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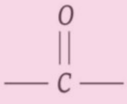
ALDEHYDE KETONES CARBOXYLIC ACIDS

Introduction

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



$$-\overset{\overset{\displaystyle O}{||}}{C}-$$

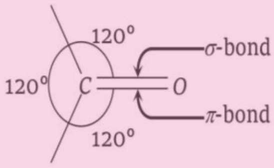
Carbonyl group

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° apart. The carbon-oxygen double bond is different than carbon-carbon double bond. Since, oxygen is more electronegative, the electrons of the bond are attracted towards oxygen. Consequently, oxygen attains a partial negative charge and carbon a partial positive charge making the bond polar. The high values of dipole moment, $\overset{\delta+}{C}=\overset{\delta-}{O}$

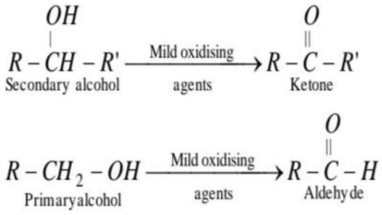
(2.3 – 2.8D) cannot be explained only on the basis of inductive effect and thus, it is proposed that carbonyl group is a resonance hybrid of the following two structures.

$$>C=O \longleftrightarrow >\overset{+}{C}-\overset{-}{O}$$



Preparation of carbonyl compounds

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



$$\underset{\text{Secondary alcohol}}{R-\overset{\overset{\displaystyle OH}{|}}{CH}-R'} \xrightarrow[\text{agents}]{\text{Mild oxidising}} \underset{\text{Ketone}}{R-\overset{\overset{\displaystyle O}{||}}{C}-R'}$$

$$\underset{\text{Primaryalcohol}}{R-CH_2-OH} \xrightarrow[\text{agents}]{\text{Mild oxidising}} \underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{||}}{C}-H}$$

Mild oxidising agents are

(a) X_2 (Halogen) (b) Fenton reagent ($FeSO_4 + H_2O_2$)

(c) $K_2Cr_2O_7 / \overset{\oplus}{H}$ (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 α,β-unsaturated aldehydes.*

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

$$R-CH_2OH \xrightarrow{Cu/300°C} R-\overset{\overset{O}{||}}{C}-H+H_2$$

$$R-\underset{}{\overset{\overset{OH}{|}}{CH}}-R' \xrightarrow{Cu/300°C} R-\overset{\overset{O}{||}}{C}-R'+H_2$$

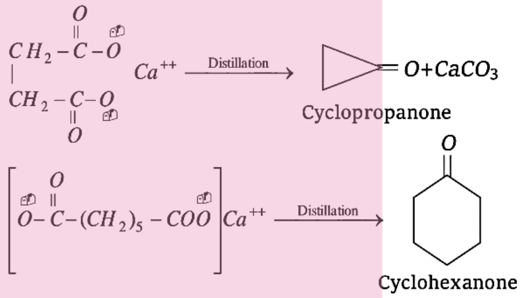
(2) **From carboxylic acids**

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

$$(RCOO)_2Ca+(R'COO)_2Ca \xrightarrow{\Delta} 2R-\overset{\overset{O}{||}}{C}-R'+2CaCO_3$$

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.



Cyclopropanone

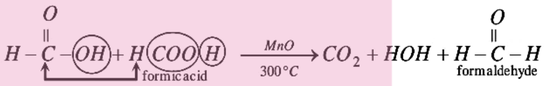
Cyclohexanone

(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.

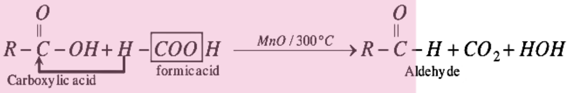
(b) If one of the carboxylic acids is $HCOOH$ then this acid undergoes decarboxylation because this acid is the only monobasic acid which undergoes decarboxylation even in the absence of catalyst.

Case I : When both molecules are $HCOOH$



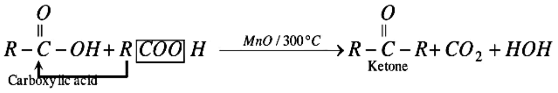
$$H-\overset{\overset{O}{||}}{C}-OH+\underset{\text{formic acid}}{HCOOH} \xrightarrow[300°C]{MnO} CO_2+HOH+\underset{\text{formaldehyde}}{H-\overset{\overset{O}{||}}{C}-H}$$

Case II : When only one molecule is formic acid.



$$\underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{||}}{C}-OH}+\underset{\text{formic acid}}{H-\boxed{COO}H} \xrightarrow{MnO/300°C} \underset{\text{Aldehyde}}{R-\overset{\overset{O}{||}}{C}-H}+CO_2+HOH$$

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



$$\underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{||}}{C}-OH+R\boxed{COO}H} \xrightarrow{MnO/300°C} \underset{\text{Ketone}}{R-\overset{\overset{O}{||}}{C}-R}+CO_2+HOH$$

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

(i) $\underset{\text{Gemdihalide}}{R-CHX_2} \xrightarrow{HOH/\overset{\ominus}{O}H} \underset{\text{Aldehyde}}{R-CHO}$

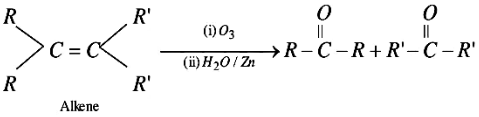
(ii) $R-\overset{\overset{X}{|}}{\underset{\underset{X}{|}}{C}}-R' \xrightarrow{HOH/\overset{\ominus}{O}H} R-\overset{\overset{O}{||}}{C}-R'$

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

(4) **From alkenes**

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

$$\underset{\text{Alkene}}{R-CH=CH-R} \xrightarrow[\text{(ii)}H_2O/Zn]{\text{(i)}O_3} R-CHO+RCHO$$



$$\underset{\text{Alkene}}{R_2C=CR'_2} \xrightarrow[\text{(ii)}H_2O/Zn]{\text{(i)}O_3} R-\overset{\overset{O}{||}}{C}-R+R'-\overset{\overset{O}{||}}{C}-R'$$

❑ *This method is used only for aliphatic carbonyl compounds.*

(ii) ***Oxo process***

$$R-CH=CH_2+CO+H_2 \xrightarrow[150°C,\ 300\ atm]{CO_2(CO)_8} R-CH_2-CH_2-CHO$$

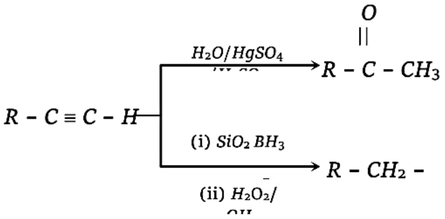
❑ *Oxo process is used only for the preparation of aldehydes.*

(iii) ***Wacker process***

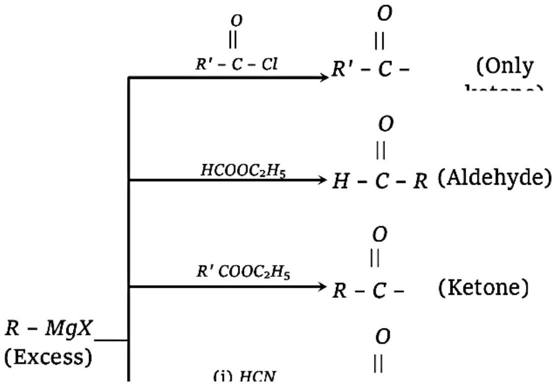
(a) $\underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow[\text{air}/Cu_2Cl_2]{PdCl_2/HOH} CH_3-CHO$

(b) $\underset{\text{Alkylethene}}{R-CH=CH_2} \xrightarrow[\text{air}/Cu_2Cl_2]{PdCl_2/HOH} R-\overset{\overset{O}{||}}{C}-CH_3$

(5) **From alkynes**

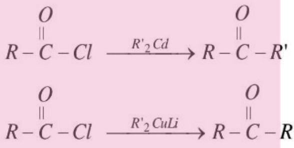


(6) **From Grignard reagents**



(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.



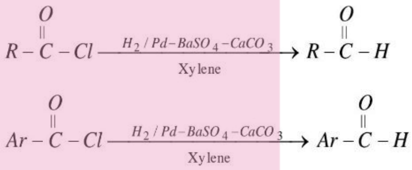
$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{R'_2Cd} R-\overset{O}{\overset{\|}{C}}-R'$$

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{R'_2CuLi} R-\overset{O}{\overset{\|}{C}}-R'$$

(Only used for the preparation of ketones)

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

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



$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{Xylene}]{H_2/Pd-BaSO_4-CaCO_3} R-\overset{O}{\overset{\|}{C}}-H$$

$$Ar-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{Xylene}]{H_2/Pd-BaSO_4-CaCO_3} Ar-\overset{O}{\overset{\|}{C}}-H$$

(Only used for aldehydes)

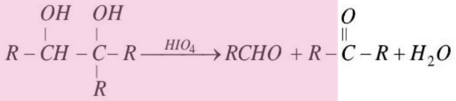
(8) **From cyanides**

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

$$\underset{\text{Alkylcyanide}}{R-C\equiv N} \xrightarrow[\text{(ii)}\ H_2O/\Delta\ \text{or steam distillation}]{\text{(i)}\ SnCl_2/HCl/\text{ether}} \underset{\text{Aldehyde}}{R-CHO}$$

(Only used for aldehydes)

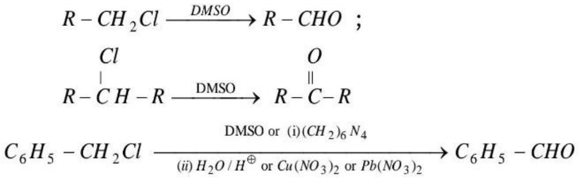
(9) **From vic diols**



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

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

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

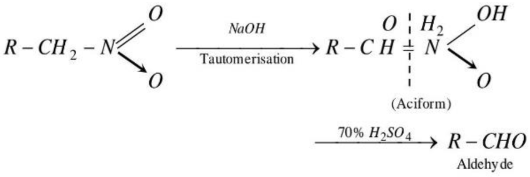


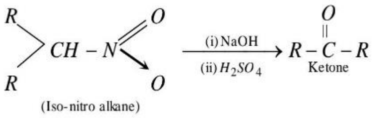
$$R-CH_2Cl \xrightarrow{DMSO} R-CHO\ ;$$

$$R-\overset{Cl}{\overset{|}{C}}H-R \xrightarrow{\text{DMSO}} R-\overset{O}{\overset{\|}{C}}-R$$

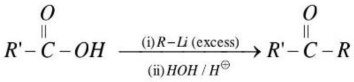
$$C_6H_5-CH_2Cl \xrightarrow[\text{(ii)}\ H_2O/H^{\oplus}\ \text{or}\ Cu(NO_3)_2\ \text{or}\ Pb(NO_3)_2]{\text{DMSO or (i)}(CH_2)_6N_4} C_6H_5-CHO$$

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





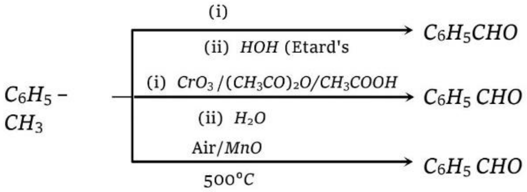
(12) **Reaction with excess of alkyl lithium :** Carboxylic acids react with excess of organo lithium compound to give lithium salt of gem diols which on hydrolysis give ketones.



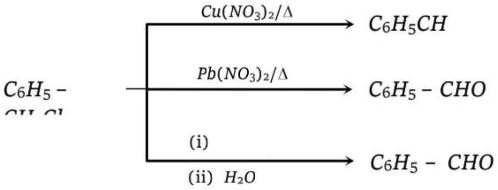
$$R'-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{(ii)}\ HOH/H^{\oplus}]{\text{(i)}\ R-Li\ \text{(excess)}} R'-\overset{O}{\overset{\|}{C}}-R$$

Preparation of only aromatic carbonyl compounds

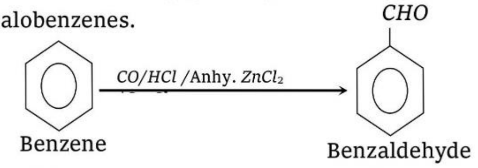
(1) **From methyl arenes**

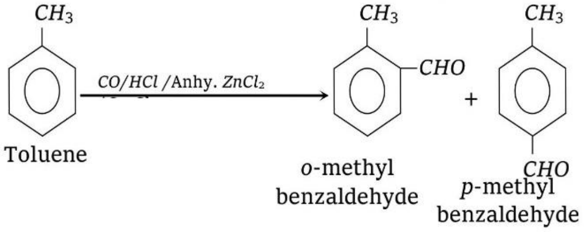


(2) **From chloro methyl**

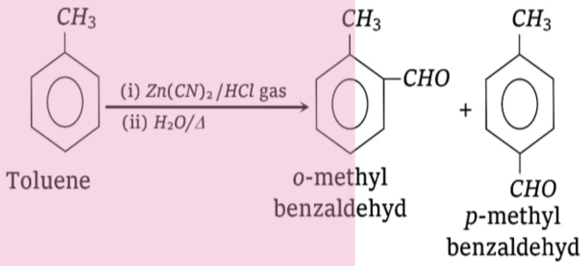


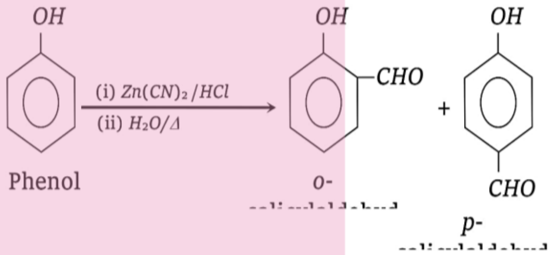
(3) **Gattermann – Koch formylation :** This reaction is mainly given by aromatic hydrocarbons and halobenzenes.

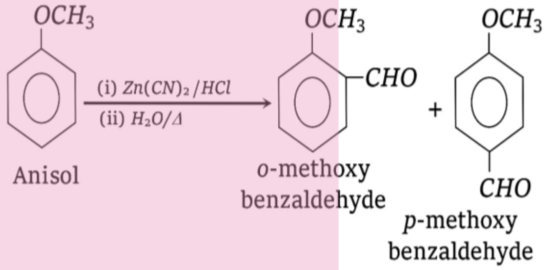




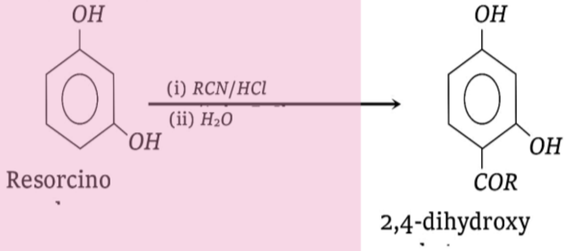
(4) **Gattermann formylation :** This reaction is mainly given by alkyl benzenes, phenols and phenolic ethers.

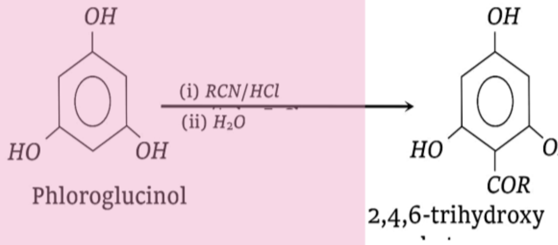




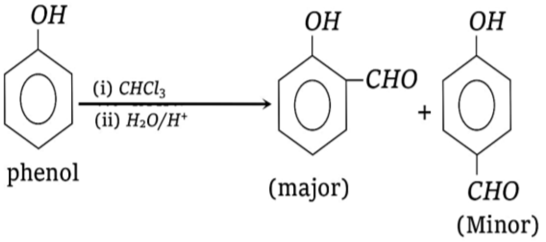


(5) **Houben – Hoesch reaction :** This reaction is given by *di* and polyhydric benzenes.





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

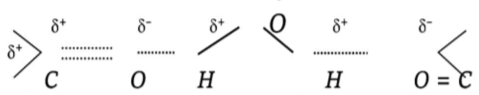


Physical properties of carbonyl compounds

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

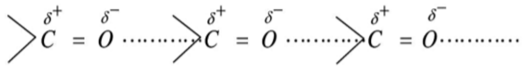
(2) **Smell :** With the exception of lower aldehydes which have unpleasant odours, aldehydes and ketones have generally pleasant smell. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones have been used in blending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

(3) **Solubility :** Aldehydes and ketones upto four carbon atoms are miscible with water. This is due to the presence of hydrogen bonding between the polar carbonyl group and water molecules as shown below :



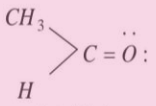
With the increase in the size of alkyl group, the solubility decreases and the compounds with more than four carbon atom are practically insoluble in water. All aldehydes and ketones are, however, soluble in organic solvents such as ether, alcohol, etc. The ketones are good solvents themselves.

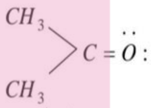
(4) **Boiling points :** The boiling points of aldehydes and ketones are higher than those of non polar compounds (hydrocarbons) or weakly polar compounds (such as ethers) of comparable molecular masses. However, their boiling points are lower than those of corresponding alcohols or carboxylic acids.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


Acetaldehyde
$\mu = 2.52$ D
b.pt. = 322 K


Acetone
$\mu = 2.88$ D
b.pt = 329 K

(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 α-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 α-hydrogen

(6) Condensation reactions and

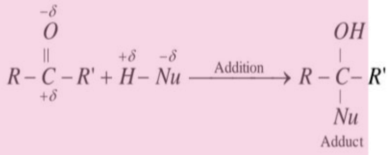
(7) Miscellaneous reactions

(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,

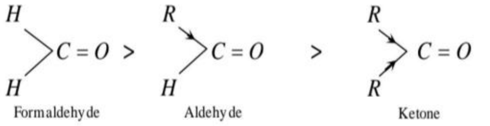


$$R-\overset{+\delta}{\underset{\|}{C}}\overset{\overset{-\delta}{O}}{}-R' + \overset{+\delta}{H}-\overset{-\delta}{Nu} \xrightarrow{\text{Addition}} R-\underset{\underset{Nu}{|}}{\overset{\overset{OH}{|}}{C}}-R' \quad \text{Adduct}$$

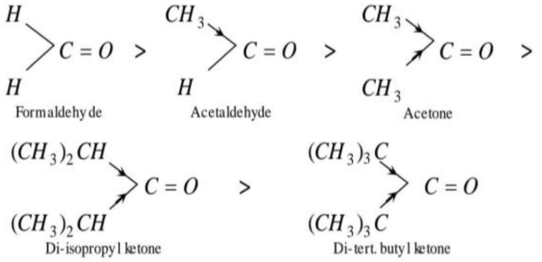
In addition reactions nucleophile adds on carbonyl carbon and electrophile on carbonyl oxygen to give adduct.

(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 stearic effects as explained below:

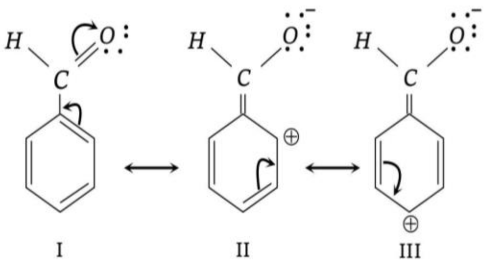
(a) *Inductive effect* : The relative reactivities of aldehydes and ketones in nucleophilic addition reactions may be attributed to the amount of positive charge on the carbon. *A greater positive charge means a higher reactivity.* If the positive charge is dispersed throughout the molecule, the carbonyl 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:

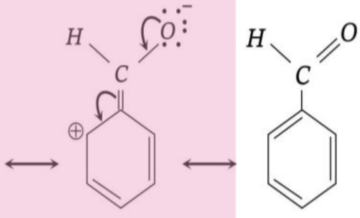

Formaldehyde Aldehyde Ketone

(b) *Stearic 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 **stearic 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:


Formaldehyde Acetaldehyde Acetone
Di-isopropyl ketone Di-tert. butyl ketone

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:





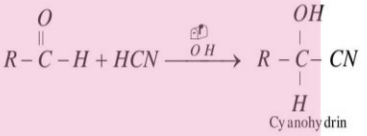
IV V

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,

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} > \underset{\text{Acetophenone}}{C_6H_5COCH_3} > \underset{\text{Benzophenone}}{C_6H_5COC_6H_5}$$

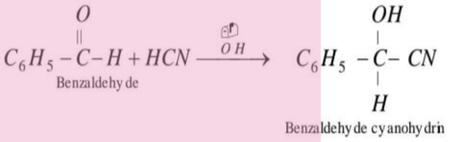
Some important examples of nucleophilic addition reactions

Addition of *HCN*



$$R-\overset{\overset{O}{\|}}{C}-H + HCN \xrightarrow{\overset{\ominus}{OH}} R-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CN$$

Cyanohydrin



$$\underset{\text{Benzaldehyde}}{C_6H_5-\overset{\overset{O}{\|}}{C}-H} + HCN \xrightarrow{\overset{\ominus}{OH}} C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CN$$

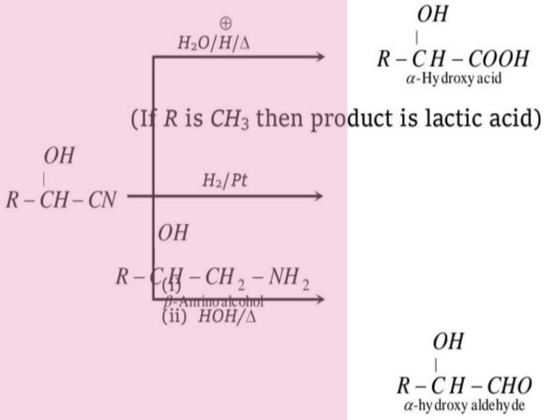
Benzaldehyde cyanohydrin

❑ *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 gives optically active cyanohydrin (racemic mixture).*

❑ *This reaction is synthetically useful reaction for the preparation of α-hydroxy acids, β-amino alcohols and α-hydroxy aldehydes.*



$$R-\overset{\overset{OH}{|}}{C}H-CN \xrightarrow{H_2O/\overset{\oplus}{H}/\Delta} \underset{\alpha\text{-Hydroxy acid}}{R-\overset{\overset{OH}{|}}{C}H-COOH}$$

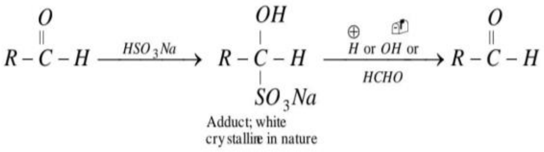
(If R is CH_3 then product is lactic acid)

$$R-\overset{\overset{OH}{|}}{C}H-CN \xrightarrow{H_2/Pt} \underset{\beta\text{-Amino alcohol}}{R-\overset{\overset{OH}{|}}{C}H-CH_2-NH_2}$$

$$R-\overset{\overset{OH}{|}}{C}H-CN \xrightarrow[\text{(ii) } HOH/\Delta]{\text{(i)}} \underset{\alpha\text{-hydroxy aldehyde}}{R-\overset{\overset{OH}{|}}{C}H-CHO}$$

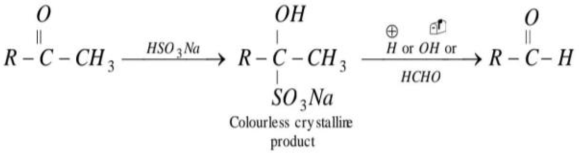
Addition of sodium bisulphite

All types of aldehydes give addition reaction with this reagent.



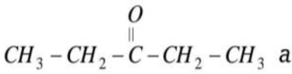
$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{HSO_3Na} \underset{\text{Adduct; white crystalline in nature}}{R-\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}-H} \xrightarrow[HCHO]{\overset{\oplus}{H}\text{ or }\overset{\ominus}{OH}\text{ or}} R-\overset{\overset{O}{\|}}{C}-H$$

Only aliphatic methyl ketones give addition reaction with sodium bisulphite.

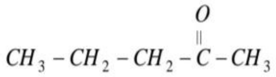


$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{HSO_3Na} \underset{\text{Colourless crystalline product}}{R-\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3} \xrightarrow[HCHO]{\overset{\oplus}{H}\text{ or }\overset{\ominus}{OH}\text{ or}} R-\overset{\overset{O}{\|}}{C}-H$$

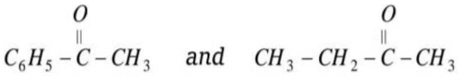
❑ *This reagent can be used for differentiation between aromatic and aliphatic methyl ketones, e.g.*



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \text{ and}$$



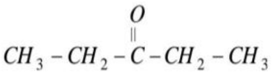
$$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$



$$C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 \quad \text{and} \quad CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

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

CH_3-CH_2-CHO and

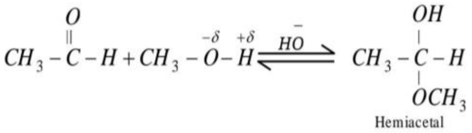


$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

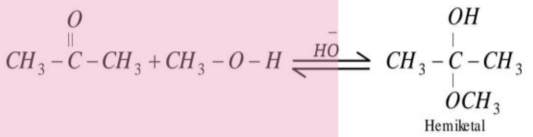
These two compounds can be separated from their mixture by the use of NaHSO₃. Higher aliphatic ketones and aromatic ketones do not react with NaHSO₃.

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.

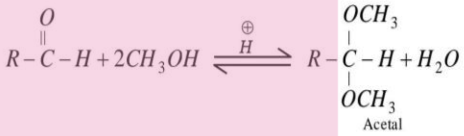


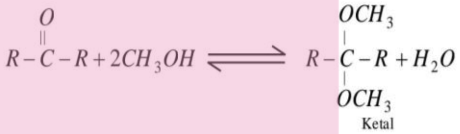
$$CH_3-\overset{\overset{O}{\|}}{C}-H + CH_3-\overset{-\delta}{O}-\overset{+\delta}{H} \xrightleftharpoons{\overset{-}{HO}} \underset{\text{Hemiacetal}}{CH_3-\underset{\underset{OCH_3}{|}}{\overset{\overset{OH}{|}}{C}}-H}$$


$$CH_3-\overset{O}{\overset{||}{C}}-CH_3+CH_3-O-H \xrightleftharpoons{\overset{-}{HO}} CH_3-\underset{OCH_3}{\overset{OH}{\overset{|}{C}}}-CH_3$$
Hemiketal

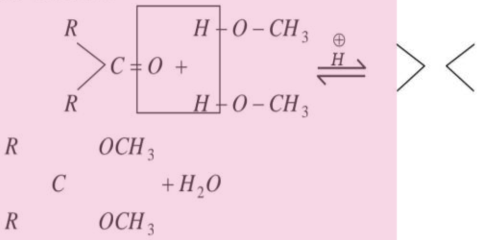
Hemiacetals and hemiketals are **α-alkoxy alcohols.**

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).


$$R-\overset{O}{\overset{||}{C}}-H+2CH_3OH \xrightleftharpoons{\overset{\oplus}{H}} R-\underset{OCH_3}{\overset{OCH_3}{\overset{|}{C}}}-H+H_2O$$
Acetal


$$R-\overset{O}{\overset{||}{C}}-R+2CH_3OH \rightleftharpoons R-\underset{OCH_3}{\overset{OCH_3}{\overset{|}{C}}}-R+H_2O$$
Ketal

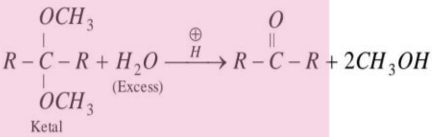
(i) Formation of acetals and ketals can be shown as follows:



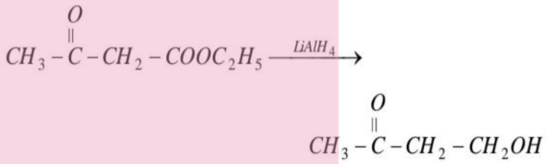
(ii) Acetals and ketals are gem dialkoxy compounds.

(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.

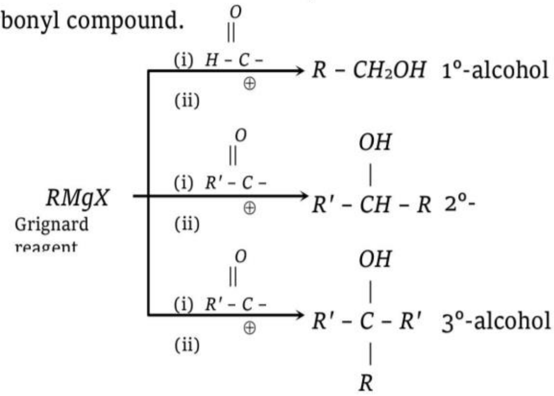

$$R-\underset{OCH_3}{\overset{OCH_3}{\overset{|}{C}}}-R+\underset{(Excess)}{H_2O} \xrightarrow{\overset{\oplus}{H}} R-\overset{O}{\overset{||}{C}}-R+2CH_3OH$$
Ketal

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 $LiAlH_4$.

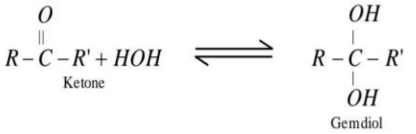

$$CH_3-\overset{O}{\overset{||}{C}}-CH_2-COOC_2H_5 \xrightarrow{LiAlH_4} CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_2OH$$

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.


$$\underset{Ketone}{R-\overset{O}{\overset{||}{C}}-R'}+HOH \rightleftharpoons \underset{Gemdiol}{R-\underset{OH}{\overset{OH}{\overset{|}{C}}}-R'}$$

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 α-carbon decreases the stability of gem diols. $+I$ group decreases stability of gem diol and hence decreases extent of hydration.

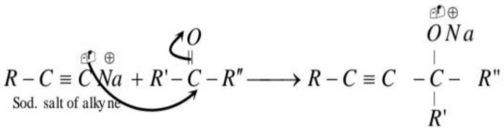
(ii) Stability of gem diols mainly depends on the presence of $-I$ group on α-carbon. More is the $-I$ power of the group more will be stability of gem diols.

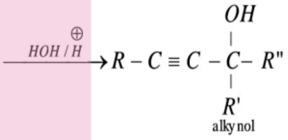
$R-\overset{O}{\overset{||}{C}}-$

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

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

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


$$\underset{Sod.\ salt\ of\ alkyne}{R-C\equiv\overset{\ominus}{C}\overset{\oplus}{Na}}+R'-\overset{O}{\overset{||}{C}}-R'' \longrightarrow R-C\equiv C-\underset{R'}{\overset{\overset{\ominus\ \oplus}{ONa}}{\overset{|}{\underset{|}{C}}}}-R''$$



$$\xrightarrow{HOH/\overset{\oplus}{H}} R-C\equiv C-\overset{\overset{OH}{|}}{\underset{\underset{R'}{|}}{C}}-R''$$

alkynol

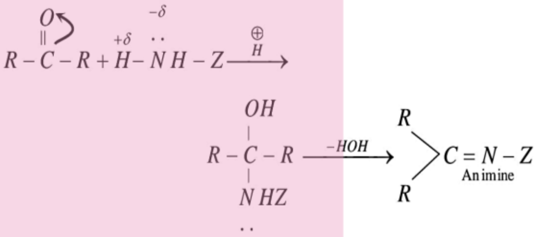
(2) **Addition followed by elimination reactions :** This reaction is given by ammonia derivatives (NH_2-Z).

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

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

Primary amines and derivatives of ammonia react with carbonyl compounds to give adduct.

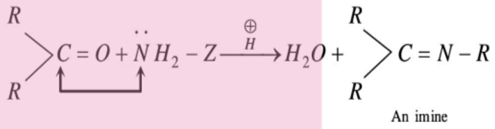
In adduct nucleophilic group has lone pair of electrons. It undergoes elimination to give product known as imine. An imine is a compound with a carbon-nitrogen double bond.



$$R-\overset{\overset{O}{\|}}{C}-R+\overset{+\delta}{H}-\overset{-\delta}{\ddot{N}}H-Z\xrightarrow{\overset{\oplus}{H}} R-\overset{\overset{OH}{|}}{\underset{\underset{NHZ}{|}}{C}}-R\xrightarrow{-HOH} \begin{matrix}R\\ \\R\end{matrix}\!\!>\!C=N-Z$$

An imine

The overall reaction can be shown as follows



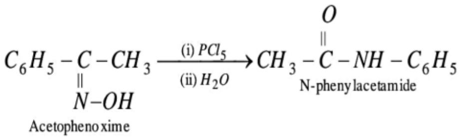
$$\begin{matrix}R\\ \\R\end{matrix}\!\!>\!C=O+\ddot{N}H_2-Z\xrightarrow{\overset{\oplus}{H}}H_2O+\begin{matrix}R\\ \\R\end{matrix}\!\!>\!C=N-R$$

An imine

Different Imine formation with NH_2-Z is given below

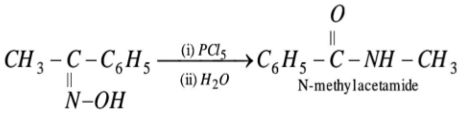
Beckmann rearrangement : Ketoxime when treated with acid at 0°C it undergoes rearrangement known as **Beckmann rearrangement.**

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.)



$$C_6H_5-\underset{\underset{N-OH}{\|}}{C}-CH_3\xrightarrow[(ii)\,H_2O]{(i)\,PCl_5}CH_3-\overset{\overset{O}{\|}}{C}-NH-C_6H_5$$

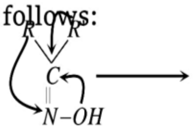
Acetophenoxime N-phenylacetamide

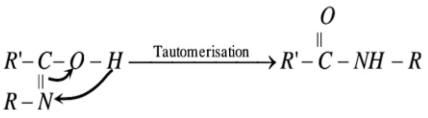


$$CH_3-\underset{\underset{N-OH}{\|}}{C}-C_6H_5\xrightarrow[(ii)\,H_2O]{(i)\,PCl_5}C_6H_5-\overset{\overset{O}{\|}}{C}-NH-CH_3$$

N-methylacetamide

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





$$\underset{R-N}{R'-\overset{}{\underset{\|}{C}}-O-H}\xrightarrow{\text{Tautomerisation}}R'-\overset{\overset{O}{\|}}{C}-NH-R$$

(3) **Oxidation of carbonyl compounds**

(i) ***Oxidation by mild oxidising agents*** **:** Mild oxidising agents oxidise only aldehydes into carboxylic acids. They do not oxidises 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. (Roschelle 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 ammonical silver nitrate solution. Its reacting species is $Ag^{\oplus}$.

❑ It oxidises aliphatic as well as aromatic aldehydes.

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

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

$CH_2=CH-CHO+Ag^{\oplus}\longrightarrow CH_2=CH-COOH+Ag$

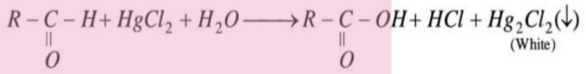
In this reaction the oxidation no. of Ag varies from +1 to 0.

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

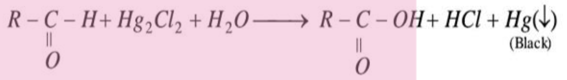
$C_5H_{11}O_5CHO+Cu_2O \text{ (or) } Ag_2O\longrightarrow \underset{\text{Gluconic acid}}{C_5H_{11}O_5COOH}$

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

(d) *Reaction with mercuric chloride solution* :



$$R-\underset{O}{\underset{\|}{C}}-H+HgCl_2+H_2O\longrightarrow R-\underset{O}{\underset{\|}{C}}-OH+HCl+\underset{\text{(White)}}{Hg_2Cl_2(\downarrow)}$$



$$R-\underset{O}{\underset{\|}{C}}-H+Hg_2Cl_2+H_2O\longrightarrow R-\underset{O}{\underset{\|}{C}}-OH+HCl+\underset{\text{(Black)}}{Hg(\downarrow)}$$

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

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

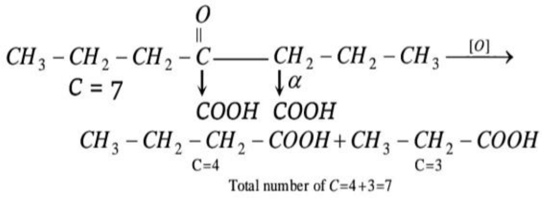
(a) *Oxidation of aldehydes* : Aldehydes are oxidised into corresponding acids.

$\underset{C=n}{RCHO}\xrightarrow{[O]}\underset{C=n}{RCOOH}$

$C_6H_5CHO\xrightarrow{KMnO_4/\overset{\ominus}{O}H/\Delta}C_6H_5COOH$

(b) *Oxidation of ketones* : Ketones undergo oxidation only in drastic conditions. During the oxidation of ketones there is breaking of carbon-carbon bond between α-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



$$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3\xrightarrow{[O]}$$

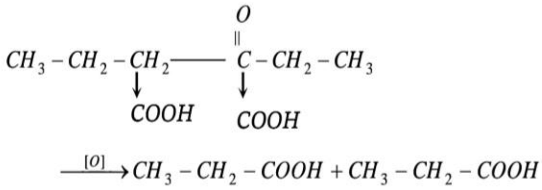
C = 7

$$\underset{C=4}{CH_3-CH_2-CH_2-COOH}+\underset{C=3}{CH_3-CH_2-COOH}$$

Total number of $C=4+3=7$

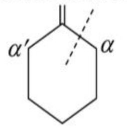
Thus number of carbons in any product is less than the number of carbons in ketone.

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



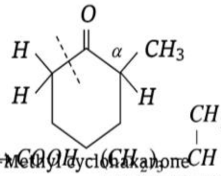
$$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3\xrightarrow{[O]}CH_3-CH_2-COOH+CH_3-CH_2-COOH$$

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.



$\xrightarrow{[O]}\underset{\text{Adipic acid}}{COOH-(CH_2)_4-COOH}$

❑ *If both α-carbons are not identical then bond breaking takes place between carbonyl carbon and the α-carbon which has maximum number of hydrogens.*

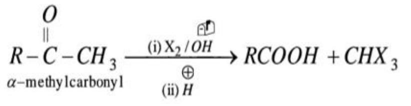


2-Methyl cyclohexanone

$\xrightarrow{[O]}\underset{\alpha\text{-Methyladipic acid}}{COOH-(CH_2)_3-\overset{CH_3}{\overset{|}{C}H}-COOH}$

(iii) ***Miscellaneous oxidation***

(a) *Haloform Reaction*

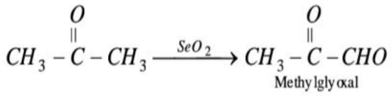


$$\underset{\alpha-\text{methylcarbonyl}}{R-\overset{O}{\overset{\|}{C}}-CH_3}\xrightarrow[\text{(ii) }\overset{\oplus}{H}]{\text{(i) }X_2/\overset{\ominus}{O}H}RCOOH+CHX_3$$

(b) *Oxidation at α-CH₂ or CH₃ by SeO₂* : SeO₂ oxidises $\alpha-CH_2-$group into keto group and $\alpha-CH_3-$group into aldehydic group.

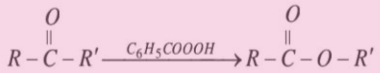
In this oxidation reactivity of CH_2 is more than the CH_3 group and Oxidation is regio selective in nature.

$CH_3-CHO\xrightarrow{SeO_2}\underset{\text{Glyoxal}}{CHO-CHO}$;



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3\xrightarrow{SeO_2}\underset{\text{Methylglyoxal}}{CH_3-\overset{O}{\overset{\|}{C}}-CHO}$$

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

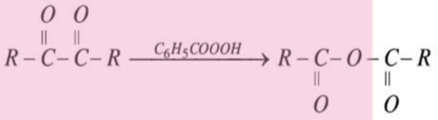


$$R-\overset{O}{\overset{||}{C}}-R' \xrightarrow{C_6H_5COOOH} R-\overset{O}{\overset{||}{C}}-O-R'$$

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 α-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.



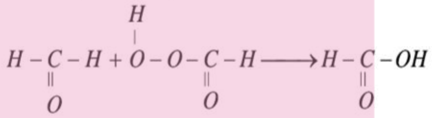
$$R-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-R \xrightarrow{C_6H_5COOOH} R-\underset{O}{\underset{||}{C}}-O-\underset{O}{\underset{||}{C}}-R$$

❑ ***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*

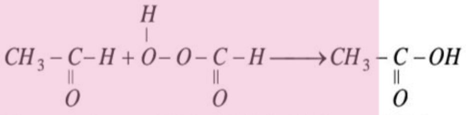
Example :

$$CH_3-CO-CH_2-CH_3 \xrightarrow{[O]} CH_3-COOH+HOOCCH_3$$

(d) *Baeyer- villiger oxidation :*



$$H-\underset{O}{\underset{||}{C}}-H+\overset{H}{\overset{|}{O}}-O-\underset{O}{\underset{||}{C}}-H \longrightarrow H-\underset{O}{\underset{||}{C}}-OH$$

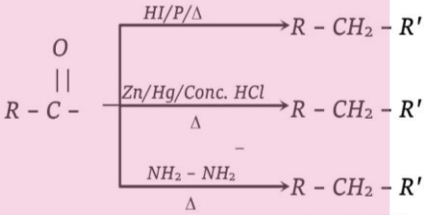


$$CH_3-\underset{O}{\underset{||}{C}}-H+\overset{H}{\overset{|}{O}}-O-\underset{O}{\underset{||}{C}}-H \longrightarrow CH_3-\underset{O}{\underset{||}{C}}-OH$$

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

(4) **Reduction of carbonyl compounds**

(i) ***Reduction of*** $\overset{O}{\overset{||}{C}}-$ ***group into*** **$-CH_2-$** ***group*** **:** Following three reagents reduce carbonyl group into $-CH_2-$ groups: (a) $HI/P/\Delta$ (b) $Zn/Hg/Conc.HCl$ and (c) $NH_2-NH_2/\overset{\ominus}{O}H$.



$$R-\overset{O}{\overset{||}{C}}- \xrightarrow{HI/P/\Delta} R-CH_2-R'$$

$$R-\overset{O}{\overset{||}{C}}- \xrightarrow[\Delta]{Zn/Hg/Conc.\ HCl} R-CH_2-R'$$

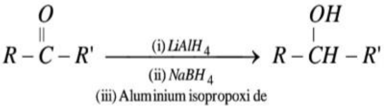
(Clemmenson reduction)

$$R-\overset{O}{\overset{||}{C}}- \xrightarrow[\Delta]{NH_2-NH_2} R-CH_2-R'$$

(Wolff-kishner

(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.

$$R-CHO \xrightarrow[\text{(ii) } NaBH_4 \text{ (iii) Aluminium isopropoxide}]{\text{(i) } LiAlH_4} R-CH_2OH$$



$$R-\overset{O}{\overset{||}{C}}-R' \xrightarrow[\text{(ii) } NaBH_4 \text{ (iii) Aluminium isopropoxide}]{\text{(i) } LiAlH_4} R-\overset{OH}{\overset{|}{CH}}-R'$$

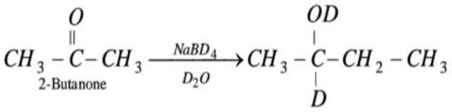
$NaBH_4$ is regioselective reducing agent because it reduced only. CHO in the presence of other reducible group.

Example :

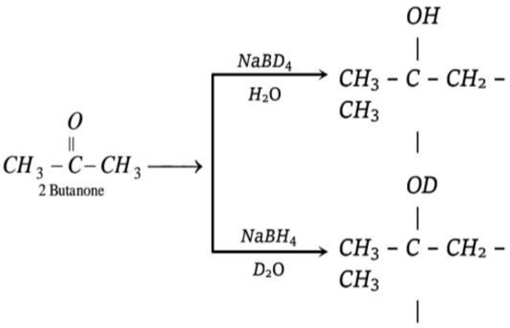
$$\underset{\text{Crotonaldehyde}}{CH_3-CH=CH-CHO} \xrightarrow{NaBH_4} \underset{\text{Crotonyl alcohol}}{CH_3-CH=CH-CH_2OH}$$

Hydride ion of $NaBH_4$ attack on carbonyl carbon during reduction.

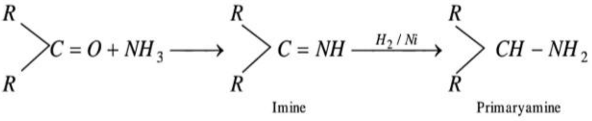
Example :



$$\underset{\text{2-Butanone}}{CH_3-\overset{O}{\overset{||}{C}}-CH_3} \xrightarrow[D_2O]{NaBD_4} CH_3-\overset{OD}{\overset{|}{\underset{D}{\underset{|}{C}}}}-CH_2-CH_3$$

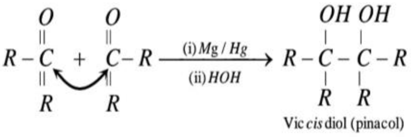


(iii) ***Reductive amination*** **:** In this reduction $-CO-$group converts into $-CH-NH_2$ group



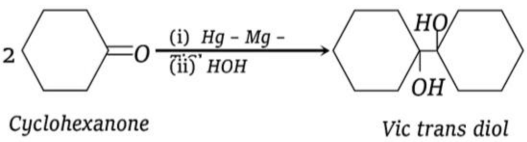
$$\overset{R}{\underset{R}{>}}C=O+NH_3 \longrightarrow \overset{R}{\underset{R}{>}}\underset{\text{Imine}}{C=NH} \xrightarrow{H_2/Ni} \overset{R}{\underset{R}{>}}\underset{\text{Primaryamine}}{CH-NH_2}$$

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

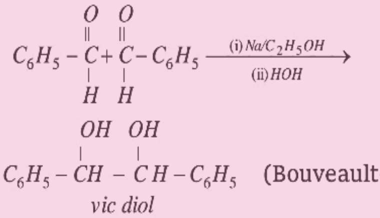


$$R-\underset{R}{\underset{||}{\overset{O}{\overset{||}{C}}}}+\underset{R}{\underset{|}{\overset{O}{\overset{||}{C}}}}-R \xrightarrow[\text{(ii) } HOH]{\text{(i) } Mg/Hg} \underset{\text{Vic cis diol (pinacol)}}{R-\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R}$$

When this reaction is carried out in the presence of $Mg/Hg/TiCl_4$, the product is vic *trans* diol.



(v) ***Reduction of benzaldehyde by Na/C₂H₅OH*** **:** Benzaldehyde undergoes reduction via coupling reaction and product is vic diol.

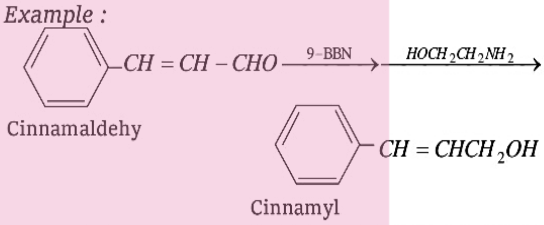


$$C_6H_5-\underset{H}{\overset{O}{\overset{\|}{\underset{|}{C}}}}+\underset{H}{\overset{O}{\overset{\|}{\underset{|}{C}}}}-C_6H_5\xrightarrow[\text{(ii)}\,HOH]{\text{(i)}\,Na/C_2H_5OH}\underset{\textit{vic diol}}{C_6H_5-\overset{OH}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH}}-C_6H_5}$$

(Bouveault-blanc reaction)

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

Example :

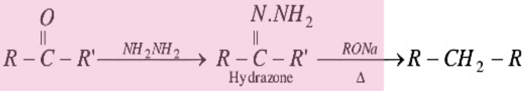


❑ *If reducing agent is NaH, reaction is called Darzen's reaction, we can also use $LiAlH_4$ in this reaction.*

❑ *If reducing agent is aluminium iso propoxide $(CH_3-\underset{CH_3}{\underset{|}{C}}H-O-)_3Al$. 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).



$$R-\overset{O}{\overset{\|}{C}}-R'\xrightarrow{NH_2NH_2}\underset{\text{Hydrazone}}{R-\overset{N.NH_2}{\overset{\|}{C}}-R'}\xrightarrow[\Delta]{RONa}R-CH_2-R$$

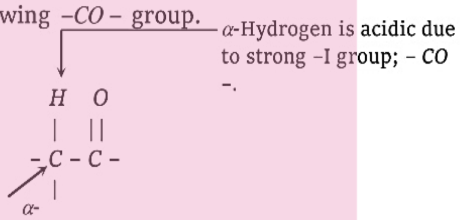
(vii) Schiff's base on reduction gives secondary amines.

$$\underset{\text{Aldehyde}}{R-CH=O}\xrightarrow{R'NH_2}\underset{\text{Schiff's base}}{R-CH=NR'}\xrightarrow{H_2/Ni}\underset{\text{Secondary amine}}{R-CH_2NHR}$$

(5) **Reactions due to α-hydrogen**

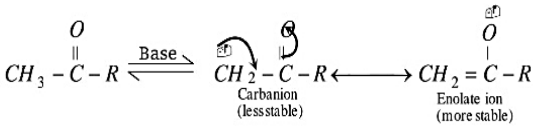
(i) ***Acidity of α-hydrogens :***

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



α-Hydrogen is acidic due to strong –I group; $-CO-$.

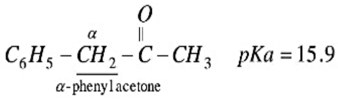
(b) Thus carbonyl compounds having α-hydrogen convert into carbanions in the presence of base. This carbanion is stabilised by delocalisation of negative charge.



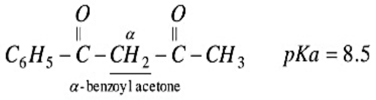
$$CH_3-\overset{O}{\overset{\|}{C}}-R\xrightleftharpoons{\text{Base}}\underset{\text{Carbanion (less stable)}}{\overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-R}\longleftrightarrow\underset{\text{Enolate ion (more stable)}}{CH_2=\overset{\overset{\ominus}{O}}{\overset{|}{C}}-R}$$

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

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



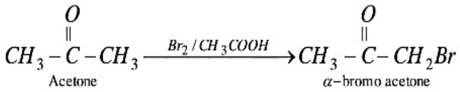
$$\underset{\alpha\text{-phenyl acetone}}{C_6H_5-\overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-CH_3}\quad pKa=15.9$$



$$\underset{\alpha\text{-benzoyl acetone}}{C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-CH_3}\quad pKa=8.5$$

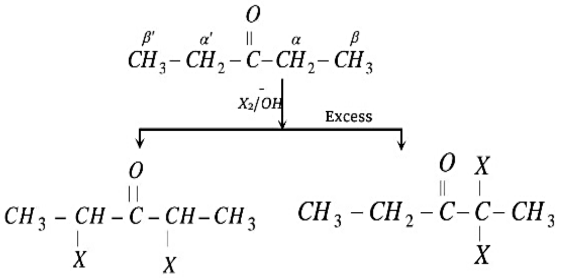
(ii) ***Halogenation*** : Carbonyl compounds having α-hydrogens undergo halogenation reactions. This reaction is catalysed by acid as well as base.

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

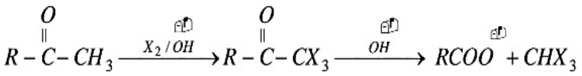


$$\underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}\xrightarrow{Br_2/CH_3COOH}\underset{\alpha\text{-bromo acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2Br}$$

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

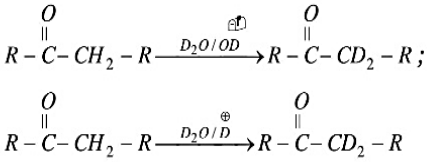


Carbonyl compounds having three α-hydrogens give **haloform** reaction.



$$R-\overset{O}{\overset{\|}{C}}-CH_3\xrightarrow{X_2/\overset{\ominus}{O}H}R-\overset{O}{\overset{\|}{C}}-CX_3\xrightarrow{\overset{\ominus}{O}H}RCO\overset{\ominus}{O}+CHX_3$$

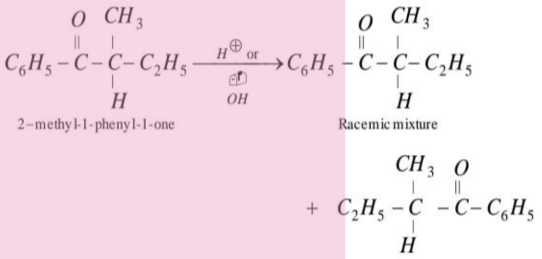
(iii) ***Deuterium exchange reaction*** : Deuterium exchange reaction is catalysed by acid $(D^{\oplus})$ as well as base $(\overset{\ominus}{OD})$. In both the cases all the hydrogens on only one α-carbon is replaced by *D*.



$$R-\overset{O}{\overset{\|}{C}}-CH_2-R\xrightarrow{D_2O/\overset{\ominus}{O}D}R-\overset{O}{\overset{\|}{C}}-CD_2-R\,;$$

$$R-\overset{O}{\overset{\|}{C}}-CH_2-R\xrightarrow{D_2O/\overset{\oplus}{D}}R-\overset{O}{\overset{\|}{C}}-CD_2-R$$

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

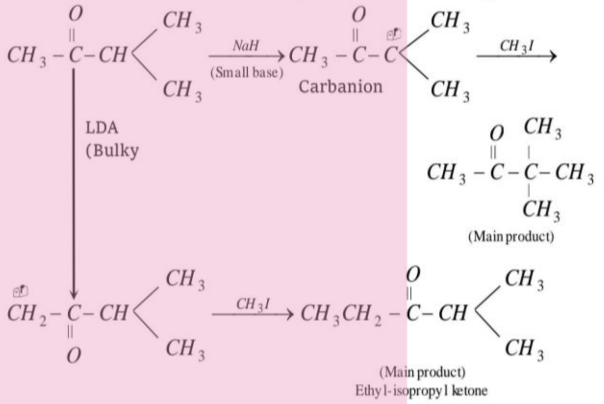


$$C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{CH_3}{C}}-C_2H_5 \xrightarrow[\overset{\ominus}{O}H]{H^{\oplus}\text{ or}} C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{CH_3}{C}}-C_2H_5 + C_2H_5-\underset{H}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5$$

2-methyl-1-phenyl-1-one

Racemic mixture

(v) ***Alkylation*** : Carbonyl compounds having α-hydrogens undergo alkylation reaction with RX in the presence of base. This reaction is S_{N^2} reaction. The best result is obtained with CH_3-X. Other halides undergo elimination in the presence of strong base.

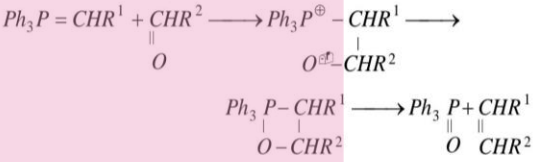


$$CH_3-\overset{O}{\overset{\|}{C}}-CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} \xrightarrow[\text{(Small base)}]{NaH} \underset{\text{Carbanion}}{CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}} \xrightarrow{CH_3I} \underset{\text{(Main product)}}{CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3}$$

$$\xrightarrow{\text{LDA (Bulky)}} \overset{\ominus}{C}H_2-\underset{O}{\underset{\|}{C}}-CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} \xrightarrow{CH_3I} \underset{\substack{\text{(Main product)}\\\text{Ethyl-isopropyl ketone}}}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}}$$

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

$$Ph_3P=CH_2+\underset{\substack{\text{Aldehyde}\\\text{or ketone}}}{>C=O} \longrightarrow \underset{\text{alkene}}{>C=CH_2} + \underset{\substack{\text{Triphenyl}\\\text{Phosphonium oxide}}}{Ph_3P=O}$$

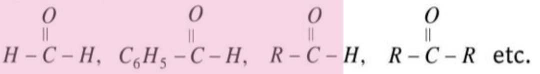


$$Ph_3P=CHR^1+\underset{O}{\underset{\|}{C}}HR^2 \longrightarrow Ph_3\overset{\oplus}{P}-\underset{\overset{\ominus}{O}-CHR^2}{\underset{|}{CHR^1}} \longrightarrow$$

$$\underset{O-CHR^2}{Ph_3\,P-CHR^1} \longrightarrow \underset{O}{\underset{\|}{Ph_3\,P}}+\underset{CHR^2}{\underset{\|}{CHR^1}}$$

(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 α-carbon is known as condensation reaction. In this addition reaction :

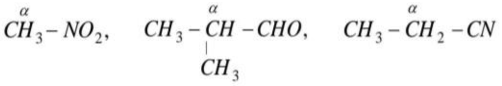
Substrate is always an organic compound having a carbonyl group, *e.g.*



$$H-\overset{O}{\overset{\|}{C}}-H,\quad C_6H_5-\overset{O}{\overset{\|}{C}}-H,\quad R-\overset{O}{\overset{\|}{C}}-H,\quad R-\overset{O}{\overset{\|}{C}}-R \text{ etc.}$$

Addition always takes place on the carbonyl group.

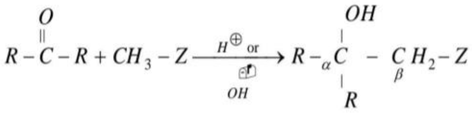
Reagents of the condensation reaction are also organic compounds having at least one hydrogen on α-carbon and α-carbon should have –I group, *e.g.*



$$\overset{\alpha}{C}H_3-NO_2,\quad CH_3-\underset{CH_3}{\underset{|}{\overset{\alpha}{C}H}}-CHO,\quad CH_3-\overset{\alpha}{C}H_2-CN$$

❑ *If substrate and reagent both are carbonyl compounds then one should have at least one α-hydrogen and other may or may not have α-hydrogen.*

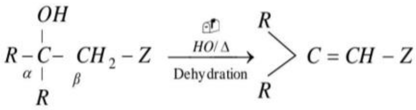
Condensation reaction always takes place in the presence of acid or base as catalyst. Best result is obtained with base at lower temp.



$$R-\overset{O}{\overset{\|}{C}}-R+CH_3-Z \xrightarrow[\overset{\ominus}{O}H]{H^{\oplus}\text{ or}} R-{}_{\alpha}\underset{R}{\overset{OH}{C}}-\underset{\beta}{C}H_2-Z$$

Condensation is carried out at lower temperature $(\le 20°C)$ because product of the reaction is alcohol which has strong –I group at β-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°C. They also undergo elimination even on strong heating.



$$R-\underset{\alpha\ R}{\overset{OH}{C}}-\underset{\beta}{C}H_2-Z \xrightarrow[\text{Dehydration}]{\overset{\ominus}{H}O/\Delta} \begin{smallmatrix}R\\R\end{smallmatrix}\!>C=CH-Z$$

(i) ***Aldol condensation***

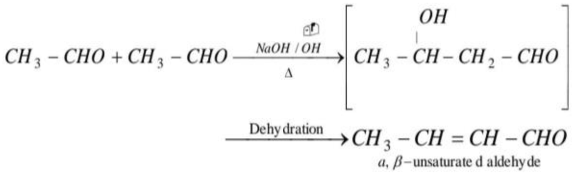
(a) This reaction takes place between two molecules of carbonyl compounds; one molecule should have at least two α-hydrogen atoms. In this reaction best result is obtained when

Both molecule are the same or

One should have no α-hydrogen atom and other should have at least two α-hydrogens.

(b) These reactions are practical when base is $NaOH$ and reaction temperature is high $(\ge 100°)$.

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



$$CH_3-CHO+CH_3-CHO \xrightarrow[\Delta]{NaOH/\overset{\ominus}{O}H} \left[CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO\right] \xrightarrow{\text{Dehydration}} \underset{\alpha,\,\beta\text{-unsaturated aldehyde}}{CH_3-CH=CH-CHO}$$

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

$CH_3 - CH = CH - CHO + CH_3 - CH = CH - CHO$

$\Big\downarrow$ NaOH

$$CH_3-CH=CH-\overset{OH}{\overset{|}{C}H}-CH_2-CH=CH-CHO$$

$\Delta \Big\downarrow -H_2O$

$CH_3 - CH = CH - CH = CH - CH = CH - CHO$

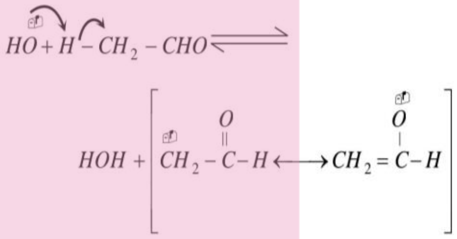
$\Big\downarrow$

$CH_3-(CH=CH-)_3-CHO$

Condensed

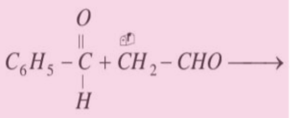
Mechanism : $C_6H_5-CHO+CH_3-CHO \xrightarrow{\overset{\ominus}{OH}/\Delta} C_6H_5-CH=CH-CHO+HOH$

Step I :

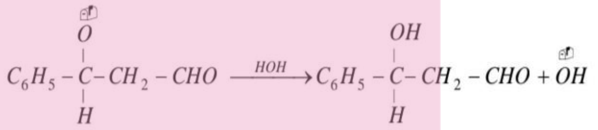


$$\overset{\ominus}{HO}+H-CH_2-CHO \rightleftharpoons HOH+\left[\overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-H \longleftrightarrow CH_2=\overset{O^{\ominus}}{\overset{|}{C}}-H\right]$$

Step II :

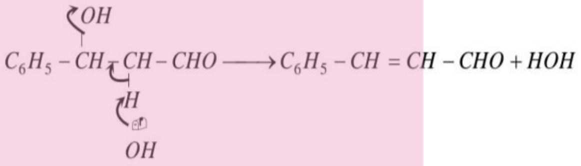


$$C_6H_5-\underset{H}{\underset{|}{\overset{O}{\overset{\|}{C}}}}+\overset{\ominus}{C}H_2-CHO \longrightarrow$$



$$C_6H_5-\underset{H}{\underset{|}{\overset{O^{\ominus}}{\overset{|}{C}}}}-CH_2-CHO \xrightarrow{HOH} C_6H_5-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-CHO+\overset{\ominus}{O}H$$

Step III :

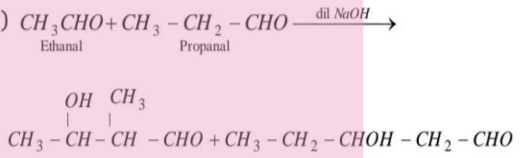


$$C_6H_5-\overset{OH}{\overset{|}{CH}}-\underset{\underset{\overset{\ominus}{O}H}{H}}{CH}-CHO \longrightarrow C_6H_5-CH=CH-CHO+HOH$$

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 α-hydrogen atom gives different possible product

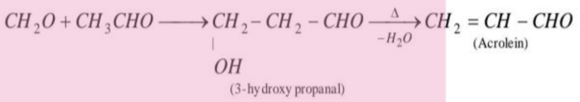
(a)



$$\underset{\text{Ethanal}}{CH_3CHO}+\underset{\text{Propanal}}{CH_3-CH_2-CHO} \xrightarrow{\text{dil } NaOH}$$

$$CH_3-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CHO+CH_3-CH_2-CHOH-CH_2-CHO$$

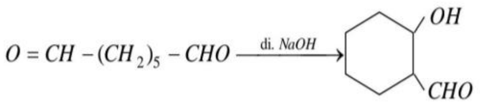
However crossed aldol condensation is important when only it the components has α-hydrogen atom.



$$CH_2O+CH_3CHO \longrightarrow \underset{\underset{\text{(3-hydroxy propanal)}}{OH}}{\underset{|}{CH_2}}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} \underset{\text{(Acrolein)}}{CH_2=CH-CHO}$$

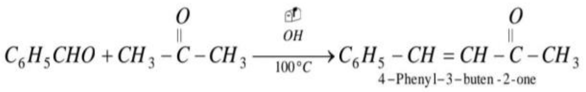
Intra molecular aldol condensation : One molecule Intramolecular condensation give aldol compounds

Example :



$O=CH-(CH_2)_5-CHO \xrightarrow{\text{di. } NaOH}$

(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 :



$$C_6H_5CHO+CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[100^\circ C]{\overset{\ominus}{OH}} \underset{\text{4-Phenyl-3-buten-2-one}}{C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3}$$

Test of aldehydes and Ketones (Distinction)

Table : 27.1

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

Some commercially important aliphatic carbonyl compounds

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**

(i) $2CH_3OH + O_2 \xrightarrow[300-400°C]{\text{Platinised asbestos}} \underset{\text{Formaldehyde}}{HCHO}$

$$CH_3OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} HCHO + H_2O$$

(ii) $CH_3OH \xrightarrow[300-400°C]{Cu \text{ or } Ag} \underset{\text{Formaldehyde}}{HCHO}$

(iii) $\underset{\text{Calcium formate}}{Ca(HCOO)_2} \xrightarrow{\text{Heat}} \underset{\text{Formaldehyde}}{HCHO}$

(iv) $CH_2 = CH_2 + O_3 \xrightarrow[Pd]{H_2} \underset{\text{Formaldehyde}}{HCHO}$

(v) $\underset{\text{Methane}}{CH_4} + O_2 \xrightarrow[\text{Catalyst}]{\text{Mo-oxide}} \underset{\text{Formaldehyde}}{HCHO}$

(vi) $CO + H_2 \xrightarrow{\text{Elec.discharge}} \underset{\text{Formaldehyde}}{HCHO}$

(2) **Physical properties**

(i) It is a colourless, pungent smelling gas.

(ii) It is extremely soluble in water. Its solubility in water may be due to hydrogen bonding between water molecules and its hydrate.

(iii) It can easily be condensed into liquid. The liquid formaldehyde boils at – 21°C.

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

(v) Its solution acts as antiseptic and disinfectant.

(3) **Uses**

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

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

(iii) It is used in silvering of mirror.

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

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

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

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

Acetaldehyde

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

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

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

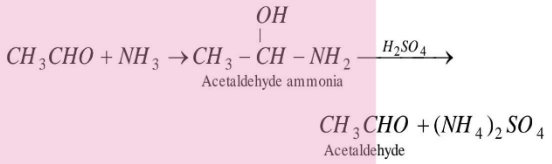
$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$[CH_3CH_2OH + O \longrightarrow CH_3CHO + H_2O] \times 3$$

$$\underset{\substack{\text{Potassium}\\\text{dichromate}}}{K_2Cr_2O_7} + \underset{\text{Ethylalcohol}}{3CH_3CH_2OH} + \underset{\text{Sulphuric acid}}{4H_2SO_4} \longrightarrow$$

$$\underset{\substack{\text{Potassium}\\\text{sulphate}}}{K_2SO_4} + \underset{\substack{\text{Chromic}\\\text{sulphate}}}{Cr_2(SO_4)_3} + \underset{\text{Acetaldehyde}}{3CH_3CHO} + \underset{\text{Water}}{7H_2O}$$

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.



$$CH_3CHO + NH_3 \rightarrow \underset{\text{Acetaldehyde ammonia}}{CH_3-\overset{\displaystyle OH}{\overset{|}{C}}H-NH_2} \xrightarrow{H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} + (NH_4)_2SO_4$$

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

(a) *By air oxidation of ethyl alcohol*

$$2CH_3CH_2OH + O_2 \xrightarrow[300^\circ C]{Ag} 2CH_3CHO + 2H_2O$$

(b) *By dehydrogenation of alcohol*

$$CH_3CH_2OH \xrightarrow[300^\circ C]{Cu} CH_3CHO$$

(c) *By hydration of acetylene*

$$CH \equiv CH + H_2O \xrightarrow[H_2SO_4(40\%)]{HgSO_4(1\%), 60^\circ C} CH_3CHO$$

(d) *From ethylene (Wacker process)*

$$H_2C = CH_2 + O_2 \xrightarrow[H_2O]{PdCl_2, CuCl_2} H_3C-CHO$$

(2) **Physical properties**

(i) Acetaldehyde is a colourless volatile liquid. It boils at 21°C.

(ii) It has a characteristic pungent smell.

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

$$CH_3CHO + H_2O \longrightarrow CH_3CH(OH)_2$$

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

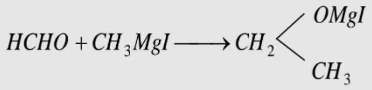
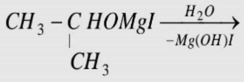
(i) In the preparation of acetic acid, acetic anhydride, ethyl acetate, chloral, 1,3-butadiene (used in rubbers), dyes and drugs.

(ii) As an antiseptic inhalent 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 : 27.2 Comparative study of formaldehyde and acetaldehyde

S.No.	**Reaction**	**Formaldehyde *HCHO***	**Acetaldehyde *CH₃CHO***
Similarities			
1.	Addition of hydrogen (a) H_2 in presence of catalyst, Ni, Pd or Pt (b) $LiAlH_4$ (ether) (c) Amalgamated zinc + conc. HCl (Clemmenson reduction)	Forms methyl alcohol $HCHO + H_2 \longrightarrow CH_3OH$ Forms methyl alcohol Forms methane $HCHO + 4H \longrightarrow CH_4 + H_2O$	Forms ethyl alcohol $CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$ Forms ethyl alcohol Forms ethane $CH_3CHO + 4H \longrightarrow C_2H_6 + H_2O$
2.	Addition of $NaHSO_3$ solution	Forms bisulphite addition product $HCHO + NaHSO_3 \longrightarrow CH_2(OH)SO_3Na$	Forms bisulphite addition product $CH_3CHO + NaHSO_3 \longrightarrow$ $CH_3CH(OH)SO_3Na$
3.	Addition of HCN	Forms formaldehyde cyanohydrin $HCHO + HCN \longrightarrow CH_2(OH)CN$	Forms acetaldehyde cyanohydrin $CH_3CHO + HCN \longrightarrow$ $CH_3CH(OH)CN$
4.	Addition of Grignard reagent followed by hydrolysis	Forms ethyl alcohol  $HCHO + CH_3MgI \longrightarrow CH_2\begin{matrix}OMgI\\CH_3\end{matrix}$ $\xrightarrow[-Mg(OH)I]{H_2O} CH_3CH_2OH$	Forms isopropyl alcohol $CH_3CHO + CH_3MgI \longrightarrow$  $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{C}}HOMgI \xrightarrow[-Mg(OH)I]{H_2O}$

			$CH_3-\underset{\underset{CH_3}{\mid}}{CH}-OH$
5.	With hydroxylamine NH_2OH	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_2NH_2)	Forms formaldehyde hydrazone $CH_2O+H_2N\ NH_2 \xrightarrow{-H_2O}$ $CH_2=NNH_2$	Forms acetaldehyde hydrazone $CH_3CH=O+H_2NNH_2 \xrightarrow{-H_2O}$ $CH_3CH=NNH_2$
7.	With phenyl hydrazine $(C_6H_5NHNH_2)$	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 $(H_2NNHCONH_2)$	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_2H_5OH) 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 $H_2C=O+2C_2H_5SH \longrightarrow$ $CH_2\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}$	Forms acetaldehyde diethyl thioacetal $CH_3CH=O+2C_2H_5SH \longrightarrow$ $CH_3CH\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}$
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	Undergoes polymerisation

$\xrightleftharpoons{\text{Evaporatio}}$

$\xrightleftharpoons[\text{dil. } H_2SO_4.]{H_2SO_4\text{Conc.}}$

$\xrightleftharpoons[\text{heat}]{\text{Room temp.}}$

$\xrightleftharpoons[\text{dil. } H_2SO_4.]{H_2SO_4\text{Conc.}}$

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

Inter conversion of formaldehyde and acetaldehyde

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

(i) $\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{H_2/Ni} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{PCl_5} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow[KCN]{\text{Alc.}}$

$\underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{Na/\text{Alcohol}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[HCl]{NaNO_2}$

$\underset{\text{Ethylalcohol}}{CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7]{H_2SO_4(\text{dil.})} \underset{\text{Acetaldehyde}}{CH_3CHO}$

(ii) $\underset{\text{Formaldehyde}}{HCHO} \xrightarrow[\text{Ether}]{CH_3MgI} CH_3CH_2OMgI \xrightarrow{H_3O^+}$

$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[300°C]{Cu} \underset{\text{Acetaldehyde}}{CH_3CHO}$

(iii) $\underset{\text{Formaldehyde}}{HCHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Formic acid}}{HCOOH} \xrightarrow{Ca(OH)_2}$

$\underset{\text{Calcium formate}}{(HCOO)_2Ca} \xrightarrow[\text{heat}]{(CH_3COO)_2Ca} \underset{\text{Acetaldehyde}}{CH_3CHO}$

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

(i) $\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3}$

$\underset{\text{Amm.acetate}}{CH_3COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2 / KOH}$

$\underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow[HCl]{NaNO_2} CH_3OH \xrightarrow[300°C]{Cu} \underset{\text{Formaldehyde}}{HCHO}$

(ii) $\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} \underset{\text{Sod.acetate}}{CH_3COONa}$

$\xrightarrow[\text{heat}]{\text{Sodalime}} \underset{\text{Methane}}{CH_4} \xrightarrow[hv]{Cl_2} CH_3Cl \xrightarrow{AgOH}$

$CH_3OH \xrightarrow[300°C]{Cu} \underset{\text{Formaldehyde}}{HCHO}$

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 :**

(i)
$\underset{\text{calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\Delta}$

(ii)
$\underset{\text{Isopropyl alcohol}}{2CH_3CHOHCH_3 + O_2} \xrightarrow{500°C}$

(iii)
$\underset{\text{2 propanol}}{CH_3CHOHCH_3} \xrightarrow[300°C]{Cu}$

(iv) (a)
$\underset{\text{propene}}{CH_3CH = CH_2} + PdCl_2 + H_2O \rightarrow$

(b) $\underset{\text{propene}}{CH_3CH = CH_2} + H_2SO_4 \rightarrow$

$\downarrow$

$CH_3CH(HSO_4)CH_3$

$\downarrow H_2O$

$\underset{\text{Isopropyl alcohol}}{CH_3CH(OH)CH_3} \xrightarrow[300°C]{Cu}$

(v) $2C_3H_5OH + H_3O \xrightarrow[500°C]{Zn(CrO_2)}$

(vi)
$2CH \equiv CH + 3H_2O \xrightarrow[420°C]{\text{catalyst}}$

$\longrightarrow CH_3COCH_3$

(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 $56°C$.

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 $56°C$.

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

(3) **Chemical properties**

CH_3COCH_3
(Acetone)

$\xrightarrow[Pd]{\text{Reduction } H_2, Ni,} \underset{\text{Isopropyl alcohol}}{CH_3CHOHCH_3}$

$\xrightarrow[\text{+ conc. } HCl]{\text{Amalgamated } Zn} \underset{\text{Propane}}{CH_3CH_2CH_3}$

$\xrightarrow{NaHSO_3} \underset{\text{Acetone sodium bisulphite derivative}}{(CH_3)_2C(OH)SO_3Na}$

$\xrightarrow{HCN} \underset{\text{Acetone cyanohydrin}}{(CH_3)_2C{<}^{OH}_{CN}}$

$\xrightarrow[\text{Ether}]{CH_3MgI} \underset{\text{Tertiary butyl alcohol}}{(CH_3)_3COH}$

$\xrightarrow{NH_2OH} \underset{\text{Acetoxime}}{(CH_3)_2C = NOH}$

$\xrightarrow{NH_2NH_2} \underset{\text{Acetone hydrazone}}{(CH_3)_2C = NNH_2}$

$\xrightarrow{C_6H_5NHNH_2} \underset{\text{Acetone phenyl hydrazone}}{(CH_3)_2C = NNHC_6H_5}$

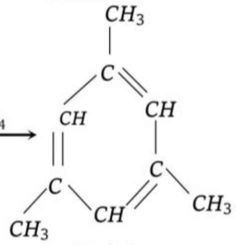
$\xrightarrow{H_2NNHCONH_2} \underset{\text{Acetone semicarbazone}}{(CH_3)_2C = NNHCONH_2}$

$\xrightarrow{PCl_5} \underset{\text{Isopropylidene chloride}}{(CH_3)_2C{<}^{Cl}_{Cl}}$

$\xrightarrow{Cl_2} \underset{\text{Trichloroacetone}}{CH_3COCCl_3}$

$\xrightarrow{I_2 + NaOH} \underset{\text{Iodoform}}{CHI_3}$

$\xrightarrow{\text{Conc. } H_2SO_4}$



Mesitylene
(1, 3, 5-trimethyl

$\xrightarrow[\text{heat}]{CaOCl_2 \text{ (Bleaching}} \underset{\text{Chloroform}}{CHCl_3}$

$\xrightarrow{K_2Cr_2O_7 + H_2SO_4} CH_3COOH + CO_2 + H_2O$

$\xrightarrow{CHCl_3} \underset{\text{Chloretone}}{(CH_3)_2C(OH)CCl_3}$

$\xrightarrow{Ba(OH)_2} \underset{\text{Diacetone alcohol}}{(CH_3)_2C(OH)CH_2COCH_3}$

$\xrightarrow{HNO_2} \underset{\text{(Oximino acetone)}}{CH_3COCH = NOH}$

$\xrightarrow{NH_3} \underset{\text{Diacetone amine}}{(CH_3)_2C(NH_2)CH_2COCH_3}$

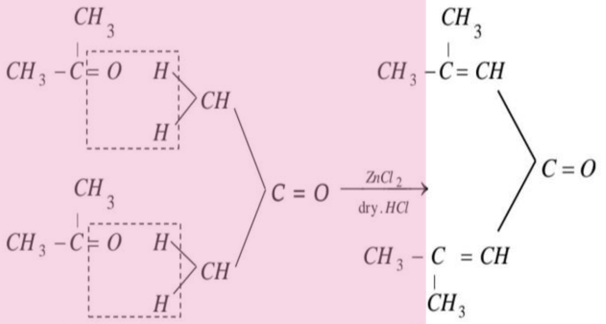
$\xrightarrow{Mg-Hg + H_2O} \underset{\text{Pinacol}}{(CH_3)_2\overset{OH}{\overset{|}{C}} - \overset{OH}{\overset{|}{C}}(CH_3)_2}$

$\xrightarrow[\text{reagent}]{\text{Schiff's}}$ No reaction

Tollen's

No reaction

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**'.



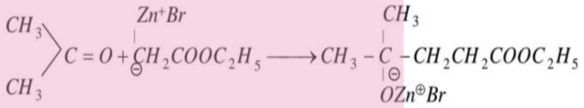
Acetone (3 phoron

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

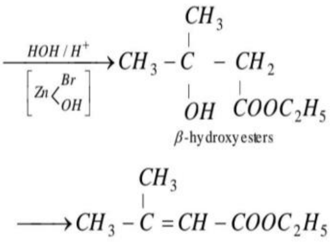
Reformatsky reaction: This reaction involves the treatment of aldehyde and ketone with a bromo acid ester in presence of metallic zinc to form β-hydroxy ester, which can be easily dehydrated into α,β-unsaturated ester.

(a) $BrCH_2COOC_2H_5 + Zn \xrightarrow{\text{Benzene}} Br - \overset{\oplus}{Zn} - \overset{\ominus}{C}H_2COOC_2H_5$ Organo zinc compound

(b) Addition to carbonyl group



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=O + \overset{Zn^{+}Br}{\underset{\ominus}{C}}H_2COOC_2H_5 \longrightarrow CH_3-\overset{CH_3}{\underset{OZn^{\oplus}Br}{C}}-CH_2CH_2COOC_2H_5$$



$$\xrightarrow[\left[Zn<^{Br}_{OH}\right]]{HOH/H^+} CH_3-\overset{CH_3}{\underset{OH}{C}}-\underset{COOC_2H_5}{CH_2} \quad \beta\text{-hydroxy esters}$$

$$\longrightarrow CH_3-\overset{CH_3}{C}=CH-COOC_2H_5$$

(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**

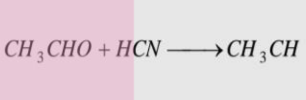
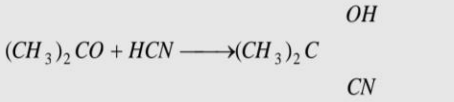
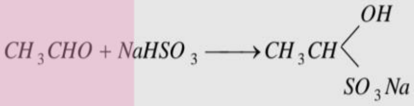
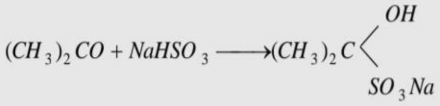
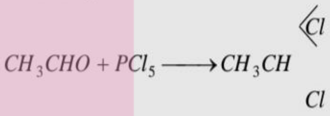
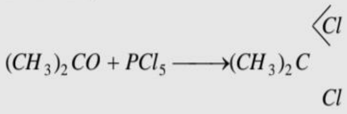
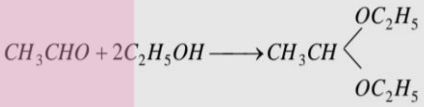
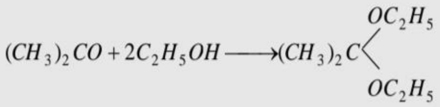
(i) ***Legal's test*** : When a few drops of freshly prepared sodium nitroprusside and sodium hydroxide solution are added to an aqueous solution of acetone, a wine colour is obtained which changes to yellow on standing.

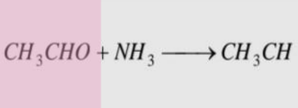
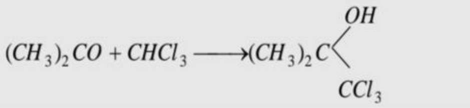
(ii) ***Indigo test*** : A small amount of orthonitrobenzaldehyde is added to about 2 *ml*. of acetone and it is diluted with *KOH* solution and stirred. A blue colour of indigotin is produced.

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

Table : 27.3 Comparison between Acetaldehyde and Acetone

Reaction	Acetaldehyde	Acetone
Similarities		
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	Forms acetone cyanohydrin

	 $CH_3CHO + HCN \longrightarrow CH_3CH\begin{matrix}OH\\CN\end{matrix}$	 $(CH_3)_2CO + HCN \longrightarrow (CH_3)_2C\begin{matrix}OH\\CN\end{matrix}$
4. Addition of $NaHSO_3$	White crystalline derivative  $CH_3CHO + NaHSO_3 \longrightarrow CH_3CH\begin{matrix}OH\\SO_3Na\end{matrix}$	White crystalline derivative  $(CH_3)_2CO + NaHSO_3 \longrightarrow (CH_3)_2C\begin{matrix}OH\\SO_3Na\end{matrix}$
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)  $CH_3CHO + PCl_5 \longrightarrow CH_3CH\begin{matrix}Cl\\Cl\end{matrix}$	Forms isopropylidene chloride (Gem dihalide)  $(CH_3)_2CO + PCl_5 \longrightarrow (CH_3)_2C\begin{matrix}Cl\\Cl\end{matrix}$
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)  $CH_3CHO + 2C_2H_5OH \longrightarrow CH_3CH\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$	Forms ketal (a diether)  $(CH_3)_2CO + 2C_2H_5OH \longrightarrow (CH_3)_2C\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$
13. With SeO_2	Forms glyoxal $CH_3CHO + SeO_2 \longrightarrow CHOCHO + Se + H_2O$	Forms methyl glyoxal $(CH_3)_2CO + SeO_2 \longrightarrow CH_3COCHO + Se + H_2O$
14. Iodoform reaction $(I_2 + NaOH)$	Forms iodoform	Forms iodoform
15. Bleaching powder	Forms chloroform	Forms chloroform
16. Aldol condensation with mild alkali	Forms aldol $2CH_3CHO \longrightarrow CH_3CHOHCH_2CHO$	Forms diacetone alcohol $2CH_3COCH_3 \longrightarrow (CH_3)_2C(OH)CH_2COCH_3$
17. Polymerisation	Undergoes polymerisation	Does not undergo polymerisation but gives condensation reaction
18. With NH_3	Forms acetaldehyde ammonia	Forms diacetone ammonia

	 $CH_3CHO + NH_3 \longrightarrow CH_3CH(OH)(NH_2)$	$(CH_3)_2CO + NH_3 + OC(CH_3)_2 \longrightarrow (CH_3)_2C(NH_2)CH_2COCH_3$
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  $(CH_3)_2CO + CHCl_3 \longrightarrow (CH_3)_2C(OH)(CCl_3)$
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^oC	56^oC
Dissimilarities		
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 :

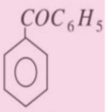
The compounds in which $-CHO$ group is attached directly to an aromatic ring, *e.g.,* benzaldehyde, C_6H_5CHO.

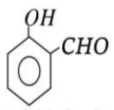
Those in which aldehyde $(-CHO)$ group is attached to side chain, *e.g.,* phenyl acetaldehyde, $C_6H_5CH_2CHO$. They closely resemble with aliphatic aldehydes.

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 :


Benzaldehy de

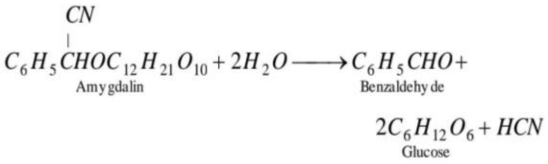

Acetopheno ne
(Methyl phenyl ketone)


Benzopheno ne
(Diphenyl ketone)


Salicylald ehyde

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



$$\underset{\text{Amygdalin}}{C_6H_5\overset{CN}{\overset{|}{C}}HOC_{12}H_{21}O_{10}} + 2H_2O \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Glucose}}{2C_6H_{12}O_6} + HCN$$

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.

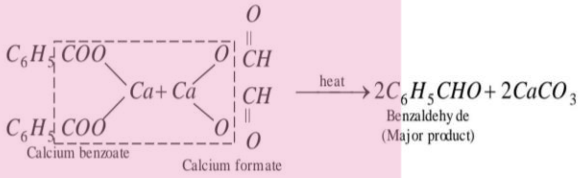
$$\underset{\text{Benzyl chloride}}{2C_6H_5CH_2Cl} + \underset{Pb(NO_3)_2}{\underset{\text{or}}{Cu(NO_3)_2}} \xrightarrow[CO_2]{\text{heat}} \underset{\text{Benzaldehyde}}{2C_6H_5CHO} + CuCl_2 + 2HNO_2$$

$$[2HNO_2 \longrightarrow NO + NO_2 + H_2O]$$

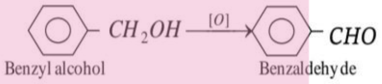
(ii) ***Rosenmund reaction*** :

$$\underset{\text{Benzyl chloride}}{C_6H_5COCl} + H_2 \xrightarrow[\text{xylene}]{Pd/BaSO_4} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

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

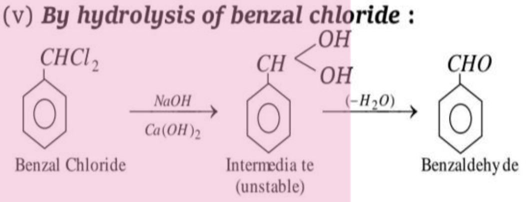


(iv) ***By oxidation of benzyl alcohol*** : This involves the treatment of benzyl alcohol with dil. HNO_3 or acidic potassium dichromate or chromic anhydride in acetic anhydride or with copper catalyst at 350^oC.



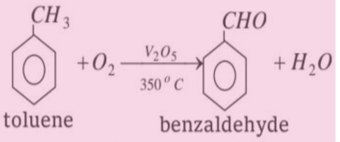
This method is used for commercial production of benzaldehyde.

(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^oC in the presence of oxides of Mn, Mo or Zr as catalyst.

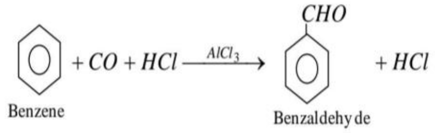
Partial oxidation of toluene with manganese dioxide and dilute sulphuric acid at 35^oC, also forms benzaldehyde.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[(CH_3CO)_2O]{CrO_3} \underset{\text{Benzylidene acetate}}{C_6H_5CH(OCOCH_3)_2} \xrightarrow{H^+/H_2O} C_6H_5CHO + 2CH_3COOH$$

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

$$\underset{\text{Brown addition product}}{C_6H_5CH_3 2CrO_2Cl_2} \xrightarrow{H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

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



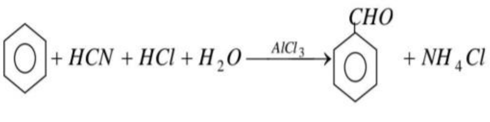
(ix) ***Gattermann reaction***

$$HC\equiv N + HCl + AlCl_3 \longrightarrow H\overset{\oplus}{C} = NH + AlCl_4^-;$$

$$\underset{\text{Benzene}}{C_6H_5H} + H\overset{+}{C} = NH \longrightarrow C_6H_5CH = \overset{+}{N}H_2$$

$$C_6H_5CH = \overset{+}{N}H_2 + H_2O + AlCl_4^- \longrightarrow C_6H_5CHO + NH_3 + AlCl_3 + HCl$$

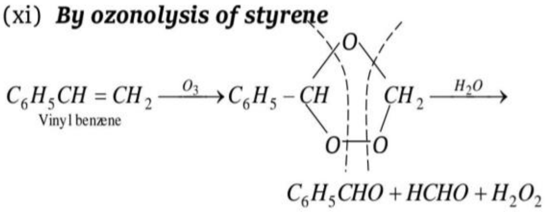
Thus,



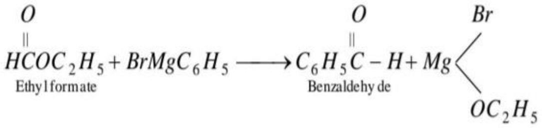
(x) ***Stephen's reaction*** : Benzaldehyde is obtained by partial reduction of phenyl cyanide with stannous chloride and passing dry HCl gas in ether solution followed by hydrolysis of the aldimine stannic chloride with water.

$$\underset{\text{Phenylcyanide}}{C_6H_5C\equiv N} \xrightarrow[\text{Ether}]{HCl/SnCl_2} \underset{\text{Aldimine complex}}{[C_6H_5CH=NH]_2H_2SnCl_6} \xrightarrow{H_2O} 2C_6H_5CHO$$

(xi) ***By ozonolysis of styrene***



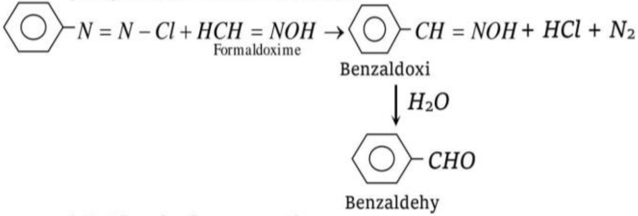
(xii) ***Grignard reaction***



$$\underset{\text{Ethyl formate}}{H\overset{O}{\overset{||}{C}}OC_2H_5} + BrMgC_6H_5 \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5\overset{O}{\overset{||}{C}}-H} + Mg\left\langle\begin{matrix}Br\\OC_2H_5\end{matrix}\right.$$

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^oC.

(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^oC).

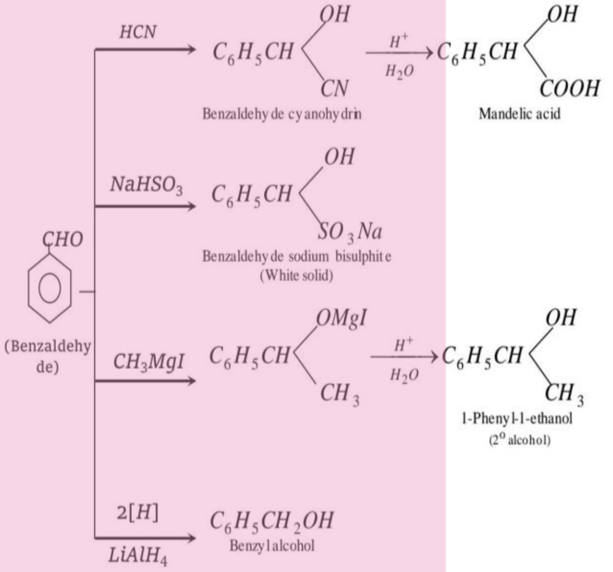
(vi) It is poisonous in nature.

(3) **Chemical properties**

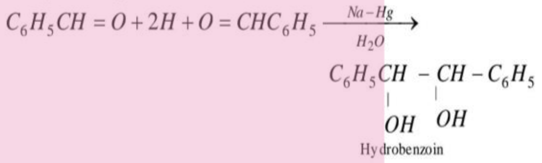
(i) ***Addition reaction:*** The carbonyl group is polar as oxygen is more electronegative than carbon,

$$>\overset{\delta^+}{C}=\overset{\delta^-}{O}$$

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

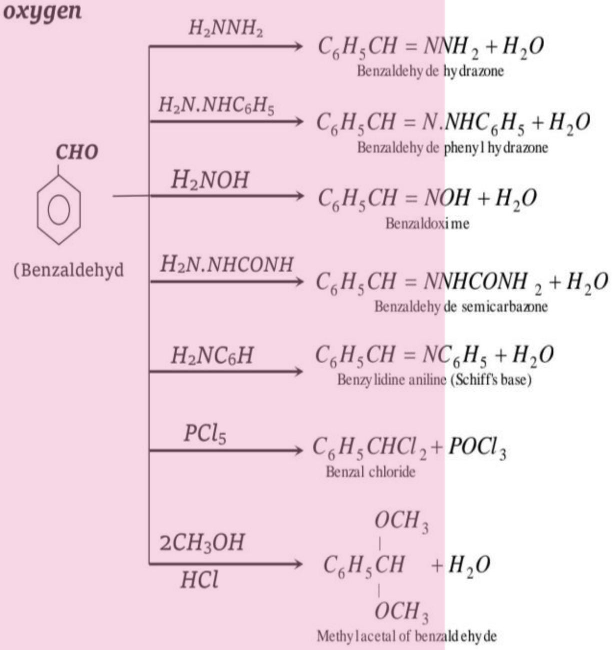


However on reduction with sodium amalgam and water, it gives hydrobenzoin,



$$C_6H_5CH=O+2H+O=CHC_6H_5 \xrightarrow[H_2O]{Na-Hg} \underset{\text{Hydrobenzoin}}{C_6H_5\underset{OH}{CH}-\underset{OH}{CH}-C_6H_5}$$

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



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

$$C_6H_5CHO \xrightarrow{[O]} C_6H_5COOH$$

Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$ and dilute 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.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+Ag_2O \longrightarrow 2Ag+\underset{\text{Benzoic acid}}{C_6H_5COOH}$$

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

$$C_6H_5CHO+4H \xrightarrow[HCl]{Zn-Hg} C_6H_5CH_3+H_2O$$

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

(vii) ***Tischenko reaction*** : On heating benzaldehyde with aluminium alkoxide (ethoxide) and a little of anhydrous $AlCl_3$ 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).

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} \xrightarrow{Al(OC_2H_5)_3} \underset{\text{Benzyl benzoate (ester)}}{C_6H_5CH_2OOCC_6H_5}$$

(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 α -hydrogen atom present which could be replaced by chlorine.

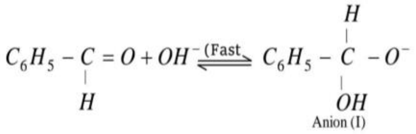
$$C_6H_5CHO+Cl_2 \xrightarrow[\Delta]{170^o C} C_6H_5COCl+HCl$$

(c) *Cannizzaro's reaction* : $\underset{\text{Benzaldehyde}}{2C_6H_5CHO} \xrightarrow{KOH}$

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}+\underset{\text{Potassium benzoate}}{C_6H_5COOK}$$

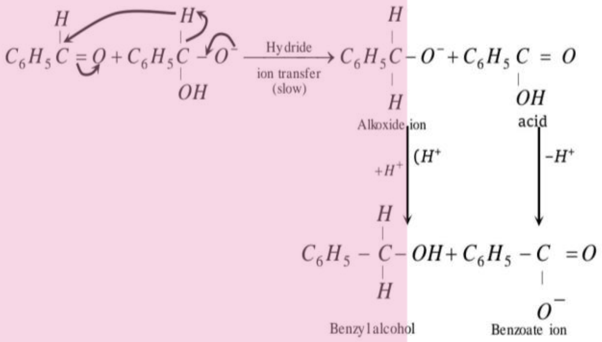
The possible Mechanism is

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



$$C_6H_5-\underset{H}{C}=O+OH^- \underset{}{\overset{\text{(Fast)}}{\rightleftharpoons}} \underset{\text{Anion (I)}}{C_6H_5-\overset{H}{\underset{OH}{C}}-O^-}$$

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.

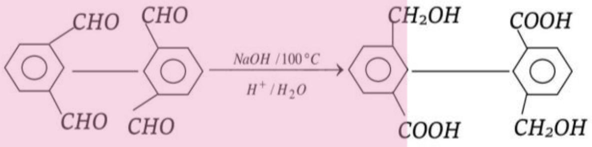
So one molecule of aldehyde acts as hydride donor and the other acts as hydride acceptor. In other words, Cannizzaro's reaction is an example of self reduction and oxidation.

❑ Two different aldehydes each having no α-hydrogen atom, exhibit crossed Cannizzaro's reaction when heated in alkaline solution.

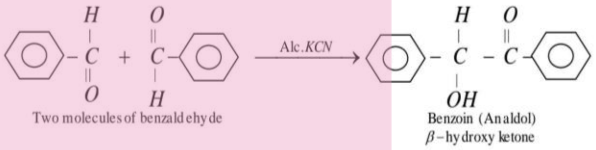
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+\underset{\text{Formaldehyde}}{HCHO}\xrightarrow[\text{heat}]{NaOH}\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}+\underset{\text{Sod. formate}}{HCOONa}$$

Aldehyde which do not have α- hydrogen ($C_6H_5-CHO, CCl_3CHO, (CH_3)_3C-CHO, CH_2O$ etc.) undergoes Cannizzaro's reaction.

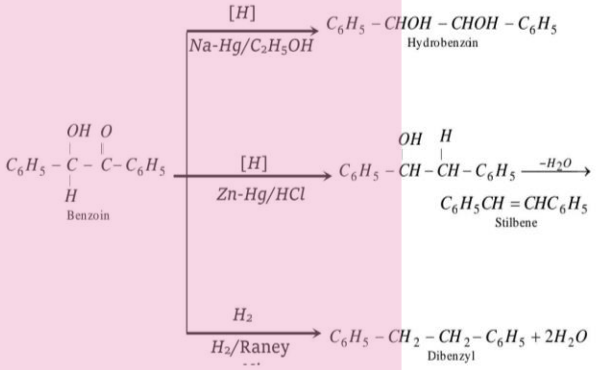
Intramolecular cannizzaro reaction



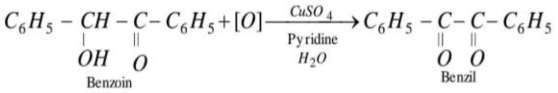
(d) *Benzoin Condensation*



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



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



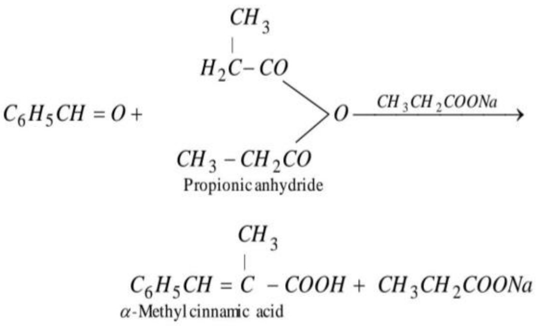
$$\underset{\text{Benzoin}}{C_6H_5-\underset{OH}{CH}-\underset{\overset{\|}{O}}{C}-C_6H_5}+[O]\xrightarrow[\substack{\text{Pyridine}\\ H_2O}]{CuSO_4}\underset{\text{Benzil}}{C_6H_5-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-C_6H_5}$$

(e) *Perkin's reaction*

$$\underset{\text{Benzaldehyde}}{C_6H_5CH\boxed{O+H_2}}\underset{\text{Acetic anhydride}}{CHCOOCOCH_3}\xrightarrow[-H_2O]{CH_3COONa}$$

$$C_6H_5CH=CHCOOCOCH_3$$

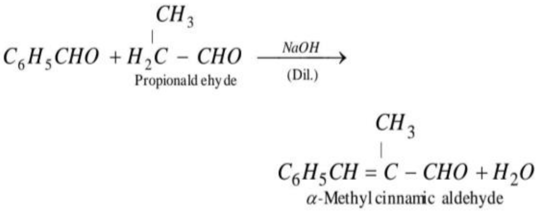
$$\xrightarrow{H_2O}\underset{\text{Cinnamic acid}}{C_6H_5CH=CHCOOH}+\underset{\text{Acetic acid}}{CH_3COOH}$$



$$C_6H_5CH=O+\underset{\text{Propionic anhydride}}{\left.\begin{matrix}\overset{CH_3}{H_2C}-CO\\ CH_3-CH_2CO\end{matrix}\right>O}\xrightarrow{CH_3CH_2COONa}$$

$$\underset{\alpha\text{-Methyl cinnamic acid}}{C_6H_5CH=\overset{CH_3}{C}-COOH}+CH_3CH_2COONa$$

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



$$C_6H_5CHO+\underset{\text{Propionaldehyde}}{H_2\overset{CH_3}{C}-CHO}\xrightarrow[\text{(Dil.)}]{NaOH}$$

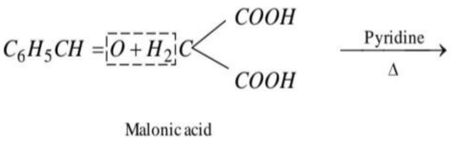
$$\underset{\alpha\text{-Methyl cinnamic aldehyde}}{C_6H_5CH=\overset{CH_3}{C}-CHO+H_2O}$$

$$C_6H_5CHO+\underset{\text{Acetone}}{H_2CHCOCH_3}\xrightarrow{NaOH\text{(Dil)}}$$

$$\underset{\text{Benzylidene acetone}}{C_6H_5CH=CHCOCH_3+H_2O}$$

(β-hydroxy ketone)

(g) Knoevenagel reaction



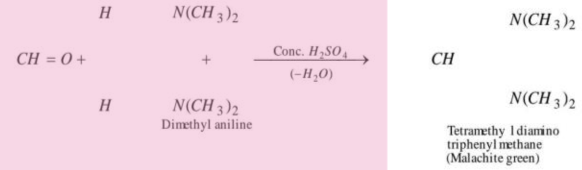
$$C_6H_5CH=\boxed{O+H_2}\underset{\text{Malonic acid}}{C\begin{matrix}COOH\\ COOH\end{matrix}}\xrightarrow[\Delta]{\text{Pyridine}}$$

$$\underset{\text{Cinnamic acid}}{C_6H_5CH=CHCOOH}+CO_2+H_2O$$

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

$$C_6H_5CH=O+\underset{\text{Aniline}}{H_2NC_6H_5}\xrightarrow[(-H_2O)]{\text{Warm}}\underset{\substack{\text{Benzylidene aniline}\\ \text{(Schiff's base)}}}{C_6H_5CH=NC_6H_5}$$

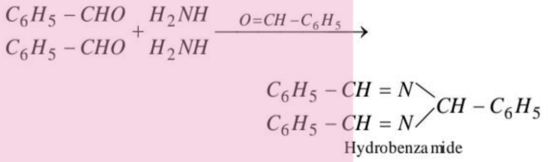
Reaction with Dimethylaniline



Dimethyl aniline

Tetramethyl diamino triphenyl methane (Malachite green)

(i) *Reaction with Ammonia* : Benzaldehyde reacts with ammonia to form hydrobenzamide aldehyde other than CH_2O give aldehyde ammonia while CH_2O forms urotropine.

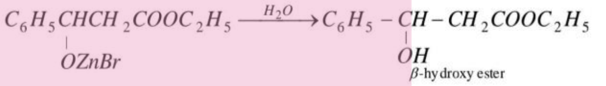


$$\begin{matrix} C_6H_5-CHO \\ C_6H_5-CHO \end{matrix} + \begin{matrix} H_2NH \\ H_2NH \end{matrix} \xrightarrow{O=CH-C_6H_5} \begin{matrix} C_6H_5-CH=N \\ C_6H_5-CH=N \end{matrix} \Big\rangle CH-C_6H_5$$

Hydrobenzamide

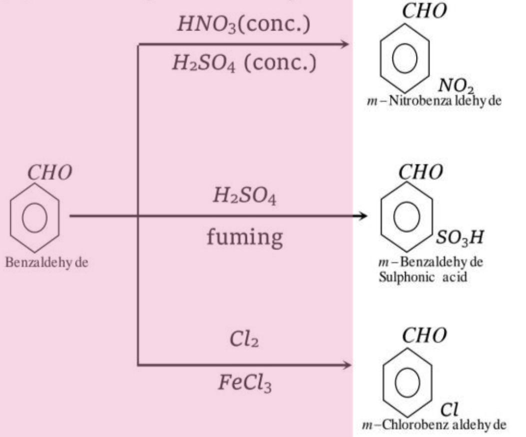
(j) *Reformatsky reaction*

$$\underset{\text{Benzaldehyde}}{C_6H_5CH=O} + Zn + \underset{\text{Bromo ethylacetate}}{Br\overset{\alpha}{C}H_2COOC_2H_5} \longrightarrow$$



$$C_6H_5\underset{\displaystyle OZnBr}{CH}CH_2COOC_2H_5 \xrightarrow{H_2O} \underset{\beta\text{-hydroxy ester}}{C_6H_5-\underset{\displaystyle OH}{CH}-CH_2COOC_2H_5}$$

(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 $NaHSO_3$ 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 $KMnO_4$ and subsequent acidification gives a white precipitate of benzoic acid on cooling.

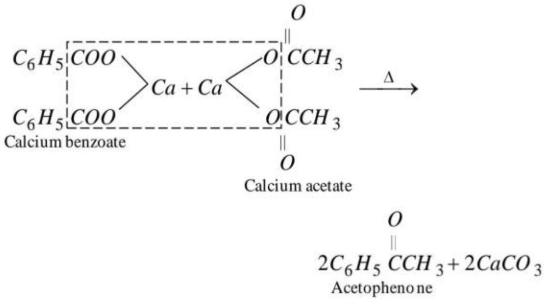
Acetophenone, $C_6H_5COCH_3$, Acetyl Benzene

(1) **Method of preparation**

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

$$\underset{\text{Benzene}}{C_6H_5\boxed{H+Cl}}\underset{\text{Acetylchloride}}{COCH_3} \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

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



Calcium benzoate

Calcium acetate

Acetophenone

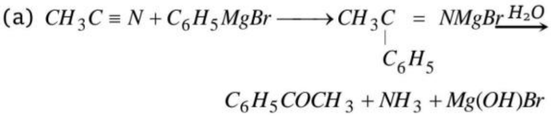
(iii) By methylation of benzaldehyde with diazomethane.

$$C_6H_5CHO + CH_2N_2 \longrightarrow C_6H_5COCH_3 + N_2$$

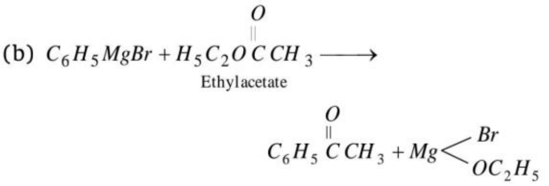
(iv) By treating benzoyl chloride with dimethyl cadmium.

$$2C_6H_5COCl + (CH_3)_2Cd \longrightarrow 2C_6H_5COCH_3 + CdCl_2$$

(v) ***By Grignard reagent***

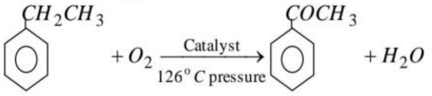


(a) $$CH_3C\equiv N + C_6H_5MgBr \longrightarrow CH_3\underset{\displaystyle C_6H_5}{C}=NMgBr \xrightarrow{H_2O} C_6H_5COCH_3 + NH_3 + Mg(OH)Br$$



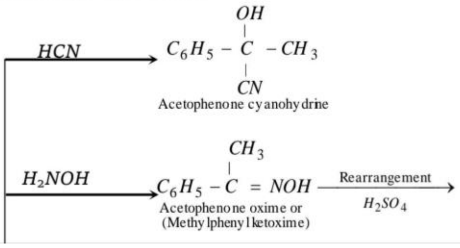
(b) $$C_6H_5MgBr + \underset{\text{Ethylacetate}}{H_5C_2O\overset{O}{\overset{\|}{C}}CH_3} \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}CH_3 + Mg\Big\langle\begin{matrix} Br \\ OC_2H_5 \end{matrix}$$

(vi) ***Commercial preparation*** : Ethylbenzene is oxidised with air at 126 ^oC under pressure in presence of a catalyst manganese acetate.



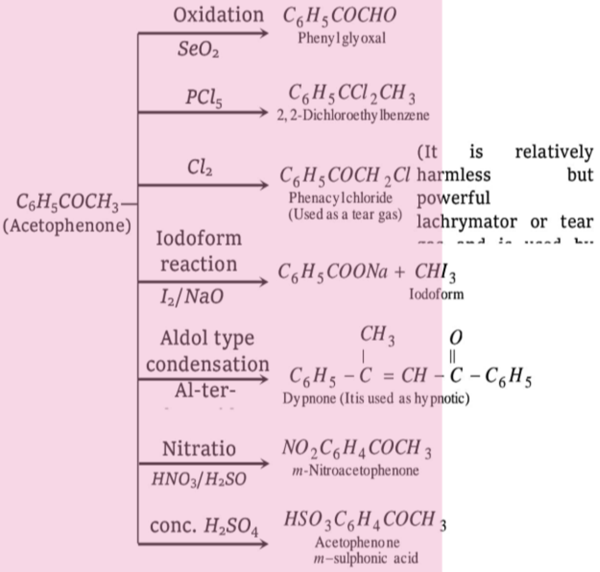
(2) ***Physical properties*** : It is a colourless crystalline solid with melting point 20^oC and boiling point 202^oC. It has characteristic pleasant odour. It is slightly soluble in water. Chemically, It is similar to acetone.

(3) ***Chemical properties*** :



Acetophenone cyanohydrine

Acetophenone oxime or (Methylphenylketoxime)



(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***

$$C_6H_5-CH_2-C_6H_5+2O \xrightarrow{HNO_3} C_6H_5COC_6H_5$$

(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 :***

$$C_6H_5COC_6H_5+2H \xrightarrow{Na-Hg} \underset{\text{Diphenylcarbinol}}{C_6H_5.CHOHC_6H_5}$$

(ii) ***Clemmenson reduction :***

$$C_6H_5COC_6H_5 \xrightarrow[HCl]{Zn/Hg} \underset{\text{Diphenylmethane}}{C_6H_5CH_2C_6H_5}+H_2O$$

(iii) ***Fusion with KOH :***

$$C_6H_5COC_6H_5+KOH \xrightarrow{\text{Fuse}} C_6H_5COOK+C_6H_6$$

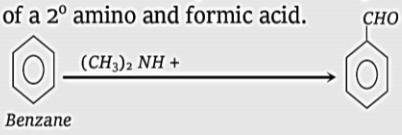
$$C_6H_5COC_6H_5+H_2O \xrightarrow[\text{Ether}]{\text{Pot. tert. Butoxide}} \underset{\text{Benzoic acid}}{C_6H_5COOH}+C_6H_6$$

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.

$$CH_2=CHCH_2OH \xrightarrow{K_2Cr_2O_7/H_2S} CH_2=CHCHO$$

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

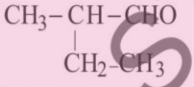


✍ Benzaldehyde although reduces Tollen's reagent. It does not reduce Fehling or Benedict solution.

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

FACT/DEFINITION TYPE QUESTIONS

1. Choose the correct IUPAC name for



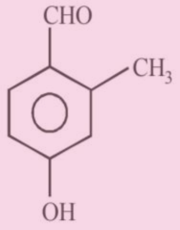
$CH_3-\underset{\underset{CH_2-CH_3}{|}}{CH}-CHO$

(a) Butan - 2- aldehyde
(b) 2- methylbutanal
(c) 3- methylisobutyraldehyde
(d) 2- ethylpropanal

2. The IUPAC name of the compound having the molecular formula Cl_3C-CH_2CHO is
(a) 3, 3, 3- trichloropropanal
(b) 1, 1, 1- trichloropropanal
(c) 2, 2, 2- trichloropropanal
(d) Chloral

3. The IUPAC name of $CH_3COCH(CH_3)_2$ is
(a) 2-methyl-3-butanone (b) 4-methylisopropyl ketone
(c) 3-methyl-2-butanone (d) Isopropylmethyl ketone

4. IUPAC name of following will be



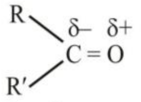
(a) 4-formyl 3-methyl 1-hydroxy benzene
(b) 4-formyl 3-methyl phenol
(c) 4-hydroxy 2-methyl benzaldehyde
(d) 4-hydroxy 2-methyl carbaldehyde

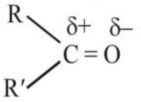
5. IUPAC name of ethyl isopropyl ketone is
(a) 4-methyl pent-3-one (b) 2-methyl pent-3-one
(c) 4-methyl pent-2-one (d) 2-methyl pent-2-one

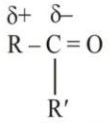
6. In $>C=O$ group sigma bond is formed by
(a) sp^2-p-overlapping (b) sp^3-p-overlapping
(c) sp-p-overlapping (d) s-p-overlapping

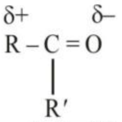
7. The π-bond in carbonyl group is formed by
(a) s-s-overlapping (b) p-p-overlapping
(c) s-p-overlapping (d) p-d-overlapping

8. Which of the following is correct for carbonyl compounds?

(a)


(b)


(c)


(d)


9. Which of the following contain an aldehyde?
(a) Vanilla beans (b) Meadow sweet
(c) Cinnamon (d) All of these

10. Which of the following have pleasant smell?
(a) Methanal (b) Propanal
(c) Ethanal (d) Hexanal

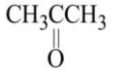
11. Which one of the following can be oxidised to the corresponding carbonyl compound?
(a) 2-hydroxy-propane
(b) Ortho-nitrophenol
(c) Phenol
(d) 2-methyl-2 hydroxy-propane

12. Which one of the following on oxidation gives a ketone ?
(a) Primary alcohol (b) Secondary alcohol
(c) Tertiary alcohol (d) All of these

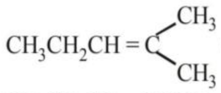
13. What is formed when a primary alcohol undergoes catalytic dehydrogenation ?
(a) Aldehyde (b) Ketone
(c) Alkene (d) Acid

14. Primary and secondary alcohols on action of reduced copper give
(a) Aldehydes and ketones respectively
(b) Ketones and aldehydes respectively
(c) Only aldehydes
(d) Only ketones

15. Which alkene on ozonolysis gives CH_3CH_2CHO and

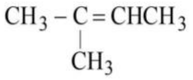


$CH_3\underset{\underset{O}{\|}}{C}CH_3$

(a)


(b) $CH_3CH_2CH=CHCH_2CH_3$

(c) $CH_3CH_2CH=CHCH_3$

(d)


$CH_3-\underset{\underset{CH_3}{|}}{C}=CHCH_3$

16. The catalyst used in Rosenmund's reduction is
(a) $HgSO_4$ (b) $Pd/BaSO_4$
(c) anhydrous $AlCl_3$ (d) anhydrous $ZnCl_2$

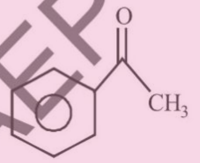
17. $C_6H_5C\equiv N + [H] \xrightarrow{SnCl_2/HCl} C_6H_5CHO + NH_3$.
The above reaction is
(a) Mendius reaction (b) Sandorn's reaction
(c) Rosenmund's reaction (d) Stephen's reaction

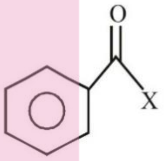
18. Benzaldehyde can be prepared by oxidation of toluene by
(a) Acidic $KMnO_4$ (b) $K_2Cr_2O_7/H^+$
(c) CrO_2Cl_2 (d) All of these

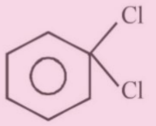
19. The oxidation of toluene to benzaldehyde by chromyl chloride is called
(a) Rosenmund reaction (b) Wurtz reaction
(c) Etard reaction (d) Fittig reaction

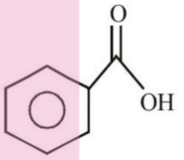
20. An aldehyde group can be present
(a) in between carbon chain
(b) at any position in carbon atom
(c) only at the end of carbon chain
(d) at the second carbon atom of the carbon chain

21. Benzaldehyde is obtained from Rosenmund's reduction of

(a) 

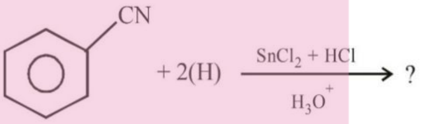
(b) 

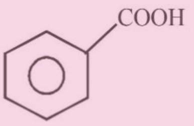
(c) 

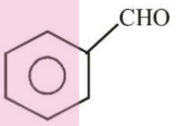
(d) 

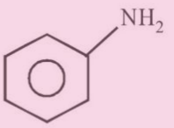
22. Which of the following is not used in the preparation of ketone?
(a) Oxidation of secondary alcohols
(b) Dehydrogenation of 2° alcohol
(c) Pyrolysis of calcium acetate
(d) Acid hydrolysis of alkyl cyanide

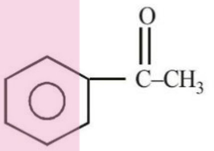
23. Product of the following reaction is



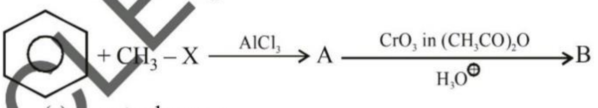
(a) 

(b) 

(c) 

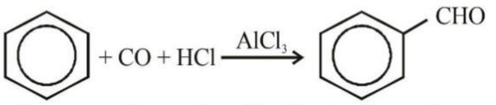
(d) 

24. Find out B in the given reactions



(a) acetophenone
(b) benzaldehyde
(c) cyclohexyl carbaldehyde
(d) benzoic acid

25. The reaction



(a) Rosenmund's reaction (b) Stephen's reaction
(c) Cannizzaro's reaction (d) Gatterman-Koch reaction

26. Which aldehyde cannot be obtained by Rosenmund's reaction?
(a) CH_3CHO (b) HCHO
(c) CH_3CH_2CHO (d) All of these

27. The conversion $PhCN \rightarrow PhCOCH_3$, can be achieved most conveniently by reaction with
(a) CH_3MgBr followed by hydrolysis
(b) $I_2 - NaOH, CH_3I$
(c) Dil. H_2SO_4 followed by reaction with CH_2N_2
(d) $LiAlH_4$ followed by reaction with CH_3I

28. Which of the following is used to prepare ketone from acyl chloride ?
(a) R-MgX (b) R_2Cd
(c) CO+HCl (d) CrO_3

29. Which of the following forces explain the boiling point of aldehydes and ketones?
(a) Hydrogen bonding (b) van der Waal's forces
(c) Dipole-dipole attraction (d) None of these

30. Which is highly soluble in water?
(a) Methanal (b) Propanal
(c) Propanone (d) Butanone

31. Propanal and propanone, both have same molecular formula(C_3H_6O), what do you expect about their boiling points?
(a) Both have same boiling point
(b) Boiling point of propanal is higher than the boiling point of propanone.
(c) Boiling point of propanal is lower than the boiling point of propanone
(d) Nothing can be predicted

32. Less reactivity of ketone is due to
(a) + I inductive effect decrease positive charge on carbonyl carbon atom
(b) steric effect of two bulky alkyl groups
(c) sp^2 hybridised carbon atom of carbonyl carbon atom
(d) Both (a) and (b)

33. Acetaldehyde reacts with
(a) Electrophiles only
(b) Nucleophiles only
(c) Free radicals only
(d) Both electrophiles and nucleophiles

34. Carbonyl compounds undergo nucleophilic addition because of
(a) electronegativity difference of carbon and oxygen atoms
(b) electromeric effect
(c) more stable anion with negative charge on oxygen atom and less stable carbonium ion
(d) None of the above

35. Which of the following statement is false ?
(a) Cannizzaro reaction is given by aldehydes in presence of alkali
(b) Aldol condensation is given by aldehydes in presence of alkali
(c) Aldol condensation is given by aldehydes and ketones in presence of acids
(d) None of the above

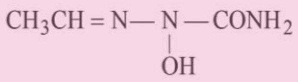
36. If formaldehyde and KOH are heated, then we get
(a) methane (b) methyl alcohol
(c) ethyl formate (d) acetylene

37. The reagent which can be used to distinguish acetophenone from benzophenone is
(a) 2,4-dinitrophenylhydrazine
(b) aqueous solution of $NaHSO_3$
(c) benedict reagent
(d) I_2 and Na_2CO_3

38. Benzaldehyde reacts with ethanoic KCN to give
(a) $C_6H_5CHOHCN$ (b) $C_6H_5CHOHCOC_6H_5$
(c) $C_6H_5CHOHCOOH$ (d) $C_6H_5CHOHCHOHC_6H_5$

39. Acetone reacts with iodine (I_2) to form iodoform in the presence of
(a) $CaCO_3$ (b) NaOH
(c) KOH (d) $MgCO_3$

40. $(CH_3)_3C–CHO$ does not undergo aldol condensation due to
(a) three electron donating methyl groups
(b) cleavage taking place between —C— CHO bond
(c) absence of alpha hydrogen atom in the molecule
(d) bulky $(CH_3)_3C$—group

41. Acetaldehyde reacts with semicarbazide and forms semicarbazone. Its structure is
(a) $CH_3CH=NNHCON=CHCH_3$
(b) $CH_3CH=NNHCONH_2$
(c) 
$CH_3CH=N—\underset{\substack{|\\ OH}}{N}—CONH_2$
(d) $CH_3CH=N—CONHNH_2$

42. Iodoform test is not given by
(a) 2-Pentanone (b) Ethanol
(c) Ethanal (d) 3-Pentanone

43. Phenylmethyl ketone can be converted into ethylbenzene in one step by which of the following reagents?
(a) $LiAlH_4$ (b) Zn-Hg/HCl
(c) $NaBH_4$ (d) CH_3MgI

44. When acetaldehyde is heated with Fehling's solution it gives a precipitate of
(a) Cu (b) CuO
(c) Cu_2O (d) $Cu(OH)_2$

45. Aldol condensation would not occur in :
(a) CH_3COCH_3 (b) CH_3CH_2CHO
(c) HCHO (d) CH_3CHO

46. Cannizzaro reaction occurs with
(a) CH_3-CH_2OH (b) C_6H_5CHO
(c) CH_3CHO (d) $CH_3-CO-CH_3$

47. Which of the following compound will show positive silver mirror test ?
(a) HCOOH (b) $CH_3(CHOH)_3CHO$
(c) $CH_3CO(CHOH)CH_3$ (d) Both (a) and (b)

48. Aldehydes and ketones are distinguished by which of the following test ?
(a) Lucas test
(b) Tollen's test
(c) $KMnO_4$ solution (Baeyer's test)
(d) None of these

49. Aldehydes and ketones are generally reduced by :
(a) Clemmensen reduction (b) H_2S
(c) H_2/Ni (d) None of these

50. In which reaction, $>C=O$ can be reduced to $>CH_2$?
(a) Wolf-Kishner reaction (b) Reimer-Tiemann reaction
(c) Wurtz reaction (d) None of these

51. A compound does not react with 2, 4-dinitrophenylhydrazine, the compound is :
(a) Acetone (b) Acetaldehdye
(c) CH_3OH (d) $CH_3CH_2COCH_3$

52. Which gives lactic acid on hydrolysis after reacting with HCN ?
(a) HCHO (b) CH_3CHO
(c) C_6H_5CHO (d) CH_3COCH_3

53. 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

54. Aldehydes can be oxidised by :
(a) Tollen's reagent (b) Fehling solution
(c) Benedict solution (d) All the above

55. 2-pentanone and 3-pentanone can be distinguished by :
(a) Cannizaro's reaction (b) Aldol condensation
(c) Iodoform reaction (d) Clemmensen's reduction

56. Cross aldol condensation occurs between
(a) two same aldehydes
(b) two same ketones
(c) two different aldehydes and ketones
(d) None of these

57. Ketone upon treatment with Grignard Reagent gives
(a) primary alcohol (b) secondary alcohol
(c) tertiary alcohol (d) aldehyde

58. When acetaldehyde reacts with alcohol then produce
(a) Acetal (b) Ketal
(c) Acetone (d) None

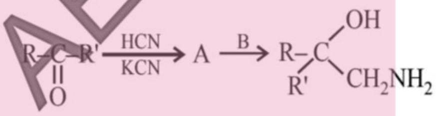
59. The product formed in Aldol condensation is
(a) a beta-hydroxy aldehyde or a beta-hydroxy ketone
(b) an alpha-hydroxy aldehyde or ketone
(c) an alpha, beta unsaturated ester
(d) a beta-hydroxy acid

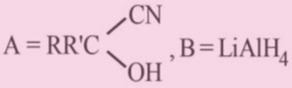
60. Clemmensen reduction of a ketone is carried out in the presence of which of the following ?
(a) Glycol with KOH (b) Zn-Hg with HCl
(c) $LiAlH_4$ (d) H_2 and Pt as catalyst

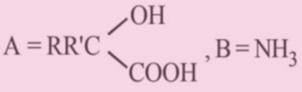
61. Which of the following products is formed when benzaldehyde is treated with CH_3MgBr and the addition product so obtained is subjected to acid hydrolysis ?
(a) A secondary alcohol (b) A primary alcohol
(c) Phenol (d) tert-Butyl alcohol

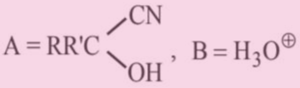
62. During reduction of aldehydes with hydrazine and potassium hydroxide, the first step is the formation of
(a) $R-CH=N-NH_2$ (b) $R-C\equiv N$
(c)  $R-\underset{\underset{O}{\|}}{C}-NH_2$ (d) $R-CH=NH$

63. A and B in the following reactions are



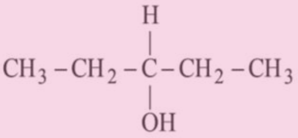
(a)  $A = RR'C\begin{smallmatrix}CN\\OH\end{smallmatrix}, B = LiAlH_4$

(b)  $A = RR'C\begin{smallmatrix}OH\\COOH\end{smallmatrix}, B = NH_3$

(c)  $A = RR'C\begin{smallmatrix}CN\\OH\end{smallmatrix}, B = H_3O^{\oplus}$

(d) $A = RR'CH_2CN, B = NaOH$

64. The product obtained by the reaction of an aldehyde and hydroxylamine is
(a) hydrazone (b) aldoxime
(c) primary amine (d) alcohol

65. Which one gives positive iodoform test ?
(a) $(CH_3)_2CHCH_2OH$
(b) C_6H_5-OH
(c)  $CH_3-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-CH_3$
(d) CH_3CH_2OH

66. The compound that neither forms semicarbazone nor oxime is
(a) HCHO (b) CH_3COCH_2Cl
(c) CH_3CHO (d) $CH_3CONHCH_3$

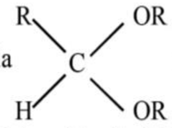
67. Schiff's reagent gives pink colour with
(a) acetaldehyde (b) acetone
(c) acetic acid (d) methyl acetate

68. Benzophenone can be converted into benzene by using
(a) fused alkali
(b) anhydrous $AlCl_3$
(c) sodium amalgam in water
(d) acidified dichromate

69. In the reaction of $NaHSO_3$ with carbonyl compounds to form bisulphite product, the nucleophile is
(a) HSO_3^- (b) SO_3Na
(c) SO_3^{--} (d) None of the above

70. Wolf-Kishner reduction is
(a) reduction of carbonyl compound into alcohol
(b) reduction of carbonyl compound into alkene
(c) reduction of carboxyl compound into alkane
(d) reduction of nitro compound into aniline

71. Tollen's reagent is
(a) ammonical $CuSO_4$
(b) ammonical $AgNO_3$
(c) alkaline solution containing complex of copper nitrate
(d) none of these

72. Compound of general formula  are called
(a) diester (b) acid anhydride
(c) hemiacetal (d) acetal

73. Imine derivatives of aldehyde and ketone is called as
(a) Schiff's reagent (b) Fehling's reagent
(c) Schiff's base (d) Schiff's acid

74. Which reaction is used for detecting the presence of carbonyl group?
(a) Reaction with hydrazine
(b) Reaction with phenyl hydrazine
(c) Reaction with hydroxylamine
(d) All of the above

75. The difference between aldol condensation and Cannizzaro's reaction is that:
(a) the former takes place in the presence of α-H-atom.
(b) the former takes place in the absence of α-H-atom.
(c) the former takes place in the presence of β-H-atom.
(d) none of the above

76. $C_6H_5CH=CHCHO \xrightarrow{X} C_6H_5CH=CHCH_2OH$
In the above sequence X can be :
(a) H_2/Ni (b) $NaBH_4$
(c) $K_2Cr_2O_7/H^+$ (d) Both (a) and (b)

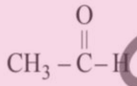
77. Which of the following pairs of compounds will undergo aldol and Cannizzaro reaction respectively ?
(i) acetone; benzaldehyde
(ii) acetaldehyde; butan–2–one
(iii) propanone; formaldehyde.
(iv) cyclopentanone, benzaldehyde
(a) (i), (ii) and (iii) (b) (ii) and (iii)
(c) (ii), (iii) and (iv) (d) (iii) and (iv)

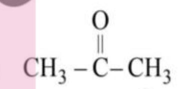
78. Two compounds benzyl alcohol and benzoic acid are formed from this compound, when this compound is heated in the presence of conc.NaOH, this compound is.
(a) Benzaldehyde (b) Benzylalcohol
(c) Acetophenone (d) Benzophenone

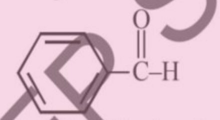
79. The reagent which does not react with both, acetone and benzaldehyde.
(a) Sodium hydrogensulphite
(b) Phenyl hydrazine
(c) Fehling's solution
(d) Grignard reagent

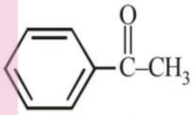
80. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution?
(a) Butan-1-ol (b) Butan-2-ol
(c) Both of these (d) None of these

81. Which of the following compounds is most reactive towards nucleophilic addition reactions?

(a) 
$CH_3-\overset{\overset{O}{||}}{C}-H$

(b) 
$CH_3-\overset{\overset{O}{||}}{C}-CH_3$

(c) 

(d) 

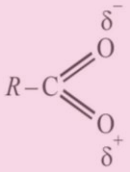
82. Which of the following does not represent the natural source of the corresponding acids ?
(a) Formic acid : Red ant
(b) Acetic acid : Vinegar
(c) Butyric acid : Rancid butter
(d) Isobutyric acid : Automobile exhausts

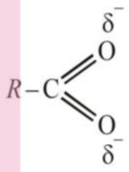
83. Vinegar is a solution of acetic acid which is :
(a) 15 – 20% (b) 20–25%
(c) 6 – 8% (d) 2 – 4%

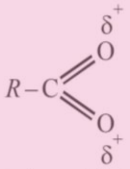
84. Methyl cyanide can be converted into acetic acid by one of the following reactions.
(a) Reduction (b) Hydrolysis
(c) Electrolysis (d) Decarboxylation

85. Toluene can be oxidised to benzoic acid by
(a) $KMnO_4$ (alk.) (b) $K_2Cr_2O_7$ (alk.)
(c) Both (a) and (b) (d) Neither (a) nor (b)

86. Which of the following does the best represent the structure of the carboxylate ion ?

(a) 

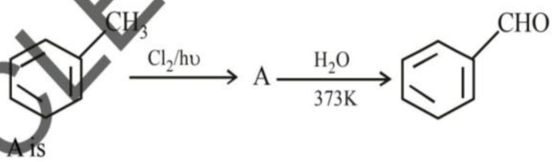
(b) 

(c) 

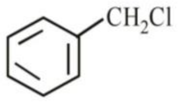
(d) None of these

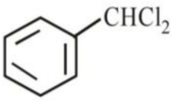
87. Select the acid(s) which cannot be prepared by Grignard reagent.
(a) Acetic acid (b) Succinic acid
(c) Formic acid (d) All of the above

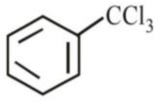
88. In the given reaction

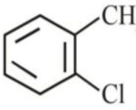


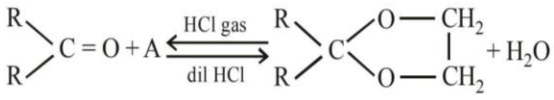
A is

(a) 

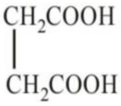
(b) 

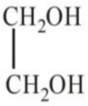
(c) 

(d) 

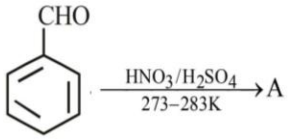
89. 

A is
(a) CH_3OH (b) CH_3COOH

(c) 
$\begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}$

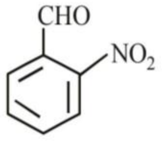
(d) 
$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$

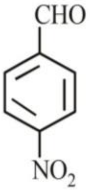
90. In the reaction

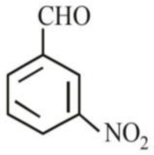


Benzaldehyde

A is

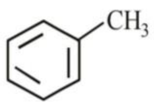
(a) 

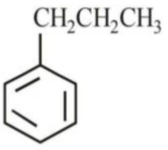
(b) 

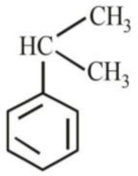
(c) 

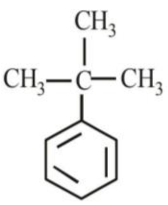
(d) Both (a) and (b)

91. Which of the following can not be oxidised to give carboxylic acid?

(a) 

(b) 

(c) 

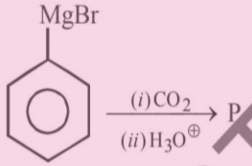
(d) 

92. Lower carboxylic acids are soluble in water due to
(a) low molecular weight (b) hydrogen bonding
(c) dissociation into ions (d) easy hydrolysis

93. Dimerisation of carboxylic acids is due to
(a) ionic bond
(b) covalent bond
(c) coordinate bond
(d) intermolecular hydrogen bond

94. Boiling points of carboxylic acids are
(a) lower than corresponding alcohols
(b) higher than corresponding alcohols
(c) equal to that of corresponding alcohols
(d) None of the above

95.

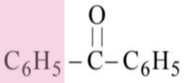


In the above reaction product 'P' is

(a)


(b)


(c)


(d)

$C_6H_5-\overset{\overset{O}{||}}{C}-C_6H_5$

96. In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it?
(a) Electronic orbitals of carbon atom are hybridised
(b) The C=O bond is weaker than the C–C bond
(c) The anion $HCOO^-$ has two reasonating structures
(d) The anion is obtained by removal of a proton from the acid molecule

97. Carboxylic acids are more acidic than phenol and alcohol because of
(a) intermolecular hydrogen bonding
(b) formation of dimers
(c) highly acidic hydrogen
(d) resonance stabilization of their conjugate base

98. Which of the following has the maximum acidic strength ?
(a) o- nitrobenzoic acid (b) m-nitrobenzoic acid
(c) p-nitrobenzoic acid (d) p-nitrophenol

99. Which of the following is the weakest acid ?

(a)


(b) CH_3COOH

(c) HCOOH

(d)


100. Which of the following acids has the smallest dissociation constant ?
(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH
(c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

101. Which one of the following esters is obtained by the esterification of propan-2-ol with ethanoic acid ?
(a) $(CH_3)_2CHCOOCH_3$ (b) $CH_3COOCH_2CH_3$
(c) $CH_3COOCH(CH_3)_2$ (d) $(CH_3)_2CHCOOCH_2CH_3$

102. The major product of nitration of benzoic acid is
(a) 3- Nitrobenzoic acid (b) 4- Nitrobenzoic acid
(c) 2-Nitrobenzoic acid (d) 2, 4- dinitrobenzoic acid

103. Among the following acids which has the lowest pK_a value?
(a) CH_3CH_2COOH (b) $(CH_3)_2CH-COOH$
(c) HCOOH (d) CH_3COOH

104. The correct order of increasing acidic strength is __________
(a) Phenol < Ethanol < Chloroacetic acid < Acetic acid
(b) Ethanol < Phenol < Chloroacetic acid < Acetic acid
(c) Ethanol < Phenol < Acetic acid < Chloroacetic acid
(d) Chloroacetic acid < Acetic acid < Phenol < Ethanol

105. Which reagent can convert acetic acid into ethanol ?
(a) Na + alcohol (b) $LiAlH_4$ + ether
(c) H_2 + Pt (d) Sn + HCl

106. Which is false in case of carboxylic acids?
(a) They are polar molecules
(b) They form H-bonds
(c) They are stronger than mineral acids
(d) They have higher b.p. than corresponding alcohols

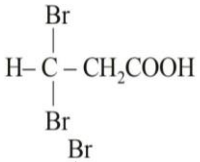
107. The elimination of CO_2 from a carboxylic acid is known as
(a) hydration (b) dehydration
(c) decarboxylation (d) carboxylation

108. The reaction of carboxylic acid gives effervescences of CO_2 with $NaHCO_3$. The CO_2 comes from.
(a) R – COOH (b) $NaHCO_3$
(c) Both (a) and (b) (d) None of these

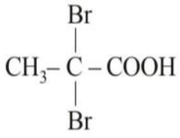
109. Acetic anhydride is obtained by the reaction of
(a) sodium and acetic acid
(b) ammonia and acetic acid
(c) ethanol and acetic acid
(d) P_2O_5 and acetic acid

110. Benzoic acid may be converted to ethyl benzoate by reaction with
(a) sodium ethoxide (b) ethyl chloride
(c) dry HCl—C_2H_5OH (d) ethanol

111. Propionic acid with Br_2/P yields a dibromo product. Its structure would be:

(a)

$H-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}-CH_2COOH$

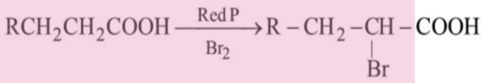
(b) CH_2Br-CH_2-COBr

(c)

$CH_3-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}-COOH$

(d) $CH_2Br-CHBr-COOH$

112. The product obtained when acetic acid is treated with phosphorus trichloride is
(a) $CH_3COOPCl_3$ (b) $ClCH_2COCl$
(c) CH_3COCl (d) $ClCH_2COOH$

113. The reaction



$$RCH_2CH_2COOH \xrightarrow[Br_2]{\text{Red P}} R-CH_2-\underset{\substack{|\\Br}}{CH}-COOH$$

is called as
(a) Reimer- Tiemann reaction
(b) Hell-Volhard Zelinsky reaction
(c) Cannizzaro reaction
(d) Sandmeyer reaction

114. Benzoic acid reacts with conc. HNO_3 and H_2SO_4 to give :
(a) 3-Nitrobenzoic acid
(b) 4-Benzene sulphonic acid
(c) 4-Nitrobenzoic acid
(d) 2-Nitrobenzoic acid

115. In the following reaction

$$RCH_2COOH \xrightarrow{Br_2/P} X \xrightarrow{\text{excess } NH_3} Y$$

The major compounds X and Y are
(a) $RCHBrCONH_2$; $RCH(NH_2)COOH$
(b) $RCHBrCOOH$; $RCH(NH_2)COOH$
(c) RCH_2COBr ; RCH_2COONH_4
(d) $RCHBrCOOH$; RCH_2CONH_2

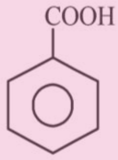
116. The yield of ester in esterification can be increased by

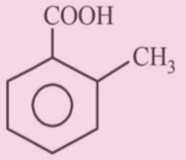
$$CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

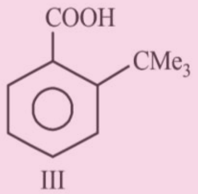
(a) removing water
(b) taking ethanol in excess
(c) taking acetic acid in excess
(d) all the above factors

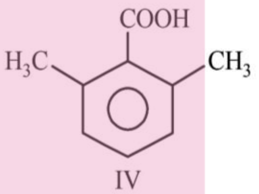
117. A carboxylic acid can best be converted into acid chloride by using
(a) PCl_5 (b) $SOCl_2$
(c) HCl (d) ClCOCOCl

118. Arrange the following four acids in their decreasing order of acidity


I


II


III


IV

(a) I > II > III > IV (b) IV > III > II > I
(c) II > IV > III > I (d) III > IV > II > I

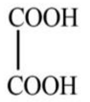
119. The strongest acid among the following is –
(a) Salicylic acid (b) *m*-hydroxybenzoic acid
(c) *p*-hydroxybenzoic acid (d) Benzoic acid

120. Among the following, the most acidic is :
(a) CH_3COOH (b) $ClCH_2COOH$
(c) $Cl_2CHCOOH$ (d) Cl_2CHCH_2COOH

121. Which of the following is the correct decreasing order of acidic strength of
(i) Methanoic acid (ii) Ethanoic acid
(iii) Propanoic acid (iv) Butanoic acid
(a) (i) > (ii) > (iii) > (iv) (b) (ii) > (iii) > (iv) > (i)
(c) (i) > (iv) > (iii) > (ii) (d) (iv) > (i) > (iii) > (ii)

122. Among the following the strongest acid is
(a) CH_3COOH (b) CH_2ClCH_2COOH
(c) $CH_2ClCOOH$ (d) CH_3CH_2COOH

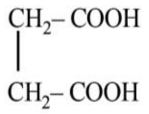
123. Arrange the following carboxylic acid in their decreasing acidity.

1. 

$$\begin{array}{c}COOH\\|\\COOH\end{array}$$

Oxalic acid

2. $HOOC-CH_2-COOH$ Malonic acid

3. 

$$\begin{array}{l}CH_2-COOH\\|\\CH_2-COOH\end{array}$$

Succinic acid

(a) 3 > 2 > 1 (b) 1 > 2 > 3
(c) 2 > 3 > 1 (d) 2 > 1 > 3

STATEMENT TYPE QUESTIONS

124. Read the following statements and choose the correct option
(i) The carbonyl carbon atom is sp^2 -hybridised
(ii) The carbonyl carbon is an electrophilic (Lewis acid) centre
(iii) The carbonyl oxygen is a nucleophilic (Lewis base) centre
(iv) Carbonyl compounds are non- polar in nature.
(a) (i), (ii) and (iv) are correct
(b) (i), (ii) and (iii) are correct
(c) (ii), (iii) and (iv) are correct
(d) (ii) and (iv) are correct

125. Which of the following statement(s) is/are true regarding preparation of aldehydes and ketones?
(i) Both can be prepared by the oxidation of the concerned alcohol with copper at about 250°C.
(ii) Both can be prepared by the oxidation of the concerned alcohol by Oppenauer oxidation.
(iii) Both can be prepared by the oxidation of respective alcohol with acidic dichromate.
(a) (i) only (b) (ii) and (iii)
(c) (i) and (iii) (d) All the three

126. Which of the following statements are *false*?
(i) No aldehyde can be prepared by the oxidation of primary alcohol with acidic $KMnO_4$.
(ii) Aldehydes having a boiling point less than 100°C can be prepared by the oxidation of primary alcohol with acidic dichromate.
(iii) Secondary alcohols on oxidation with PCC in dichloromethane give carboxylic acids having lesser number of carbon atoms
(iv) Tertiary alcohols can't be oxidised at all
(a) (ii) and (iii) (b) (ii), (iii) and (iv)
(c) (i), (iii) and (iv) (d) (i), (ii) and (iii)

127. Read the following statements and choose the correct option
(i) The boiling points of aldehydes and ketones are lower than those of alcohols of similar molecular masses
(ii) Alcohols show intermolecular hydrogen bonding whereas aldehydes and ketones do not show intermolecular hydrogen bonding.
(iii) The lower members of aldehydes and ketones are miscible with water in all proportions, because they form hydrogen bond with water.
(iv) The solubility of aldehydes and ketones increases rapidly on increasing the length of alkyl chain
(a) TTFF (b) TFFT
(c) FTTT (d) TTTF

128. Aldehydes are generally more reactive than ketones in nucleophilic addition reactions. Which of the following statements accounts for this ?
(i) Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon
(ii) Aldehydes show resonance whereas ketones do not
(iii) Electronically, the presence of two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively.
(iv) Electronically carbonyl carbon atom in ketones is more electrophilic than in aldehydes
(a) (i) and (iii) (b) (i) and (iv)
(c) (ii) and (iii) (d) (ii) and (iv)

129. $2C_6H_5CHO \xrightarrow[H_2O]{OH^-} C_6H_5CH_2OH + C_6H_5COO^-$
Which of the following statements are correct regarding the above reduction of benzaldehyde to benzyl alcohol?
(i) One hydrogen is coming from H_2O as H^+ and another from C_6H_5CHO as H^-
(ii) One hydrogen is coming from H_2O as H^- and another from C_6H_5CHO as H^+
(iii) One hydrogen from H_2O and another from C_6H_5CHO, both in the form of H^-
(iv) The reduction is an example of disproportionation reaction
(a) (i), (ii) and (iii) (b) (i) and (iv)
(c) (ii), (iii) and (iv) (d) (iii) and (iv)

130. Which of the following statement(s) is/are true regarding esterification of a carboxylic acid with an alcohol ?
(i) It is carried out in presence of a strong acid which acts as a catalyst.
(ii) The strong acid makes the carbonyl carbon more electrophilic, and hence causes the alcohol, a strong nucleophile to attack on the carbonyl carbon.
(iii) The strong acid makes the carbonyl group more electrophilic which is thus attacked easily by an alcohol, a weak nucleophile.
(iv) Esterification can be done even in absence of a strong acid.
(a) (i) and (ii) (b) (i) and (iii)
(c) (i) only (d) (iv) only

MATCHING TYPE QUESTIONS

131. Match the columns

	Column-I (Common names)		**Column-II (IUPAC names)**
(A)	Cinnamaldehyde	(p)	Pentanal
(B)	Acetophenone	(q)	Prop-2-enal
(C)	Valeraldehyde	(r)	4-Methylpent-3-en-2-one
(D)	Acrolein	(s)	3-Phenylprop-2-enal
(E)	Mesityl oxide	(t)	1-Phenylethanone

(a) A – (s), B – (t), C – (p), D – (q), E – (r)
(b) A – (p), B – (q), C – (s), D – (t), E – (r)
(c) A – (t), B – (s), C – (p), D – (r), E – (q)
(d) A – (q), B – (t), C – (r), D – (s), E – (p)

132. Match the columns

	Column-I		**Column-II**
(A)	$R-CO-CH_3 \xrightarrow{Zn-Hg/HCl} R-CH_2-CH_3$	(p)	Friedel-Craft's reaction
(B)	$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5COONa + C_6H_5CH_2OH$	(q)	Kolbe's reaction
(C)	$C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Anhyd.} C_6H_5COCH_3$	(r)	Clemmensen's reaction
(D)	$C_6H_5OH + CO_2 + NaOH \rightarrow HOC_6H_4COONa$	(s)	Cannizzaro's reaction

(a) A – (p), B – (q), C – (r), D – (s)
(b) A – (q), B – (p), C – (r), D – (s)
(c) A – (r), B – (s), C – (p), D – (q)
(d) A – (s), B – (r), C – (p), D – (q)

133. Match the columns

	Column-I		**Column-II**
(A)	Etard reaction	(p)	Alcoholic KOH
(B)	Hydroxylation	(q)	Anhydrous $AlCl_3$
(C)	Dehydrohalogenation	(r)	Chromyl chloride
(D)	Friedel-Crafts reaction	(s)	Dilute alkaline $KMnO_4$

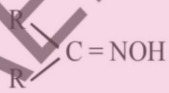
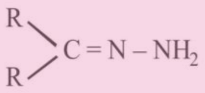
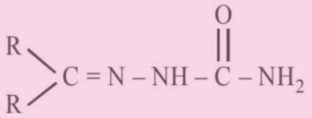
(a) A – (p), B – (q), C – (r), D – (q)
(b) A – (s), B – (r), C – (p), D – (q)
(c) A – (r), B – (s), C – (p), D – (q)
(d) A – (q), B – (p), C – (s), D – (r)

134. Match the columns

	Column-I (Reactions)		Column-II (Reagents)
(A)	Benzophenone → Diphenylmethane	(p)	$LiAlH_4$
(B)	Benzaldehyde → 1-Phenylethanol	(q)	DIBAL–H
(C)	Cyclohexanone → Cyclohexanol	(r)	Zn(Hg)/Conc HCl
(D)	Phenyl benzoate → Benzaldehyde	(s)	CH_3MgBr

(a) A – (p), B – (s), C – (r), D – (q)
(b) A – (q), B – (s), C – (p), D – (r)
(c) A – (s), B – (r), C – (q), D – (p)
(d) A – (r), B – (s), C – (p), D – (q)

135. Match the columns

	Column-I		Column-II
(A)		(p)	Oxime
(B)		(q)	Semicarbazone
(C)		(r)	Imine
(D)		(s)	Hydrazone

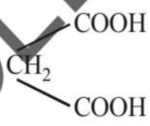
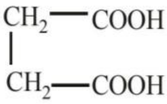
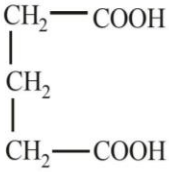
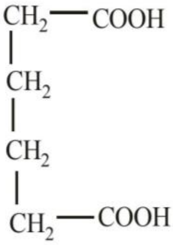
(a) A – (q), B – (s), C – (p), D – (r)
(b) A – (r), B – (p), C– (s), D– (q)
(c) A – (r), B – (s), C – (p), D– (q)
(d) A – (s), B – (r), C – (q), D– (p)

136. Match the acids given in Column-I with their correct IUPAC names given in Column-II.

	Column-I (Acids)		Column-II (IUPAC names)
(A)	Phthalic acid	(p)	Hexane-1, 6-dioic acid
(B)	Oxalic acid	(q)	Benzene-1, 2-dicarboxylic acid
(C)	Succinic acid	(r)	Pentane-1, 5-dioic acid
(D)	Adipic acid	(s)	Butane-1, 4-dioic acid
(E)	Glutaric acid	(t)	Ethane-1, 2-dioic acid

(a) A – (t), B – (q), C – (r), D – (p), E – (s)
(b) A – (p), B – (s), C – (t), D – (q), E – (r)
(c) A – (q), B – (t), C – (s), D – (p), E – (r)
(d) A – (r), B – (t), C – (p), D – (s), E – (q)

137. Match the columns

	Column-I		Column-II
(A)		(p)	Glutaric acid
(B)	 $\begin{array}{l}CH_2-COOH\\ \vert\\ CH_2-COOH\end{array}$	(q)	Adipic acid
(C)	 $\begin{array}{l}CH_2-COOH\\ \vert\\ CH_2\\ \vert\\ CH_2-COOH\end{array}$	(r)	Succinic acid
(D)	 $\begin{array}{l}CH_2-COOH\\ \vert\\ CH_2\\ \vert\\ CH_2\\ \vert\\ CH_2-COOH\end{array}$	(s)	Malonic acid

(a) A – (q), B – (p), C – (s), D – (r)
(b) A – (r), B – (p), C – (s), D – (q)
(c) A – (s), B – (r), C – (p), D – (q)
(d) A – (r), B – (q), C – (s), D – (p)

ASSERTION-REASON TYPE QUESTIONS

Directions : Each of these questions contain two statements, Assertion and Reason. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.

(a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
(c) Assertion is correct, reason is incorrect
(d) Assertion is incorrect, reason is correct.

138. **Assertion :** The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.

Reason : There is a weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.

139. **Assertion :** Formaldehyde is a planar molecule.

Reason : It contains sp^2 hybridised carbon atom.

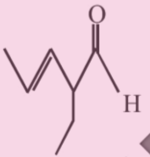
140. **Assertion :** Compounds containing –CHO group are easily oxidised to corresponding carboxylic acids.

Reason : Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.

141. **Assertion :** The molecular mass of acetic acid in benzene is 120 instead of 60.
Reason : The carboxylic acids exist as cyclic dimers in which the two molecules of the acid are held together by two strong hydrogen bonds.

CRITICAL THINKING TYPE QUESTIONS

142. IUPAC name of the following compound is



(a) 2-(2-propenyl) butanal
(b) 2-(1-propenyl) butanal
(c) 4-formyl 4-ethyl but-2-ene
(d) 2-ethyl pent-3-en-l-al

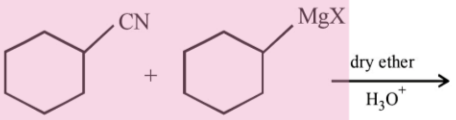
143. Observe the following structures and pick up the correct statement.

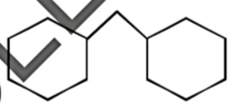
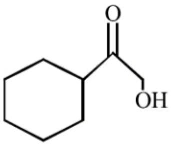
$>C=O$ (I) $>C=\overset{+}{O}H$ (II)

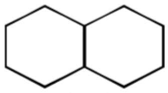
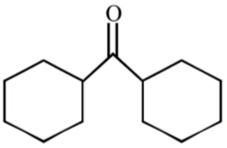
(a) Carbonyl carbon of I is more electrophilic than that of II
(b) Carbonyl carbon of I is less electrophilic than that of II
(c) Carbonyl carbon of both structures have equal electrophilic character
(d) It depends upon the complete structure of the compound

144. The boiling points of aldehydes and ketones lie in between alkanes and alcohols of comparable masses because
(a) alkanes are polar
(b) aldehydes and ketones are non-polar
(c) alkanes are non-polar and aldehydes and ketones contain polar $>C=O$ group and lower alcohols have H-bonding.
(d) alkanes are held together by weak van der Waal's forces (being non-polar), aldehydes and ketones contain polar $>C=O$ group and held together by strong dipole-dipole attraction and lower alcohols have H-bonding, which is stronger than dipole-dipole attraction.

145. Product of the following reaction is



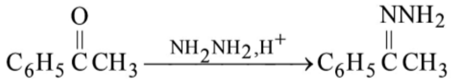
(a) 
(b) 

(c) 
(d) 

146. Which of the following reagent reacts in different ways with CH_3CHO, HCHO and C_6H_5CHO ?
(a) Fehling solution (b) $C_6H_5NHNH_2$
(c) Ammonia (d) HCl

147. A new carbon - carbon bond is formed in
(i) Aldol condensation (ii) Kolbe's reaction
(iii) Reimer-Tiemann reaction
(iv) Wurtz Fittig reaction
(a) (i) and (iii) (b) (ii) and (iii)
(c) (i), (ii) and (iiv) (d) All the four

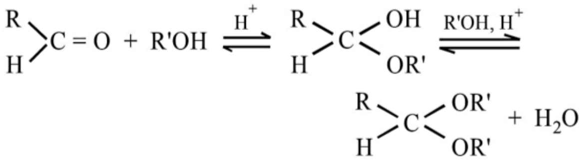
148. Which of the following is an example of nucleophilic addition ?

(a) 
$$C_6H_5\overset{\overset{O}{||}}{C}CH_3 \xrightarrow{NH_2NH_2,H^+} C_6H_5\overset{\overset{NNH_2}{||}}{C}CH_3$$

(b) 
$$C_6H_5\overset{\overset{O}{||}}{C}CH_3 \xrightarrow{LiAlH_4} C_6H_5\overset{\overset{OH}{|}}{C}HCH_3$$

(c) Both (a) and (b)
(d) None of the two

149. Acetal formation is a reversible reaction


$$\underset{H}{\overset{R}{>}}C=O + R'OH \overset{H^+}{\rightleftharpoons} \underset{H}{\overset{R}{>}}C\underset{OR'}{\overset{OH}{<}} \overset{R'OH,\ H^+}{\rightleftharpoons} \underset{H}{\overset{R}{>}}C\underset{OR'}{\overset{OR'}{<}} + H_2O$$

Under what conditions, the reaction can be forced to proceed only in right (forward) direction ?
(a) Using excess of alcohol
(b) Using high temperature
(c) Using dilute acid and excess of alcohol
(d) Using dry acid and excess of alcohol

150. In the crossed Cannizzaro reaction involving HCHO as one of the components
(a) HCHO is always oxidised because of electronic effect
(b) HCHO is always oxidised because of steric effect
(c) both of the above statements are true
(d) none of the above statement is true

151. Which of the following acts as a nucleophile in the aldol condensation of ethanal?
(i) OH^- (ii) $H_2\ddot{O}:$
(iii) $^-CH_2CHO$
(a) Only (i) (b) (i) and (ii)
(c) (i) and (iii) (d) All the three

152. Which of the following acts as a nucleophile in the Cannizzaro reaction involving benzaldehyde ?

(i) OH^- (ii) $\overset{-}{C}_6H_4CHO$

(iii) $C_6H_5CH(OH)O^-$ (iv) $H_2\ddot{O}:$

(a) (i) and (iv) (b) (i) and (ii)

(c) (i) and (iii) (d) Only (i)

153. Which of the following undergoes haloform reaction ?

(i) $CH_3CH_2COCH_2Cl$ (ii) $C_6H_5COCH_3$

(iii) $C_6H_5COCHCl_2$ (iv) $CH_3CH_2COCCl_3$

(a) Only (ii) (b) (ii) and (iv)

(c) (i), (ii) and (iv) (d) All the four

154. When ethanal reacts with propanal in the presence of a base, the number of products formed is

(a) 2 (b) 3

(c) 4 (d) 5

155. Aldehydes and ketones will not form crystalline derivatives with

(a) sodium bisulphite

(b) phenylhydrazine

(c) semicarbazide hydrochloride

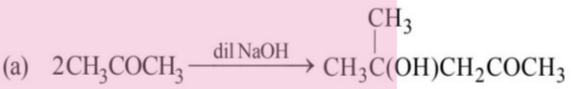
(d) dihydrogen sodium phosphate.

156. Which of the following compound will undergo self aldol condensation in the presence of cold dilute alkali ?

(a) $CH_2{=}CH-CHO$ (b) $CH{\equiv}C-CHO$

(c) C_6H_5CHO (d) CH_3CH_2CHO.

157. Which of the following is an example of aldol condensation?



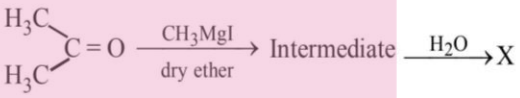
(a) $2CH_3COCH_3 \xrightarrow{\text{dil NaOH}} CH_3\overset{\overset{\large CH_3}{|}}{C}(OH)CH_2COCH_3$

(b) $2HCHO \xrightarrow{\text{dil NaOH}} CH_3OH$

(c) $C_6H_5CHO + HCHO \xrightarrow{\text{dil NaOH}} C_6H_5CH_2OH$

(d) None of the above

158. Identify X,



$(CH_3)_2C{=}O \xrightarrow[\text{dry ether}]{CH_3MgI} \text{Intermediate} \xrightarrow{H_2O} X$

(a) CH_3OH (b) Ethyl alcohol

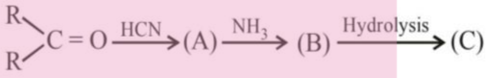
(c) Methyl cyanide (d) tert-Butyl alcohol

159. An organic compound of formula, C_3H_6O forms phenyl hydrazone, but gives negative Tollen's test. The compound is

(a) $CH_3CH_2COCH_3$ (b) CH_3CH_2CHO

(c) CH_3COCH_3 (d) Both (a) and (c)

160.



$R_2C{=}O \xrightarrow{HCN} (A) \xrightarrow{NH_3} (B) \xrightarrow{\text{Hydrolysis}} (C)$

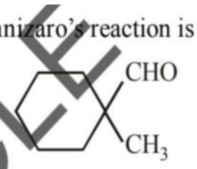
Compound (C) in above reaction is

(a) α-hydroxy acid (b) α-amino acid

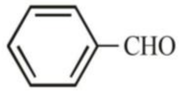
(c) α-amino alkanol (d) α-amino β-hydroxy acid

161. Cannizaro's reaction is not given by ____________

(a)



(b)



(c) HCHO (d) CH_3CHO

162. Benzophenone can be obtained by____________.

(i) Benzoyl chloride + Benzene + $AlCl_3$

(ii) Benzoyl chloride + Diphenyl cadmium

(iii) Benzoyl chloride + Phenyl magnesium chloride

(iv) Benzene + Carbon monoxide + $ZnCl_2$

(a) (i), (ii) and (iii) (b) (ii) and (iii)

(c) (iii) and (iv) (d) (i), (ii) and (iv)

163. Which of the following conversions can be carried out by Clemmensen Reduction ?

(i) Benzaldehyde into benzyl alcohol

(ii) Cyclohexanone into cyclohexane

(iii) Benzoyl chloride into benzaldehyde

(iv) Benzophenone into diphenyl methane

(a) (ii) and (iv) (b) (i) and (iv)

(c) (i) and (iii) (d) (iii) and (iv)

164. Benzaldehyde is less reactive than propanal because

(i) the carbon atom of the carbonyl group of benzaldehyde is less electrophilic as in propanal.

(ii) the carbon atom of the carbonyl group of benzaldehyde is more electrophilic as in propanal.

(iii) carbonyl group in benzaldehyde is more polar due to resonance

(iv) carbonyl group in benzaldehyde is less polar due to resonance

(a) (i) and (iii) (b) (i) and (iv)

(c) (i) only (d) (iv) only

165. Addition of hydrogen cyanide to aldehydes and ketones occurs in presence of a base.The role of base is to

(i) catalyse the reaction

(ii) generate CN^- ion

(iii) slow down the reaction

(iv) to stabilize the cyanohydrins

(a) (i) and (iii) (b) (i) and (ii)

(c) (i) and (iv) (d) (ii) and (iv)

166. Addition of alcohols to aldehydes and ketones takes place in presence of dry HCl gas because it

(i) Protonates the oxygen of the carbonyl compounds

(ii) Increases the electrophilicity of the carbonyl carbon

(iii) Removes the excess moisture from the reaction

(iv) Helps the reaction to move in the forward direction

(a) (i), (ii) and (iv) (b) (i), (ii), (iii) and (iv)

(c) (ii) ,(iii), and (iv) (d) (i), (iii) and (iv)

167. When benzaldehyde and acetaldehyde undergoes reaction with the 2, 4–DNP ?

(a) Benzaldehyde reacts slowly than acetaldehyde

(b) Acetaldehyde reacts slowly than benzaldehyde

(c) Both reacts equally

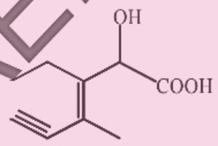
(d) Both do not react with 2, 4-DNP

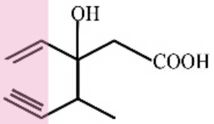
168. Suppose the reaction of compound containing ketone as functional group is carried in basic medium of NaOH. Which of the following will one use to protect the unwanted reaction due presence of carbonyl moiety.
(a) $NaHSO_3$
(b) HCN
(c) ethylene glycol and HCl
(d) None of these

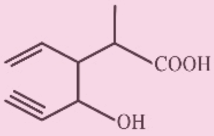
169. A compound $C_5H_{10}O$ forms orange–red precipitate upon reaction with 2,4–DNP, but does not give positive Tollen's test and iodoform test. Possible compound is
(a) 2, 2–dimethylpropanal (b) 3–methylbutan–2–one
(c) Pentan–3–one (d) None of the above

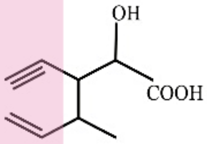
170. Nitration of the compound is carried out, this compound gives red–orange ppt. with 2,4–DNP, this compound undergoes Cannizzaro reaction but not aldol, than possible product due to nitration is
(a) 3–nitroacetophenone
(b) (2–nitro)–2–phenylethanal
(c) (2–nitro)–1–phenylpropan–2–one
(d) 3–nitrobezaldehyde

171. Structure of the compound whose IUPAC name is 3-ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid is :

(a)


(b)


(c)


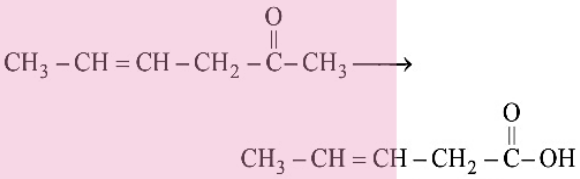
(d)


172. The end product *B* in the sequence of reactions,

$$R-X \xrightarrow{CN^-} A \xrightarrow{NaOH} B \text{ is}$$

(a) an alkane
(b) a carboxylic acid
(c) sodium salt of carboxylic acid
(d) a ketone

173. Which is the most suitable reagent for the following conversion?



$$CH_3-CH=CH-CH_2-\overset{\overset{\large O}{||}}{C}-CH_3 \longrightarrow CH_3-CH=CH-CH_2-\overset{\overset{\large O}{||}}{C}-OH$$

(a) Tollen's reagent (b) Benzoyl peroxide
(c) I_2 and NaOH solution (d) Sn and NaOH solution

174. In the given reaction,

$$(C_6H_5CO)_2O \xrightarrow{H_2O} I$$

$$C_6H_5COOCOCH_3 \xrightarrow{H_2O} II$$

Identify the product(s) formed in the given reaction.

	I	II
(a)	2 molecules of benzoic acid	2 molecules of ethanoic acid
(b)	2 molecules of benzoic acid	1 molecules of benzoic acid and 1 molecule of ethanoic acid
(c)	1 molecule of ethanoic acid	1 molecule of benzoic acid
(d)	1 molecule of benzoic acid	1 molecule of butanoic acid

175. Ethanoic acid can't be obtained by which of the following reaction ?

(i) $C_2H_5Cl \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) KCN}}$

(ii) $CH_3Cl \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) AgCN}}$

(iii) $CH_3CH=CH_2 \xrightarrow[\text{heat}]{KMnO_4\,/\,OH^-}$

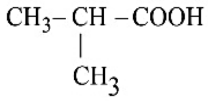
(iv) $CH_3Br \xrightarrow[\substack{\text{(ii) } CO_2 \\ \text{(iii) } H_3O^+}]{\text{(i) Mg}}$

(a) (iii) and (iv) (b) (i) and (ii)
(c) (ii) and (iii) (d) (i) and (iv)

176. Primary alcohols can be readily oxidised to carboxylic acids by.
(i) $KMnO_4$ in neutral medium.
(ii) $KMnO_4$ in acidic or alkaline medium.
(iii) $K_2Cr_2O_7$ in alkaline medium.
(iv) $K_2Cr_2O_7$ in acidic medium.
(a) (i), (ii) and (iv) (b) (i), (ii) and (iii)
(c) (ii) and (iii) (d) (i) and (iii)

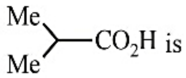
177. Which of the following is correct order of acidity?
(a) $HCOOH > CH_3COOH > ClCH_2COOH > C_2H_5COOH$
(b) $ClCH_2COOH > HCOOH > CH_3COOH > C_2H_5COOH$
(c) $CH_3COOH > HCOOH > ClCH_2COOH > C_2H_5COOH$
(d) $C_2H_5COOH > CH_3COOH > HCOOH > ClCH_2COOH$

178. An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br_2 to given $CH_3CH_2NH_2$. A is :
(a) CH_3COOH (b) $CH_3CH_2CH_2COOH$

(c)


$$\underset{\underset{\large CH_3}{|}}{CH_3-CH}-COOH$$

(d) CH_3CH_2COOH

179. The correct order of increasing acid strength of the compounds
(A) CH_3CO_2H (B) $MeOCH_2CO_2H$
(C) CF_3CO_2H (D)


is
(a) D < A < B < C (b) A < D < B < C
(c) B < D < A < C (d) D < A < C < B

180. Through which of the following reactions number of carbon atoms can be increased in the chain?

(i) Grignard reaction (ii) Cannizzaro's reaction
(iii) Aldol condensation (iv) HVZ reaction

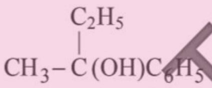
Choose the correct option.

(a) Only (iii) and (i) (b) Only (iii) and (ii)
(c) Only (iii) and (iv) (d) (i), (ii), (iii) and (iv)

181. In a set of the given reactions, acetic acid yielded a product C.

$$CH_3COOH + PCl_5 \longrightarrow A \xrightarrow[\text{Anh. }AlCl_3]{C_6H_6} B \xrightarrow[\text{Ether}]{C_2H_5MgBr} C$$

Product C would be

(a) 
$CH_3-\overset{C_2H_5}{\overset{|}{C}}(OH)C_6H_5$ (b) $CH_3CH(OH)C_2H_5$

(c) $CH_3COC_6H_5$ (d) $CH_3CH(OH)C_6H_5$

182.  $\xrightarrow{K_2Cr_2O_7+H_2SO_4}$ Z. Here Z is

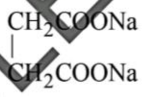
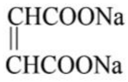
(a) 
(b) $(CH_3)_3CCOOH$
(c) Both (a) and (b)
(d) 

183. RCOOH can be reduced to RCH_2OH by

(i) $NaBH_4$ (ii) $LiAlH_4$
(iii) Na/C_2H_5OH (iv) H_2/Catalyst

(a) (ii) and (iv) (b) (i) and (iii)
(c) (i), (ii) and (iv) (d) (i), (iii) and (iv)

184. Kolbe's electrolytic method can be applied on

(i) 
$\begin{array}{l}CH_2COONa\\ |\\ CH_2COONa\end{array}$ (ii) 
$\begin{array}{l}CHCOONa\\ ||\\ CHCOONa\end{array}$

(iii) C_6H_5COOK (iv) CH_3COOK

(a) (i), (ii) and (iv) (b) (i), (ii) and (iii)
(c) (ii), (iii) and (iv) (d) (iii) and (iv)

185. Which of the following represents the correct order of the acidity in the given compounds?

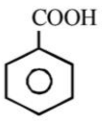
(a) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$

(b) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$

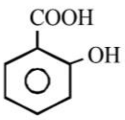
(c) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

(d) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

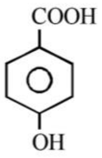
186. The correct order for the acidic character of the following carboxylic acids is



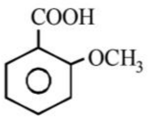
I



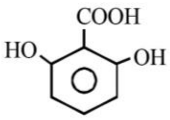
II



III



IV



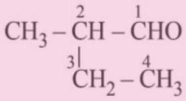
V

(a) IV > I > II > III > V (b) V > II > III > I > IV
(c) V > II > IV > III > I (d) V > II > IV > I > III

HINTS AND SOLUTIONS

FACT/DEFINITION TYPE QUESTIONS

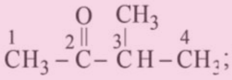
1. (b)



$$\overset{2}{C}H_3-\overset{2}{C}H-\overset{1}{C}HO \quad (\text{with } {}^{3}CH_2-{}^{4}CH_3 \text{ on C-2})$$

2. (a)

3. (c)



$$\overset{1}{C}H_3-\overset{\overset{O}{\|}}{\underset{2}{C}}-\overset{CH_3}{\underset{3}{\overset{|}{C}}}H-\overset{4}{C}H_3$$; 3-methyl-2-butanone

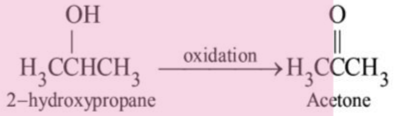
4. (c) 5. (b) 6. (a) 7. (b)

8. (b) O is more electronegative than C.

9. (d) Vanillin -vanilla beans
Salicylaldehyde - meadow sweet
Cinnamaldehyde -from cinnamon.

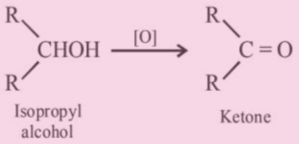
10. (d) The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant.

11. (a) Carbonyl compounds (aldehydes and ketones) are obtained by the oxidation of 1° and 2° alcohols respectively. Among the given options, only (a) is 2° alcohol hence it can be oxidized to ketone.



$$\underset{\text{2–hydroxypropane}}{H_3C\overset{OH}{\overset{|}{C}}HCH_3} \xrightarrow{\text{oxidation}} \underset{\text{Acetone}}{H_3C\overset{O}{\overset{\|}{C}}CH_3}$$

12. (b) Secondary alcohols on oxidation give ketones.
Note : Primary alcohols form aldehydes.



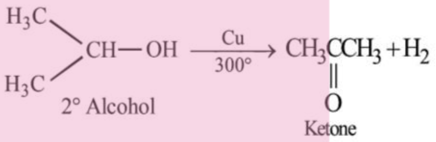
$$\underset{\text{Isopropyl alcohol}}{R_2CHOH} \xrightarrow{[O]} \underset{\text{Ketone}}{R_2C=O}$$

13. (a) 1° Alcohols on catalytic dehydrogenation give aldehydes.

$$\underset{1^\circ\text{alcohol}}{RCH_2OH} \xrightarrow[300^\circ C]{Cu} \underset{\text{Aldehyde}}{RCHO + H_2}$$

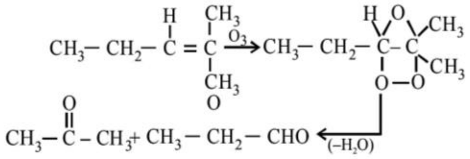
14. (a) Alcohols are oxidized by removal of H_2 in presence of a heated metal catalyst (Cu)

$$\underset{1^\circ\text{alcohol}}{CH_3CH_2OH} \xrightarrow[300^\circ]{Cu} \underset{\text{Aldehyde}}{CH_3CHO + H_2}$$

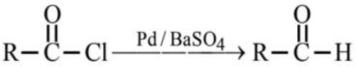


$$\underset{2^\circ\text{ Alcohol}}{(H_3C)_2CH-OH} \xrightarrow[300^\circ]{Cu} \underset{\text{Ketone}}{CH_3\underset{O}{\underset{\|}{C}}CH_3} + H_2$$

15. (a)



16. (b) Catalyst used in Rosenmund reduction is Pd/$BaSO_4$. Rosenmund reduction is used for reduction of acid chloride.



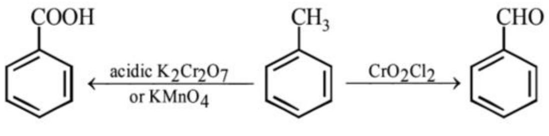
$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{Pd/BaSO_4} R-\overset{O}{\overset{\|}{C}}-H$$

17. (d) Phenyl cyanide is reduced into benzaldehyde in the presence of $SnCl_2/HCl$ reagent. This reaction is known as **Stephen's reaction**.

$$C_6H_5C\equiv N + 2[H] \xrightarrow[HCl]{SnCl_2}$$

$$C_6H_5CH=NH \xrightarrow{H_2O/H^+} C_6H_5CHO + NH_3$$

18. (c)



(Etard reaction)

Acidic $KMnO_4$ and $K_2Cr_2O_7$ oxidise toluene to benzoic acid but CrO_2Cl_2 oxidises it to benzaldehyde.

19. (c) 20. (c) 21. (b) 22. (d) 23. (b)

24. (a) 25. (d)

26. (b) Formyl chloride is unstable at room temperature.

27. (a) Alkanenitriles (other than methanenitrile) and benzonitrile give ketones with Grignard reagents.

28. (b)

29. (c) $>C=O \longleftrightarrow >\overset{+}{C}-\overset{-}{O}$; the polarity exists in carbonyl group due to resonance.

30. (a) Solubility decreases with increase in mol. wt.

31. (c) Propanone has symmetrical structure.

32. (d)

33. (b) Acetaldehyde reacts only with nucleophiles. Since the mobile p electrons of carbon–oxygen double bond are strongly pulled towards oxygen, carbonyl carbon is electron-deficient and carbonyl oxygen is electron-rich. The electron deficient (acidic) carbonyl carbon is most susceptible to attack by electron rich nucleophilic reagents, that is, by base. Hence the typical reaction of aldehydes and ketones is nucleophilic addition.

34. (c)

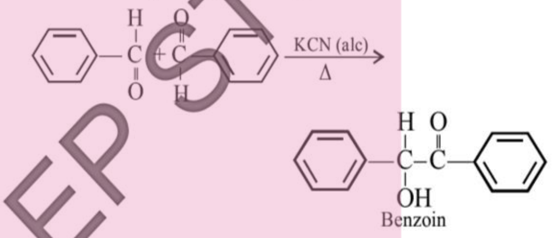
35. **(d)** Cannizzaro reaction is given by aldehydes having no α-hydrogen atom in the presence of conc. alkali, aldol condensation is given by aldehydes and ketones having at least one α-atom in presence of alkali or in presence of acids

36. **(b)** Aldehydes containing no α-hydrogen atom on warming with 50% NaOH or KOH undergo disproportionation i.e. self oxidation - reduction known as Cannizzaro's reaction.

$$2HCHO \xrightarrow{50\%\,NaOH} HCOONa + CH_3OH$$

37. **(d)** I_2 and Na_2CO_3 react with acetophenone ($C_6H_5COCH_3$) to give yellow ppt. of CHI_3 but benzophenone ($C_6H_5COC_6H_5$) does not and hence can be used to distinguish between them.

38. **(b)** When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide, two molecules of benzaldehyde condense together to form benzoin



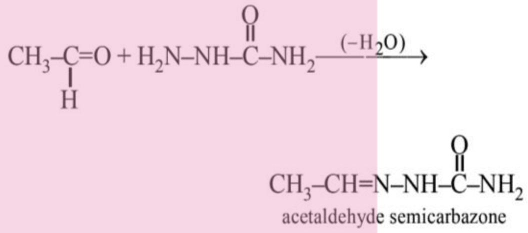
39. **(b)** $\underset{\text{Acetone}}{CH_3COCH_3} + 3I_2 + 4NaOH \longrightarrow$

$$\underset{\text{Iodoform}}{CHI_3} + 3NaI + CH_3COONa + 3H_2O$$

Thus acetone reacts with iodine to form iodoform in the presence of NaOH.

40. **(c)** Aldol condensation is given by the compounds which contain α hydrogen atom. As the given compound does not contain α hydrogen atom. Hence it does not undergo aldol condensation.

41. **(b)**

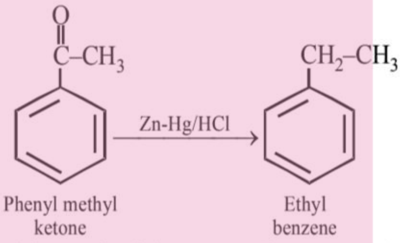


$$\underset{\displaystyle H}{\underset{|}{CH_3\text{–}C}}{=}O + H_2N\text{–}NH\text{–}\overset{O}{\overset{\|}{C}}\text{–}NH_2 \xrightarrow{(-H_2O)}$$

$$\underset{\text{acetaldehyde semicarbazone}}{CH_3\text{–}CH{=}N\text{–}NH\text{–}\overset{O}{\overset{\|}{C}}\text{–}NH_2}$$

42. **(d)** Iodoform test is exhibited by ethyl alcohol, acetaldehyde, acetone, methyl ketone and those alcohols which possess $CH_3CH(OH)$-group. As 3-pentanone does not contain CH_3CO-group therefore it does not give iodoform test.

43. **(b)**



This reaction is known as Clemmensen's reduction.

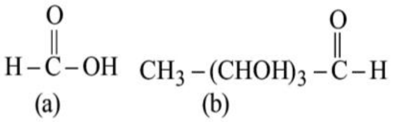
44. **(c)** $CH_3CHO + \underset{\text{Fehling solution}}{2Cu^{2+} + OH^-} \rightarrow CH_3COOH + \underset{\text{(red)}}{Cu_2O\downarrow}$

45. **(c)** Aldol condensation is given by carbonyl compounds which have α-hydrogen atoms.

∵ HCHO does not have any α-hydrogen atom, so it does not give aldol condensation.

46. **(b)** Cannizzaro reaction is given by aldehydes and ketones which do not have α-hydrogen atom. Benzaldehyde (C_6H_5CHO) does not have α-H atom and hence gives Cannizzaro reaction.

47. **(d)** Compounds having – CHO group reduce Tollen's reagent to silver mirror. It is called silver mirror test.

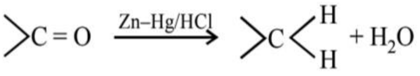


$$\underset{\text{(a)}}{H-\overset{O}{\overset{\|}{C}}-OH} \qquad \underset{\text{(b)}}{CH_3-(CHOH)_3-\overset{O}{\overset{\|}{C}}-H}$$

Both (a) and (b) have $-\overset{O}{\overset{\|}{C}}-H$ group so both of them give positive silver mirror test.

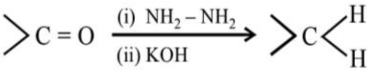
48. **(b)** Tollen's reagent is ammonical $AgNO_3$. Aldehydes form silver mirror with it and ketones do not show any change. So Tollen's reagent is used to distinguish between aldehydes and ketones.

49. **(a)** Aldehydes and ketones are reduced to alkanes by Clemmensen reduction.



$$>C=O \xrightarrow{\text{Zn–Hg/HCl}} >C<^{H}_{H} + H_2O$$

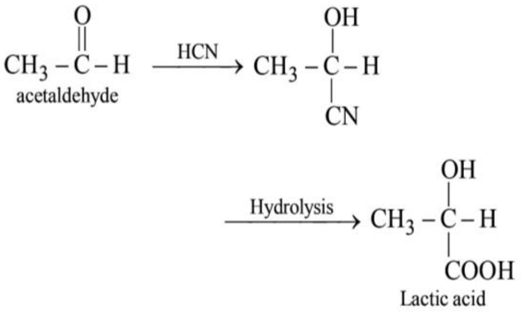
50. **(a)** Wolf- Kishner reduction



$$>C=O \xrightarrow[\text{(ii) KOH}]{\text{(i) } NH_2-NH_2} >C<^{H}_{H}$$

51. **(c)** Only aldehydes and ketones react with 2, 4-dinitrophenylhydrazine.

52. **(b)**



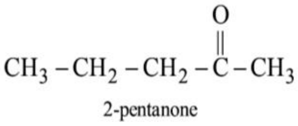
$$\underset{\text{acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{HCN} CH_3-\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H$$

$$\xrightarrow{\text{Hydrolysis}} \underset{\text{Lactic acid}}{CH_3-\underset{\underset{\displaystyle COOH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H}$$

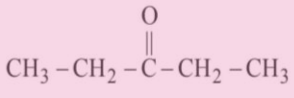
53. **(d)** HCHO does not undergo iodoform test, while acetaldehyde undergoes iodoform test (I_2 in presence of base) to form yellow precipitate of iodoform.

54. **(d)** Aldehydes can be oxidised by all the three given reagents.

55. **(c)** Iodoform test is given by compounds which have CH_3CO group.



$$\underset{\text{2-pentanone}}{CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3}$$



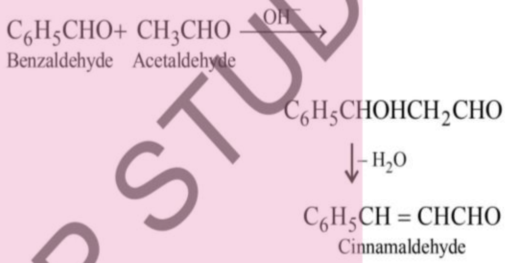
$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$$

3-pentanone

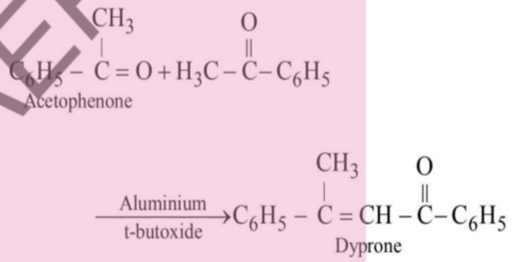
∵ 2-pentanone has CH_3CO group, so it gives iodoform test, while 3-pentanone does not have CH_3CO group, so it does not give iodoform test.

56. **(c)** In cross aldol condensation aromatic aldehydes or ketones (with or without α-hydrogen) react with aldehydes, ketones or esters having α-hydrogen atoms in the presence of dilute alkali to form a β-unsaturated carbonyl compound.

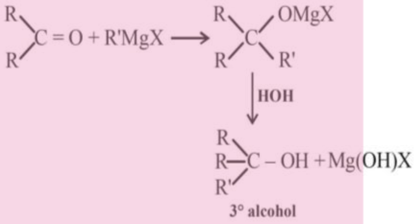
Example,

(i) 

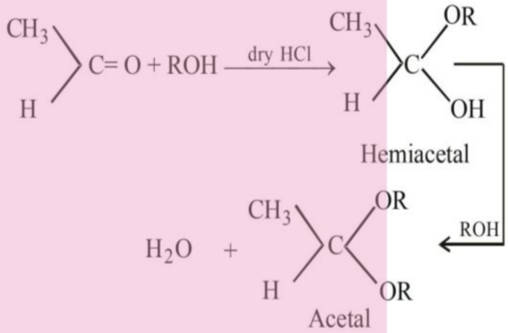
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+\underset{\text{Acetaldehyde}}{CH_3CHO}\xrightarrow{OH^-}C_6H_5CHOHCH_2CHO\xrightarrow{-H_2O}\underset{\text{Cinnamaldehyde}}{C_6H_5CH=CHCHO}$$

(ii) 

$$\underset{\text{Acetophenone}}{C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{C}=O}+H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5\xrightarrow[\text{t-butoxide}]{\text{Aluminium}}\underset{\text{Dyprone}}{C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5}$$

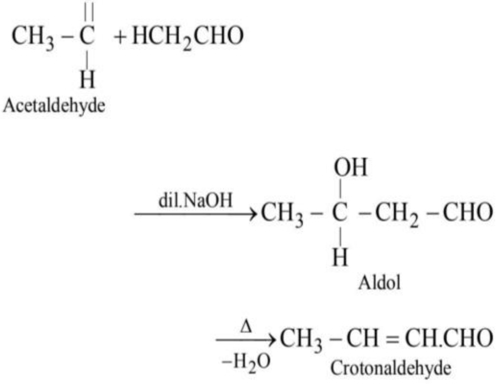
57. **(c)** 

58. **(a)** When acetaldehyde is treated with alcohol in the presence of dry HCl , then acetal is formed



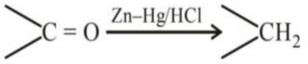
Hence, option (a) is correct.

59. **(a)** Aldehydes and ketones having at least one α-hydrogen atom in presence of dilute alkali give β-hydroxy aldehyde or β-hydroxy ketone

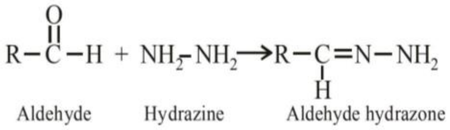


$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{C}}}+HCH_2CHO\xrightarrow{\text{dil.NaOH}}\underset{\text{Aldol}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-CHO}\xrightarrow[-H_2O]{\Delta}\underset{\text{Crotonaldehyde}}{CH_3-CH=CH.CHO}$$

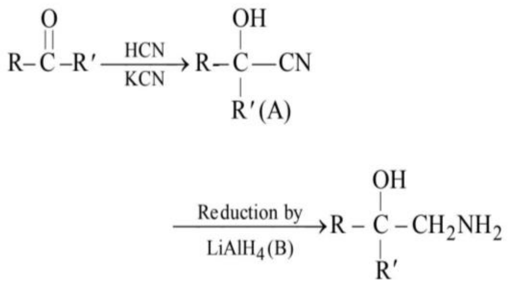
60. **(b)** Clemmensen reduction is



61. **(a)** Aldehydes, other than formaldehyde, when treated with RMgX give 2° alcohols.

62. **(a)** 

$$\underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H}+\underset{\text{Hydrazine}}{NH_2-NH_2}\longrightarrow\underset{\text{Aldehyde hydrazone}}{R-\underset{\underset{\displaystyle H}{|}}{C}=N-NH_2}$$

63. **(a)** 

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R'\xrightarrow[KCN]{HCN}R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R'(A)}{|}}{C}}-CN\xrightarrow[\text{LiAlH}_4(B)]{\text{Reduction by}}R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-CH_2NH_2$$

64. **(b)**

65. **(d)** Iodoform test is given by compounds having $CH_3CO–$ group or secondary alcohols having $CH_3–$ as one of alkyl groups, i.e., CH_3CHOHR or CH_3CH_2OH because it is readily oxidised by halogen (present in reagent) to CH_3CHO which has $CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O$ group.

66. **(d)**

67. **(a)** Aldehydes (e.g. CH_3CHO) restore the pink colour of Schiff's reagent.

68. **(a)** $C_6H_5COC_6H_5+KOH\xrightarrow{\text{fusion}}$

$$C_6H_6+C_6H_5COO^-K^+$$

69. **(c)** The nucleophile is SO_3^{--} not HSO_3^-, SO_3Na

70. **(c)** Wolf-Kishner reduction is reduction of carboxyl compound into alkane.

71. **(b)** Ammonical $AgNO_3$ is Tollen's reagent.

72. (d) **73.** (c)

74. (d) These reactions lead to replacement of oxygen atom of carbonyl group to form hydrazones and oximes.

75. (a) Cannizzaro's reaction is shown by aldehydes lacking α-H-atom. Aldol condensation reactions are shown by aldehydes having α-H-atoms.

76. (b) $NaBH_4$ selectively reduces the aldehyde group to alcohol without affecting double bond in a organic compound. So, X is $NaBH_4$.

$$C_6H_5CH=CHCHO \xrightarrow{NaBH_4} C_6H_5CH=CHCH_2OH$$

77. (a) All ketones in (i), (ii) and (iii) contain abstractable alpha–proton while all aldehydes do not contain alpha–hydrogen.

78. (a) Benzaldehyde undergoes Cannizzaro reaction, which forms benzoic acid and benzylalcohol as the product.

79. (c) **80.** (b) **81.** (a)

82. (d) Automobile exhausts are artificial source of isobutyric acid.

83. (c) Vinegar is 6 - 8% solution of acetic acid.

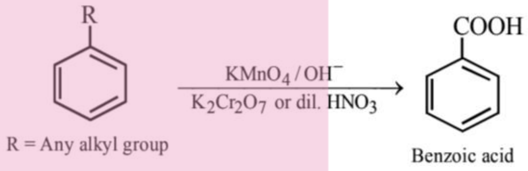
84. (b) The overall reaction involved is

$$CH_3CN \xrightarrow{H_2O} CH_3CONH_2 \xrightarrow{H_2O}$$

$$CH_3-COO^{-}\overset{\oplus}{N}H_4 \xrightarrow{HCl} CH_3COOH + NH_4Cl$$

On reduction cyanides yield 1° amines. They do not undergo decarboxylation or electrolysis.

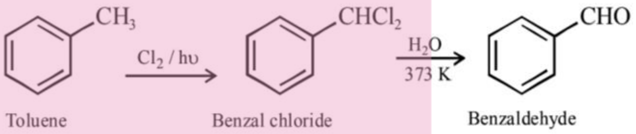
85. (a)



86. (b) Both C–O bonds are identical and each O possesses partial negative charge.

87. (c) Formic acid cannot be prepared by Grignard reagent.

88. (b)



89. (d)

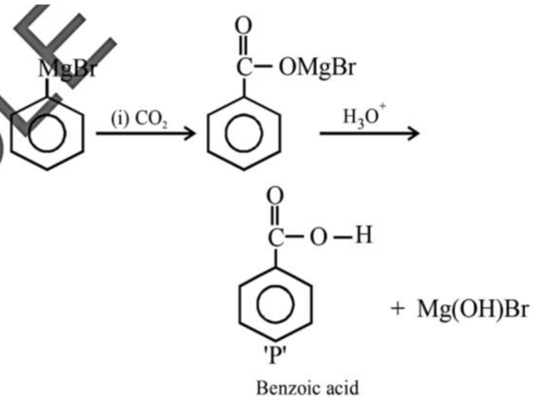
90. (c) Carbonyl group acts as a deactivating and metadirecting group.

91. (d) Primary and secondary alkyl groups oxidised to give carboxylic acid while tertiary alkyl group remain unaffected.

92. (b) **93.** (d)

94. (b) Due to H-bonding.

95. (b) Grignard reagent forms addition product with bubbled carbondioxide which on hydrolysis with HCl yields benzoic acid.



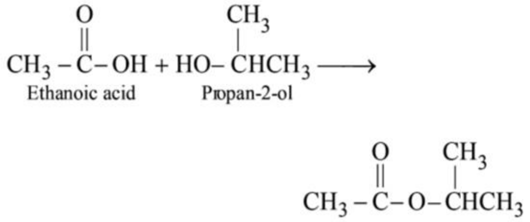
96. (c)

97. (d) In carboxylates (conjugate base of carboxylic acids), resonance is more significant because the two resonating structures are similar, while in phenoxide, the resonating structures are not equivalent, alkoxide ions do not show resonance.

98. (a) **99.** (a)

100. (c) Bromine is less electronegative than F, further in $BrCH_2CH_2COOH$, Br is more away from the –COOH group than in $CH_3CHBrCOOH$.

101. (c)



$$\underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Propan-2-ol}}{HO-\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3} \longrightarrow$$

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$$

102. (a)

103. (c) $pK_a = -\log K_a$; HCOOH is the strongest acid and hence it has the highest K_a or lowest pK_a value.

104. (c)

105. (b) $LiAlH_4$ in presence of ether can be used to convert acetic acid into ethanol.

$$\underset{\text{acetic acid}}{CH_3COOH} + 3LiAlH_4 \xrightarrow{\text{ether}}$$

$$[CH_3CH_2O]_4AlLi + 2LiAlO_2 + 4H_2$$

$$[CH_3CH_2O]_4AlLi \xrightarrow{H^+} \underset{\text{ethanol}}{CH_3CH_2OH}$$

106. (c) Carboxylic acids are weak acids.

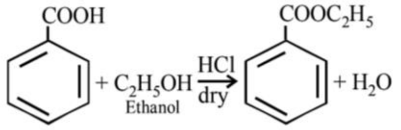
107. (c) Removal of CO_2 from carboxylic acid is called decarboxylation.

108. (b) It is a test for –COOH gp.;

$$R\text{–}COOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow.$$

109. (d)

110. (c)



This process is known as esterification.

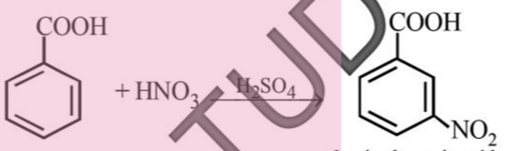
111. (c) This reaction is an example of Hell - Volhard Zelinsky reaction. In this reaction acids containing α – H on treatment with X_2 /P give di-halo substituted acid.

$$CH_3-CH_2COOH \xrightarrow{Br_2/P} CH_3-CBr_2-COOH$$

112. (c) $3CH_3COOH + PCl_3 \longrightarrow \underset{\text{Acetyl Chloride}}{CH_3COCl} + \underset{\text{Phosphorous acid}}{H_3PO_3}$

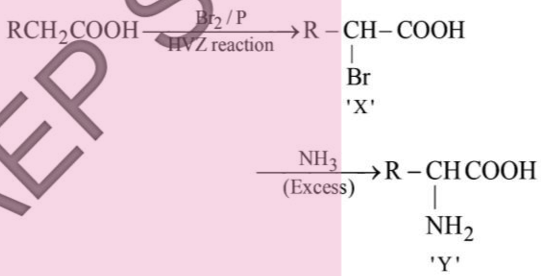
113. (b)

114. (a) –COOH group when attached to benzene ring deactivates the ring and substitution occurs at m-position. (HNO_3 + H_2SO_4) is a source of $^+NO_2$ (electrophile) which attacks at m-position.



3- nitrobenzoic acid

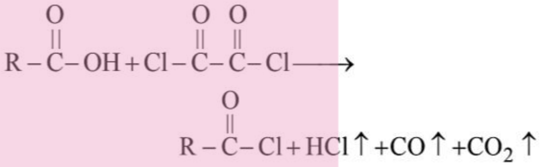
115. (b)



$$RCH_2COOH \xrightarrow[\text{HVZ reaction}]{Br_2/P} \underset{\text{'X'}}{R-\underset{\substack{|\\Br}}{CH}-COOH} \xrightarrow[\text{(Excess)}]{NH_3} \underset{\text{'Y'}}{R-\underset{\substack{|\\NH_2}}{CH}COOH}$$

116. (d) The yield of product in a reversible reaction can be increased by (i) removing one of the products, (ii) taking either of the reactant in excess.

117. (d) Use of $SOCl_2$ and ClCOCOCl forms gaseous by-products which can be easily removed, giving better yield of RCOCl. Further, oxalyl chaloride is particularly easy to use becasue any excess of it can be easily evaporated due to its low b.p. (62°C)



$$R-\overset{\overset{O}{||}}{C}-OH+Cl-\overset{\overset{O}{||}}{C}-\overset{\overset{O}{||}}{C}-Cl \longrightarrow R-\overset{\overset{O}{||}}{C}-Cl+HCl\uparrow+CO\uparrow+CO_2\uparrow$$

118. (b)

119. (a) Salicylic acid, because it stabilizes the corresponding salicylate ion by intramolecular H-bonding.

120. (c) $Cl_2CHCOOH$ is most acidic because it has two chlorine at α-position.

121. (a) An electron releasing substituent (+I) intensify the negative charge on the anion resulting in the decrease of stability and thus decreases the acidity of the acid. Hence acid character decreases as the + I-effect of the alkyl group increases as

$$CH_3^- < CH_3CH_2^- < CH_3CH_2CH_2^- < CH_3CH_2CH_2CH_2^-$$

Hence the order becomes : (i) > (ii) > (iii) > (iv)

122. (c) Chlorine is electron withdrawing group. Further inductive effect is stronger at α position than β-position. i.e.,

$$\overset{\alpha}{C}H_2ClCOOH > \overset{\beta}{C}H_2\,Cl\overset{\alpha}{C}H_2\,COOH$$

123. (b)

STATEMENT TYPE QUESTIONS

124. (b) Carbonyl compounds have substantial dipole moments and are polar in nature. The high polarity of the carbonyl group is due to resonance.

125. (a) Primary alcohols on oxidation give carboxylic acids as the final product, of course through aldehydes. Oppenauer oxidation involves oxidation of 2° alcohols to ketones, and not for the oxidation of 1° alcohols.

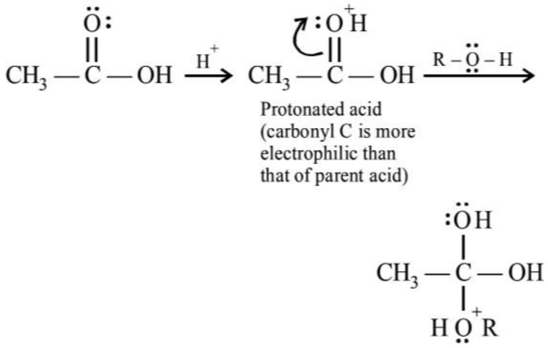
126. (c) If the aldehyde has a boiling point less than 100°C, it can be prepared by the oxidation of 1° alcohols with regular oxidising agents like acidic permanganate or dichromate. Since the aldehyde has a lower boiling point than the alcohol, it is distilled off as soon as it is formed ; so further oxidation to a carboxylic acid is minimized.

127. (d) The solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.

128. (a) Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively than in former.

129. (b) The hydrogen atom that is added to the carbonyl carbon of the aldehyde in the reduction is derived directly from the other aldehyde molecule as a hydride ion. The second hydrogen that is added to the negatively charged oxygen is coming from the solvent (consult mechanism of Cannizzaro reaction). Oxidation of one molecule of the compound at the expense of other molecule of the same compound is known as disproportionation.

130. (b) First two steps of the esterification make the question clear



MATCHING TYPE QUESTIONS

131. (a) 132. (c) 133. (b) 134. (d) 135. (b)
136. (c) 137. (c)

ASSERTION-REASON TYPE QUESTIONS

138. (a) 139. (a) 140. (b)

141. (a) The molecular mass of acetic acid in benzene is 120 instead of 60 because the carboxylic acids exists as cyclic dimers in which two molecules of the acid are held together by two strong hydrogen bond.

CRITICAL THINKING TYPE QUESTIONS

142. (d)

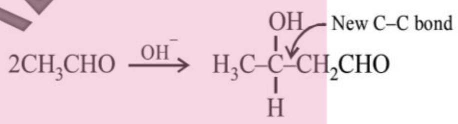
143. (b) In structure II, presence of positive charge on oxygen causes the displacement of π electrons toward oxygen, making carbon more electron deficient than that in unprotonated carbonyl group.

144. (c) It is the reason for the given fact.

145. (d)

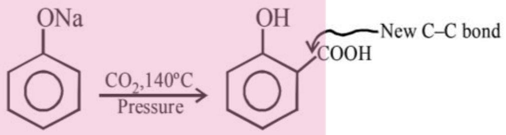
146. (c) With ammonia, HCHO forms hexamethylenetetramine, CH_3CHO gives acetaldehydeammonia addition product, while C_6H_5CHO gives hydrobenzamide.

147. (d) Aldol condensation :

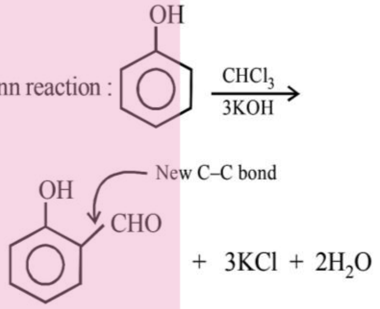


$$2CH_3CHO \xrightarrow{OH^-} H_3C-\overset{OH}{\underset{H}{C}}-CH_2CHO$$

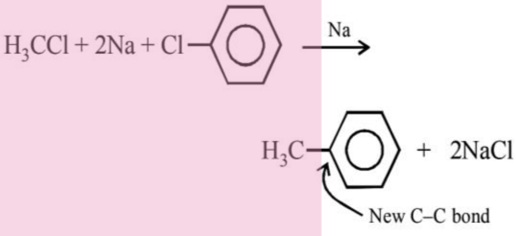
Kolbe reaction :



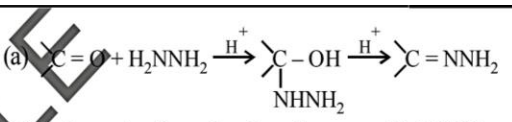
Reimer-Tiemann reaction :



Wurtz Fittig reaction :

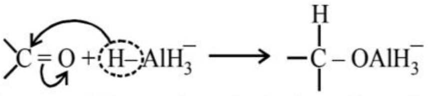


148. (c) (a)



$$>C=O+H_2NNH_2 \xrightarrow{H^+} >\underset{NHNH_2}{C}-OH \xrightarrow{H^+} >C=NNH_2$$

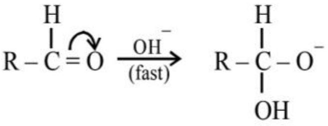
(b) In the reduction of carbonyl group with $LiAlH_4$ or $NaBH_4$, a hydride ion is transferred from the metal to the carbonyl carbon (nucleophilic addition)



$$>C=O+H-AlH_3^- \longrightarrow -\overset{H}{\underset{|}{C}}-OAlH_3^-$$

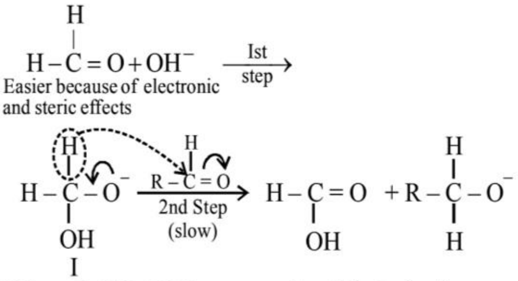
149. (d) Being reversible reaction, the backward reaction i.e. acetal -hemiacetal step can be restricted by minimizing water content, i.e. by using dry HCl. The step hemiacetal - aldehyde can be restricted by using excess of alcohol.

150. (c) First step in Cannizzaro reaction is the nucleophilic addition of OH^- on the carbonyl carbon.

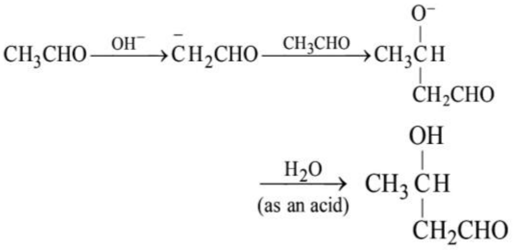


$$R-\overset{H}{C}=O \xrightarrow[\text{(fast)}]{OH^-} R-\overset{H}{\underset{OH}{C}}-O^-$$

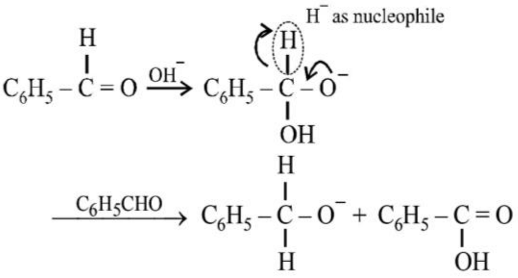
Higher the electron deficiency on cabonyl carbon, more easier will be the attack of the nucleophile (OH^-) on its carbon. Futher, the attack of OH^- on the carbonyl carbon is more easy in case of HCHO because its carbon is least hindered having two hydrogens (steric effect). Thus the intermediate I is formed very easily which donates hydride ion to another aldehyde and thus itself oxidised.



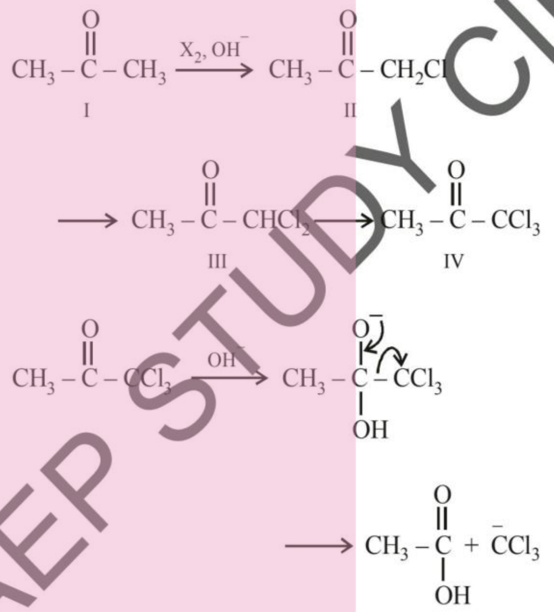
151. (c) OH^- and $^-CH_2CHO$ act as nucleophile in the first two steps.



152. (c)



153. (d) If we observe the haloform reaction carefully, we see that $-COCH_3$ group is first halogenated to the trihalo $-COCX_3$ through monohalogeno and dihalogeno compound. It is the $-COCX_3$ part which then undergoes nucleophilic addition. The product easily loses $-CX_3$ since it is a very good leaving group.



$$\underset{I}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow{X_2,\,OH^-} \underset{II}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2Cl}$$

$$\longrightarrow \underset{III}{CH_3-\overset{\overset{O}{\|}}{C}-CHCl_2} \longrightarrow \underset{IV}{CH_3-\overset{\overset{O}{\|}}{C}-CCl_3}$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CCl_3 \xrightarrow{OH^-} CH_3-\underset{OH}{\overset{O^-}{C}}-CCl_3$$

$$\longrightarrow CH_3-\underset{OH}{\overset{\overset{O}{\|}}{C}} + \overset{-}{C}Cl_3$$

Thus all compounds (I to IV) are ultimately converted to $CHCl_3$ (chloroform).

154. (c) $2CH_3CHO \longrightarrow 1^{st}$ Product,

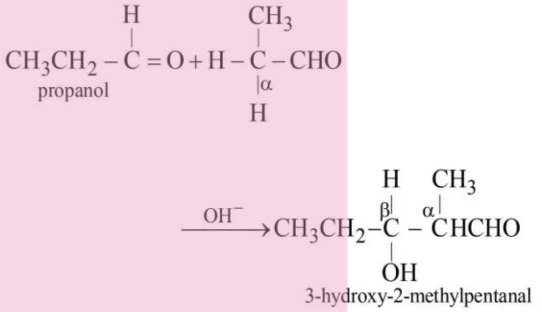
$2\,CH_3CH_2CHO \longrightarrow 2^{nd}$ Product

$CH_3CH_2CHO + \overset{\alpha}{C}H_3CHO \longrightarrow 3^{rd}$ Product;

$CH_3\overset{\alpha}{C}H_2CHO + CH_3CHO \longrightarrow 4^{th}$ Product

155. (d) Dihydrogen sodium phosphate (NaH_2PO_4) does not have a lone pair of electrons on the P atom. As such it can not act as a nucleophile and hence does not react with aldehydes and ketones.

156. (d) Aldehydes which contain a α-hydrogen on a saturated carbon, i.e., CH_3CH_2CHO undergo aldol condensation.



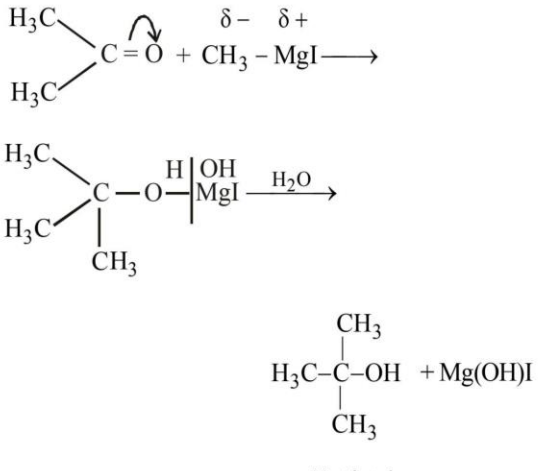
$$\underset{\text{propanol}}{CH_3CH_2-\overset{H}{C}=O} + H-\underset{H}{\overset{CH_3}{C}}{}_{\alpha}-CHO \xrightarrow{OH^-} CH_3CH_2-\underset{OH}{\overset{H}{\overset{\beta}{C}}}-\overset{CH_3}{\overset{\alpha}{C}}HCHO$$

3-hydroxy-2-methylpentanal

157. (a) Aldol condensation involves an aldehyde or ketone having an α–hydrogen atom. This type of condensation occurs in presence of dilute base (i.e., dil NaOH).

Only CH_3COCH_3 will give aldol condensation (Both HCHO and C_6H_5CHO lack α-hydrogen).

158. (d)

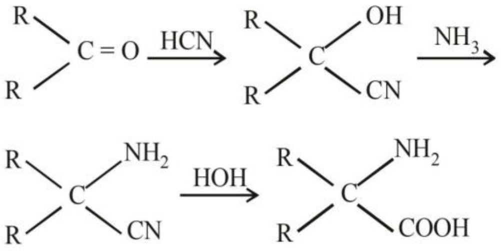


$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>C=O + \overset{\delta-}{CH_3}-\overset{\delta+}{MgI} \longrightarrow \begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\underset{CH_3}{C}-O-\overset{H|OH}{|MgI} \xrightarrow{H_2O} H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH + Mg(OH)I$$

Tert butyl alcohol

159. (d) Ketones do not respond to Tollen's test. Aldehydes respond to Tollen's test.

160. (b)



$$\begin{matrix}R\\R\end{matrix}\!\!>C=O \xrightarrow{HCN} \begin{matrix}R\\R\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\CN\end{matrix} \xrightarrow{NH_3} \begin{matrix}R\\R\end{matrix}\!\!>C<\!\!\begin{matrix}NH_2\\CN\end{matrix} \xrightarrow{HOH} \begin{matrix}R\\R\end{matrix}\!\!>C<\!\!\begin{matrix}NH_2\\COOH\end{matrix}$$

161. (d) **162. (a)** **163. (a)**

164. (b) The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.

165. (b) Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. This reaction occurs very slowly with pure HCN. Therefore, it is catalysed by a base and the generated cyanide ion (CN^-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrins

166. (b) Dry hydrogen chloride protonates the oxygen of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon facilitating the nucleophilic attack by the alcohol molecule. Dry HCl gas also absorbs the water produced in these reactions thereby shifting the equilibrium in the forward direction.

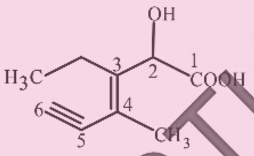
167. (a) Because of resonance in benzaldehyde which is not possible in case of acetaldehyde the positive charge on the carbonyl carbon decreases and hence there is decrease in reactivity.

168. (c) Acetal formed upon reaction of ethylene glycol and HCl, which is unaffected by base hence unwanted reaction does not occur due to presence of carbonyl group.

169. (c) 2, 2-dimethyl propanal gives Tollen's test and 3-methylbutan-2-one gives iodoform test.

170. (d)

171. (a)



IUPAC name of the structure is 3-ethyl-2-hydroxy -4-methylhex-3-en-5-ynoic acid.

172. (c) $R-X \xrightarrow{CN^-} R-CN \xrightarrow{NaOH} RCOONa$

173. (c)

174. (b) $(C_6H_5CO)_2O \xrightarrow{H_2O} 2C_6H_5-COOH$

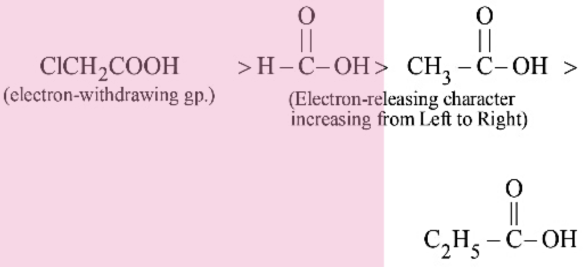
benzoic anhydride — benzoic acid

$C_6H_5COOCOCH_3 \xrightarrow{H_2O} C_6H_5COOH + CH_3COOH$

bezoyl ethanoic anhydride — benzoic acid — ethanoic acid

175. (b) **176. (a)**

177. (b) Recall that presence of electron-withdrawing group increases, while presence of electron-releasing group decreases the acidity of carboxylic acids.



$$ClCH_2COOH > H-\overset{\overset{O}{||}}{C}-OH > CH_3-\overset{\overset{O}{||}}{C}-OH > C_2H_5-\overset{\overset{O}{||}}{C}-OH$$

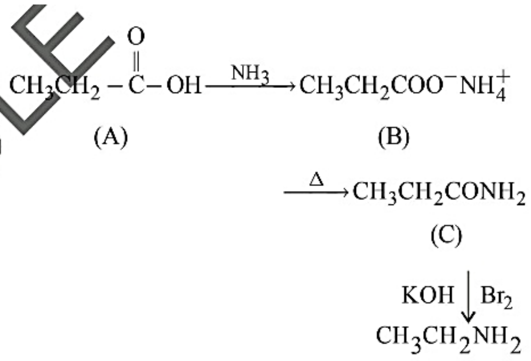
(electron-withdrawing gp.)

(Electron-releasing character increasing from Left to Right)

178. (d) $A \xrightarrow[(I)]{NH_3} B \xrightarrow[II]{\Delta} C \xrightarrow[KOH,(III)]{Br_2} CH_3CH_2NH_2$

Reaction (III) is a Hofmann bromamide reaction. Now formation of $CH_3CH_2NH_2$ is possible only from a compound $CH_3CH_2CONH_2$(C) which can be obtained from the compound $CH_3CH_2COO^-NH_4^+$(B).

Thus (A) should be CH_3CH_2COOH



$$CH_3CH_2-\overset{\overset{O}{||}}{C}-OH \xrightarrow{NH_3} CH_3CH_2COO^-NH_4^+ \xrightarrow{\Delta} CH_3CH_2CONH_2 \xrightarrow[KOH]{Br_2} CH_3CH_2NH_2$$

(A) (B) (C)

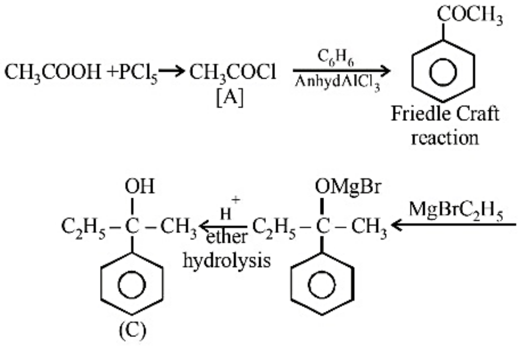
179. (a) The correct order of increasing acid strength

$$CF_3COOH > MeOCH_2COOH > CH_3COOH > (Me)_2CH.COOH$$

Electron withdrawing groups increase the acid strength and electron donating groups decrease the acid strength.

180. (a) Grignard reagents and nitriles are useful for converting alkyl halide into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides.

181. (a)



182. (c) An alkyl group attached to benzene ring can be oxidised only when it contains at least one α-hydrogen atom. Thus here $-CH_3$ group is oxidised and Me_3C- group not. However, Me_3C- group may cause oxidation of the benzene ring to $-COOH$.

183. (a) **184. (a)**

185. (c) Electron withdrawing substituent (like halogen, $-NO_2$, C_6H_5 etc.) would disperse the negative charge and hence stabilise the carboxylate ion and thus increase acidity of the parent acid. On the other hand, electron-releasing substituents would intensify the negative charge, destabilise the carboxylate ion and thus decrease acidity of the parent acid.

Electronegativity decreases in order

$$F > Cl > Br$$

and hence –I effect also decreases in the same order, therefore the correct option is

$$[FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH]$$

186. (d) V is most stable because its anion is stabilized to a greater extent through H – bonding with H atom of OH present on both *ortho*-positions ; followed by II in which one OH group is present. Compound IV comes next to II because here –OCH_3 group is present in *ortho* position which although is not capable of forming H–bonding yet more acidic than *p*-HOC_6H_4COOH (III) due to ortho effect. Compound III is less acidic than benzoic acid because of electron-releasing group in the para position. Thus