



## **CLASSROOM STUDY PACKAGE**

# **CHEMISTRY**

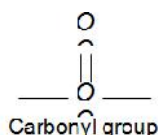
**ALDEHYDES AND KETONES**

**JEE EXPERT**

# ALDEHYDES AND KETONES

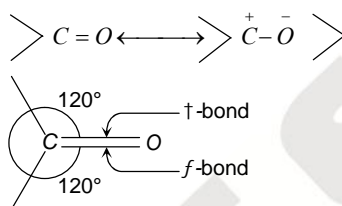
## Introduction

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



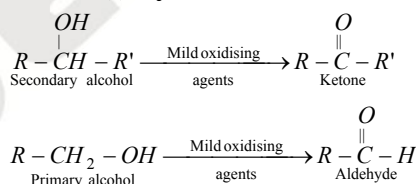
Both aldehyde and ketones possess the same general formula  $C_nH_{2n}O$ .

**Structure :** Carbonyl carbon atom is joined to three atoms by sigma bonds. Since these bonds utilise  $sp^2$ -orbitals, they lie in the same plane and are  $120^\circ$  apart. The carbon-oxygen double bond is different than carbon-carbon double bond. Since, oxygen is more electronegative, the electrons of the bond are attracted towards oxygen. Consequently, oxygen attains a partial negative charge and carbon a partial positive charge making the bond polar. The high values of dipole moment,  $\overset{+}{C} = \overset{-}{O}$  (2.3 – 2.8D) cannot be explained only on the basis of inductive effect and thus, it is proposed that carbonyl group is a resonance hybrid of the following two structures.



## Preparation of carbonyl compounds

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



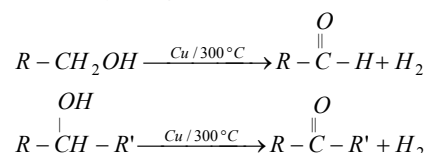
Mild oxidising agents are

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

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

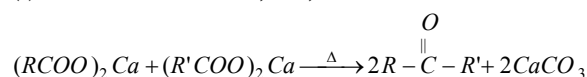
□ The yield of aldehydes is usually low by this methods. The allylic alcohols can be converted to aldehydes by treating with oxidising agent pyridinium chloro-chromate ( $C_5H_5NH^+CrO_3Cl^-$ ). It is abbreviated as PCC and is called **Collin's reagent**. This reagent is used in non-aqueous solvents like  $CH_2Cl_2$  (dichloro methane). It is prepared by mixing pyridine,  $CrO_3$  and  $HCl$  in dichloromethane. This is a very good reagent because it checks the further oxidation of aldehydes to carboxylic acids and is suitable method for preparing  $\alpha,\beta$ -unsaturated aldehydes.

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



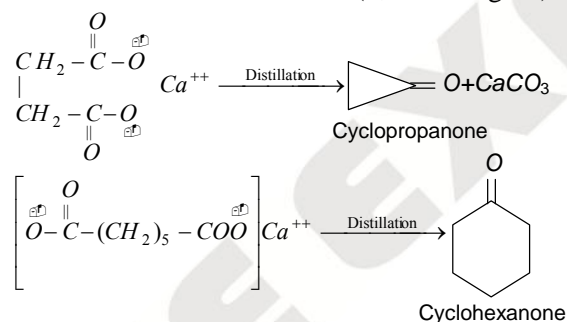
(2) **From carboxylic acids**

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



Thus in the product, one alkyl group comes from one carboxylic acid and other alkyl group from other carboxylic acid.

Calcium salts of dibasic acid (1, 4 and higher) on distillation give cyclic ketones.

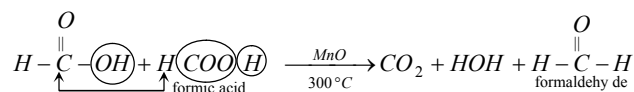


(ii) **Decarboxylation or Dehydration of acids by MnO/300°C.**

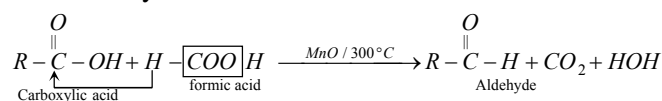
(a) This reaction takes place between two molecules of carboxylic acids. Both may be the same or different.

(b) If one of the carboxylic acids is  $HCOOH$  then this acid undergoes decarboxylation because this acid is the only monobasic acid which undergoes decarboxylation even in the absence of catalyst.

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



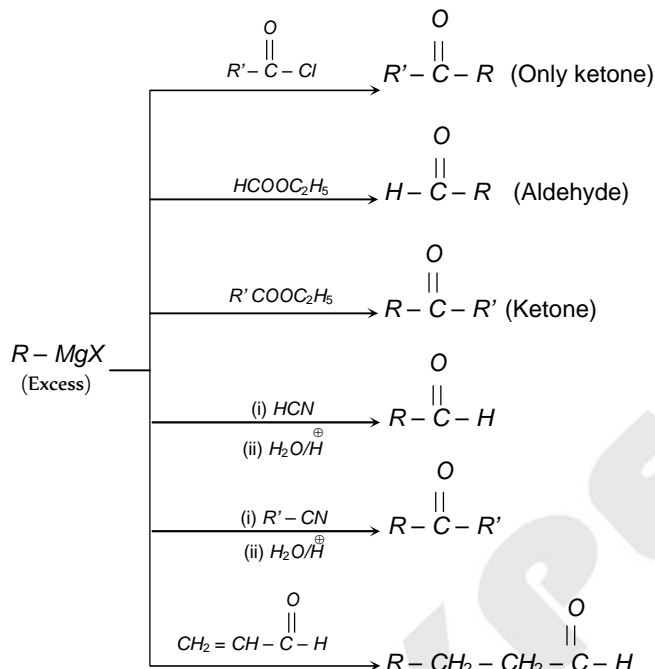
**Case II :** When only one molecule is formic acid.



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

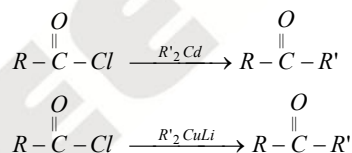


## (6) From Grignard reagents



## (7) From acid chloride

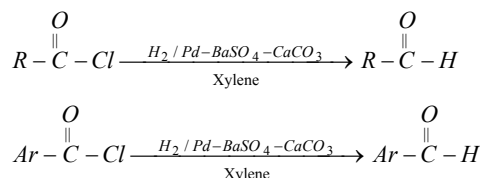
(i) Acid chlorides give nucleophilic substitution reaction with dialkyl cadmium and dialkyl lithium cuprate to give ketones. This is one of the most important method for the preparation of ketones from acid chlorides.



(Only used for the preparation of ketones)

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

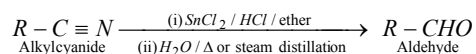
(ii) **Rosenmunds reduction** : This reduction takes place in the presence of Lindlars catalyst.



(Only used for aldehydes)

## (8) From cyanides

(i) **Stephen aldehyde synthesis** : Conversion of cyanides into aldehydes by partial reduction with  $\text{SnCl}_2 / \text{HCl}$ , followed by hydrolysis, is known as Stephens aldehyde synthesis.



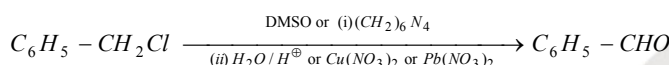
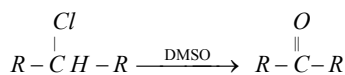
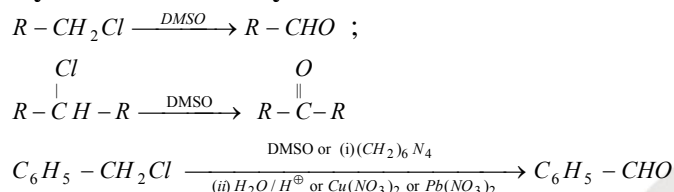
(Only used for aldehydes)

(9) **From vic diols**

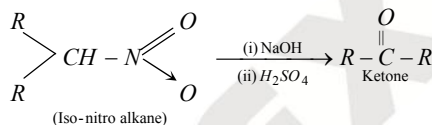
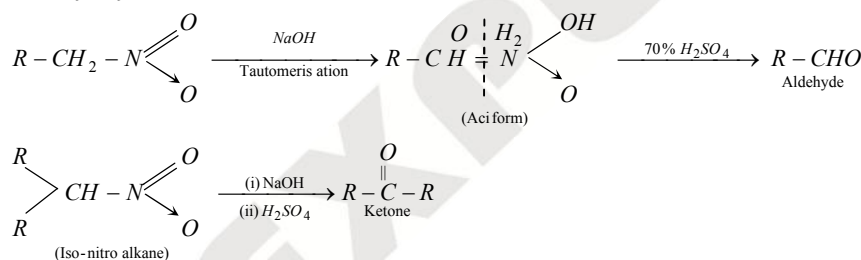
$$R-\overset{\overset{OH}{|}}{CH}-\underset{\underset{R}{|}}{C}-\overset{\overset{OH}{|}}{C}-R \xrightarrow{HIO_4} RCHO + R-\overset{\overset{O}{||}}{C}-R + H_2O$$

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

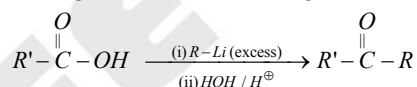
(10) **From Alkyl halides and benzyl halides**



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

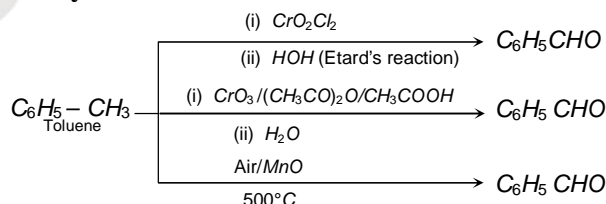


(12) **Reaction with excess of alkyl lithium :** Carboxylic acids react with excess of organo lithium compound to give lithium salt of gem diols which on hydrolysis give ketones.

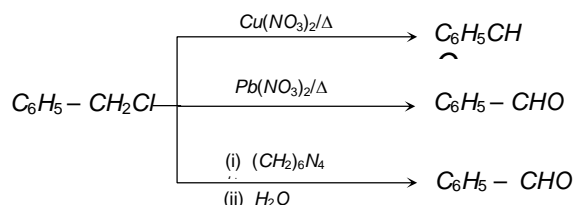


### Preparation of only aromatic carbonyl compounds :

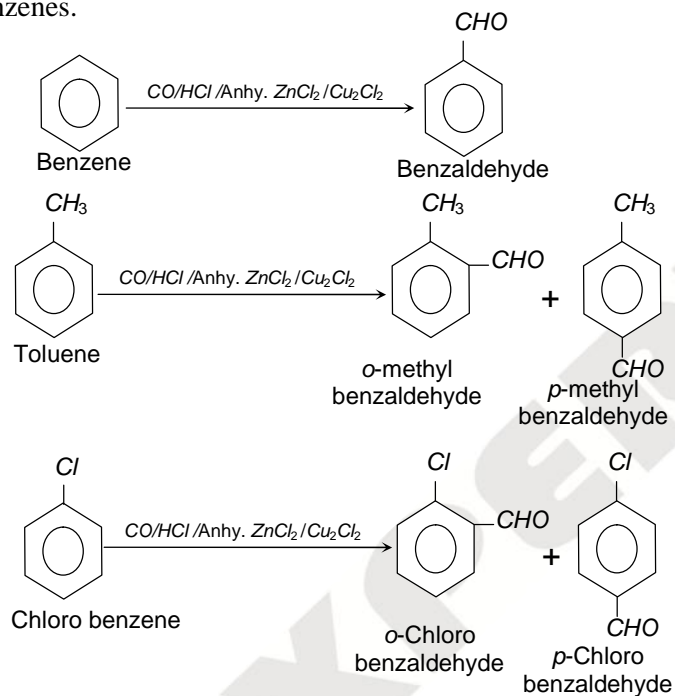
(1) **From methyl arenes**



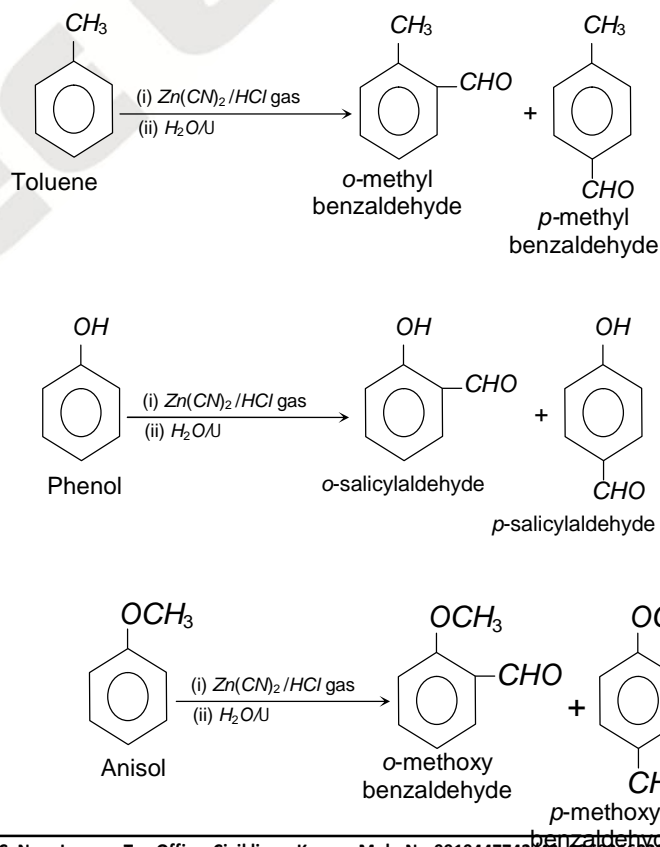
(2) **From chloro methyl**



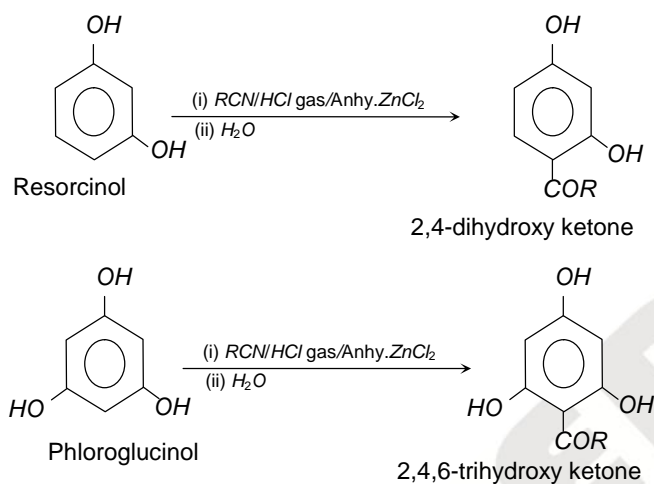
- (3) **Gattermann – Koch formylation** : This reaction is mainly given by aromatic hydrocarbons and halobenzenes.



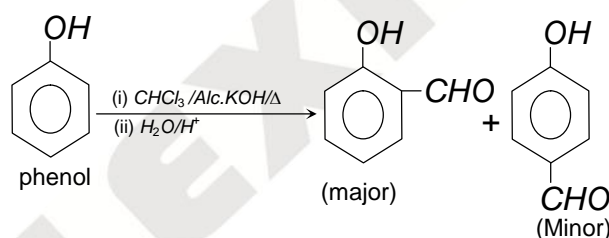
- (4) **Gattermann formylation** : This reaction is mainly given by alkyl benzenes, phenols and phenolic ethers.



- (5) **Houben – Hoesch reaction** : This reaction is given by di and polyhydric benzenes.

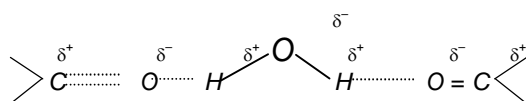


- (6) **Reimer – Tiemann reaction** : Phenol gives o- and p- hydroxy benzaldehyde in this reaction.



### Physical properties of carbonyl compounds

- Physical state** : Methanal is a pungent smell gas. Ethanal is a volatile liquid, boiling points 294 K. Other aldehydes and ketones containing up to eleven carbon atoms are colourless liquids while higher members are solids.
- Smell** : With the exception of lower aldehydes which have unpleasant odours, aldehydes and ketones have generally pleasant smell. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones have been used in blending of perfumes and flavouring agents.
- Solubility** : Aldehydes and ketones upto four carbon atoms are miscible with water. This is due to the presence of hydrogen bonding between the polar carbonyl group and water molecules as shown below :

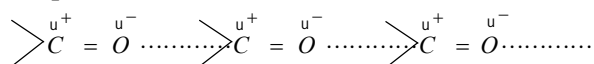


With the increase in the size of alkyl group, the solubility decreases and the compounds with more than four carbon atom are practically insoluble in water. All aldehydes and



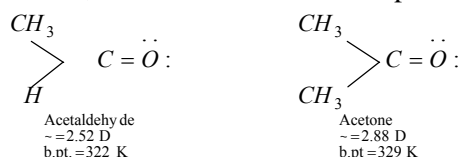
ketones are, however, soluble in organic solvents such as ether, alcohol, etc. The ketones are good solvents themselves.

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



However, these dipole-dipole interactions are weaker than the intermolecular hydrogen bonding in alcohols and carboxylic acids. Therefore, boiling points of aldehydes and ketones are relatively lower than the alcohols and carboxylic acids of comparable molecular masses.

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



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

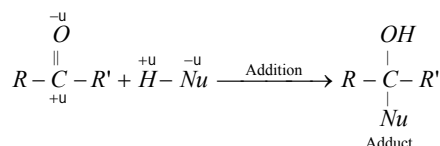
### Chemical properties of carbonyl compounds :

Carbonyl compounds give chemical reactions due to carbonyl group and  $\alpha$ -hydrogens. Chemical reactions of carbonyl compounds can be classified into following categories.

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

#### (1) Nucleophilic addition reactions

- (i) Carbonyl compounds give nucleophilic addition reaction with those reagents which on dissociation give electrophile as well as nucleophile.
- (ii) If nucleophile is weak then addition reaction is carried out in the presence of acid as catalyst.
- (iii) Product of addition reactions can be written as follows,

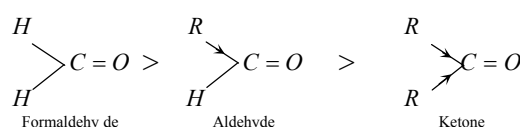


In addition reactions nucleophile adds on carbonyl carbon and electrophile on carbonyl oxygen to give adduct.

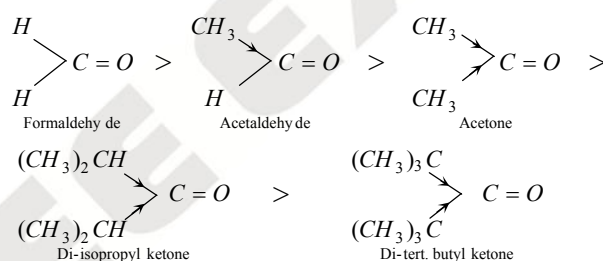
- (iv) **Relative reactivity of aldehydes and ketones :** Aldehydes and ketones readily undergo nucleophilic addition reactions. However, ketones are less reactive than aldehydes. This is

due to electronic and steric effects as explained below:

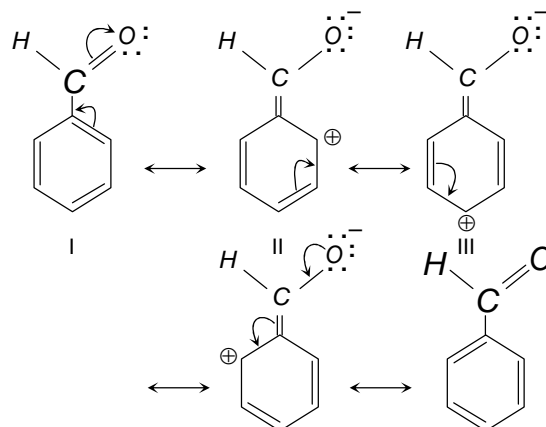
(a) Inductive effect : The relative reactivities of aldehydes and ketones in nucleophilic addition reactions may be attributed to the amount of positive charge on the carbon. A greater positive charge means a higher reactivity. If the positive charge is dispersed throughout the molecule, the carbonyl compound becomes more stable and its reactivity decreases. Now, alkyl group is an electron releasing group (+I inductive effect). Therefore, electron releasing power of two alkyl groups in ketones is more than that of one alkyl group in aldehyde. As a result, the electron deficiency of carbon atom in the carbonyl group is satisfied more in ketones than in aldehydes. Therefore, the reduced positive charge on carbon in case of ketones discourages the attack of nucleophiles. Hence ketones are less reactive than aldehydes. Formaldehyde with no alkyl groups is the most reactive of the aldehydes and ketones. Thus, the order of reactivity is:



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



In general, **aromatic aldehydes and ketones are less reactive than the corresponding aliphatic analogues**. For example, benzaldehyde is less reactive than aliphatic aldehydes. This can be easily understood from the resonating structures of benzaldehyde as shown below:

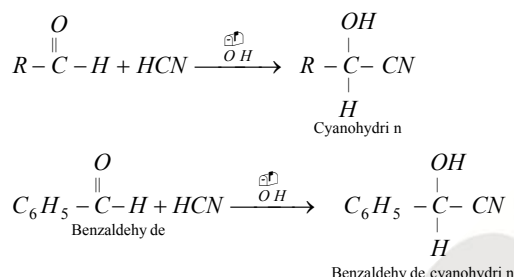


It is clear from the resonating structures that due to electron releasing resonance effect of the benzene ring, the magnitude of the positive charge on the carbonyl group decreases and consequently it becomes less susceptible to the nucleophilic attack. Thus, aromatic aldehydes and ketones are less reactive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

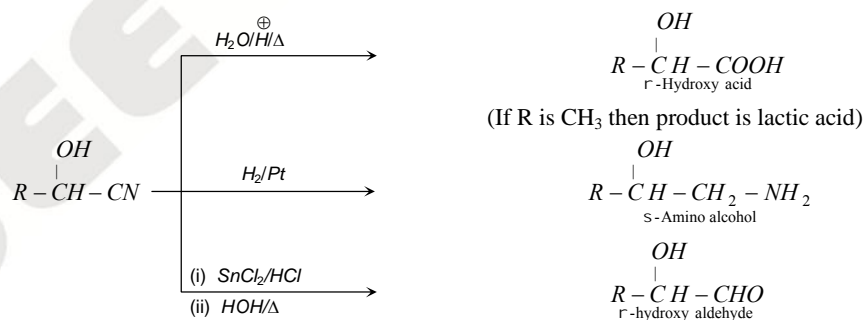


**Some important examples of nucleophilic addition reactions :**

#### Addition of HCN

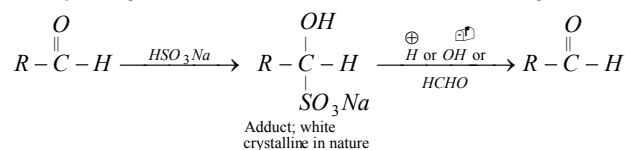


- Because HCN is a toxic gas, the best way to carry out this reaction is to generate hydrogen cyanide during the reaction by adding HCl to a mixture of the carbonyl compound and excess of NaCN.
- Benzophenone does not react with HCN.
- Except formaldehyde, all other aldehydes give optically active cyanohydrin (racemic mixture).
- This reaction is synthetically useful reaction for the preparation of  $\alpha$ -hydroxy acids,  $\beta$ -amino alcohols and  $\alpha$ -hydroxy aldehydes.

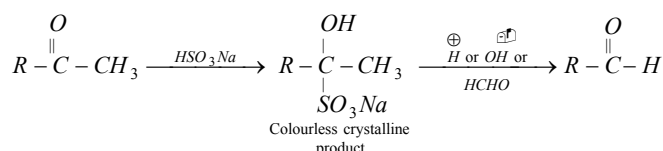


#### Addition of sodium bisulphite :

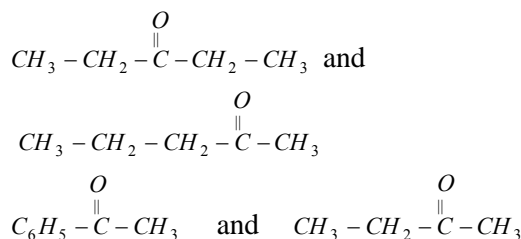
All types of aldehydes give addition reaction with this reagent.



Only aliphatic methyl ketones give addition reaction with sodium bisulphite.



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



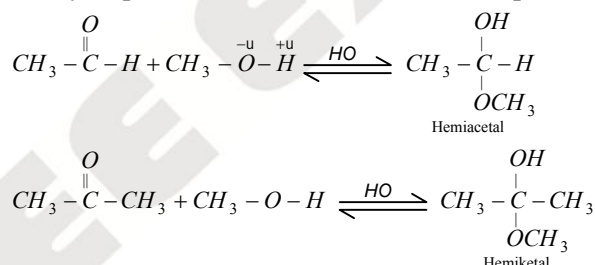
□ This reagent can be used for the separation of aldehydes and aliphatic methyl ketones from the mixture, e.g.



These two compounds can be separated from their mixture by the use of  $NaHSO_3$ . Higher aliphatic ketones and aromatic ketones do not react with  $NaHSO_3$ .

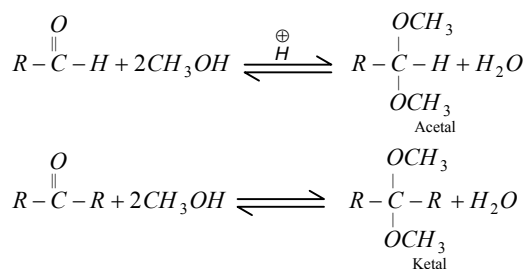
**Addition of alcohols :** Carbonyl compounds give addition reaction with alcohols. This reaction is catalysed by acid and base. Nature of product depends on the catalyst.

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

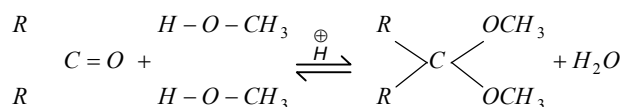


Hemiacetals and hemiketals are **α-alkoxy alcohols**.

**Case II : Addition catalysed by acid :** In the presence of an acid one equivalent of carbonyl compound reacts with two equivalents of alcohol. Product of the reaction is acetal (in case of aldehyde) or ketal (in case of ketone).



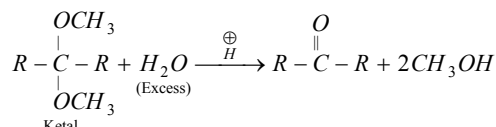
(i) Formation of acetals and ketals can be shown as follows:



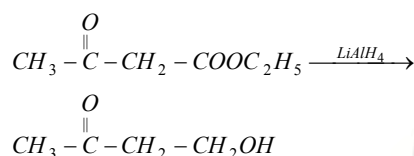
(ii) Acetals and ketals are gem dialkoxy compounds.

(iii) High yield of acetals or ketals are obtained if the water eliminated from the reaction is removed as it formed because the reaction is reversible.

(iv) Acetals and ketals can be transformed back to corresponding aldehyde or ketone in the presence of excess of water.

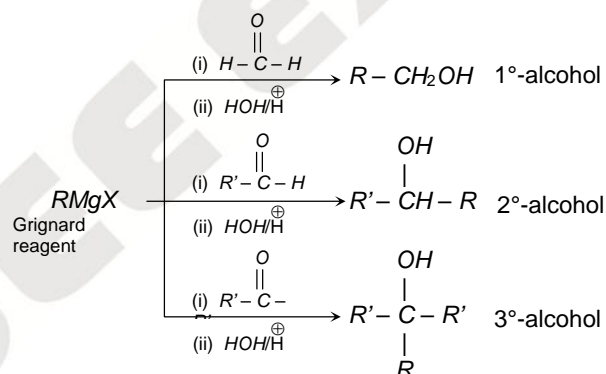


This reaction is very useful reaction for the protection of carbonyl group which can be deprotected by hydrolysis. Glycol is used for this purpose. Suppose we want to carry out the given conversion by  $LiAlH_4$ .

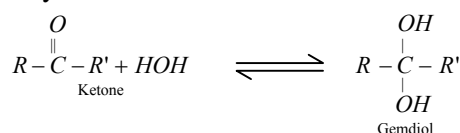


This can be achieved by protection of  $>C=O$  group and then by deprotection

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



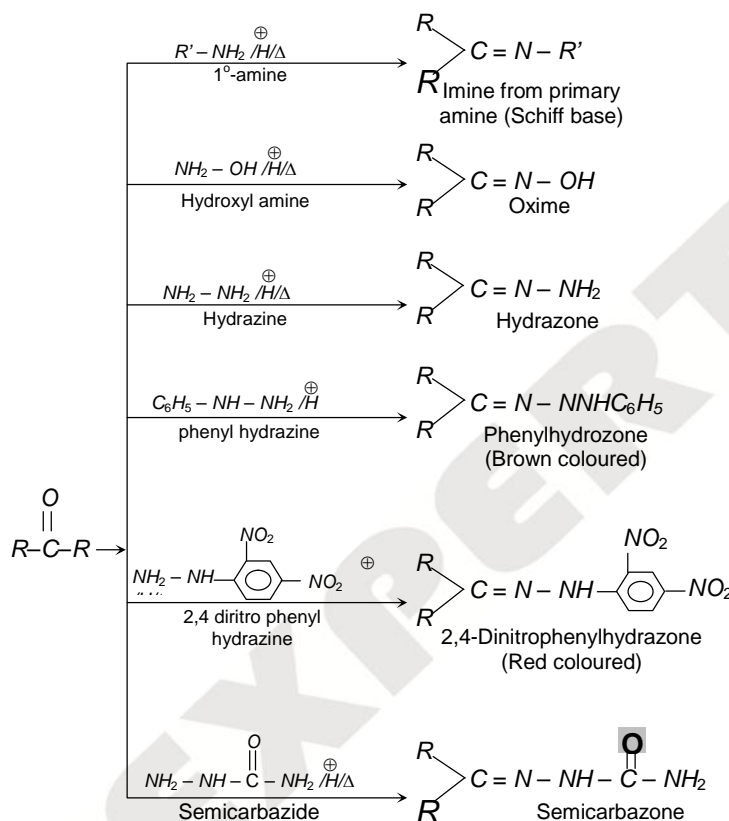
**Addition of water :** Carbonyl compounds react with water to give gem diols. This reaction is catalysed by acid. The reaction is reversible reaction.



Gem diols are highly unstable compounds hence equilibrium favours the backward direction. The extent to which an aldehyde or ketone is hydrated depends on the stability of gem diol. Stability of gem diols depend on the following factors:

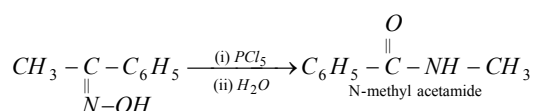
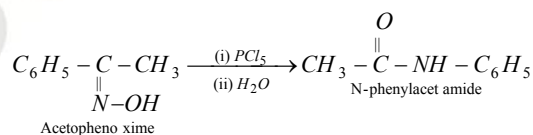
(i) Steric hindrance by +I group around  $\alpha$ -carbon decreases the stability of gem diols. +I



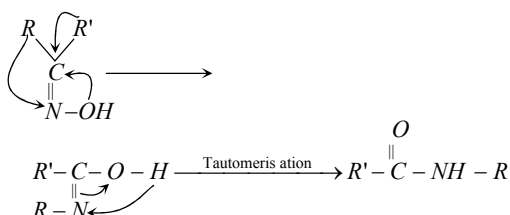


**Beckmann rearrangement :** Ketoxime when treated with acid at  $0^\circ\text{C}$  it undergoes rearrangement known as **Beckmann rearrangement**.

Thus acid catalysed conversion of ketoximes to N-substituted amides is called Beckmann rearrangement. Acid catalyst used are proton acids ( $H_2SO_4, HCl, H_3PO_4$ ) and Lewis acids ( $PCl_5, SOCl_2, PhSO_2Cl, RCOCl, SO_3, BF_3$  etc.)



In short product of the rearrangement can be obtained as follows:



(3) **Oxidation of carbonyl compounds**

(i) **Oxidation by mild oxidising agents** : Mild oxidising agents oxidise only aldehydes into carboxylic acids. They do not oxidise ketones. Main oxidising agents are:

(a) Fehling solution : It is a mixture of two Fehling solution: Fehling solution No. 1 : It contains  $CuSO_4$  solution and NaOH.

Fehling solution No. 2 : It contains sodium potassium tartrate. (Rochelle salt).

(b) Benedict's solution : This solution contains  $CuSO_4$ , NaOH and sodium or potassium citrate.

□ Reacting species of both solutions is  $Cu^{++}$  oxidation no. of Cu varies from 2 to 1.

□ These two oxidising agents oxidise only aliphatic aldehydes and have no effect on any other functional groups

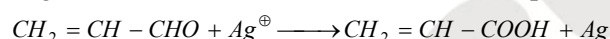
Benedict's solution and Fehling solutions are used as a reagent for the test of sugar (glucose) in blood sample.

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

□ It oxidises aliphatic as well as aromatic aldehydes.

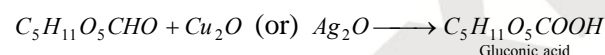


□ This reagent has no effect on carbon-carbon multiple bond.



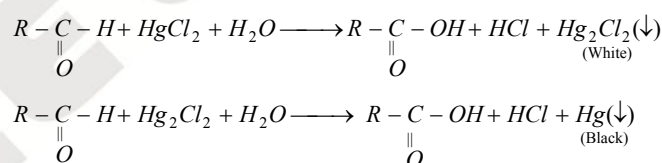
In this reaction the oxidation no. of Ag varies from +1 to 0.

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



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

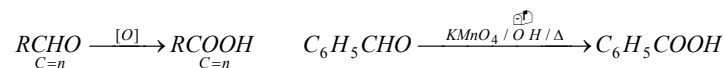
(d) Reaction with mercuric chloride solution :



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

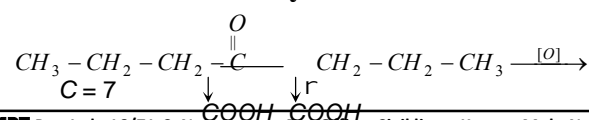
(ii) **Oxidation by strong oxidising agents** : Main strong oxidising agents are  $KMnO_4 / OH^{\oplus} / \Delta$ ,  $KMnO_4 / H^{\oplus} / \Delta$ ,  $K_2Cr_2O_7 / H^{\oplus} / \Delta$  and conc  $HNO_3 / \Delta$ . These agents oxidise aldehydes as well as ketones.

(a) Oxidation of aldehydes : Aldehydes are oxidised into corresponding acids.

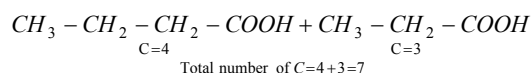


(b) Oxidation of ketones : Ketones undergo oxidation only in drastic conditions. During the oxidation of ketones there is breaking of carbon-carbon bond between  $\alpha$ -carbon and carbonyl carbon. In this process both carbons convert into carboxylic groups. This leads to the formation of two moles of monocarboxylic acids.

**Case I : Oxidation of symmetrical ketones**

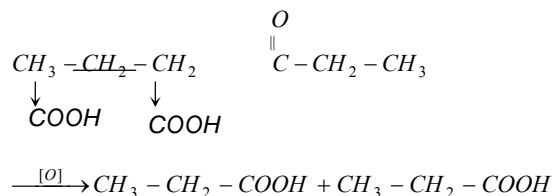




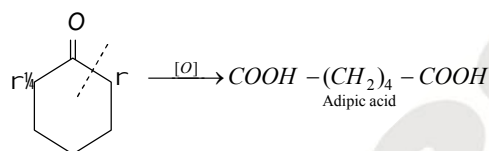


Thus number of carbons in any product is less than the number of carbons in ketone.

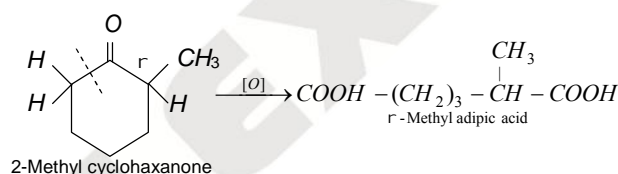
**Case II : Oxidation of unsymmetrical ketones :** In case of unsymmetrical ketones  $\alpha$ -carbon whose bond breaks always belongs to the alkyl group which has more number of carbons. This rule is known as Popoff's rule.



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

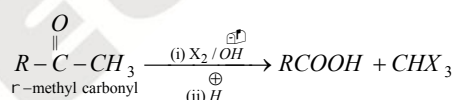


□ If both  $\alpha$ -carbons are not identical then bond breaking takes place between carbonyl carbon and the  $\alpha$ -carbon which has maximum number of hydrogens.



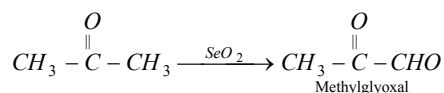
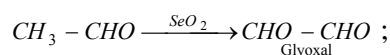
### (iii) Miscellaneous oxidation

#### (a) Haloform Reaction

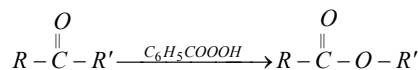


(b) Oxidation at  $\alpha$ -CH<sub>2</sub> or CH<sub>3</sub> by SeO<sub>2</sub> : SeO<sub>2</sub> oxidises  $\text{r} - \text{CH}_2 -$  group into keto group and  $\text{r} - \text{CH}_3 -$  group into aldehydic group.

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



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

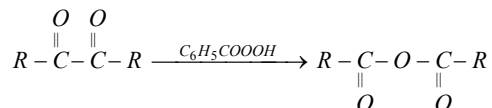


In case of aldehyde there is insertion of atomic oxygen (obtained from peracid) between

carbonyl carbon and hydrogen of carbonyl carbon.

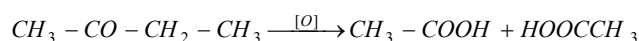
In case of ketone, insertion of oxygen takes place between carbonyl carbon and  $\alpha$ -carbon. Thus the product is ester. This is one of the most important reaction for the conversion of ketones into esters.

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

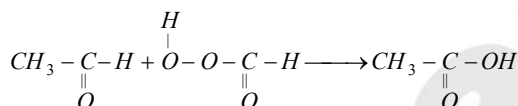
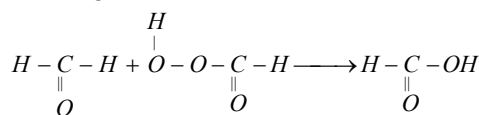


❑ **Popoff's rule** : Oxidation of unsymmetrical ketones largely take place in such a way that the smaller alkyl group remains attached to the CO group during the formation of two molecules of acids. This is known as Popoff's rule

Example :



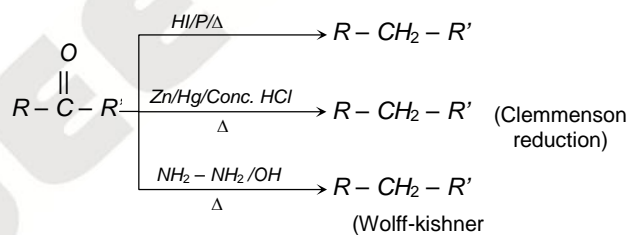
(d) Baeyer- villiger oxidation :



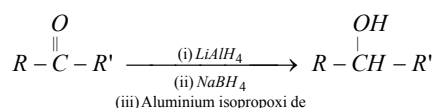
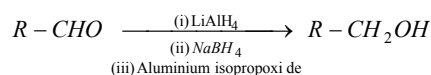
❑ Reaction will be held if the oxidising agent is performic acid.

#### (4) Reduction of carbonyl compounds

(i) **Reduction of  $\text{C}=\text{O}$  group into  $-\text{CH}_2-$  group** : Following three reagents reduce carbonyl group into  $-\text{CH}_2-$  groups: (a)  $\text{HI} / \text{P} / \Delta$  (b)  $\text{Zn} / \text{Hg} / \text{Conc. HCl}$  and (c)  $\text{NH}_3 - \text{NH}_2 / \text{OH}^-$ .

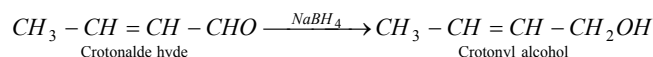


(ii) **Reduction of carbonyl compounds into hydroxy compounds :** Carbonyl group converts into  $-CHOH-$  group by  $LiAlH_4$ ,  $NaBH_4$ ,  $Na / C_2H_5OH$  and aluminium isopropoxide.

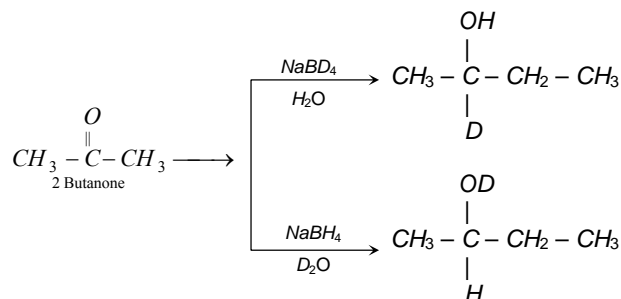
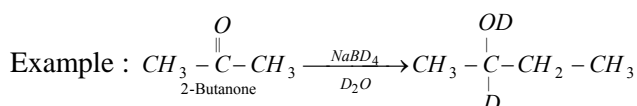


$\text{NaBH}_4$  is regioselective reducing agent because it reduced only. CHO in the presence of other reducible group.

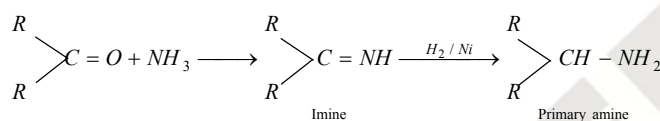
Example :



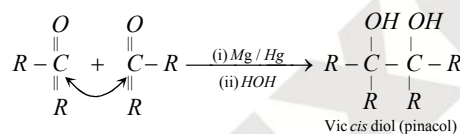
Hydride ion of  $\text{NaBH}_4$  attack on carbonyl carbon during reduction.



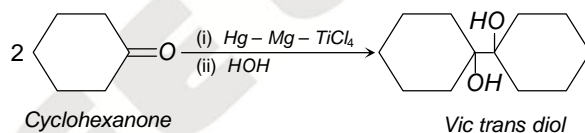
(iii) **Reductive amination** : In this reduction  $-\text{CO}-$  group converts into  $-\text{CH}-\text{NH}_2$  group



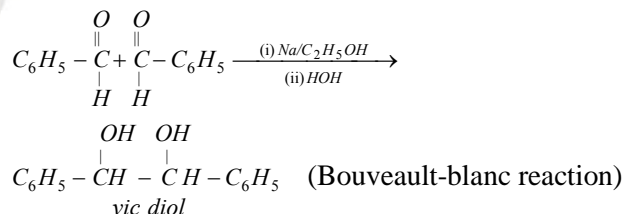
(iv) **Reduction of ketones by Mg or Mg/Hg** : In this case ketones undergo reduction via coupling reaction and product is vic cis diol.



When this reaction is carried out in the presence of  $\text{Mg} / \text{Hg} / \text{TiCl}_4$ , the product is vic trans diol.

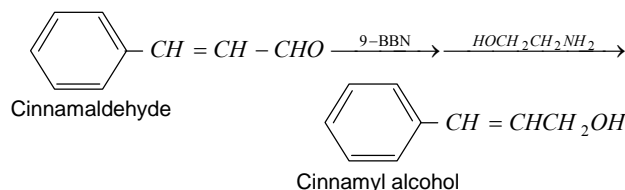


(v) **Reduction of benzaldehyde by  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$**  : Benzaldehyde undergoes reduction via coupling reaction and product is vic diol.



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

Example :



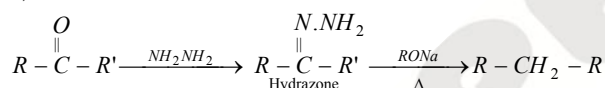
□ If reducing agent is NaH, reaction is called Darzen's reaction, we can also use  $\text{LiAlH}_4$  in this reaction.

□ If reducing agent is aluminium iso propoxide  $(\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{O})_3\text{Al}$ . Product will be alcohol.

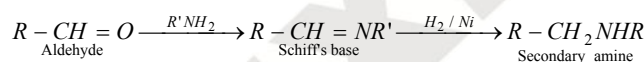
This reaction is called Meerwein – pondorff verley reduction (MPV reduction).

□ The percentage yield of alkanes can be increased by using diethylene glycol in Wolf Kishner reduction. Then reaction is called Huang – Millan conversion.

(vi) Hydrazones when treated with base like alkoxide give hydrocarbon (Wolf – Kishner reduction).



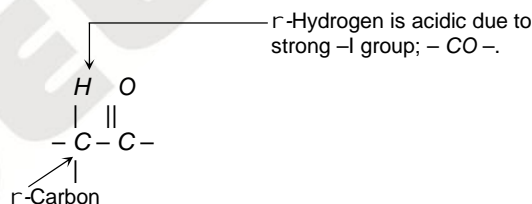
(vii) Schiff's base on reduction gives secondary amines.



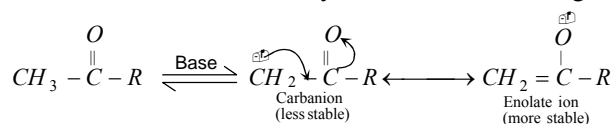
## (5) Reactions due to $\alpha$ -hydrogen

### (i) Acidity of $\alpha$ -hydrogens :

(a)  $\alpha$ -hydrogen of carbonyl compounds are acidic in character due to the presence of the electron withdrawing  $-\text{CO}-$  group.

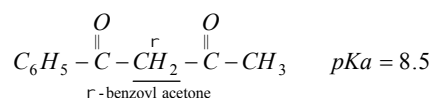
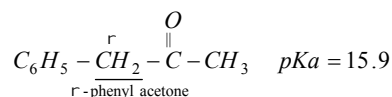


(b) Thus carbonyl compounds having  $\alpha$ -hydrogen convert into carbanions in the presence of base. This carbanion is stabilised by delocalisation of negative charge.



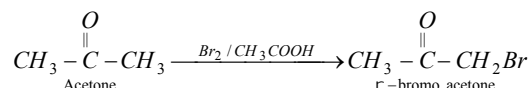
(c) The acidity of  $\alpha$ -hydrogen is more than ethyne.  $\text{pK}_a$  value of aldehydes and ketones are generally 19 – 20 where as  $\text{pK}_a$  value of ethyne is 25.

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

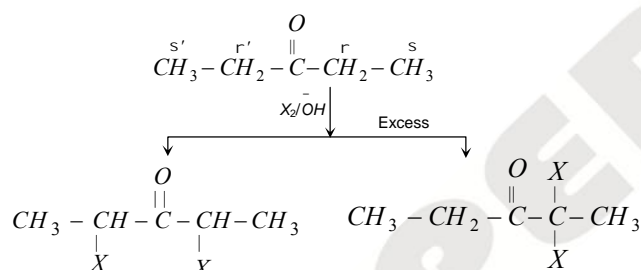


(ii) **Halogenation** : Carbonyl compounds having  $\alpha$ -hydrogens undergo halogenation reactions. This reaction is catalysed by acid as well as base.

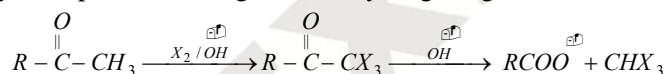
(a) Acid catalysed halogenation : This gives only monohalo derivative.



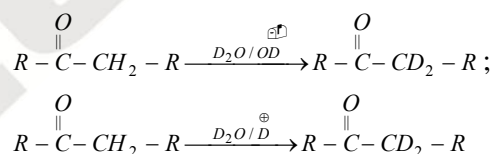
(b) Base catalysed halogenation : In the presence of base all  $\alpha$ -hydrogens of the same carbon is replaced by halogens.



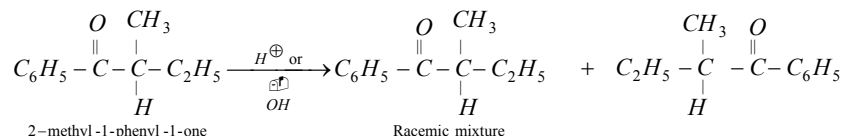
Carbonyl compounds having three  $\alpha$ -hydrogens give **haloform** reaction.



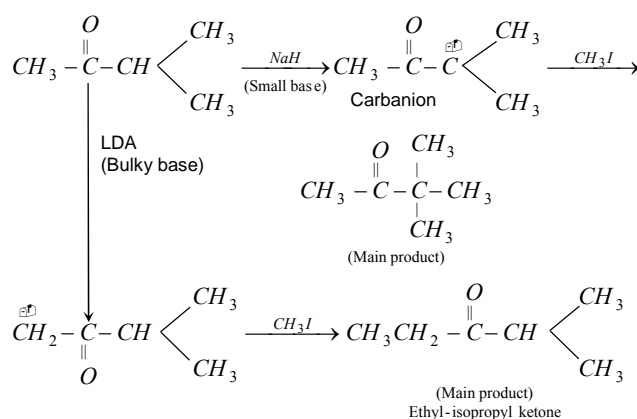
(iii) **Deuterium exchange reaction** : Deuterium exchange reaction is catalysed by acid ( $D^+$ ) as well as base ( $OD^-$ ). In both the cases all the hydrogens on only one  $\alpha$ -carbon is replaced by D.



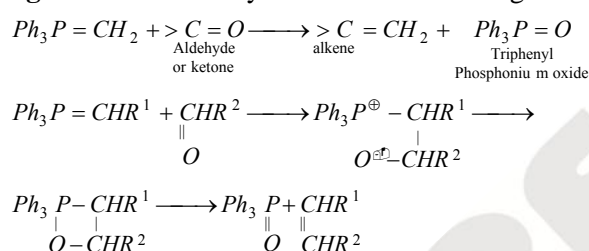
(iv) **Racemisation** : Ketones whose  $\alpha$ -carbon is chiral undergo Racemisation in the presence of acid as well as base.



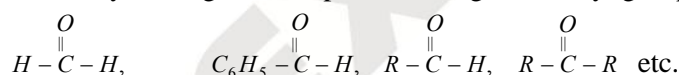
(v) **Alkylation** : Carbonyl compounds having  $\alpha$ -hydrogens undergo alkylation reaction with  $RX$  in the presence of base. This reaction is  $S_N2$  reaction. The best result is obtained with  $CH_3-X$ . Other halides undergo elimination in the presence of strong base.



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

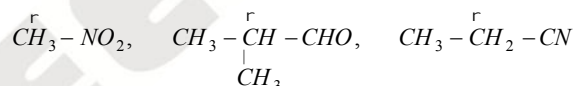


- (6) **Condensation reaction of carbonyl compounds** : Nucleophilic addition reaction of compounds having carbonyl group with those compounds which have at least one acidic hydrogen at  $\alpha$ -carbon is known as condensation reaction. In this addition reaction :  
Substrate is always an organic compound having a carbonyl group, e.g.



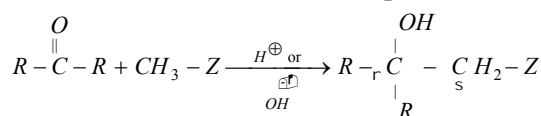
Addition always takes place on the carbonyl group.

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



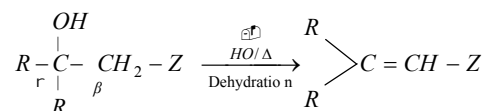
□ If substrate and reagent both are carbonyl compounds then one should have at least one  $\alpha$ -hydrogen and other may or may not have  $\alpha$ -hydrogen.

Condensation reaction always takes place in the presence of acid or base as catalyst. Best result is obtained with base at lower temp.



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

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



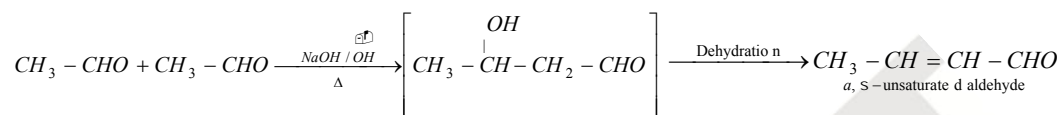
## (i) Aldol condensation

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

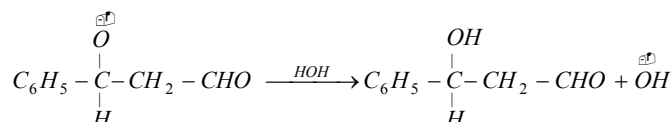
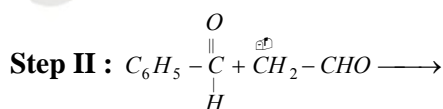
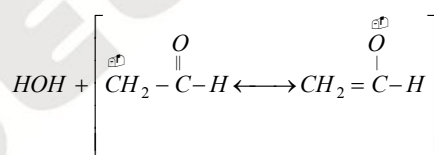
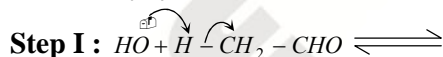
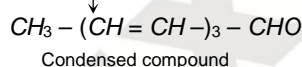
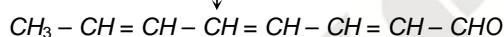
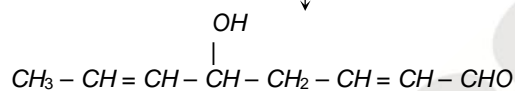
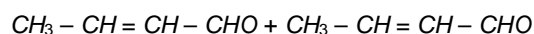
One should have no  $\alpha$ -hydrogen atom and other should have at least two  $\alpha$ -hydrogens.

(b) These reactions are practical when base is NaOH and reaction temperature is high ( $\geq 100^\circ$ ).

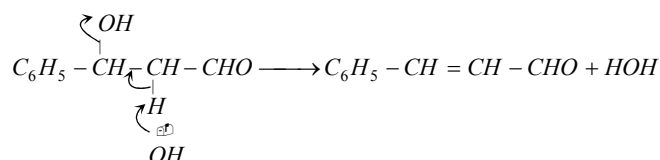
(c) The reaction is two step reaction. First step is aldol formation and second step is dehydration of aldol.



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

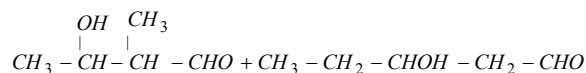
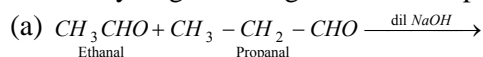


**Step III :**

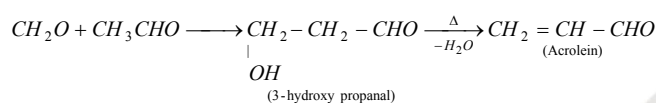


In aldol condensation, dehydration occurs readily because the double bond that forms is conjugated, both with the carbonyl group and with the benzene ring. The conjugation system is thereby extended.

**Crossed aldol condensation :** Aldol condensation between two different aldehydes or two different ketones or one aldehyde and another ketone provided at least one of the components have  $\alpha$ -hydrogen atom gives different possible product

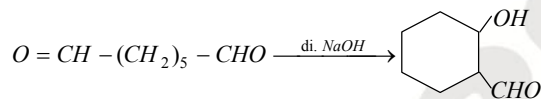


However crossed aldol condensation is important when only it the components has  $\alpha$ -hydrogen atom.

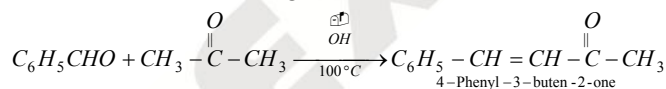


**Intra molecular aldol condensation :** One molecule Intramolecular condensation give aldol compounds

Example :



(ii) **Claisen – Schmidt reaction :** Crossed aldol condensation between aromatic aldehyde and aliphatic ketone or mixed ketone is known as Claisen – Schmidt reaction. Claisen – Schmidt reactions are useful when bases such as sodium hydroxide are used because under these conditions ketones do not undergo self condensation. Some examples of this reaction are :



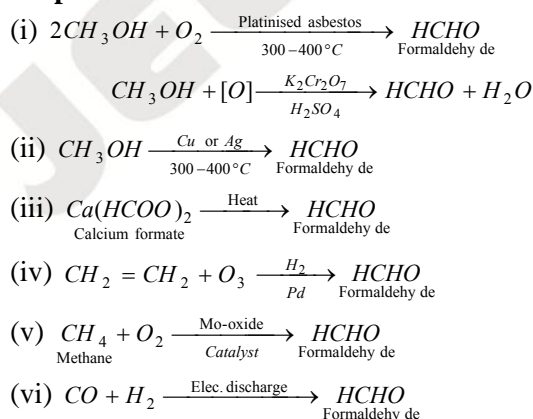


**Test of aldehydes and Ketones (Distinction)****Table :**

Test	<u>Aldehydes</u>	<u>Ketones</u>
With Schiff's reagent	Give pink colour.	No colour.
With Fehling's solution	Give red precipitate.	No precipitate is formed.
With Tollen's reagent	Black precipitate or silver mirror is formed.	No black precipitate or silver mirror is formed.
With saturated sodium bisulphite solution in water	Crystalline compound (colourless) is formed.	Crystalline compound (colourless) is formed.
With 2, 4-dinitrophenyl hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.
With sodium hydroxide	Give brown resinous mass (formaldehyde does not give this test).	No reaction.
With sodium nitroprusside and few drops of sodium hydroxide	A deep red colour (formaldehyde does not respond to this test).	Red colour which changes to orange.

**Some commercially important aliphatic:****Carbonyl compounds:**

**Formaldehyde:** Formaldehyde is the first member of the aldehyde series. It is present in green leaves of plants where its presence is supposed to be due to the reaction of  $CO_2$  with water in presence of sunlight and chlorophyll.

**(1) Preparation****(2) Physical properties**

- It is a colourless, pungent smelling gas.
- It is extremely soluble in water. Its solubility in water may be due to hydrogen bonding between water molecules and its hydrate.
- It can easily be condensed into liquid. The liquid formaldehyde boils at  $-21^\circ C$ .
- It causes irritation to skin, eyes, nose and throat.

(v) Its solution acts as antiseptic and disinfectant.

(3) **Uses**

(i) The 40% solution of formaldehyde (formalin) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens.

(ii) It is used in the preparation of hexamethylene tetramine (urotropine) which is used as an antiseptic and germicide.

(iii) It is used in silvering of mirror.

(iv) It is employed in manufacture of synthetic dyes such as para-rosaniline, indigo, etc.

(v) It is used in the manufacture of formamint (by mixing formaldehyde with lactose) – a throat lozenges.

(vi) It is used for making synthetic plastics like bakelite, urea-formaldehyde resin, etc.

(vii) Rongalite – a product obtained by reducing formaldehyde sodium bisulphite derivative with zinc dust and ammonia and is used as a reducing agent in vat dyeing.

### Acetaldehyde

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

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

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

(ii) By dehydrogenation of ethyl alcohol. The vapours of ethyl alcohol are passed over copper at 300°C.

(iii) By heating the mixture of calcium acetate and calcium formate.

(iv) By heating ethylidene chloride with caustic soda or caustic potash solution.

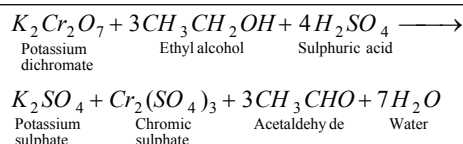
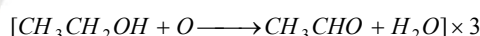
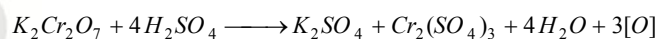
(v) By the reduction of acetyl chloride with hydrogen in presence of a catalyst palladium suspended in barium sulphate (Rosenmund's reaction).

(vi) By the reduction of  $CH_3CN$  with stannous chloride and HCl in ether and hydrolysis (Stephen's method).

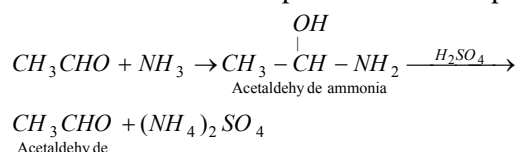
(vii) By hydration of acetylene with dil.  $H_2SO_4$  and  $HgSO_4$  at 60°C.

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

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

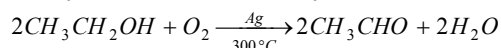


To recover acetaldehyde, the distillate is treated with dry ammonia when crystallised product, acetaldehyde ammonia, is formed. It is filtered and washed with dry ether. The dried crystals are then distilled with dilute sulphuric acid when pure acetaldehyde is collected.

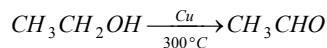


(x) **Manufacture** : Acetaldehyde can be manufactured by one of the following methods:

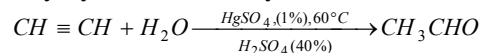
(a) By air oxidation of ethyl alcohol



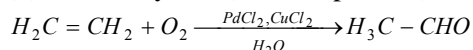
(b) By dehydrogenation of alcohol



(c) By hydration of acetylene



(d) From ethylene (Wacker process)

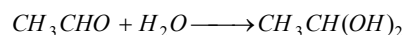


(2) **Physical properties**

(i) Acetaldehyde is a colourless volatile liquid. It boils at  $21^\circ\text{C}$ .

(ii) It has a characteristic pungent smell.

(iii) It is soluble in water, chloroform, ethyl alcohol and ether. Its aqueous solution has a pleasant odour. In water, it is hydrated to a considerable extent to form ethylidene diol.



(3) **Uses** : Acetaldehyde is used :

(i) In the preparation of acetic acid, acetic anhydride, ethyl acetate, chloral, 1,3-butadiene (used in rubbers), dyes and drugs.

(ii) As an antiseptic inhalant in nose troubles.

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

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

Table : Comparative study of formaldehyde and acetaldehyde

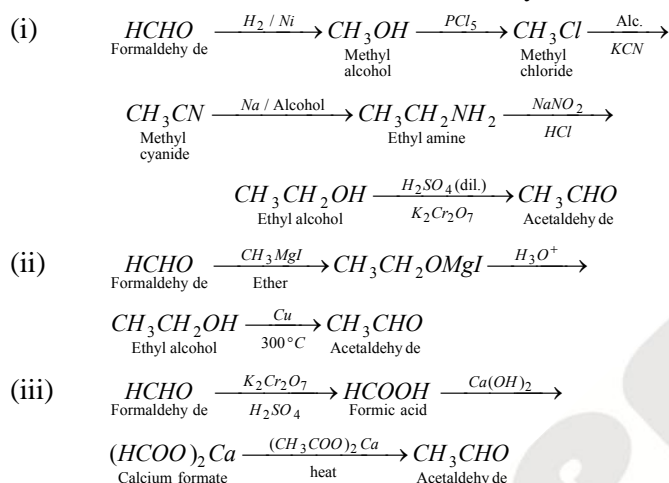
S.No.	Reaction	Formaldehyde HCHO	Acetaldehyde CH <sub>3</sub> CHO
<b>Similarities</b>			
1.	Addition of hydrogen (a) H <sub>2</sub> in presence of catalyst, Ni, Pd or Pt (b) LiAlH <sub>4</sub> (ether) (c) Amalgamated zinc + conc. HCl (Clemmenson reduction)	Forms methyl alcohol $HCHO + H_2 \longrightarrow CH_3OH$ Forms methyl alcohol Forms methane $HCHO + 4H \longrightarrow CH_4 + H_2O$	Forms ethyl alcohol $CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$ Forms ethyl alcohol Forms ethane $CH_3CHO + 4H \longrightarrow C_2H_6 + H_2O$
2.	Addition of NaHSO <sub>3</sub> solution	Forms bisulphite addition product $HCHO + NaHSO_3 \longrightarrow CH_2(OH)SO_3Na$	Forms bisulphite addition product $CH_3CHO + NaHSO_3 \longrightarrow CH_3CH(OH)SO_3Na$
3.	Addition of HCN	Forms formaldehyde cyanohydrin $HCHO + HCN \longrightarrow CH_2(OH)CN$	Forms acetaldehyde cyanohydrin $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$
4.	Addition of Grignard reagent followed by hydrolysis	Forms ethyl alcohol $HCHO + CH_3MgI \longrightarrow CH_2 \begin{matrix} OMgI \\ CH_3 \end{matrix}$ $\xrightarrow[-Mg(OH)I]{H_2O} CH_3CH_2OH$	Forms isopropyl alcohol $CH_3CHO + CH_3MgI \longrightarrow CH_3 - C \begin{matrix} HOMgI \\   \\ CH_3 \end{matrix}$ $\xrightarrow[-Mg(OH)I]{H_2O} CH_3 - CH - OH$ $ $ $CH_3$
5.	With hydroxylamine NH <sub>2</sub> OH	Forms formaldoxime $CH_2 = O + H_2NOH \xrightarrow{-H_2O} CH_2 = NOH$	Forms acetaldoxime $CH_3CH = O + H_2NOH \xrightarrow{-H_2O} CH_3CH = NOH$
6.	With hydrazine (NH <sub>2</sub> NH <sub>2</sub> )	Forms formaldehyde hydrazone $CH_2O + H_2NNH_2 \xrightarrow{-H_2O} CH_2 = NNH_2$	Forms acetaldehyde hydrazone $CH_3CH = O + H_2NNH_2 \xrightarrow{-H_2O} CH_3CH = NNH_2$
7.	With phenyl hydrazine (C <sub>6</sub> H <sub>5</sub> NHNH <sub>2</sub> )	Forms formaldehyde phenyl hydrazone $CH_2 = O + H_2NNHC_6H_5 \xrightarrow{-H_2O} CH_2 = NNHC_6H_5$	Forms acetaldehyde phenyl hydrazone $CH_3CH = O + H_2NNHC_6H_5 \xrightarrow{-H_2O} CH_3CH = NNHC_6H_5$
8.	With semicarbazide (H <sub>2</sub> NNHCONH <sub>2</sub> )	Forms formaldehyde semicarbazone $CH_2 = O + H_2NNHCONH_2 \xrightarrow{-H_2O} CH_2 = NNHCONH_2$	Forms acetaldehyde semicarbazone $CH_3CH = O + H_2NNHCONH_2 \xrightarrow{-H_2O} CH_3CH = NNHCONH_2$
9.	With alcohol (C <sub>2</sub> H <sub>5</sub> OH) in presence of acid	Forms ethylal $H_2C = O + 2C_2H_5OH \xrightarrow{HCl} CH_2 \begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix}$	Forms acetaldehyde diethyl acetal $CH_3CHO + 2C_2H_5OH \xrightarrow{HCl} CH_3CH \begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix}$

10.	With thioalcohols ( $C_2H_5SH$ ) in presence of acid	Forms thio ethylal $H_2C = O + 2C_2H_5SH \longrightarrow$ $CH_2 \begin{matrix} \swarrow SC_2H_5 \\ \searrow SC_2H_5 \end{matrix}$	Forms acetaldehyde diethyl thioacetal $CH_3CH = O + 2C_2H_5SH \longrightarrow$ $CH_3CH \begin{matrix} \swarrow SC_2H_5 \\ \searrow SC_2H_5 \end{matrix}$
11.	Oxidation with acidified $K_2Cr_2O_7$	Forms formic acid $HCHO + O \longrightarrow HCOOH$	Forms acetic acid $CH_3CHO + O \longrightarrow CH_3COOH$
12.	With Schiff's reagent	Restores pink colour of Schiff's reagent	Restores pink colour of Schiff's reagent
13.	With Tollen's reagent	Gives black precipitate of Ag or silver mirror $Ag_2O + HCHO \longrightarrow 2Ag + HCOOH$	Gives black precipitate of Ag or silver mirror $Ag_2O + CH_3CHO \longrightarrow$ $2Ag + CH_3COOH$
14.	With Fehling's solution or Benedict's solution	Gives red precipitate of cuprous oxide $2CuO + HCHO \longrightarrow Cu_2O + HCOOH$	Gives red precipitate of cuprous oxide $2CuO + CH_3CHO \longrightarrow$ $Cu_2O + CH_3COOH$
15.	Polymerisation	Undergoes polymerisation $nHCHO \xrightleftharpoons[\text{Room temp.}]{\text{Evaporation}} (HCHO)_n$ Paraformaldehyde $3HCHO \xrightleftharpoons[\text{heat}]{\text{Room temp.}} (HCHO)_3$ Metaformaldehyde	Undergoes polymerisation $3CH_3CHO \xrightleftharpoons[\text{dil. } H_2SO_4, \text{ distill}]{H_2SO_4 \text{ Conc.}} (CH_3CHO)_3$ Paraldehyde $4CH_3CHO \xrightleftharpoons[\text{dil. } H_2SO_4, \text{ distill}]{H_2SO_4 \text{ Conc.}} (CH_3CHO)_4$ Metaldehyde
<b>Dissimilarities</b>			
16.	With $PCl_5$	No reaction	Forms ethylidene chloride $CH_3CHO + PCl_5 \longrightarrow CH_3CH \begin{matrix} \swarrow Cl \\ \searrow Cl \end{matrix} + POCl_3$
17.	With chlorine	No reaction	Forms chloral $CH_3CHO + 3Cl_2 \longrightarrow CCl_3CHO + 3HCl$
18.	With $SeO_2$	No reaction	Forms glyoxal $CH_3CHO + SeO_2 \longrightarrow CHO \cdot CHO + Se + H_2O$
19.	Iodoform reaction ( $I_2 + NaOH$ )	No reaction	Forms iodoform $CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$
20.	With dil. alkali (Aldol condensation)	No reaction	Forms aldol $CH_3CHO + HCH_2CHO \longrightarrow CH_3CH(OH)CH_2CHO$
21.	With conc. NaOH (Cannizzaro's reaction)	Forms sodium formate and methyl alcohol $2HCHO + NaOH \longrightarrow HCOONa + CH_3OH$	Forms a brown resinous mass
22.	With ammonia	Forms hexamethylene tetramine (urotropine) $6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$	Forms addition product, acetaldehyde ammonia $CH_3CHO + NH_3 \longrightarrow CH_3CH \begin{matrix} \swarrow OH \\ \searrow NH_2 \end{matrix}$
23.	With phenol	Forms bakelite plastic	No reaction

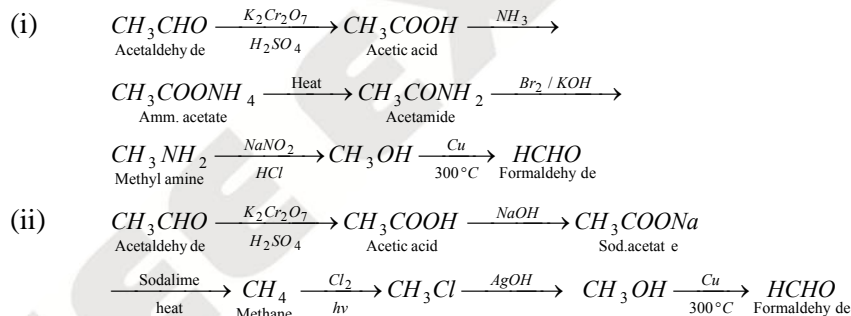
24.	With urea	Forms urea-formaldehyde plastic	No reaction
25.	Condensation in presence of $Ca(OH)_2$	Form formose (a mixture of sugars)	No reaction

### Inter conversion of formaldehyde and acetaldehyde

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

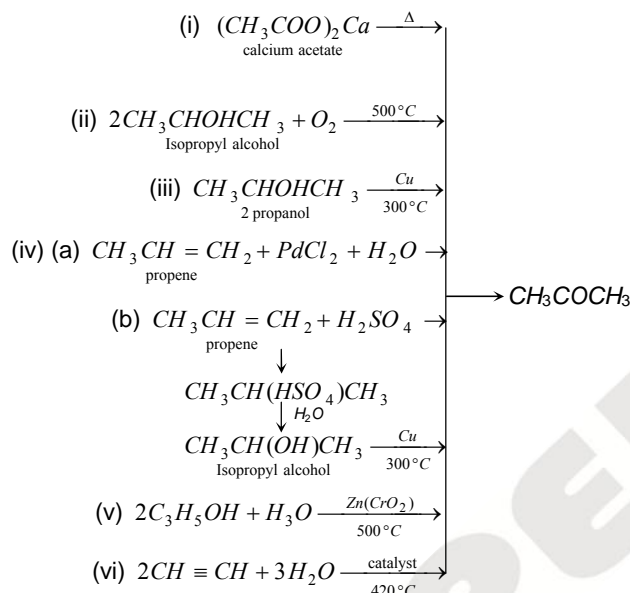


#### (2) Descent of series : Conversion of acetaldehyde into formaldehyde



**Acetone :**

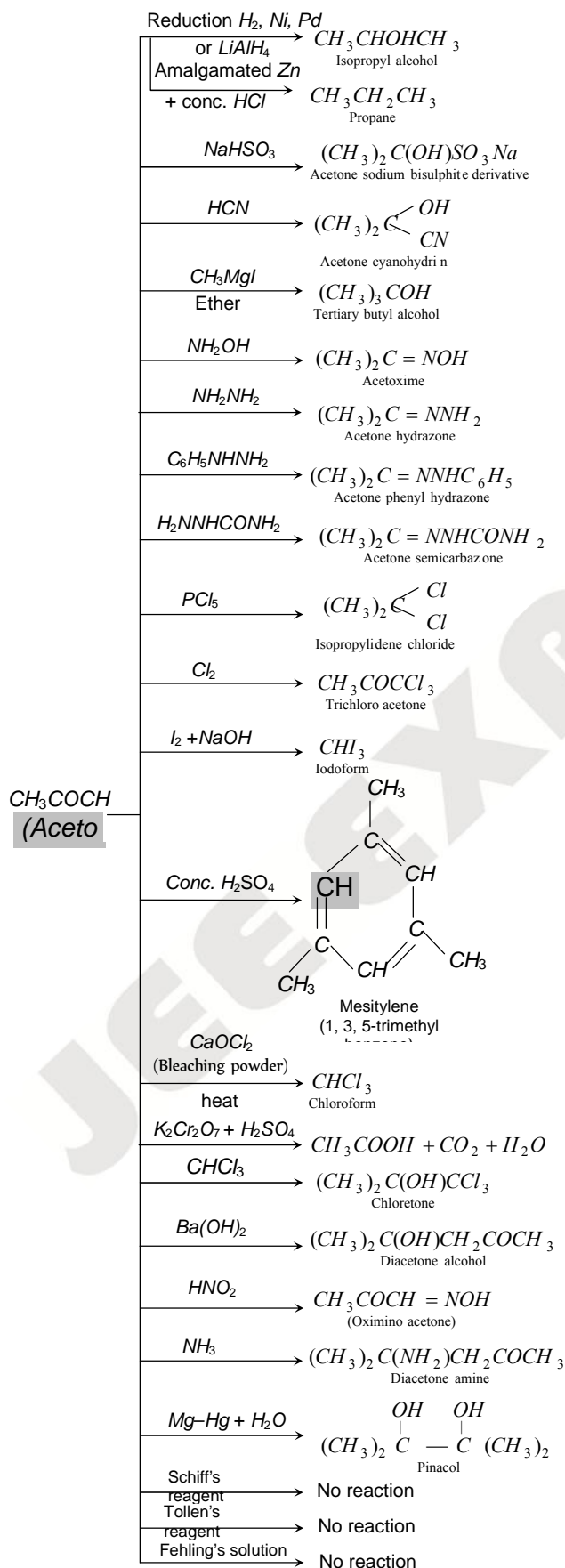
It is a symmetrical (simple) ketone and is the first member of the homologous series of ketones. In traces, it is present in blood and urine.

**(1) Preparation :**

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

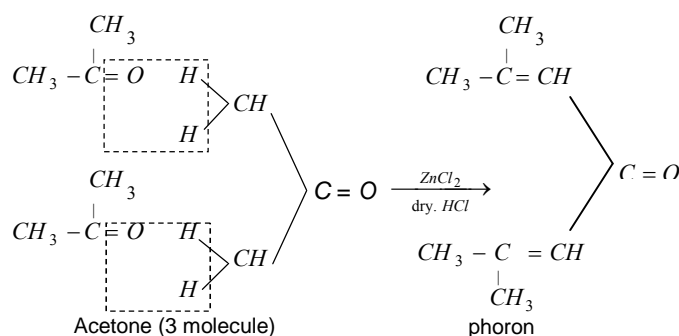
- (2) **Physical properties :**
- (i) It is a colourless liquid with characteristic pleasant odour.
  - (ii) It is inflammable liquid. It boils at  $56^\circ C$ .
  - (iii) It is highly miscible with water, alcohol and ether.

## (3) Chemical properties



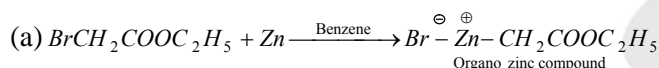


If acetone would be in excess in ketal condensation or catalyst ( $ZnCl_2$  / dry  $HCl$ ) is used then three moles of acetone undergoes condensation polymerisation and form a compound called 'Phorone'.

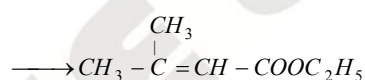
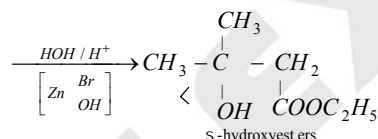
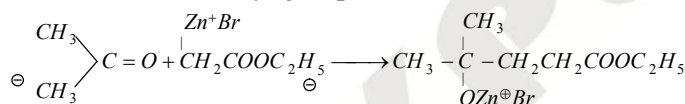


Molecular mass of phorone = 3 mole of acetone – 2 mole of  $H_2O$

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



(b) Addition to carbonyl group



#### (4) Uses

- (i) As a solvent for cellulose acetate, cellulose nitrate, celluloid, lacquers, resins, etc.
- (ii) For storing acetylene.
- (iii) In the manufacture of cordite – a smoke less powder explosive.
- (iv) In the preparation of chloroform, iodoform, sulphonal and chloretone.
- (v) As a nailpolish remover.
- (vi) In the preparation of an artificial scent (ionone), plexiglass (unbreakable glass) and synthetic rubber.

#### (5) Tests

- (i) **Legal's test :** When a few drops of freshly prepared sodium nitroprusside and sodium hydroxide solution are added to an aqueous solution of acetone, a wine colour is obtained which changes to yellow on standing.
- (ii) **Indigo test :** A small amount of orthonitrobenzaldehyde is added to about 2 ml. of acetone and it is diluted with KOH solution and stirred. A blue colour of indigotin is produced.
- (iii) **Iodoform test :** Acetone gives iodoform test with iodine and sodium hydroxide or iodine and ammonium hydroxide.

Table : Comparison between Acetaldehyde and Acetone:

Reaction	Acetaldehyde	Acetone
<b>Similarities</b>		
1. Reduction with $H_2$ and Ni or $LiAlH_4$	Forms ethyl alcohol $CH_3CHO + H_2 \xrightarrow{Ni} CH_3CH_2OH$	Forms isopropyl alcohol $CH_3COCH_3 + H_2 \longrightarrow CH_3CHOHCH_3$
2. Clemmensen's reduction (Zn/Hg and conc. HCl)	Forms ethane (an alkane) $CH_3CHO + 4H \longrightarrow CH_3CH_3 + H_2O$	Forms propane (an alkane) $CH_3COCH_3 + 4H \longrightarrow CH_3CH_2CH_3 + H_2O$
3. Addition of HCN	Forms acetaldehyde cyanohydrin $CH_3CHO + HCN \longrightarrow CH_3CH \begin{matrix} OH \\ \diagdown \\ CN \end{matrix}$	Forms acetone cyanohydrin $(CH_3)_2CO + HCN \longrightarrow (CH_3)_2C \begin{matrix} OH \\ \diagdown \\ CN \end{matrix}$
4. Addition of $NaHSO_3$	White crystalline derivative $CH_3CHO + NaHSO_3 \longrightarrow CH_3CH \begin{matrix} OH \\ \diagdown \\ SO_3Na \end{matrix}$	White crystalline derivative $(CH_3)_2CO + NaHSO_3 \longrightarrow (CH_3)_2C \begin{matrix} OH \\ \diagdown \\ SO_3Na \end{matrix}$
5. Grignard reagent followed by hydrolysis	Forms isopropyl alcohol $CH_3CHO + CH_3MgI \longrightarrow (CH_3)_2CH-OMgI$ $\xrightarrow{H_2O} CH_3CHOHCH_3$	Forms tertiary butyl alcohol $(CH_3)_2CO + CH_3MgI \longrightarrow (CH_3)_3COMgI$ $\xrightarrow{H_2O} (CH_3)_3COH$
6. With hydroxylamine ( $NH_2OH$ )	Forms acetaldoxime (an oxime) $CH_3CHO + H_2NOH \longrightarrow CH_3CH=NOH$	Forms acetoxime (an oxime) $(CH_3)_2CO + H_2NOH \longrightarrow (CH_3)_2C=NOH$
7. With hydrazine ( $NH_2NH_2$ )	Forms acetaldehyde hydrazone $CH_3CHO + H_2NNH_2 \longrightarrow CH_3CH=NNH_2$	Forms acetone hydrazone $(CH_3)_2CO + H_2NNH_2 \longrightarrow (CH_3)_2C=NNH_2$
8. With phenyl hydrazine ( $C_6H_5NHNH_2$ )	Forms acetaldehyde phenylhydrazone $CH_3CHO + H_2NNHC_6H_5 \longrightarrow$ $CH_3CH=NNHC_6H_5$	Forms acetone phenyl hydrazone $(CH_3)_2CO + H_2NNHC_6H_5 \longrightarrow$ $(CH_3)_2C=NNHC_6H_5$
9. With semicarbazide ( $H_2NNHCONH_2$ )	Forms acetaldehyde semicarbazone $CH_3CHO + H_2NNHCONH_2 \longrightarrow$ $CH_3CH=NNHCONH_2$	Forms acetone semicarbazone $(CH_3)_2CO + H_2NNHCONH_2 \longrightarrow$ $(CH_3)_2C=NNHCONH_2$
10. With $PCl_5$	Forms ethylidene chloride (Gem dihalide) $CH_3CHO + PCl_5 \longrightarrow CH_3CH \begin{matrix} Cl \\ \diagdown \\ Cl \end{matrix}$	Forms isopropylidene chloride (Gem dihalide) $(CH_3)_2CO + PCl_5 \longrightarrow (CH_3)_2C \begin{matrix} Cl \\ \diagdown \\ Cl \end{matrix}$
11. With chlorine	Forms chloral (Gem trihalide) $CH_3CHO + Cl_2 \longrightarrow CCl_3CHO$	Forms trichloro acetone (Gem trihalide) $CH_3COCH_3 + Cl_2 \longrightarrow CCl_3COCH_3$

12. With alcohols	Forms acetal (a diether) $CH_3CHO + 2C_2H_5OH \longrightarrow CH_3CH \begin{matrix} \swarrow OC_2H_5 \\ \searrow OC_2H_5 \end{matrix}$	Forms ketal (a diether) $(CH_3)_2CO + 2C_2H_5OH \longrightarrow (CH_3)_2C \begin{matrix} \swarrow OC_2H_5 \\ \searrow OC_2H_5 \end{matrix}$
13. With $SeO_2$	Forms glyoxal $CH_3CHO + SeO_2 \longrightarrow CHOCHO + Se + H_2O$	Forms methyl glyoxal $(CH_3)_2CO + SeO_2 \longrightarrow CH_3COCHO + Se + H_2O$
14. Iodoform reaction ( $I_2 + NaOH$ )	Forms iodoform	Forms iodoform
15. Bleaching powder	Forms chloroform	Forms chloroform
16. Aldol condensation with mild alkali	Forms aldol $2CH_3CHO \longrightarrow CH_3CHOHCH_2CHO$	Forms diacetone alcohol $2CH_3COCH_3 \longrightarrow (CH_3)_2C(OH)CH_2COCH_3$
17. Polymerisation	Undergoes polymerisation	Does not undergo polymerisation but gives condensation reaction
18. With $NH_3$	Forms acetaldehyde ammonia $CH_3CHO + NH_3 \longrightarrow CH_3CH \begin{matrix} \swarrow OH \\ \searrow NH_2 \end{matrix}$	Forms diacetone ammonia $(CH_3)_2CO + NH_3 + OC(CH_3)_2 \longrightarrow (CH_3)_2C(NH_2)CH_2COCH_3$
19. With conc. $NaOH$	Forms brownish resinous mass	No reaction
20. With $HNO_2$	No reaction	Forms oximino acetone $CH_3COCH_3 + HNO_2 \longrightarrow CH_3COCH = NOH$
21. With chloroform	No reaction	Forms chloretone $(CH_3)_2CO + CHCl_3 \longrightarrow (CH_3)_2C \begin{matrix} \swarrow OH \\ \searrow CCl_3 \end{matrix}$
22. With alk. sodium nitroprusside	Deep red colour	Red colour changes to yellow on standing
23. With sodium nitroprusside + Pyridine	Blue colour	No effect
24. Boiling point	$21^\circ C$	$56^\circ C$
<b>Dissimilarities</b>		
25. With Schiff's reagent	Pink colour	Does not give pink colour

26. With Fehling's solution	Gives red precipitate	No reaction
27. With Tollen's reagent	Gives silver mirror	No reaction
28. Oxidation with acidified $K_2Cr_2O_7$	Easily oxidised to acetic acid $CH_3CHO + O \longrightarrow CH_3COOH$	Oxidation occurs with difficulty to form acetic acid $CH_3COCH_3 + O \longrightarrow CH_3COOH + CO_2 + H_2O$

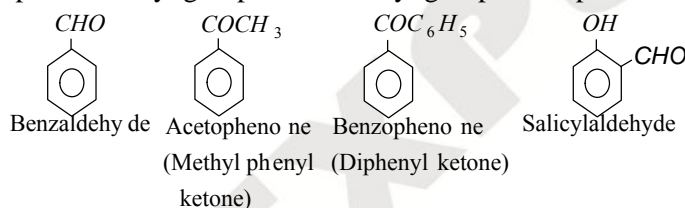
### Aromatic Carbonyl Compounds

Aromatic aldehydes are of two types :

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

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

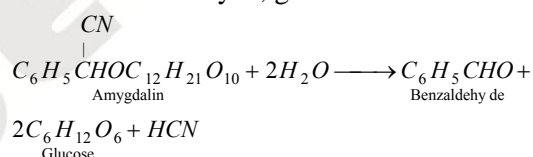
Aromatic ketones are compounds in which a carbonyl group ( $>C=O$ ) is attached to either two aryl groups or one aryl group and one alkyl group. Examples are :



**Benzaldehyde,  $C_6H_5CHO$  or**



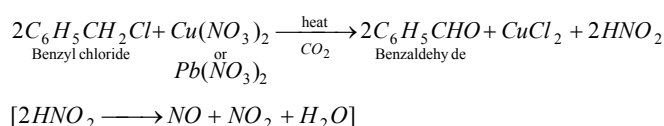
Benzaldehyde is the simplest aromatic aldehyde. It occurs in bitter almonds in the form of its glucoside, **amygdalin** ( $C_{20}H_{27}O_{11}N$ ). When amygdalin is boiled with dilute acids, it hydrolyses into benzaldehyde, glucose and HCN



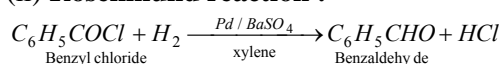
Benzaldehyde is also known as oil of bitter almonds.

#### (1) Method of preparation

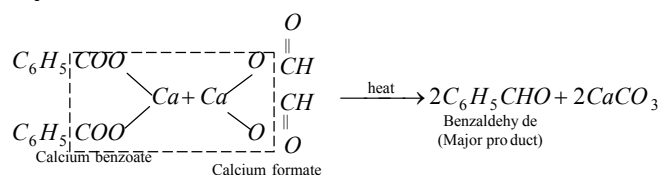
(i) **Laboratory method** : It is conveniently prepared by boiling benzyl chloride with copper nitrate or lead nitrate solution in a current of carbon dioxide.



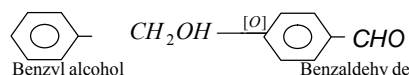
(ii) **Rosenmund reaction** :



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

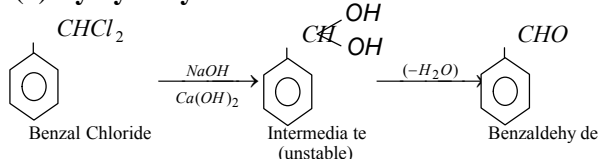


(iv) **By oxidation of benzyl alcohol :** This involves the treatment of benzyl alcohol with dil.  $\text{HNO}_3$  or acidic potassium dichromate or chromic anhydride in acetic anhydride or with copper catalyst at  $350^\circ\text{C}$ .



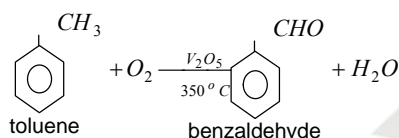
This method is used for commercial production of benzaldehyde.

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



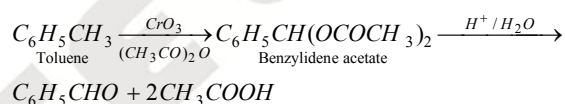
This is also an industrial method.

(vi) **By oxidation of Toluene**

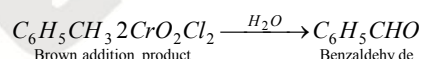


Commercially the oxidation of toluene is done with air and diluted with nitrogen (to prevent complete oxidation) at  $500^\circ\text{C}$  in the presence of oxides of  $\text{Mn}$ ,  $\text{Mo}$  or  $\text{Zr}$  as catalyst.

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



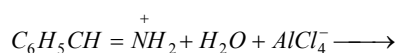
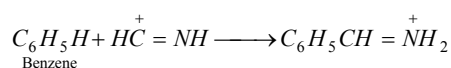
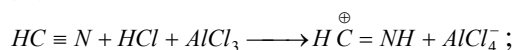
(vii) **Etard's reaction :**  $\text{C}_6\text{H}_5\text{CH}_3 + 2\text{CrO}_2\text{Cl}_2 \longrightarrow$

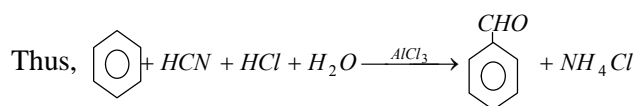
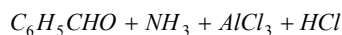


(viii) **Gattermann-koch aldehyde synthesis :** Benzene is converted into benzaldehyde by passing a mixture of carbon monoxide and  $\text{HCl}$  gas under high pressure into the ether solution of benzene in presence of anhydrous aluminium chloride and cuprous chloride.

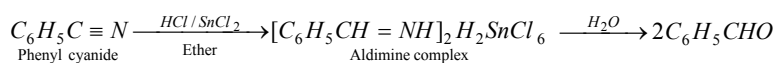


(ix) **Gattermann reaction**

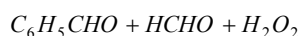
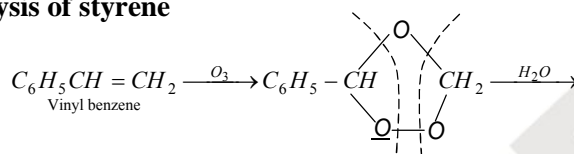




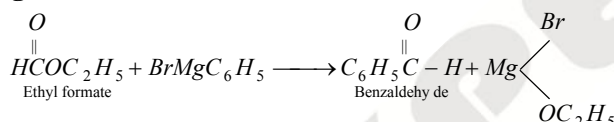
(x) **Stephen's reaction** : Benzaldehyde is obtained by partial reduction of phenyl cyanide with stannous chloride and passing dry  $HCl$  gas in ether solution followed by hydrolysis of the aldimine stannic chloride with water.



(xi) **By ozonolysis of styrene**

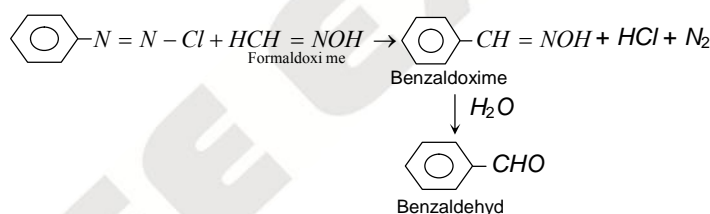


(xii) **Grignard reaction**



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

(xiii) **From Diazonium salt**

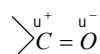


## (2) Physical properties

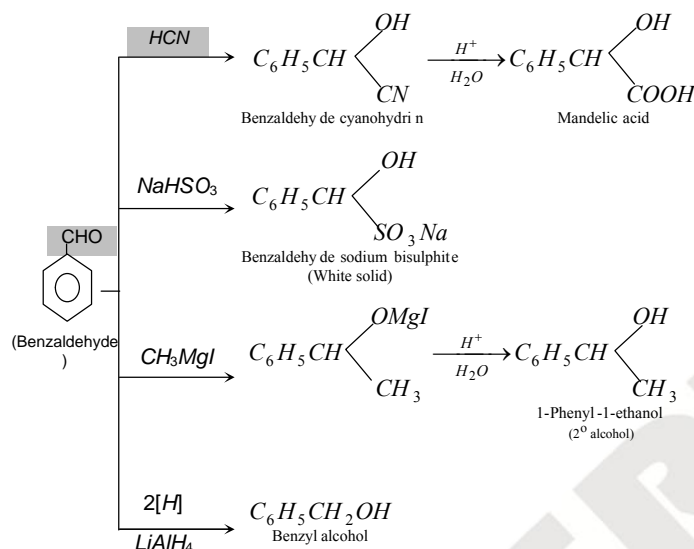
- (i) Benzaldehyde is a colourless oily liquid. Its boiling point is  $179^\circ C$ .
- (ii) It has smell of bitter almonds.
- (iii) It is sparingly soluble in water but highly soluble in organic solvents.
- (iv) It is steam volatile.
- (v) It is heavier than water (sp. gr. 1.0504 at  $15^\circ C$ ).
- (vi) It is poisonous in nature.

## (3) Chemical properties

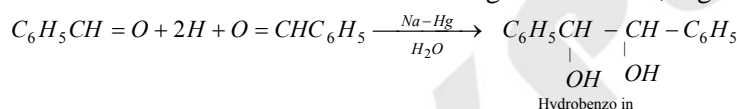
(i) **Addition reaction**: The carbonyl group is polar as oxygen is more electronegative than carbon,



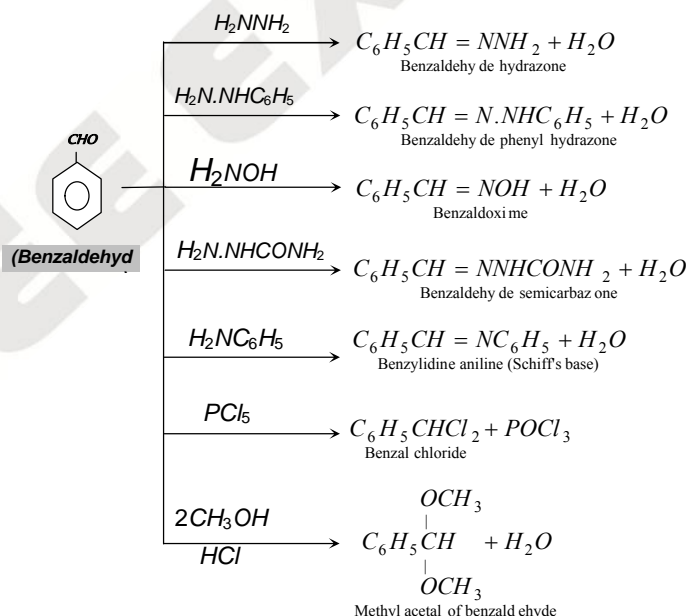
Thus, The positive part of the polar reagent always goes to the carbonyl oxygen and negative part goes to carbonyl carbon.



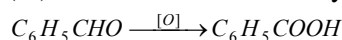
However on reduction with sodium amalgam and water, it gives hydrobenzoin,



## (ii) Reactions involving replacement of carbonyl oxygen



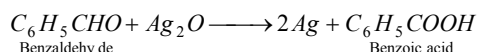
(iii) **Oxidation** : Benzaldehyde is readily oxidised to benzoic acid even on exposure to air.



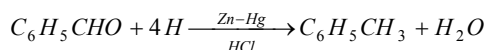
Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ , alkaline  $\text{KMnO}_4$  and dilute  $\text{HNO}_3$  can be used as oxidising agents for oxidation.

(iv) **Reducing properties** : Benzaldehyde is a weak reducing agent. It reduces ammonical

silver nitrate solution (Tollen's reagent) to give silver mirror but does not reduce Fehling's solution.

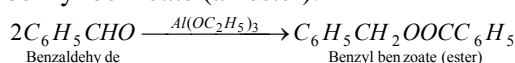


(v) **Clemmensen's reduction** : With amalgamated zinc and conc. HCl, benzaldehyde is reduced to toluene.



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

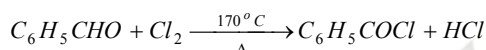
(vii) **Tischenko reaction** : On heating benzaldehyde with aluminium alkoxide (ethoxide) and a little of anhydrous  $AlCl_3$  or  $ZnCl_2$ , it undergoes an intermolecular oxidation and reduction (like aliphatic aldehydes) to form acid and alcohol respectively as such and react to produce benzyl benzoate (an ester).



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

(a) With fehling's solution : No reaction

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



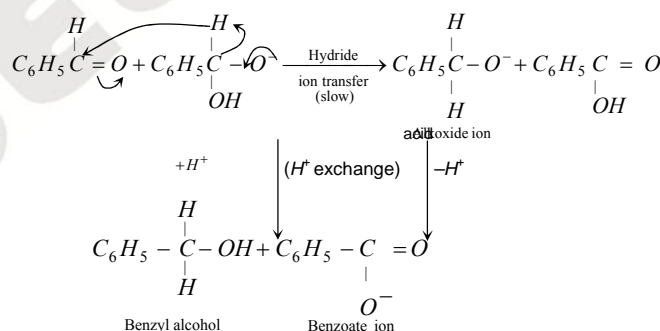
(c) Cannizzaro's reaction :  $2C_6H_5CHO \xrightarrow{KOH} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Potassium benzoate}}{C_6H_5COOK}$

The possible Mechanism is

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



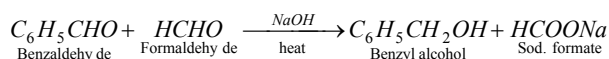
**Second step** is the transfer of hydride ion directly to the another aldehyde molecule, the latter is thus reduced to alkoxide ion and the former (ion I) is oxidised to an acid.



**Third Step** is exchange of protons to give most stable pair alcohol and acid anion.

So one molecule of aldehyde acts as hydride donor and the other acts as hydride acceptor. In other words, Cannizzaro's reaction is an example of self reduction and oxidation.

□ Two different aldehydes each having no  $\alpha$ -hydrogen atom, exhibit crossed Cannizzaro's reaction when heated in alkaline solution.

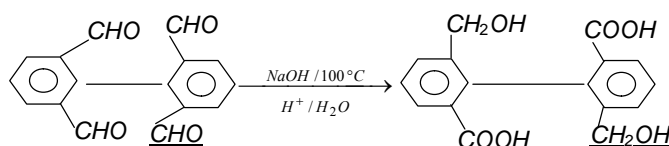


Aldehyde which do not have  $\alpha$ -hydrogen ( $C_6H_5 - CHO$ ,  $CCl_3CHO$ ,  $(CH_3)_3C - CHO$ ,  $CH_2O$  etc.)

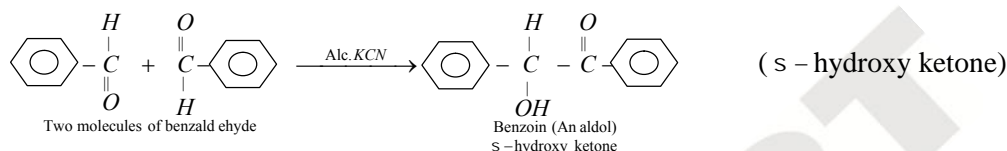


undergoes Cannizzaro's reaction.

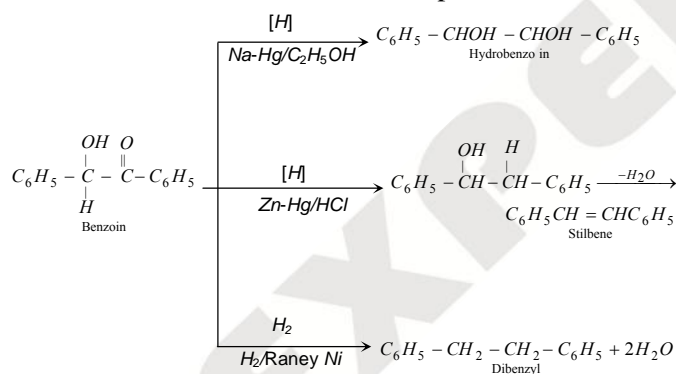
### Intramolecular cannizzaro reaction



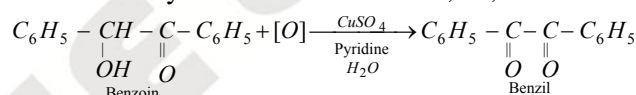
### (d) Benzoin Condensation



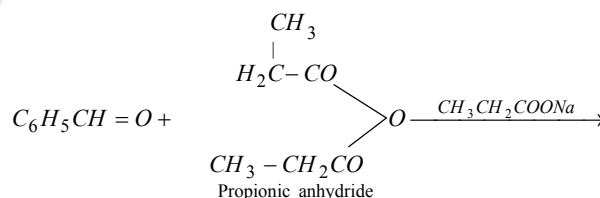
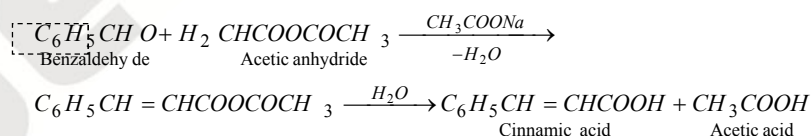
Benzoin can also be reduced to a number of product i.e.,



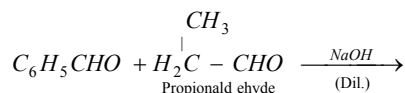
Benzoin can be readily oxidised to a diketone, i.e., benzil.

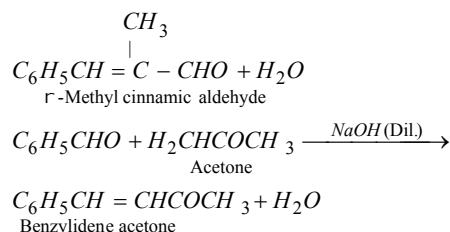


### (e) Perkin's reaction

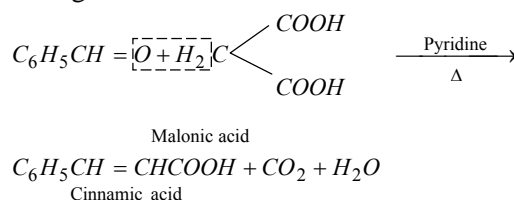


### (f) Claisen condensation [Claisen-schmidt reaction]

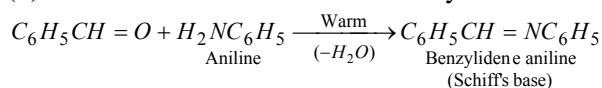




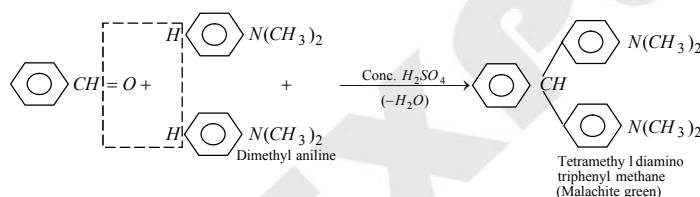
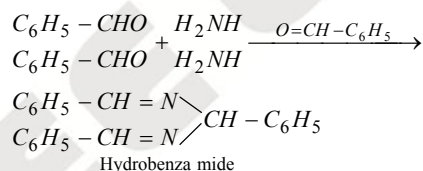
## (g) Knoevenagel reaction



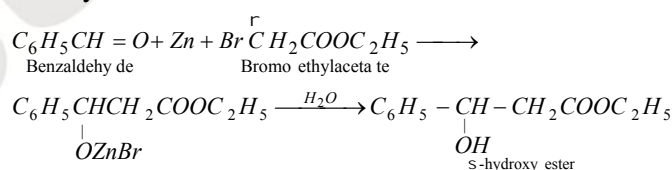
## (h) Reaction with aniline : Benzaldehyde reacts with aniline and forms Schiff's base



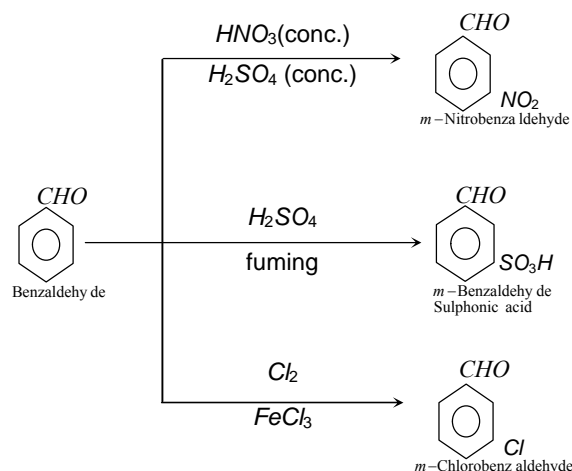
## Reaction with Dimethylaniline

(i) Reaction with Ammonia : Benzaldehyde reacts with ammonia to form hydrobenzamide aldehyde other than  $\text{CH}_2\text{O}$  give aldehyde ammonia while  $\text{CH}_2\text{O}$  forms urotropine.

## (j) Reformatsky reaction



(k) Reaction of benzene ring



(4) **Uses :** Benzaldehyde is used,

- (i) In perfumery
- (ii) In manufacture of dyes
- (iii) In manufacture of benzoic acid, cinnamic acid, cinnamaldehyde, Schiff's base, etc.

(5) **Tests :** (i) Benzaldehyde forms a white precipitate with  $\text{NaHSO}_3$  solution.

(ii) Benzaldehyde forms a yellow precipitate with 2 : 4 dinitrophenyl hydrazine.

(iii) Benzaldehyde gives pink colour with Schiff's reagent.

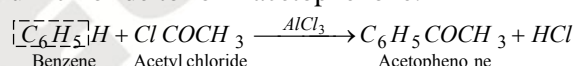
(iv) Benzaldehyde forms black precipitate or silver mirror with Tollen's reagent.

(v) Benzaldehyde on treatment with alkaline  $\text{KMnO}_4$  and subsequent acidification gives a white precipitate of benzoic acid on cooling.

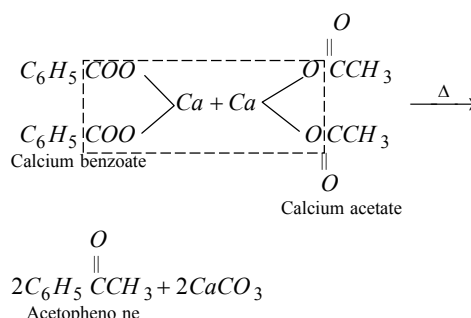
### Acetophenone, $\text{C}_6\text{H}_5\text{COCH}_3$ , Acetyl Benzene

(1) **Method of preparation**

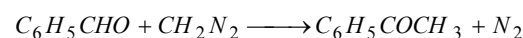
(i) **Friedel-Craft's reaction :** Acetyl chloride reacts with benzene in presence of anhydrous aluminium chloride to form acetophenone.



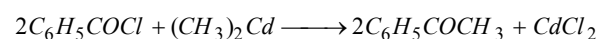
(ii) By distillation of a mixture of calcium benzoate and calcium acetate.



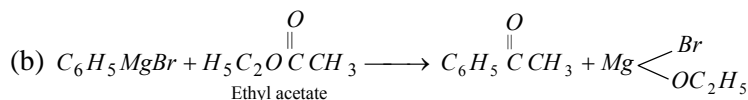
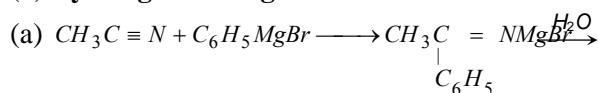
(iii) By methylation of benzaldehyde with diazomethane.



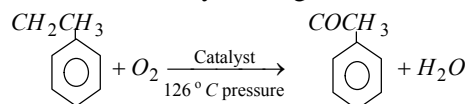
(iv) By treating benzoyl chloride with dimethyl cadmium.



## (v) By Grignard reagent

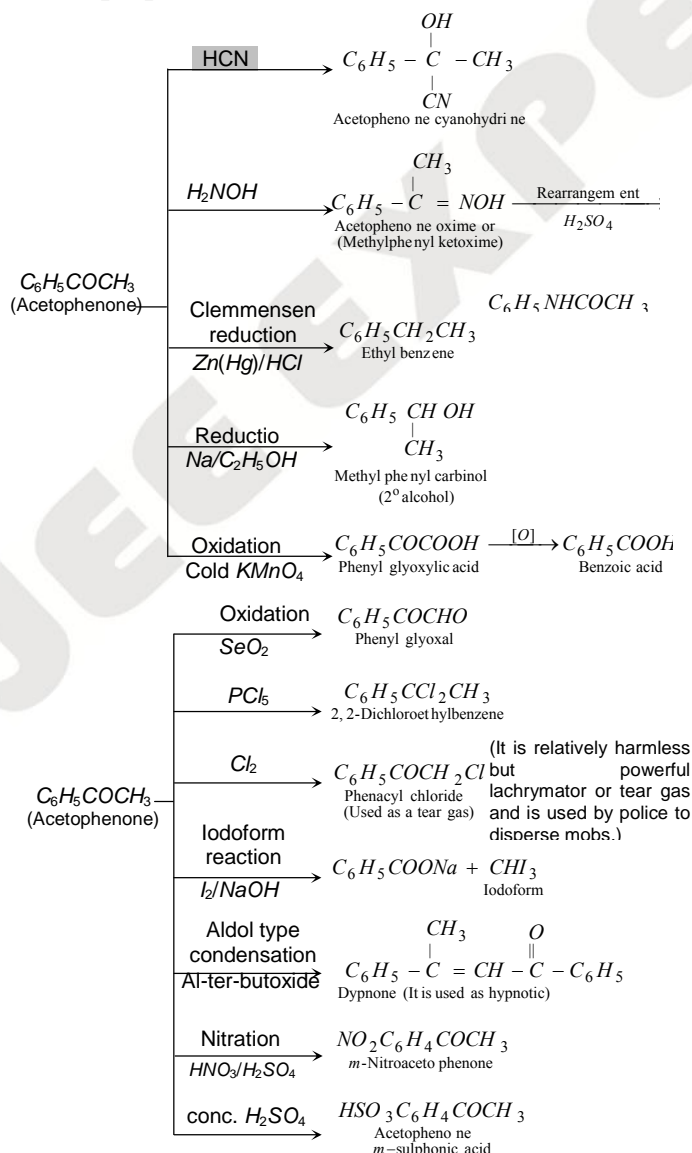


(vi) **Commercial preparation** : Ethylbenzene is oxidised with air at  $126^\circ\text{C}$  under pressure in presence of a catalyst manganese acetate.



(2) **Physical properties** : It is a colourless crystalline solid with melting point  $20^\circ\text{C}$  and boiling point  $202^\circ\text{C}$ . It has characteristic pleasant odour. It is slightly soluble in water. Chemically, It is similar to acetone.

(3) **Chemical properties** :

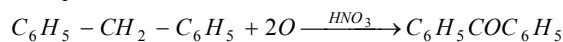


- (4) **Uses :** It is used in perfumery and as a sleep producing drug.

**Benzophenone,  $C_6H_5COC_6H_5$**

**(1) Method of preparation**

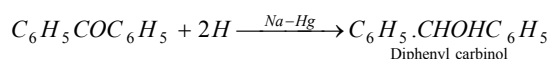
**(i) From alkyl benzenes**



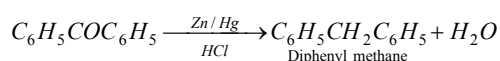
- (2) Physical properties :** It is a colourless, pleasant smelling solid.

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

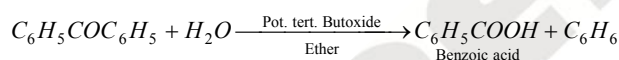
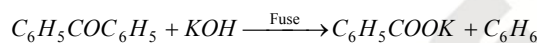
**(i) Reduction :**



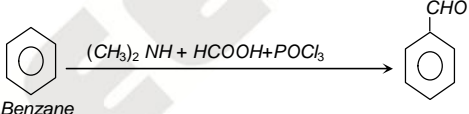
**(ii) Clemmenson reduction :**



**(iii) Fusion with KOH :**



### TIPS & TRICKS

- Acidified  $K_2Cr_2O_7$  i.e., chromic acid sulphuric acid mixture is known as Jone's reagent. When used as an oxidising agent unlike acidified  $KMnO_4$  it does not diffect a double bond.  
 $CH_2=CHCH_2OH \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_2=CHCHO$
- Vilsmeier reaction : this reaction involves the conversion of aromatic compounds to aldehydes in the presence of a 2° amino and formic acid.  


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

\*\*\*\*\*

# EXERCISE - I

## OBJECTIVE QUESTION

- Reaction of acetaldehyde with HCN followed by hydrolysis gives a compound which shows  
 (a) Optical isomerism (b) Geometrical isomerism  
 (c) Metamerism (d) Tautomerism
- In aldehydes and ketones, carbon of carbonyl group is  
 (a)  $sp^3$  hybridised (b)  $sp^2$  hybridised  
 (c)  $sp$  hybridised (d) Unhybridised
- The IUPAC name of the following structure is  

$$\begin{array}{c} CH_3 \quad O \\ | \quad || \\ CH_3 - CH - C - CH_2 - CH_2OH \end{array}$$
  
 (a) 1-hydroxy 4-methyl 3-pentanone (b) 2-methyl 5-hydroxy 3-pentanone  
 (c) 4-methyl 3-oxo 1-pentanol (d) Hexanol-1, one-3
- Glyoxal** is  
 (a)  $CH_2O - CH_2O$  (b)  $\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$  (c)  $\begin{array}{c} CHO \\ | \\ CHO \end{array}$  (d)  $\begin{array}{c} CH_2OH \\ | \\ CHO \end{array}$
- Aldehydes are isomeric with  
 (a) Ketones (b) Ethers (c) Alcohols (d) Fatty acids
- Which of the following compounds does not contain an  $-OH$  group  
 (a) Phenol (b) Carboxylic acid (c) Aldehydes (d) Alcohols
- IUPAC name of  $CH_3COCH_3$  is  
 (a) Acetone (b) 2-propanone (c) Dimethyl ketone (d) Propanal
- What is the compound called if remaining two valencies of a carbonyl group are satisfied by two alkyl groups  
 (a) Aldehyde (b) Ketone (c) Acid (d) Acid chloride
- $\begin{array}{c} OH \\ | \\ CH_3 - C - CN \\ | \\ H \end{array}$  is  
 (a) Acetaldehyde cyanohydrin (b) Acetone cyanohydrin  
 (c) Cyanoethanol (d) Ethanol nitrile
- Ethanedial has which functional group(s)  
 (a) One ketonic (b) Two aldehydic (c) One double bond (d) Two double bond

11. In the group  $\begin{smallmatrix} R' \\ \diagup \\ C \\ \diagdown \\ R \end{smallmatrix} = O$  the carbonyl carbon is joined to other atoms by  
(a) Two sigma and one pi bonds (b) Three sigma and one pi bonds  
(c) One sigma and two pi bonds (d) Two sigma and two pi bonds
12. Which of the following types of isomerism is shown by pentanone  
(a) Chain isomerism (b) Position isomerism  
(c) Functional isomerism (d) All of these
13. IUPAC name of  $CCl_3CHO$  is  
(a) Chloral (b) Trichloro acetaldehyde  
(c) 1, 1, 1-trichloroethanal (d) 2, 2, 2-trichloroethanal
14. Which of the following is a mixed ketone  
(a) Pentanone (b) Acetophenone (c) Benzophenone (d) Butanone
15. Chloral is  
(a)  $CCl_3CHO$  (b)  $CCl_3COCH_3$  (c)  $CCl_3COCCl_3$  (d)  $CCl_3CH_2OH$
16. Carbonyl compounds are usually  
(a) Ethers, aldehydes, ketones and carboxylic acids  
(b) Aldehydes, ketones and carboxylic acids  
(c) Aldehydes and ketones  
(d) Carboxylic acids
17. Acetone and acetaldehyde are  
(a) Position isomers (b) Functional isomers  
(c) Not isomers (d) Chain isomers
18. Which of the aldehyde is most reactive ?  
(a)  $C_6H_5-CHO$  (b)  $CH_3CHO$   
(c)  $HCHO$  (d) All the equally reactive

## EXERCISE - II

### Preparation

- The end product in the following sequence of reaction is  

$$HC \equiv CH \xrightarrow[20\% H_2SO_4]{1\% HgSO_4} A \xrightarrow{CH_3MgX} B \xrightarrow{[O]} \text{product}$$

(a) Acetic acid (b) Isopropyl alcohol  
(c) Acetone (d) Ethanol
- In the following reaction, product P is  $R - \overset{\overset{O}{\parallel}}{C} - Cl \xrightarrow[Pd - BaSO_4]{H_2} P$   

(a)  $RCH_2OH$  (b)  $R COOH$   
(c)  $RCHO$  (d)  $RCH_3$
- Acetophenone is prepared from  

(a) Rosenmund reaction (b) Sandmeyer reaction  
(c) Wurtz reaction (d) Friedel craft reaction
- Compound which gives acetone on ozonolysis  

(a)  $CH_3 - CH = CH - CH_3$  (b)  $(CH_3)_2C = C(CH_3)_2$   
(c)  $C_6H_5CH = CH_2$  (d)  $CH_3CH = CH_2$
- $CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_2 - COOC_2H_5 \xrightarrow[H_2O]{NaOH} A$ ,  
 product 'A' in the reaction is  

(a)  $CH_3COOH$  (b)  $C_2H_5OH$  (c)  $CH_3COCH_3$  (d)  $C_2H_5CHO$
- Which one of the following compounds is prepared in the laboratory from benzene by a substitution reaction  

(a) Glyoxal (b) Cyclohexane  
(c) Acetophenone (d) Hexabromo cyclohexane
- Ketones ( $R - \overset{\overset{O}{\parallel}}{C} - R_1$ ) where  $R = R_1 =$  alkyl group. It can be obtained in one step by  

(a) Hydrolysis of esters (b) Oxidation of primary alcohol  
(c) Oxidation of secondary alcohol (d) Reaction of acid halide with alcohols
- Predict the product 'B' in the sequence of reaction  $HC \equiv CH \xrightarrow[HgSO_4]{30\% H_2SO_4} A \xrightarrow{NaOH} B$   

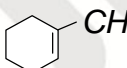
(a)  $CH_3COONa$  (b)  $CH_3COOH$   
(c)  $CH_3CHO$  (d)  $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_2CHO$
- $CH_3COCl \xrightarrow[Pd / BaSO_4]{2H} CH_3CHO + HCl$ ;  
 The above reaction is called  

(a) Reimer-Tiemann reaction (b) Cannizzaro reaction  
(c) Rosenmund reaction (d) Reformatsky reaction



10. The oxidation of toluene to benzaldehyde by chromyl chloride is called  
 (a) Cannizzaro reaction (b) Wurtz reaction  
 (c) Etard reaction (d) Reimer-Tiemann reaction
11. From which of the following tertiary butyl alcohol is obtained by the action of methyl magnesium iodide  
 (a)  $HCHO$  (b)  $CH_3CHO$  (c)  $CH_3COCH_3$  (d)  $CO_2$
12. Catalyst used in Rosenmund reduction is  
 (a)  $Pd / BaSO_4$  (b) Zn-Hg couple (c)  $LiAlH_4$  (d)  $Ni / H_2$
13.  $CH_3 - CH_2 - C \equiv CH \xrightarrow[H_2O]{R}$  Butanone, R is  
 (a)  $Hg^{++}$  (b)  $KMnO_4$  (c)  $KClO_3$  (d)  $K_2Cr_2O_7$
14. Dry heating of calcium acetate gives  
 (a) Acetaldehyde (b) Ethane (c) Acetic acid (d) Acetone
15. Identify the product C in the series  
 $CH_3CN \xrightarrow{Na / C_2H_5OH} A \xrightarrow{HNO_2} B \xrightarrow{\text{Tollen's reagent}} C$   
 (a)  $CH_3COOH$  (b)  $CH_3CH_2NHOH$  (c)  $CH_3CONH_2$  (d)  $CH_3CHO$
16. Acetophenone is prepared by the reaction of which of the following in the presence of  $AlCl_3$  catalyst  
 (a) Phenol and acetic acid (b) Benzene and acetone  
 (c) Benzene and acetyl chloride (d) Phenol and acetone
17. Isopropyl alcohol on oxidation gives  
 (a) Acetone (b) Acetaldehyde (c) Ether (d) Ethylene
18. On heating calcium acetate and calcium formate, the product formed is  
 (a)  $CH_3COCH_3$  (b)  $CH_3CHO$  (c)  $HCHO + CaCO_3$  (d)  $CH_3CHO + CaCO_3$
19. Which of the following compound gives a ketone with Grignard reagent  
 (a) Formaldehyde (b) Ethyl alcohol (c) Methyl cyanide (d) Methyl iodide
20. In the Rosenmund's reduction,  $BaSO_4$  taken with catalyst Pd acts as  
 (a) Promotor (b) Catalytic poison  
 (c) Cooperator (d) Absorber
21. The Clemmenson reduction of acetone yields  
 (a) Ethanol (b) Ethanal (c) Propane (d) Propanol
22. Catalyst  $SnCl_2 / HCl$  is used in  
 (a) Stephen's reduction (b) Cannizzaro reaction  
 (c) Clemmensen's reduction (d) Rosenmund's reduction

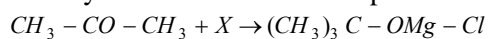
23. Methyl ethyl ketone is prepared by the oxidation of  
 (a) 2-propanol (b) 1-butanol (c) 2-butanol (d) t-butyl alcohol
24. Benzaldehyde can be prepared by oxidation of toluene by  
 (a) Acidic  $KMnO_4$  (b)  $K_2Cr_2O_7$  (c)  $CrO_2Cl_2$  (d) All of these
25.  $C_6H_6 + CO + HCl \xrightarrow{\text{Anhy } AlCl_3} X + HCl$   
 Compound X is  
 (a)  $C_6H_5CH_3$  (b)  $C_6H_5CH_2Cl$  (c)  $C_6H_5CHO$  (d)  $C_6H_5COOH$
26. Which of the following gases when passed through warm dilute solution of  $H_2SO_4$  in presence of  $HgSO_4$  gives acetaldehyde  
 (a)  $CH_4$  (b)  $C_2H_6$  (c)  $C_2H_4$  (d)  $C_2H_2$
27.  $CH_3COCH_3$  can be obtained by  
 (a) Heating acetaldehyde with methanol (b) Oxidation of propyl alcohol  
 (c) Oxidation of isopropyl alcohol (d) Reduction of propionic acid
28. Propyne on hydrolysis in presence of HCl and  $HgSO_4$  gives  
 (a) Acetaldehyde (b) Acetone (c) Formaldehyde (d) None of these
29. Which of the following on reaction with  $NH_3$  gives urinary antiseptic compound  
 (a) HCHO (b)  $CH_3CHO$  (c)  $C_6H_5CHO$  (d)  $C_6H_5CH_2CHO$
30. The oxidation product of 2-propanol with hot conc.  $HNO_3$  is  
 (a) Ethanoic acid (b) Propanone (c) Propanal (d) None of these
31. Hydrolysis of ozonide of 1-butene gives  
 (a) Ethylene only (b) Acetaldehyde and Formaldehyde  
 (c) Propionaldehyde and Formaldehyde (d) Acetaldehyde only  
 (e) Acetaldehyde and Oxalic acid
32. Ketones are prepared by  
 (a) Clemmensen's reduction (b) Cannizzaro reaction  
 (c) Rosenmund's reduction (d) Oppenauer's oxidation
33.  $O_3$  reacts with  $CH_2 = CH_2$  to form ozonide. On hydrolysis it forms  
 (a) Ethylene oxide (b) HCHO (c) Ethylene glycol (d) Ethyl alcohol
34. Ethyne on reaction with water in the presence of  $HgSO_4$  and  $H_2SO_4$  gives  
 (a) Acetone (b) Acetaldehyde (c) Acetic acid (d) Ethyl alcohol

35.  $CH_3 - CH_2 - C \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} A$ , the compound A is
- (a)  $CH_3 - CH_2 - \overset{\overset{O}{\parallel}}{C} - CH_3$  (b)  $CH_3 - CH_2 - CH_2 - CHO$   
 (c)  $CH_3 - CH_2 - CH_2 - COOH$  (d) None of these
36. When a mixture of methane and oxygen is passed through heated molybdenum oxide, the main product formed is  
 (a) Methanoic acid (b) Ethanal (c) Methanol (d) Methanal
37. Benzoin is  
 (a) Compound containing an aldehyde and a ketonic group  
 (b)  $\alpha$ ,  $\beta$ -unsaturated acid  
 (c)  $\alpha$ -hydroxy aldehyde  
 (d)  $\alpha$ -hydroxy ketone
38. The oxidation of benzyl chloride with lead nitrate gives  
 (a) Benzyl alcohol (b) Benzoic acid  
 (c) Benzaldehyde (d) p-chlorobenzaldehyde
39.  $R - CH = CH_2 + CO + H_2 \xrightarrow[High Pressure]{High Temp} RCH_2CH_2CHO$ . The above reaction is  
 (a) Mendius reaction (b) Oxo process  
 (c) Sandorn's reaction (d) Stephen's reaction
40. Glycerol reacts with potassium bisulphate to produce  
 (a) Allyl iodide (b) Allyl sulphate  
 (c) Acryl aldehyde (d) Glycerol trisulphate
41. The reagent used in Gatterman Koch aldehyde synthesis is  
 (a)  $Pb / BaSO_4$  (b) alkaline  $KMnO_4$  (c) acidic  $KMnO_4$  (d)  $CO + HCl$
42.  On reductive ozonolysis yields  
 (a) 6-oxoheptanal (b) 6-oxoheptanoic acid  
 (c) 6-hydroxyheptanal (d) 3-hydroxypentanal
43. An alkene of molecular formula  $C_9H_{18}$  on ozonolysis gives 2,2 dimethyl propanal & 2-butanone, then the alkene is  
 (a) 2, 2, 4-trimethyl -3-hexene (b) 2, 2, 6-trimethyl-3-hexene  
 (c) 2, 3, 4-trimethyl-2-hexene (d) 2, 2, 4-trimethyl-2-hexene  
 (e) 2, 2dimethyl-2-heptene

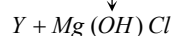
## EXERCISE -III

### Properties

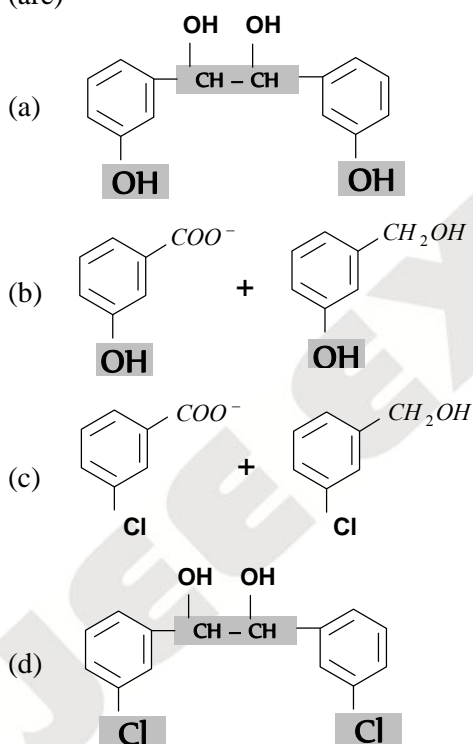
1. Identify the reactant X and the product Y



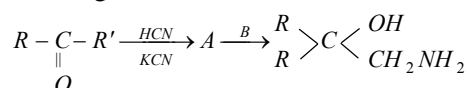
↓ Hydrolysis



- (a)  $X = MgCl_2$ ;  $Y = CH_3CH = CH_2$                       (b)  $X = CH_3MgCl$ ;  $Y = C_2H_5COCH_3$   
 (c)  $X = CH_3MgCl$ ;  $Y = (CH_3)_3C - OH$                       (d)  $X = C_2H_5MgCl$ ;  $Y = (CH_3)_3C - OH$
2. When m-chlorobenzaldehyde is treated with 50% KOH solution, the product (s) obtained is (are)

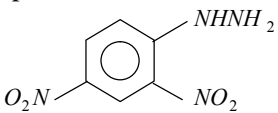


3. A and B in the following reactions are



- (a)  $A = RR'C \begin{matrix} CN \\ < \\ OH \end{matrix}$ ,  $B = LiAlH_4$                       (b)  $A = RR'C \begin{matrix} OH \\ < \\ COOH \end{matrix}$ ,  $B = NH_3$   
 (c)  $A = RR'C \begin{matrix} CN \\ < \\ OH \end{matrix}$ ,  $B = H_3O^+$                       (d)  $A = RR'CH_2CN$ ,  $B = NaOH$

4. Reduction of Aldehydes and Ketones to hydrocarbon take place in the presence of  
 (a) Zn amalgam and HCl acid (b)  $Pd / BaSO_4$   
 (c) Anhydrous  $AlCl_3$  (d) Ni/Pt
5. Reduction of  $>C=O$  to  $CH_2$  can be carried out with  
 (a) Catalytic reduction (b)  $Na / C_2H_5OH$   
 (c) Wolf-Kischner reduction (d)  $LiAlH_4$
6. For  $C_6H_5CHO$  which of the following is incorrect  
 (a) On oxidation it yields benzoic acid (b) It is used in perfumery  
 (c) It is an aromatic aldehyde (d) On reduction yields phenol
7. Grignard reagent on reaction with acetone forms  
 (a) Tertiary alcohol (b) Secondary alcohol  
 (c) Acetic acid (d) Acetaldehyde
8. Which of the following is incorrect  
 (a)  $FeCl_3$  is used in the detection of phenols  
 (b) Fehling solution is used in the detection of glucose  
 (c) Tollen's reagent is used in detection of unsaturation  
 (d)  $NaHSO_3$  is used in the detection of carbonyl compounds
9. Consider the following statement Acetophenone can be prepared by  
 (1) Oxidation of 1-phenylethanol  
 (2) Reaction of benzalcohol with methyl magnesium bromide  
 (3) Friedel craft's reaction of benzene with acetyl chloride  
 (4) Distillation of calcium benzoate [SCRA 2001]  
 (a) 1 and 2 (b) 1 and 4 (c) 1 and 3 (d) 3 and 4
10. Which one of the following pairs is not correctly matched  
 (a)  $>C=O \xrightarrow{\text{Clemenson's reduction}} >CH_2$  (b)  $>C=O \xrightarrow{\text{Wolf-Kishner reduction}} >CHOH$   
 (c)  $-COCl \xrightarrow{\text{Rosenmund's reduction}} CHO$  (d)  $-C \equiv N \xrightarrow{\text{Stephen reduction}} CHO$
11. Which of the following gives aldol condensation reaction  
 (a)  $C_6H_5OH$  (b)  $C_6H_5 - \overset{\overset{O}{\parallel}}{C} - C_6H_5$   
 (c)  $CH_3CH_2 - \overset{\overset{O}{\parallel}}{C} - CH_3$  (d)  $(CH_3)_3C - \overset{\overset{O}{\parallel}}{C} - CH_3$
12. Which of the following products is formed when benzaldehyde is treated with  $CH_3MgBr$  and the addition product so obtained is subjected to acid hydrolysis  
 (a) Secondary alcohol (b) A primary alcohol  
 (c) Phenol (d) Tert-Butyl alcohol

13. Aldol condensation will not be observed in  
 (a) Chloral (b) Phenyl acetaldehyde  
 (c) Hexanal (d) Ethanol
14. Which of the following compounds containing carbonyl group will give coloured crystalline compound with
- 
- (a)  $CH_3COCl$  (b)  $CH_3COCH_3$  (c)  $CH_3CO(OC_2H_5)$  (d)  $CH_3CONH_2$   
 (e)  $HO(C_6H_4)COOH$
15. Which of the following organic compounds exhibits positive Fehling test as well as iodoform test  
 (a) Methanal (b) Ethanol (c) Propanone (d) Ethanal
16. Which of the following compound will undergo self aldol condensation in the presence of cold dilute alkali  
 (a)  $C_6H_5CHO$  (b)  $CH_3CH_2CHO$   
 (c)  $CH \equiv C - CHO$  (d)  $CH_2 = CH - CHO$
17. Acetaldehyde when treated with dilute NaOH gives  
 (a)  $CH_3CH_2OH$  (b)  $CH_3COOH$   
 (c)  $CH_3 - \underset{\substack{| \\ OH}}{CH} - CH_2 - CHO$  (d)  $CH_3 - CH_3$
18.  $C_2H_5CHO$  and  $(CH_3)_2CO$  can be distinguished by testing with  
 (a) Phenyl hydrazine (b) Hydroxylamine  
 (c) Fehling solution (d) Sodium bisulphite
19. Which of the following will undergo aldol condensation  
 (a) Acetaldehyde (b) Propanaldehyde  
 (c) Benzaldehyde (d) Trideuteroacetaldehyde
20. Which of the following oxidation reactions can be carried out with chromic acid in aqueous acetone at  $5 - 10^\circ C$   
 (a)  $CH_3(CH_2)_3C \equiv \underset{\substack{| \\ OH}}{C} - CH - CH_3 \rightarrow$   
 $CH_3(CH_2)_3C \equiv \overset{\substack{O \\ ||}}{C} - CH_3$   
 (b)  $CH_3(CH_2)_3CH = CH - CH_2OH \rightarrow$   
 $CH_3(CH_2)_3CH = CH - CHO$   
 (c)  $C_6H_5CH_3 \rightarrow C_6H_5COOH$   
 (d)  $CH_3(CH_2)_3CH_2OH \rightarrow CH_3(CH_2)_3CHO$

21. Acetaldehyde cannot show  
(a) Iodoform test (b) Lucas test (c) Benedict's test (d) Tollen's test
22. Benzaldehyde + NaOH  $\rightarrow$   
(a) Benzyl alcohol (b) Benzoic alcohol (c) Hydrobenzamide (d) Cinnamic acid
23. The following reagent converts  $C_6H_5COCHO$  to  $C_6H_5CHOHCOONa$   
(a) Aq. NaOH (b) Acidic  $Na_2S_2O_3$   
(c)  $Na_2CrO_4 / H_2SO_4$  (d)  $NaNO_2 / HCl$
24. Benzyl alcohol and sodium benzoate is obtained by the action of sodium hydroxide on benzaldehyde. This reaction is known as  
(a) Perkin's reaction (b) Cannizzaro's reaction  
(c) Sandmeyer's reaction (d) Claisen condensation
25. To distinguish between formaldehyde and acetaldehyde, we require  
(a) Tollen's reagent (b) Fehling's solution  
(c) Schiff's reagent (d) Caustic soda solution
26. Which of the following does not give iodoform test  
(a)  $CH_3CH_2OH$  (b)  $CH_3OH$  (c)  $CH_3CHO$  (d)  $PhCOCH_3$
27. Which of the following will not give iodoform test  
(a) Ethanal (b) Ethanol (c) 2-propanone (d) 3-pentanone
28. Which of the following will not give the iodoform test  
(a) Acetophenone (b) Ethanal (c) Benzophenone (d) Ethanol
29. Haloform test is given by the following substance  
(a) HCHO (b)  $(CH_3)_2CO$  (c)  $CH_3OCH_3$  (d)  $CH_3CH_2Cl$
30. Dimethyl ketones are usually characterised through  
(a) Tollen's reagent (b) Iodoform test  
(c) Schiff's test (d) Benedict's reagent
31. The light yellow compound produced when acetone reacts with iodine and alkali, is  
(a)  $CH_3.CO.CH_2I$  (b)  $CH_3I$  (c)  $CHI_3$  (d) None of these
32. If formaldehyde and KOH are heated, then we get  
(a) Acetylene (b) Methane (c) Methyl alcohol (d) Ethyl formate
33. Which of the following reagent reacts differently with  $HCHO$ ,  $CH_3CHO$  and  $CH_3COCH_3$   
(a) HCN (b)  $NH_2NH_2$  (c)  $NH_2OH$  (d)  $NH_3$
34. Acetaldehyde reacts with  $C_2H_5MgCl$  the final product is  
(a) An aldehyde (b) A ketone  
(c) A primary alcohol (d) A secondary alcohol

35. Treatment of propionaldehyde with dilute NaOH solution gives  
 (a)  $CH_3CH_2COOCH_2CH_2CH_3$  (b)  $CH_3CH_2CHOHCH(CH_3)CHO$   
 (c)  $CH_3CH_2CHOHCH_2CH_2CHO$  (d)  $CH_3CH_2COCH_2CH_2CHO$
36. Aldol condensation of acetaldehyde involves the formation of which of the following intermediate  
 (a) Acetate ion (b) A carbanion (c) A carbonium ion (d) A free radical
37.  $3CH_3COCH_3 \xrightarrow{HCl} (CH_3)_2C=CH-CO-CH=C(CH_3)_2$   
 This polymer (B) is obtained when acetone is saturated with hydrogen chloride gas, B can be  
 (a) Phorone (b) Formose (c) Diacetone alcohol (d) Mesityl oxide
38. Aromatic aldehydes undergo disproportionation in presence of sodium or potassium hydroxide to give corresponding alcohol and acid. The reaction is known as  
 (a) Wurtz's reaction (b) Cannizzaro reaction  
 (c) Friedel-Craft's reaction (d) Claisen reaction
39. m-chlorobenzaldehyde on reaction with conc. KOH at room temperature gives  
 (a) Potassium m-chlorobenzoate and m-hydroxy benzaldehyde  
 (b) m-hydroxy benzaldehyde and m-chlorobenzyl alcohol  
 (c) m-chlorobenzyl alcohol and m-hydroxy benzyl alcohol  
 (d) Potassium m-chlorobenzoate and m-chlorobenzyl alcohol
40. Which of the following does not give yellow precipitate with  $NaOH + KI$   
 (a) Acetone (b) Acetaldehyde  
 (c) Benzaldehyde (d) Acetophenone
41. The alkaline  $CuSO_4$  containing sodium potassium tartrate does not react with  
 (a)  $CH_3CHO$  (b)  $C_2H_5CHO$  (c)  $C_6H_5CH_2CHO$  (d)  $C_6H_5CHO$
42. Correct order of reactivity of  $CH_3CHO$ ,  $C_2H_5COCH_3$  and  $CH_3COCH_3$  is  
 (a)  $CH_3CHO > CH_3COCH_3 > CH_3COC_2H_5$  (b)  $C_2H_5COCH_3 > CH_3COCH_3 > CH_3CHO$   
 (c)  $CH_3COCH_3 > CH_3CHO > C_2H_5COCH_3$  (d)  $CH_3COCH_3 > C_2H_5COCH_3 > CH_3CHO$
43. One mole of an organic compound requires 0.5 mole of oxygen to produce an acid. The compound may be  
 (a) Alcohol (b) Ether (c) Ketone (d) Aldehyde
44. Aldehydes can be oxidised by  
 (a) Tollen's reagent (b) Fehling solution  
 (c) Benedict solution (d) All of these
45. Silver mirror is a test for  
 (a) Aldehydes (b) Thio alcohols (c) Amines (d) Ethers



46.  $CH_3CH = CHCHO$  is oxidised to  $CH_3CH = CHCOOH$  using  
(a) Alkaline  $KMnO_4$  (b) Selenium dioxide (c) Ammoniacal  $AgNO_3$  (d) All of these
47. Which of the following does not turn Schiff's reagent to pink  
(a) Formaldehyde (b) Benzaldehyde (c) Acetone (d) Acetaldehyde
48. Fehling's test is positive for  
(a) Acetaldehyde (b) Benzaldehyde (c) Ether (d) Alcohol
49. Acetaldehyde and acetone differ in their reaction with  
(a) Sodium bisulphite (b) Ammonia  
(c) Phosphorus pentachloride (d) Phenyl hydrazine
50. The final product formed when acetaldehyde is reduced with sodium and alcohol is  
(a) Ethylene (b) Ethyl alcohol (c) Ethene (d) All of these
51. The compound obtained by the reduction of propionaldehyde by amalgamated zinc and concentrated HCl is  
(a) Propanol (b) Propane (c) Propene (d) All of these
52. Formaldehyde when treated with KOH gives methanol and potassium formate. The reaction is known as  
(a) Perkin reaction (b) Claisen reaction  
(c) Cannizzaro reaction (d) Knoevenagel reaction
53. Aldehydes and ketones give addition reaction with  
(a) Hydrazine (b) Phenyl hydrazine  
(c) Semicarbazide (d) Hydrogen cyanide  
(e) All of these
54. Acetaldehyde reacts with  
(a) Electrophiles only (b) Nucleophiles only  
(c) Free radicals only (d) Both electrophiles and nucleophiles
55. The typical reactions of aldehyde is  
(a) Electrophilic addition (b) Nucleophilic substitution  
(c) Nucleophilic addition (d) Nucleophilic elimination
56. Which will not give acetamide on reaction with ammonia  
(a) Acetic acid (b) Acetyl chloride (c) Acetic anhydride (d) Methyl formate
57. The addition of  $HCN$  to carbonyl compounds is an example of  
(a) Nucleophilic substitution (b) Electrophilic addition  
(c) Nucleophilic addition (d) Electrophilic substitution
58. Which of the following reagents is used to distinguish acetone and acetophenone  
(a)  $NaHSO_3$  (b) Grignard reagent (c)  $Na_2SO_4$  (d)  $NH_4Cl$

59. The product formed by the reaction of chlorine with benzaldehyde in the absence of a catalyst is  
 (a) Chlorobenzene (b) Benzyl chloride  
 (c) Benzoyl Chloride (d) o-Chlorobenzaldehyde
60. Which of the following compound is resistant to nucleophilic attack by hydroxyl ions  
 (a) Methyl acetate (b) Acetonitrile (c) Dimethyl ether (d) Acetamide
61. Glucose molecule reacts with X number of molecules of phenylhydrazine to yield osazone. The value of X is  
 (a) One (b) Two (c) Three (d) Four
62. In which of the following reactions aromatic aldehyde is treated with acid anhydride in presence of corresponding salt of the acid to give unsaturated aromatic acid  
 (a) Friedel-Craft's reaction (b) Perkin reaction  
 (c) Wurtz reaction (d) None of these
63.  $2\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3 \xrightarrow[\text{H}^+]{\text{Mg/Hg}}$  Product, product in the reaction is  
 (a)  $\text{H}_3\text{C} - \underset{\text{OH}}{\underset{\parallel}{\text{C}}} - \underset{\text{OH}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$  (b)  $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{O} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$   
 (c)  $\text{CH}_3 - \underset{\text{OH}}{\underset{\parallel}{\text{C}}} - \underset{\text{OH}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$  (d) None of these
64. Cinnamic acid is formed when  $\text{C}_6\text{H}_5 - \text{CHO}$  condenses with  $(\text{CH}_3\text{CO})_2\text{O}$  in presence of  
 (a) Conc.  $\text{H}_2\text{SO}_4$  (b) Sodium acetate  
 (c) Sodium metal (d) Anhydrous  $\text{ZnCl}_2$
65. A mixture of benzaldehyde and formaldehyde on heating with aqueous  $\text{NaOH}$  solution gives  
 (a) Benzyl alcohol and sodium formate (b) Sodium benzoate and methyl alcohol  
 (c) Sodium benzoate and sodium formate (d) Benzyl alcohol and methyl alcohol
66. The reaction,  
 $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{OCH}_3 + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}^+ \text{ or } \text{OH}^-}$   
 $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{OC}_2\text{H}_5 + \text{CH}_3\text{OH}$  is called  
 (a) Perkin's reaction (b) Claisen Schmidt reaction  
 (c) Esterification (d) Trans-esterification
67. Formaldehyde reacts with ammonia to give urotropine. The formula of urotropine is  
 (a)  $(\text{CH}_2)_6\text{N}_4$  (b)  $(\text{CH}_2)_4\text{N}_3$  (c)  $(\text{CH}_2)_6\text{N}_6$  (d)  $(\text{CH}_2)_3\text{N}_3$
68. Aldol condensation will not take place in  
 (a)  $\text{HCHO}$  (b)  $\text{CH}_3\text{CH}_2\text{CHO}$  (c)  $\text{CH}_3\text{CHO}$  (d)  $\text{CH}_3\text{COCH}_3$

69. Contents of three bottles were found to react  
(i) Neither with Fehling's solution nor with Tollen's reagent  
(ii) Only with Tollen's reagent but not with Fehling's solution  
(iii) With both Tollen's reagent and Fehling's solution.  
If they contained either ethanal (acetaldehyde) or propanone (acetone) or benzal (benzaldehyde), which bottle contained which  
(a) In (i) benzal, in (ii) ethanal and in (iii) propanone  
(b) In (i) benzal, in (ii) propanone and in (iii) ethanal  
(c) In (i) propanone, in (ii) benzal and in (iii) ethanal  
(d) In (i) propanone, in (ii) ethanal and in (iii) benzal
70. Action of hydrazine on aldehydes and ketones gives compound of the general structure  
(a)  $>C=N-NH_2$   
(b)  $>C=N-OH$   
(c)  $>C=N-NH-CONH_2$   
(d)  $>C=N-NH-C_6H_5$
71. The reaction in which sodium cyanide is used  
(a) Perkin reaction  
(b) Reimer-Tiemann reaction  
(c) Benzoin condensation  
(d) Rosenmund reaction
72. Which one of the following reactions is a method for the conversion of a ketone into a hydrocarbon  
(a) Aldol condensation  
(b) Reimer-Tiemann reaction  
(c) Cannizzaro reaction  
(d) Wolf-Kishner reduction
73. Bakelite is a polymer of  
(a)  $HCHO$  + phenol  
(b)  $HCHO$  + aldehyde (acetaldehyde)  
(c) Phenol +  $H_2SO_4$   
(d)  $HCHO$  + acetone
74. Clemmenson reduction involves  $>C=O$  to  $>CH_2$  in presence of  
(a)  $Zn/Hg$   
(b) Alcohol  
(c)  $Zn$  dust  
(d)  $Zn$  / alcohol
75. Aldol condensation involving  $CH_3CHO + CH_3CHO$  gives the product  
(a)  $CH_3CHOHCH_2CHO$   
(b)  $CH_3COCH_2CH_3$   
(c)  $CH_3CH=CH_2$   
(d) None of these
76. Enol content is highest in  
(a) Acetone  
(b) Acetophenone  
(c) Acetic acid  
(d) Acetyl acetone
77. Which one of the following reacts with  $HCN$  and Tollen's reagent, but is not oxidised by Fehling's solution  
(a) Methanal  
(b) Ethanal  
(c) Benzaldehyde  
(d) Acetone

78. During reaction of benzaldehyde with alkali one of the product is  
 (a) Phenol (b) Benzyl alcohol  
 (c) Benzene (d) Benzophenone
79. Cannizzaro reaction is given by  
 (a) HCHO (b)  $CH_3COCH_3$  (c)  $CH_3CHO$  (d)  $CH_3CH_2OH$
80. The reaction  $C_6H_5CHO + CH_3CHO \rightarrow C_6H_5CH=CH-CHO$  is known as  
 (a) Perkin's reaction (b) Claisen condensation  
 (c) Benzoin condensation (d) Cannizzaro's reaction
81. When two molecules of acetaldehyde condense in the presence of dilute alkali, it forms  
 (a) Acetal (b) Sodium formate (c) Aldol (d) Mesitylene  
 (e) None of these
82. Acetaldehyde on treatment with dil. NaOH followed by heating gives  
 (a)  $CH_3CH_2CH_2CH_2OH$  (b)  $CH_3CH_2CH_2CHO$   
 (c)  $CH_3-CH=CHCHO$  (d)  $CH_3-CH=CHCH_2OH$
83. Reaction  $R_2C=O + HCN \rightarrow R_2C(OH)CN$  is  
 (a) Electrophilic substitution (b) Electrophilic addition  
 (c) Nucleophilic addition (d) Nucleophilic substitution
84. Benzaldehyde on reaction with acetophenone in the presence of sodium hydroxide solution gives  
 (a)  $C_6H_5CH=CHCOC_6H_5$  (b)  $C_6H_5COCH_2C_6H_5$   
 (c)  $C_6H_5CH=CHC_6H_5$  (d)  $C_6H_5CH(OH)COC_6H_5$
85. Aldehydes and ketones can be reduced to hydrocarbon by using  
 (a)  $LiAlH_4$  (b)  $H_2 / Pd - BaSO_4$   
 (c)  $Na - Hg / HCl$  (d)  $NH_2 - NH_2 / C_2H_5ONa$
86. An important reaction of acetone is autocondensation in presence of concentrated sulphuric acid to give the aromatic compound  
 (a) Mesitylene (b) Mesityl oxide (c) Trioxan (d) Phorone
87. Identify the organic compound which, on heating with strong solution of NaOH, partly converted into an acid salt and partly into alcohol  
 (a) Benzyl alcohol (b) Acetaldehyde  
 (c) Acetone (d) Benzaldehyde
88. Which of the following does not give brick red precipitate with Fehling solution  
 (a) Acetone (b) Acetaldehyde (c) Formalin (d) D-glucose

89. Acetaldehyde and acetone can be distinguished by  
 (a) Molisch test (b) Bromoform test (c) Solubility in water (d) Tollen's test
90. Which compound is soluble in  $H_2O$   
 (a)  $HCHO$  (b)  $CH_3CHO$  (c)  $CH_3COCH_3$  (d) All
91.  $CH_3CHO + CH_3MgBr \rightarrow \text{Product} \xrightarrow{H_2O} A$   
 What is A ?  
 (a) Primary alcohol (b) Secondary alcohol (c) Tertiary alcohol (d) Ketone
92. Which gives lactic acid on hydrolysis after reacting with  $HCN$   
 (a)  $HCHO$  (b)  $CH_3CHO$  (c)  $C_6H_5CHO$  (d)  $CH_3COCH_3$
93.  $CH_3CHO$  react with aqueous  $NaOH$  solution to form  
 (a) 3-hydroxy butanal (b) 2-hydroxy butanal  
 (c) 4-hydroxy butanal (d) 3-hydroxy butanol
94. Fehling solution react with  $HCHO$  to form precipitate of  
 (a) White colour (b) Yellow colour (c) Red colour (d) Blue colour
95. Product in following reaction is  
 $CH_3MgI + HCHO \rightarrow \text{Product}$   
 (a)  $CH_3CHO$  (b)  $CH_3OH$  (c)  $C_2H_5OH$  (d)  $CH_3-O-CH_3$
96.  $A \xrightarrow[800^\circ C]{\Delta} CH_2 = C = O$ , Reactant 'A' in the reaction is  
 (a)  $CH_3CH_2CHO$  (b)  $CH_3CHO$  (c)  $CH_3 - \underset{\underset{O}{||}}{C} - CH_3$  (d)  $C_2H_5OH$
97. Only an aldehyde having..... can undergo the aldol condensation  
 (a) At least one beta H atom (b) At least one alpha H atom  
 (c) An aromatic ring (d) No alpha H atom
98. Clemenson's reduction of ketones is carried out in  
 (a)  $H_2$  with Pd catalyst (b) Glycol with  $KOH$   
 (c)  $LiAlH_4$  in water (d)  $Zn-Hg$  with  $HCl$
99. Reaction  

$$\begin{array}{c} R \\ | \\ >C=O \\ | \\ R \end{array} \xrightarrow[\text{KOH / glycol}]{H_2NNH_2} \begin{array}{c} R \\ | \\ >C< \\ | \\ R \end{array} \begin{array}{c} H \\ / \\ H \end{array} + N_2 + H_2$$
 is called  
 (a) Wolff-Kishner reaction (b) Tischenko reaction  
 (c) Reformatsky reaction (d) Gattermann reaction
100. Propanal on treatment with dilute sodium hydroxide forms  
 (a)  $CH_3CH_2CH_2CH_2CHO$  (b)  $CH_3CH_2CH(OH)CH_2CHO$   
 (c)  $CH_3CH_2CH(OH)CH(CH_3)CHO$  (d)  $CH_3CH_2COONa$

101. Identify the product  $Y$  in the sequence  $CH_3CHO + CH_3MgI \xrightarrow{\text{Ether}} X \xrightarrow{H_2O/H^+} Y$   
 (a)  $CH_3OH$  (b)  $CH_3CH_2OH$  (c)  $(CH_3)_2CHOH$  (d)  $(CH_3)_3COH$
102. What is the name of reaction when benzaldehyde changes into benzyl alcohol  
 (a) Friedel-Craft's reaction (b) Kolbe's reaction  
 (c) Wurtz reaction (d) Cannizzaro reaction
103. The reagent that gives an orange coloured precipitate with acetaldehyde  
 (a)  $NH_2OH$  (b)  $NaHSO_3$  (c) Iodine (d) 2, 4-DNP
104. Which one is used in the manufacture of mirror  
 (a) Red lead (litharge) (b) Ammoniacal  $AgNO_3$   
 (c) Ammoniacal  $AgNO_3 +$  Red lead (d) Ammoniacal  $AgNO_3 + HCHO$
105. When  $CH_3COCH_3$  reacts with  $Cl_2$  and  $NaOH$ , which of the following is formed  
 (a)  $CHCl_3$  (b)  $CCl_4$  (c)  $CCl_2H_2$  (d)  $CH_3Cl$
106. Which gives difference between aldehyde and ketone  
 (a) Fehling's solution (b) Tollen's reagent  
 (c) Schiff's reagent (d) Benedict's solution  
 (e) All of these
107. Aldehyde turns pink with  
 (a) Benedict solution (b) Schiff reagent  
 (c) Fehling solution (d) Tollen's reagent  
 (e) Mollisch reagent
108. Which of the following would undergo aldol condensation  
 (a)  $CCl_3.CHO$  (b)  $CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - CHO$  (c)  $CH_3.CH_2.CHO$  (d)  $HCHO$
109. The reaction of acetaldehyde with conc.  $KMnO_4$  gives  
 (a)  $CH_3COOH$  (b)  $CH_3CH_2OH$  (c)  $HCHO$  (d)  $CH_3OH$
110. When acetaldehyde is heated with Tollen's reagent, following is obtained  
 (a) Methyl alcohol (b) Silver acetate  
 (c) Silver mirror (d) Formaldehyde
111. Boiling point of acetone is  
 (a)  $56^\circ C$  (b)  $60^\circ C$  (c)  $100^\circ C$  (d)  $90^\circ C$
112. Urotropine is  
 (a) Hexamethylene tetramine (b) Hexaethylene tetramine  
 (c) Hexamethylene diamine (d) None of these

113. Magenta is  
(a) Alkaline phenolphthalein (b) Methyl red  
(c) p-rosaniline hydrochloride (d) Red litmus
114. An aldehyde on oxidation gives  
(a) An alcohol (b) An acid (c) A ketone (d) An ether
115. The reaction of an aldehyde with hydroxylamine gives a product which is called  
(a) Aminohydroxide (b) Hydrazone (c) Semicarbazone (d) Oxime
116. Cannizzaro reaction is not shown by  
(a) HCHO (b)  $C_6H_5CHO$  (c)  $CH_3CHO$  (d) All of these
117. When acetone is heated with hydroxylamine, the compound formed is  
(a) Cyanohydrin (b) Oxime (c) Semicarbazone (d) Hydrazone
118. The product of the reaction between ammonia and formaldehyde is  
(a) Urotropine (b) Formamide (c) Paraformaldehyde (d) Methanol
119. Which of the following products is obtained by the oxidation of propionaldehyde  
(a) Acetic acid (b) Formic acid and acetic acid  
(c) Propanoic acid (d) n-propyl alcohol
120. When acetaldehyde reacts with  $PCl_5$ , the resulting compound is  
(a) Ethyl chloride (b) Ethylene chloride  
(c) Ethylidene chloride (d) Trichloro acetaldehyde
121. Benzaldehyde and acetaldehyde can be differentiated by  
(a) HCN (b)  $NH_2OH$  (c) Hydrazine (d) NaOH solution
122. In the presence of a dilute base  $C_6H_5CHO$  and  $CH_3CHO$  react together to give a product. The product is  
(a)  $C_6H_5CH_3$  (b)  $C_6H_5CH_2CH_2OH$   
(c)  $C_6H_5CH_2OH$  (d)  $C_6H_5CH=CHCHO$
123. Grignard's reagent reacts with ethanal (acetaldehyde) and propanone to give  
(a) Higher aldehydes with ethanal and higher ketones with propanone  
(b) Primary alcohols with ethanal and secondary alcohols with propanone  
(c) Ethers with ethanal and alcohols with propanone  
(d) Secondary alcohols with ethanal and tertiary alcohols with propanone
124. Base catalysed aldol condensation occurs with  
(a) Benzaldehyde  
(b) 2, 2-dimethyl propionaldehyde  
(c) Acetaldehyde  
(d) Formaldehyde

125. Benzaldehyde reacts with ammonia to form  
(a) Benzaldehyde ammonia (b) Urotropine  
(c) Hydrobenzamide (d) Aniline
126. Glucose + Tollen's reagent → Silver mirror shows  
(a) Presence of acidic group (b) Presence of alkaline group  
(c) Presence of ketonic group (d) Presence of aldehyde group
127. Fehling solution is  
(a) Ammoniacal cuprous chloride solution  
(b) Acidified copper sulphate solution  
(c) Copper sulphate and sodium hydroxide + Rochelle salt  
(d) None of these
128. Reduction of an aldehyde produces  
(a) Primary alcohol (b) Monocarboxylic acid  
(c) Secondary alcohol (d) Tertiary alcohol
129. Which of the following on reaction with conc. NaOH gives an alcohol  
(a) Methanal (b) Ethanal (c) Propanal (d) Butanal
130. Schiff's reagent is  
(a) Magenta colour solution decolourised with sulphurous acid  
(b) Ammoniacal cobalt chloride solution  
(c) Ammoniacal manganese sulphate solution  
(d) Magenta solution decolourised with chlorine
131. Pyrolysis of acetone gives  $CH_2 = C = O$  called  
(a) Methylene oxide (b) Methyl carbon monoxide  
(c) Ketene (d) Methone
132. Which one of the following on oxidation will not give a carboxylic acid with the same number of carbon atoms  
(a)  $CH_3COCH_3$  (b)  $CCl_3CH_2CHO$  (c)  $CH_3CH_2CH_2OH$  (d)  $CH_3CH_2CHO$
133. Acetal is obtained by reacting in the presence of dry HCl and alcohol with  
(a) Aldehyde (b) Ketone (c) Ether (d) Carboxylic acid
134. The reagent with which both aldehyde and acetone react easily is  
(a) Fehling's reagent (b) Grignard reagent (c) Schiff's reagent (d) Tollen's reagent
135. Phenylmethanol can be prepared by reducing the benzaldehyde with  
(a)  $CH_3Br$  (b) Zn and HCl (c)  $CH_3Br$  and Na (d)  $CH_3I$  and Mg
136. Which of the following is used in the manufacture of thermosetting plastics  
(a) Formaldehyde (b) Acetaldehyde (c) Acetone (d) Benzaldehyde

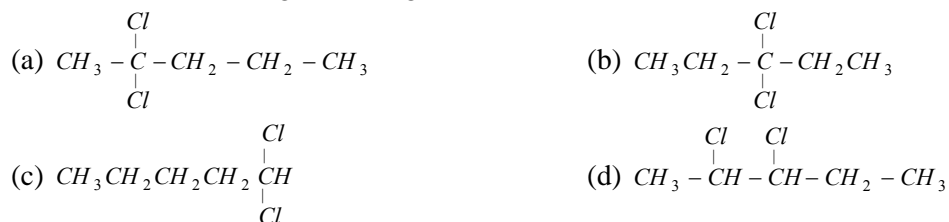


137. Which compound undergoes iodoform reaction  
(a)  $\text{HCHO}$  (b)  $\text{CH}_3\text{CHO}$  (c)  $\text{CH}_3\text{OH}$  (d)  $\text{CH}_3\text{COOH}$
138. Which does not react with Fehling solution  
(a) Acetaldehyde (b) Benzaldehyde (c) Glucose (d) Formic acid
139. Which of the following compound will react with ethanolic KCN  
(a) Ethane (b) Acetyl chloride  
(c) Chlorobenzene (d) Benzaldehyde
140. Schiff's reagent gives pink colour with  
(a) Aldehydes (b) Ethers (c) Ketones (d) Carboxylic acid
141. Acetaldehyde reacts with  $\text{Cl}_2$  (in excess) to give  
(a) Chloral (b) Chloroform  
(c) Acetic acid (d) Trichloroacetic acid
142. The compound which reacts with Fehling solution is  
(a)  $\text{C}_6\text{H}_5\text{COOH}$  (b)  $\text{HCOOH}$  (c)  $\text{C}_6\text{H}_5\text{CHO}$  (d)  $\text{CH}_2\text{ClCH}_3$
143. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid  
(a) Butanal (b) Benzaldehyde (c) Phenol (d) Benzoic acid
144. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon  
(a) Acetamide (b) Acetic acid (c) Ethyl acetate (d) Butan-2-one
145. Three molecules of acetone in the presence of dry HCl form  
(a) Mesitylene (b) Phorone (c) Glyoxal (d) Mesityl oxide
146. Aldehydes and ketones can be reduced to corresponding hydrocarbons by  
(a) Refluxing with water  
(b) Refluxing with strong acids  
(c) Refluxing with soda amalgam and water  
(d) Refluxing with zinc amalgam and concentrated HCl  
(e) Passing the vapour under heated  $\text{PbO}_2$
147. Acetone reacts with iodine to form iodoform in the presence of  
(a)  $\text{CaCO}_3$  (b)  $\text{NaOH}$  (c)  $\text{KOH}$  (d)  $\text{MgCO}_3$
148. Cyanohydrin of which of the following forms lactic acid  
(a)  $\text{CH}_3\text{CH}_2\text{CHO}$  (b)  $\text{CH}_3\text{CHO}$  (c)  $\text{HCHO}$  (d)  $\text{CH}_3\text{COCH}_3$
149. Which of the following is used to detect aldehydes  
(a) Million's test (b) Tollen's reagent  
(c) Neutral ferric chloride solution (d) Molisch's test

150. Which of the following aldehydes give red precipitate with Fehling solution ?  
 (a) Benzaldehyde (b) Salicylaldehyde  
 (c) Acetaldehyde (d) None of these
151.  $A \longrightarrow (CH_3)_2C = CHCOCH_3$  A is  
 (a) Acetone (b) Acetaldehyde  
 (c) Propionaldehyde (d) Formaldehyde
152. The aldehyde which react with NaOH to produce an alcohol and sodium salt is  
 (a) HCHO (b)  $CH_3CHO$  (c)  $CH_3CH_2CHO$  (d)  $CH_3CH_2CH_2CHO$
153. Acetaldehyde and Acetone can be distinguished by  
 (a) Iododorm test (b) Nitroprusside test  
 (c) Fehling's solution test (d) DNP test
154.  $OCH - CHO \xrightarrow{OH^-} HOH_2C - COOH$  The reaction given is  
 (a) Aldol condensation (b) Knoevenagel reaction  
 (c) Cannizzaro reaction (d) None of these
155. The order of susceptibility of nucleophilic attack on aldehydes follows the order  
 (a)  $1^\circ > 3^\circ > 2^\circ$  (b)  $1^\circ > 2^\circ > 3^\circ$  (c)  $3^\circ > 2^\circ > 1^\circ$  (d)  $2^\circ > 3^\circ > 1^\circ$
156. In Wolf-Kishner reduction, the carbonyl group of aldehydes and ketones is converted into  
 (a)  $>CH_2$  group (b)  $-CH_3$  group (c)  $-CH_2OH$  group (d)  $>CHOH$  group
157. Which of the following react with  $NaHSO_3$   
 (a)  $CH_3COCH_3$  (b)  $CH_3CHO$  (c)  $HCHO$  (d) All of these
158. Fehling solution is  
 (a)  $CuSO_4$  + lime (b)  $CuSO_4 + NaOH(aq)$  (c)  $CuSO_4 + Na_2CO_3$  (d) None of these
159. Wolf kishner reduction, reduces  
 (a)  $-COOH$  group (b)  $-C \equiv C -$  group (c)  $-CHO$  group (d)  $-O -$  group
160. A compound has a vapour density of 29. On warming an aqueous solution of alkali, it gives a yellow precipitate. The compound is  
 (a)  $CH_3CH_2CHO$  (b)  $CH_3CHOHCH_3$  (c)  $CH_3COCH_3$  (d)  $CH_3CH_2COOH$
161. Which responds to +ve iodoform test ?  
 (a) Butanol (b) Butan-1-al (c) Butanol-2 (d) 3-pentanone
162. The correct order of reactivity of  $PhMgBr$  with  
 $Ph - \overset{\overset{O}{\parallel}}{C} - Ph$  (I)  $CH_3 - \overset{\overset{O}{\parallel}}{C} - H$  (II)  $CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_3$  (III) is  
 (a) (I) > (II) > (III) (b) (III) > (II) > (I) (c) (II) > (III) > (I) (d) (I) > (III) > (II)

163. The pair of compounds in which both the compounds give positive test with Tollen's reagent is  
(a) Glucose and Sucrose (b) Fructose and Sucrose  
(c) Acetophenone and Hexanal (d) Glucose and Fructose
164. The most appropriate reagent to distinguish between acetaldehyde and formaldehyde is  
(a) Fehling's solution (b) Tollen's reagent  
(c) Schiff's reagent (d) Iodine in presence of base
165. Silver mirror test can be used to distinguish between  
(a) Ketone and acid (b) Phenol and acid  
(c) Aldehyde and acid (d) Alcohol and phenol
166. Paraldehyde is  
(a) A trimer of formaldehyde (b) A trimer of acetaldehyde  
(c) A hexamer of formaldehyde (d) A hexamer of acetaldehyde
167. Paraldehyde is used as a  
(a) Medicine (b) Poison (c) Polymer (d) Dye
168. Formalin is an aqueous solution of  
(a) Formic acid (b) Formaldehyde  
(c) Fluorescein (d) Furfuraldehyde
169. Hexamethylene tetramine is used as  
(a) Analgesic (b) Antipyretic  
(c) Urinary antiseptic (d) All of these
170. Methyl ketone group is identified by  
(a) Iodoform test (b) Fehling solution  
(c) Tollen's reagent (d) Schiff's reagent
171. Which of the following does not give Fehling solution test?  
(a) Acetone (b) Propanal (c) Ethanal (d) Butanal
172. How will you convert butan-2-one to propanoic acid?  
(a) Tollen's reagent (b) Fehling's solution  
(c)  $\text{NaOH/I}_2/\text{H}^+$  (d)  $\text{NaOH/NaI/H}^+$
173. Ketones react with Mg-Hg over water gives  
(a) Pinacolone (b) Pinacols (c) Alcohols (d) None of these
174. Which of the following will form two isomers with semi carbazide  
(a) Benzaldehyde (b) Acetone  
(c) Benzoquinone (d) Benzophenone

175. A compound  $A \rightarrow C_5H_{10}Cl_2$  on hydrolysis gives  $C_5H_{10}O$  which reacts with  $NH_2OH$ , forms iodoform but does not give fehling test.  $A$  is



176.  $CH_3 - CHO + HCN \rightarrow A$ ; Compound  $A$  on hydrolysis gives



177. Which one does not give cannizzaro's reaction

- (a) Benzaldehyde  
 (b) 2-methyl propanal  
 (c) p-methoxy benzaldehyde  
 (d) 2,2 dimethyl propanal  
 (e) Formaldehyde

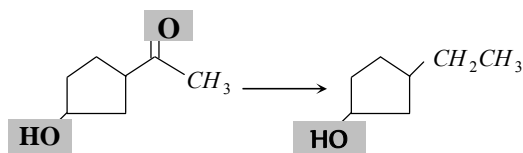
## EXERCISE - IV

- Which of the following will fail to react with potassium dichromate and dilute sulphuric acid  
 (a) Ethyl alcohol (ethanol) (b) Acetaldehyde (ethanal)  
 (c) Secondary propyl alcohol (2-propanol) (d) Acetone (propanone)
- Acetone and acetaldehyde are differentiated by  
 (a)  $\text{NaOH} + \text{I}_2$  (b)  $\text{Ag}(\text{NH}_3)_2^+$  (c)  $\text{HNO}_2$  (d)  $\text{I}_2$
- Which of the following will react with water  
 (a)  $\text{CHCl}_3$  (b)  $\text{Cl}_3\text{CCHO}$   
 (c)  $\text{CCl}_4$  (d)  $\text{ClCH}_2\text{CH}_2\text{Cl}$
- An organic compound 'A' has the molecular formula  $\text{C}_3\text{H}_6\text{O}$ , it undergoes iodoform test. When saturated with dil.  $\text{HCl}$  it gives 'B' of molecular formula  $\text{C}_9\text{H}_{14}\text{O}$ . A and B respectively are  
 (a) Propanal and mesitylene  
 (b) Propanone and mesityl oxide  
 (c) Propanone and 2,6-dimethyl-2,5-heptadien-4-one  
 (d) Propanone and mesitylene oxide
- Which alkene is formed from the following reaction  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{PPh}_3 + 2 - \text{Butanone}$   
 (a) 3-Methyl-3-heptene (b) 4-Methyl-3-heptene  
 (c) 5-Methyl-3-heptene (d) 1-Methyl-5-methane
- Compound 'A' (molecular formula  $\text{C}_3\text{H}_8\text{O}$ ) is treated with acidified potassium dichromate to form a product 'B' (molecular formula  $\text{C}_3\text{H}_6\text{O}$ ). 'B' forms a shining silver mirror on warming with ammoniacal silver nitrate. 'B' when treated with an aqueous solution of  $\text{H}_2\text{NCONHNH}_2 \cdot \text{HCl}$  and sodium acetate gives a product 'C'. Identify the structure of 'C'  
 (a)  $\text{CH}_3\text{CH}_2\text{CH}=\text{NNHCONH}_2$  (b)  $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\text{NNHCONH}_2}$   
 (c)  $\text{CH}_3\text{CH}=\underset{\text{CH}_3}{\text{NCONHNH}_2}$  (d)  $\text{CH}_3\text{CH}_2\text{CH}-\text{NCONHNH}_2$
- Which is not true about acetophenone  
 (a) Reacts to form 2,4-dinitrophenyl hydrazine  
 (b) Reacts with Tollen's reagent to form silver mirror  
 (c) Reacts with  $\text{I}_2 / \text{NaOH}$  to form iodoform  
 (d) On oxidation with alkaline  $\text{KMnO}_4$  followed by hydrolysis gives benzoic acid

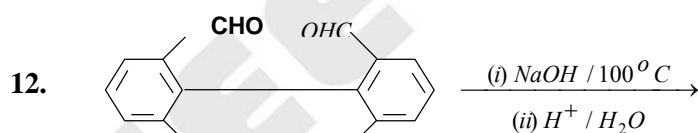
8. The enol form of acetone, after treatment with  $D_2O$ , gives



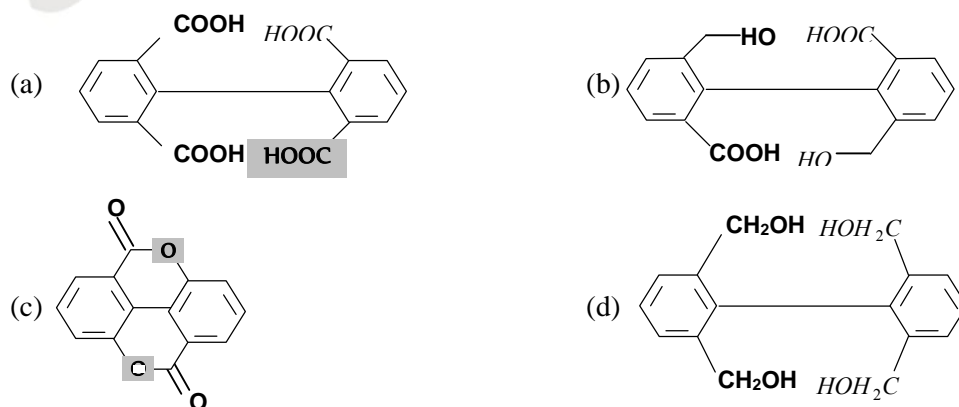
9. The appropriate reagent for the transformation



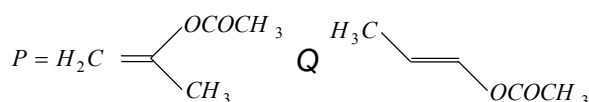
- (a)  $Zn(Hg), HCl$  (b)  $NH_2NH_2OH^-$  (c)  $H_2 / Ni$  (d)  $NaBH_4$
10. Which of the following has the most acidic hydrogen
- (a) 3-hexanone (b) 2, 4-hexanedione  
(c) 2, 5-hexanedione (d) 2, 3-hexanedione
11. Which of the following will be most readily dehydrated in acidic conditions



Major Product is

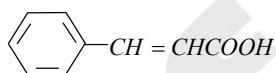
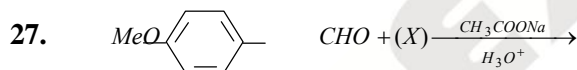


13. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is  
 (a)  $\text{MeCOCl}$  (b)  $\text{MeCHO}$  (c)  $\text{MeCOOMe}$  (d)  $\text{MeCOOCOMe}$
14. Which of the following will give yellow precipitate with  $\text{I}_2 / \text{NaOH}$   
 (a)  $\text{ICH}_2\text{COCH}_2\text{CH}_3$  (b)  $\text{CH}_3\text{COOCOCH}_3$   
 (c)  $\text{CH}_3\text{CONH}_2$  (d)  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
15. The product of acid hydrolysis of P and Q can be distinguished by



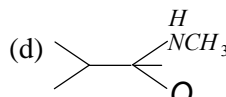
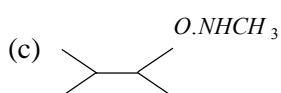
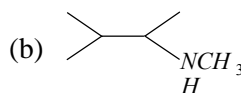
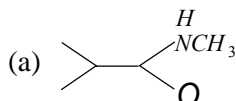
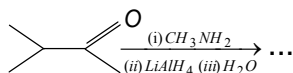
- (a) Lucas Reagent (b) 2,4-DNP (c) Fehling's Solution (d)  $\text{NaHSO}_3$
16. On vigorous oxidation by permanganate solution  $(\text{CH}_3)_2\text{C} = \text{CH} - \text{CH}_2\text{CH}_2\text{CH}_3$  gives  
 (a)  $\begin{array}{c} \text{OH} \quad \text{OH} \\ | \quad | \\ \text{CH}_3 - \text{C} - \text{CH} - \text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$  (b)  $\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CH}_3 \end{array} \text{CHCO}_2\text{H} + \text{CH}_3\text{COOH}$   
 (c)  $\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CH}_3 \end{array} \text{CHOH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (d)  $\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CH}_3 \end{array} \text{C} = \text{O} + \text{CH}_3\text{CH}_2\text{COOH}$
17. Which of the following reactions give benzo phenone  
 (a)  $2\text{C}_6\text{H}_6 + \text{CCl}_4 \xrightarrow[\text{(ii) } \text{H}_2\text{O}]{\text{(i) } \text{AlCl}_3}$  (b)  $\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{COCl} \xrightarrow{\text{AlCl}_3}$   
 (c)  $o - \text{CH}_3\text{C}_6\text{H}_4\text{COC}_6\text{H}_5 \xrightarrow{\text{Heat}}$  (d)  $o - \text{HOOC} - \text{C}_6\text{H}_4 - \text{COC}_6\text{H}_5 \xrightarrow[260^\circ\text{C}]{\text{Cu}}$
18. Aldehyde and ketones can decolourize by  
 (a) Bromine water (b) Quick lime (c) dil.  $\text{H}_2\text{SO}_4$  (d) None of these
19. Which of the following statements regarding chemical properties of acetophenone are wrong  
 (1) It is reduced to methyl phenyl carbinol by sodium and ethanol  
 (2) It is oxidised to benzoic acid with acidified  $\text{KMnO}_4$   
 (3) It does not undergo iodoform electrophilic substitution like nitration at meta position  
 (4) It does not undergo iodoform reaction with iodine and alkali  
 (a) 1 and 2 (b) 2 and 4 (c) 3 and 4 (d) 1 and 3
20. The product(s) obtained via oxymercuration ( $\text{HgSO}_4 + \text{H}_2\text{SO}_4$ ) of 1-butyne would be  
 (a)  $\text{CH}_3\text{CH}_2\text{COCH}_3$  (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$   
 (c)  $\text{CH}_3\text{CH}_2\text{CHO} + \text{HCHO}$  (d)  $\text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH}$

21. The most reactive compound towards formation of cyanohydrin on treatment with KCN followed by acidification is  
 (a) Benzaldehyde (b) p-Nitrobenzaldehyde  
 (c) Phenyl acetaldehyde (d) p-Hydroxybenzaldehyde
22. The key step in cannizzaro's reaction is the intermolecular shift of  
 (a) Proton (b) Hydride ion  
 (c) Hydronium ion (d) Hydrogen bond
23. Benzophenone does not react with  
 (a)  $RNH_2$  (b)  $SO_3$  (c)  $NaOH$  (d)  $Na_2CO_3$
24. The most suitable reagent for the conversion of  $RCH_2OH \rightarrow RCHO$  is  
 (a)  $KMnO_4$  (b)  $K_2Cr_2O_7$   
 (c)  $CrO_3$  (d) PCC (Pyridine chloro chromate)
25. The conversion of acetophenone to acetanilide is best accomplished by using :  
 (a) Backmann rearrangement (b) Curtius rearrangement  
 (c) Lossen rearrangement (d) Hofmann rearrangement
26. Which of the following will not give iodoform test ?  
 (a) Isopropyl alcohol (b) Ethanol (c) Ethanal (d) Benzyl alcohol



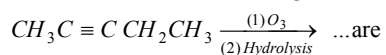
The compound (X) is

- (a)  $CH_3COOH$  (b)  $BrCH_2 - COOH$  (c)  $(CH_3CO)_2O$  (d)  $CHO - COOH$
28. The major organic product formed from the following reaction





29. Products of the following reaction



- (a)  $CH_3CHO + CH_3CH_2CHO$  (b)  $CH_3COOH + CH_3CH_2CHO$   
(c)  $CH_3COOH + HOOCCH_2CH_3$  (d)  $CH_3COOH + CO_2$

30. A compound, containing only carbon, hydrogen and oxygen, has a molecular weight of 44. On complete oxidation it is converted into a compound of molecular weight 60. The original compound is

- (a) An aldehyde (b) An acid  
(c) An alcohol (d) an ether

## EXERCISE - V

### ASSERTION & REASON

Read the assertion and reason carefully to mark the correct option out of the options given below :

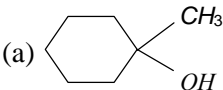
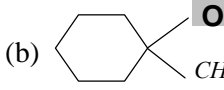
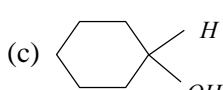
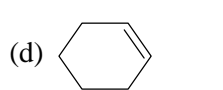
- (a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
- (c) If assertion is true but reason is false.
- (d) If the assertion and reason both are false.
- (e) If assertion is false but reason is true.

1. Assertion : Acetic acid does not undergo haloform reaction.  
Reason : Acetic acid has no  $\alpha$  hydrogens.
2. Assertion : Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.  
Reason : Cyanide ( $\text{CN}^-$ ) is a strong nucleophile.
3. Assertion : Lower aldehyde and ketones are soluble in water but the solubility decreases as molecular mass increases.  
Reason : Aldehydes and ketones can be distinguished by Tollen's reagent.
4. Assertion : Acetaldehyde on treatment with alkaline gives aldol.  
Reason : Acetaldehyde molecules contains  $\alpha$  hydrogen atom.
5. Assertion : Acetylene on treatment with alkaline  $\text{KMnO}_4$  produce acetaldehyde.  
Reason : Alkaline  $\text{KMnO}_4$  is a reducing agent.
6. Assertion : Acetophenone and benzophenone can be distinguished by iodoform test.  
Reason : Acetophenone and benzophenone both are carbonyl compounds.
7. Assertion : Isobutanal does not give iodoform test  
Reason : It does not have  $\alpha$ -hydrogen.
8. Assertion : Benzaldehyde is more reactive than ethanol towards nucleophilic attack.  
Reason : The overall effect of  $-I$  and  $+R$  effect of phenyl group decreases the electron density on the carbon atom of  $>C=O$  group in benzaldehyde.
9. Assertion : Aldol condensation can be catalysed both by acids and bases.  
Reason :  $\beta$ -Hydroxy aldehydes or ketones readily undergo acid catalysed dehydration.
10. Assertion : Ketones are less reactive than aldehydes.  
Reason : Ketones do not give schiff's test.
11. Assertion : Oximes are less acidic than hydroxyl amine.  
Reason : Oximes of aldehydes and ketones show geometrical isomerism.

12. Assertion : The bond energy of  $>C=O$  is less than  $>C=C<$  in alkenes.  
Reason : The carbon atom in carbonyl group is  $sp^2$  hybridised.
13. Assertion :  $R-C\equiv O^+$  is more stable than  $R-C^+=O$ .  
Reason : Resonance in carbonyl compound provides  $C^+$  and  $O^-$ .
14. Assertion : Formaldehyde cannot be prepared by Rosenmund's reduction.  
Reason : Acid chlorides can be reduced into aldehydes with hydrogen in boiling xylene using palladium or platinum as a catalyst supported on barium sulphate. This is known as Rosenmund's reduction.
15. Assertion :  $CH_3CHO$  reacts with  $NH_3$  to form urotropine.  
Reason : Urotropine is used as medicine in case of urinary troubles.
16. Assertion :  $\alpha$ -Hydrogen atoms in aldehydes and ketones are acidic.  
Reason : The anion left after the removal of  $\alpha$ -hydrogen is stabilized by inductive effect.
17. Assertion : 2, 2-Dimethyl propanal undergoes Cannizzaro reaction with concentrated NaOH.  
Reason : Cannizzaro is a disproportionation reaction.
18. Assertion : Benzaldehyde undergoes aldol condensation.  
Reason : Aldehydes that do not have  $\alpha$ -hydrogen undergo aldol condensation.

# SELF EVALUATION TEST

- Benzophenone can be converted into benzene using
  - Fused alkali
  - Anhydrous  $AlCl_3$
  - Sodium amalgam in water
  - Acidified dichromate
- The reagent(s) which can be used to distinguish acetophenone from benzophenone is (are)
  - 2, 4-dinitrophenyl hydrazine
  - Aqueous solution of  $NaHSO_3$
  - Benedict reagent
  - $I_2$  and  $Na_2CO_3$
- When acetaldehyde is heated with Fehling solution, it gives a red precipitate of
  - $Cu$
  - $CuO$
  - $Cu_2O$
  - $Cu(OH)_2$
- The general order of reactivity of carbonyl compounds for nucleophilic addition reactions is
  - $H_2C=O > RCHO > ArCHO > R_2C=O > Ar_2C=O$
  - $ArCHO > Ar_2C=O > RCHO > R_2C=O > H_2C=O$
  - $Ar_2C=O > R_2C=O > ArCHO > RCHO > H_2C=O$
  - $H_2C=O > R_2C=O > Ar_2C=O > RCHO > ArCHO$
- Which of the following gives an alcohol and salt of carboxylic acid when reacted with conc.  $NaOH$ 
  - $CH_3CHO$
  - $C_6H_5CHO$
  - $CH_3COCH_3$
  - $C_6H_5COCH_3$
- Which of the following compounds would undergo Cannizzaro's reaction
  - Propionaldehyde
  - Benzaldehyde
  - Bromobenzene
  - Acetaldehyde
- $NaOH / H^+$  reacts with
  - $C_6H_5OCH_3$
  - $CH_3OH$
  - $CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_3$
  - $C_2H_5OH$
- The product of following reaction Self Evaluation TEST  

$$\text{Cyclohexanone} \xrightarrow{H_2 / Pt} \text{is}$$
  - 
  - 
  - 
  - 
- Which of the following aldehydes is most reactive towards nucleophilic addition reactions
  - $HCHO$
  - $CH_3CHO$
  - $C_2H_5CHO$
  - $CH_3COCH_3$
- Which one of the following gives iodoform test
  - Formaldehyde
  - Ethyl alcohol
  - Benzyl alcohol
  - Benzaldehyde

11. The active ion in Tollen's reagent is  
 (a)  $Cu^+$  (b)  $Cu(NH_3)_2^+$  (c)  $Ag^+$  (d)  $Ag(NH_3)_2^+$
12. Among the following compounds, which will react with acetone to give a product containing  $>C=N-$   
 (a)  $C_6H_5NH_2$  (b)  $(CH_3)_3N$  (c)  $C_6H_5NHC_6H_5$  (d)  $C_6H_5NHNH_2$
13. Which of the following does not give yellow precipitate with  $I_2$  and  $NaOH$   
 (a)  $C_2H_5OH$  (b)  $CH_3CHO$  (c)  $CH_3COCH_3$  (d)  $HCHO$
14. In this reaction  

$$CH_3CHO + HCN \xrightarrow{H^+/OH^-} CH_3CH(OH)COOH$$
  
 an asymmetric centre is generated. The acid obtained would be  
 (a) 20% *D* + 80% *L*-isomer (b) *D*-isomer  
 (c) *L*-isomer (d) 50% *D* + 50% *L*-isomer
15. Aldehydes are produced in atmosphere by  
 (a) Oxidation of secondary alcohols  
 (b) Reduction of alkenes  
 (c) Reaction of oxygen atoms with hydrocarbons  
 (d) Reaction of oxygen atoms with ozone
16. Which of the following compounds will give positive test with Tollen's reagent  
 (a) Acetamide (b) Acetaldehyde  
 (c) Acetic acid (d) Acetone
17.  $ArH + R-\overset{\overset{O}{\parallel}}{C}-Cl \xrightarrow{\text{Lewis acid}} Ar-\overset{\overset{O}{\parallel}}{C}-R + HCl$  is an example of  
 (a) Friedel-Craft's alkylation (b) Friedel-Craft's acylation  
 (c) Cannizzaro reaction (d) Claisen condensation
18. Which of the following fails to answer the iodoform test.  
 (a) Pentanone-1 (b) Pentanone-2  
 (c) Propanone-2 (d) Ethanol
19. The reagent used for the separation of acetaldehyde from acetophenone is  
 (a)  $NaHSO_4$  (b)  $C_6H_5NHNH_2$   
 (c)  $NH_2OH$  (d)  $NaOH - I_2$

\*\*\*\*\*

# ANSWER KEY

## INTRODUCTION

1	a	2	b	3	a	4	c	5	a
6	c	7	b	8	b	9	a	10	b
11	b	12	d	13	d	14	b	15	a
16	c	17	c	18	c				

## PREPARATION

1	c	2	c	3	d	4	b	5	b,c
6	c	7	c	8	d	9	c	10	c
11	c	12	a	13	a	14	d	15	d
16	c	17	a	18	d	19	c	20	b
21	c	22	a	23	c	24	c	25	c
26	d	27	c	28	b	29	a	30	b
31	c	32	d	33	b	34	b	35	a
36	d	37	d	38	c	39	b	40	c
41	d	42	a	43	a				

## PROPERTIES

1	c	2	c	3	a	4	a	5	c
6	d	7	a	8	c	9	c	10	b
11	c	12	a	13	a	14	b	15	d
16	b	17	c	18	c	19	abd	20	abcd
21	b	22	a	23	a	24	b	25	d
26	b	27	d	28	c	29	b	30	b
31	c	32	c	33	d	34	d	35	c
36	b	37	a	38	b	39	d	40	c
41	d	42	a	43	d	44	d	45	a
46	c	47	c	48	a	49	b	50	b

**[CHEMISTRY]****[ALDEHYDES AND KETONES]**

51	b	52	c	53	d	54	b	55	c
56	d	57	c	58	a	59	c	60	c
61	b	62	b	63	a	64	b	65	a
66	d	67	a	68	a	69	c	70	a
71	c	72	d	73	a	74	a	75	a
76	d	77	c	78	b	79	a	80	b
81	c	82	c	83	c	84	a	85	d
86	a	87	d	88	a	89	d	90	d
91	b	92	b	93	a	94	c	95	c
96	a	97	b	98	d	99	a	100	c
101	c	102	d	103	d	104	d	105	a
106	e	107	b	108	c	109	a	110	c
111	a	112	a	113	c	114	b	115	d
116	c	117	b	118	a	119	c	120	c
121	d	122	d	123	d	124	c	125	c
126	d	127	c	128	a	129	a	130	a
131	c	132	a	133	a	134	b	135	b
136	a	137	b	138	b	139	d	140	a
141	a	142	b	143	b	144	d	145	b
146	d	147	b	148	b	149	b	150	c
151	a	152	a	153	c	154	c	155	b
156	a	157	d	158	d	159	c	160	a
161	c	162	c	163	d	164	d	165	c
166	d	167	a	168	b	169	c	170	a
171	a	172	c	173	b	174	a	175	a
176	e	177	b						

## CRITICAL THINKING QUESTIONS

1	d	2	bc	3	b	4	c	5	a
6	a	7	b	8	b	9	b	10	b
11	a	12	b	13	a	14	a,d	15	c
16	d	17	b,d	18	d	19	c	20	a
21	b	22	b	23	d	24	d	25	a
26	d	27	c	28	b	29	c	30	a

## ASSERTION &amp; REASON

1	c	2	d	3	b	4	a	5	d
6	b	7	c	8	a	9	b	10	b
11	e	12	e	13	b	14	b	15	e
16	c	17	b	18	d				



# HINTS & SOLUTION

## Introduction

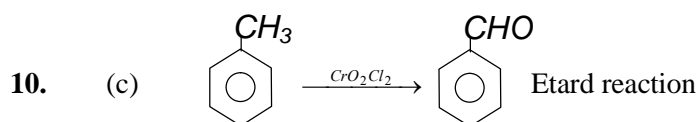
1. (a) 
$$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{H} \\ \text{Acetaldehyde} \end{array} + \begin{array}{c} \text{HCN} \\ \text{Hydrogen} \\ \text{Cyanide} \end{array} \longrightarrow \begin{array}{c} \text{OH} \\ | \\ \text{CH}_3 - \text{C} - \text{H} \\ | \\ \text{CN} \\ \text{Acetaldehyde} \\ \text{Cynohydrin} \end{array} \quad (\text{optically active})$$
2. (b) 
$$> \text{C} = \text{O}$$
  
 $sp^2$  hybridised
7. (b) 
$$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_3 \\ \text{2 propanone} \end{array}$$
10. (b)  $\text{CHOCHO}$
11. (b) 
$$\begin{array}{c} \text{R} \nearrow \text{C} \xleftarrow{f} \text{O} \\ \text{R} \nwarrow \uparrow \end{array}$$
13. (d) 
$$\begin{array}{c} \text{Cl} \quad \text{O} \\ | \quad \parallel \\ \text{Cl} - \text{C} - \text{C} - \text{H} \\ | \\ \text{Cl} \\ \text{2, 2, 2, trichloro ethanal} \end{array}$$
18. (c) Among Carbonyl Compounds, reactivity decrease with increase in alkyl groups as alkyl groups (+I effect) decrease positive character on C-atom. Thus, the correct order of reactivity is  
 $\text{HCHO} > \text{CH}_3\text{CHO} > \text{C}_6\text{H}_5\text{CHO}$

## Preparation

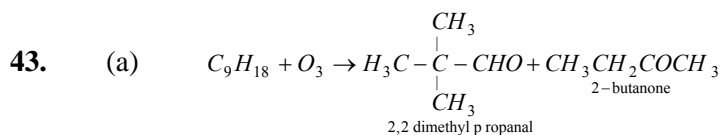
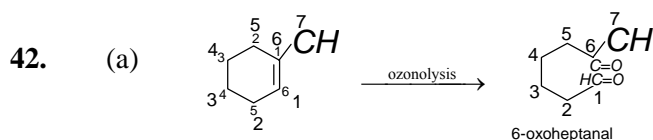
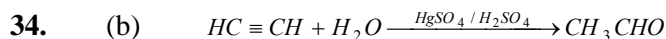
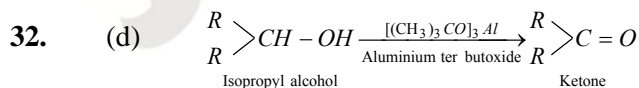
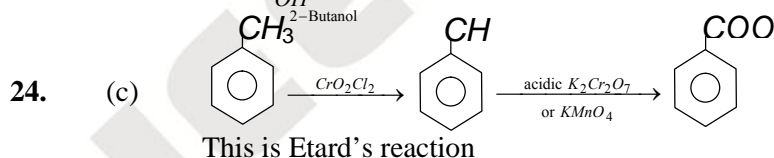
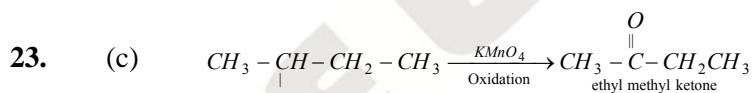
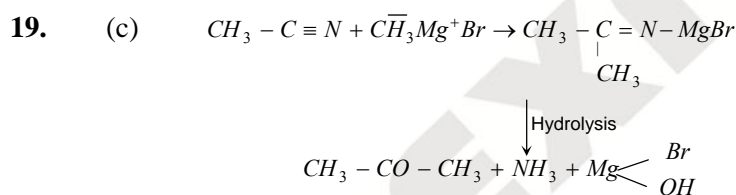
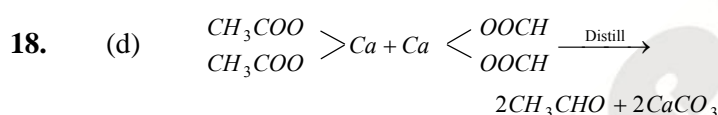
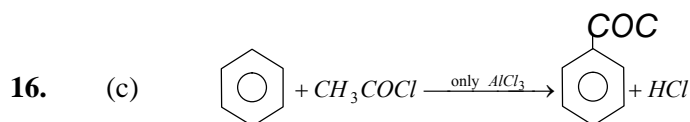
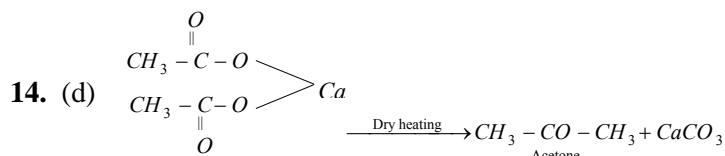
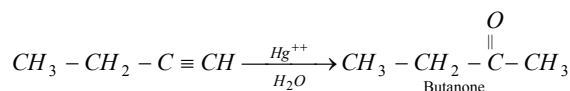
1. (c) 
$$\text{HC} \equiv \text{CH} \xrightarrow[20\% \text{H}_2\text{SO}_4]{1\% \text{HgSO}_4} \text{CH}_3\text{CHO} \xrightarrow[\text{H}_2\text{O}]{\text{CH}_3\text{MgX}} \text{CH}_3\text{CHOHCH}_3 \xrightarrow[\text{Acetone}]{[\text{O}]} \text{CH}_3\text{COCH}_3$$
4. (b) 
$$(\text{CH}_3)_2\text{C} = \text{C}(\text{CH}_3)_2 \xrightarrow{\text{O}_3} 2\text{CH}_3 - \text{CO} - \text{CH}_3$$
5. (c) Ketonic hydrolysis:  $\text{CH}_3 - \text{CO} - \text{CH}_2\text{COOC}_2\text{H}_5$   
$$\xrightarrow[\text{H}_2\text{O}]{\text{NaOH}} \text{CH}_3\text{COCH}_3 + \text{C}_2\text{H}_5\text{OH} + \text{CO}_2$$
6. (c) 
$$\text{C}_6\text{H}_6 + \text{CH}_3\text{COCl} \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{COCH}_3 + \text{HCl}$$

It is Friedel-Crafts reaction. Acetophenone

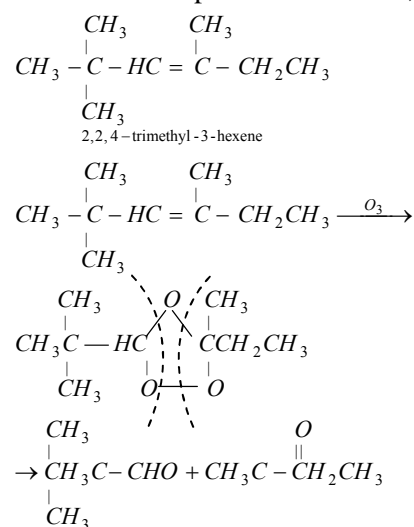
9. (c) 
$$\text{CH}_3\text{COCl} \xrightarrow[\text{Pd / BaSO}_4]{2\text{H}} \text{CH}_3\text{CHO} + \text{HCl}$$



13. (a) It is hydration of alkynes.



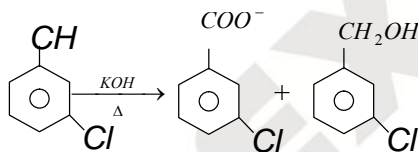
On the basis of product formation, it would be alkene



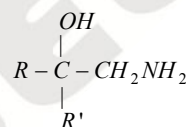
## Properties

1. (c)  $CH_3COCH_3 + CH_3MgCl \rightarrow (CH_3)_3C - OMgCl$   
(X)  
 $\xrightarrow{\text{hydrolysis}} (CH_3)_3C - OH + Mg(OH)Cl$   
(Y)

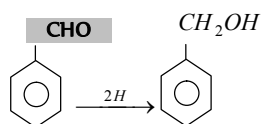
2. (c) It is cannizzaro reaction – 2



3. (a) 
$$R-CO-R' \xrightarrow{HCN} R-\overset{\overset{|}{CN}}{\underset{\underset{(A)}{|}}{C}}-R' \xrightarrow{LiAlH_4}$$



- 5.** (c) Reduction of  $>C=O$  to  $CH_2$  can be carried out with Wolf Kischner reduction.

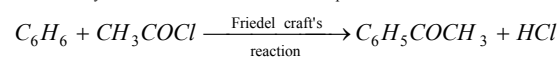


- 6. (d)**

Benzalde      Benzylalc

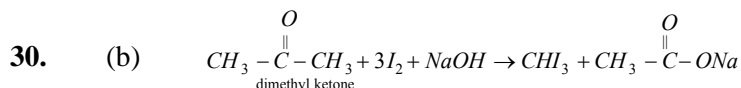
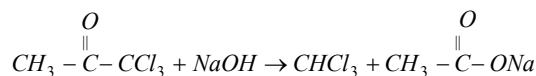
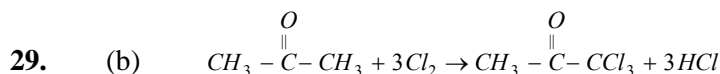
on reduction it gives benzylalcohol and not phenol.

9. (c) 
$$\underset{\text{1-Phenylethanol}}{C_6H_5CHOHCH_3} \xrightarrow{[O]} \underset{\text{Acetophenone}}{C_6H_5COCH_3}$$

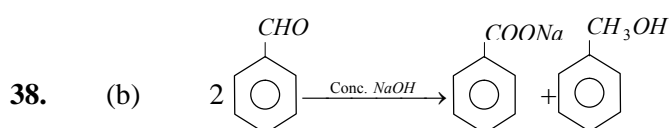


- 10.** (b) Wolf-Kishner reduction does not convert  $>CO$  to  $CHOH$  but converts it to  $>CH_2$ .

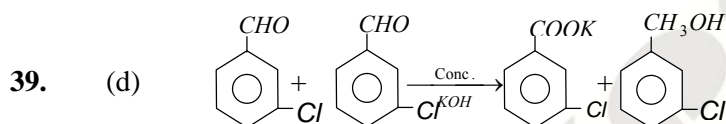
11. (c) Although both  $CH_3CH_2COCH_3$  and  $(CH_3)_3CCOCH_3$  contain  $\alpha$ -hydrogen, yet  $(CH_3)_3CCOCH_3$  does not undergo Aldol condensation due to steric hindrance.
12. (a)  $C_6H_5CHO \xrightarrow[H^+ / H_2O]{CH_3MgBr} C_6H_5CH(OH)CH_3$   
Benzaldehyde  $\quad \quad \quad$   $2^\circ$  Alcohol
13. (a) Chloral  $CCl_3CHO$ , has no  $\alpha$ -hydrogen atom and hence does not undergo aldol condensation.
14. (b) Among the given compounds only acetone gives crystalline coloured derivative with 2, 4 DNP.
15. (d) Ethanal among the given compounds gives positive iodoform test.
17. (c)  $2CH_3CHO \xrightarrow[NaOH]{dil.} CH_3 - \overset{OH}{\underset{|}{CH}} - CH_2CHO$
18. (c)  $C_2H_5CHO + 2Cu^{+2} + 5OH^- \rightarrow \underset{\text{Red ppt}}{Cu_2O} + 3H_2O + C_2H_5COO^-$   
 $CH_3COCH_3 + 2Cu^{+2} + 5OH^- \rightarrow \text{No reaction}$
19. (abd) Deuterium behaves like  $H$  and hence trideuteroacetaldehyde also undergoes aldol condensation but benzaldehyde does not since it has no  $\alpha$ -hydrogen.
21. (b)  $1^\circ$  Primary alcohol  $\xrightarrow{ZnCl_2 / HCl}$  White turbidity only heating  
 $2^\circ$  Alcohol  $\xrightarrow{ZnCl_2 / HCl}$  White turbidity after 5 min heating  
 $3^\circ$  Alcohol  $\xrightarrow{ZnCl_2 / HCl}$  easily in seconds
24. (b) Benzaldehyde on treatment with 50% aqueous or ethanolic alkali solution undergoes Cannizzaro's reaction like  $HCHO$  (no  $\alpha$ -hydrogen atom) i.e., one molecule is oxidised and one is reduced with the formation of benzoic acid and benzyl alcohol respectively.  
 $2C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$
25. (d)  $2HCHO \xrightarrow[Conc.]{NaOH} CH_3OH + HCOONa$   
It is a Cannizzaro's reaction.  
 $2CH_3CHO \xrightarrow[dil.]{NaOH} CH_3 - \overset{OH}{\underset{|}{CH}} - CH_2 - CHO$   
It is aldol condensation reaction.
27. (d)  $CH_3 - CH_2 - \overset{O}{\parallel} C - CH_2 - CH_3$  do not have  $CH_3 - \overset{O}{\parallel} C -$  Group



31. (c)  $\text{CHI}_3$  is yellow compound when iodine reacts with  $\text{NaOH}$  and ketone.



This reaction is called as Cannizzaro's reaction.



41. (d) The solution represented is fehling's and it has no tendency to oxidise benzaldehyde.

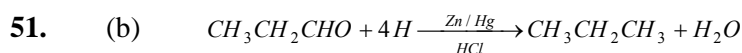
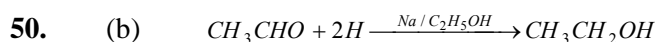
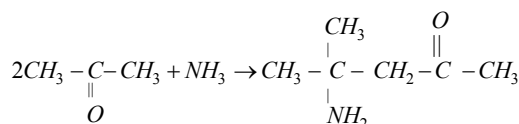
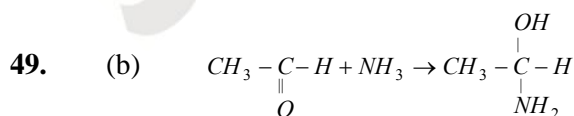
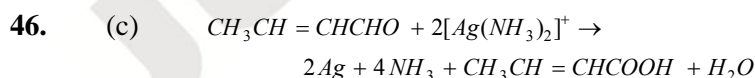
42. (a) Increasing alkyl group the reactivity decreases.



44. (d) All test for Aldehyde because ketone require strong oxidising agent.



45. (a) Silver mirror test is the test of aldehyde.



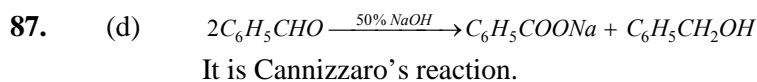
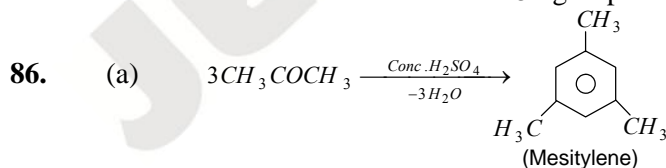
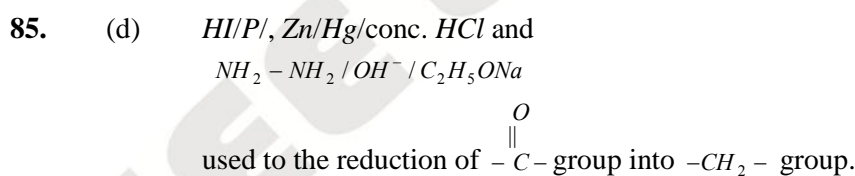
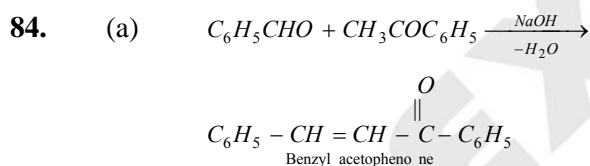
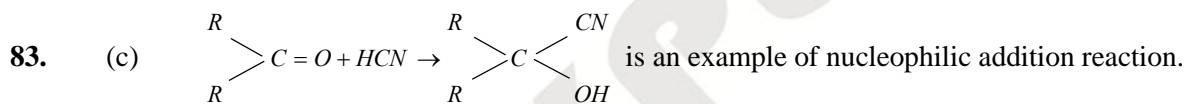
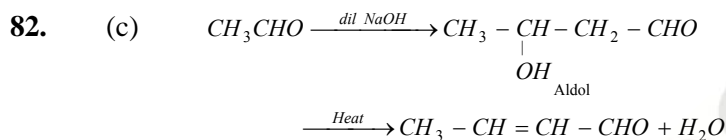
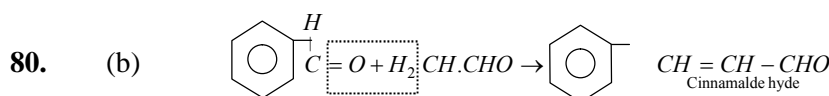
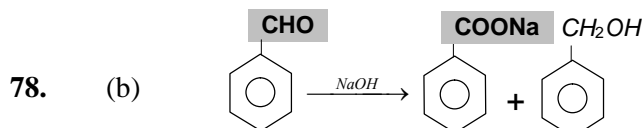
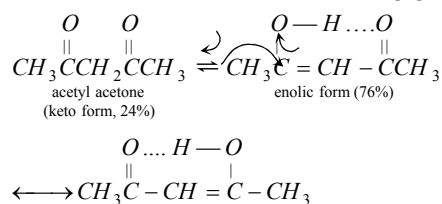
This reaction is called clemmenson's reduction.

52. (c) In cannizaro's reaction the one substance is oxidized and other is reduced.  

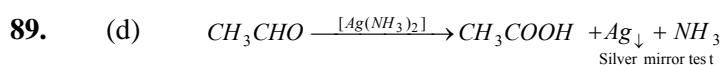
$$HCHO + HCHO \xrightarrow{KOH} CH_3OH + HCOOK$$
55. (c) Nucleophilic as addition of  $HCN$ ,  $NaHSO_3$  etc.
57. (c) Addition of  $HCN$  to carbonyl compounds is an example of nucleophilic addition.
58. (a) Acetone forms sodium bisulphate adduct but acetophenone does not. Aromatic ketones do not give addition product with  $NaHSO_3$ .
59. (c) 
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + Cl_2 \rightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + HCl$$
60. (c)  $CH_3 \rightarrow \ddot{O} \leftarrow CH_3$  The electron density of oxygen is highly increased therefore resistant to its nucleophilic attack.
63. (a) 
$$2CH_3 - \underset{\text{Acetone}}{CO} - CH_3 \xrightarrow[H_2O]{Mg/Hg} H_3C - \underset{\substack{| \\ OH}}{\overset{CH_3}{C}} - \underset{\substack{| \\ OH}}{\overset{CH_3}{C}} - CH_3$$
  
(Pinacol)
64. (b) 
$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3CO_2Na} C_6H_5CH = CHCO_2H$$
  
It is Perkin's reaction.
65. (a) Crossed aldol reaction gives benzyl alcohol and sodium formate.  

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{NaOH(aq)} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. formate}}{HCOONa}$$
66. (d) The substitution of alkoxy group of ester by an alcohol, is called trans-esterification. It occurs in presence of either an acid or base.
67. (a) 
$$6HCHO + 4NH_3 \rightarrow \underset{\text{Urotropine}}{(CH_2)_6N_4} + 6H_2O$$
68. (a) In  $HCHO$  because  $\alpha$ -Hydrogen atom is absent.
71. (c) 
$$C_6H_5 - \overset{\overset{O}{||}}{C} - H + H - \overset{\overset{O}{||}}{C} - C_6H_5 \xrightarrow{alc\ NaCN} C_6H_5 - \overset{\overset{OH}{|}}{CH} - \overset{\overset{O}{||}}{C} - C_6H_5$$
  
Benzoin
72. (d) 
$$CH_3 - \overset{\overset{O}{||}}{C} - CH_3 \xrightarrow[KOH / Glycol]{NH_2-NH_2} CH_3 - CH_2 - CH_3 + H_2O + N_2$$
75. (a) 
$$2CH_3CHO \xrightarrow[dil]{NaOH} CH_3 - \underset{\substack{| \\ OH}}{CH} - CH_2 - CHO$$
  
(Aldol)

76. (d) The amount of enolic form is highest (76%) in acetyl acetone because keto group is a much better electron-withdrawing group.

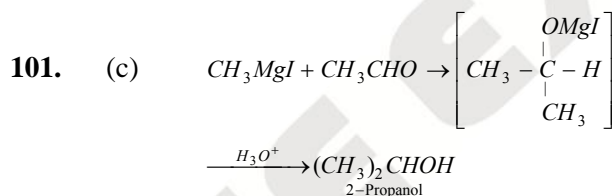
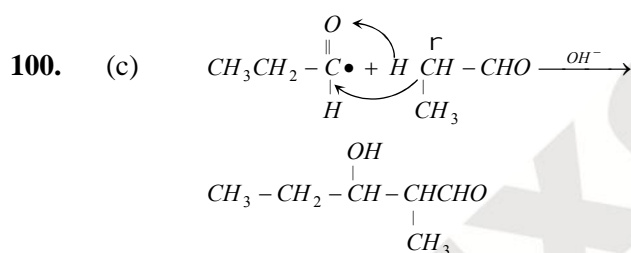
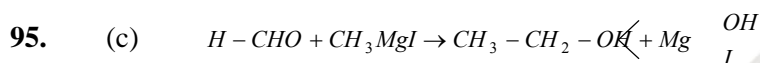
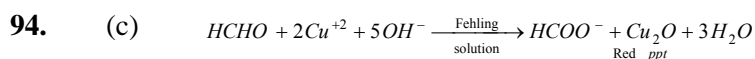
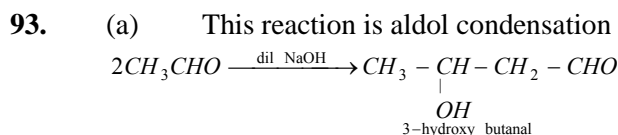
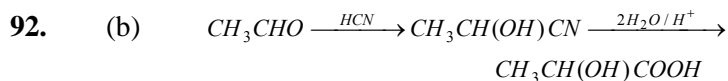
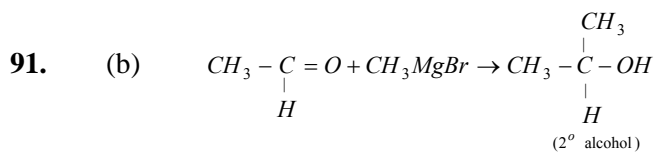


88. (a) Because acetone require stronger oxidising agent and hence not oxidized with Fehling solution to give brick red ppt.

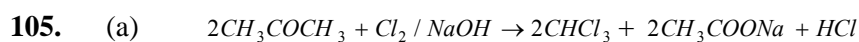
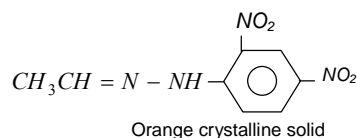
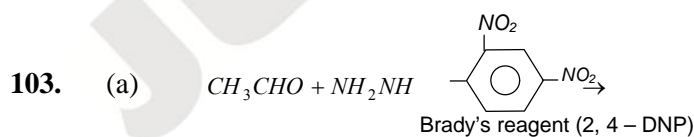


While acetone do not react.

90. (d) Due to H-bonding all are soluble in water.



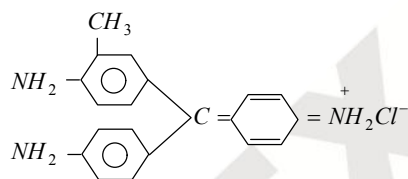
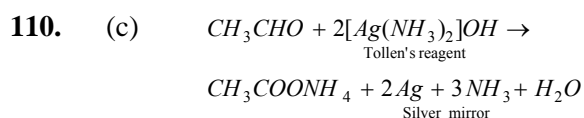
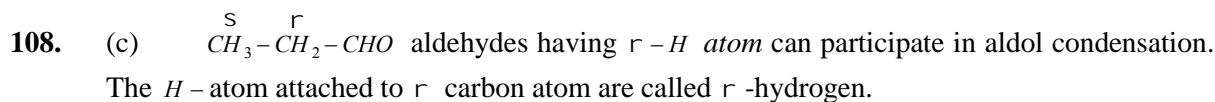
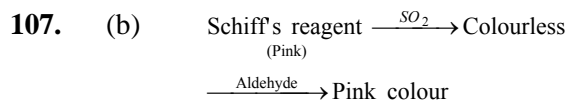
102. (d) Cannizzaro's reaction involve self oxidation and self reduction.



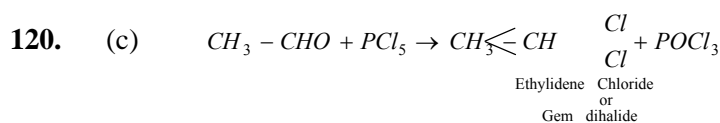
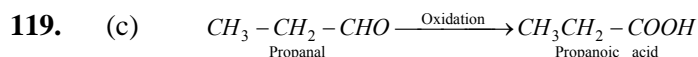
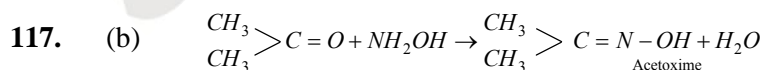
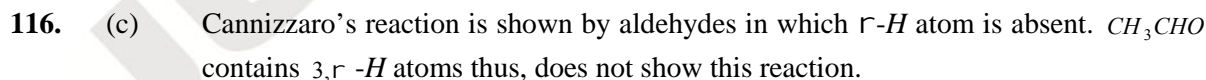
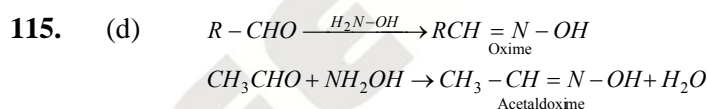
106. (e) Fehling solution  $\Rightarrow$  Alkaline  $\text{CuSO}_4 + \text{Na} - \text{K}$  tartarate  
 Tollen's reagent  $\Rightarrow \text{NH}_4\text{OH} + \text{AgNO}_3$   
 Schiff's reagent  $\Rightarrow$  *P*-rosaniline hydrochloride or magenta  
 Benedict's solution  $\Rightarrow$  Alkaline  $\text{CuSO}_4 +$  Citrate ions



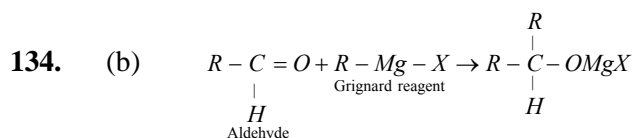
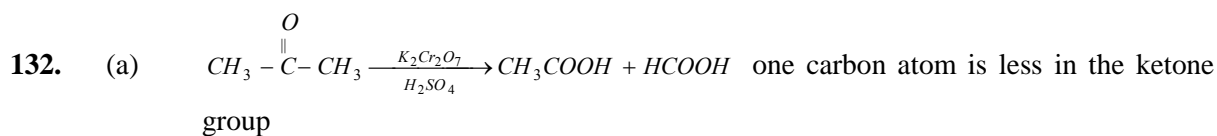
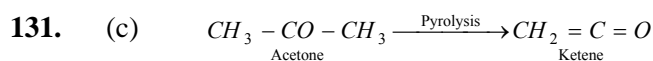
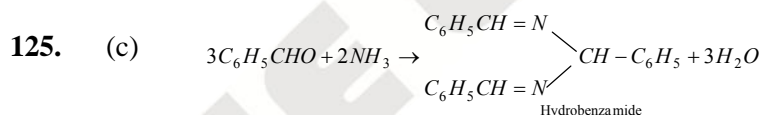
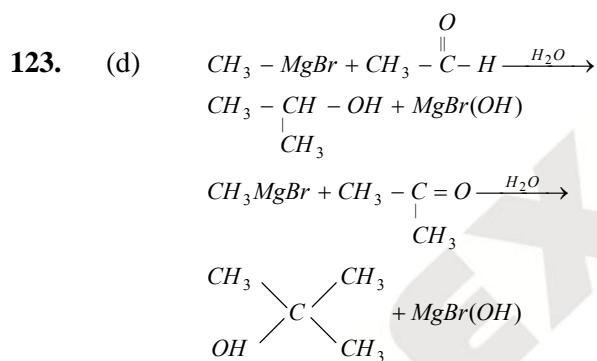
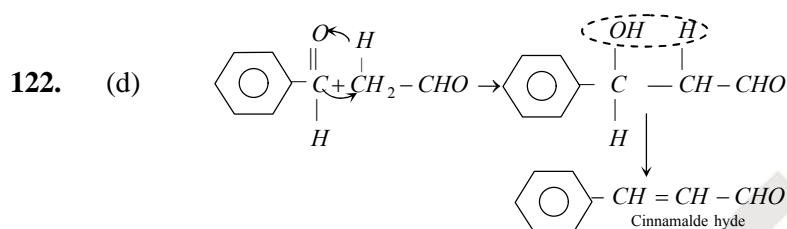
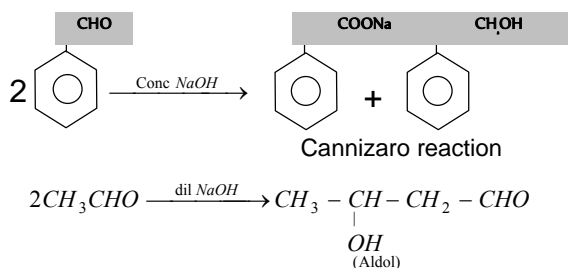
All these reagents are used to distinguish between aldehydes and ketones. Aldehydes reacts with all these reagents while ketones do not react.

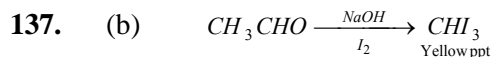
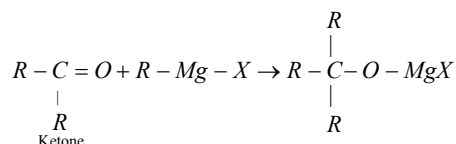


It is used for the identification of aldehydes.

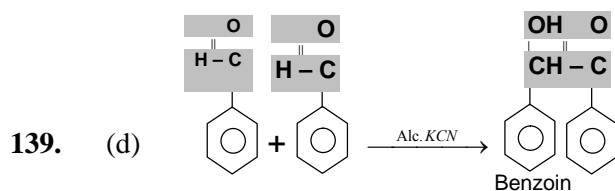


121. (d) Benzaldehyde gives cannizaro's reaction whereas acetaldehyde gives aldol condensation.





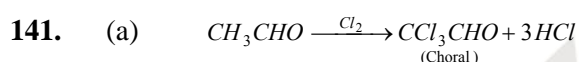
138. (b) Fehling solution is a weak oxidising agent therefore unable to oxidise benzaldehyde.



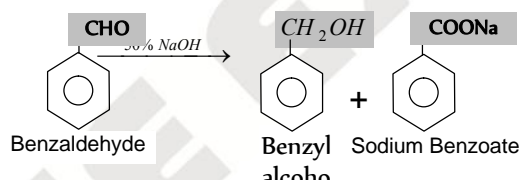
This reaction is called benzoin condensation.

140. (a) Aldehyde + Schiff's reagent  $\rightarrow$  Pink colour  
(Colourless)

Ketone do not give this test.

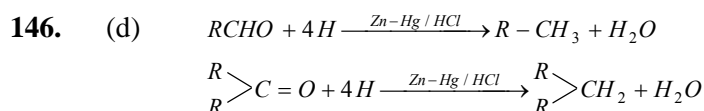
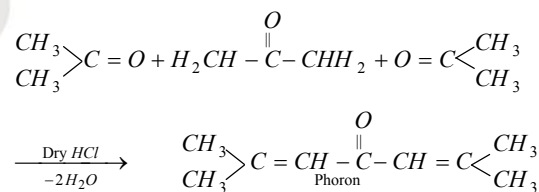


143. (b) Benzaldehyde will undergo Cannizzaro's reaction on treatment with 50% NaOH to produce benzyl alcohol and benzoic acid as it does not contain  $\alpha$ -hydrogen

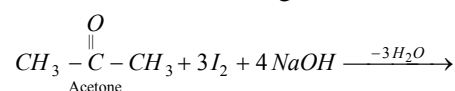


144. (d) Butane 2-one will get reduced into butane when treated with Zinc and hydrochloric acid following Clemmensen reduction, whereas Zn/HCl do not reduce ester, acid, amide

145. (b) Phoron

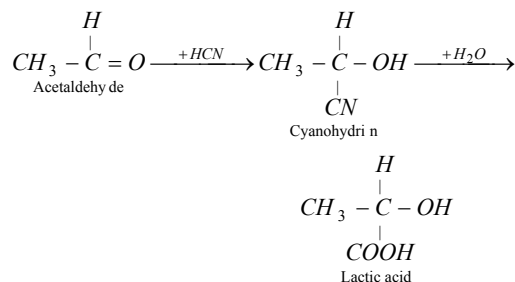


147. (b) Acetone on iodination gives iodoform in the presence of NaOH



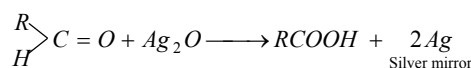


148. (b) We know that



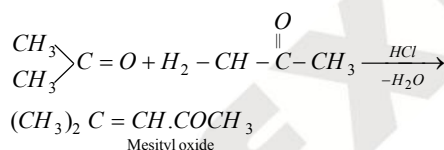
Thus Lactic acid is formed.

149. (b) Tollen's reagent is used to detect aldehydes. Aldehyde reduce Tollen's reagent to give Silver mirror while these are oxidised to acid.

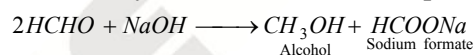


150. (c) Only aliphatic aldehyde reduce fehling solution. Hence, acetaldehyde give red ppt. with fehling solution.

151. (a) Two molecules of acetone condense in presence of dry  $HCl$  gas to form mesityl oxide.



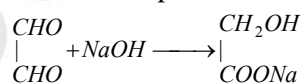
152. (a) Formaldehyde and  $NaOH$  reacts to produce alcohol and sodium salt of an acid.



This reaction is Cannizzaro's reaction

153. (c) Acetaldehyde reduces Fehling solution giving red ppt. while acetone do not.

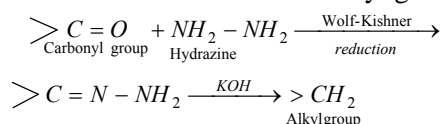
154. (c) It is an example of Cannizzaro reaction



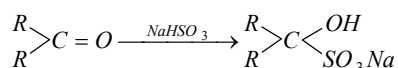
155. (b)  $R - \overset{+u}{\underset{\parallel}{C}} - H$  ; Susceptibility of nucleophilic attack on aldehyde is decreased by electron

releasing effect of  $R$  group. Decreasing order of aldehyde towards nucleophilic attack is  $1^\circ > 2^\circ > 3^\circ R$  group.

156. (a) Wolf kischner reduction : Hydrazine ( $NH_2 - NH_2$ ) followed by reaction with strong base like  $KOH$  reduce carbonyl group into alkyl group.



157. (d) Ketones and Aldehyde add to  $\text{NaHSO}_3$  to give white precipitate



158. (d) Fehling's solution is the solution of  $\text{CuSO}_4 + \text{NaOH}$  + Roschel salt (Sodium potassium tartarate). Aldehyde give red precipitate with Fehling's solution.

159. (c) It reduce  $-\text{CHO}$  group into hydrocarbon.

160. (a) Molecular weight of the compound

$$= 2 \times \text{Vapour density}$$

$$= 2 \times 29 = 58$$

Molecular weight of  $\text{CH}_3\text{CH}_2\text{CHO}$ ,  $\text{CH}_3\text{CHOHCH}_3$ ,  $\text{CH}_3\text{COCH}_3$  and  $\text{CH}_3\text{CH}_2\text{COOH}$  are 58, 60, 58 and 74 respectively. Both  $\text{CH}_3\text{CH}_2\text{CHO}$  and  $\text{CH}_3\text{COCH}_3$  have molecular weight 58 but only aldehyde i.e.,  $\text{CH}_3\text{CH}_2\text{CHO}$  on warming with aqueous alkali gives yellow precipitate.

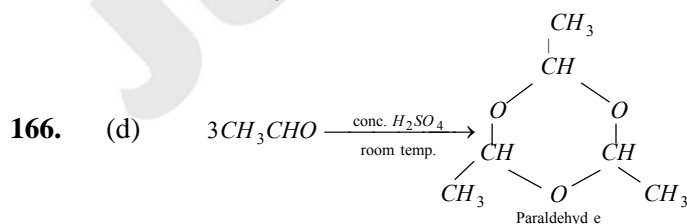
161. (c)  $\text{CH}_3 - \text{CH}_2 - \overset{\text{OH}}{\underset{\text{2 butanol}}{\text{CH}}} - \text{CH}_3$  contain  $\text{CH}_3 - \overset{\text{OH}}{\text{CH}} -$  group by which it give +ve iodoform test.

162. (c) In nucleophilic addition reaction, the carbonyl compound will respond in preference which is sterically more exposed and electronically have intact positive charge over carbonyl carbon. So reactivity order towards reaction with  $\text{phMgBr}$  is (II) > (III) > (I).

163. (d) Tollen's reagent oxidizes the compound having aldehyde group like glucose and also oxidizes  $\alpha$ -hydroxy ketones having  $-\text{COCH}_2\text{OH}$  group as in fructose.

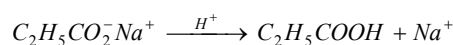
164. (d) Acetaldehyde have  $\text{CH}_3\text{CO}-$  group so it give positive iodoform test with  $\text{I}_2$  and  $\text{NaOH}$  while formaldehyde does not have  $-\text{CH}_3\text{CO}$  group so it will not give the positive haloform test.

165. (c) Aldehyde reduce silver mirror whereas acid do not reduce silver mirror.

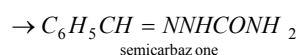
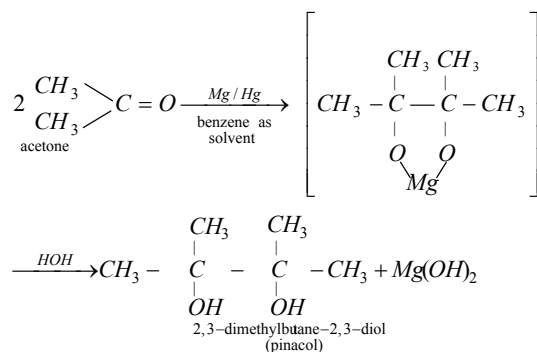


168. (b) Formaline contains 40%  $\text{HCHO}$ , 8%  $\text{CH}_3\text{OH}$  and 52% water. It is used as biological preservative.

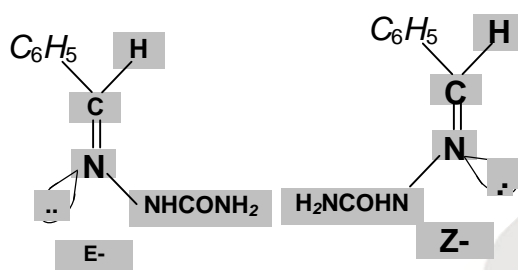
172. (c)  $\text{C}_2\text{H}_5 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3 + \text{I}_2 + \text{NaOH} \rightarrow \text{C}_2\text{H}_5\text{CO}_2^- \text{Na}^+ + \text{CHI}_3$



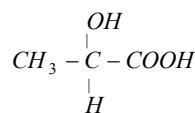
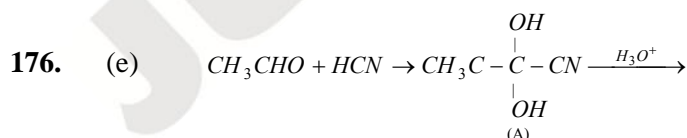
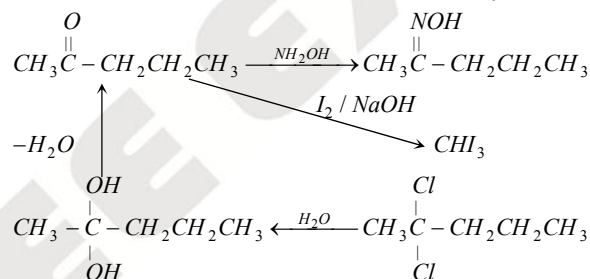
173. (b) Two molecules of ketones undergo reduction in the presence of  $\text{Mg/Hg}$  to form pinacol.



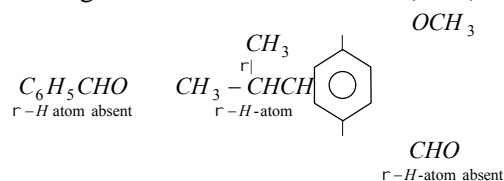
The product shows *E* and *Z* configuration

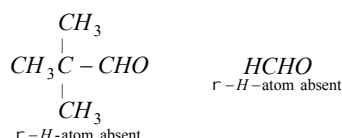


175. (a) As *A* reacts with hydroxylamine it means *A* may be aldehyde or ketone. but it does not react with fehling solution hence *A* must be a ketone. Secondly it forms iodoform which is a characteristic reaction of methyl ketone.



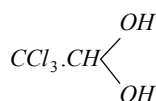
177. (b) Aldehyde, which does not have the  $\alpha$ -H atom, gives cannizzaro's reaction on heating with conc. alkali solution (50%)





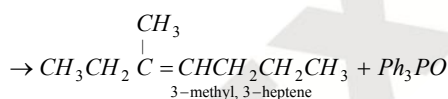
## Critical Thinking Questions

- (d) Acetone oxidise by  $K_2Cr_2O_7$  & conc.  $H_2SO_4$  into carboxylic acid. It is not oxidised by dilute  $H_2SO_4$ .
- (b) Acetaldehyde react with tollen's reagent while ketone do not react with tollen's reagent.
- (b)  $CCl_3 - CHO + H_2O \rightarrow CCl_3 \cdot CHO \cdot H_2O \rightarrow$   
(Chloral hydrate)

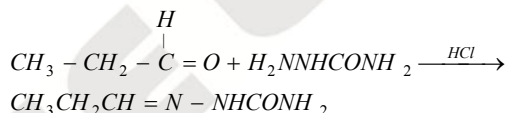


- (c) The compound A with formula  $C_3H_6O$  gives iodoform test, it is propanone forms a compound B having carbon atoms three times, the number of carbon atoms in propanone, it is 2, 6-dimethyl-2, 5-heptadien-4-one.

- (a) 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2 - \text{C} = \text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} = \text{PPh}_3 \\ \text{2-Butanone} \end{array}$$

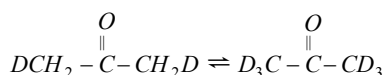
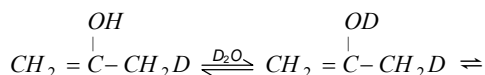
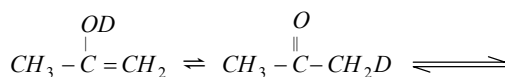


- (a) 
$$\begin{array}{ccc} \text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{OH} & \xrightarrow{[O]} & \text{CH}_3 - \text{CH}_2 - \text{CHO} \\ \text{(A)} & & \text{(B)} \end{array}$$



- (b) Acetophenone is a ketone and does not react with Tollen's reagent to give silver mirror.

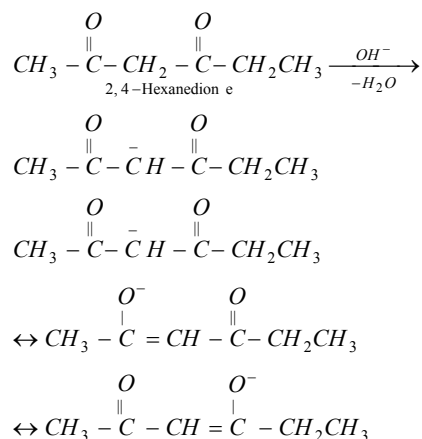
- (b) 
$$\begin{array}{c} \text{O} \\ || \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \text{Acetone (ketoform)} \end{array} \left[ \begin{array}{c} \text{OH} \\ | \\ \text{CH}_3 - \text{C} = \text{CH}_2 \\ \text{enol form} \end{array} \right] \rightleftharpoons$$



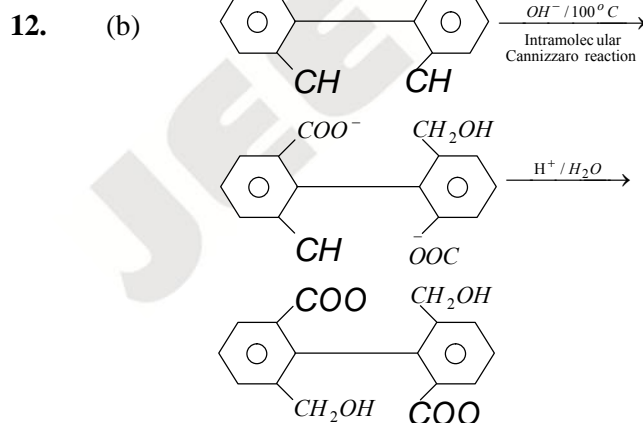
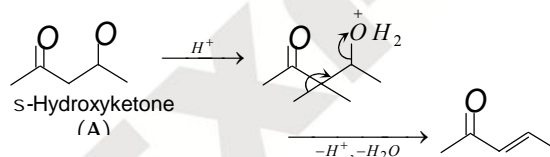
The enol form of acetone on treatment with  $D_2O$  undergoes enolisation, deuteration (addition of  $D_2O$ ) and dehydration (removal of  $H_2O$ ). The repeated enolisation, deuteration and dehydration ultimately gives  $CD_3 \cdot COCD_3$  (B).

9. (b) Both  $Zn(Hg), HCl$  and  $NH_2NH_2, OH^-$  can reduce  $-COCH_3$  group to  $-CH_2-CH_3$  group, but  $HCl$  will also bring about dehydration of alcohol to form alkene. Therefore, appropriate reagent for the conversion is  $NH_2NH_2, OH^-$ .

10. (b) 2, 4-hexanedione (a 1, 3-diketone) has the most acidic hydrogen. This is because the carbanion left after the removal of  $H^+$  is resonance stabilised in this case.

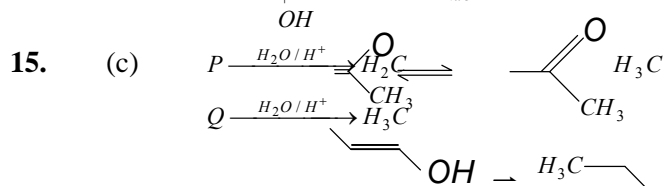
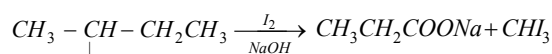
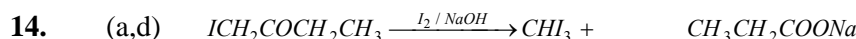


11. (a) Aldols (S-hydroxy aldehydes or S-hydroxyketones) readily undergo dehydration to form  $\alpha, \beta$ -unsaturated aldehydes or ketones.

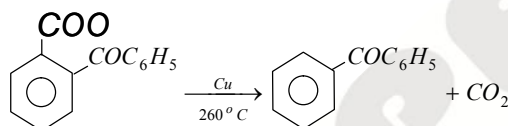
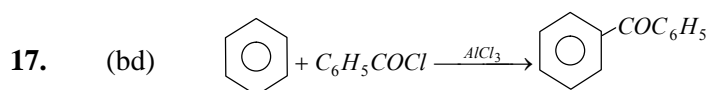
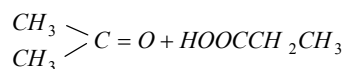
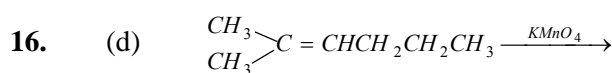


13. (a) Amongst aldehyde & the acid derivatives, acid chloride are the most susceptible to nucleophilic attack due to strong  $-I$  effect & weak  $+R$  effect of the  $Cl$ -atom as a result of which carbonyl carbon has the highest electron deficiency. The actual order is  $MeCOCl > MeCOOCOMe > MeCOOMe > MeCHO$ .



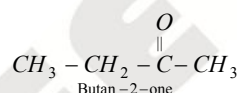
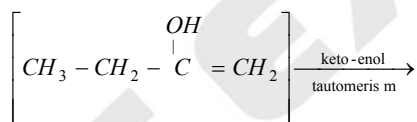
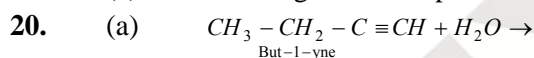


Ketone (non-reducing) and aldehyde (reducing) can be distinguished by Fehling solution.



18. (d) Aldehyde & ketone are colourless & stable compound

19. (c) It undergoes electrophilic substitution at *m*-position and also gives iodoform test.

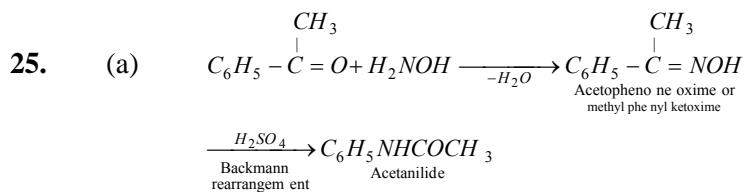


21. (b) Due to electron withdrawing nature of  $NO_2$  group, the partial +ve charge on the carbon atom of the  $>C=O$  group in *p*-nitrobenzaldehyde increases and hence becomes more susceptible to nucleophilic attack by  $CN^-$  ion.

22. (b) Cannizzaro reaction is an example of hydride ion ( $H^-$ ) transfer reaction.

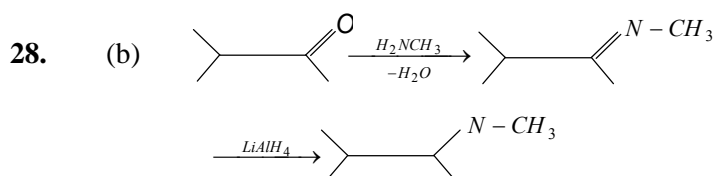
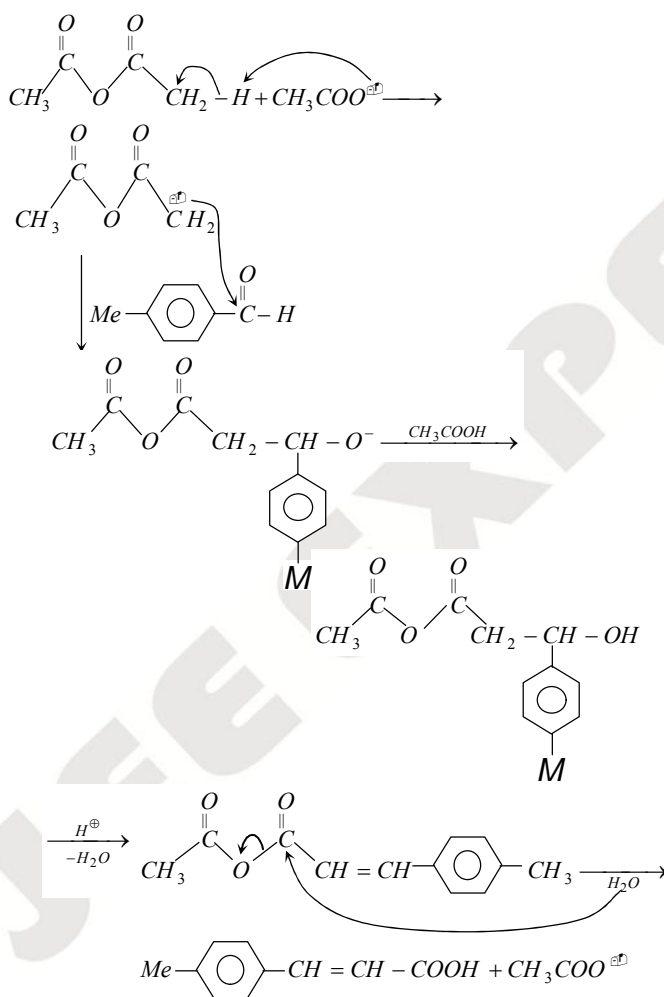
23. (d) Except  $Na_2CO_3$  benzophenone react with rest of option.

24. (d) The alcohol can be converted to aldehyde group by treating with oxidising agent Pyridinium chloro chromate ( $C_5H_5N^+HCrO_3Cl^-$ ) it is abbreviated as PCC and is called Collin's reagent. This reagent is used in non aqueous solvent like  $CH_2Cl_2$ . It is a very good reagent because it checks the further oxidation of aldehyde to carboxylic acid while rest oxidising agent oxidise aldehyde into carboxylic acid.



26. (d) Benzyl alcohol does not have the  $\text{CH}_3\text{CO} -$  group or  $\text{CH}_3\text{CH}_2\text{O}^-$  so it will not give the positive iodoform test.

27. (c) This is perkin reaction





Acetaldehyde, acetone and methyl ketones having  $CH_3CO$  group undergo haloform reaction. The halogen atoms of the methyl group are first replaced by hydrogen atoms. This reaction is used as a test of  $CH_3CO$ -group. Due to absence of  $CH_3CO$ -group isobutanal does not give iodoform test.

8. (a) Benzaldehyde is less reactive than ethanol towards nucleophilic attack. The combined effect of  $-I$  and  $+R$  effect of phenyl group is electron donating which increases the electron density on the carbon atom of the  $>C=O$  in benzaldehyde.
9. (b) Both carbanions (formed in presence of base) and enol form (formed in presence of an acid) act as nucleophiles and hence add on the carbonyl group of aldehydes and ketones to give aldols.
10. (b) The positive inductive effect of two alkyl groups in ketones makes the carbon atom less positive and makes it less reactive in comparison to aldehydes.
11. (e) Oximes are more acidic because, there is a delocalisation of  $f$  electrons (*i.e.*, resonance) and it stabilises it and its conjugate acid. But no such resonance exists in hydroxyl amine base ( $NH_2O^-$ )
12. (e) The bond energy of carbonyl group is  $179 \text{ Kcal mol}^{-1}$  and in  $>C=C<$  the bond energy is  $145.8 \text{ Kcal}$ . The carbonyl group shows resonance and thus possesses higher bond energy.  $>C=O \leftrightarrow >C^+ - O^-$
13. (b) Both carbon and oxygen are nonmetals and try to complete their octet. In  $R-C \equiv O^+$  each has complete octet whereas in  $R-C^+ = O$ , carbon atom has incomplete octet.
14. (b)  $HCHO$  cannot be prepared by Rosenmund's reduction because formyl chloride is unstable at room temperature.
15. (e)  $HCHO$  reacts with  $NH_3$  to form urotropine  $6HCHO + 4NH_3 \rightarrow (CH_2)_6N_4 + 6H_2O$
16. (c) The anion left after the removal of  $\alpha$ -hydrogen is stabilized by resonance effect.
17. (b) Aldehydes which do not contain  $\alpha$ -hydrogens undergo Cannizzaro reaction.  

$$\begin{array}{c}
 CH_3 \\
 | \\
 H_3C - C^r - CHO \\
 | \\
 CH_3
 \end{array}$$

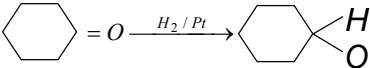
2, 2 dimethyl propanal (no  $\alpha$  hydrogen)
18. (d) Aldehydes having a methyl or methylene group in the  $\alpha$ -position or more correctly having atleast one hydrogen atom in the  $\alpha$ -position undergo dimerisation in presence of a base at low temperature to form  $\beta$ -hydroxy aldehydes called aldols.

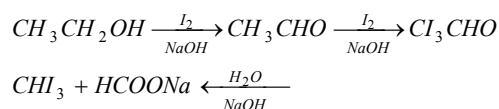
# SELF EVALUATION TEST

## ANSWER & SOLUTION

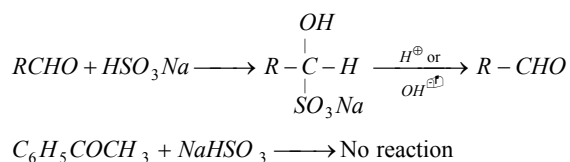
- (a) 
$$\begin{array}{ccc} C_6H_5COC_6H_5 + KOH & \xrightarrow{\text{Fusion}} & C_6H_6 + C_6H_5COOK \\ \text{Benzophenone} & & \text{Benzene} \quad \text{Pot. benzoate} \end{array}$$

$$C_6H_5COOK + KOH \xrightarrow{\Delta} K_2CO_3 + C_6H_6$$
  
Benzene
- (d) Acetophenone gives iodoform reaction while benzophenone does not give this.
- (c) 
$$CH_3CHO + \underbrace{2Cu^{+2} + 5OH^-}_{\text{Fehling solution}} \rightarrow CH_3COO^- + \underbrace{Cu_2O}_{\text{Red ppt.}} + 3H_2O$$
- (a) The size of the alkyl group. Causes hindrance to attacking group. As the number and size of the alkyl groups increase the hindrance to the attack of nucleophile also increases.  
Thus the reactivity follows the order  
 $H_2C=O > RCHO > ArCHO > R_2C=O > Ar_2C=O$ .
- (b) Benzaldehyde does not have the  $\alpha$ -hydrogen so it will undergo Cannizzaro's reaction.  
$$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$$
- (b)  $C_6H_5CHO$  Aldehydes – Those aldehyde in which  $\alpha$ -H atom is absent can participate in Cannizzaro's reaction.
- (c) 
$$2CH_3-CO-CH_3 \xrightarrow{\text{dil NaOH}}$$

$$\begin{array}{c} OH \qquad \qquad O \\ | \qquad \qquad || \\ CH_3 - C - CH_2 - C - CH_3 \\ | \qquad \qquad \text{(Diacetone alcohol)} \\ CH_3 \end{array}$$
- (c) 
- (a) Because alkyl group is absent and they have +ve inductive effect and increases the electron density on the carbonyl group.
- (b) The compound having  $\alpha$ -hydrogen will give iodoform test. Ethyl alcohol and secondary alcohols also give positive iodoform test because by the action of halogens in alkaline medium, they are oxidised to acetaldehyde and methyl ketones respectively.



11. (d) During reaction  $Ag^+$  gets reduced Ag metal and forms silver mirror.
12. (a,d)  $C_6H_5NH_2$  and  $C_6H_5NH.NH_2$  will give the compounds containing  $>C=N$ -group.
13. (d)  $HCHO \xrightarrow{I_2 / NaOH}$  No reaction
14. (d)  $CH_3CHO + HCN \rightarrow CH_3CHOHCN \xrightarrow{\text{hydrolysis}} CH_3CHOHCOOH$   
D+L isomer of lactic acid
15. (c) Aldehydes are compounds containing C, H and O. So hydrocarbons react with atmospheric oxygen to give aldehydes.
16. (b) Tollen's reagent is ammoniacal silver nitrate solution. Its reacting species is  $Ag^+$ . It oxidises aliphatic as well as aromatic aldehydes.  
 $R-CHO + Ag^+ \xrightarrow[\text{reaction}]{\text{Redox}} RCOOH + Ag$
17. (b)  $ArH + R-CO-Cl \xrightarrow{\text{anhyd. } AlCl_3} Ar-CO-R + HCl$   
This reaction is Friedel-Craft's acylation.
18. (a) 1-pentanone is an impossible compound does not have  $CH_3-\overset{\overset{O}{\parallel}}{C}-$  group.
19. (a)  $NaHSO_3$  gives the addition reaction with Aldehyde and only aliphatic ketone. Acetophenone is the aromatic ketone so it does not give the addition product with  $NaHSO_3$  aldehyde from the addition product with  $NaHSO_3$  which on treatment with acid or base give again aldehyde.



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