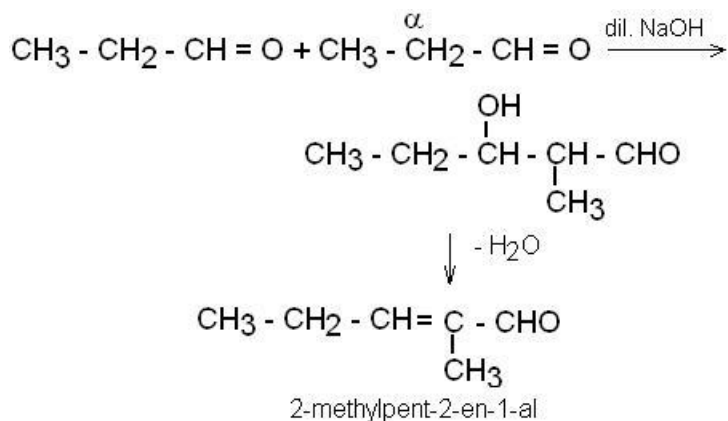
### (2) Cross aldol condensation



### # A-A Condensation

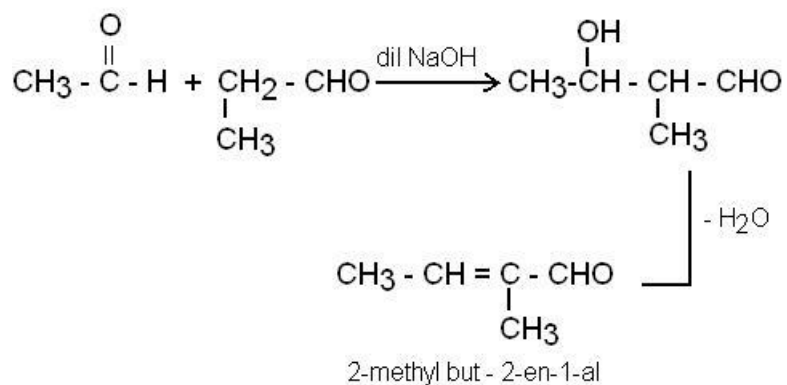


### # B-B Condensation

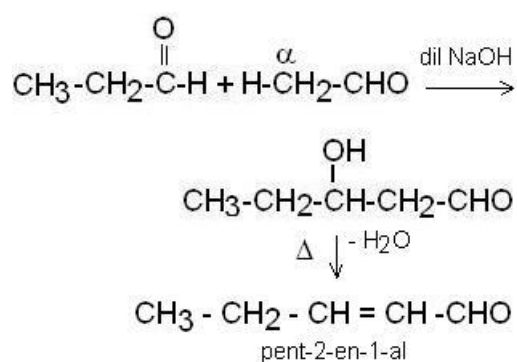


# ALDEHYDES AND KETONE

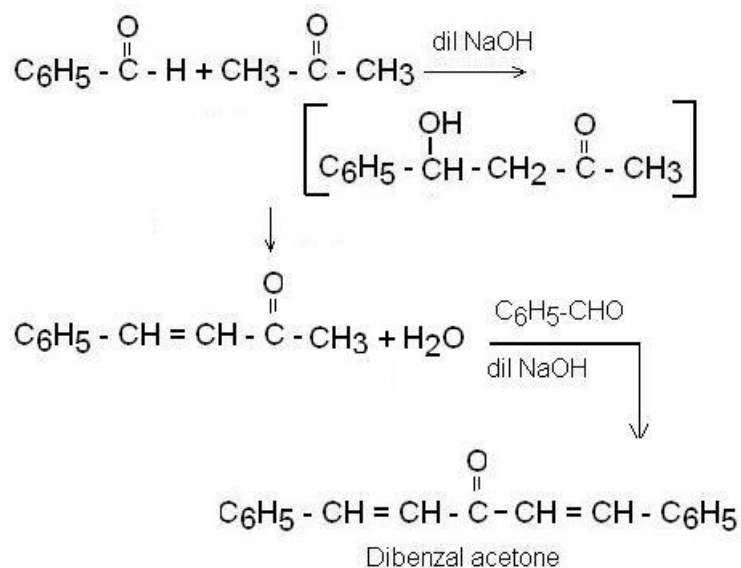
## # A-B Condensation



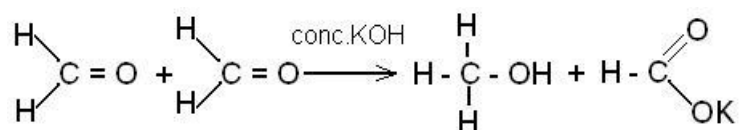
## # B-A Condensation



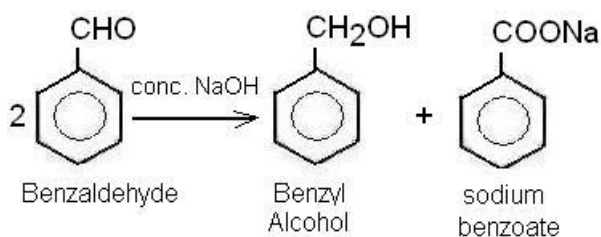
### (3) Claisen – Schmidt condensation



### 5. Cannizzaro reaction

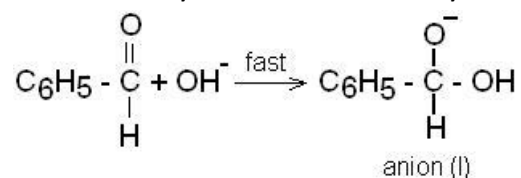


## ALDEHYDES AND KETONE

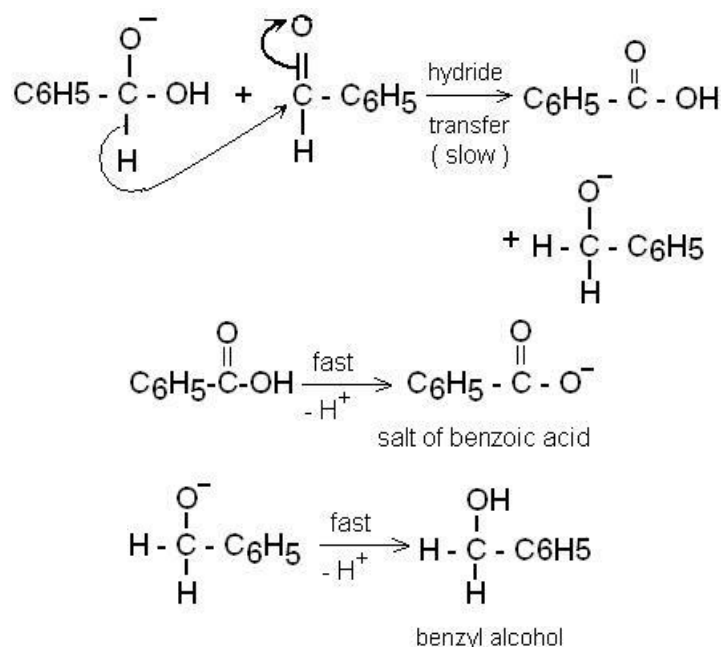


### Mechanism

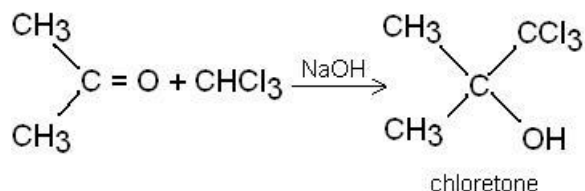
Step I : The  $\text{OH}^-$  ion attacks the carbonyl carbon to form hydroxyl alkoxide



Step II : Anion (I) acts as hydride ion donor to the second molecule of aldehyde. In the final step of the reaction, the acid and the alkoxide ion transfer  $\text{H}^+$  to acquire stability.

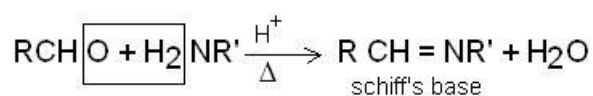


### 6. Reaction with chloroform

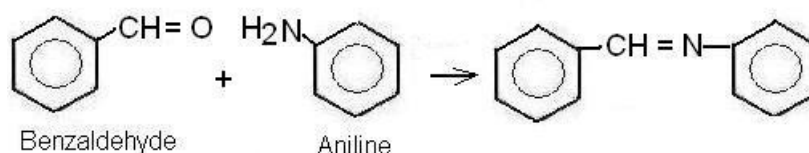


Chloroform is used as hypnotic.

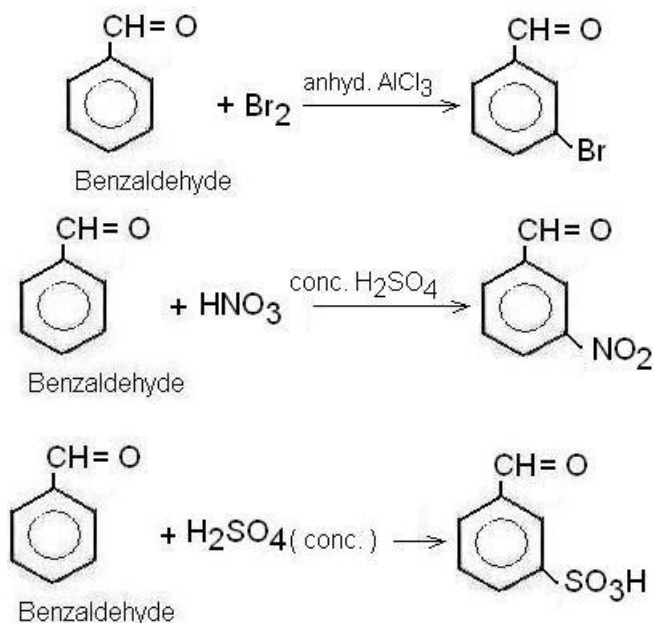
### 7. Reaction with primary amine



## ALDEHYDES AND KETONE



### 8. Electrophilic substitution reaction of aromatic carbonyl compounds



### USES OF ALDEHYDES AND KETONES

#### (a) Uses of formaldehyde

- The 40% solution of formaldehyde in water ( formaline) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens
- It is used for silvering of mirrors
- It is used for making synthetic plastics, like Bakelite, urea- formaldehyde resin etc

#### (b) Uses of acetaldehyde

- It is used in preparation of acetic acid, dyes, drugs, etc
- As an antiseptic inhalant in nose troubles

#### (c) Uses of benzaldehyde

- As flavouring agent in perfume industry
- In manufacture of dyes.

#### (d) Uses of acetone

- As a solvent for cellulose acetate, resin etc.
- As a nailpolish remover
- In the preparation of an artificial scent and synthetic rubber