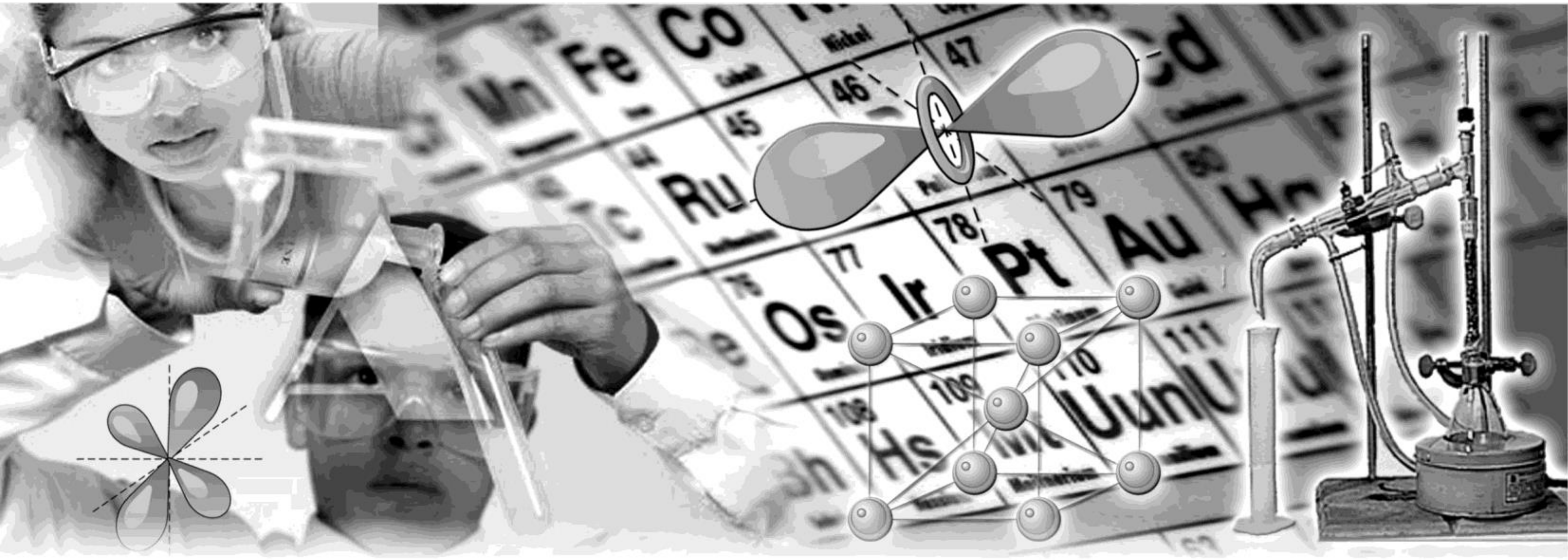


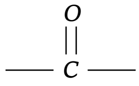
Chapter

27

Aldehydes and Ketones

Introduction

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



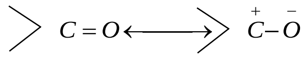
$$-\overset{\overset{\large O}{||}}{C}-$$

Carbonyl group

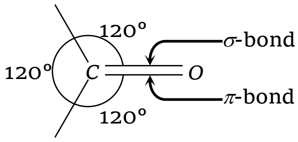
Both aldehyde and ketones possess the same general formula $C_nH_{2n}O$.

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.

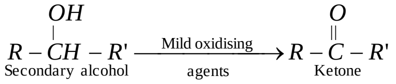


$$>C=O \longleftrightarrow >\overset{+}{C}-\overset{-}{O}$$

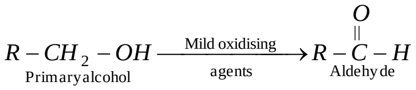


Preparation of carbonyl compounds

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



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



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

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*.**

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

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

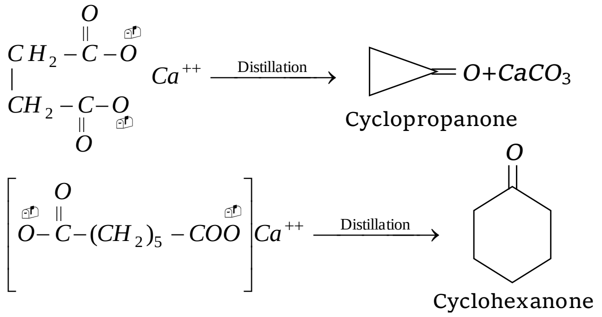
(2) **From carboxylic acids**

(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.

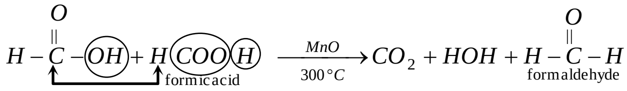


(ii) ***Decarboxylation or Dehydration of acids by MnO/300°C*.**

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

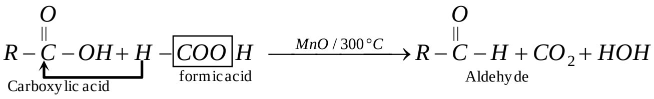
(b) If one of the carboxylic acids is $HCOOH$ then this acid undergoes decarboxylation because this acid is the only monobasic acid which undergoes decarboxylation even in the absence of catalyst.

Case I : When both molecules are $HCOOH$



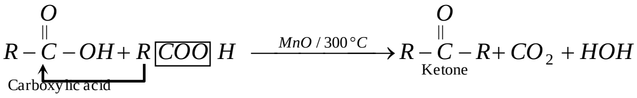
$$H-\overset{\overset{O}{\|}}{C}-OH+\underbrace{H\,COO\,H}_{\text{formic acid}} \xrightarrow[300°C]{MnO} CO_2+HOH+\underbrace{H-\overset{\overset{O}{\|}}{C}-H}_{\text{formaldehyde}}$$

Case II : When only one molecule is formic acid.



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

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



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

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

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

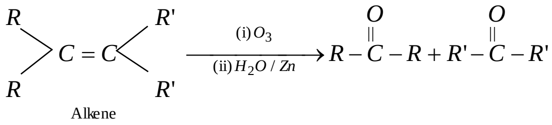
(ii) $$R-\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}}-R' \xrightarrow{HOH/\overset{\ominus}{O}H} R-\overset{\overset{O}{\|}}{C}-R'$$

❑ *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

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



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

(ii) ***Oxo process***

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

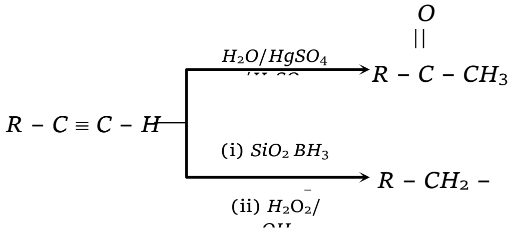
❑ *Oxo process is used only for the preparation of aldehydes.*

(iii) ***Wacker process***

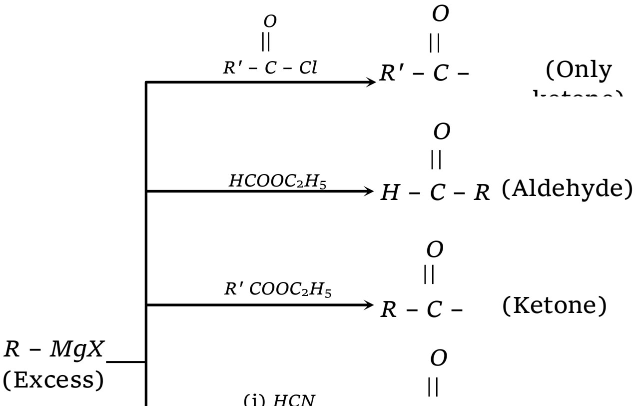
(a) $$\underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow[\text{air}/Cu_2Cl_2]{PdCl_2/HOH} CH_3-CHO$$

(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**

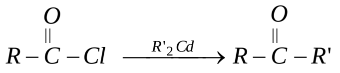


(6) **From Grignard reagents**

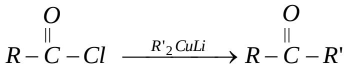


(7) **From acid chloride**

(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.



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

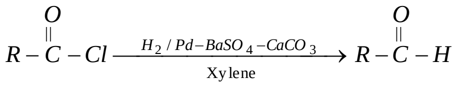


$$R-\overset{\overset{O}{||}}{C}-Cl \xrightarrow{R'_2CuLi} R-\overset{\overset{O}{||}}{C}-R'$$

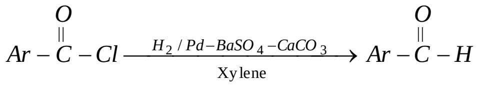
(Only used for the preparation of ketones)

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.



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

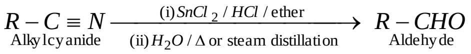


$$Ar-\overset{\overset{O}{||}}{C}-Cl \xrightarrow[\text{Xylene}]{H_2/Pd-BaSO_4-CaCO_3} Ar-\overset{\overset{O}{||}}{C}-H$$

(Only used for aldehydes)

(8) **From cyanides**

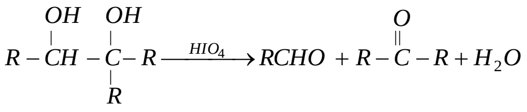
(i) ***Stephen aldehyde synthesis*** **:** Conversion of cyanides into aldehydes by partial reduction with $SnCl_2/HCl$, followed by hydrolysis, is known as Stephens aldehyde synthesis.



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

(Only used for aldehydes)

(9) **From vic diols**



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

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

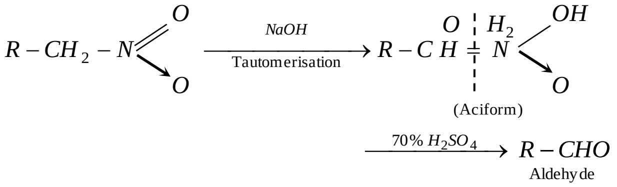
(10) **From Alkyl halides and benzyl halides**

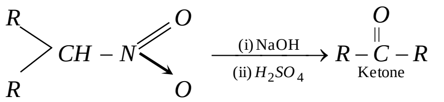
$$R-CH_2Cl \xrightarrow{DMSO} R-CHO \;;$$

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

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

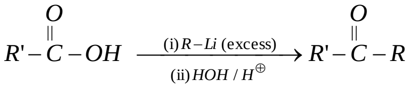
(11) **From nitro alkanes :** Nitro alkanes having at least one α -hydrogen atom give carbonyl compounds on treatment with conc $NaOH$ followed by 70% H_2SO_4. The reaction is known as **Nef** carbonyl synthesis.





(Iso-nitro alkane)

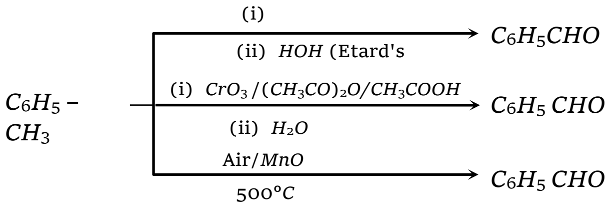
(12) **Reaction with excess of alkyl lithium :** Carboxylic acids react with excess of organo lithium compound to give lithium salt of gem diols which on hydrolysis give ketones.



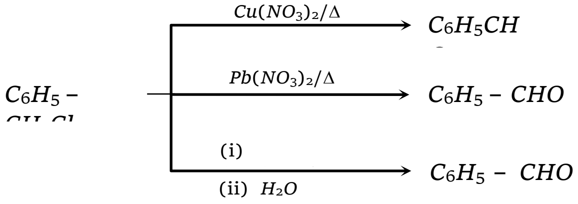
$$R'-\overset{\overset{O}{||}}{C}-OH \xrightarrow[\text{(ii)}HOH/H^{\oplus}]{\text{(i)}R-Li\text{ (excess)}} R'-\overset{\overset{O}{||}}{C}-R$$

Preparation of only aromatic carbonyl compounds

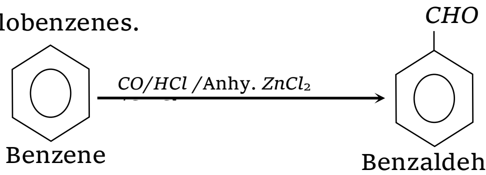
(1) **From methyl arenes**



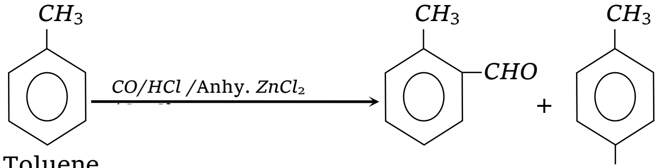
(2) **From chloro methyl**



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

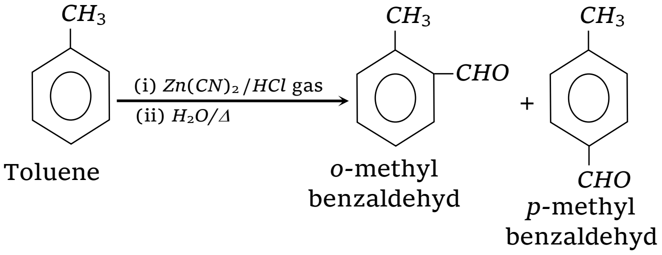


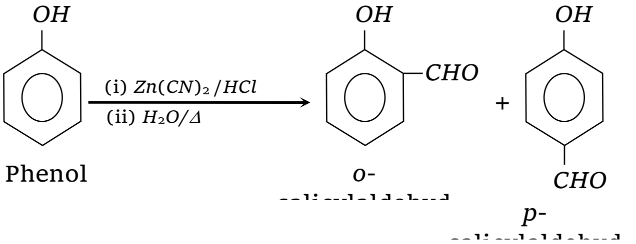
Benzene Benzaldehyde

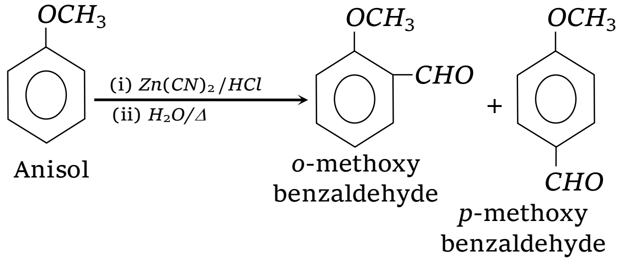


Toluene *o*-methyl benzaldehyde *p*-methyl benzaldehyde

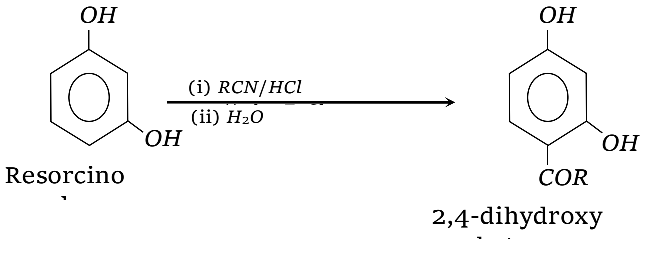
(4) **Gattermann formylation :** This reaction is mainly given by alkyl benzenes, phenols and phenolic ethers.

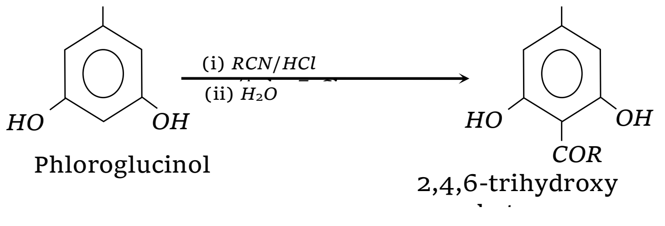




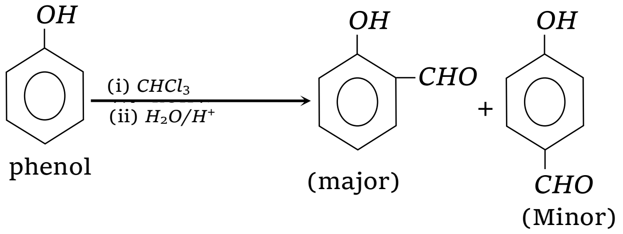


(5) **Houben – Hoesch reaction :** This reaction is given by *di* and polyhydric benzenes.





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

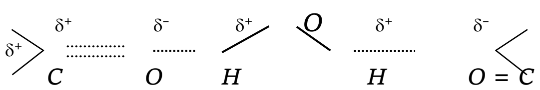


Physical properties of carbonyl compounds

(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.

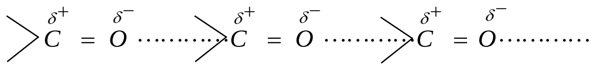
(2) **Smell :** With the exception of lower aldehydes which have unpleasant odours, aldehydes and ketones have generally pleasant smell. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones have been used in blending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



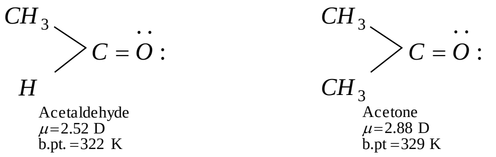
With the increase in the size of alkyl group, the solubility decreases and the compounds with more than four carbon atom are practically insoluble in water. All aldehydes and ketones are, however, soluble in organic solvents such as ether, alcohol, etc. The ketones are good solvents themselves.

(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.



(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

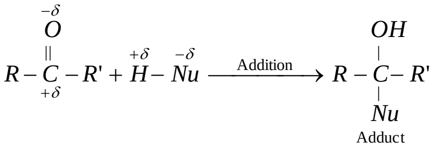
(7) Miscellaneous reactions

(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,

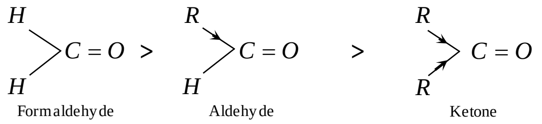


$$R-\overset{\overset{-\delta}{O}}{\underset{+\delta}{\overset{\|}{C}}}-R' + \overset{+\delta}{H}-\overset{-\delta}{Nu} \xrightarrow{\text{Addition}} \underset{\text{Adduct}}{R-\overset{\overset{OH}{|}}{\underset{\underset{Nu}{|}}{C}}-R'}$$

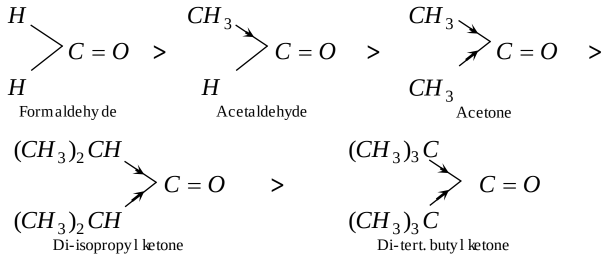
In addition reactions nucleophile adds on carbonyl carbon and electrophile on carbonyl oxygen to give adduct.

(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:

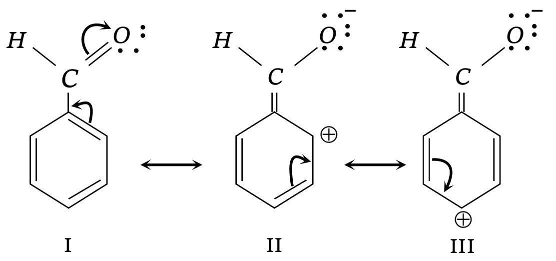
(a) *Inductive effect* : The relative reactivities of aldehydes and ketones in nucleophilic addition reactions may be attributed to the amount of positive charge on the carbon. *A greater positive charge means a higher reactivity*. If the positive charge is dispersed throughout the molecule, the carbonyl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

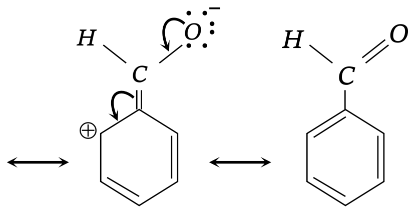


(b) *Stearic effect* : The size of the alkyl group is more than that of hydrogen. In aldehydes, there is one alkyl group but in ketones, there are two alkyl groups attached to the carbonyl group. The alkyl groups are larger than a hydrogen atom and these cause hindrance to the attacking group. This is 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:



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:





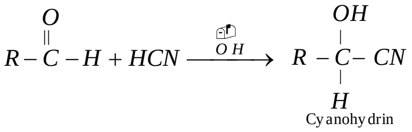
IV V

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,

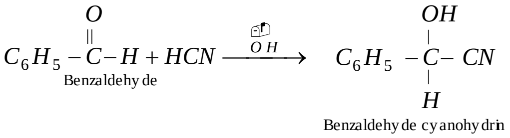
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} > \underset{\text{Acetophenone}}{C_6H_5COCH_3} > \underset{\text{Benzopheno ne}}{C_6H_5COC_6H_5}$$

Some important examples of nucleophilic addition reactions

Addition of *HCN*



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



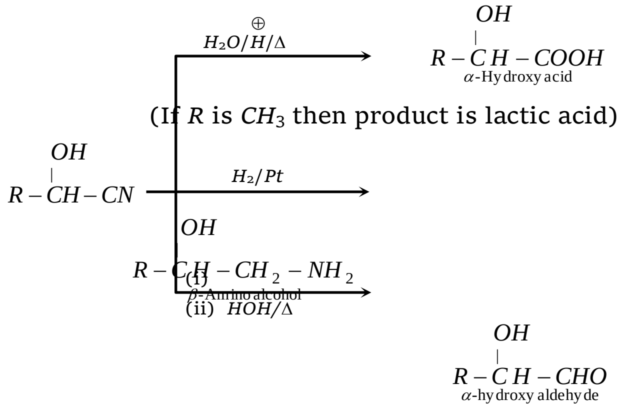
$$\underset{\text{Benzaldehyde}}{C_6H_5-\overset{\overset{O}{\|}}{C}-H} + HCN \xrightarrow{\overset{\ominus}{O H}} \underset{\text{Benzaldehyde cyanohydrin}}{C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CN}$$

❑ *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).*

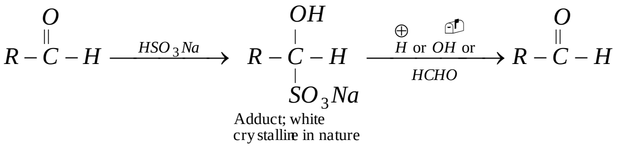
❑ *This reaction is synthetically useful reaction for the preparation of α-hydroxy acids, β-amino alcohols and α-hydroxy aldehydes.*



(If R is CH_3 then product is lactic acid)

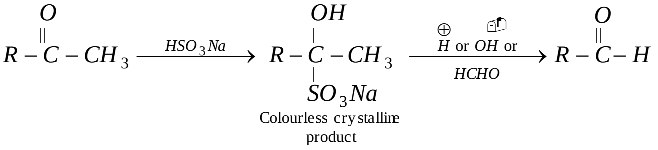
Addition of sodium bisulphite

All types of aldehydes give addition reaction with this reagent.



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

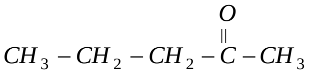
Only aliphatic methyl ketones give addition reaction with sodium bisulphite.



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

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

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

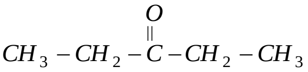


$$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

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

❑ *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*

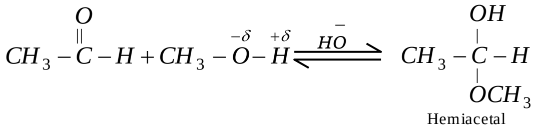


$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

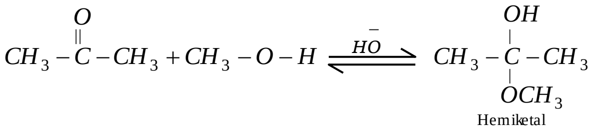
These two compounds can be separated from their mixture by the use of $NaHSO_3$. Higher aliphatic ketones and aromatic ketones do not react with $NaHSO_3$.

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

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



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

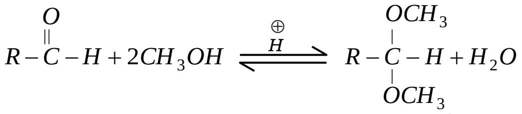


$$CH_3-\overset{O}{\overset{||}{C}}-CH_3+CH_3-O-H \overset{H\bar{O}}{\rightleftharpoons} CH_3-\underset{OCH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_3$$

Hemiketal

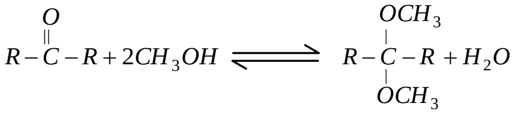
Hemiacetals and hemiketals are **α-alkoxy alcohols**.

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).



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

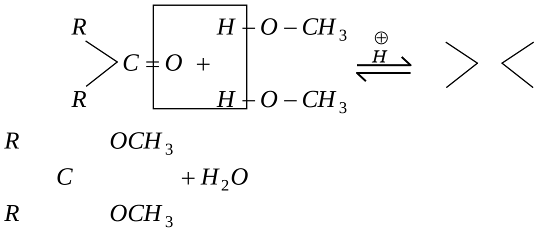
Acetal



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

Ketal

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

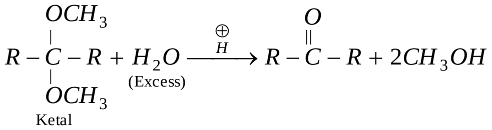


$$\begin{matrix} R & & H-O-CH_3 \\ & >C=O\ + & \\ R & & H-O-CH_3 \end{matrix} \underset{H}{\overset{\oplus}{\rightleftharpoons}} \begin{matrix} R & & OCH_3 \\ & C & & +H_2O \\ R & & OCH_3 \end{matrix}$$

(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.

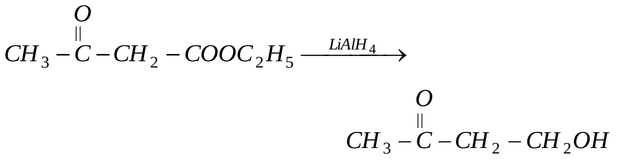
(iv) Acetals and ketals can be transformed back to corresponding aldehyde or ketone in the presence of excess of water.



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

Ketal

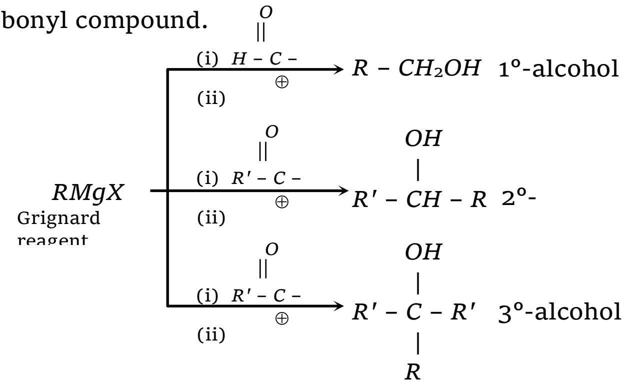
This reaction is very useful reaction for the protection of carbonyl group which can be deprotected by hydrolysis. Glycol is used for this purpose. Suppose we want to carry out the given conversion by $LiAlH_4$.



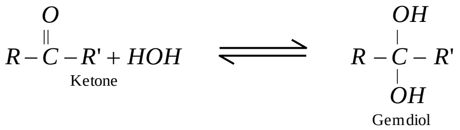
$$CH_3-\overset{O}{\overset{||}{C}}-CH_2-COOC_2H_5 \xrightarrow{LiAlH_4} CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_2OH$$

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.



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

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:

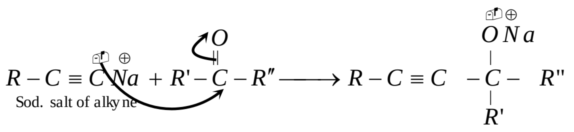
(i) Steric hindrance by $+I$ group around α-carbon decreases the stability of gem diols. $+I$ group decreases stability of gem diol and hence decreases extent of hydration.

(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.

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

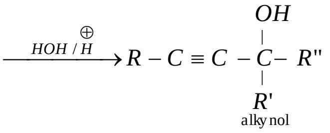
More is the strength of hydrogen bond more will be the stability of gem diol.

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



$$R-C\equiv\overset{\ominus}{C}\overset{\oplus}{Na}+R'-\overset{O}{\overset{||}{C}}-R'' \longrightarrow R-C\equiv C-\underset{R'}{\overset{\overset{\ominus\ \oplus}{ONa}}{\underset{|}{\overset{|}{C}}}}-R''$$

Sod. salt of alkyne



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

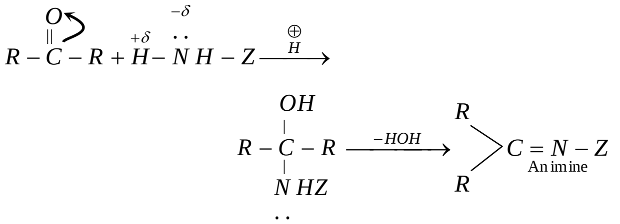
(2) **Addition followed by elimination reactions :** This reaction is given by ammonia derivatives (NH_2-Z).

(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.

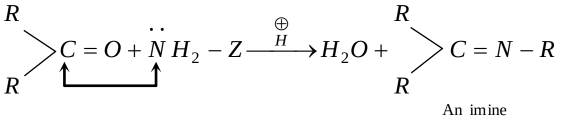
In adduct nucleophilic group has lone pair of electrons. It undergoes elimination to give product known as imine. An imine is a compound with a carbon-nitrogen double bond.



$$R-\overset{O}{\overset{\|}{C}}-R+\overset{+\delta}{H}-\overset{-\delta}{\ddot{N}}H-Z\xrightarrow{\overset{\oplus}{H}}$$

$$R-\underset{\ddot{N}HZ}{\overset{OH}{C}}-R\xrightarrow{-HOH}\begin{matrix}R\\R\end{matrix}\!\!>\underset{\text{An imine}}{C=N-Z}$$

The overall reaction can be shown as follows



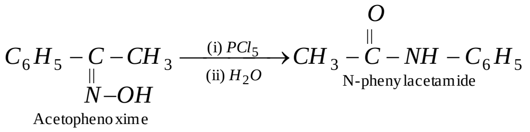
$$\begin{matrix}R\\R\end{matrix}\!\!>C=O+\ddot{N}H_2-Z\xrightarrow{\overset{\oplus}{H}}H_2O+\begin{matrix}R\\R\end{matrix}\!\!>C=N-R$$

An imine

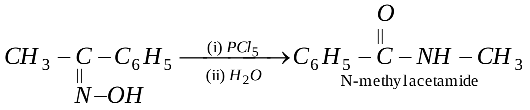
Different Imine formation with NH_2-Z is given below

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.)

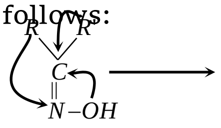


$$C_6H_5-\underset{\underset{\text{Acetophenoxime}}{N-OH}}{\underset{\|}{C}}-CH_3\xrightarrow[\text{(ii) }H_2O]{\text{(i) }PCl_5}CH_3-\underset{\text{N-phenylacetamide}}{\overset{O}{\overset{\|}{C}}-NH-C_6H_5}$$

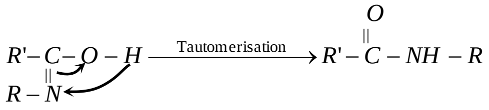


$$CH_3-\underset{N-OH}{\underset{\|}{C}}-C_6H_5\xrightarrow[\text{(ii) }H_2O]{\text{(i) }PCl_5}C_6H_5-\underset{\text{N-methylacetamide}}{\overset{O}{\overset{\|}{C}}-NH-CH_3}$$

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



$$\overset{R\quad R'}{\underset{\underset{N-OH}{\|}}{C}}\longrightarrow$$



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

(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.

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

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

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

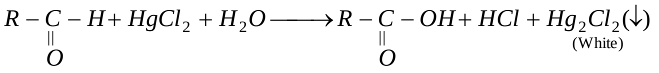
In this reaction the oxidation no. of *Ag* varies from +1 to 0.

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

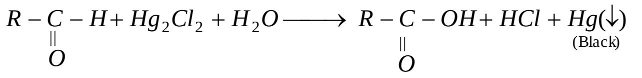
$$C_5H_{11}O_5CHO+Cu_2O\ (or)\ Ag_2O\longrightarrow \underset{\text{Gluconic acid}}{C_5H_{11}O_5COOH}$$

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* :



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



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

(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.

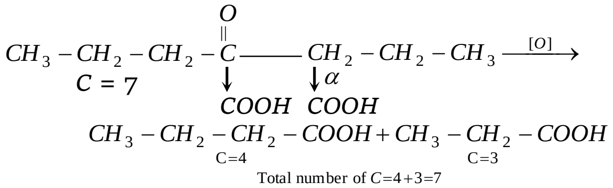
(a) *Oxidation of aldehydes* : Aldehydes are oxidised into corresponding acids.

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

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

(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



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

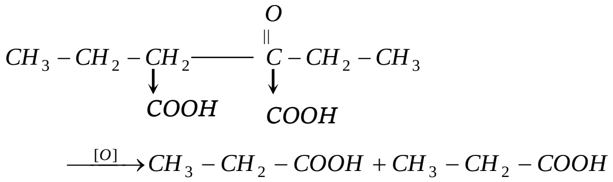
C = 7

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

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

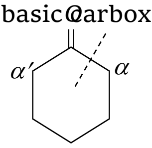
Thus number of carbons in any product is less than the number of carbons in ketone.

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.*



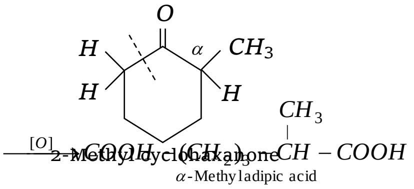
$$CH_3-CH_2-CH_2-\overset{\overset{O}{||}}{C}-CH_2-CH_3\xrightarrow{[O]}CH_3-CH_2-COOH+CH_3-CH_2-COOH$$

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.*

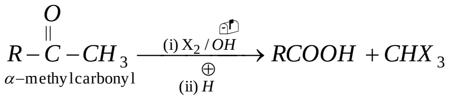


2-Methyl cyclohexanone

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

(iii) ***Miscellaneous oxidation***

(a) *Haloform Reaction*

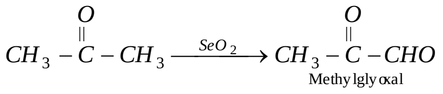


$$\underset{\alpha-\text{methylcarbonyl}}{R-\overset{\overset{O}{||}}{C}-CH_3}\xrightarrow[\text{(ii) }\overset{\oplus}{H}]{\text{(i) }X_2/\overset{\ominus}{OH}}RCOOH+CHX_3$$

(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.

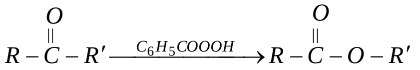
In this oxidation reactivity of CH_2 is more than the CH_3 group and Oxidation is regio selective in nature.

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



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

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

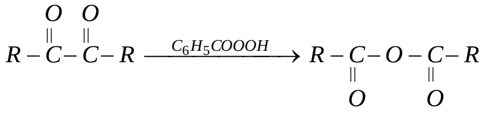


$$R-\overset{O}{\overset{||}{C}}-R' \xrightarrow{C_6H_5COOOH} R-\overset{O}{\overset{||}{C}}-O-R'$$

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.



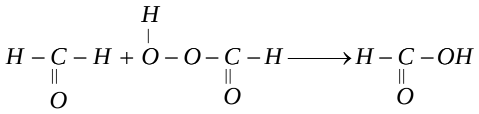
$$R-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-R \xrightarrow{C_6H_5COOOH} R-\underset{O}{\underset{||}{C}}-O-\underset{O}{\underset{||}{C}}-R$$

❑ ***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*

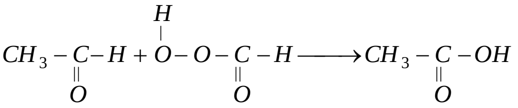
Example :

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

(d) *Baeyer- villiger oxidation* :



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

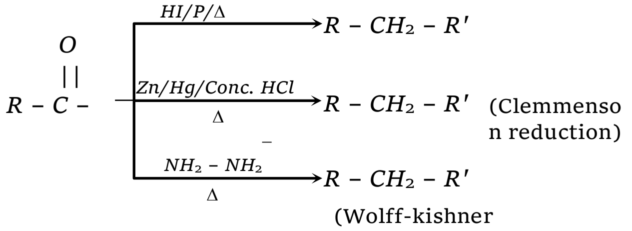


$$CH_3-\underset{O}{\underset{||}{C}}-H+\overset{H}{\overset{|}{O}}-O-\underset{O}{\underset{||}{C}}-H \longrightarrow CH_3-\underset{O}{\underset{||}{C}}-OH$$

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

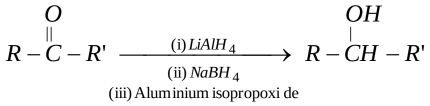
(4) **Reduction of carbonyl compounds**

(i) ***Reduction of*** $\overset{O}{\overset{||}{C}}$ ***– group into –CH₂ – 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/OH.



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

$$R-CHO \xrightarrow[\text{(ii) } NaBH_4,\ \text{(iii) Aluminium isopropoxide}]{\text{(i) LiAlH}_4} R-CH_2OH$$



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

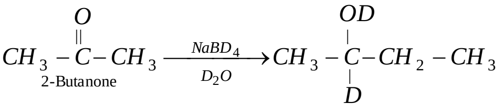
$NaBH_4$ is regioselective reducing agent because it reduced only. CHO in the presence of other reducible group.

Example :

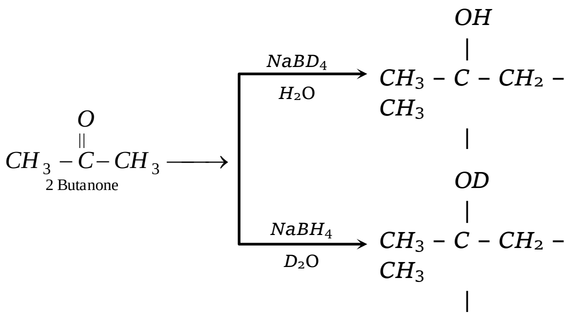
$$\underset{\text{Crotonaldehyde}}{CH_3-CH=CH-CHO} \xrightarrow{NaBH_4} \underset{\text{Crotonyl alcohol}}{CH_3-CH=CH-CH_2OH}$$

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

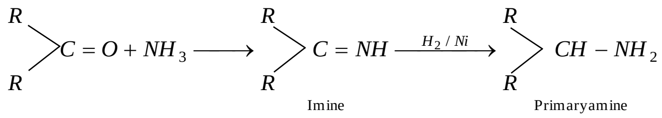
Example :



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



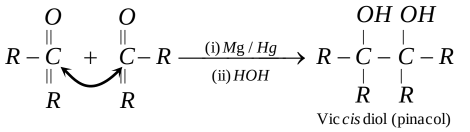
(iii) ***Reductive amination*** **:** In this reduction $-CO-$ group converts into $-CH-NH_2$ group



$$\begin{matrix}R\\ \ \ \end{matrix}\!\!>C=O+NH_3 \longrightarrow \begin{matrix}R\\ R\end{matrix}\!\!>C=NH \xrightarrow{H_2/Ni} \begin{matrix}R\\ R\end{matrix}\!\!>CH-NH_2$$

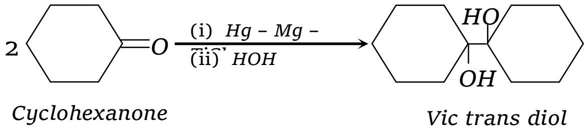
$$\text{Imine} \qquad \text{Primaryamine}$$

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

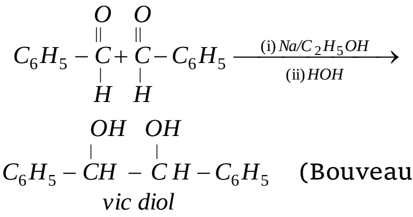


$$R-\underset{R}{\underset{||}{\overset{O}{\overset{||}{C}}}}+\underset{R}{\underset{||}{\overset{O}{\overset{||}{C}}}}-R \xrightarrow[\text{(ii)} HOH]{\text{(i)} Mg/Hg} \underset{\text{Vic } cis \text{ diol (pinacol)}}{R-\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R}$$

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.



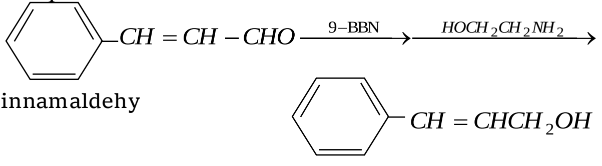
$$C_6H_5-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}}+\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}}-C_6H_5\xrightarrow[\text{(ii)}\,HOH]{\text{(i)}\,Na/C_2H_5OH}$$

$$\underset{\text{vic diol}}{C_6H_5-\overset{\overset{OH}{|}}{C}H-\overset{\overset{OH}{|}}{C}H-C_6H_5}$$

(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 :



$$C_6H_5-CH=CH-CHO\xrightarrow{9\text{–BBN}}\xrightarrow{HOCH_2CH_2NH_2}C_6H_5-CH=CHCH_2OH$$

Cinnamaldehy

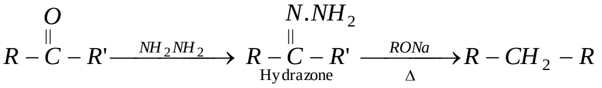
Cinnamyl

❑ *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* $(CH_3-\underset{\underset{CH_3}{|}}{C}H-O-)_3Al$. *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).



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

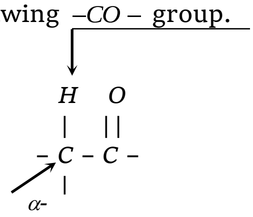
(vii) Schiff's base on reduction gives secondary amines.

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

(5) **Reactions due to α-hydrogen**

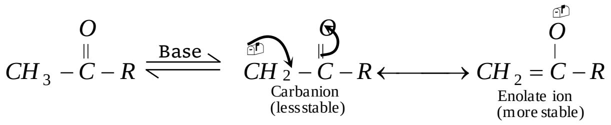
(i) ***Acidity of α-hydrogens* :**

(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 –.

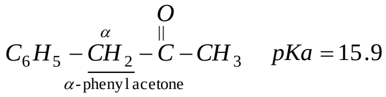
(b) Thus carbonyl compounds having α-hydrogen convert into carbanions in the presence of base. This carbanion is stabilised by delocalisation of negative charge.



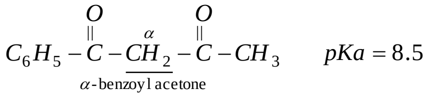
$$CH_3-\overset{\overset{O}{\|}}{C}-R\underset{}{\overset{\text{Base}}{\rightleftharpoons}}\underset{\substack{\text{Carbanion}\\ \text{(less stable)}}}{\overset{\ominus}{C}H_2-\overset{\overset{O}{\|}}{C}-R}\longleftrightarrow\underset{\substack{\text{Enolate ion}\\ \text{(more stable)}}}{CH_2=\overset{\overset{\overset{\ominus}{O}}{|}}{C}-R}$$

(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.



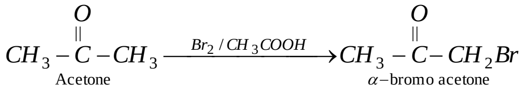
$$\underset{\alpha\text{-phenyl acetone}}{C_6H_5-\overset{\alpha}{CH_2}-\overset{\overset{O}{\|}}{C}-CH_3}\quad pKa=15.9$$



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

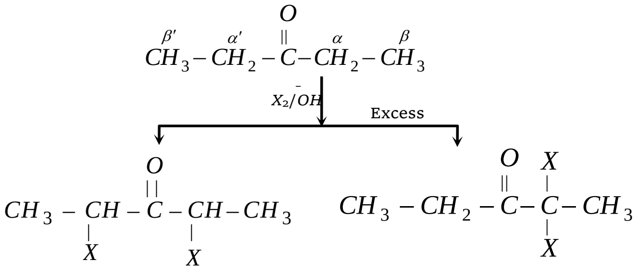
(ii) ***Halogenation*** **:** Carbonyl compounds having α-hydrogens undergo halogenation reactions. This reaction is catalysed by acid as well as base.

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



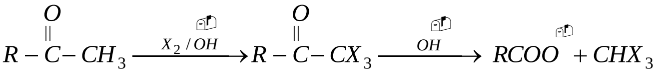
$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}\xrightarrow{Br_2/CH_3COOH}\underset{\alpha\text{–bromo acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2Br}$$

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



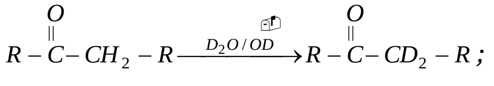
$$\overset{\beta'}{CH_3}-\overset{\alpha'}{CH_2}-\overset{\overset{O}{\|}}{C}-\overset{\alpha}{CH_2}-\overset{\beta}{CH_3}\xrightarrow{X_2/\overset{-}{O}H,\ \text{Excess}}CH_3-\underset{\underset{X}{|}}{CH}-\overset{\overset{O}{\|}}{C}-\underset{\underset{X}{|}}{CH}-CH_3\ ;\ CH_3-CH_2-\overset{\overset{O}{\|}}{C}-\overset{\overset{X}{|}}{\underset{\underset{X}{|}}{C}}-CH_3$$

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

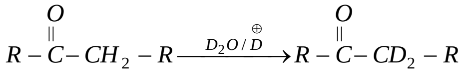


$$R-\overset{\overset{O}{\|}}{C}-CH_3\xrightarrow{X_2/\overset{\ominus}{O}H}R-\overset{\overset{O}{\|}}{C}-CX_3\xrightarrow{\overset{\ominus}{O}H}RCO\overset{\ominus}{O}+CHX_3$$

(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.

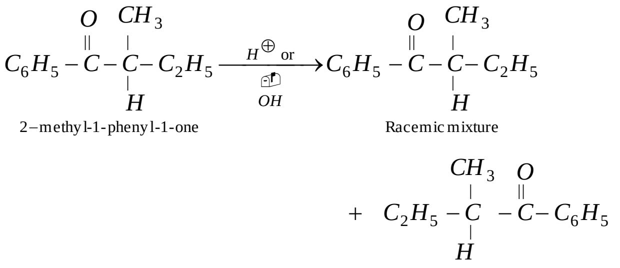


$$R-\overset{\overset{O}{\|}}{C}-CH_2-R\xrightarrow{D_2O/\overset{\ominus}{O}D}R-\overset{\overset{O}{\|}}{C}-CD_2-R\ ;$$



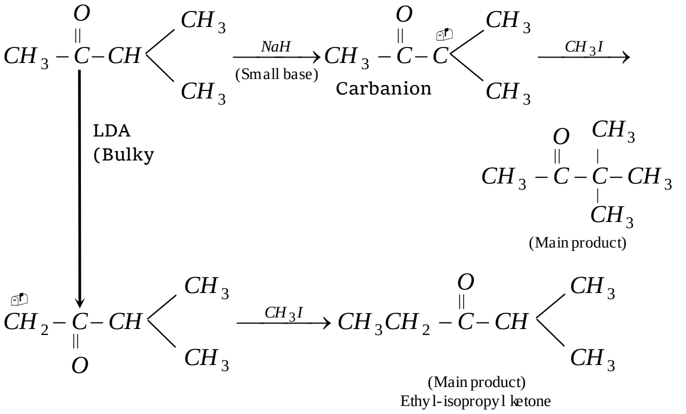
$$R-\overset{\overset{O}{\|}}{C}-CH_2-R\xrightarrow{D_2O/\overset{\oplus}{D}}R-\overset{\overset{O}{\|}}{C}-CD_2-R$$

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



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

(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.

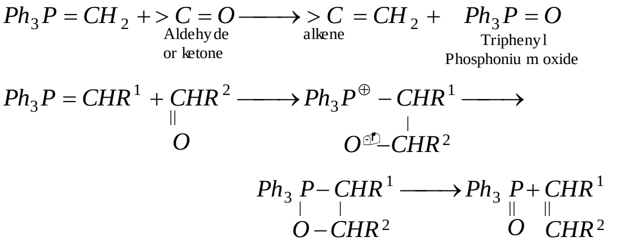


$$CH_3-\overset{\overset{O}{\|}}{C}-CH\begin{matrix}CH_3\\CH_3\end{matrix} \xrightarrow[\text{(Small base)}]{NaH} \underset{\text{Carbanion}}{CH_3-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{C}\begin{matrix}CH_3\\CH_3\end{matrix}} \xrightarrow{CH_3I} \underset{\text{(Main product)}}{CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\ove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

$$\downarrow \text{LDA (Bulky}$$

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

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



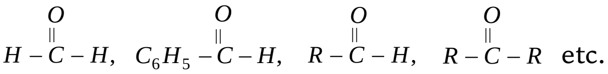
$$Ph_3P=CH_2 + \underset{\substack{\text{Aldehyde}\\ \text{or ketone}}}{>C=O} \longrightarrow \underset{\text{alkene}}{>C=CH_2} + \underset{\substack{\text{Triphenyl}\\ \text{Phosphonium oxide}}}{Ph_3P=O}$$

$$Ph_3P=CHR^1 + \underset{\underset{O}{\|}}{C}HR^2 \longrightarrow \begin{array}{l} Ph_3P^{\oplus}-CHR^1 \\ \qquad\ \ | \\ \quad\ O^{\ominus}-CHR^2 \end{array} \longrightarrow$$

$$\begin{array}{l} Ph_3\,P-CHR^1 \\ \quad\ \ |\quad\ | \\ \quad O-CHR^2 \end{array} \longrightarrow \begin{array}{l} Ph_3\,P+CHR^1 \\ \qquad\ \|\quad\ \| \\ \qquad O\ \ CHR^2 \end{array}$$

(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 :

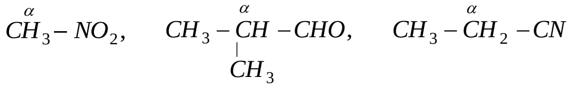
Substrate is always an organic compound having a carbonyl group, *e.g.*



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

Addition always takes place on the carbonyl group.

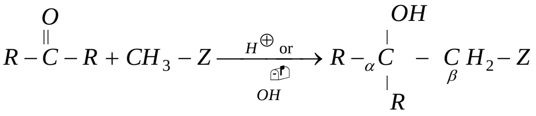
Reagents of the condensation reaction are also organic compounds having at least one hydrogen on α-carbon and α-carbon should have –I group, *e.g.*



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

❑ *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.*

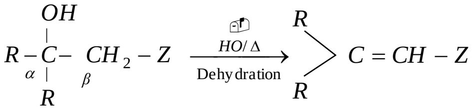
Condensation reaction always takes place in the presence of acid or base as catalyst. Best result is obtained with base at lower temp.



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

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.



$$R-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{\underset{\alpha}{C}}}-\underset{\beta}{CH_2}-Z \xrightarrow[\text{Dehydration}]{\overset{\ominus}{HO}/\Delta} \begin{matrix}R\\R\end{matrix}\!>C=CH-Z$$

(i) ***Aldol condensation***

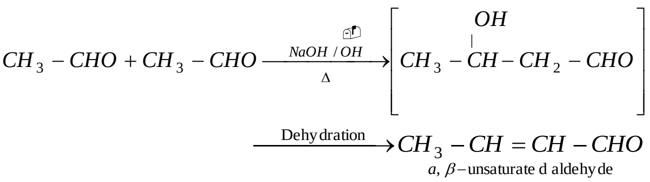
(a) This reaction takes place between two molecules of carbonyl compounds; one molecule should have at least two α-hydrogen atoms. In this reaction best result is obtained when

Both molecule are the same or

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

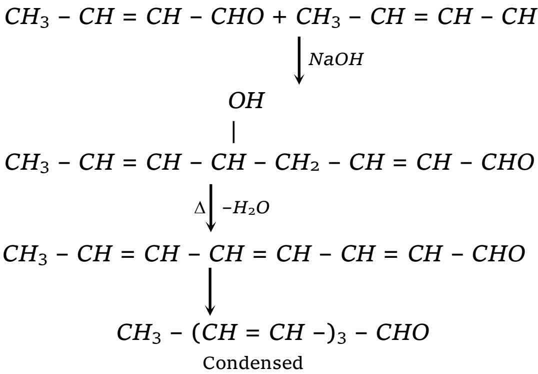
(b) These reactions are practical when base is $NaOH$ and reaction temperature is high $(\ge 100°)$.

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



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

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



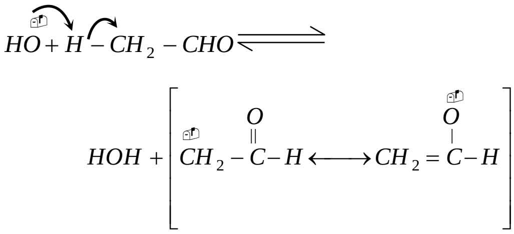
$$CH_3-CH=CH-CHO+CH_3-CH=CH-CHO$$
$$\Big\downarrow NaOH$$
$$CH_3-CH=CH-\overset{\overset{OH}{|}}{CH}-CH_2-CH=CH-CHO$$
$$\Delta\Big\downarrow -H_2O$$
$$CH_3-CH=CH-CH=CH-CH=CH-CHO$$
$$\Big\downarrow$$
$$CH_3-(CH=CH-)_3-CHO$$

Condensed compound

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

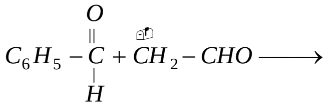
$$C_6H_5-CH=CH-CHO+HOH$$

Step I :

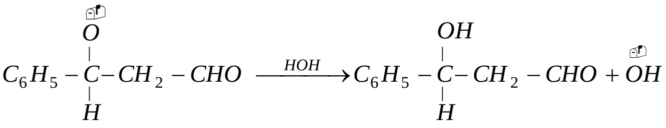


$$HO^{\ominus}+H-CH_2-CHO\rightleftharpoons HOH+\left[\overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-H\longleftrightarrow CH_2=\overset{O^{\ominus}}{\overset{|}{C}}-H\right]$$

Step II :

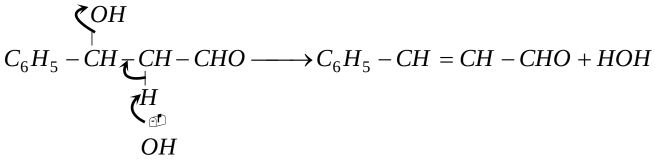


$$C_6H_5-\underset{H}{\underset{|}{\overset{O}{\overset{\|}{C}}}}+\overset{\ominus}{C}H_2-CHO\longrightarrow$$



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

Step III :

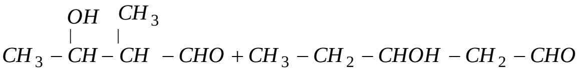


$$C_6H_5-\overset{OH}{\overset{|}{CH}}-\underset{\underset{\overset{\ominus}{OH}}{H}}{\underset{|}{CH}}-CHO\longrightarrow C_6H_5-CH=CH-CHO+HOH$$

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.

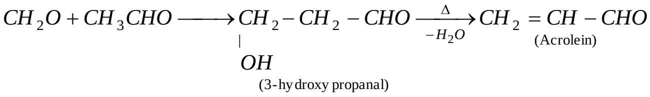
Crossed aldol condensation : Aldol condensation between two different aldehydes or two different ketones or one aldehyde and another ketone provided at least one of the components have α-hydrogen atom gives different possible product

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



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

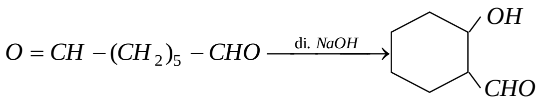
However crossed aldol condensation is important when only it the components has α-hydrogen atom.



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

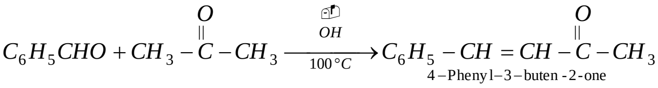
Intra molecular aldol condensation : One molecule Intramolecular condensation give aldol compounds

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 :



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

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.

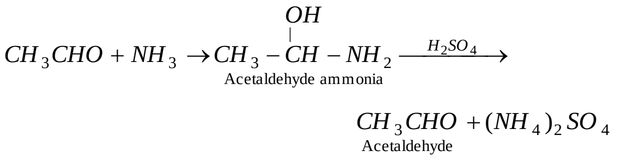
(ix) ***Laboratory preparation* :** Acetaldehyde is prepared in the laboratory by oxidation of ethyl alcohol with acidified potassium dichromate or acidified sodium dichromate.

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

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

$$\underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + \underset{\text{Ethylalcohol}}{3CH_3CH_2OH} + \underset{\text{Sulphuric acid}}{4H_2SO_4} \longrightarrow \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Chromic sulphate}}{Cr_2(SO_4)_3} + \underset{\text{Acetaldehyde}}{3CH_3CHO} + \underset{\text{Water}}{7H_2O}$$

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.



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

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

(a) *By air oxidation of ethyl alcohol*

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

(b) *By dehydrogenation of alcohol*

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

(c) *By hydration of acetylene*

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

(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 :

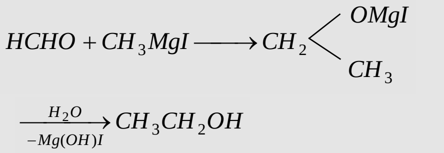
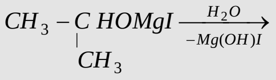
(i) In the preparation of acetic acid, acetic anhydride, ethyl acetate, chloral, 1,3-butadiene (used in rubbers), dyes and drugs.

(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 $CH_3CHO + CH_3MgI \longrightarrow$  $CH_3-\underset{\underset{CH_3}{|}}{C}HOMgI \xrightarrow[-Mg(OH)I]{H_2O}$

			$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-OH$
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 $H_2C=O+2C_2H_5OH\xrightarrow{HCl}$ $CH_2\left<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.$	Forms acetaldehyde diethyl acetal $CH_3CHO+2C_2H_5OH\xrightarrow{HCl}$ $CH_3CH\left<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.$
10.	With thioalcohols (C_2H_5SH) in presence of acid	Forms thio ethylal $H_2C=O+2C_2H_5SH\longrightarrow$ $CH_2\left<\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}\right.$	Forms acetaldehyde diethyl thioacetal $CH_3CH=O+2C_2H_5SH\longrightarrow$ $CH_3CH\left<\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}\right.$
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

$\overset{\text{Evaporatio}}{\rightleftharpoons}$

$\underset{\text{dil. }H_2SO_4.}{\overset{H_2SO_4\text{Conc.}}{\rightleftharpoons}}$

$\underset{\text{heat}}{\overset{\text{Room temp.}}{\rightleftharpoons}}$

$\underset{\text{dil. }H_2SO_4.}{\overset{H_2SO_4\text{Conc.}}{\rightleftharpoons}}$

		$nHCHO \quad \underset{\text{Paraformaldehyde}}{(HCHO)_n}$ $3HCHO$ $\underset{\text{Metaformaldehyde}}{(HCHO)_3}$	$3CH_3CHO$ $\underset{\text{Paraldehyde}}{(CH_3CHO)_3}$ $4CH_3CHO$ $\underset{\text{Metaldehyde}}{(CH_3CHO)_4}$
Dissimilarities			
16.	With PCl_5	No reaction	Forms ethylidene chloride $CH_3CHO + PCl_5 \longrightarrow CH_3CH\begin{matrix}Cl\\Cl\end{matrix}$ $+POCl_3$
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 $CH_3CHO + NH_3 \longrightarrow$ $CH_3CH\begin{matrix}OH\\NH_2\end{matrix}$
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) $\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{H_2/Ni} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{PCl_5} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow[KCN]{\text{Alc.}}$

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

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

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

$$\rightarrow CH_3COCH_3$$

(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**

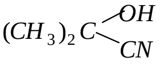
CH_3COCH_3 (Acetone)

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

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

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

$\xrightarrow{HCN}$



$(CH_3)_2C\begin{smallmatrix}OH\\CN\end{smallmatrix}$

Acetone cyanohydrin

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

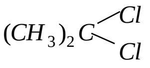
$\xrightarrow{NH_2OH}$ $\underset{\text{Acetoxime}}{(CH_3)_2C=NOH}$

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

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

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

$\xrightarrow{PCl_5}$



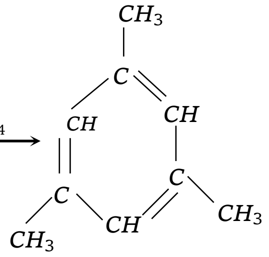
$(CH_3)_2C\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$

Isopropylidene chloride

$\xrightarrow{Cl_2}$ $\underset{\text{Trichloro acetone}}{CH_3COCCl_3}$

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

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



Mesitylene

(1, 3, 5-trimethyl

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

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

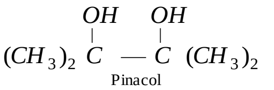
$\xrightarrow{CHCl_3}$ $\underset{\text{Chloretone}}{(CH_3)_2C(OH)CCl_3}$

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

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

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

$\xrightarrow{Mg\text{–}Hg + H_2O}$



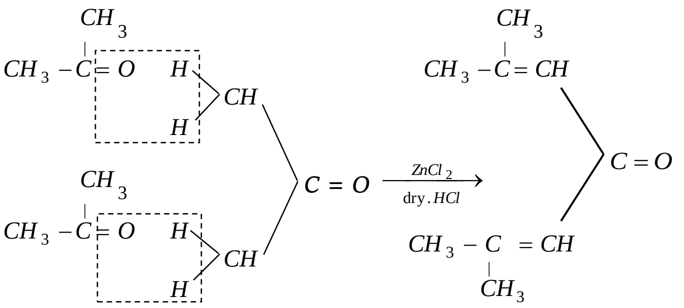
$(CH_3)_2\overset{OH}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}(CH_3)_2$

Pinacol

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

$\xrightarrow{\text{Tollen's}}$ No reaction

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

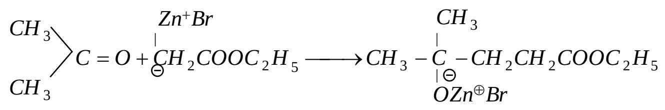

Acetone (3 phoron

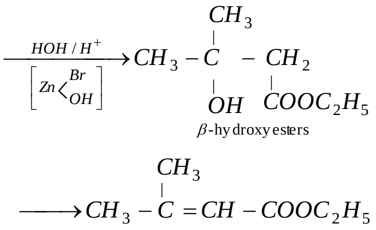
Molecular mass of phorone = 3 mole of acetone – 2 mole of H_2O

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

(b) Addition to carbonyl group




$$\xrightarrow[\left[Zn\langle^{Br}_{OH}\right]]{HOH/H^+} CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}} - \underset{\underset{COOC_2H_5}{|}}{CH_2}$$

β-hydroxy esters

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

(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**

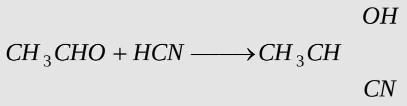
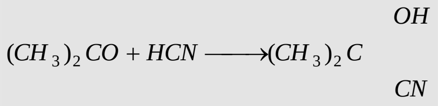
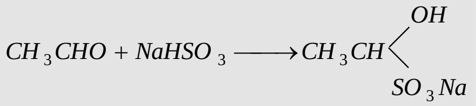
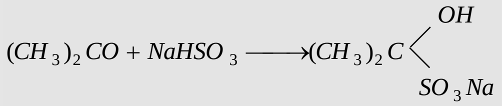
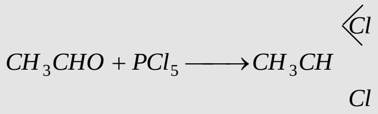
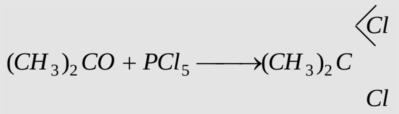
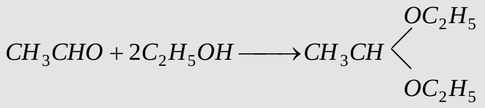
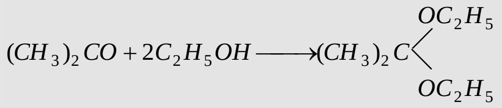
(i) ***Legal's test*** **:** When a few drops of freshly prepared sodium nitroprusside and sodium hydroxide solution are added to an aqueous solution of acetone, a wine colour is obtained which changes to yellow on standing.

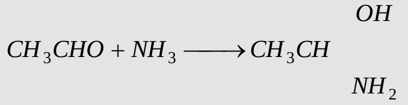
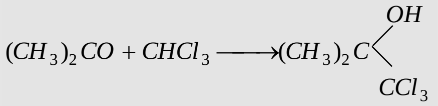
(ii) ***Indigo test*** **:** A small amount of orthonitrobenzaldehyde is added to about 2 *ml.* of acetone and it is diluted with *KOH* solution and stirred. A blue colour of indigotin is produced.

(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

	 $CH_3CHO + HCN \longrightarrow CH_3CH\left\langle\begin{matrix}OH\\CN\end{matrix}\right.$	 $(CH_3)_2CO + HCN \longrightarrow (CH_3)_2C\left\langle\begin{matrix}OH\\CN\end{matrix}\right.$
4. Addition of $NaHSO_3$	White crystalline derivative  $CH_3CHO + NaHSO_3 \longrightarrow CH_3CH\left\langle\begin{matrix}OH\\SO_3Na\end{matrix}\right.$	White crystalline derivative  $(CH_3)_2CO + NaHSO_3 \longrightarrow (CH_3)_2C\left\langle\begin{matrix}OH\\SO_3Na\end{matrix}\right.$
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)  $CH_3CHO + PCl_5 \longrightarrow CH_3CH\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right.$	Forms isopropylidene chloride (Gem dihalide)  $(CH_3)_2CO + PCl_5 \longrightarrow (CH_3)_2C\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right.$
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)  $CH_3CHO + 2C_2H_5OH \longrightarrow CH_3CH\left\langle\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.$	Forms ketal (a diether)  $(CH_3)_2CO + 2C_2H_5OH \longrightarrow (CH_3)_2C\left\langle\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.$
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 $CH_3COCH_3 + O \longrightarrow CH_3COOH + CO_2 + H_2O$

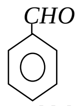
Aromatic Carbonyl Compounds

Aromatic aldehydes are of two types :

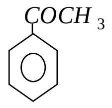
The compounds in which $-CHO$ group is attached directly to an aromatic ring, *e.g.,* benzaldehyde, C_6H_5CHO .

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.

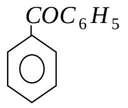
Aromatic ketones are compounds in which a carbonyl group $(>C=O)$ is attached to either two aryl groups or one aryl group and one alkyl group. Examples are :



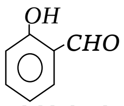
Benzaldehyde



Acetophenone (Methyl phenyl ketone)

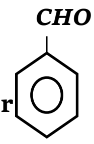


Benzophenone (Diphenyl ketone)

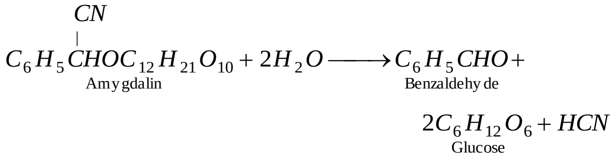


Salicylaldehyde

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.

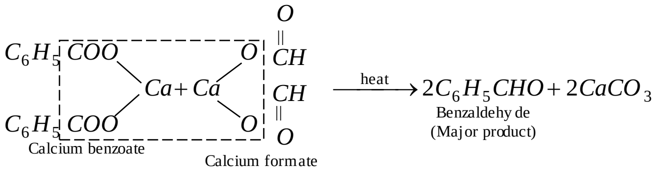
$$\underset{\text{Benzyl chloride}}{2C_6H_5CH_2Cl} + \underset{\substack{\text{or} \\ Pb(NO_3)_2}}{Cu(NO_3)_2} \xrightarrow[CO_2]{\text{heat}} \underset{\text{Benzaldehyde}}{2C_6H_5CHO} + CuCl_2 + 2HNO_2$$

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

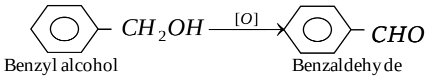
(ii) ***Rosenmund reaction*** **:**

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

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

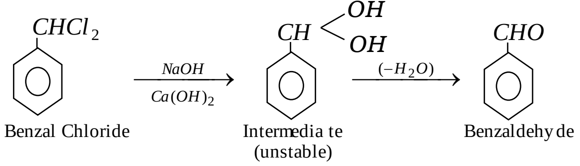


(iv) ***By oxidation of benzyl alcohol*** **:** This involves the treatment of benzyl alcohol with dil. HNO_3 or acidic potassium dichromate or chromic anhydride in acetic anhydride or with copper catalyst at 350^oC.



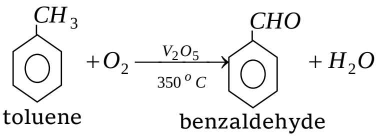
This method is used for commercial production of benzaldehyde.

(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.

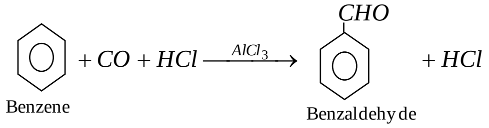
Partial oxidation of toluene with manganese dioxide and dilute sulphuric acid at 35^oC, also forms benzaldehyde.

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

(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.



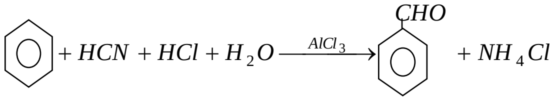
(ix) ***Gattermann reaction***

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

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

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

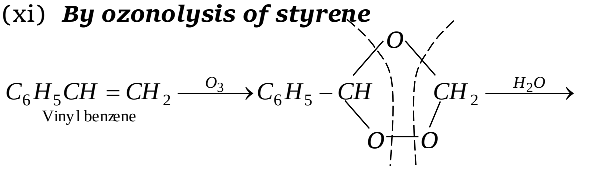
Thus,



(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.

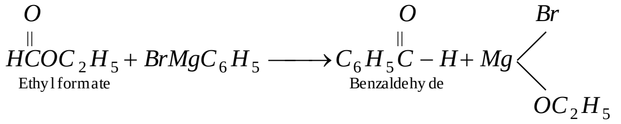
$$\underset{\text{Phenyl cyanide}}{C_6H_5C\equiv N} \xrightarrow[\text{Ether}]{HCl/SnCl_2} \underset{\text{Aldimine complex}}{[C_6H_5CH=NH]_2H_2SnCl_6} \xrightarrow{H_2O} 2C_6H_5CHO$$

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



$$C_6H_5CHO + HCHO + H_2O_2$$

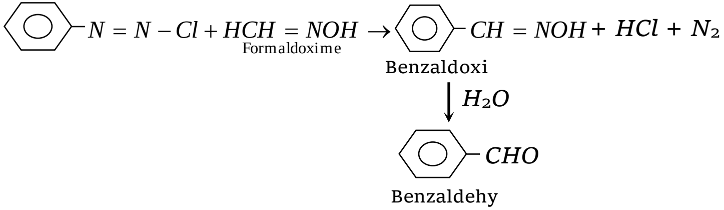
(xii) ***Grignard reaction***



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

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).

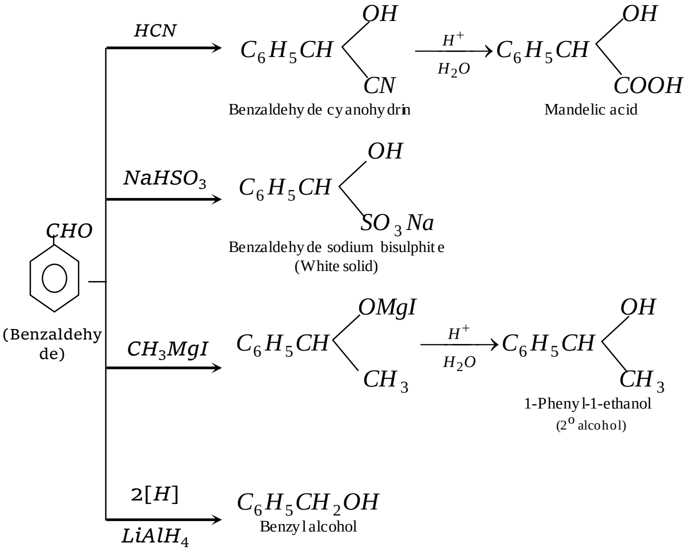
(vi) It is poisonous in nature.

(3) **Chemical properties**

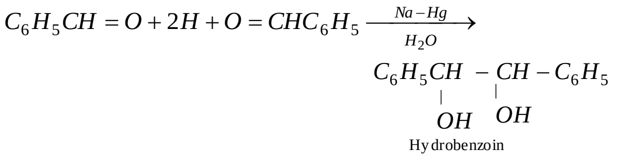
(i) ***Addition reaction*:** The carbonyl group is polar as oxygen is more electronegative than carbon,

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

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

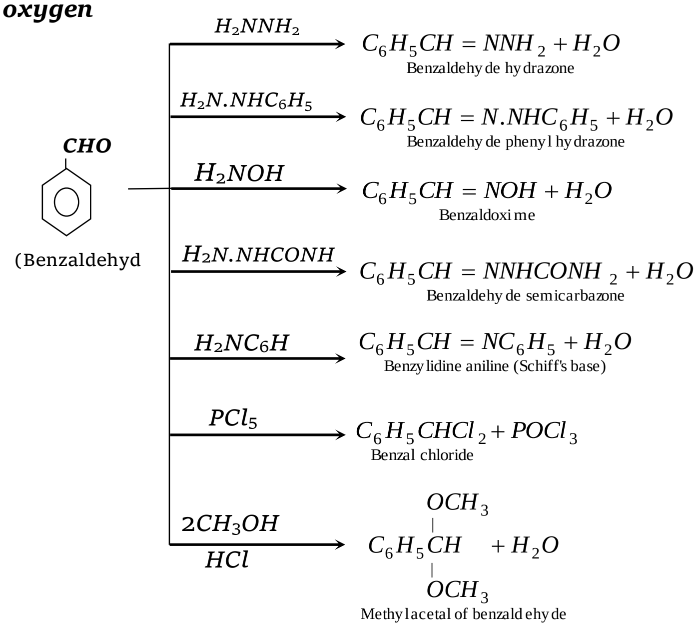


However on reduction with sodium amalgam and water, it gives hydrobenzoin,



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

(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.

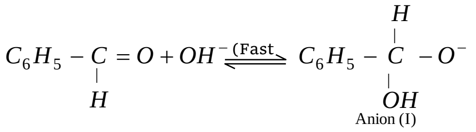
$$C_6H_5CHO+Cl_2 \xrightarrow[\Delta]{170^o C} C_6H_5COCl+HCl$$

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

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

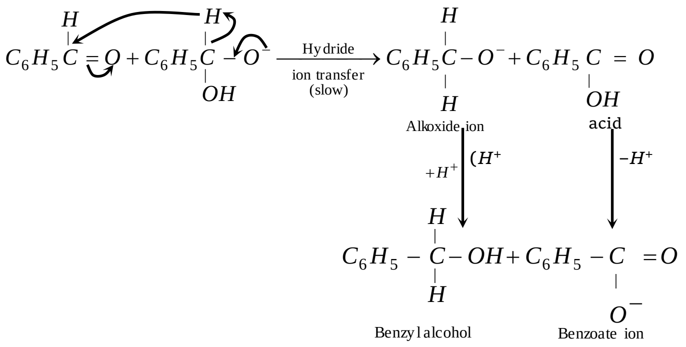
The possible Mechanism is

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



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

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.



$$C_6H_5\overset{H}{C}=O+C_6H_5\underset{OH}{\overset{H}{C}}-O^- \xrightarrow[\text{ion transfer (slow)}]{\text{Hydride}} \underset{\text{Alkoxide ion}}{C_6H_5\underset{H}{\overset{H}{C}}-O^-}+\underset{\text{acid}}{C_6H_5\underset{OH}{C}=O}$$

$$\downarrow +H^+\ (H^+ \qquad\qquad \downarrow -H^+$$

$$\underset{\text{Benzyl alcohol}}{C_6H_5-\underset{H}{\overset{H}{C}}-OH}+\underset{\text{Benzoate ion}}{C_6H_5-\underset{O^-}{C}=O}$$

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

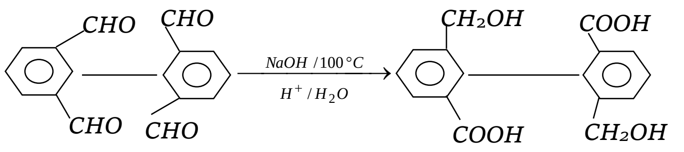
So one molecule of aldehyde acts as hydride donor and the other acts as hydride acceptor. In other words, Cannizzaro's reaction is an example of self reduction and oxidation.

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

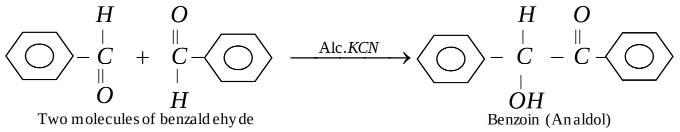
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+\underset{\text{Formaldehyde}}{HCHO}\xrightarrow[\text{heat}]{NaOH}\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}+\underset{\text{Sod. formate}}{HCOONa}$$

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



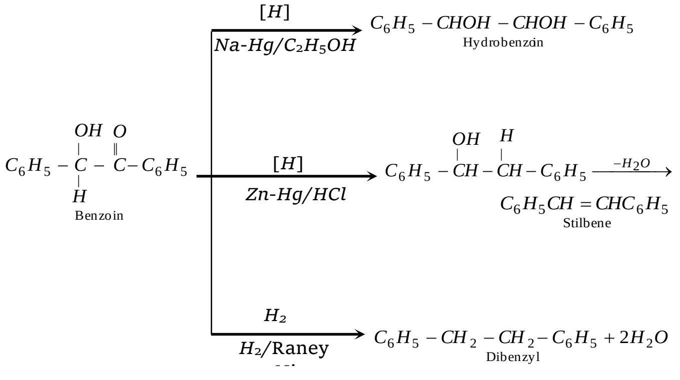
(d) *Benzoin Condensation*



Two molecules of benzaldehyde

Benzoin (An aldol)
β–hydroxy ketone

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

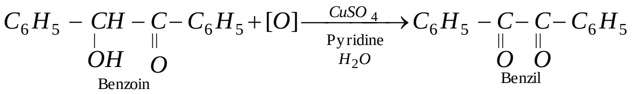


$$\underset{\text{Benzoin}}{C_6H_5-\underset{H}{\overset{OH}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5}\xrightarrow[\text{Na-Hg/}C_2H_5OH]{[H]}\underset{\text{Hydrobenzoin}}{C_6H_5-CHOH-CHOH-C_6H_5}$$

$$\xrightarrow[\text{Zn-Hg/HCl}]{[H]}C_6H_5-\overset{OH}{CH}-\overset{H}{CH}-C_6H_5\xrightarrow{-H_2O}\underset{\text{Stilbene}}{C_6H_5CH=CHC_6H_5}$$

$$\xrightarrow[H_2\text{/Raney}]{H_2}\underset{\text{Dibenzyl}}{C_6H_5-CH_2-CH_2-C_6H_5}+2H_2O$$

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



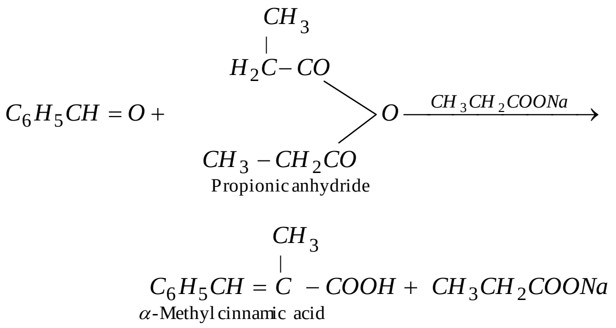
$$\underset{\text{Benzoin}}{C_6H_5-\underset{OH}{CH}-\underset{O}{\underset{\|}{C}}-C_6H_5}+[O]\xrightarrow[\text{Pyridine}\ H_2O]{CuSO_4}\underset{\text{Benzil}}{C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-C_6H_5}$$

(e) *Perkin's reaction*

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

$$C_6H_5CH=CHCOOCOCH_3$$

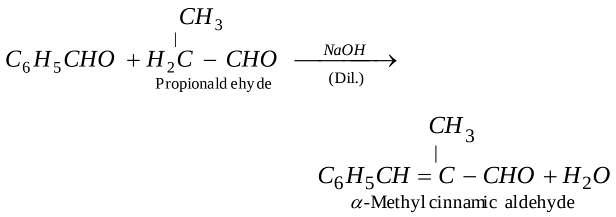
$$\xrightarrow{H_2O}\underset{\text{Cinnamic acid}}{C_6H_5CH=CHCOOH}+\underset{\text{Acetic acid}}{CH_3COOH}$$



$$C_6H_5CH=O+\underset{\text{Propionic anhydride}}{\begin{matrix}H_2\overset{CH_3}{C}-CO\\ \quad\ \ \rangle O\\ CH_3-CH_2CO\end{matrix}}\xrightarrow{CH_3CH_2COONa}$$

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

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



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

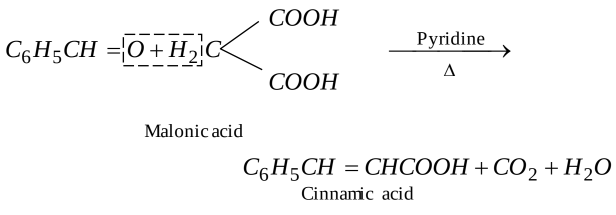
$$\underset{\alpha\text{-Methyl cinnamic aldehyde}}{C_6H_5CH=\overset{CH_3}{C}-CHO}+H_2O$$

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

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

(β – hydroxy ketone)

(g) *Knoevenagel reaction*



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

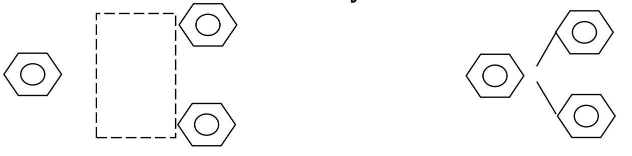
Malonic acid

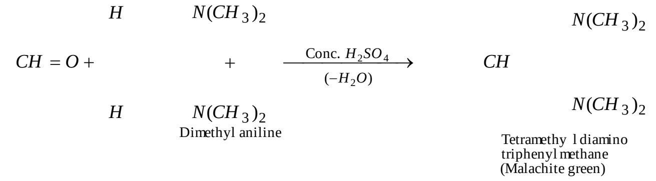
$$\underset{\text{Cinnamic acid}}{C_6H_5CH=CHCOOH}+CO_2+H_2O$$

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

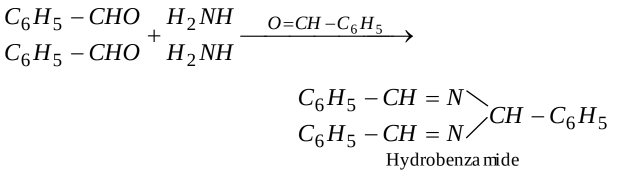
$$C_6H_5CH=O+\underset{\text{Aniline}}{H_2NC_6H_5}\xrightarrow[(-H_2O)]{\text{Warm}}\underset{\substack{\text{Benzylidene aniline}\\ \text{(Schiff's base)}}}{C_6H_5CH=NC_6H_5}$$

Reaction with Dimethylaniline





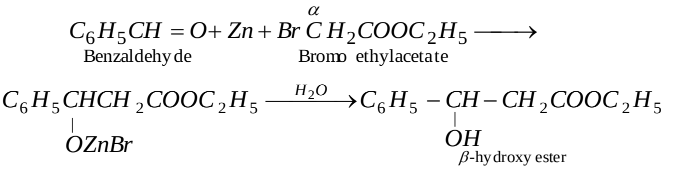
(i) *Reaction with Ammonia* : Benzaldehyde reacts with ammonia to form hydrobenzamide aldehyde other than CH_2O give aldehyde ammonia while CH_2O forms urotropine.



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

Hydrobenza mide

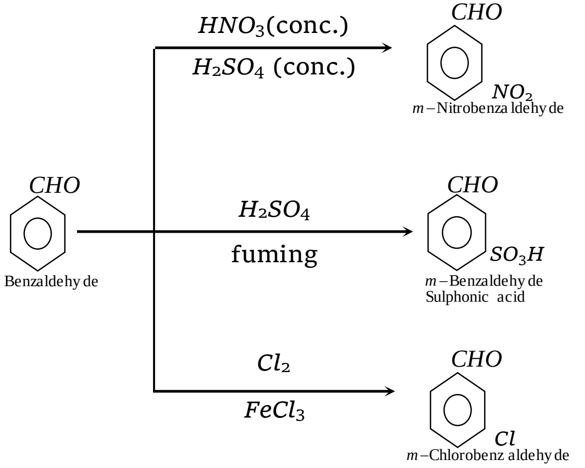
(j) *Reformatsky reaction*



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

$$\underset{OZnBr}{C_6H_5\overset{}{C}HCH_2COOC_2H_5} \xrightarrow{H_2O} \underset{\beta\text{-hydroxy ester}}{C_6H_5-\underset{OH}{CH}-CH_2COOC_2H_5}$$

(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.

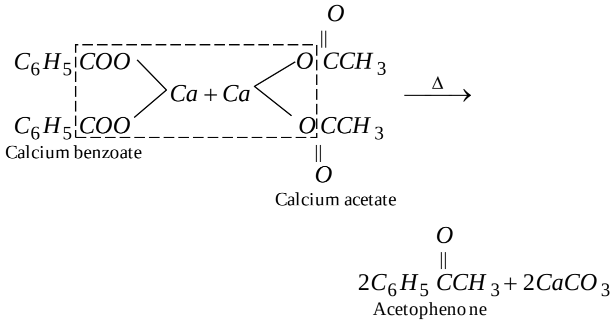
Acetophenone, $C_6H_5COCH_3$, Acetyl Benzene

(1) **Method of preparation**

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

$$\underset{\text{Benzene}}{C_6H_5\boxed{H+Cl}}\underset{\text{Acetyl chloride}}{COCH_3} \xrightarrow{AlCl_3} \underset{\text{Acetopheno ne}}{C_6H_5COCH_3} + HCl$$

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



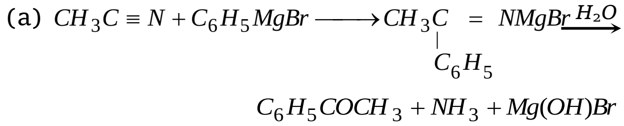
(iii) By methylation of benzaldehyde with diazomethane.

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

(iv) By treating benzoyl chloride with dimethyl cadmium.

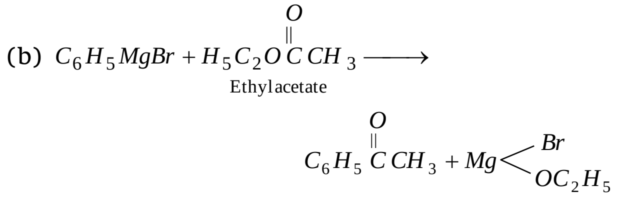
$$2C_6H_5COCl + (CH_3)_2Cd \longrightarrow 2C_6H_5COCH_3 + CdCl_2$$

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



(a) $CH_3C \equiv N + C_6H_5MgBr \longrightarrow CH_3\underset{C_6H_5}{C} = NMgBr \xrightarrow{H_2O}$

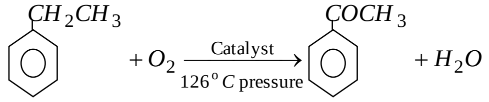
$$C_6H_5COCH_3 + NH_3 + Mg(OH)Br$$



(b) $C_6H_5MgBr + \underset{\text{Ethylacetate}}{H_5C_2O\overset{O}{\overset{||}{C}}CH_3} \longrightarrow$

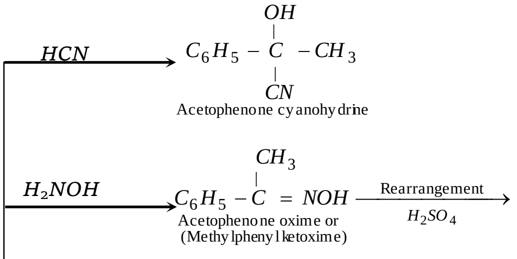
$$C_6H_5\overset{O}{\overset{||}{C}}CH_3 + Mg\langle\begin{matrix} Br \\ OC_2H_5 \end{matrix}$$

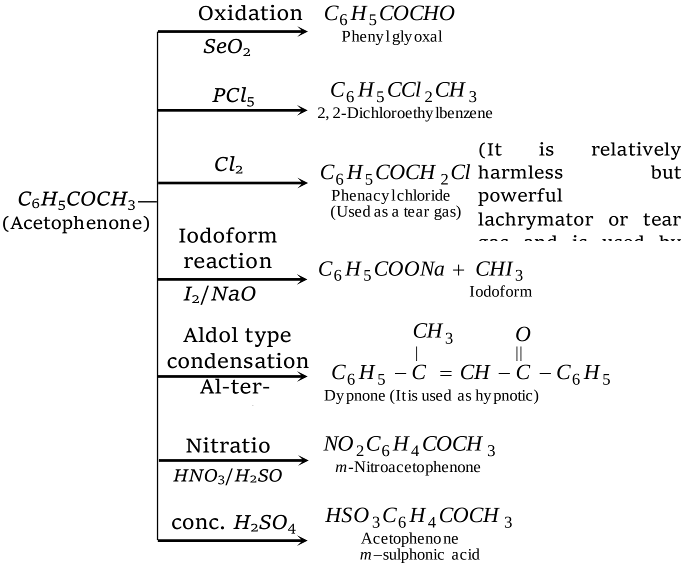
(vi) ***Commercial preparation :*** Ethylbenzene is oxidised with air at 126^oC under pressure in presence of a catalyst manganese acetate.



(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 :***





(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 :***

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

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

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

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

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

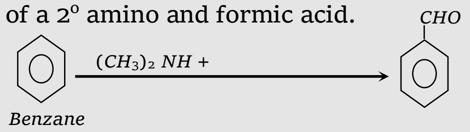
$$C_6H_5COC_6H_5+H_2O\xrightarrow[\text{Ether}]{\text{Pot. tert. Butoxide}}\underset{\text{Benzoic acid}}{C_6H_5COOH}+C_6H_6$$

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.

OT Ordinary Thinking

Objective Questions

Introduction

1. Reaction of acetaldehyde with HCN followed by hydrolysis gives a compound which shows**[MP PET 1997]**

(a) Optical isomerism (b) Geometrical isomerism

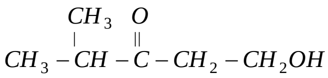
(c) Metamerism (d) Tautomerism

2. In aldehydes and ketones, carbon of carbonyl group is **[MP PMT 1995; RPET 1999, 2000]**

(a) sp^3 hybridised (b) sp^2 hybridised

(c) sp hybridised (d) Unhybridised

3. The IUPAC name of the following structure is



$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle O}{||}}{C}-CH_2-CH_2OH$ **[MP PMT 1995]**

(a) 1-hydroxy 4-methyl 3-pentanone

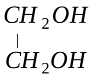
(b) 2-methyl 5-hydroxy 3-pentanone

(c) 4-methyl 3-*oxo* 1-pentanol

(d) Hexanol-1, one-3

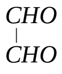
4. **Glyoxal** is **[BVP 2003]**

(a) CH_2O-CH_2O (b)



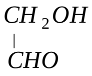
$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$

(c)



$\begin{matrix}CHO\\|\\CHO\end{matrix}$

(d)



$\begin{matrix}CH_2OH\\|\\CHO\end{matrix}$

5. Aldehydes are isomeric with

(a) Ketones (b) Ethers

(c) Alcohols (d) Fatty acids

6. Which of the following compounds does not contain an $-OH$ group **[CPMT 1982]**

(a) Phenol (b) Carboxylic acid

(c) Aldehydes (d) Alcohols

7. IUPAC name of CH_3COCH_3 is **[MP PET 1991]**

(a) Acetone (b) 2-propanone

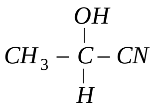
(c) Dimethyl ketone (d) Propanal

8. What is the compound called if remaining two valencies of a carbonyl group are satisfied by two alkyl groups **[CPMT 1990]**

(a) Aldehyde (b) Ketone

(c) Acid (d) Acid chloride

9.



$CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CN$ is

(a) Acetaldehyde cyanohydrin

(b) Acetone cyanohydrin

(c) Cyanoethanol

(d) Ethanol nitrile

10. Ethanedial has which functional group(s)

(a) One ketonic (b) Two aldehydic

(c) One double bond (d) Two double bond

11. In the group $\begin{matrix}R'\\R\end{matrix}\!>C=O$ the carbonyl carbon is joined to other atoms by

(a) Two sigma and one pi bonds

(b) Three sigma and one pi bonds

(c) One sigma and two pi bonds

(d) Two sigma and two pi bonds

12. Which of the following types of isomerism is shown by pentanone **[MP PMT 1995]**

(a) Chain isomerism (b) Position isomerism

(c) Functional isomerism (d) All of these

13. IUPAC name of CCl_3CHO is **[MP PMT/PET 1988]**

(a) Chloral (b) Trichloro acetaldehyde

(c) 1, 1, 1-trichloroethanal (d)2, 2, 2-trichloroethanal

14. Which of the following is a mixed ketone**[AFMC 1997]**

(a) Pentanone (b) Acetophenone

(c) Benzophenone (d) Butanone

15. Chloral is **[CPMT 1976, 84]**

(a) CCl_3CHO (b) CCl_3COCH_3

(c) CCl_3COCCl_3 (d) CCl_3CH_2OH

16. Carbonyl compounds are usually

(a) Ethers, aldehydes, ketones and carboxylic acids

(b) Aldehydes, ketones and carboxylic acids

(c) Aldehydes and ketones

(d) Carboxylic acids

17. Acetone and acetaldehyde are **[KCET 1998]**

(a) Position isomers (b) Functional isomers

(c) Not isomers (d) Chain isomers

18. Which of the aldehyde is most reactive ?**[DCE 2004]**

(a) C_6H_5-CHO (b) CH_3CHO

(c) $HCHO$ (d) All the equally reactive

Preparation

1. The end product in the following sequence of reaction is

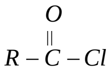
$$HC\equiv CH\xrightarrow[20\%H_2SO_4]{1\%\text{HgSO}_4}A\xrightarrow{CH_3MgX}B\xrightarrow{[O]}$$

[Bihar CEE 2002]

(a) Acetic acid (b) Isopropyl alcohol

(c) Acetone (d) Ethanol

2. In the following reaction, product P is



$R-\overset{\overset{\displaystyle O}{||}}{C}-Cl\xrightarrow[Pd-BaSO_4]{H_2}P$ **[CBSE PMT 1991, 2000, 02; Kerala CET 2001;**

IIT 1992; AIIMS 1997; AFMC 1998]

(a) RCH_2OH (b) $RCOOH$

(c) $RCHO$ (d) RCH_3

3. Acetophenone is prepared from **[CPMT 2003]**

(a) Rosenmund reaction

(b) Sandmayer reaction

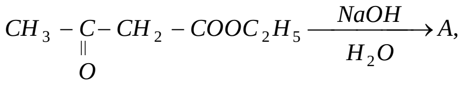
(c) Wurtz reaction

(d) Friedel craft reaction

4. Compound which gives acetone on ozonolysis **[UPSEAT 2003]**

(a) $CH_3-CH=CH-CH_3$ (b) $(CH_3)_2C=C(CH_3)_2$

(c) $C_6H_5CH=CH_2$ (d) $CH_3CH=CH_2$

5. 

$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-COOC_2H_5\xrightarrow[H_2O]{NaOH}A,$

product '*A*' in the reaction is **[RPMT 2003]**

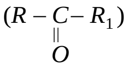
(a) CH_3COOH (b) C_2H_5OH

(c) CH_3COCH_3 (d) C_2H_5CHO

6. Which one of the following compounds is prepared in the laboratory from benzene by a substitution reaction **[EAMCET 2003]**

(a) Glyoxal (b) Cyclohexane

(c) Acetophenone (d) Hexabromo cyclohexane

7. Ketones  $(R-\underset{\underset{O}{\|}}{C}-R_1)$ where $R=R_1=$ alkyl group. It can be obtained in one step by **[CBSE PMT 1997]**

(a) Hydrolysis of esters

(b) Oxidation of primary alcohol

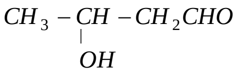
(c) Oxidation of secondary alcohol

(d) Reaction of acid halide with alcohols

8. Predict the product '*B*' in the sequence of reaction

$HC\equiv CH\xrightarrow[HgSO_4]{30\%H_2SO_4}A\xrightarrow{NaOH}B$ **[CBSE PMT 2001]**

(a) CH_3COONa (b) CH_3COOH

(c) CH_3CHO (d)  $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2CHO$

9. $CH_3COCl\xrightarrow[Pd/BaSO_4]{2H}CH_3CHO+HCl;$

The above reaction is called **[JIPMER 1997]**

(a) Reimer-Tiemann reaction (b) Cannizzaro reaction

(c) Rosenmund reaction (d) Reformatsky reaction

10. The oxidation of toluene to benzaldehyde by chromyl chloride is called **[CBSE PMT 1996; AFMC 1998, 99; AIIMS 2000; JIPMER 2001; AFMC 2001; DCE 2004]**

(a) Cannizzaro reaction (b) Wurtz reaction

(c) Etard reaction (d) Reimer-Tiemann reaction

11. From which of the following tertiary butyl alcohol is obtained by the action of methyl magnesium iodide **[MP CET 2000]**

(a) $HCHO$ (b) CH_3CHO

(c) CH_3COCH_3 (d) CO_2

12. Catalyst used in Rosenmund reduction is **[Bihar MEE 1997]**

(a) $Pd\ /\ BaSO_4$ (b) *Zn-Hg* couple

(c) $LiAlH_4$ (d) Ni/H_2

13. $CH_3-CH_2-C\equiv CH\xrightarrow[H_2O]{R}$ Butanone, *R* is **[BHU 2003]**

(a) Hg^{++} (b) $KMnO_4$

(c) $KClO_3$ (d) $K_2Cr_2O_7$

14. Dry heating of calcium acetate gives **[DPMT 1979, 81, 96; NCERT 1981; KCET 1993; Bihar CEE 1995; MNR 1986; MP PMT 1997; MP PET 1993, 95; JIPMER 2002; AIIMS 1996; CPMT 1982, 86, 96, 2003; RPMT 2002]**

(a) Acetaldehyde (b) Ethane

(c) Acetic acid (d) Acetone

15. Identify the product *C* in the series

$CH_3CN\xrightarrow{Na/C_2H_5OH}A\xrightarrow{HNO_2}B\xrightarrow{\text{Tollen's reagent}}C$ **[MP PET 1999]**

(a) CH_3COOH (b) CH_3CH_2NHOH

(c) CH_3CONH_2 (d) CH_3CHO

16. Acetophenone is prepared by the reaction of which of the following in the presence of $AlCl_3$ catalyst **[AIIMS 1996]**

(a) Phenol and acetic acid

(b) Benzene and acetone

(c) Benzene and acetyl chloride

(d) Phenol and acetone

17. Isopropyl alcohol on oxidation gives **[RPMT 1997; BHU 1997]**

(a) Acetone (b) Acetaldehyde

(c) Ether (d) Ethylene

18. On heating calcium acetate and calcium formate, the product formed is **[DPMT 1984; EAMCET 1985; MP PMT 1996, 92; KCET 1990; CPMT 1979, 82, 84; BIT 1992; RPET 2000]**

(a) CH_3COCH_3 (b) CH_3CHO

(c) $HCHO+CaCO_3$ (d) $CH_3CHO+CaCO_3$

19. Which of the following compound gives a ketone with Grignard reagent **[CPMT 1988; MP PET 1997]**

(a) Formaldehyde (b) Ethyl alcohol

(c) Methyl cyanide (d) Methyl iodide

20. In the Rosenmund's reduction, $BaSO_4$ taken with catalyst *Pd* acts as

(a) Promotor (b) Catalytic poison

(c) Cooperator (d) Absorber

21. The Clemmenson reduction of acetone yields
(a) Ethanol
(b) Ethanal
(c) Propane
(d) Propanol

22. Catalyst $SnCl_2/HCl$ is used in **[BHU 1995]**
(a) Stephen's reduction
(b) Cannizzaro reaction
(c) Clemmensen's reduction
(d) Rosenmund's reduction

23. Methyl ethyl ketone is prepared by the oxidation of
[IIT-JEE 1987; MP PMT 1992]
(a) 2-propanol
(b) 1-butanol
(c) 2-butanol
(d) *t*-butyl alcohol

24. Benzaldehyde can be prepared by oxidation of toluene by
[BHU 1986]
(a) Acidic $KMnO_4$
(b) $K_2Cr_2O_7$
(c) CrO_2Cl_2
(d) All of these

25. $C_6H_6 + CO + HCl \xrightarrow{\text{Anhy } AlCl_3} X + HCl$
Compound X is **[DPMT 1979, 83]**
(a) $C_6H_5CH_3$
(b) $C_6H_5CH_2Cl$
(c) C_6H_5CHO
(d) C_6H_5COOH

26. Which of the following gases when passed through warm dilute solution of H_2SO_4 in presence of $HgSO_4$ gives acetaldehyde
(a) CH_4
(b) C_2H_6
(c) C_2H_4
(d) C_2H_2

27. CH_3COCH_3 can be obtained by
(a) Heating acetaldehyde with methanol
(b) Oxidation of propyl alcohol
(c) Oxidation of isopropyl alcohol
(d) Reduction of propionic acid

28. Propyne on hydrolysis in presence of HCl and $HgSO_4$ gives **[DPMT 1980; CPMT 1983]**
(a) Acetaldehyde
(b) Acetone
(c) Formaldehyde
(d) None of these

29. Which of the following on reaction with NH_3 gives urinary antiseptic compound **[MP PMT 1999]**
(a) $HCHO$
(b) CH_3CHO
(c) C_6H_5CHO
(d) $C_6H_5CH_2CHO$

30. The oxidation product of 2-propanol with hot conc. HNO_3 is
(a) Ethanoic acid
(b) Propanone
(c) Propanal
(d) None of these

31. Hydrolysis of ozonide of 1-butene gives **[Kerala PMT 2003]**
(a) Ethylene only
(b) Acetaldehyde and Formaldehyde
(c) Propionaldehyde and Formaldehyde
(d) Acetaldehyde only
(e) Acetaldehyde and Oxalic acid

32. Ketones are prepared by
(a) Clemmensen's reduction
(b) Cannizzaro reaction
(c) Rosenmund's reduction
(d) Oppenaur's oxidation

33. O_3 reacts with $CH_2=CH_2$ to form ozonide. On hydrolysis it forms **[MP PET 1986, 90]**
(a) Ethylene oxide
(b) $HCHO$
(c) Ethylene glycol
(d) Ethyl alcohol

34. Ethyne on reaction with water in the presence of $HgSO_4$ and H_2SO_4 gives **[UPSEAT 1999; BVP 2003]**
(a) Acetone
(b) Acetaldehyde
(c) Acetic acid
(d) Ethyl alcohol

35. $CH_3-CH_2-C\equiv CH \xrightarrow[H_2SO_4]{HgSO_4} A$, the compound A is
[Orissa JEE 2004]
(a) $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$
(b) $CH_3-CH_2-CH_2-CHO$
(c) $CH_3-CH_2-CH_2-COOH$
(d) None of these

36. When a mixture of methane and oxygen is passed through heated molybdenum oxide, the main product formed is
[KCET 2004]
(a) Methanoic acid
(b) Ethanal
(c) Methanol
(d) Methanal

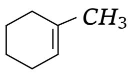
37. Benzoin is **[EAMCET 1986]** **[KCET 2004]**
(a) Compound containing an aldehyde and a ketonic group
(b) α, β-unsaturated acid
[CBSE PMT 1992]
(c) α-hydroxy aldehyde
(d) α-hydroxy ketone

38. The oxidation of benzyl chloride with lead nitrate gives
[MP PMT 2004]
(a) Benzyl alcohol
(b) Benzoic acid
(c) Benzaldehyde
(d) *p*-chlorobenzaldehyde

39. $R-CH=CH_2+CO+H_2$
$\xrightarrow[\text{High Pressure}]{\text{High Temp}} RCH_2CH_2CHO.$ **[DPMT 2004]**
The above reaction is
(a) Mendius reaction
(b) Oxo process
(c) Sandorn's reaction
(d) Stephen's reaction

40. Glycerol reacts with potassium bisulphate to produce
[JIPMER 1997] **[Pb. CET 2003]**
(a) Allyl iodide
(b) Allyl sulphate
(c) Acryl aldehyde
(d) Glycerol trisulphate

41. The reagent used in Gatterman Koch aldehyde synthesis is
[CPMT 2004]
(a) $Pb/BaSO_4$
(b) alkaline $KMnO_4$
(c) acidic $KMnO_4$
(d) $CO+HCl$



42. On reductive ozonolysis yields **[Orissa JEE 2005]**

(a) 6-oxoheptanal (b) 6-oxoheptanoic acid

(c) 6-hydroxyheptanal (d) 3-hydroxypentanal

43. An alkene of molecular formula C_9H_{18} on ozonolysis gives 2,2 dimethyl propanal & 2-butanon, then the alkene is **[Kerala CET 2005]**

(a) 2, 2, 4-trimethyl –3-hexene

(b) 2, 2, 6-trimethyl-3-hexene

(c) 2, 3, 4-trimethyl-2-hexene

(d) 2, 2, 4-trimethyl-2-hexene

(e) 2, 2dimethyl-2-heptene

Properties

1. Identify the reactant X and the product Y

$$\begin{array}{c} CH_3-CO-CH_3+X\rightarrow (CH_3)_3\,C-OMg-Cl \\ \big\downarrow \text{Hydrolysis} \\ Y+Mg\,(OH)\,Cl \end{array}$$

[Kerala PMT 2003]

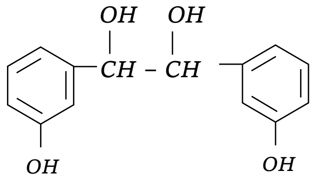
(a) $X=MgCl_2;\; Y=CH_3CH=CH_2$

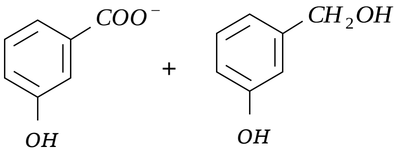
(b) $X=CH_3MgCl; Y=C_2H_5COCH_3$

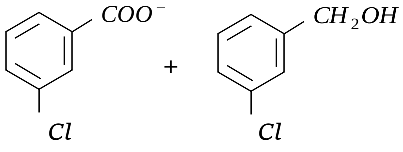
(c) $X=CH_3MgCl; Y=(CH_3)_3\;C-OH$

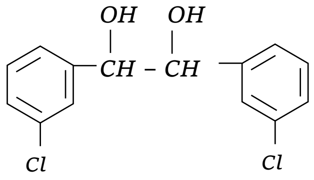
(d) $X=C_2H_5MgCl; Y=(CH_3)_3C-OH$

2. When *m*-chlorobenzaldehyde is treated with 50% *KOH* solution, the product (*s*) obtained is (are) **[CBSE PMT 2003]**

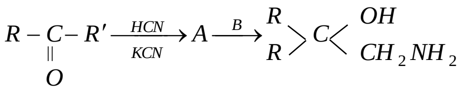
(a) 

(b) 

(c) 

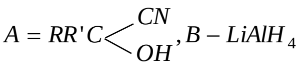
(d) 

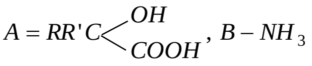
3. A and B in the following reactions are

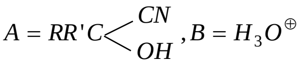


$$R-\underset{\underset{O}{\|}}{C}-R'\xrightarrow[KCN]{HCN}A\xrightarrow{B}\begin{smallmatrix}R\\R\end{smallmatrix}\!\!>C<\!\!\begin{smallmatrix}OH\\CH_2NH_2\end{smallmatrix}$$

[CBSE PMT 2003]

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

4. Reduction of Aldehydes and Ketones to hydrocarbon take place in the presence of **[CPMT 2003]**

(a) *Zn* amalgam and *HCl* acid

(b) $Pd/BaSO_4$

(c) Anhydrous $AlCl_3$

(d) *Ni*/*Pt*

5. Reduction of $>C=O$ to CH_2 can be carried out with **[DCE 2000]**

(a) Catalytic reduction (b) Na/C_2H_5OH

(c) Wolf-Kischner reduction (d) $LiAlH_4$

6. For C_6H_5CHO which of the following is incorrect **[CPMT 1985]**

(a) On oxidation it yields benzoic acid

(b) It is used in perfumery

(c) It is an aromatic aldehyde

(d) On reduction yields phenol

7. Grignard reagent on reaction with acetone forms **[BHU 1995; RPMT 2002; Roorkee 1990]**

(a) Tertiary alcohol (b) Secondary alcohol

(c) Acetic acid (d) Acetaldehyde

8. Which of the following is incorrect **[CBSE PMT 2001]**

(a) $FeCl_3$ is used in the detection of phenols

(b) Fehling solution is used in the detection of glucose

(c) Tollen's reagent is used in detection of unsaturation

(d) $NaHSO_3$ is used in the detection of carbonyl compounds

9. Consider the following statement Acetophenone can be prepared by

(1) Oxidation of 1-phenylethanol

(2) Reaction of benzalthanol with methyl magnesium bromide

(3) Friedel craft's reaction of benzene with acetyl chloride

(4) Distillation of calcium benzoate [SCRA 2001]

(a) 1 and 2 (b) 1 and 4

(c) 1 and 3 (d) 3 and 4

10. Which one of the following pairs is not correctly matched

[SCRA 2001]

(a) $>C=O \xrightarrow{\text{Clemenson's reduction}} >CH_2$

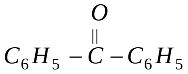
(b) $>C=O \xrightarrow{\text{Wolf-Kishner reduction}} >CHOH$

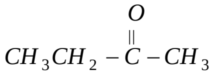
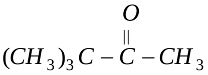
(c) $-COCl \xrightarrow{\text{Rosenmund's reduction}} CHO$

(d) $-C\equiv N \xrightarrow{\text{Stephen reduction}} CHO$

11. Which of the following gives aldol condensation reaction

[CPMT 2001]

(a) C_6H_5OH (b) 
$C_6H_5-\overset{\overset{O}{||}}{C}-C_6H_5$

(c) 
$CH_3CH_2-\overset{\overset{O}{||}}{C}-CH_3$ (d) 
$(CH_3)_3C-\overset{\overset{O}{||}}{C}-CH_3$

12. Which of the following products is formed when benzaldehyde is treated with CH_3MgBr and the addition product so obtained is subjected to acid hydrolysis

[Haryana CEET 2000]

(a) Secondary alcohol (b) A primary alcohol

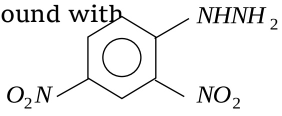
(c) Phenol (d) Tert-Butyl alcohol

13. Aldol condensation will not be observed in **[GATE 2001]**

(a) Chloral (b) Phenyl acetaldehyde

(c) Hexanal (d) Ethanol

14. Which of the following compounds containing carbonyl group will give coloured crystalline compound with



[Kerala (Med.) 2001]

(a) CH_3COCl (b) CH_3COCH_3

(c) $CH_3CO(OC_2H_5)$ (d) CH_3CONH_2

(e) $HO(C_6H_4)COOH$

15. Which of the following organic compounds exhibits positive Fehling test as well as iodoform test

[MP PET 1994; KCET 2001]

(a) Methanal (b) Ethanol

(c) Propanone (d) Ethanal

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

[CBSE PMT 1994]

(a) C_6H_5CHO (b) CH_3CH_2CHO

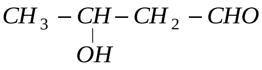
(c) $CH\equiv C-CHO$ (d) $CH_2=CH-CHO$

17. Acetaldehyde when treated with dilute $NaOH$ gives

[EAMCET 1998]

(a) CH_3CH_2OH

(b) CH_3COOH

(c) 
$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$

(d) CH_3-CH_3

18. C_2H_5CHO and $(CH_3)_2CO$ can be distinguished by testing with

MP PMT 1996; RPMT 1997, 99]

(a) Phenyl hydrazine (b) Hydroxylamine

(c) Fehling solution (d) Sodium bisulphite

19. Which of the following will undergo aldol condensation

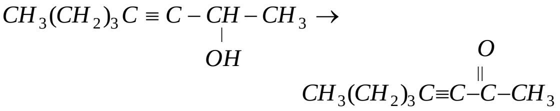
[IIT 1998]

(a) Acetaldehyde (b) Propanaldehyde

(c) Benzaldehyde (d) Trideuteroacetaldehyde

20. Which of the following oxidation reactions can be carried out with chromic acid in aqueous acetone at $5-10^oC$

[Roorkee Qualifying 1998]

(a) 
$CH_3(CH_2)_3C\equiv C-\underset{\underset{OH}{|}}{CH}-CH_3 \rightarrow CH_3(CH_2)_3C\equiv C-\overset{\overset{O}{||}}{C}-CH_3$

(b) $CH_3(CH_2)_3CH=CH-CH_2OH \rightarrow CH_3(CH_2)_3CH=CH-CHO$

(c) $C_6H_5CH_3 \rightarrow C_6H_5COOH$

(d) $CH_3(CH_2)_3CH_2OH \rightarrow CH_3(CH_2)_3CHO$

21. Acetaldehyde cannot show **[AIIMS 1997]**

(a) Iodoform test (b) Lucas test

(c) Benedict's test (d) Tollen's test

22. Benzaldehyde $+NaOH \rightarrow$

[CPMT 1997, 2001; CBSE PMT 1999; Pb. PMT 1999]

(a) Benzyl alcohol (b) Benzoic alcohol

(c) Hydrobenzamide (d) Cinnamic acid

23. The following reagent converts C_6H_5COCHO to $C_6H_5CHOHCOONa$ **[Roorkee Qualifying 1998]**

(a) Aq. $NaOH$ (b) Acidic $Na_2S_2O_3$

(c) Na_2CrO_4/H_2SO_4 (d) $NaNO_2/HCl$

24. Benzyl alcohol and sodium benzoate is obtained by the action of sodium hydroxide on benzaldehyde. This reaction is known as

(a) Perkin's reaction (b) Cannizzaro's reaction

(c) Sandmeyer's reaction (d)Claisen condensation

25. To distinguish between formaldehyde and acetaldehyde, we require

(a) Tollen's reagent (b) Fehling's solution

(c) Schiff's reagent (d) Caustic soda solution

26. Which of the following does not give iodoform test

[AIIMS 1992; MP PMT 1990, 96; CET Pune 1998 DPMT 1981; CPMT 1976]

(a) CH_3CH_2OH (b) CH_3OH

(c) CH_3CHO (d) $PhCOCH_3$

27. Which of the following will not give iodoform test

[Kurukshetra CEE 1991; Bihar CEE 1995; CBSE PMT 1998; MP PMT 2004]

(a) Ethanal (b) Ethanol

(c) 2-propanone (d) 3-pentanone

28. Which of the following will not give the iodoform test

[MNR 1994]

(a) Acetophenone (b) Ethanal

(c) Benzophenone (d) Ethanol

29. Haloform test is given by the following substance

[EAMCET 1988]

(a) $HCHO$ (b) $(CH_3)_2CO$

(c) CH_3OCH_3 (d) CH_3CH_2Cl

30. Dimethyl ketones are usually characterised through

[MNR 1992]

(a) Tollen's reagent (b) Iodoform test

(c) Schiff's test (d) Benedict's reagent

31. The light yellow compound produced when acetone reacts with iodine and alkali, is **[MP PMT 1992; EAMCET 1993]**

(a) $CH_3.CO.CH_2I$ (b) CH_3I

(c) CHI_3 (d) None of these

32. If formaldehyde and KOH are heated, then we get

[MP PET 1999; KCET 2000]

(a) Acetylene (b) Methane

(c) Methyl alcohol (d) Ethyl formate

33. Which of the following reagent reacts differently with $HCHO, CH_3CHO$ and CH_3COCH_3 **[MP PET 1999]**

(a) HCN (b) NH_2NH_2

(c) NH_2OH (d) NH_3

34. Acetaldehyde reacts with C_2H_5MgCl the final product is

[Pb. CET 1985]

(a) An aldehyde (b) A ketone

(c) A primary alcohol (d) A secondary alcohol

35. Treatment of propionaldehyde with dilute $NaOH$ solution gives **[MNR 1992]**

(a) $CH_3CH_2COOCH_2CH_2CH_3$

(b) $CH_3CH_2CHOHCH(CH_3)CHO$

(c) $CH_3CH_2CHOHCH_2CH_2CHO$

(d) $CH_3CH_2COCH_2CH_2CHO$

36. Aldol condensation of acetaldehyde involves the formation of which of the following intermediate **[Pb. CET 1986]**

(a) Acetate ion (b) A carbanion

(c) A carbonium ion (d) A free radical

37. $3CH_3COCH_3 \xrightarrow{HCl} (CH_3)_2C=CH-CO-CH=C(CH_3)_2$

This polymer (B) is obtained when acetone is saturated with hydrogen chloride gas, B can be

(a) Phorone (b) Formose

(c) Diacetone alcohol (d) Mesityl oxide

38. Aromatic aldehydes undergo disproportionation in presence of sodium or potassium hydroxide to give corresponding alcohol and acid. The reaction is known as **[MNR 1987]**

(a) Wurtz's reaction (b) Cannizzaro reaction

(c) Friedel-Craft's reaction (d) Claisen reaction

39. *m*-chlorobenzaldehyde on reaction with conc. KOH at room temperature gives **[IIT-JEE 1991]**

(a) Potassium *m*-chlorobenzoate and *m*-hydroxy benzaldehyde

(b) *m*-hydroxy benzaldehyde and *m*-chlorobenzyl alcohol

(c) *m*-chlorobenzyl alcohol and *m*-hydroxy benzyl alcohol

(d) Potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol

40. Which of the following does not give yellow precipitate with $NaOH + KI$

(a) Acetone (b) Acetaldehyde

(c) Benzaldehyde (d) Acetophenone

41. The alkaline $CuSO_4$ containing sodium potassium tartrate does not react with **[MP PMT 1997]**

(a) CH_3CHO (b) C_2H_5CHO

(c) $C_6H_5CH_2CHO$ (d) C_6H_5CHO

42. Correct order of reactivity of $CH_3CHO, C_2H_5COCH_3$ and CH_3COCH_3 is **[MP PMT 1991]**

(a) $CH_3CHO > CH_3COCH_3 > CH_3COC_2H_5$

(b) $C_2H_5COCH_3 > CH_3COCH_3 > CH_3CHO$

(c) $CH_3COCH_3 > CH_3CHO > C_2H_5COCH_3$

(d) $CH_3COCH_3 > C_2H_5COCH_3 > CH_3CHO$

43. One mole of an organic compound requires 0.5 mole of oxygen to produce an acid. The compound may be

[NCERT 1981]

(a) Alcohol (b) Ether

(c) Ketone (d) Aldehyde

44. Aldehydes can be oxidised by **[NCERT 1983]**

(a) Tollen's reagent (b) Fehling solution

(c) Benedict solution (d) All of these

45. Silver mirror is a test for **[DPMT 1983; CBSE PMT 1988]**

(a) Aldehydes (b) Thio alcohols

(c) Amines (d) Ethers

46. $CH_3CH=CHCHO$ is oxidised to $CH_3CH=CHCOOH$ using

(a) Alkaline $KMnO_4$ (b) Selenium dioxide

(c) Ammoniacal $AgNO_3$ (d) All of these

47. Which of the following does not turn Schiff's reagent to pink

[DPMT 1981; CPMT 1989]

(a) Formaldehyde (b) Benzaldehyde

(c) Acetone (d) Acetaldehyde

48. Fehling's test is positive for **[KCET 1993]**

(a) Acetaldehyde (b) Benzaldehyde

(c) Ether (d) Alcohol

49. Acetaldehyde and acetone differ in their reaction with

[KCET 1989]

(a) Sodium bisulphite

(b) Ammonia

(c) Phosphorus pentachloride

(d) Phenyl hydrazine

50. The final product formed when acetaldehyde is reduced with sodium and alcohol is **[BHU 1976]**

(a) Ethylene (b) Ethyl alcohol

(c) Ethene (d) All of these

51. The compound obtained by the reduction of propionaldehyde by amalgamated zinc and concentrated HCl is **[MP PMT 1983]**

(a) Propanol (b) Propane

(c) Propene (d) All of these

52. Formaldehyde when treated with KOH gives methanol and potassium formate. The reaction is known as

[MP PET 1997]

(a) Perkin reaction (b) Claisen reaction

(c) Cannizzaro reaction (d) Knoevenagel reaction

53. Aldehydes and ketones give addition reaction with

[KCET 1992]

(a) Hydrazine (b) Phenyl hydrazine

(c) Semicarbazide (d) Hydrogen cyanide

(e) All of these

54. Acetaldehyde reacts with **[CBSE PMT 1991]**

(a) Electrophiles only

(b) Nucleophiles only

(c) Free radicals only

(d) Both electrophiles and nucleophiles

55. The typical reactions of aldehyde is **[Pb. CET 1986]**

(a) Electrophilic addition (b)Nucleophilic substitution

(c) Nucleophilic addition (d)Nucleophilic elimination

56. Which will not give acetamide on reaction with ammonia

[CPMT 1985]

(a) Acetic acid (b) Acetyl chloride

(c) Acetic anhydride (d) Methyl formate

57. The addition of HCN to carbonyl compounds is an example of **[Haryana CEET 2000]**

(a) Nucleophilic substitution

(b) Electrophilic addition

(c) Nucleophilic addition

(d) Electrophilic substitution

58. Which of the following reagents is used to distinguish acetone and acetophenone**[RPMT 2002; KCET 1**

(a) $NaHSO_3$ (b) Grignard reagent

(c) Na_2SO_4 (d) NH_4Cl

59. The product formed by the reaction of chlorine with benzaldehyde in the absence of a catalyst is

[Tamil Nadu CET 2002]

(a) Chlorobenzene (b) Benzyl chloride

(c) Benzoyl Chloride (d) *o*-Chlorobenzaldehyde

60. Which of the following compound is resistant to nucleophilic attack by hydroxyl ions

[CBSE PMT 1998; KCET (Med.) 2001; AFMC 2001]

(a) Methyl acetate (b) Acetonitrile

(c) Dimethyl ether (d) Acetamide

61. Glucose molecule reacts with X number of molecules of phenylhydrazine to yield osazone. The value of X is

[CBSE PMT 1998]

(a) One (b) Two

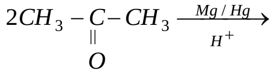
(c) Three (d) Four

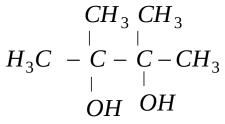
62. In which of the following reactions aromatic aldehyde is treated with acid anhydride in presence of corresponding salt of the acid to give unsaturated aromatic acid

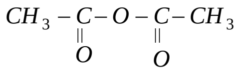
[BHU 1998, KCET (Med.) 2001]

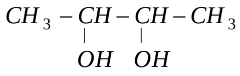
(a) Friedel-Craft's reaction (b) Perkin reaction

(c) Wurtz reaction (d) None of these

63. 
$2CH_3-\underset{\underset{O}{||}}{C}-CH_3 \xrightarrow[H^+]{Mg/Hg}$ Product, product in the reaction is **[RPMT 2003]**

(a) 
$H_3C-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3$

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

(c) 
$CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3$

(d) None of these

64. Cinnamic acid is formed when C_6H_5-CHO condenses with $(CH_3CO)_2O$ in presence of**[Orissa JEE 2003**

(a) Conc. H_2SO_4 (b) Sodium acetate

(c) Sodium metal (d) Anhydrous $ZnCl_2$

65. A mixture of benzaldehyde and formaldehyde on heating with aqueous $NaOH$ solution gives

[IIT-JEE (Screening) 2001]

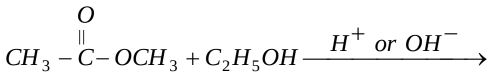
(a) Benzyl alcohol and sodium formate

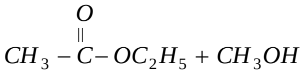
(b) Sodium benzoate and methyl alcohol

(c) Sodium benzoate and sodium formate

(d) Benzyl alcohol and methyl alcohol

66. The reaction,


$CH_3-\overset{\overset{O}{||}}{C}-OCH_3+C_2H_5OH \xrightarrow{H^+ \text{ or } OH^-}$



$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5+CH_3OH$ is called **[MP PMT 2003]**

(a) Perkin's reaction (b) Claisen Schmidt reaction

(c) Esterification (d) Trans-esterification

67. Formaldehyde reacts with ammonia to give urotropine. The formula of urotropine is

[MP PMT 1989, 96, 2003; AIIMS 1982; NCERT 1987; MP PET 1990, 91, 2000; CPMT 1978, 82, 86, 97; KCET 2003]

(a) $(CH_2)_6N_4$ (b) $(CH_2)_4N_3$

(c) $(CH_2)_6N_6$ (d) $(CH_2)_3N_3$

68. Aldol condensation will not take place in

[CBSE PMT 1996, 99; RPMT 1999; CPMT 1988, 04]

(a) $HCHO$ (b) CH_3CH_2CHO

(c) CH_3CHO (d) CH_3COCH_3

69. Contents of three bottles were found to react

(i) Neither with Fehling's solution nor with Tollen's reagent

(ii) Only with Tollen's reagent but not with Fehling's solution

(iii) With both Tollen's reagent and Fehling's solution.

If they contained either ethanal (acetaldehyde) or propanone (acetone) or benzal (benzaldehyde), which bottle contained which

(a) In (i) benzal, in (ii) ethanal and in (iii) propanone

(b) In (i) benzal, in (ii) propanone and in (iii) ethanal

(c) In (i) propanone, in (ii) benzal and in (iii) ethanal

(d) In (i) propanone, in (ii) ethanal and in (iii) benzal

70. Action of hydrazine on aldehydes and ketones gives compound of the general structure

(a) $>C=N-NH_2$

(b) $>C=N-OH$

(c) $>C=N-NH-CONH_2$

(d) $>C=N-NH-C_6H_5$

71. The reaction in which sodium cyanide is used

[MP PET/PMT 1998]

(a) Perkin reaction (b) Reimer-Tiemann reaction

(c) Benzoin condensation (d)Rosenmund reaction

72. Which one of the following reactions is a method for the conversion of a ketone into a hydrocarbon

[MP PET/PMT 1998; CBSE PMT 1989]

(a) Aldol condensation (b) Reimer-Tiemann reaction

(c) Cannizzaro reaction (d) Wolf-Kishner reduction

73. Bakelite is a polymer of **[DPMT 1996; MP PET 2002]**

(a) $HCHO+$ phenol

(b) $HCHO+$ aldehyde (acetaldehyde)

(c) Phenol $+H_2SO_4$

(d) $HCHO+$ acetone

74. Clemmenson reduction involves $>C=O$ to $>CH_2$ in presence of **[DPMT 1996]**

(a) $Zn\ /\ Hg$ (b) Alcohol

(c) Zn dust (d) Zn / alcohol

75. Aldol condensation involving $CH_3CHO+CH_3CHO$ gives the product **[DPMT 1996]**

(a) $CH_3CHOHCH_2CHO$ (b) $CH_3COCH_2CH_3$

(c) $CH_3CH=CH_2$ (d) None of these

76. Enol content is highest in

(a) Acetone (b) Acetophenone

(c) Acetic acid (d) Acetyl acetone

77. Which one of the following reacts with HCN and Tollen's reagent, but is not oxidised by Fehling's solution

(a) Methanal (b) Ethanal

(c) Benzaldehyde (d) Acetone

78. During reaction of benzaldehyde with alkali one of the product is

(a) Phenol (b) Benzyl alcohol

(c) Benzene (d) Benzophenone

79. Cannizzaro reaction is given by **[DPMT 1996]**

(a) $HCHO$ (b) CH_3COCH_3

(c) CH_3CHO (d) CH_3CH_2OH

80. The reaction

$C_6H_5CHO+CH_3CHO\rightarrow C_6H_5CH=CH-CHO$

is known as **[BHU 1996]**

(a) Perkin's reaction (b) Claisen condensation

(c) Benzoin condensation (d)Cannizzaro's reaction

81. When two molecules of acetaldehyde condense in the presence of dilute alkali, it forms**[Bihar MEE 1996]**

(a) Acetal (b) Sodium formate

(c) Aldol (d) Mesitylene

(e) None of these

82. Acetaldehyde on treatment with dil. $NaOH$ followed by heating gives

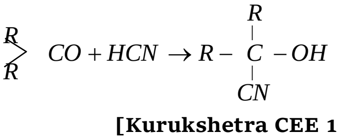
(a) $CH_3CH_2CH_2CH_2OH$

(b) $CH_3CH_2CH_2CHO$

(c) $CH_3-CH=CHCHO$

(d) $CH_3-CH=CHCH_2OH$

83. Reaction



$\frac{R}{R}\!>CO+HCN\rightarrow R-\underset{\underset{CN}{|}}{\overset{\overset{R}{|}}{C}}-OH$ is

[Kurukshetra CEE 1998; IIT 1990]

(a) Electrophilic substitution

(b) Electrophilic addition

(c) Nucleophilic addition

(d) Nucleophilic substitution

84. Benzaldehyde on reaction with acetophenone in the presence of sodium hydroxide solution gives **[BVP 20**

(a) $C_6H_5CH = CHCOC_6H_5$

(b) $C_6H_5COCH_2C_6H_5$

(c) $C_6H_5CH = CHC_6H_5$

(d) $C_6H_5CH(OH)COC_6H_5$

85. Aldehydes and ketones can be reduced to hydrocarbon by using **[Orissa JEE 2003]**

(a) $LiAlH_4$ (b) $H_2 / Pd - BaSO_4$

(c) $Na - Hg / HCl$ (d) $NH_2 - NH_2 / C_2H_5ONa$

86. An important reaction of acetone is autocondensation in presence of concentrated sulphuric acid to give the aromatic compound **[KCET 2003; MP PET 1986, 89; MP PMT 1992, 2000]**

(a) Mesitylene (b) Mesityl oxide

(c) Trioxan (d) Phorone

87. Identify the organic compound which, on heating with strong solution of $NaOH$, partly converted into an acid salt and partly into alcohol**[KCET 2003]**

(a) Benzyl alcohol (b) Acetaldehyde

(c) Acetone (d) Benzaldehyde

88. Which of the following does not give brick red precipitate with Fehling solution **[AIIMS 1996]**

(a) Acetone (b) Acetaldehyde

(c) Formalin (d) *D*-glucose

89. Acetaldehyde and acetone can be distinguished by **[AIIMS 1996; DCE 1999; Pb. CET 2000]**

(a) Molisch test (b) Bromoform test

(c) Solubility in water (d) Tollen's test

90. Which compound is soluble in H_2O **[RPMT 1997]**

(a) $HCHO$ (b) CH_3CHO

(c) CH_3COCH_3 (d) All

91. $CH_3CHO + CH_3MgBr \rightarrow \text{Product} \xrightarrow{H_2O} A$

What is A ? **[RPMT 1997]**

(a) Primary alcohol (b) Secondary alcohol

(c) Tertiary alcohol (d) Ketone

92. Which gives lactic acid on hydrolysis after reacting with HCN **[UPSEAT 2003; MP PMT 2003]**

(a) $HCHO$ (b) CH_3CHO

(c) C_6H_5CHO (d) CH_3COCH_3

93. CH_3CHO react with aqueous $NaOH$ solution to form

[MP PMT 1992]

(a) 3-hydroxy butanal (b) 2-hydroxy butanal

(c) 4-hydroxy butanal (d) 3-hydroxy butanol

94. Fehling solution react with $HCHO$ to form precipitate of

[MP PMT 1992]

(a) White colour (b) Yellow colour

(c) Red colour (d) Blue colour

95. Product in following reaction is

$CH_3MgI + HCHO \rightarrow \text{Product}$

[RPMT 2003; BHU 1998, 2005; DCE 1999]

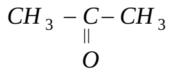
(a) CH_3CHO (b) CH_3OH

(c) C_2H_5OH (d) $CH_3 - O - CH_3$

96. $A \xrightarrow[800^oC]{\Delta} CH_2 = C = O$, Reactant '$A$' in the reaction is

[RPMT 2003]

(a) CH_3CH_2CHO (b) CH_3CHO

(c) 
$CH_3 - \underset{\underset{O}{||}}{C} - CH_3$ (d) C_2H_5OH

97. Only an aldehyde having..... can undergo the aldol condensation **[KCET 1998]**

(a) At least one beta H atom

(b) At least one alpha H atom

(c) An aromatic ring

(d) No alpha H atom

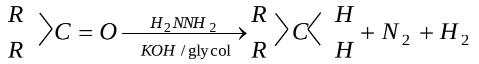
98. Clemenson's reduction of ketones is carried out in

[BHU 2000]

(a) H_2 with Pd catalyst (b) Glycol with KOH

(c) $LiAlH_4$ in water (d) $Zn - Hg$ with HCl

99. Reaction


$$\begin{matrix} R \\ R \end{matrix}\rangle C = O \xrightarrow[KOH/\text{glycol}]{H_2NNH_2} \begin{matrix} R \\ R \end{matrix}\rangle C\langle \begin{matrix} H \\ H \end{matrix} + N_2 + H_2$$

is called

[MP PET 2003]

(a) Wolff–Kishner reaction (b)Tischenko reaction

(c) Reformatsky reaction (d)Gattermann reaction

100. Propanal on treatment with dilute sodium hydroxide forms

[Kerala CET 2000]

(a) $CH_3CH_2CH_2CH_2CH_2CHO$

(b) $CH_3CH_2CH(OH)CH_2CH_2CHO$

(c) $CH_3CH_2CH(OH)CH(CH_3)CHO$

(d) CH_3CH_2COONa

101. Identify the product Y in the sequence $CH_3CHO + CH_3Mgl \xrightarrow{\text{Ether}} X \xrightarrow{H_2O/H^+} Y$

[Kerala (Med.) 2001]

(a) CH_3OH (b) CH_3CH_2OH

(c) $(CH_3)_2CHOH$ (d) $(CH_3)_3COH$

102. What is the name of reaction when benzaldehyde changes into benzyl alcohol**[CPMT 1996; RPET 1999]**

(a) Friedel-Craft's reaction (b) Kolbe's reaction

(c) Wurtz reaction (d) Cannizzaro reaction

103. The reagent that gives an orange coloured precipitate with acetaldehyde

[EAMCET 1997; Pb. PMT 2004; AIIMS 1987]

(a) NH_2OH (b) $NaHSO_3$

(c) Iodine (d) 2, 4-*DNP*

104. Which one is used in the manufacture of mirror

[MP PET 1992]

(a) Red lead (litharge)

(b) Ammoniacal $AgNO_3$

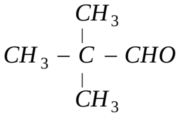
(c) Ammoniacal $AgNO_3 +$ Red lead

(d) Ammoniacal $AgNO_3 + HCHO$

105. When CH_3COCH_3 reacts with Cl_2 and $NaOH$, which of the following is formed **[CPMT 1996]**
(a) $CHCl_3$ (b) CCl_4
(c) CCl_2H_2 (d) CH_3Cl

106. Which gives difference between aldehyde and ketone **[CPMT 1994]**
(a) Fehling's solution (b) Tollen's reagent
(c) Schiff's reagent (d) Benedict's solution
(e) All of these

107. Aldehyde turns pink with **[Bihar MEE 1997]**
(a) Benedict solution (b) Schiff reagent
(c) Fehling solution (d) Tollen's reagent
(e) Mollisch reagent

108. Which of the following would undergo aldol condensation **[MP PMT 1986; BHU 1995]**
(a) $CCl_3.CHO$ (b)

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CHO$
(c) $CH_3.CH_2.CHO$ (d) $HCHO$

109. The reaction of acetaldehyde with conc. $KMnO_4$ gives **[DPMT 1982; AIIMS 1996]**
(a) CH_3COOH (b) CH_3CH_2OH
(c) $HCHO$ (d) CH_3OH

110. When acetaldehyde is heated with Tollen's reagent, following is obtained **[CPMT 1989; MP PET/PMT 1988]**
(a) Methyl alcohol (b) Silver acetate
(c) Silver mirror (d) Formaldehyde

111. Boiling point of acetone is **[CPMT 1975, 89]**
(a) 56^oC (b) 60^oC
(c) 100^oC (d) 90^oC

112. Urotropine is
(a) Hexamethylene tetramine
(b) Hexaethylene tetramine
(c) Hexamethylene diamine
(d) None of these

113. Magenta is **[DPMT 1982; Kurukshetra CEE 1998]**
(a) Alkaline phenolphthalein
(b) Methyl red
(c) *p*-rosaniline hydrochloride
(d) Red litmus

114. An aldehyde on oxidation gives **[CPMT 1973, 03; DPMT 1983; Manipal MEE 1995]**
(a) An alcohol (b) An acid
(c) A ketone (d) An ether

115. The reaction of an aldehyde with hydroxylamine gives a product which is called **[MP PET 1993; AFMC 2002]**
(a) Aminohydroxide (b) Hydrazone
(c) Semicarbazone (d) Oxime

116. Cannizzaro reaction is not shown by **[BHU 1980; IIT 1983; KCET 1993; Bihar MEE 1995; RPMT 1997, 2000, 02]**
(a) $HCHO$ (b) C_6H_5CHO
(c) CH_3CHO (d) All of these

117. When acetone is heated with hydroxylamine, the compound formed is **[MP PMT 1993]**
(a) Cyanohydrin (b) Oxime
(c) Semicarbazone (d) Hydrazone

118. The product of the reaction between ammonia and formaldehyde is **[MP PMT 1993]**
(a) Urotropine (b) Formamide
(c) Paraformaldehyde (d) Methanol

119. Which of the following products is obtained by the oxidation of propionaldehyde **[CPMT 1989]**
(a) Acetic acid
(b) Formic acid and acetic acid
(c) Propanoic acid
(d) *n*-propyl alcohol

120. When acetaldehyde reacts with PCl_5, the resulting compound is **[MP PMT 1992, 93]**
(a) Ethyl chloride (b) Ethylene chloride
(c) Ethylidene chloride (d) Trichloro acetaldehyde

121. Benzaldehyde and acetaldehyde can be differentiated by
(a) HCN (b) NH_2OH
(c) Hydrazine (d) $NaOH$ solution

122. In the presence of a dilute base C_6H_5CHO and CH_3CHO react together to give a product. The product is **[MP PET 1994]**
(a) $C_6H_5CH_3$ (b) $C_6H_5CH_2CH_2OH$
(c) $C_6H_5CH_2OH$ (d) $C_6H_5CH=CHCHO$

123. Grignard's reagent reacts with ethanal (acetaldehyde) and propanone to give
(a) Higher aldehydes with ethanal and higher ketones with propanone
(b) Primary alcohols with ethanal and secondary alcohols with propanone
(c) Ethers with ethanal and alcohols with propanone
(d) Secondary alcohols with ethanal and tertiary alcohols with propanone

124. Base catalysed aldol condensation occurs with **[IIT-JEE 1991]**
(a) Benzaldehyde

(b) 2, 2-dimethyl propionaldehyde
(c) Acetaldehyde
(d) Formaldehyde

125. Benzaldehyde reacts with ammonia to form **[CPMT 1989; AFMC 1998]**
(a) Benzaldehyde ammonia
(b) Urotropine
(c) Hydrobenzamide
(d) Aniline

126. Glucose + Tollen's reagent → Silver mirror shows **[CPMT 1997]**
(a) Presence of acidic group
(b) Presence of alkaline group
(c) Presence of ketonic group
(d) Presence of aldehyde group

127. Fehling solution is **[MP PMT 1989]**
(a) Ammoniacal cuprous chloride solution
(b) Acidified copper sulphate solution
(c) Copper sulphate and sodium hydroxide + Rochelle salt
(d) None of these

128. Reduction of an aldehyde produces **[MP PMT 1994; MP PET 2001]**
(a) Primary alcohol (b) Monocarboxylic acid
(c) Secondary alcohol (d) Tertiary alcohol

129. Which of the following on reaction with conc. $NaOH$ gives an alcohol **[MP PET 1996]**
(a) Methanal (b) Ethanal
(c) Propanal (d) Butanal

130. Schiff's reagent is **[MP PMT 1989]**
(a) Magenta colour solution decolourised with sulphurous acid
(b) Ammoniacal cobalt chloride solution
(c) Ammoniacal manganese sulphate solution
(d) Magenta solution decolourised with chlorine

131. Pyrolysis of acetone gives $CH_2 = C = O$ called
(a) Methylene oxide
(b) Methyl carbon monoxide
(c) Ketene
(d) Methone

132. Which one of the following on oxidation will not give a carboxylic acid with the same number of carbon atoms **[CBSE PMT 1992; MP PET 1996]**
(a) CH_3COCH_3 (b) CCl_3CH_2CHO
(c) $CH_3CH_2CH_2OH$ (d) CH_3CH_2CHO

133. Acetal is obtained by reacting in the presence of dry HCl and alcohol with **[MP PET 1996]**
(a) Aldehyde (b) Ketone
(c) Ether (d) Carboxylic acid

134. The reagent with which both aldehyde and acetone react easily is **[CPMT 1973, 74, 89; BIT 1992]**
(a) Fehling's reagent (b) Grignard reagent
(c) Schiff's reagent (d) Tollen's reagent

135. Phenylmethanol can be prepared by reducing the benzaldehyde with **[CBSE PMT 1997]**
(a) CH_3Br (b) Zn and HCl
(c) CH_3Br and Na (d) CH_3I and Mg

136. Which of the following is used in the manufacture of thermosetting plastics
(a) Formaldehyde (b) Acetaldehyde
(b) Acetone (d) Benzaldehyde

137. Which compound undergoes iodoform reaction **[DPMT 1984; CPMT 1989]**
(a) $HCHO$ (b) CH_3CHO
(c) CH_3OH (d) CH_3COOH

138. Which does not react with Fehling solution **[MNR 1983, 93]**
(a) Acetaldehyde (b) Benzaldehyde
(c) Glucose (d) Formic acid

139. Which of the following compound will react with ethanolic KCN **[IIT-JEE 1984]**
(a) Ethane (b) Acetyl chloride
(c) Chlorobenzene (d) Benzaldehyde

140. Schiff's reagent gives pink colour with **[EAMCET 1980; MP PMT 2000]**
(a) Aldehydes (b) Ethers
(c) Ketones (d) Carboxylic acid

141. Acetaldehyde reacts with Cl_2 (in excess) to give **[MP PMT 1997]**
(a) Chloral (b) Chloroform
(c) Acetic acid (d) Trichloroacetic acid

142. The compound which reacts with Fehling solution is **[CPMT 1989]**
(a) C_6H_5COOH (b) $HCOOH$
(c) C_6H_5CHO (d) CH_2ClCH_3

143. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid
(a) Butanal (b) Benzaldehyde
(c) Phenol (d) Benzoic acid

144. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon **[AIEEE 2004]**
(a) Acetamide (b) Acetic acid
(c) Ethyl acetate (d) Butan–2–one

145. Three molecules of acetone in the presence of dry HCl form

[MP PET 2004]

(a) Mesitylene (b) Phorone
(c) Glyoxal (d) Mesityl oxide

146. Aldehydes and ketones can be reduced to corresponding hydrocarbons by

(a) Refluxing with water
(b) Refluxing with strong acids
(c) Refluxing with soda amalgam and water
(d) Refluxing with zinc amalgam and concentrated HCl
(e) Passing the vapour under heated PbO_2

[MHCET 2004]

147. Acetone reacts with iodine to form iodoform in the presence of

(a) $CaCO_3$ (b) $NaOH$
(c) KOH (d) $MgCO_3$

148. Cyanohydrin of which of the following forms lactic acid

[MHCET 2003]

(a) CH_3CH_2CHO (b) CH_3CHO
(c) $HCHO$ (d) CH_3COCH_3

149. Which of the following is used to detect aldehydes

[MHCET 2004]

(a) Million's test
(b) Tollen's reagent
(c) Neutral ferric chloride solution
(d) Molisch's test

150. Which of the following aldehydes give red precipitate with Fehling solution ?

(a) Benzaldehyde (b) Salicylaldehyde
(c) Acetaldehyde (d) None of these

151. $A \longrightarrow (CH_3)_2C = CHCOCH_3$ A is **[MHCET 2004]**

(a) Acetone (b) Acetaldehyde
(c) Propionaldehyde (d) Formaldehyde

152. The aldehyde which react with $NaOH$ to produce an alcohol and sodium salt is

(a) $HCHO$ (b) CH_3CHO
(c) CH_3CH_2CHO (d) $CH_3CH_2CH_2CHO$

153. Acetaldehyde and Acetone can be distinguished by

[DCE 2003]

(a) Iododorm test
(b) Nitroprusside test
(c) Fehling's solution test
(d) DNP test

154. $OCH - CHO \xrightarrow{OH^-} HOH_2C - COOH$

The reaction given is **[DCE 2003]**

(a) Aldol condensation (b) Knovengel reaction
(c) Cannizzaro reaction (d) None of these

155. The order of susceptibility of nucleophilic attack on aldehydes follows the order

(a) $1^\circ > 3^\circ > 2^\circ$ (b) $1^\circ > 2^\circ > 3^\circ$
(c) $3^\circ > 2^\circ > 1^\circ$ (d) $2^\circ > 3^\circ > 1^\circ$

156. In Wolf-Kishner reduction, the carbonyl group of aldehydes and ketones is converted into

[Kerala PMT 2004]

(a) $>CH_2$ group (b) $-CH_3$ group
(c) $-CH_2OH$ group (d) $>CHOH$ group

157. Which of the following react with $NaHSO_3$

[Pb. CET 2003]

(a) CH_3COCH_3 (b) CH_3CHO
(c) $HCHO$ (d) All of these

158. Fehling solution is **[Pb. CET 2003]**

[BHU 2004; CPMT 2004]

(a) $CuSO_4$ + lime (b) $CuSO_4 + NaOH(aq)$
(c) $CuSO_4 + Na_2CO_3$ (d) None of these

159. Wolf kishner reduction, reduces

(a) $-COOH$ group (b) $-C \equiv C-$ group
(c) $-CHO$ group (d) $-O-$ group

160. A compound has a vapour density of 29. On warming an aqueous solution of alkali, it gives a yellow precipitate. The compound is

(a) CH_3CH_2CHO (b) $CH_3CHOHCH_3$
(c) CH_3COCH_3 (d) CH_3CH_2COOH

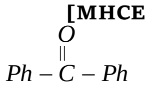
161. Which responds to +ve iodoform test ?**[Orissa JEE 2004]**

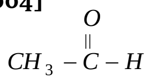
(a) Butanol (b) Butan-1-al
(c) Butanol-2 (d) 3-pentanone

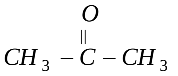
162. The correct order of reactivity of $PhMgBr$ with

[IIT-JEE (Screening) 2004]

[MHCET 2004]


$Ph-\overset{\overset{O}{\parallel}}{C}-Ph$


$CH_3-\overset{\overset{O}{\parallel}}{C}-H$


$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$ is

(I) (II) (III)

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

163. The pair of compounds in which both the compounds give positive test with Tollen's reagent is

[Pb. PMT 2004]

[IIT-JEE (Screening) 2004]

(a) Glucose and Sucrose
(b) Fructose and Sucrose
(c) Acetophenone and Hexanal
(d) Glucose and Fructose

164. The most appropriate reagent to distinguish between acetaldehyde and formaldehyde is**[UPSEAT 2004]**

(a) Fehling's solution
(b) Tollen's reagent
(c) Schiff's reagent
(d) Iodine in presence of base

165. Silver mirror test can be used to distinguish between

[MP PET 2004]

(a) Ketone and acid (b) Phenol and acid

(c) Aldehyde and acid (d) Alcohol and phenol

166. Paraldehyde is **[CPMT 1985; MP PET 1992, 96; RPMT 2000]**

(a) A trimer of formaldehyde

(b) A trimer of acetaldehyde

(c) A hexamer of formaldehyde

(d) A hexamer of acetaldehyde

167. Paraldehyde is used as a **[CBSE PMT 1989]**

(a) Medicine (b) Poison

(c) Polymer (d) Dye

168. Formalin is an aqueous solution of **[BHU 1979; DPMT 1983]**

(a) Formic acid (b) Formaldehyde

(c) Fluorescein (d) Furfuraldehyde

169. Hexamethylene tetramine is used as **[MP PMT 1979, 84]**

(a) Analgesic (b) Antipyretic

(c) Urinary antiseptic (d) All of these

170. Methyl ketone group is identified by **[BCECE 2005]**

(a) Iodoform test (b) Fehling solution

(c) Tollen's reagent (d) Shiff's reagent

171. Which of the following does not give Fehling solution test? **[BCECE 2005]**

(a) Acetone (b) Propanal

(c) Ethanal (d) Butanal

172. How will you convert butan–2–one to propanoic acid? **[IIT 2005]**

(a) Tollen's reagent (b) Fehling's solution

(c) $NaOH/I_2/H^+$ (d) $NaOH/NaI/H^+$

173. Ketones react with Mg-Hg over water gives **[AFMC 2005]**

(a) Pinacolone (b) Pinacols

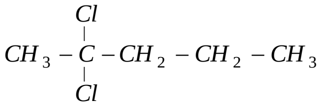
(c) Alcohols (d) None of these

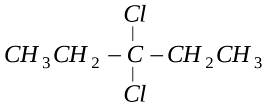
174. Which of the following will form two isomers with semi carbazide **[Orissa JEE 2005]**

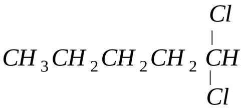
(a) Benzaldehyde (b) Acetone

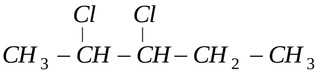
(c) Benzoquinone (d) Benzophenone

175. A compound $A \rightarrow C_5H_{10}Cl_2$ on hydrolysis gives $C_5H_{10}O$ which reacts with NH_2OH, forms iodoform but does not give fehling test. A is **[DPMT 2005]**

(a) 
$CH_3-\underset{Cl}{\overset{Cl}{C}}-CH_2-CH_2-CH_3$

(b) 
$CH_3CH_2-\underset{Cl}{\overset{Cl}{C}}-CH_2CH_3$

(c) 
$CH_3CH_2CH_2CH_2\underset{Cl}{\overset{Cl}{CH}}$

(d) 
$CH_3-\overset{Cl}{CH}-\overset{Cl}{CH}-CH_2-CH_3$

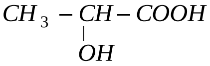
176. $CH_3-CHO+HCN \rightarrow A$; Compound A on hydrolysis gives **[Kerala CET 2005]**

(a) CH_3-CH_2-COOH

(b) $CH_3-CH_2-CH_2-NH_2$

(c) $CH_3-CO-COOH$

(d) $CH_3CO-CH=NOH$

(e) 
$CH_3-\underset{OH}{CH}-COOH$

177. Which one does not give cannizzaro's reaction **[Kerala CET 2005]**

(a) Benzaldehyde

(b) 2-methyl propanal

(c) *p*-methoxy benzaldehyde

(d) 2,2 dimethyl propanal

(e) Formaldehyde

Critical Thinking

Objective Questions

1. Which of the following will fail to react with potassium dichromate and dilute sulphuric acid

(a) Ethyl alcohol (ethanol)

(b) Acetaldehyde (ethanal)

(c) Secondary propyl alcohol (2-propanol)

(d) Acetone (propanone)

2. Acetone and acetaldehyde are differentiated by **[CPMT 1987, 93]**

(a) $NaOH+I_2$ (b) $Ag(NH_3)_2^+$

(c) HNO_2 (d) I_2

3. Which of the following will react with water **[IIT 1998]**

(a) $CHCl_3$ (b) Cl_3CCHO

(c) CCl_4 (d) $ClCH_2CH_2Cl$

4. An organic compound 'A' has the molecular formula C_3H_6O, it undergoes iodoform test. When saturated with dil. HCl is gives 'B' of molecular formula $C_9H_{14}O$. A and B respectively are **[Tamil Nadu CE**

(a) Propanal and mesitylene

(b) Propanone and mesityl oxide

(c) Propanone and 2,6–dimethyl –2, 5-heptadien–4–one

(d) Propanone and mesitylene oxide

5. Which alkene is formed from the following reaction $CH_3CH_2CH_2CH = PPh_3 + 2-\text{Butanone}$ **[Manipal 2001]**

(a) 3- Methyl-3-heptene

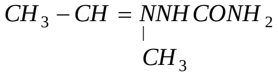
(b) 4-Methyl-3-heptene

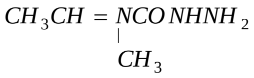
(c) 5-Methyl-3-heptene

(d) 1-Methyl-5- methane

6. Compound '*A*' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product '*B*' (molecular formula C_3H_6O). '*B*' forms a shining silver mirror on warming with ammoniacal silver nitrate. '*B*' when treated with an aqueous solution of $H_2NCONHNH_2.HCl$ and sodium acetate gives a product '*C*'. Identify the structure of '*C*' **[IIT-JEE (Screening) 2002]**

(a) $CH_3CH_2CH = NNHCONH_2$

(b)

$CH_3 - \underset{\substack{|\\ CH_3}}{CH} = NNHCONH_2$

(c)

$CH_3CH = \underset{\substack{|\\ CH_3}}{N}CONHNH_2$

(d) $CH_3CH_2CH - NCONHNH_2$

7. Which is not true about acetophenone **[Manipal 2002]**

(a) Reacts to form 2, 4-dinitorphenyl hydrazine

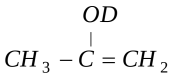
(b) Reacts with Tollen's reagent to form silver mirror

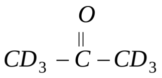
(c) Reacts with $I_2 / NaOH$ to form iodoform

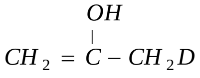
(d) On oxidation with alkaline $KMnO_4$ followed by hydrolysis gives benzoic acid

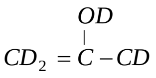
8. The enol form of acetone, after treatment with D_2O, gives

[IIT-JEE (Screening) 1999]

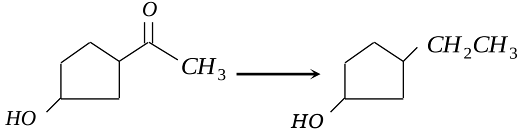
(a)

$CH_3 - \overset{\substack{OD\\ |}}{C} = CH_2$

(b)

$CD_3 - \overset{\substack{O\\ \|}}{C} - CD_3$

(c)

$CH_2 = \overset{\substack{OH\\ |}}{C} - CH_2D$

(d)

$CD_2 = \overset{\substack{OD\\ |}}{C} - CD$

9. The appropriate reagent for the transformation



[IIT-JEE (Screening) 2000]

(a) $Zn(Hg), HCl$

(b) $NH_2NH_2OH^-$

(c) H_2 / Ni

(d) $NaBH_4$

10. Which of the following has the most acidic hydrogen

[IIT-JEE (Screening) 2000]

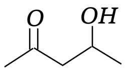
(a) 3-hexanone

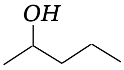
(b) 2, 4-hexanedione

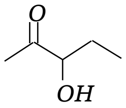
(c) 2, 5-hexanedione

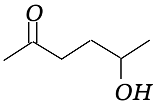
(d) 2, 3-hexanedione

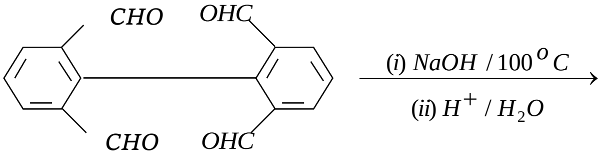
11. Which of the following will be most readily dehydrated in acidic conditions **[IIT-JEE (Screening) 2000]**

(a)


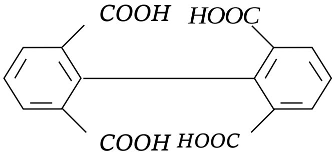
(b)


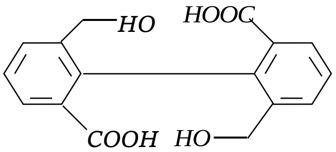
(c)


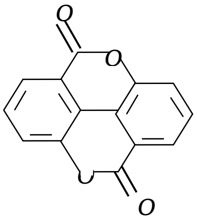
(d)


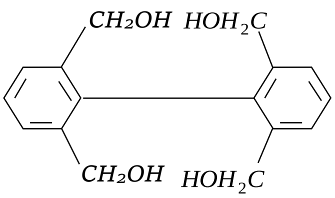
12.


Major Product is **[IIT-JEE (Screening) 2003]**

(a)


(b)


(c)


(d)


13. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is **[IIT 1997]**

(a) $MeCOCl$

(b) $MeCHO$

(c) $MeCOOMe$

(d) $MeCOOCOMe$

14. Which of the following will give yellow precipitate with $I_2 / NaOH$

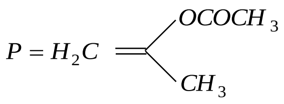
(a) $ICH_2COCH_2CH_3$

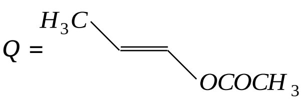
(b) $CH_3COOCOCH_3$

(c) CH_3CONH_2

(d) $CH_3CH(OH)CH_2CH_3$

15. The product of acid hydrolysis of P and Q can be distinguished by **[IIT-JEE (Screening) 2003]**



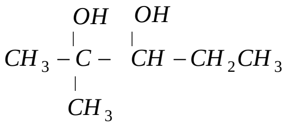


(a) Lucas Reagent (b) 2,4-DNP

(c) Fehling's Solution (d) $NaHSO_3$

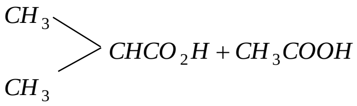
16. On vigorous oxidation by permanganate solution $(CH_3)_2C=CH-CH_2CH_2CH_3$ gives **[AIEEE 2002]**

(a)



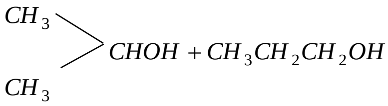
$CH_3-\overset{OH}{\underset{CH_3}{C}}-\overset{OH}{CH}-CH_2CH_3$

(b)



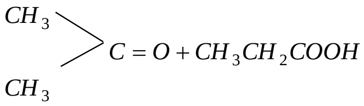
$(CH_3)_2CHCO_2H+CH_3COOH$

(c)



$(CH_3)_2CHOH+CH_3CH_2CH_2OH$

(d)



$(CH_3)_2C=O+CH_3CH_2COOH$

17. Which of the following reactions give benzo phenone

[Roorkee Qualifying 1998]

(a) $2C_6H_6+CCl_4\xrightarrow[\text{(ii)}H_2O]{\text{(i)}AlCl_3}$

(b) $C_6H_6+C_6H_5COCl\xrightarrow{AlCl_3}$

(c) $o-CH_3C_6H_4COC_6H_5\xrightarrow{\text{Heat}}$

(d) $o-HOOC-C_6H_4-COC_6H_5\xrightarrow[260^oC]{Cu}$

18. Aldehyde and ketones can decolourize by**[CPMT 2003]**

(a) Bromine water (b) Quick lime

(c) dil. H_2SO_4 (d) None of these

19. Which of the following statements regarding chemical properties of acetophenone are wrong

(1) It is reduced to methyl phenyl carbinol by sodium and ethanol

(2) It is oxidised to benzoic acid with acidified $KMnO_4$

(3) It does not undergo iodoform electrophilic substitution like nitration at meta position

(4) It does not undergo iodoform reaction with iodine and alkali **[Tamil Nadu CET 2001]**

(a) 1 and 2 (b) 2 and 4

(c) 3 and 4 (d) 1 and 3

20. The product(s) obtained via oxymercuration $(HgSO_4+H_2SO_4)$ of 1-butyne would be **[IIT-JEE 1999]**

(a) $CH_3CH_2COCH_3$

(b) $CH_3CH_2CH_2CHO$

(c) $CH_3CH_2CHO+HCHO$

(d) $CH_3CH_2COOH+HCOOH$

21. The most reactive compound towards formation of cyanohydrin on treatment with KCN followed by acidification is **[GATE 2001]**

(a) Benzaldehyde (b) p-Nitrobenzaldehyde

(c) Phenyl acetaldehyde (d) p-Hydroxybenzaldehyde

22. The key step in cannizzaro's reaction is the intermolecular shift of **[Orissa JEE 2003]**

(a) Proton (b) Hydride ion

(c) Hydronium ion (d) Hydrogen bond

23. Benzophenone does not react with **[BHU 2003]**

(a) RNH_2 (b) SO_3

(c) $NaOH$ (d) Na_2CO_3

24. The most suitable reagent for the conversion of $RCH_2OH\rightarrow RCHO$ is **[AIIMS 2004]**

(a) $KMnO_4$

(b) $K_2Cr_2O_7$

(c) CrO_3

(d) PCC (Pyridine chloro chromate)

25. The conversion of acetophenone to acetanilide is best accomplished by using :

(a) Backmann rearrangement

(b) Curtius rearrangement

(c) Lossen rearrangement

(d) Hofmann rearrangement

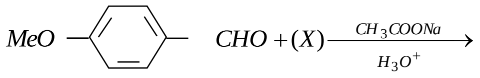
26. Which of the following will not give iodoform test ?

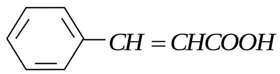
[UPSEAT 2004]

(a) Isopropyl alcohol (b) Ethanol

(c) Ethanal (d) Benzyl alcohol

27.



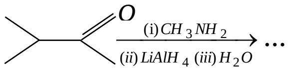


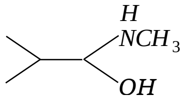
The compound (X) is **[IIT-JEE 2005]**

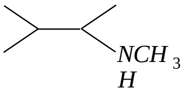
(a) CH_3COOH (b) $BrCH_2-COOH$

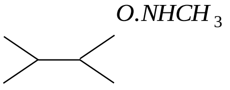
(c) $(CH_3CO)_2O$ (d) $CHO-COOH$

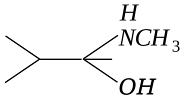
28. The major organic product formed from the following reaction **[CBSE PMT 2005]**



(a)


(b)


(c)


(d)


29. Products of the following reaction

$CH_3C \equiv C\,CH_2CH_3 \xrightarrow[(2)\,Hydrolysis]{(1)\,O_3}$ ...are **[CBSE PMT 2005]**

(a) $CH_3CHO + CH_3CH_2CHO$

(b) $CH_3COOH + CH_3CH_2CHO$

(c) $CH_3COOH + HOOCCH_2CH_3$

(d) $CH_3COOH + CO_2$

30. A compound, containing only carbon, hydrogen and oxygen, has a molecular weight of 44. On complete oxidation it is converted into a compound of molecular weight 60. The original compound is **[KCET 2005]**

(a) An aldehyde (b) An acid

(c) An alcohol (d) an ether

AR Assertion & Reason

For AIIMS Aspirants

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

(a) If both assertion and reason are true and the reason is the correct explanation of the assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of the assertion.

(c) If assertion is true but reason is false.

(d) If the assertion and reason both are false.

(e) If assertion is false but reason is true.

1. Assertion : Acetic acid does not undergo haloform reaction.

Reason : Acetic acid has no alpha hydrogens. **[IIT 1998]**

2. Assertion : Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.

Reason : Cyanide (CN^-) is a strong nucleophile. **[IIT 1998]**

3. Assertion : Lower aldehyde and ketones are soluble in water but the solubility decreases as molecular mass increases.

Reason : Aldehydes and ketones can be distinguished by Tollen's reagent. **[AIIMS 1994**

4. Assertion : Acetaldehyde on treatment with alkaline gives aldol.

Reason : Acetaldehyde molecules contains α hydrogen atom. **[AIIMS 1997]**

5. Assertion : Acetylene on treatment with alkaline $KMnO_4$ produce acetaldehyde.

Reason : Alkaline $KMnO_4$ is a reducing agent. **[AIIMS 2000]**

6. Assertion : Acetophenone and benzophenone can be distinguished by iodoform test.

Reason : Acetophenone and benzophenone both are carbonyl compounds. **[AIIMS 2002]**

7. Assertion : Isobutanal does not give iodoform test

Reason : It does not have α-hydrogen. **[AIIMS 2004]**

8. Assertion : Benzaldehyde is more reactive than ethanol towards nucleophilic attack.

Reason : The overall effect of –I and +R effect of phenyl group decreases the electron density on the carbon atom of $>C=O$ group in benzaldehyde.

9. Assertion : Aldol condensation can be catalysed both by acids and bases.

Reason : β-Hydroxy aldehydes or ketones readily undergo acid catalysed dehydration.

10. Assertion : Ketones are less reactive than aldehydes.

Reason : Ketones do not give schiff's test.

11. Assertion : Oximes are less acidic than hydroxyl amine.

Reason : Oximes of aldehydes and ketones show geometrical isomerism.

12. Assertion : The bond energy of $>C=O$ is less than $>C=C<$ in alkenes.

Reason : The carbon atom in carbonyl group is sp^2 hybridised.

13. Assertion : $R-C\equiv 0^+$ is more stable than $R-C^+=0$.

Reason : Resonance in carbonyl compound provides C^+ and O^-.

14. Assertion : Formaldehyde cannot be prepared by Rosenmund's reduction.

Reason : Acid chlorides can be reduced into aldehydes with hydrogen in boiling xylene using palladium or platinum as a catalyst supported on barium sulphate. This is known as Rosenmund's reduction.

15. Assertion : CH_3CHO reacts with NH_3 to form urotropine.

Reason : Urotropine is used as medicine in case of urinary troubles.

16. Assertion : α-Hydrogen atoms in aldehydes and ketones are acidic.

Reason : The anion left after the removal of α-hydrogen is stabilized by inductive effect.

17. Assertion : 2, 2–Dimethyl propanal undergoes Cannizzaro reaction with concentrated $NaOH$.

Reason : Cannizzaro is a disproportionation reaction.

18. Assertion : Benzaldehyde undergoes aldol condensation.

Reason : Aldehydes that do not have α–hydrogen undergo aldol condensation.

Answers

Introduction

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

Preparation

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

Properties

1	c	2	c	3	a	4	a	5	c
6	d	7	a	8	c	9	c	10	b
11	c	12	a	13	a	14	b	15	d
16	b	17	c	18	c	19	abd	20	abcd
21	b	22	a	23	a	24	b	25	d
26	b	27	d	28	c	29	b	30	b
31	c	32	c	33	d	34	d	35	c
36	b	37	a	38	b	39	d	40	c
41	d	42	a	43	d	44	d	45	a
46	c	47	c	48	a	49	b	50	b
51	b	52	c	53	d	54	b	55	c
56	d	57	c	58	a	59	c	60	c
61	b	62	b	63	a	64	b	65	a
66	d	67	a	68	a	69	c	70	a
71	c	72	d	73	a	74	a	75	a
76	d	77	c	78	b	79	a	80	b
81	c	82	c	83	c	84	a	85	d
86	a	87	d	88	a	89	d	90	d
91	b	92	b	93	a	94	c	95	c
96	a	97	b	98	d	99	a	100	c
101	c	102	d	103	d	104	d	105	a
106	e	107	b	108	c	109	a	110	c
111	a	112	a	113	c	114	b	115	d
116	c	117	b	118	a	119	c	120	c
121	d	122	d	123	d	124	c	125	c
126	d	127	c	128	a	129	a	130	a
131	c	132	a	133	a	134	b	135	b
136	a	137	b	138	b	139	d	140	a
141	a	142	b	143	b	144	d	145	b
146	d	147	b	148	b	149	b	150	c
151	a	152	a	153	c	154	c	155	b
156	a	157	d	158	d	159	c	160	a
161	c	162	c	163	d	164	d	165	c
166	d	167	a	168	b	169	c	170	a
171	a	172	c	173	b	174	a	175	a
176	e	177	b						

Critical Thinking Questions

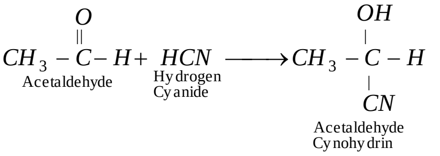
1	d	2	bc	3	b	4	c	5	a
6	a	7	b	8	b	9	b	10	b
11	a	12	b	13	a	14	a,d	15	c
16	d	17	b,d	18	d	19	c	20	a
21	b	22	b	23	d	24	d	25	a
26	d	27	c	28	b	29	c	30	a

Assertion & Reason

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

Answers and Solutions

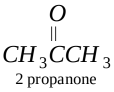
Introduction

1. (a) 

$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H}+\underset{\text{Hydrogen Cyanide}}{HCN}\longrightarrow \underset{\text{Acetaldehyde Cynohydrin}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}-H}$$

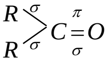
(optically active)

2. (b) $\underset{sp^2\text{ hybridised}}{>C=O}$

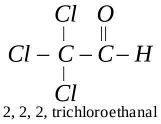
7. (b) 

$\underset{\text{2 propanone}}{CH_3\overset{\overset{\displaystyle O}{||}}{C}CH_3}$

10. (b) $CHOCHO$

11. (b) 

$\begin{matrix} R \overset{\sigma}{\searrow} \\ R \underset{\sigma}{\nearrow} \end{matrix} C \overset{\pi}{\underset{\sigma}{=}} O$

13. (d) 

$\underset{\text{2, 2, 2, trichloroethanal}}{Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\overset{\overset{\displaystyle O}{||}}{C}-H}$

18. (c) Among Carbonyl Compounds, reactivity decrease with increase in alkyl groups as alkyl groups ($+I$ effect) decrease positive character on C-atom. Thus, the correct order of reactivity is

$HCHO > CH_3CHO > C_6H_5CHO$

Preparation

1. (c) $HC \equiv CH \xrightarrow[20\% H_2SO_4]{1\% HgSO_4} \underset{(A)}{CH_3CHO} \xrightarrow[H_2O]{CH_3MgX}$

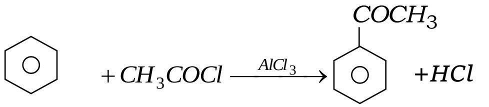
$\underset{(B)}{CH_3CHOHCH_3} \xrightarrow{[O]} \underset{\text{Acetone}}{CH_3COCH_3}$

4. (b) $(CH_3)_2C = C(CH_3)_2 \xrightarrow{O_3} 2CH_3 - CO - CH_3$

5. (c) Ketonic hydrolysis: $CH_3 - CO - CH_2COOC_2H_5$

$\xrightarrow[H_2O]{NaOH} CH_3COCH_3 + C_2H_5OH + CO_2$

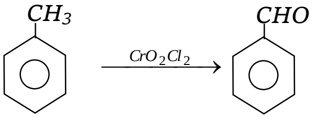
6. (c)



It is Friedel-Crafts reaction. Acetophenone

9. (c) $CH_3COCl \xrightarrow[Pd / BaSO_4]{2H} CH_3CHO + HCl$

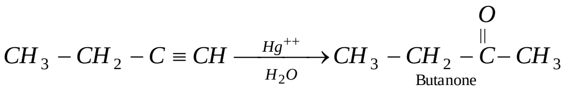
10. (c)



Etard reaction

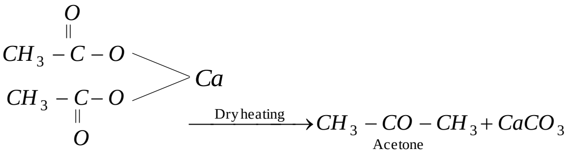
11. (c) $\underset{Acetone}{CH_3COCH_3} \xrightarrow{CH_3MgI} \underset{tert-\text{Butyl alcohol}}{(CH_3)_3COH}$

13. (a) It is hydration of alkynes.



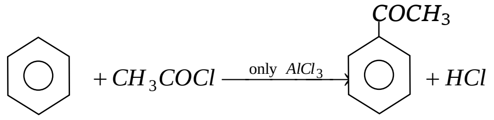
$CH_3 - CH_2 - C \equiv CH \xrightarrow[H_2O]{Hg^{++}} CH_3 - CH_2 - \underset{\text{Butanone}}{\overset{\overset{O}{\|}}{C}} - CH_3$

14. (d)



$\begin{matrix} CH_3 - \overset{\overset{O}{\|}}{C} - O \\ CH_3 - \underset{\underset{O}{\|}}{C} - O \end{matrix} > Ca \xrightarrow{\text{Dry heating}} CH_3 - \underset{\text{Acetone}}{CO} - CH_3 + CaCO_3$

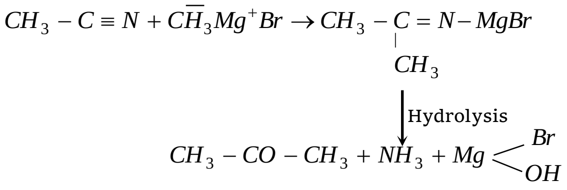
16. (c)



18. (d) $\begin{matrix} CH_3COO \\ CH_3COO \end{matrix} > Ca + Ca < \begin{matrix} OOCH \\ OOCH \end{matrix} \xrightarrow{\text{Distill}}$

$2CH_3CHO + 2CaCO_3$

19. (c)

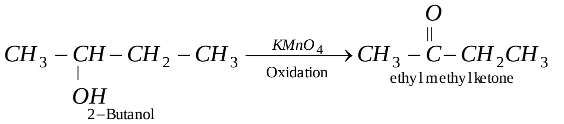


$CH_3 - C \equiv N + \overset{-}{C}H_3Mg^+Br \to CH_3 - \underset{\underset{CH_3}{|}}{C} = N - MgBr$

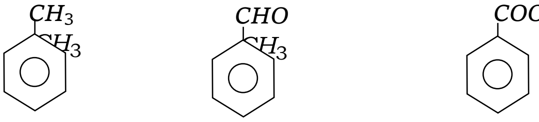
$\downarrow$ Hydrolysis

$CH_3 - CO - CH_3 + NH_3 + Mg <^{Br}_{OH}$

23. (c)



$\underset{2-\text{Butanol}}{CH_3 - \underset{\underset{OH}{|}}{CH} - CH_2 - CH_3} \xrightarrow[\text{Oxidation}]{KMnO_4} \underset{\text{ethyl methyl ketone}}{CH_3 - \overset{\overset{O}{\|}}{C} - CH_2CH_3}$



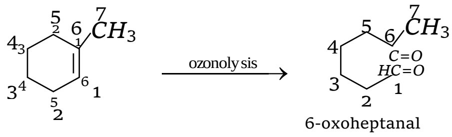
24. (c) $\xrightarrow{CrO_2Cl_2}$ $\xrightarrow[\text{or } KMnO_4]{\text{acidic } K_2Cr_2O_7}$

This is Etard's reaction

32. (d) $\underset{\text{Isopropyl alcohol}}{\begin{matrix} R \\ R \end{matrix} > CH - OH} \xrightarrow[\text{Aluminium ter butoxide}]{[(CH_3)_3CO]_3Al} \underset{\text{Ketone}}{\begin{matrix} R \\ R \end{matrix} > C = O}$

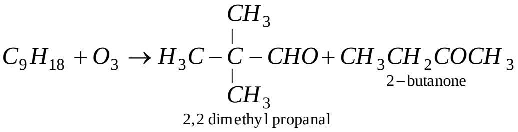
34. (b) $HC \equiv CH + H_2O \xrightarrow{HgSO_4 / H_2SO_4} CH_3CHO$

42. (a)



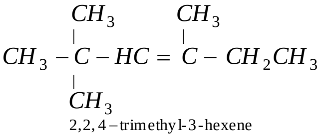
6-oxoheptanal

43. (a)

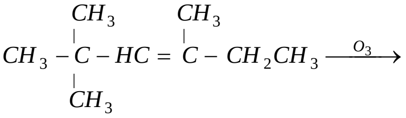


$C_9H_{18} + O_3 \to \underset{2,2\ \text{dimethyl propanal}}{H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CHO} + \underset{2-\text{butanone}}{CH_3CH_2COCH_3}$

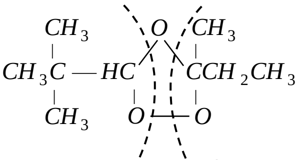
On the basis of product formation, it would be alkene

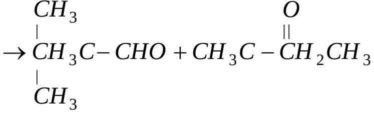


$\underset{2,2,4-\text{trimethyl-3-hexene}}{CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - HC = \overset{\overset{CH_3}{|}}{C} - CH_2CH_3}$



$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - HC = \overset{\overset{CH_3}{|}}{C} - CH_2CH_3 \xrightarrow{O_3}$





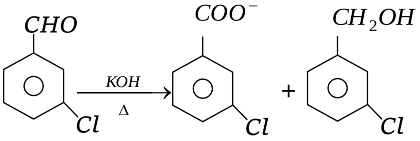
$\to CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CHO + CH_3\overset{\overset{O}{\|}}{C} - CH_2CH_3$

Properties

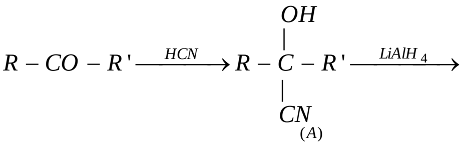
1. (c) $CH_3COCH_3 + CH_3MgCl \to \underset{(X)}{(CH_3)_3C - OMgCl}$

$\xrightarrow{\text{hydrolysis}} \underset{(Y)}{(CH_3)_3C - OH} + Mg(OH)Cl$

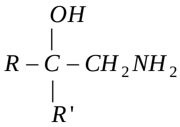
2. (c) It is cannizzaro reaction –2



3. (a)



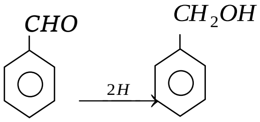
$R - CO - R' \xrightarrow{HCN} R - \underset{\underset{\underset{(A)}{CN}}{|}}{\overset{\overset{OH}{|}}{C}} - R' \xrightarrow{LiAlH_4}$



$$R-\underset{R'}{\overset{OH}{C}}-CH_2NH_2$$

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

6. (d)



Benzaldehy Benzylalco

on reduction it gives benzylalcohol and not phenol.

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

$C_6H_6 + CH_3COCl \xrightarrow[\text{reaction}]{\text{Friedel craft's}} C_6H_5COCH_3 + HCl$

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

11. (c) Although both $CH_3CH_2COCH_3$ and $(CH_3)_3CCOCH_3$ contain α-hydrogen, yet $(CH_3)_3CCOCH_3$ does not undergo Aldol condensation due to steric hindrance.

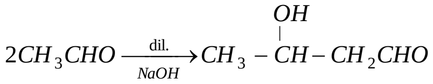
12. (a) $\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow[H^+/H_2O]{CH_3MgBr} \underset{2°\text{Alcohol}}{C_6H_5CH(OH)CH_3}$

13. (a) Chloral CCl_3CHO, has no α-hydrogen atom and hence does not undergo aldol condensation.

14. (b) Among the given compounds only acetone gives crystalline coloured derivative with 2, 4 DNP.

15. (d) Ethanal among the given compounds gives positive iodoform test.

17. (c)



$$2CH_3CHO \xrightarrow[NaOH]{\text{dil.}} CH_3-\overset{OH}{CH}-CH_2CHO$$

18. (c) $C_2H_5CHO + 2Cu^{+2} + 5OH^- \rightarrow \underset{\text{Red ppt}}{Cu_2O} + 3H_2O + C_2H_5COO^-$

$CH_3COCH_3 + 2Cu^{+2} + 5OH^- \rightarrow \text{No reaction}$

19. (abd)Deuterium behaves like H and hence trideuteroacetaldehyde also undergoes aldol condensation but benzaldehyde does not since it has no α-hydrogen.

21. (b) 1^o Primary alcohol $\xrightarrow{ZnCl_2/HCl}$

White turbidity only heating

2^o $Alcohol \xrightarrow{ZnCl_2/HCl}$ White turbidity

after 5 min heating

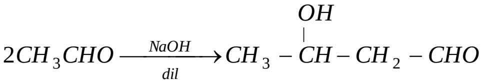
3^o Alcohol $\xrightarrow{ZnCl_2/HCl}$ easily in seconds

24. (b) Benzaldehyde on treatment with 50% aqueous or ethanolic alkali solution undergoes Cannizzaro's reaction like $HCHO$ (no α-hydrogen atom) *i.e.*, one molecule is oxidised and one is reduced with the formation of benzoic acid and benzyl alcohol respectively.

$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$

25. (d) $2HCHO \xrightarrow[Conc.]{NaOH} CH_3OH + HCOONa$

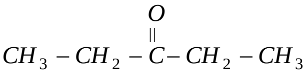
It is a Cannizzaro's reaction.



$$2CH_3CHO \xrightarrow[dil]{NaOH} CH_3-\overset{OH}{CH}-CH_2-CHO$$

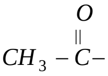
It is aldol condensation reaction.

27. (d)



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

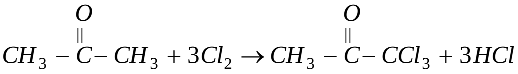
do not have



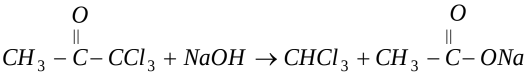
$$CH_3-\overset{O}{\overset{||}{C}}-$$

group

29. (b)

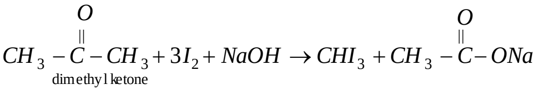


$$CH_3-\overset{O}{\overset{||}{C}}-CH_3 + 3Cl_2 \rightarrow CH_3-\overset{O}{\overset{||}{C}}-CCl_3 + 3HCl$$



$$CH_3-\overset{O}{\overset{||}{C}}-CCl_3 + NaOH \rightarrow CHCl_3 + CH_3-\overset{O}{\overset{||}{C}}-ONa$$

30. (b)

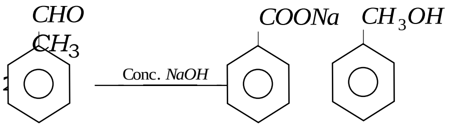


$$\underset{\text{dimethyl ketone}}{CH_3-\overset{O}{\overset{||}{C}}-CH_3} + 3I_2 + NaOH \rightarrow CHI_3 + CH_3-\overset{O}{\overset{||}{C}}-ONa$$

31. (c) CHI_3 is yellow compound when iodine reacts with $NaOH$ and ketone.

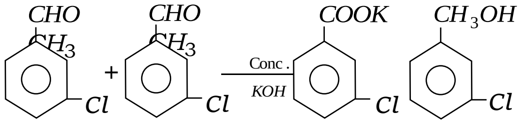
32. (c) $HCHO + HCHO \xrightarrow{KOH} HCOOK + CH_3OH$

38. (b)



This reaction is called as Cannizzaro's reaction.

39. (d)



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

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

43. (d) $RCHO + \frac{1}{2}O_2 \rightarrow RCOOH$

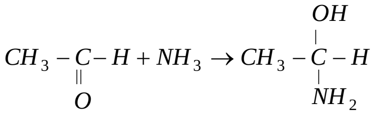
44. (d) All test for Aldehyde because ketone require strong oxidising agent.

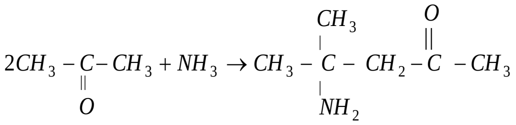
$2[Ag(NH_3)_2]^+ + RCHO \rightarrow RCOOH + 2Ag + 4NH_3 + H_2O$

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

46. (c) $CH_3CH=CHCHO + 2[Ag(NH_3)_2]^+ \rightarrow$

$2Ag + 4NH_3 + CH_3CH=CHCOOH + H_2O$

49. (b)

$CH_3-\underset{\underset{O}{\|}}{C}-H+NH_3\rightarrow CH_3-\overset{\overset{OH}{|}}{\underset{\underset{NH_2}{|}}{C}}-H$


$2CH_3-\underset{\underset{O}{\|}}{C}-CH_3+NH_3\rightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{NH_2}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

50. (b) $CH_3CHO+2H\xrightarrow{Na/C_2H_5OH}CH_3CH_2OH$

51. (b) $CH_3CH_2CHO+4H\xrightarrow[HCl]{Zn/Hg}CH_3CH_2CH_3+H_2O$

This reaction is called clemmenson's reduction.

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

$HCHO+HCHO\xrightarrow{KOH}CH_3OH+HCOOK$

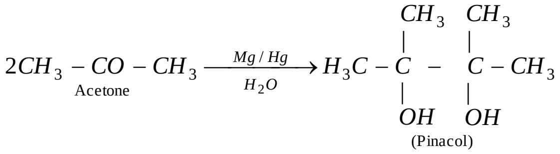
55. (c) Nucleophilic as addition of HCN, $NaHSO_3$ *etc*.

57. (c) Addition of HCN to carbonyl compounds is an example of nucleophilic addition.

58. (a) Acetone forms sodium bisulphate adduct but acetophenone does not. Aromatic ketones do not gives addition product with $NaHSO_3$.

59. (c) $\underset{\text{Benzaldehyde}}{C_6H_5CHO}+Cl_2\rightarrow\underset{\text{Benzoyl chloride}}{C_6H_5COCl}+HCl$

60. (c) $CH_3\rightarrow\ddot{\underset{\cdot\cdot}{O}}\leftarrow CH_3$ The electron density of oxygen is highly increased therefore resistant its nucleophilic attack.

63. (a)

$2\underset{\text{Acetone}}{CH_3-CO-CH_3}\xrightarrow[H_2O]{Mg/Hg}\underset{\text{(Pinacol)}}{H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3}$

64. (b) $C_6H_5CHO+(CH_3CO)_2O\xrightarrow{CH_3CO_2Na}$

$C_6H_5CH=CHCO_2H$

It is Perkin's reaction.

65. (a) Crossed aldol reaction gives benzyl alcohol and sodium formate.

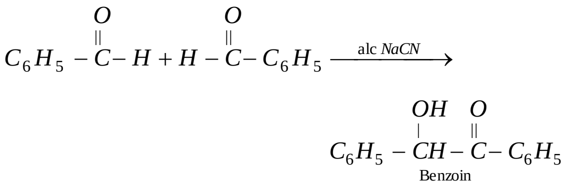
$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+\underset{\text{Formaldehyde}}{HCHO}\xrightarrow{NaOH\ (aq)}$

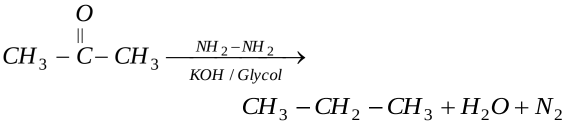
$\underset{\text{Benzylalcohol}}{C_6H_5CH_2OH}+\underset{\text{Sod. formate}}{HCOONa}$

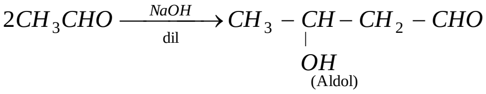
66. (d) The substitution of alkoxy group of ester by an alcohol, is called trans-esterification. It occurs in presence of either an acid or base.

67. (a) $6HCHO+4NH_3\rightarrow\underset{\text{Urotropine}}{(CH_2)_6N_4}+6H_2O$

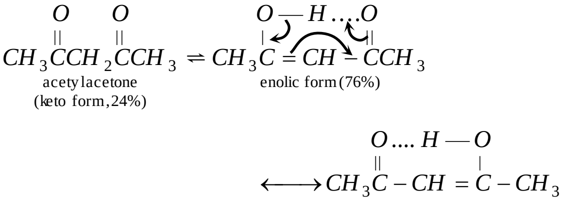
68. (a) In $HCHO$ because α-Hydrogen atom is absent.

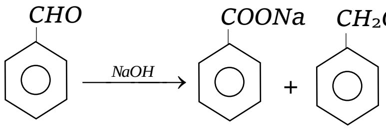
71. (c)

$C_6H_5-\overset{\overset{O}{\|}}{C}-H+H-\overset{\overset{O}{\|}}{C}-C_6H_5\xrightarrow{\text{alc } NaCN}\underset{\text{Benzoin}}{C_6H_5-\overset{\overset{OH}{|}}{CH}-\overset{\overset{O}{\|}}{C}-C_6H_5}$

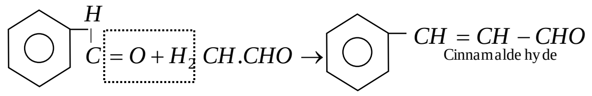
72. (d)

$CH_3-\overset{\overset{O}{\|}}{C}-CH_3\xrightarrow[KOH/Glycol]{NH_2-NH_2}CH_3-CH_2-CH_3+H_2O+N_2$

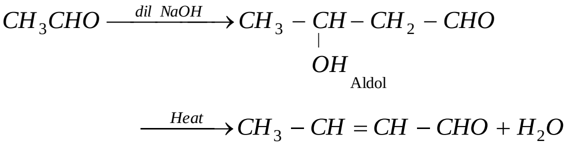
75. (a)

$2CH_3CHO\xrightarrow[\text{dil}]{NaOH}\underset{\text{(Aldol)}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO}$

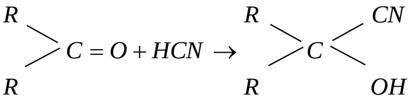
76. (d) The amount of enolic form is highest (76%) in acetyl acetone because keto group is a much better electron-withdrawing group.

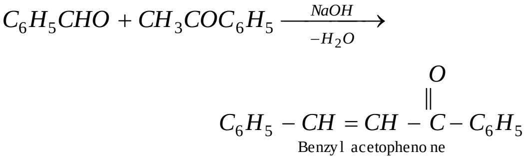

$\underset{\text{(keto form, 24\%)}}{\underset{\text{acetylacetone}}{CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}CH_3}}\rightleftharpoons\underset{\text{enolic form (76\%)}}{CH_3\overset{O-H\ldots O}{C=CH-C}CH_3}\longleftrightarrow CH_3\overset{O\ldots H-O}{C-CH=C}-CH_3$

78. (b)


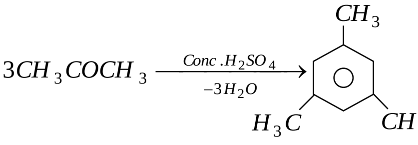
80. (b)


82. (c)

$CH_3CHO\xrightarrow{dil\ NaOH}\underset{\text{Aldol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO}\xrightarrow{Heat}CH_3-CH=CH-CHO+H_2O$

83. (c)

$\begin{matrix}R\\R\end{matrix}\!\!>C=O+HCN\rightarrow\begin{matrix}R\\R\end{matrix}\!\!>C<\!\!\begin{matrix}CN\\OH\end{matrix}$ is an example of nucleophilic addition reaction.

84. (a)

$C_6H_5CHO+CH_3COC_6H_5\xrightarrow[-H_2O]{NaOH}\underset{\text{Benzyl acetophenone}}{C_6H_5-CH=CH-\overset{\overset{O}{\|}}{C}-C_6H_5}$

85. (d) $HI/P/$, $Zn/Hg/$conc. HCl and $NH_2-NH_2/OH^-/C_2H_5ONa$ used to the reduction of $-\overset{\overset{O}{\|}}{C}-$ group into $-CH_2-$ group.

86. (a)


(Mesitylene)

87. (d) $2C_6H_5CHO\xrightarrow{50\%\ NaOH}C_6H_5COONa+C_6H_5CH_2OH$

It is Cannizzaro's reaction.

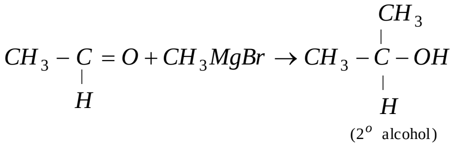
88. (a) Because acetone require stronger oxidising agent and hence not oxidized with Fehling solution to give brick red *ppt*.

89. (d) $CH_3CHO \xrightarrow{[Ag(NH_3)_2]} CH_3COOH + \underset{\text{Silver mirror test}}{Ag_\downarrow} + NH_3$

While acetone do not react.

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

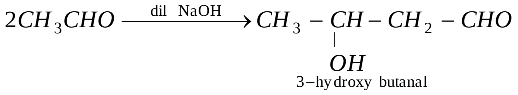
91. (b)



$$CH_3-\underset{\substack{|\\ H}}{C}=O+CH_3MgBr\rightarrow \underset{(2^o\ \text{alcohol})}{CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ H}}{C}}-OH}$$

92. (b) $CH_3CHO \xrightarrow{HCN} CH_3CH(OH)CN \xrightarrow{2H_2O/H^+} CH_3CH(OH)COOH$

93. (a) This reaction is aldol condensation

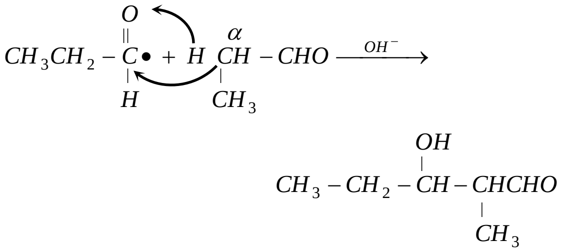


$$2CH_3CHO \xrightarrow{\text{dil NaOH}} \underset{3-\text{hydroxy butanal}}{CH_3-\underset{\substack{|\\ OH}}{CH}-CH_2-CHO}$$

94. (c) $HCHO+2Cu^{+2}+5OH^- \xrightarrow[\text{solution}]{\text{Fehling}} HCOO^- + \underset{\text{Red } ppt}{Cu_2O} + 3H_2O$

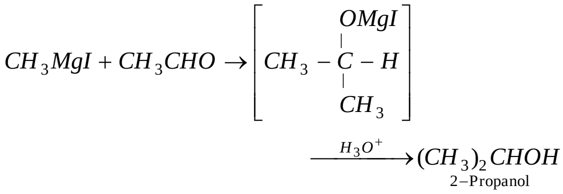
95. (c) $H-CHO+CH_3MgI\rightarrow CH_3-CH_2-OH+Mg\langle\begin{smallmatrix}OH\\ I\end{smallmatrix}$

100. (c)



$$CH_3CH_2-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ H}}{C}}\bullet + H\ \overset{\alpha}{\underset{\substack{|\\ CH_3}}{CH}}-CHO \xrightarrow{OH^-} CH_3-CH_2-\overset{\substack{OH\\ |}}{CH}-\underset{\substack{|\\ CH_3}}{CH}CHO$$

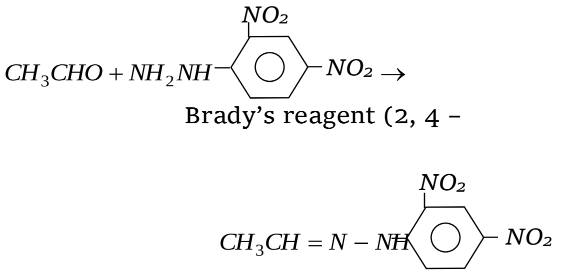
101. (c)



$$CH_3MgI+CH_3CHO\rightarrow\left[CH_3-\overset{\substack{OMgI\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-H\right]\xrightarrow{H_3O^+}\underset{2-\text{Propanol}}{(CH_3)_2CHOH}$$

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

103. (a)



Brady's reagent (2, 4 –

Orange crystalline

105. (a) $2CH_3COCH_3 + Cl_2/NaOH \rightarrow 2CHCl_3 + 2CH_3COONa + HCl$

106. (e) Fehling solution $\Rightarrow$ Alkaline $CuSO_4 + Na-K$ tartarate

Tollen's reagent $\Rightarrow$ $NH_4OH + AgNO_3$

Schiff's reagent $\Rightarrow$ *P*-rosaniline hydrochloride or magneta

Benedict's solution $\Rightarrow$ Alkaline $CuSO_4$ + Citrate ions

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

107. (b) $\underset{\text{(Pink)}}{\text{Schiff's reagent}} \xrightarrow{SO_2} \text{Colourless} \xrightarrow{\text{Aldehyde}} \text{Pink colour}$

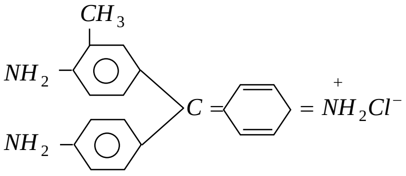
108. (c) $\overset{\beta}{CH_3}-\overset{\alpha}{CH_2}-CHO$ aldehydes having $\alpha-H$ *atom* can participate in aldol condensation. The $H-$atom attached to α carbon atom are called α -hydrogen.

109. (a) $\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{Oxidation}]{KMnO_4} \underset{\text{Acetic acid}}{CH_3COOH}$

110. (c) $CH_3CHO + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]OH} \rightarrow CH_3COONH_4 + \underset{\text{Silver mirror}}{2Ag} + 3NH_3 + H_2O$

112. (a) It is used as a medicine to treat urinary infections.

113. (c) *p*-rosaniline hydrochloride.



It is used for the identification of aldehydes.

115. (d) $R-CHO \xrightarrow{H_2N-OH} \underset{\text{Oxime}}{RCH=N-OH}$

$CH_3CHO + NH_2OH \rightarrow \underset{\text{Acetaldoxime}}{CH_3-CH=N-OH} + H_2O$

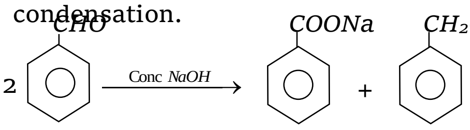
116. (c) Cannizzaro's reaction is shown by aldehydes in which α-*H* atom is absent. CH_3CHO contains $3, \alpha$ -*H* atoms thus, does not show this reaction.

117. (b) $\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>C=O+NH_2OH\rightarrow \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\underset{\text{Acetoxime}}{C=N-OH}+H_2O$

119. (c) $\underset{\text{Propanal}}{CH_3-CH_2-CHO} \xrightarrow{\text{Oxidation}} \underset{\text{Propanoic acid}}{CH_3CH_2-COOH}$

120. (c) $CH_3-CHO+PCl_5\rightarrow \underset{\substack{\text{Ethylidene Chloride}\\ \text{or}\\ \text{Gem dihalide}}}{CH_3-CH\langle\begin{smallmatrix}Cl\\ Cl\end{smallmatrix}} + POCl_3$

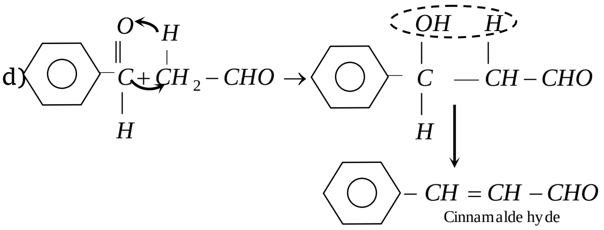
121. (d) Benzaldehyde gives cannizaro's reaction whereas acetaldehyde gives aldol condensation.



Cannizaro

$$2CH_3CHO \xrightarrow{\text{dil } NaOH} CH_3-\underset{\substack{OH\\ \text{(Aldol)}}}{CH}-CH_2-CHO$$

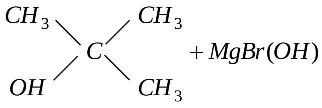
122. (d)



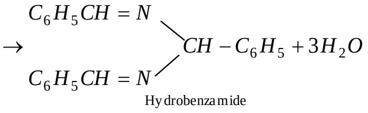
123. (d) $CH_3-MgBr+CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{H_2O}$

$$CH_3-\underset{CH_3}{CH}-OH+MgBr(OH)$$

$$CH_3MgBr+CH_3-\underset{CH_3}{C}=O \xrightarrow{H_2O}$$



125. (c) $3C_6H_5CHO+2NH_3 \rightarrow$



127. (c) $CuSO_4+NaOH+\text{Roschelle salt}(Na-K\text{ tartarate})$

128. (a) $\underset{\text{Aldehyde}}{R-CHO} \xrightarrow{\text{Reduction}} \underset{1^o\text{ alcohol}}{R-CH_2-OH}$

129. (a) $HCHO+HCHO \xrightarrow[\text{Conc}]{NaOH} CH_3OH+HCOONa$

131. (c) $\underset{\text{Acetone}}{CH_3-CO-CH_3} \xrightarrow{\text{Pyrolysis}} \underset{\text{Ketene}}{CH_2=C=O}$

132. (a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH+HCOOH$

one carbon atom is less in the ketone group

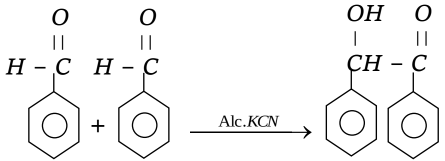
134. (b) $\underset{\text{Aldehyde}}{R-\underset{H}{C}=O}+\underset{\text{Grignard reagent}}{R-Mg-X} \rightarrow R-\overset{R}{\underset{H}{C}}-OMgX$

$$\underset{\text{Ketone}}{R-\underset{R}{C}=O}+R-Mg-X \rightarrow R-\overset{R}{\underset{R}{C}}-O-MgX$$

137. (b) $CH_3CHO \xrightarrow[I_2]{NaOH} \underset{\text{Yellowppt}}{CHI_3}$

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

139. (d)



Benzoin

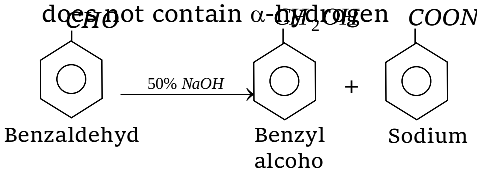
This reaction is called benzoin condensation.

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

Ketone do not give this test.

141. (a) $CH_3CHO \xrightarrow{Cl_2} \underset{\text{(Choral)}}{CCl_3CHO}+3HCl$

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



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

145. (b) Phoron

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C=O+H_2CH-\overset{O}{\overset{\|}{C}}-CHH_2+O=C<\begin{matrix}CH_3\\CH_3\end{matrix}$$

$$\xrightarrow[-2H_2O]{\text{Dry } HCl} \underset{\text{Phoron}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>C=CH-\overset{O}{\overset{\|}{C}}-CH=C<\begin{matrix}CH_3\\CH_3\end{matrix}}$$

146. (d) $RCHO+4H \xrightarrow{Zn-Hg/HCl} R-CH_3+H_2O$

$$\begin{matrix}R\\R\end{matrix}\!>C=O+4H \xrightarrow{Zn-Hg/HCl} \begin{matrix}R\\R\end{matrix}\!>CH_2+H_2O$$

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

$$\underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}+3I_2+4NaOH \xrightarrow{-3H_2O}$$

$$\underset{\text{Iodoform}}{CHI_3}+\underset{\text{Sodium acetate}}{CH_3COONa}+\underset{\text{Sodium iodide}}{3NaI}$$

148. (b) We know that

$$\underset{\text{Acetaldehyde}}{CH_3-\overset{H}{C}=O} \xrightarrow{+HCN} \underset{\text{Cyanohydrin}}{CH_3-\overset{H}{\underset{CN}{C}}-OH} \xrightarrow{+H_2O}$$

$$\underset{\text{Lactic acid}}{CH_3-\overset{H}{\underset{COOH}{C}}-OH}$$

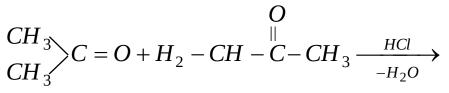
Thus Lactic acid is formed.

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

$$\begin{matrix}R\\H\end{matrix}\!>C=O+Ag_2O \longrightarrow RCOOH+\underset{\text{Silver mirror}}{2Ag}$$

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

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



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O+H_2-CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3\xrightarrow[-H_2O]{HCl}$$

$$\underset{\text{Mesity loxide}}{(CH_3)_2\,C=CH.COCH_3}$$

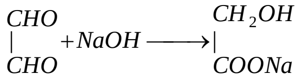
152. (a) Formaldehyde and $NaOH$ reacts to produce alcohol and sodium salt of an acid.

$$2HCHO+NaOH\longrightarrow\underset{\text{Alcohol}}{CH_3OH}+\underset{\text{Sodium formate}}{HCOONa}$$

This reaction is Cannizzaro's reaction

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

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



$$\begin{matrix}CHO\\|\\CHO\end{matrix}+NaOH\longrightarrow\begin{matrix}CH_2OH\\|\\COONa\end{matrix}$$

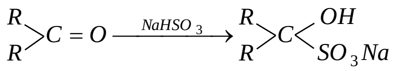
155. (b) $R-\overset{+\delta}{\underset{\underset{\displaystyle O}{\|}}{C}}-H$; Susceptibility of nucleophilic attack on aldehyde is decreased by electron releasing effect of R group. Decreasing order of aldehyde towards nucleophilic attack is 1° > 2° > 3° R group.

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

$$\underset{\text{Carbonyl group}}{>C=O}+\underset{\text{Hydrazine}}{NH_2-NH_2}\xrightarrow[\textit{reduction}]{\text{Wolf-Kishner}}$$

$$>C=N-NH_2\xrightarrow{KOH}\underset{\text{Alkylgroup}}{>CH_2}$$

157. (d) Ketones and Aldehyde add to $NaHSO_3$ to give white precipitate



$$\begin{matrix}R\\R\end{matrix}\!\!>C=O\xrightarrow{NaHSO_3}\begin{matrix}R\\R\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\SO_3Na\end{matrix}$$

158. (d) Fehling's solution is the solution of $CuSO_4+NaOH$ + Roschel salt (Sodium potassium tartarate). Aldehyde give red precipitate with Fehling's solution.

159. (c) It reduce $-CHO$ group into hydrocarbon.

160. (a) Molecular weight of the compound

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

$=2\times29=58$

Molecular weight of CH_3CH_2CHO, $CH_3CHOHCH_3$, CH_3COCH_3 and CH_3CH_2COOH are 58, 60, 58 and 74 respectively. Both CH_3CH_2CHO and CH_3COCH_3 have molecular weight 58 but only aldehyde *i.e.,* CH_3CH_2CHO on warming with aqueous alkali gives yellow precipitate.

161. (c) $\underset{\text{2 butanol}}{CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3}$ contain $CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-$ group by which it give +ve iodoform test.

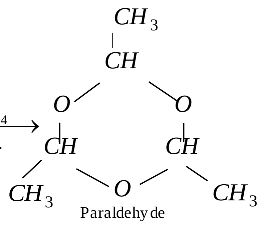
162. (c) In nucleophilic addition reaction, the carbonyl compound will respond in preference which is sterically more exposed and electronically have intact positive charge over carbonyl carbon. So reactivity order towards reaction with *phMgBr* is (II) > (III) > (I).

163. (d) Tollen's reagent oxidizes the compound having aldehyde group like glucose and also oxidizes α-hydroxy ketones having $-COCH_2OH$ group as in fructose.

164. (d) Acetaldehyde have CH_3CO- group so it give positive iodoform test with I_2 and $NaOH$ while formaldehyde does not have $-CH_3CO$ group so it will not give the positive haloform test.

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

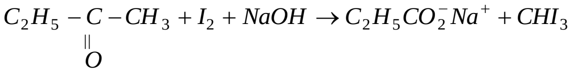
166. (d) $3CH_3CHO\xrightarrow[\text{room temp.}]{\text{conc. }H_2SO_4}$



Paraldehyde

168. (b) Formaline contains $40\%\,HCHO, 8\%\,CH_3OH$ and 52% water. It is used as biological preservative.

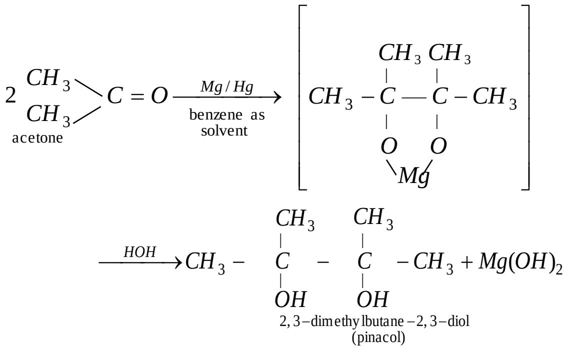
172. (c)



$$C_2H_5-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3+I_2+NaOH\rightarrow C_2H_5CO_2^-Na^++CHI_3$$

$$C_2H_5CO_2^-Na^+\xrightarrow{H^+}C_2H_5COOH+Na^+$$

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



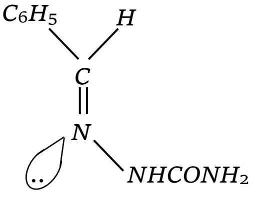
$$2\underset{\text{acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O}\xrightarrow[\text{benzene as solvent}]{Mg/Hg}\left[\begin{matrix}&CH_3&CH_3&\\&|&|&\\CH_3-&C&—C&-CH_3\\&|&|&\\&O&O&\\&&\!\!\!\!\diagdown Mg&\end{matrix}\right]$$

$$\xrightarrow{HOH}\underset{\substack{\text{2, 3-dimethylbutane-2, 3-diol}\\\text{(pinacol)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3}+Mg(OH)_2$$

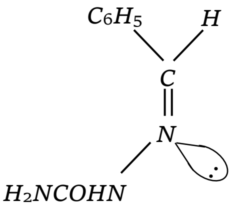
174. (a) $C_6H_5CH=O+H_2NNHCONH_2$

$$\rightarrow\underset{\text{semicarbazone}}{C_6H_5CH=NNHCONH_2}$$

The product shows E and Z configuration

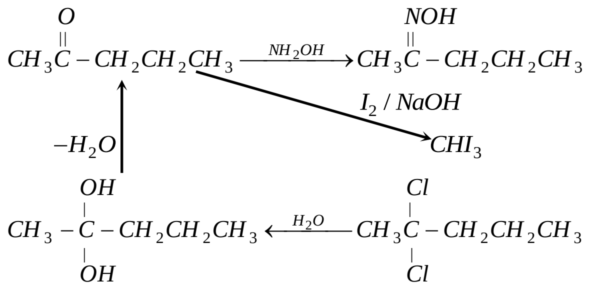


E-



Z-

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

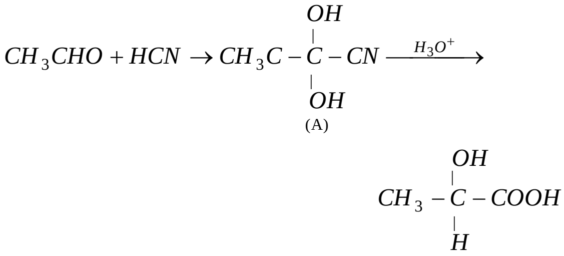


$$CH_3\overset{O}{\overset{||}{C}}-CH_2CH_2CH_3 \xrightarrow{NH_2OH} CH_3\overset{NOH}{\overset{||}{C}}-CH_2CH_2CH_3$$

$$CH_3\overset{O}{\overset{||}{C}}-CH_2CH_2CH_3 \xrightarrow{I_2/NaOH} CHI_3$$

$$CH_3-\underset{OH}{\overset{OH}{C}}-CH_2CH_2CH_3 \xleftarrow{H_2O} CH_3\underset{Cl}{\overset{Cl}{C}}-CH_2CH_2CH_3;\quad CH_3-\underset{OH}{\overset{OH}{C}}-CH_2CH_2CH_3 \xrightarrow{-H_2O} CH_3\overset{O}{\overset{||}{C}}-CH_2CH_2CH_3$$

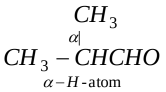
176. (e)



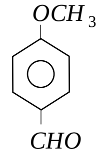
$$CH_3CHO+HCN \rightarrow \underset{(A)}{CH_3\underset{OH}{\overset{OH}{C}}-CN} \xrightarrow{H_3O^+} CH_3-\underset{H}{\overset{OH}{C}}-COOH$$

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

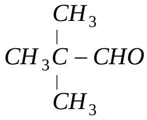
$\underset{\alpha-H \text{ atom absent}}{C_6H_5CHO}$



$$\underset{\alpha-H\text{-atom}}{CH_3-\overset{CH_3}{\overset{\alpha|}{C}}HCHO}$$



$\alpha-H$-atom absent



$$CH_3\underset{CH_3}{\overset{CH_3}{C}}-CHO$$

$\alpha-H$-atom absent

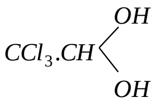
$\underset{\alpha-H-\text{atom absent}}{HCHO}$

Critical Thinking Questions

1. (d) Acetone oxidise by $K_2Cr_2O_7$ & conc. H_2SO_4 into carboxylic acid. It is not oxidised by dilute H_2SO_4.

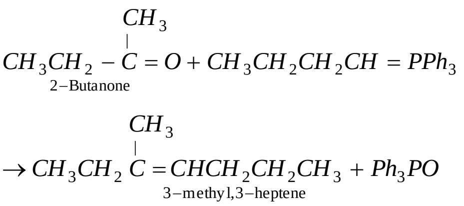
2. (b) Acetaldehyde react with tollen's reagent while ketone do not react with tollen's reagent.

3. (b) $CCl_3-CHO+H_2O \rightarrow \underset{\text{(Chloral hydrate)}}{CCl_3.CHO.H_2O} \rightarrow$



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

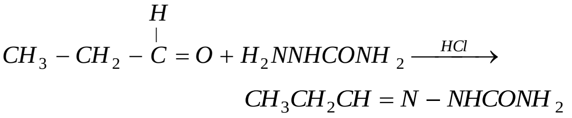
5. (a)



$$\underset{2-\text{Butanone}}{CH_3CH_2-\overset{CH_3}{C}=O}+CH_3CH_2CH_2CH=PPh_3$$

$$\rightarrow \underset{3-\text{methyl},3-\text{heptene}}{CH_3CH_2\overset{CH_3}{C}=CHCH_2CH_2CH_3}+Ph_3PO$$

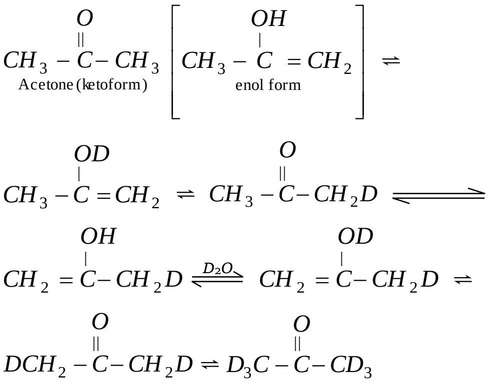
6. (a) $\underset{(A)}{CH_3-CH_2-CH_2OH} \xrightarrow{[O]} \underset{(B)}{CH_3-CH_2-CHO}$



$$CH_3-CH_2-\overset{H}{C}=O+H_2NNHCONH_2 \xrightarrow{HCl} CH_3CH_2CH=N-NHCONH_2$$

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

8. (b)



$$\underset{\text{Acetone (ketoform)}}{CH_3-\overset{O}{\overset{||}{C}}-CH_3}\left[\underset{\text{enol form}}{CH_3-\overset{OH}{C}=CH_2}\right] \rightleftharpoons$$

$$CH_3-\overset{OD}{C}=CH_2 \rightleftharpoons CH_3-\overset{O}{\overset{||}{C}}-CH_2D \rightleftharpoons$$

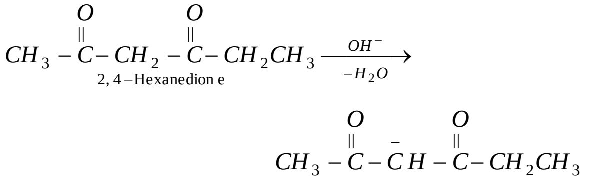
$$CH_2=\overset{OH}{C}-CH_2D \overset{D_2O}{\rightleftharpoons} CH_2=\overset{OD}{C}-CH_2D \rightleftharpoons$$

$$DCH_2-\overset{O}{\overset{||}{C}}-CH_2D \rightleftharpoons D_3C-\overset{O}{\overset{||}{C}}-CD_3$$

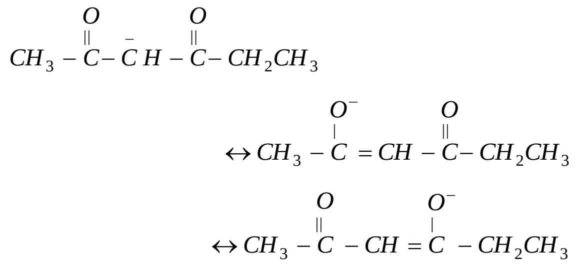
The enol form of acetone on treatment with D_2O undergoes enolisation, deutration (addition of D_2O) and dehydration (removal of H_2O). The repeated enolisation, deutration and dehydration ultimately gives $CD_3.COCD_3$ (B).

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

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



$$\underset{2,4-\text{Hexanedione}}{CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-CH_2CH_3} \xrightarrow[-H_2O]{OH^-} CH_3-\overset{O}{\overset{||}{C}}-\overset{-}{C}H-\overset{O}{\overset{||}{C}}-CH_2CH_3$$

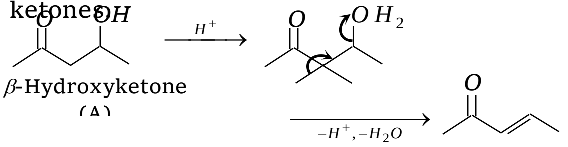


$$CH_3-\overset{\overset{O}{\|}}{C}-\bar{C}H-\overset{\overset{O}{\|}}{C}-CH_2CH_3$$

$$\leftrightarrow CH_3-\overset{\overset{O^-}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-CH_2CH_3$$

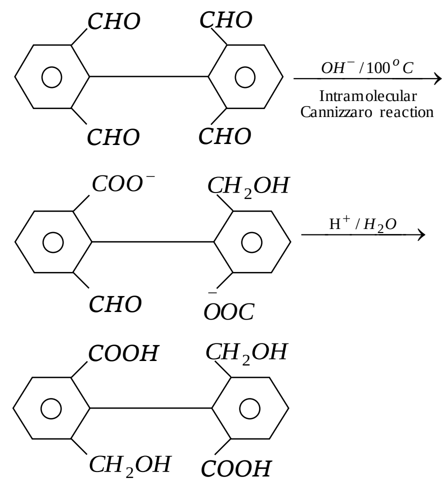
$$\leftrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH=\overset{\overset{O^-}{|}}{C}-CH_2CH_3$$

11. (a) Aldols (β-hydroxy aldehydes or β-hydroxyketones) readily undergo dehydration to form α, β-unsaturated aldehydes or ketones.



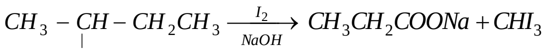
β-Hydroxyketone (A)

12. (b)



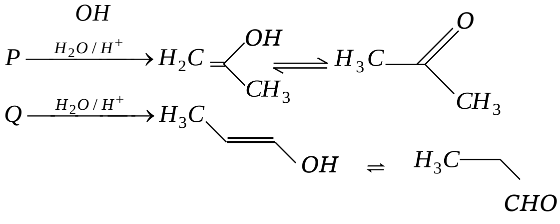
13. (a) Amongst aldehyde & the acid derivatives, acid chloride are the most susceptible to nucleophilic attack due to strong $-I$ effect & weak $+R$ effect of the Cl-atom as a result of which carbonyl carbon has the highest electron deficiency. The actual order is $MeCOCl > MeCOOCOMe > MeCOOMe > MeCHO$.

14. (ad) $ICH_2COCH_2CH_3 \xrightarrow{I_2 / NaOH} CHI_3 + CH_3CH_2COONa$



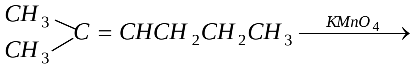
$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2CH_3 \xrightarrow[NaOH]{I_2} CH_3CH_2COONa + CHI_3$$

15. (c)

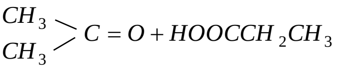


Ketone (non-reducing) and aldehyde (reducing) can be distinguished by Fehling solution.

16. (d)

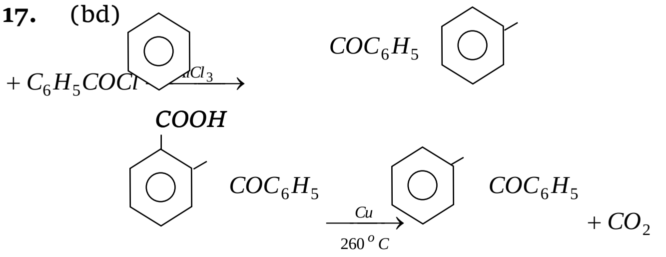


$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CHCH_2CH_2CH_3 \xrightarrow{KMnO_4}$$



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O + HOOCCH_2CH_3$$

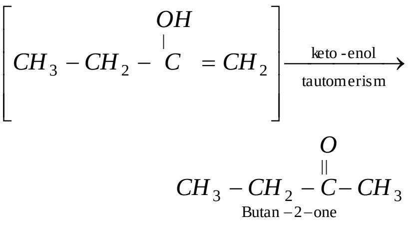
17. (bd)



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

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

20. (a) $\underset{\text{But}-1-\text{yne}}{CH_3-CH_2-C\equiv CH} + H_2O \rightarrow$



$$\left[CH_3-CH_2-\overset{\overset{OH}{|}}{C}=CH_2\right] \xrightarrow[\text{tautomerism}]{\text{keto-enol}} \underset{\text{Butan}-2-\text{one}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$$

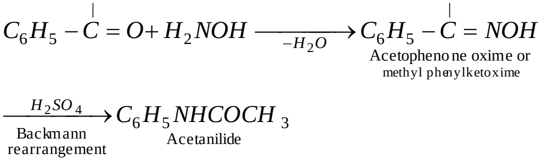
21. (b) Due to electron withdrawing nature of NO_2 group, the partial +ve charge on the carbon atom of the $>C=O$ group in p-nitrobenzaldehyde increases and hence becomes more susceptible to nucleophilic attack by CN^- ion.

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

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

24. (d) The alcohol can be converted to aldehyde group by treating with oxidising agent Pyridinium chloro chromate ($C_6H_5\overset{\oplus}{N}HCrO_3Cl^-$) it is abbreviated as PCC and is called Collin's reagent. This reagent is used in non aqueous solvent like CH_2Cl_2 It is a very good reagent because it checks the further oxidation of aldehyde to carboxylic acid while rest oxidising agent oxidise aldehyde into carboxylic acid.

25. (a)

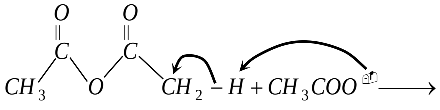


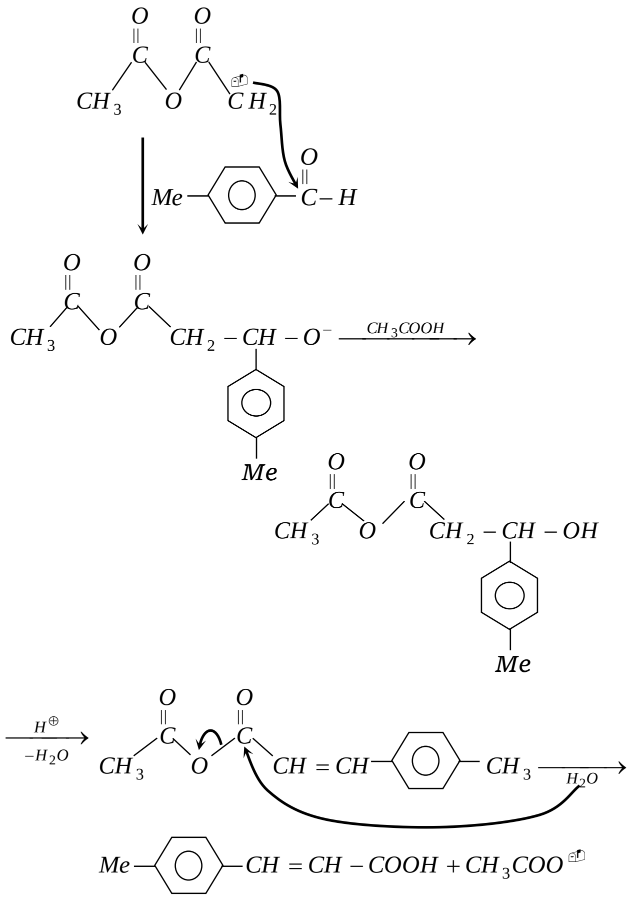
$$C_6H_5-\overset{\overset{CH_3}{|}}{C}=O + H_2NOH \xrightarrow[-H_2O]{} \underset{\substack{\text{Acetophenone oxime or}\\ \text{methyl phenylketoxime}}}{C_6H_5-\overset{\overset{CH_3}{|}}{C}=NOH}$$

$$\xrightarrow[\substack{\text{Backmann}\\ \text{rearrangement}}]{H_2SO_4} \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3}$$

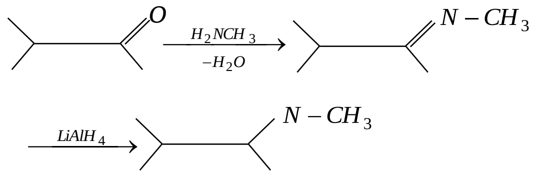
26. (d) Benzyl alcohol does not have the CH_3CO- group or $CH_3CH_2O^-$ so it will not give the positive iodoform test.

27. (c) This is perkin reaction

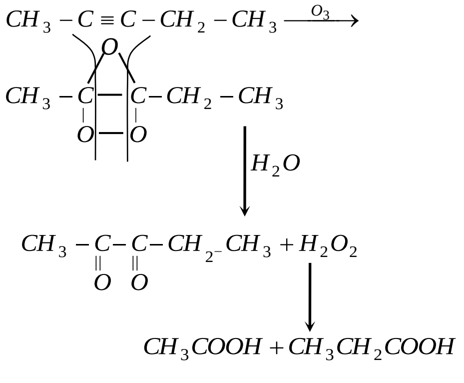




28. (b)



29. (c)



30. (a) On complete oxidation the obtained compound shows increament in molecular weight of only 16. It means only one oxygen atom is added here. This condition is fulfilled by only aldehyde which on oxidation gives acid.

$RCHO \xrightarrow{[O]} RCOOH$

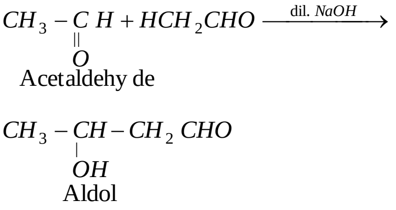
Hence, original compound must be

$$\underset{\text{mol. wt. 44}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{mol. wt. 60}}{CH_3COOH}$$

Assertion & Reason

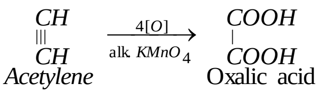
3. (b) It is true that lower aldehyde and ketones are soluble in water but as the molecular mass increases their solubility decreases. On adding Tollen's reagent to a solution of Carbonyl compound if silver mirror is obtained than it is aldehyde. Therefore Tollen's reagent is used for the identification of aldehydes and ketones. Here, assertion and reason both are true but the reason is not the correct explanation of assertion.

4. (a) Carbonyl compounds having α-hydrogen atom condenses to produce aldol in presence of alkali.



$$\underset{\text{Acetaldehy de}}{CH_3-\underset{\underset{O}{\|}}{C}H} + HCH_2CHO \xrightarrow{\text{dil. } NaOH} \underset{\text{Aldol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_2\,CHO}$$

5. (d) Acetylene, on treatment with alkaline $KMnO_4$ is oxidised to produce oxalic acid.

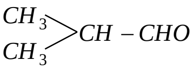


$$\underset{\text{Acetylene}}{\overset{CH}{\underset{CH}{|||}}} \xrightarrow[\text{alk. } KMnO_4]{4[O]} \underset{\text{Oxalic acid}}{\overset{COOH}{\underset{COOH}{|}}}$$

Therefore, both assertion and reason are false.

6. (b) Acetophenone and benzophenone can be distinguish by iodoform test. Both are carbonyl compounds. Assertion and reason both are true but reason is not the correct explanation of assertion.

7. (c)



Isobutanol has α-hydrogen atom.

Acetaldehyde, acetone and methyl ketones having CH_3CO group undergo haloform reaction. The halogen atoms of the methyl group are first replaced by hydrogen atoms. This reaction is used as a test of CH_3CO-

group. Due to absence of CH_3CO –group isobutanal does not give iodoform test.

8. (a) Benzaldehyde is less reactive than ethanol towards nucleophilic attack. The combined effect of $-I$ and $+R$ effect of phenyl group is electron donating which increases the electron density on the carbon atom of the $C=O$ in benzaldehyde.

9. (b) Both carbanions (formed in presence of base) and enol form (formed in presence of an acid) act as nucleophiles and hence add on the carbonyl group of aldehydes and ketones to give aldols.

10. (b) The positive inductive effect of two alkyl groups in ketones makes the carbon atom less positive and makes it less reactive in comparison to aldehydes.

11. (e) Oximes are more acidic because, there is a delocalisation of π electrons (*i.e.,* resonance) and it stabilises it and its conjugate acid. But no such resonance exists in hydroxyl amine base (NH_2O^-)

12. (e) The bond energy of carbonyl group is 179 *Kcal* mol^{-1} and in $<C=C$ the bond energy is 145.8 *Kcal*. The carbonyl group shows resonance and thus possesses higher bond energy. $C=O$ C^+-O^-

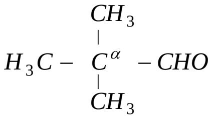
13. (b) Both carbon and oxygen are nonmetals and try to complete their octet. In $R-C\equiv O^+$ each has complete octet whereas in $R-C^+=O,$ carbon atom has in complete octet.

14. (b) *HCHO* cannot be prepared by Rosenmund's reduction because formyl chloride is unstable at room temperature.

15. (e) *HCHO* reacts with NH_3 to form urotropine $6HCHO+4NH_3\rightarrow(CH_2)_6N_4+6H_2O$

16. (c) The anion left after the removal of α-hydrogen is stabilized by resonance effect.

17. (b) Aldehydes which do not contain α-hydrogens undergo Cannizzaro reaction.



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^{\alpha}}}-CHO$$

2, 2 dimethyl propanal (no α hydrogen)

18. (d) Aldehydes having a methyl or methylene group in the α-position or more correctly having atleast one hydrogen atom in the α-position undergo dimerisation in presence of a base at low temperature to form β-hydroxy aldehydes called aldols.

Aldehydes and Ketones

SET Self Evaluation Test -27

1. Benzophenone can be converted into benzene using

[Tamil Nadu CET 2001]

(a) Fused alkali

(b) Anhydrous $AlCl_3$

(c) Sodium amalgam in water

(d) Acidified dichromate

2. The reagent(s) which can be used to distinguish acetophenone from benzophenone is (are)

[CBSE PMT 1990]

(a) 2, 4-dinitrophenyl hydrazine

(b) Aqueous solution of $NaHSO_3$

(c) Benedict reagent

(d) I_2 and Na_2CO_3

3. When acetaldehyde is heated with Fehling solution, it gives a red precipitate of **[MP PET 1989, 93; IIT 1982; MP PET/PMT 1998; RPMT 2002]**

(a) Cu (b) CuO

(c) Cu_2O (d) $Cu(OH)_2$

4. The general order of reactivity of carbonyl compounds for nucleophilic addition reactions is **[CBSE PMT 1995]**

(a) $H_2C=O > RCHO > ArCHO > R_2C=O > Ar_2C=O$

(b) $ArCHO > Ar_2C=O > RCHO > R_2C=O > H_2C=O$

(c) $Ar_2C=O > R_2C=O > ArCHO > RCHO > H_2C=O$

(d) $H_2C=O > R_2C=O > Ar_2C=O > RCHO > ArCHO$

5. Which of the following gives an alcohol and salt of carboxylic acid when reacted with conc. $NaOH$

[MP PMT 1999]

(a) CH_3CHO

(b) C_6H_5CHO

(c) CH_3COCH_3

(d) $C_6H_5COCH_3$

6. Which of the following compounds would undergo Cannizzaro's reaction

[CPMT 1989; AFMC 1991; MNR 1995]

(a) Propionaldehyde

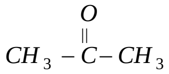
(b) Benzaldehyde

(c) Bromobenzene

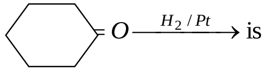
(d) Acetaldehyde

7. $NaOH / H^+$ reacts with **[BHU 2003]**

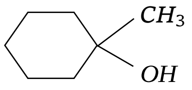
(a) $C_6H_5OCH_3$ (b) CH_3OH

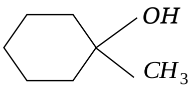
(c) 
$CH_3-\overset{\overset{O}{||}}{C}-CH_3$ (d) C_2H_5OH

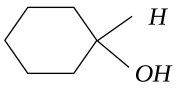
8. The product of following reaction

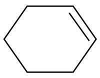


[Kerala CET 2000]

(a) 

(b) 

(c) 

(d) 

9. Which of the following aldehydes is most reactive towards nucleophilic addition reactions

[Roorkee 1992; RPMT 1997]

(a) $HCHO$ (b) CH_3CHO

(c) C_2H_5CHO (d) CH_3COCH_3

10. Which one of the following gives iodoform test

[AIIMS 1996]

(a) Formaldehyde

(b) Ethyl alcohol

(c) Benzyl alcohol

(d) Benzaldehyde

11. The active ion in Tollen's reagent is

(a) Cu^+ (b) $Cu(NH_3)_2^+$

(c) Ag^+ (d) $Ag(NH_3)_2^+$

12. Among the following compounds, which will react with acetone to give a product containing $>C=N-$

[IIT 1998]

(a) $C_6H_5NH_2$

(b) $(CH_3)_3N$

(c) $C_6H_5NHC_6H_5$

(d) $C_6H_5NHNH_2$

13. Which of the following does not give yellow precipitate with I_2 and $NaOH$ **[MP PET 1996]**

(a) C_2H_5OH (b) CH_3CHO

(c) CH_3COCH_3 (d) $HCHO$

14. In this reaction

$$CH_3CHO + HCN$$
$$\downarrow$$
$$CH_3CH(OH)CN \xrightarrow{H^+/OH^-} CH_3CH(OH)COOH$$

an asymmetric centre is generated. The acid obtained would be

(a) 20% D + 80% L-isomer

(b) D-isomer

(c) L-isomer

(d) 50% D + 50% L-isomer

15. Aldehydes are produced in atmosphere by **[NCERT 1982]**

(a) Oxidation of secondary alcohols

(b) Reduction of alkenes

(c) Reaction of oxygen atoms with hydrocarbons

(d) Reaction of oxygen atoms with ozone

16. Which of the following compounds will give positive test with Tollen's reagent

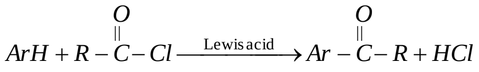
[CBSE PMT 1994; Kurukshetra CEE 1998; AFMC 2002]

(a) Acetamide

(b) Acetaldehyde

(c) Acetic acid

(d) Acetone

17. 

$$ArH + R-\overset{\overset{O}{||}}{C}-Cl \xrightarrow{\text{Lewis acid}} Ar-\overset{\overset{O}{||}}{C}-R + HCl$$ is an example of

(a) Friedel-Craft's alkylation

(b) Friedel-Craft's acylation

(c) Cannizzaro reaction

(d) Claisen condensation

[CBSE PMT 2003]

18. Which of the following fails to answer the iodoform test.

[CBSE PMT 1989]

(a) Pentanone–1

(b) Pentanone–2

(c) Propanone–2

(d) Ethanol

19. The reagent used for the separation of acetaldehyde from acetophenone is

(a) $NaHSO_4$

(b) $C_6H_5NHNH_2$

(c) NH_2OH

(d) $NaOH - I_2$

Answers and Solutions

(SET -27)

1. (a) $\underset{\text{Benzopheno ne}}{C_6H_5COC_6H_5} + KOH \xrightarrow{\text{Fusion}} \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Pot. benzoate}}{C_6H_5COOK}$

$C_6H_5\boxed{COOK + KO}H \xrightarrow{\Delta} K_2CO_3 + \underset{\text{Benzene}}{C_6H_6}$

2. (d) Acetophenone gives iodoform reaction while benzophenone does give this.

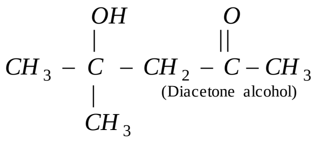
3. (c) $CH_3CHO + \underbrace{2Cu^{+2} + 5OH^-}_{\text{Fehling solution}} \rightarrow CH_3COO^- + \underset{\text{Red ppt.}}{Cu_2O} + 3H_2O$

4. (a) The size of the alkyle group. Causes hindrance to attacking group. As the number and size of the alkyl groups incirease the hindrance to the attack of nucleophile also increases.
Thus the reactivity follows the order
$H_2C = O > RCHO > ArCHO > R_2C = O > Ar_2C = O$.

5. (b) Benzaldehyde does not have the α-hydrogen so it will undergoes cannizzaro's reaction.
$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$

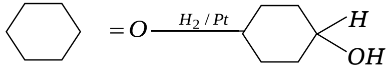
6. (b) C_6H_5CHO Aldehydes – Those aldehyde in which $\alpha - H$ atom is absent can participate in Cannizzaro's reaction.

7. (c) $2CH_3 - CO - CH_3 \xrightarrow{dil\ NaOH}$



$CH_3 - \overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_2 - \overset{\overset{O}{||}}{C} - CH_3$ (Diacetone alcohol)

8. (c)



9. (a) Because alkyl group is absent and they have $+ve$ inductive effect and increases the electron density on the carbonyl group.

10. (b) The compound having α-hydrogen will give iodoform test. Ethyl alcohol and secondary alcohols also give positive iodoform test because by the action of halogens in alkaline medium, they are oxidesed to acetaldehyde and methyl ketones respectively.

$$CH_3CH_2OH \xrightarrow[NaOH]{I_2} CH_3CHO \xrightarrow[NaOH]{I_2} CI_3CHO$$

$$CHI_3 + HCOONa \xleftarrow[NaOH]{H_2O}$$

11. (d) During reaction Ag^+ gets reduced Ag metal and forms silver mirror.

12. (ad) $C_6H_5NH_2$ and $C_6H_5NH.NH_2$ will give the compounds containing $> C = N$ -group.

13. (d) $HCHO \xrightarrow{I_2 / NaOH}$ No reaction

14. (d) $CH_3CHO + HCN \rightarrow CH_3CHOHCN \xrightarrow{\text{hydrolysis}}$

$$\underset{\text{D+L isomer of lactic acid}}{CH_3CHOHCOOH}$$

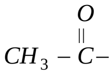
15. (c) Aldehydes are compounds containing C, H and O. So hydrocarbons react with atmospheric oxygen to give aldehydes.

16. (b) Tollen's reagent is ammonical silver nitrate solution. Its reacting species is Ag^+. It oxidises aliphatic as well as aromatic aldehydes.

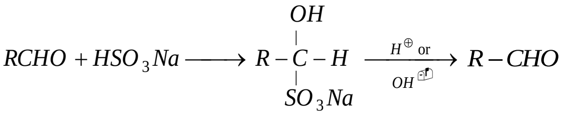
$R - CHO + Ag^+ \xrightarrow[\text{reaction}]{\text{Redox}} RCOOH + Ag$

17. (b) $ArH + R - CO - Cl \xrightarrow{\text{anhyd. } AlCl_3} Ar - CO - R + HCl$

This reaction is Friedel–Craft's acylation.

18. (a) 1-pentanone is an impossible compound does not have  $CH_3 - \overset{\overset{O}{||}}{C} -$ group.

19. (a) $NaHSO_3$ gives the addition reaction with Aldehyde and only aliphatic ketone. Acetophenone is the aromatic ketone so it does not give the addition product with $NaHSO_3$ aldehyde from the addition product with $NaHSO_3$ which on treatment with acid or base give again aldehyde.



$RCHO + HSO_3Na \longrightarrow R - \overset{\overset{OH}{|}}{\underset{\underset{SO_3Na}{|}}{C}} - H \xrightarrow[OH^{\ominus}]{H^{\oplus} \text{ or}} R - CHO$

***

$C_6H_5COCH_3 + NaHSO_3 \longrightarrow$ No reaction