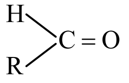
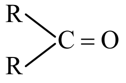
20 Aldehydes and Ketones

QUICK LOOK

Aldehydes are the compounds which have general formula RCHO, Ketones are compounds having general formula $RR'CO$. The groups R and R' may be aliphatic or aromatic, similar or different alkyl/ aryl groups.


An aldehyde

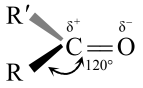

A ketone

Both aldehydes and ketones contain the carbonyl group, C = O, and are often referred to collectively as carbonyl compounds. It is the carbonyl group that governs mainly the chemistry of aldehydes and ketones.

Structure of Carbonyl Group

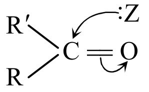
Carbonyl carbon is joined to three other atoms by σ bonds; since these bonds utilize sp^2 orbitals, they lie in a plane, and are 120° apart. The remaining p-orbitals of carbon overlaps a p-orbital of oxygen to form a π bond; carbon and oxygen are thus joined by a double bond. The part of the molecule immediately surrounding carbonyl carbon lie in a plane.

The electrons of a carbonyl double bond hold together atoms of quite different electro-negativity and hence the electrons are not equally shared; in particular the polar π-cloud is pulled strongly towards the more electronegative atom, oxygen.

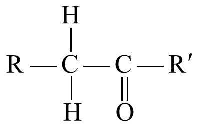


The carbonyl group, C = 0, governs the chemistry of aldehydes and ketones. It does this in two ways:

- By providing a site for nucleophilic addition, and



- By increasing the acidity of hydrogen atoms attached to the alpha carbon.

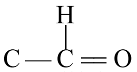


$$R-\underset{H}{\overset{H}{C}}-\underset{O}{\overset{}{\underset{\|}{C}}}-R'$$

Nomenclature: The common name of aldehydes is derived from the names of the corresponding carboxylic acids by replacing –*ic* acid by –aldehyde. The longest chain containing the –CHO group is considered the parent structure and named by replacing –*e* of the corresponding alkane by –al. The position of the substituent is indicated by a number, the carbonyl carbon always being considered C-1. Here, as with the carbonyl acids, the C-2 of the IUPAC name corresponds to alpha of the common name.

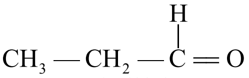
$$C-\overset{H}{\overset{|}{C}}=O$$

Formaldehyde
Methanal



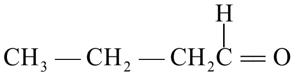
$$C-\overset{H}{\overset{|}{C}}=O$$

Acetaldehyde
Ethanal



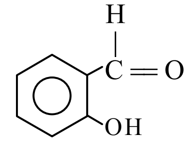
$$CH_3-CH_2-\overset{H}{\overset{|}{C}}=O$$

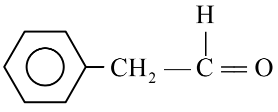
Propionaldehyde
Propanal

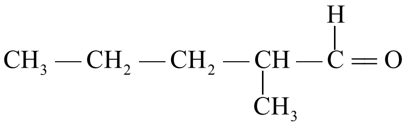


$$CH_3-CH_2-CH_2\overset{H}{\overset{|}{C}}=O$$

n-Butyraldehyde
Butanal

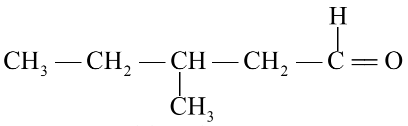

Salicyladehyde
(o-Hydroxybenzaldehyde)


Phenylacetaldehyde
(Phenylethanal)



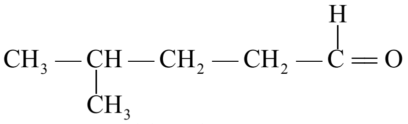
$$CH_3-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-\overset{H}{\overset{|}{C}}=O$$

2-Methylpentanal



$$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{H}{\overset{|}{C}}=O$$

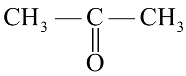
3-Methylpentanal



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-\overset{H}{\overset{|}{C}}=O$$

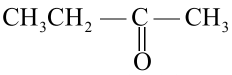
4-Methylpentanal

The simple aliphatic ketone has the common name acetone. For most other aliphatic ketones we name the two groups that are attached to carbonyl carbon and follow these names by the word ketone. A ketone in which the carbonyl group is attached to a benzene ring is named as phenone, as illustrated below. The positions of various groups are indicated by numbers.



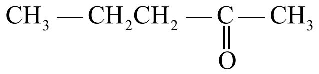
$$CH_3-\underset{O}{\underset{\|}{C}}-CH_3$$

Acetone
Propanone



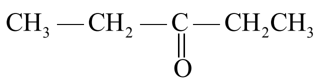
$$CH_3CH_2-\underset{O}{\underset{\|}{C}}-CH_3$$

Methyl ethyl ketone Butaone



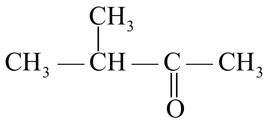
$$CH_3-CH_2CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

Methyl-n-propyl ketone
2-Pentanone



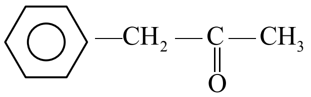
$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_3$$

3-Pentanone

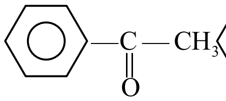


$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-CH_3$$

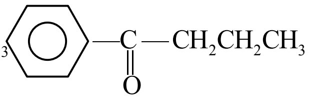
3-Methyl-2-butanone



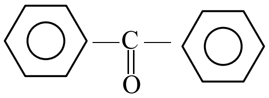
1-Phenyl-2-propanone



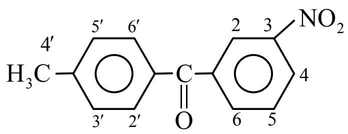
Acetophenone



n–butyrophenon



Benzophenone

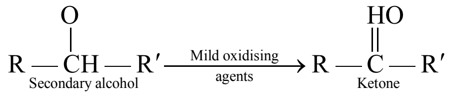


3-Nitro-4′-methylbenzophenon

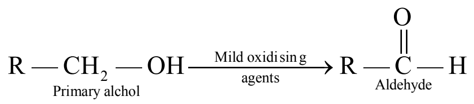
Preparation of Carbonyl Compounds

From Alcohols

- **By oxidation**



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



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

Mild oxidising agents are

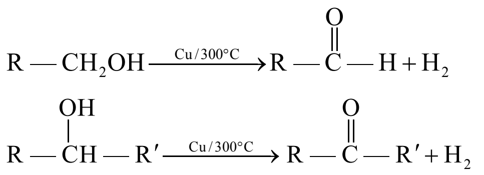
(i) X_2 (Halogen) (ii) Fenton reagent $(FeSO_4 + H_2O_2)$

(iii) $K_2Cr_2O_7 / \overset{\oplus}{H}$ (iv) Jones reagent

(v) Sarret reagent (vi) MnO_2

(vii) 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 these 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.
- **Dehydrogenation of 11° and 2° alcohols by Cu/300°or Ag/300°C.**

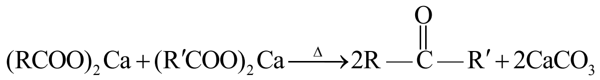


$$R-CH_2OH\xrightarrow{Cu/300^\circ C}R-\overset{\overset{O}{\|}}{C}-H+H_2$$

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

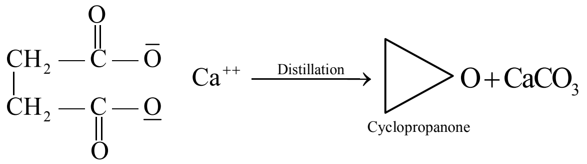
From Carboxylic Acids

- **Distillation of Ca, Ba, Sr or Th salts of monobasic acids**

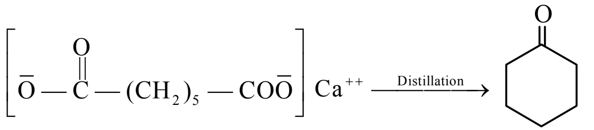


$$(RCOO)_2Ca+(R'COO)_2Ca\xrightarrow{\Delta}2R-\overset{\overset{O}{\|}}{C}-R'+2CaCO_3$$

Thus in the product, one alkyl group comes from one carboxylic acid and other alkyl group from other carboxylic acid. Calcium salts of dibasic acid (1, 4 and higher) on distillation give cyclic ketones.



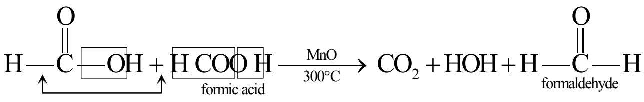
Cyclopropanone



Cyclohexanone

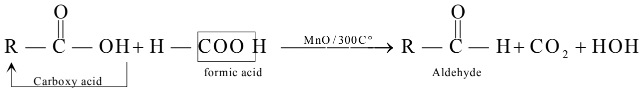
- **Decarboxylation or Dehydration of acids by MnO/ 300°C.**
- This reaction takes place between two molecules of carboxylic acids. Both may be the same or different.
- If one of the carboxylic acids is HCOOH then this acid undergoes decarboxylation because this acid is the only monobasic acid which undergoes decarboxylation even in the absence of catalyst.

Case (i): When both molecules are HCOOH



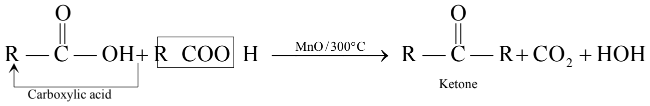
$$H-\overset{\overset{O}{\|}}{C}\boxed{-O}H+\underset{\text{formic acid}}{\boxed{H\,CO}\boxed{O}\,H}\xrightarrow[300^\circ C]{MnO}CO_2+HOH+H-\overset{\overset{O}{\|}}{\underset{\text{formaldehyde}}{C}}-H$$

Case (ii): When only one molecule is formic acid.



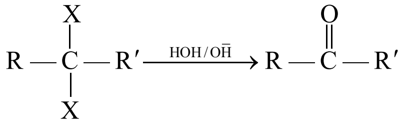
$$\underbrace{R-\overset{\overset{O}{\|}}{C}-OH}_{\text{Carboxy acid}}+\underset{\text{formic acid}}{H-\boxed{COO\ H}}\xrightarrow{MnO/300C^{\circ}}\underset{\text{Aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H}+CO_2+HOH$$

Case (iii): When none of the molecule is formic acid.



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

From Gem Dihalides: Gem dihalides on hydrolysis give carbonyl compound

- $\underset{\text{Gemdihalide}}{R-CHX_2}\xrightarrow{HOH/\bar{O}H}\underset{\text{Aldehyde}}{R-CHO}$
- 

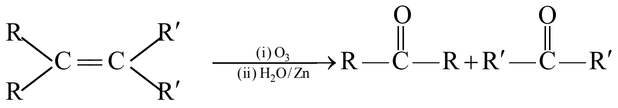
$$R-\underset{X}{\overset{X}{\overset{|}{\underset{|}{C}}}}-R'\xrightarrow{HOH/\bar{O}H}R-\overset{\overset{O}{\|}}{C}-R'$$

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

From Alkenes

- **Ozonolysis:** Alkenes on reductive ozonolysis give carbonyl compounds

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



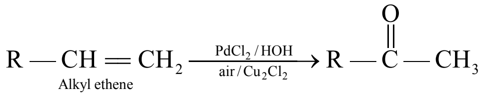
$$\begin{matrix}R\\ \end{matrix}\!\!>C=C<\!\!\begin{matrix}R'\\R'\end{matrix}\ \ (R,R)\xrightarrow[\text{(ii) }H_2O/Zn]{\text{(i) }O_3}R-\overset{\overset{O}{\|}}{C}-R+R'-\overset{\overset{O}{\|}}{C}-R'$$

This method is used only for aliphatic carbonyl compounds.

- **Oxo process**

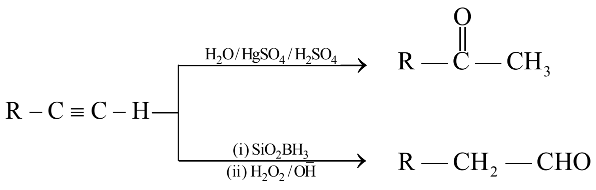
  $R-CH=CH_2+CO+H_2\xrightarrow[150^{\circ}C,\ 300\ \text{atm}]{CO_2(CO)_8}$

  $R-CH_2-CH_2-CHO$

  Oxo process is used only for the preparation of aldehydes.
- **Wacker process**
- $\underset{\text{Ethene}}{CH_2=CH_2}\xrightarrow[\text{air}/Cu_2Cl_2]{PdCl_2/HOH}CH_3-CHO$
- 

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

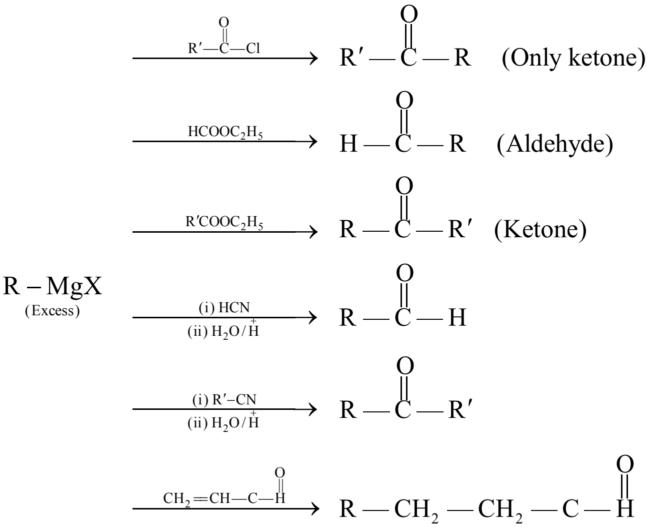
From Alkynes



$$R-C\equiv C-H\xrightarrow{H_2O/HgSO_4/H_2SO_4}R-\overset{\overset{O}{\|}}{C}-CH_3$$

$$R-C\equiv C-H\xrightarrow[\text{(ii) }H_2O_2/\bar{O}H]{\text{(i) }SiO_2BH_3}R-CH_2-CHO$$

From Grignard Reagents



$$\underset{\text{(Excess)}}{R-MgX}\xrightarrow{R'-\overset{\overset{O}{\|}}{C}-Cl}R'-\overset{\overset{O}{\|}}{C}-R\quad\text{(Only ketone)}$$

$$\xrightarrow{HCOOC_2H_5}H-\overset{\overset{O}{\|}}{C}-R\quad\text{(Aldehyde)}$$

$$\xrightarrow{R'COOC_2H_5}R-\overset{\overset{O}{\|}}{C}-R'\quad\text{(Ketone)}$$

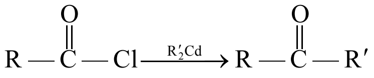
$$\xrightarrow[\text{(ii) }H_2O/\overset{+}{H}]{\text{(i) }HCN}R-\overset{\overset{O}{\|}}{C}-H$$

$$\xrightarrow[\text{(ii) }H_2O/\overset{+}{H}]{\text{(i) }R'-CN}R-\overset{\overset{O}{\|}}{C}-R'$$

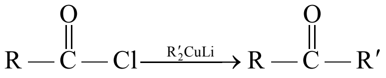
$$\xrightarrow{CH_2=CH-\overset{\overset{O}{\|}}{C}-H}R-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$$

From Acid Chloride

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



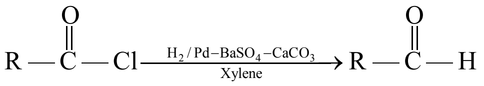
$$R-\overset{\overset{O}{\|}}{C}-Cl\xrightarrow{R_2'Cd}R-\overset{\overset{O}{\|}}{C}-R'$$



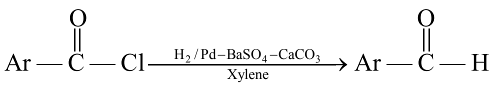
$$R-\overset{\overset{O}{\|}}{C}-Cl\xrightarrow{R_2'CuLi}R-\overset{\overset{O}{\|}}{C}-R'$$

  (Only used for the preparation of ketones)

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

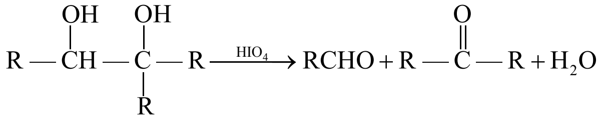
From Cyanides

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

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

  (Only used for aldehydes)

From Vic Diols



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

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

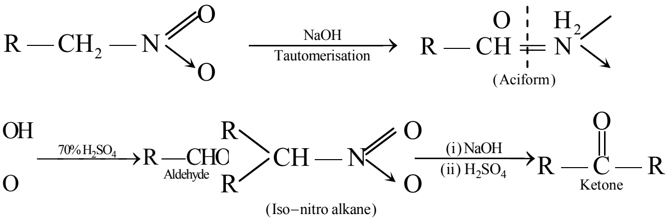
From Alkyl Halides and Benzyl Halides

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

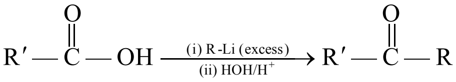
$$R-\overset{Cl}{\overset{|}{CH}}-R \xrightarrow{DMSO} R-\overset{O}{\overset{\|}{C}}-R$$

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

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.



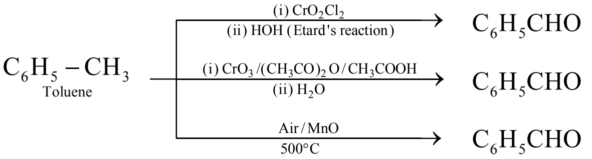
Reaction with Excess of Alkyl Lithium: Carboxylic acids react with excess of organo lithium compound to give lithium salt of gem diols which on hydrolysis give ketones.



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

Preparation of Only Aromatic Carbonyl Compounds

From Methyl Arenes

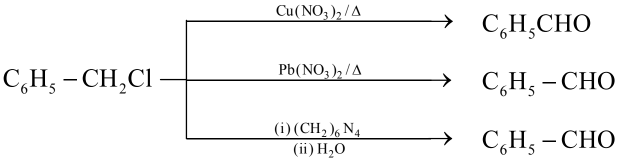


$$C_6H_5-CH_3\ (Toluene) \xrightarrow[(ii)\ HOH\ (Etard's\ reaction)]{(i)\ CrO_2Cl_2} C_6H_5CHO$$

$$C_6H_5-CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ CrO_3/(CH_3CO)_2O/CH_3COOH} C_6H_5CHO$$

$$C_6H_5-CH_3 \xrightarrow[500^\circ C]{Air/MnO} C_6H_5CHO$$

From Chloro Methyl

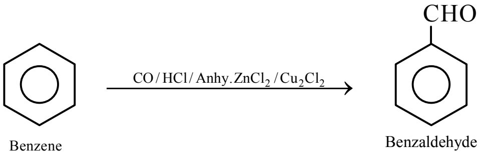


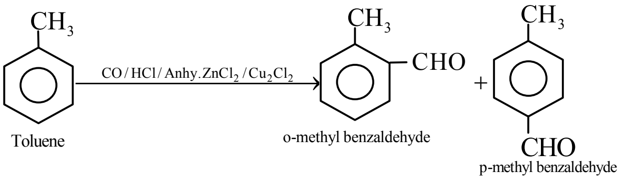
$$C_6H_5-CH_2Cl \xrightarrow{Cu(NO_3)_2/\Delta} C_6H_5CHO$$

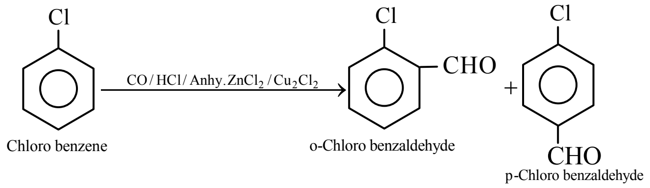
$$C_6H_5-CH_2Cl \xrightarrow{Pb(NO_3)_2/\Delta} C_6H_5-CHO$$

$$C_6H_5-CH_2Cl \xrightarrow[(ii)\ H_2O]{(i)\ (CH_2)_6N_4} C_6H_5-CHO$$

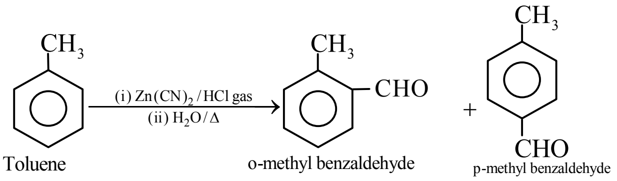
Gattermann–Koch Formylation: This reaction is mainly given by aromatic hydrocarbons and halobenzenes.

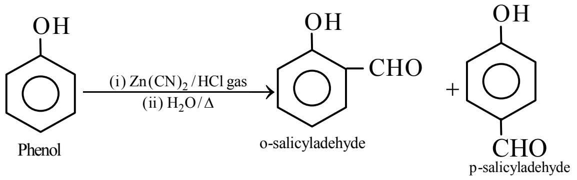


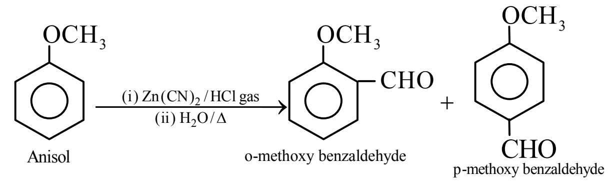




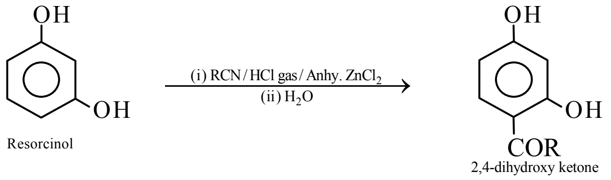
Gattermann Formylation: This reaction is mainly given by alkyl benzenes, phenols and phenolic ethers.

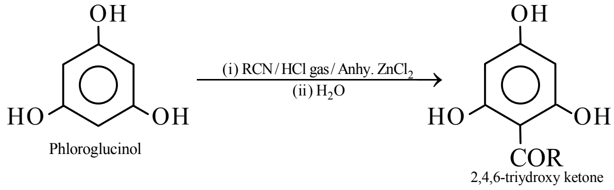




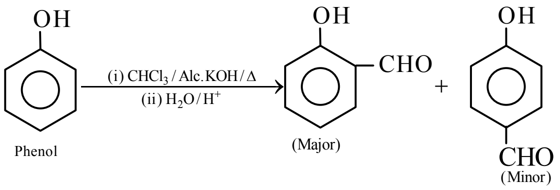


Houben –Hoesch Reaction: This reaction is given by di and polyhydric benzenes.





Reimer– Tiemann Reaction: Phenol gives o- and p- hydroxy benzaldehyde in this reaction.



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.

Preparation

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

  $CH_3OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} HCHO + H_2O$
- $CH_3OH \xrightarrow[300-400°C]{\text{Cu or Ag}} \underset{\text{Formaldehyde}}{HCHO}$
- $\underset{\text{Calcium formate}}{Ca(HCOO)_2} \xrightarrow{\text{Heat}} \underset{\text{Formaldehyde}}{HCHO}$
- $CH_2 = CH_2 + O_3 \xrightarrow[Pd]{H_2} \underset{\text{Formaldehyde}}{HCHO}$
- $\underset{\text{Methane}}{CH_4} + O_2 \xrightarrow[\text{Catalyst}]{\text{Mo-oxide}} \underset{\text{Formaldehyde}}{HCHO}$
- $CO + H_2 \xrightarrow{\text{Elec discharge}} \underset{\text{Formaldehyde}}{HCHO}$

Uses

- The 40% solution of formaldehyde (formalin) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens.
- It is used in the preparation of hexamethylene tetramine (urotropine) which is used as an antiseptic and germicide.
- It is used in silvering of mirror.
- It is employed in manufacture of synthetic dyes such as para-rosaniline, indigo, etc.
- It is used in the manufacture of formamint (by mixing formaldehyde with lactose) – a throat lozenges.
- It is used for making synthetic plastics like bakelite, urea-formaldehyde resin, etc.

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.

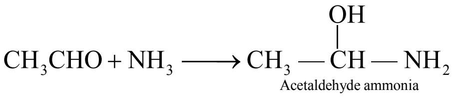
Acetaldehyde: Acetaldehyde is the second member of the aldehyde series. It occurs in certain fruits. It was first prepared by Scheele in 1774 by oxidation of ethyl alcohol.

Preparation

- By oxidation of ethyl alcohol with acidified potassium dichromate or with air in presence of a catalyst like silver at 300°C.
- By dehydrogenation of ethyl alcohol. The vapours of ethyl alcohol are passed over copper at 300°C.
- By heating the mixture of calcium acetate and calcium formate.
- By heating ethylidene chloride with caustic soda or caustic potash solution.
- By the reduction of acetyl chloride with hydrogen in presence of a catalyst palladium suspended in barium sulphate (Rosenmund's reaction).
- By the reduction of CH_3CN with stannous chloride and HCl in ether and hydrolysis (Stephen's method).
- By hydration of acetylene with dil. H_2SO_4 and $HgSO_4$ at 60°C.
- By ozonolysis of butene-2 and subsequent breaking of ozonide.
- **Laboratory preparation:** Acetaldehyde is prepared in the laboratory by oxidation of ethyl alcohol with acidified potassium dichromate or acidified sodium dichromate.

  $$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$
  $$[CH_3CH_2OH + O \longrightarrow CH_3CHO + H_2O] \times 3$$
  $$\underset{\substack{\text{Potassium}\\\text{dichromate}}}{K_2Cr_2O_7} + \underset{\text{Ethyl alcohol}}{3CH_3CH_2OH} + \underset{\text{Sulphuric acid}}{4H_2SO_4} \longrightarrow$$
  $$\underset{\substack{\text{Potassium}\\\text{sulphate}}}{K_2SO_4} + \underset{\substack{\text{Chromic}\\\text{sulphate}}}{Cr_2(SO_4)_3} + \underset{\text{Acetaldehyde}}{3CH_3CHO} + \underset{\text{Water}}{7H_2O}$$

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



$$CH_3CHO + NH_3 \longrightarrow \underset{\text{Acetaldehyde ammonia}}{CH_3 - \overset{\overset{OH}{|}}{CH} - NH_2}$$

$$\xrightarrow{H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} + (NH_4)_2SO_4$$

Manufacture: Acetaldehyde can be manufactured by one of the following methods:

- By air oxidation of ethyl alcohol

  $2CH_3CH_2OH + O_2 \xrightarrow[300°C]{Ag} 2CH_3CHO + 2H_2O$
- By dehydrogenation of alcohol

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

- By hydration of acetylene

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

- From ethylene (Wacker process)

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

Uses

- In the preparation of acetic acid, acetic anhydride, ethyl acetate, chloral, 1,3-butadiene (used in rubbers), dyes and drugs.
- As an antiseptic inhalent in nose troubles.
- In the preparation of paraldehyde (hypnotic and sporofic) and metaldehyde (solid fuel).
- In the preparation of acetaldehyde ammonia (a rubber accelerator).

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.

Preparation

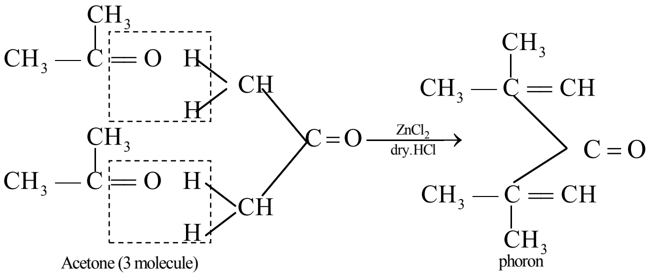
- $\underset{\text{calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\Delta} CH_3COCH_3$
- $\underset{\text{Isopropyl alcohol}}{2CH_3CHOHCH_3} + O_2 \xrightarrow{500°C} CH_3COCH_3$
- $\underset{\text{2 propanol}}{CH_3CHOHCH_3} \xrightarrow[300°C]{Cu} CH_3COCH_3$
- (i) $\underset{\text{propene}}{CH_3CH = CH_2} + PdCl_2 + H_2O \longrightarrow CH_3COCH_3$

  (ii) $\underset{\text{propene}}{CH_3CH = CH_2} + H_2SO_4 \longrightarrow$

  $CH_3CH(HSO_4)CH_3 \xrightarrow{H_2O}$

  $\underset{\text{Isopropyl alcohol}}{CH_3CH(OH)CH_3} \xrightarrow[300°C]{Cu} CH_3COCH_3$
- $2C_3H_5OH + H_3O \xrightarrow[500°C]{Zn(CrO_2)} CH_3COCH_3$
- $2CH \equiv CH + 3H_2O \xrightarrow[420°C]{catalyst} CH_3COCH_3$

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

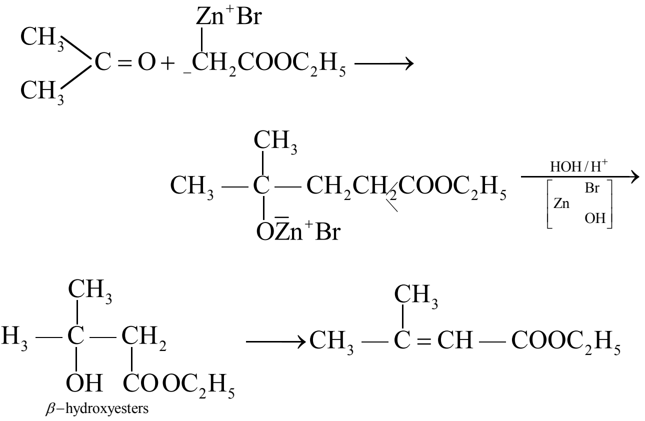


Molecular mass of phorone = 3 mole of acetone –2 mole of H_2O

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

$$BrCH_2COOC_2H_5 + Zn \xrightarrow{Benzene} Br - \overset{+}{Z}n - \underset{\text{Organo zinc compound}}{\overline{C}H_2COOC_2H_5}$$

- Addition to carbonyl group



Uses

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

Tests

- **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.

- **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.
- **Iodoform test:** Acetone gives iodoform test with iodine and sodium hydroxide or iodine and ammonium hydroxide.

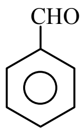
Aromatic Carbonyl Compounds

Aromatic aldehydes are of two types:

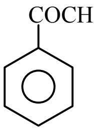
The compounds in which – CHO group is attached directly to an aromatic ring, *e.g.,* benzaldehyde, C_6H_5CHO.

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.

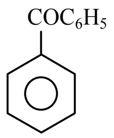
Aromatic ketones are compounds in which a carbonyl group (> C = O) is attached to either two aryl groups or one aryl group and one alkyl group. Examples are:



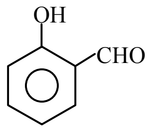
Benzaldehyde



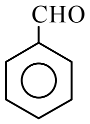
Acetophenone
(Methyl phenyl ketone)



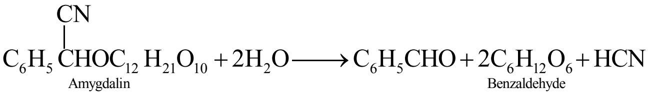
Benzophenone
(Diphenyl ketone)



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



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

Benzaldehyde is also known as oil of bitter almonds.

Preparation

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

$$2C_6H_5CH_2Cl + \underset{\underset{\textstyle Pb(NO_3)_2}{\text{or}}}{Cu(NO_3)_2} \xrightarrow[CO_2]{\text{heat}}$$

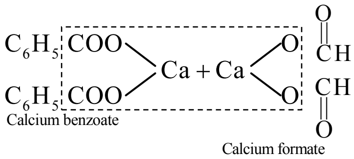
$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + CuCl_2 + 2HNO_2$$

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

- **Rosenmund reaction**

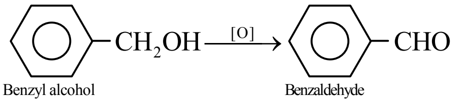
$$\underset{\text{Benzyl chloride}}{C_6H_5COCl} + H_2 \xrightarrow[\text{xylene}]{Pd/BaSO_4} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

- **By dry distillation of a mixture of calcium benzoate and calcium formate**



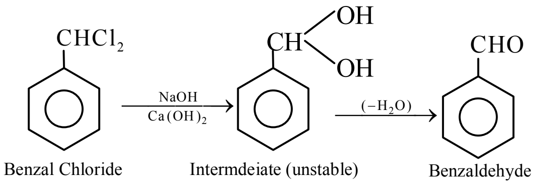
$$\xrightarrow{\text{heat}} \underset{\substack{\text{Benzaldehyde}\\ \text{(Major product)}}}{2C_6H_5CHO} + 2CaCO_3$$

- **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°C.



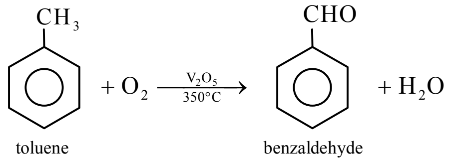
This method is used for commercial production of benzaldehyde.

- **By hydrolysis of benzal chloride**



This is also an industrial method.

- **By oxidation of toluene**



Commercially the oxidation of toluene is done with air and diluted with nitrogen (to prevent complete oxidation) at 500°C 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°C, also forms benzaldehyde.

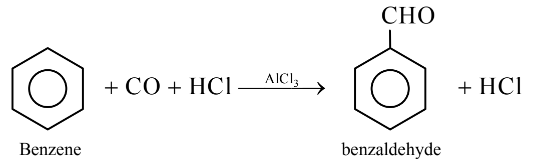
$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[(CH_3CO)_2O]{CrO_3} \underset{\text{Benzylidene acetate}}{C_6H_5CH(OCOCH_3)_2} \xrightarrow{H^+/H_2O}$$

$$C_6H_5CHO + 2CH_3COOH$$

- **Etard's reaction**: $C_6H_5CH_3 + 2CrO_2Cl_2 \longrightarrow$

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

- **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



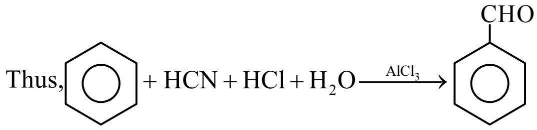
solution of benzene in presence of anhydrous aluminium chloride and cuprous chloride.

- **Gattermann reaction**

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

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

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

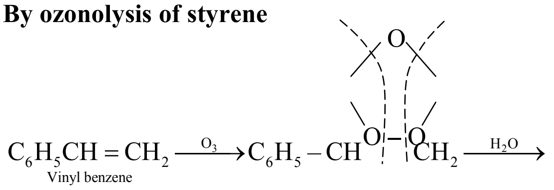


$+ NH_4Cl$

- **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.

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

- **By ozonolysis of styrene**



$$\underset{\text{Vinyl benzene}}{C_6H_5CH = CH_2} \xrightarrow{O_3} C_6H_5-CH\overset{O}{\underset{O-O}{}}CH_2 \xrightarrow{H_2O}$$

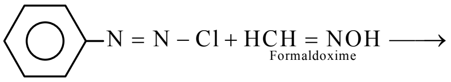
$$C_6H_5CHO + HCHO + H_2O_2$$

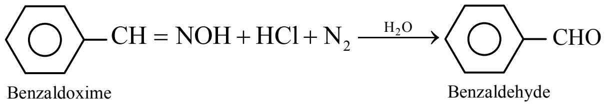
- **Grignard reaction**

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

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

- **From Diazonium salt**





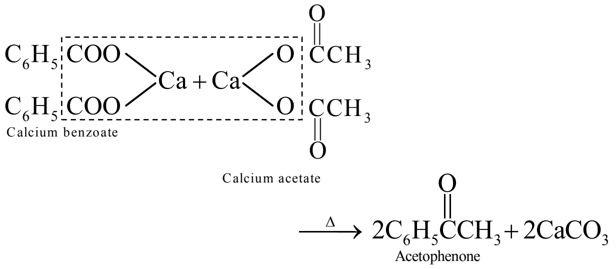
Acetophenone, $C_6H_5COCH_3$, Acetyl Benzene

Preparation

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

$$\underset{\text{Benzene}}{C_6H_5\,H} + \underset{\text{Acetyl chloride}}{Cl\,COCH_3} \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

- By distillation of a mixture of calcium benzoate and calcium acetate.



$$\underset{\text{Calcium benzoate}}{(C_6H_5COO)_2Ca} + \underset{\text{Calcium acetate}}{Ca(O\overset{\overset{O}{\|}}{C}CH_3)_2} \xrightarrow{\Delta} \underset{\text{Acetophenone}}{2C_6H_5\overset{\overset{O}{\|}}{C}CH_3} + 2CaCO_3$$

- By methylation of benzaldehyde with diazomethane.

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

- By treating benzoyl chloride with dimethyl cadmium.

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

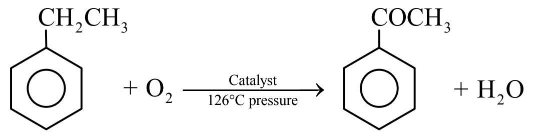
- **By grignard reagent**

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

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

$$C_6H_5MgBr + H_5C_2O\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}CH_3 + Mg\left\langle\begin{matrix}Br\\OC_2H_5\end{matrix}\right.$$

- **Commercial preparation:** Ethylbenzene is oxidised with air at 126°C under pressure in presence of catalyst manganese acetate.



Uses: It is used in perfumery and as a sleep producing drug.

Benzophenone, $C_6H_5COC_6H_5$

Preparation

From alkyl benzenes

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

MULTIPLE CHOICE QUESTIONS

Formaldehyde, Acetaldehyde and Acetone

1. In the group $\overset{R'}{\underset{R}{}}\!\!>C=O$ 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

2. IUPAC name of CCl_3CHO is:

a. Chloral
b. Trichloro acetaldehyde
c. 1, 1, 1-trichloroethanal
d. 2, 2, 2-trichloroethanal

3. On heating calcium acetate and calcium formate, the product formed is:

a. CH_3COCH_3
b. CH_3CHO
c. $HCHO + CaCO_3$
d. $CH_3CHO + CaCO_3$

4. Which of the following compound gives a ketone with Grignard reagent?

a. Formaldehyde
b. Ethyl alcohol
c. Methyl cyanide
d. Methyl iodide

Aromatic Carbonyl Compounds: Benzophenone, C_6H_5 CO C_6H_5

5. The oxidation of benzyl chloride with lead nitrate gives:

a. Benzyl alcohol
b. Benzoic acid
c. Benzaldehyde
d. *p*-chlorobenzaldehyde

6. During reaction of benzaldehyde with alkali one of the product is:

a. Phenol
b. Benzyl alcohol
c. Benzene
d. Benzophenone

7. The reaction

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

is known as:

a. Perkin's reaction
b. Claisen condensation
c. Benzoin condensation
d. Cannizzaro's reaction

8. Benzaldehyde and acetaldehyde can be differentiated by:

a. HCN
b. NH_2OH
c. Hydrazine
d. NaOH solution

9. In the presence of a dilute base C_6H_5CHO and CH_3CHO react together to give a product. The product is:

a. $C_6H_5CH_3$
b. $C_6H_5CH_2CH_2OH$
c. $C_6H_5CH_2OH$
d. $C_6H_5CH = CHCHO$

Preparation

10. The end product in the following sequence of reaction is:

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

a. Acetic acid
b. Isopropyl alcohol
c. Acetone
d. Ethanol

11. Compound which gives acetone on ozonolysis?

a. $CH_3-CH=CH-CH_3$
b. $(CH_3)_2C=C(CH_3)_2$
c. $C_6H_5CH=CH_2$
d. $CH_3CH=CH_2$

12.

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

Product 'A' in the reaction is :

a. CH_3COOH
b. C_2H_5OH
c. CH_3COCH_3
d. C_2H_5CHO

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

The above reaction is called:

a. Reimer-Tiemann reaction
b. Cannizzaro reaction
c. Rosenmund reaction
d. Reformatsky reaction

14. From which of the following tertiary butyl alcohol is obtained by the action of methyl magnesium iodide?

a. HCHO
b. CH_3CHO
c. CH_3COCH_3
d. CO_2

15. $CH_3-CH_2-C\equiv CH \xrightarrow[H_2O]{R}$ Butanone, R is :

a. Hg^{++}
b. $KMnO_4$
c. $KClO_3$
d. $K_2Cr_2O_7$

16. Dry heating of calcium acetate gives:

a. Acetaldehyde
b. Ethane
c. Acetic acid
d. Acetone

17. Methyl ethyl ketone is prepared by the oxidation of:

a. 2-propanol
b. 1-butanol
c. 2-butanol
d. *t*-butyl alcohol

18. Ethyne on reaction with water in the presence of $HgSO_4$ and H_2SO_4 gives:

a. Acetone
b. Acetaldehyde
c. Acetic acid
d. Ethyl alcohol

Properties

19. Consider the following statement Acetophenone can be prepared by:

(A) Oxidation of 1-phenylethanol
(B) Reaction of benzalthanol with methyl magnesium bromide
(C) Friedel craft's reaction of benzene with acetyl chloride

(D) Distillation of calcium benzoate

a. A and B **b.** A and D

c. A and C **d.** C and D

20. Which one of the following pairs is not correctly matched?

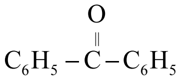
a. $>C=O \xrightarrow{\text{Clemenson's reduction}} >CH_2$

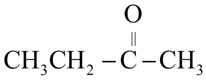
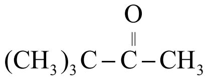
b. $>C=O \xrightarrow{\text{Wolf -Kishner reduction}} >CHOH$

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

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

21. Which of the following gives aldol condensation reaction?

a. C_6H_5OH **b.** 
$C_6H_5-\overset{\overset{O}{\parallel}}{C}-C_6H_5$

c. 
$CH_3CH_2-\overset{\overset{O}{\parallel}}{C}-CH_3$ **d.** 
$(CH_3)_3C-\overset{\overset{O}{\parallel}}{C}-CH_3$

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

a. Secondary alcohol **b.** A primary alcohol

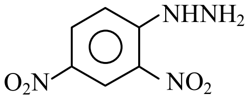
c. Phenol **d.** Tert-Butyl alcohol

23. Aldol condensation will not be observed in :

a. Chloral **b.** Phenyl acetaldehyde

c. Hexanal **d.** Ethanol

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



a. CH_3COCl **b.** CH_3COCH_3

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

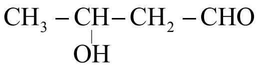
25. Which of the following organic compounds exhibits positive Fehling test as well as iodoform test?

a. Methanal **b.** Ethanol

c. Propanone **d.** Ethanal

26. Acetaldehyde when treated with dilute NaOH gives?

a. CH_3CH_2OH **b.** CH_3COOH

c. 
$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$ **d.** CH_3-CH_3

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

a. Phenyl hydrazine **b.** Hydroxylamine

c. Fehling solution **d.** Sodium bisulphite

28. Which of the following will undergo aldol condensation?

a. Acetaldehyde **b.** Propanaldehyde

c. Benzaldehyde **d.** Trideuteroacetaldehyde

29. Acetaldehyde cannot show:

a. Iodoform test **b.** Lucas test

c. Benedict's test **d.** Tollen's test

30. 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

31. To distinguish between formaldehyde and acetaldehyde, we require:

a. Tollen's reagent **b.** Fehling's solution

c. Schiff's reagent **d.** Caustic soda solution

32. Dimethyl ketones are usually characterised through:

a. Tollen's reagent **b.** Iodoform test

c. Schiff's test **d.** Benedict's reagent

33. The light yellow compound produced when acetone reacts with iodine and alkali, is?

a. $CH_3.CO.CH_2I$ **b.** CH_3I

c. CHI_3 **d.** None of these

34. If formaldehyde and KOH are heated, then we get:

a. Acetylene **b.** Methane

c. Methyl alcohol **d.** Ethyl formate

35. The alkaline $CuSO_4$ containing sodium potassium tart rate does not react with:

a. CH_3CHO **b.** C_2H_5CHO

c. $C_6H_5CH_2CHO$ **d.** C_6H_5CHO

36. Correct order of reactivity of $CH_3CHO, C_2H_5COCH_3$ and CH_3COCH_3 is:

a. $CH_3CHO > CH_3COCH_3 > CH_3COC_2H_5$

b. $C_2H_5COCH_3 > CH_3COCH_3 > CH_3CHO$

c. $CH_3COCH_3 > CH_3CHO > C_2H_5COCH_3$

d. $CH_3COCH_3 > C_2H_5COCH_3 > CH_3CHO$

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

a. Alcohol **b.** Ether

c. Ketone **d.** Aldehyde

38. Aldehydes can be oxidised by:

a. Tollen's reagent **b.** Fehling solution

c. Benedict solution **d.** All of these

39. Acetaldehyde and acetone differ in their reaction with:

a. Sodium bisulphite **b.** Ammonia

c. Phosphorus pentachloride **d.** Phenyl hydrazine

40. The compound obtained by the reduction of propionaldehyde by amalgamated zinc and concentrated HCl is:

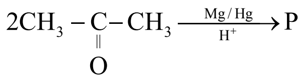
a. Propanol
b. Propane
c. Propene
d. All of these

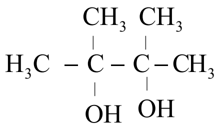
41. Formaldehyde when treated with KOH gives methanol and potassium formate. The reaction is known as?

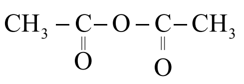
a. Perkin reaction
b. Claisen reaction
c. Cannizzaro reaction
d. Knoevenagel reaction

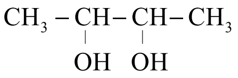
42. Which of the following reagents is used to distinguish acetone and acetophenone?

a. $NaHSO_3$
b. Grignard reagent
c. Na_2SO_4
d. NH_4Cl

43. 
$2CH_3-\underset{\overset{\|}{O}}{C}-CH_3 \xrightarrow[H^+]{Mg/Hg}$ Product, product in the reaction is:

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

b. 
$CH_3-\underset{\overset{\|}{O}}{C}-O-\underset{\overset{\|}{O}}{C}-CH_3$

c. 
$CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3$

d. None of these

44. Cinnamic acid is formed when C_6H_5-CHO condenses with $(CH_3CO)_2O$ in presence of?

a. Conc. H_2SO_4
b. Sodium acetate
c. Sodium metal
d. Anhydrous $ZnCl_2$

45. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives:

a. Benzyl alcohol and sodium formate
b. Sodium benzoate and methyl alcohol
c. Sodium benzoate and sodium formate
d. Benzyl alcohol and methyl alcohol

46. Aldehydes and ketones can be reduced to hydrocarbon by using:

a. $LiAlH_4$
b. $H_2/Pd-BaSO_4$
c. $Na-Hg/HCl$
d. NH_2-NH_2/C_2H_5ONa

47. Which of the following does not give brick red precipitate with Fehling solution?

a. Acetone
b. Acetaldehyde
c. Formalin
d. D-glucose

48. CH_3CHO react with aqueous NaOH solution to form:

a. 3-hydroxy butanal
b. 2-hydroxy butanal
c. 4-hydroxy butanal
d. 3-hydroxy butanol

49. Identify the product Y in the sequence:

$$CH_3CHO+CH_3MgI \xrightarrow{Ether} X \xrightarrow{H_2O/H^+} Y$$

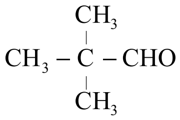
a. CH_3OH
b. CH_3CH_2OH
c. $(CH_3)_2CHOH$
d. $(CH_3)_3COH$

50. Which gives difference between aldehyde and ketone?

a. Fehling's solution
b. Tollen's reagent
c. Schiff's reagent
d. Benedict's solution
e. All of these

51. Which of the following would undergo aldol condensation?

a. $CCl_3.CHO$

b. 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CHO$

c. $CH_3.CH_2.CHO$
d. HCHO

52. Cannizzaro reaction is not shown by:

a. HCHO
b. C_6H_5CHO
c. CH_3CHO
d. All of these

53. Which one of the following on oxidation will not give a carboxylic acid with the same number of carbon atoms?

a. CH_3COCH_3
b. CCl_3CH_2CHO
c. $CH_3CH_2CH_2OH$
d. CH_3CH_2CHO

54. Schiff's reagent gives pink colour with:

a. Aldehydes
b. Ethers
c. Ketones
d. Carboxylic acid

55. Acid to give the corresponding hydrocarbon:

a. Acetamide
b. Acetic acid
c. Ethyl acetate
d. Butan–2–one

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

a. Benzaldehyde
b. Salicylaldehyde
c. Acetaldehyde
d. None of these

57. The order of susceptibility of nucleophilic attack on aldehydes follows the order:

a. 1° > 3° > 2°
b. 1° > 2° > 3°
c. 3° > 2° > 1°
d. 2° > 3° > 1°

58. Fehling solution is:

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

59. 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

60. The most appropriate reagent to distinguish between acetaldehyde and formaldehyde is:

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

NCERT EXEMPLAR PROBLEMS

More than One Answer

61. Which of the following will undergo aldol condensation?

a. Acetaldehyde **b.** Propanaldehyde
c. Benzaldehyde **d.** Trideuteroacetaldehyde

62. 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.** $CH_3CH(OH)CH_2CH_3$

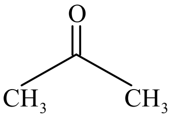
63. Which of the following reactions give benzo phenone?

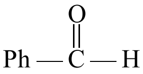
a. $2C_6H_6 + CCl_4 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlCl_3}$
b. $C_6H_6 + C_6H_5COCl \xrightarrow{AlCl_3}$
c. $o-CH_3C_6H_4COC_6H_5 \xrightarrow{\text{Heat}}$
d. $o-HOOC-C_6H_4-COC_6H_5 \xrightarrow[260°C]{Cu}$

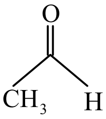
64. Which of the following are examples of aldol condensation?

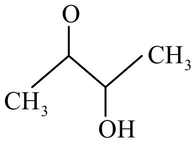
a. $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CHOHCH_2CHO$
b. $2CH_3COCH_3 \xrightarrow{\text{dil. NaOH}} CH_3C(OH)(CH_3)CH_2COCH_3$
c. $2HCHO \xrightarrow{\text{dil. NaOH}} CH_3OH$
d. $C_6H_5CHO + HCHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH_2OH$

65. Which of the following will respond to Feling's solution?

a.


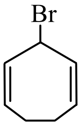
b.

$Ph-\overset{\overset{O}{\|}}{C}-H$

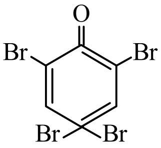
c.


d.


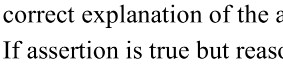
66. Which of the following compounds can be used as a source of Br^+?

a. HOBr

b.


c.


d. HBr

67.

$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{SeO_2}$ A will:

a. reduct Tollens reagent **b.** give iodoform test
c. form dioxime **d.** give Cannizaro reaction

68. Reaction of acetaldehyde with HCN followed by hydrolysis gives a compound which shows?

a. Optical isomerism **b.** Geometrical isomerism
c. Metamerism **d.** Tautomerism

69. IUPAC name of CH_3COCH_3 is:

a. Acetone **b.** 2-propanone
c. Dimethyl ketone **d.** Propanal

70. IUPAC name of CCl_3CHO is:

a. Chloral **b.** Trichloro acetaldehyde
c. 1, 1, 1-trichloroethanal **d.** 2, 2, 2-trichloroethanal

71. Which of the aldehyde is most reactive?

a. C_6H_5-CHO **b.** CH_3CHO
c. HCHO **d.** All the equally reactive

Assertion and Reason

Note: Read the Assertion (A) and Reason (R) 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.

72. **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.

73. **Assertion:** Acetaldehyde on treatment with alkaline gives aldol.

Reason: Acetaldehyde molecules contains α hydrogen atom.

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

Reason: Alkaline $KMnO_4$ is a reducing agent.

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

Reason: Acetophenone and benzophenone both are carbonyl compounds.

76. **Assertion:** Isobutanal does not give iodoform test
Reason: It does not have α- hydrogen.

77. **Assertion:** Aldol condensation can be catalysed both by acids and bases.
Reason: β- Hydroxy aldehydes or ketones readily undergo acid catalysed dehydration.

78. **Assertion:** Ketones are less reactive than aldehydes.
Reason: Ketones do not give schiff's test.

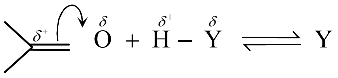
79. **Assertion:** Oximes are less acidic than hydroxyl amine.
Reason: Oximes of aldehydes and ketones show geometrical isomerism.

80. **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.

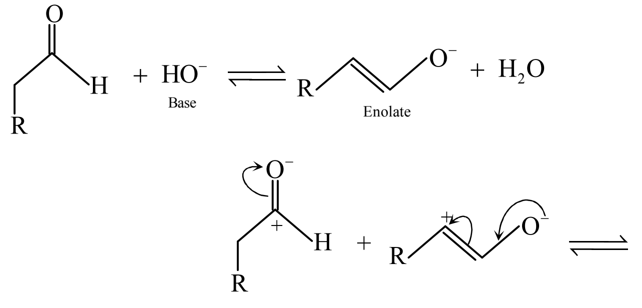
81. **Assertion:** CH_3CHO reacts with NH_3 to form urotropine.
Reason: Urotropine is used as medicine in case of urinary troubles.

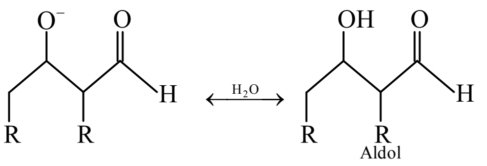
Comprehension Based

Paragraph –I

Aldehydes and ketones are polar molecule. Nucleophiles attack on carbonyl group $(>C=O)$ at carbon (positively charged) and electrophiles are attacked by oxygen. The characteristic reaction of aldehyde and ketone is nucleophilic addition to the carbon of carbonyl group 

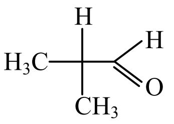
Aldehydes and ketones undergo condensation only when the consist α-hydrogen atom. The reaction takes place in presence of dilute alkali and one aldehyde molecule is partially converted to its enolate anion by the base. The enolate ion undergoes nucleophilic addition to the carbonyl group. The alkoxide formed in nucleophilic addition step, abstracts a proton form the solvent to give aldol, which consists aldehydic and hydroxyl group.

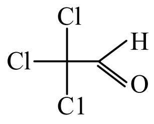


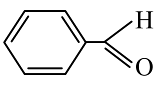


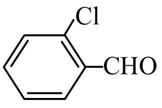
The reactivity of carbonyl compounds for nucleophilic addition reaction is inversely proportional to +I effect. In absence of $\alpha-$H atom, the aldehydes undergo Cannizzaro's reaction.

82. Which of the following undergoes aldol condensation?

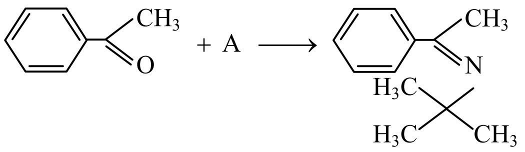
a. 

b. 

c. 

d. 

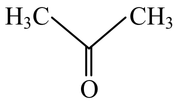
83. In the reaction A is:



a. $(CH_3)_2-NH$ **b.** $(CH_3)_3-N$
c. $(CH_3)_3C-NH_2$ **d.** None of these

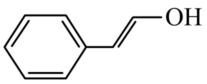
84. Which one is most reactive for addition of alcohol on carbonyl group?

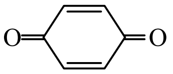
a. C_6H_5CHO **b.** HCHO

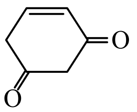
c. 

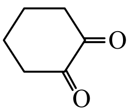
d. $CH_3\cdot CHO$

85. Tautomerism is not exhibited by:

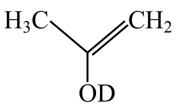
a. 

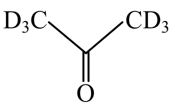
b. 

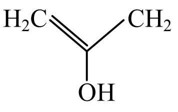
c. 

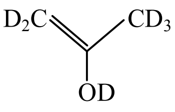
d. 

86. The enol form of acetone after treatment with D_2O gives:

a. 

b. 

c. 

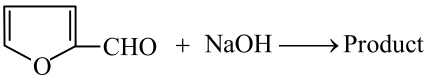
d. 

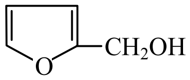
87. Which does not undergo intermolecular Cannizzaro's reaction?

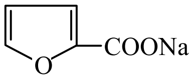
a. m-chloro benzaldehyde **b.** 2-methyl propanal

c. Glyoxalic acid **d.** glyoxal

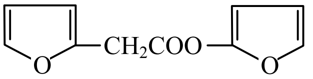
88. The product formed in the reaction are



(I)


(II)


(III)

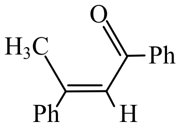

(IV)


a. I, III **b.** II, III

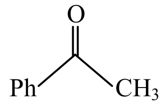
c. III, IV **d.** I, II

Paragraph –II

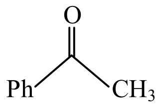
A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound L, whereas K on reaction with KOH gives only M.

M =


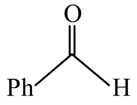
89. Compound H is formed by the reaction of

a.


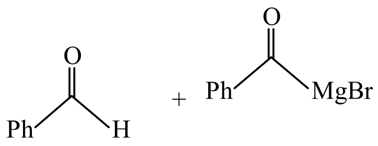
+ PhMgBr

b.


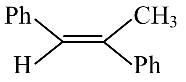
+ $PhCH_2MgBr$

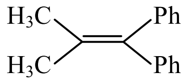
c.


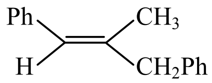
+ $PhCH_2MgBr$

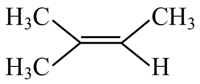
d.


90. The structure of compound I is:

a.


b.


c.


d.


91. The structure of compounds J, K and L, respectively, are:

a. $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$

b. $PhCHO$, $PhCH_2CHO$ and $PhCOO^-K^+$

c. $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$

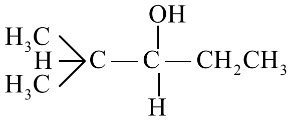
d. $PhCHO$, $PhCOCH_3$ and $PhCOO^-K^+$

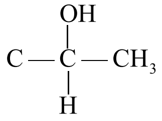
Paragraph –VII

An acyclic hydrocarbon P, having molecular formula C_6H_{10} gave acetone as the only organic product through the following sequence of reactions, in which Q is intermediate organic compound

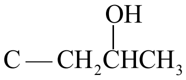
$$\underset{(C_6H_{10})}{P}\xrightarrow[\substack{2.\ NaBH_4/\text{ethanol}\\3.\text{dil.acid}}]{1.\text{dil.}H_2O_4/HgSO_4}Q\xrightarrow[\substack{2.\ O_3\\3.Zn/H_2O}]{1.\text{conc.}H_2O_4(\text{catalytic amount})(-H_2O)}$$

92. The structure of the compound Q is:

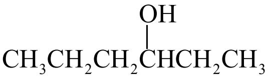
a.


b.


$C-\overset{OH}{\underset{H}{C}}-CH_3$

c.


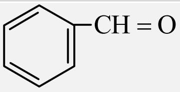
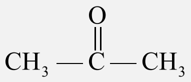
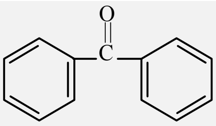
$C-CH_2\overset{OH}{C}HCH_3$

d.


$CH_3CH_2CH_2\overset{OH}{C}HCH_2CH_3$

Match the Column

93. Match the following columns:

Column I	**Column II**
(A) 	**1.** Aldol condensation
(B)  $CH_3-\overset{O}{\overset{\|\|}{C}}-CH_3$	**2.** Cannizzaro reaction
(C) $H-CH=O$	**3.** Benzoin condensation
(D) 	**4.** Claisen-Schmidt reaction

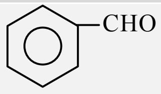
a. A→2,4; B→3,4; C→2,4; D→2

b. A→2,3,4; B→1,4; C→1,4; D-→3

c. A→1,3,4; B-→4; C→2,4; D→4

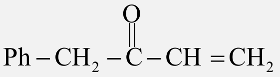
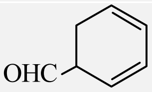
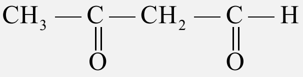
d. A→2,3,4; B→1,4; C→2,4; D→4

94. Match the following columns:

Column I	Column II
(A) 	**1.** Haloform reaction
(B) HCHO	**2.** Fehling solution
(C) $CH_3 \cdot CHO$	**3.** Cannizzaro's reaction
(D) $CH_3 \cdot CO \cdot CH_3$	**4.** Knovenagel reaction

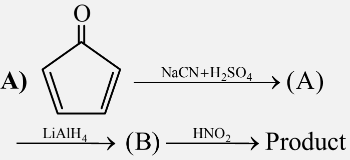
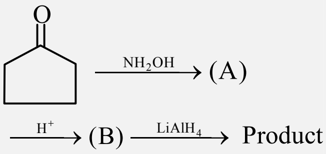
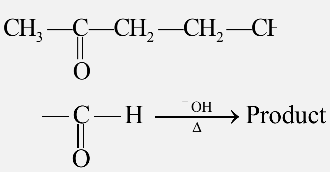
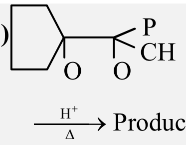
a. A→1,4; B-→2,4; C→1,2,4; D→1,4
b. A→3,4; B→2,3,4; C→1,2,4; D→1,4
c. A→3,4; B→1,3,4; C-→1,4; D→1,4
d. A→1,4; B→2,3; C→1,4; D→3,4

95. Match the following columns:

Column I	Column II
(A)  $Ph-CH_2-\overset{\overset{O}{\|}}{C}-CH=CH_2$	**1.** 1, 4 addition
(B) 	**2.** Tautomerism
(C) $CH_3-CH=CH-CH=CH_2$	**3.** $AgNO_3 / NH_4OH$
(D)  $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-H$	**4.** 2, 4 DNP test

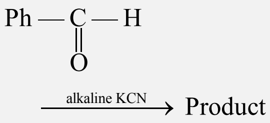
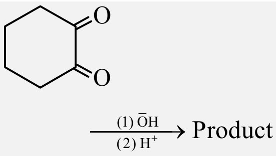
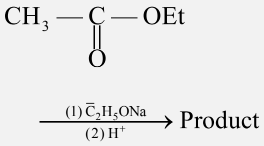
a. A→1,2,4; B→1,2,3,4; C→1; D→2,3,4
b. A→1,2; B→3,4; C→1; D→2,3,4
c. A→1,4; B→1,2,,4; C-→1; D→1,2,3,4
d. A→2,4; B→1,2,3,4; C→1; D→2,3

96. Match the following columns:

Column I	Column II
(A) 	**1.** Formation of six member ring take plane
(B) 	**2.** Final product is ketone
(C)  $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-H \xrightarrow[\Delta]{^-OH}$ Product	**3.** Final product fomed will give positive tollen's test
(D) 	**4.** Final product will react with 2, 4 DNP

a. A-→1,2; B→1,3; C→1,3,4; D-→1,2,4
b. A→1,2,4; B→1; C→1,2,4; D→1,2,4
c. A→2,4; B-→1,2; C→1,2,3,4; D→1,2,4
d. A→4; B→1,2,3; C→1,2,4; D→1,3,4

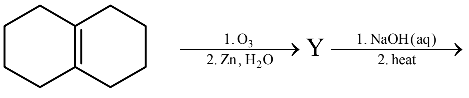
97. Match the following columns:

Column I	Column II
(A)  $Ph-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\text{alkaline KCN}}$ Product	**1.** Final product formed give positive tollen test
(B) 	**2.** Final product give test with 2, 4 DNP
(C)  $CH_3-\underset{\underset{O}{\|}}{C}-OEt \xrightarrow[(2)\ H^+]{(1)\ \bar{C}_2H_5ONa}$ Product	**3.** Final product react with $NaOCO_3$ and liberated CO_2 gas
(D) $Ph-CH=O \xrightarrow[(2)\ H_3O^+;\ \Delta]{(1)\ \bar{C}_2H_5ONa}$	**4.** Final product react with Na and liberated H_2 gas

a. A→1,4; B→1,3,4; C→2; D→1,4
b. A→3,4; B→1,3,4; C→1,2; D→3,4
c. A→3,4; B→1,4; C→2,4; D→3,4
d. A→1,2,4; B→3,4; C→2; D→3,4

Integer

98. In the scheme given below, the total number of intra-molecular aldol condensation products formed from 'Y' is



99. Consider all possible isomeric ketones including stereiosmers of MW = 100. All these isomers are independently reacted with $NaBH_4$ (Note: Stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are:

100. How many aldol products can form when 2-butanone and propanaldehyde reacts in presence of dilute base?

ANSWER

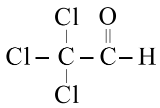
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
b	d	d	c	b	b	b	d	d	c
11.	**12.**	**13.**	**14.**	**15.**	**16.**	**17.**	**18.**	**19.**	**20.**
b	c	c	c	a	d	d	b	c	b
21.	**22.**	**23.**	**24.**	**25.**	**26.**	**27.**	**28.**	**29.**	**30.**
c	a	a	b	d	c	c	a,b,d	b	b
31.	**32.**	**33.**	**34.**	**35.**	**36.**	**37.**	**38.**	**39.**	**40.**
d	b	c	c	d	a	d	d	b	b
41.	**42.**	**43.**	**44.**	**45.**	**46.**	**47.**	**48.**	**49.**	**50.**
c	a	c	b	a	d	a	a	c	e
51.	**52.**	**53.**	**54.**	**55.**	**56.**	**57.**	**58.**	**59.**	**60.**
c	c	a	a	d	c	b	d	a	d
61.	**62.**	**63.**	**64.**	**65.**	**66.**	**67.**	**68.**	**69.**	**70.**
a,b,d	a,d	b	a,b	c,d	a,c	all	a	b	d
71.	**72.**	**73.**	**74.**	**75.**	**76.**	**77.**	**78.**	**79.**	**80.**
c	b	a	d	b	c	b	b	e	b
81.	**82.**	**83.**	**84.**	**85.**	**86.**	**87.**	**88.**	**89.**	**90.**
e	a	c	a	b	a	d	d	b	a
91.	**92.**	**93.**	**94.**	**95.**	**96.**	**97.**	**98.**	**99.**	**100.**
d	b	d	b	a	b	d	1	5	6

SOLUTION

Multiple Choice Questions

1. **(b)** $\begin{matrix}R\\R\end{matrix}\!>\!C\overset{\pi}{\underset{\sigma}{=}}O$

2. **(d)**



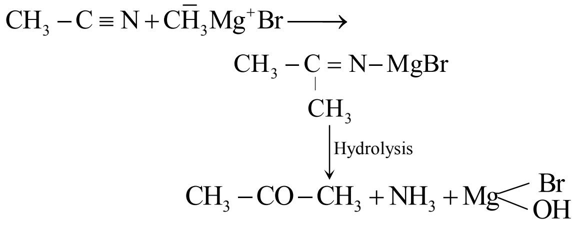
$Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-\overset{\overset{O}{||}}{C}-H$

2, 2, 2, trichloroethanal

3. **(d)** $\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\!\!>\!Ca+Ca\!<\!\begin{matrix}OOCH\\OOCH\end{matrix}$

$$\xrightarrow{\text{Distill}} 2CH_3CHO+2CaCO_3$$

4. **(c)**



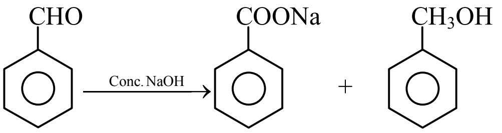
$CH_3-C\equiv N+\overset{-}{C}H_3Mg^{+}Br\longrightarrow$

$CH_3-\underset{\underset{CH_3}{|}}{C}=N-MgBr$

$\Big\downarrow$ Hydrolysis

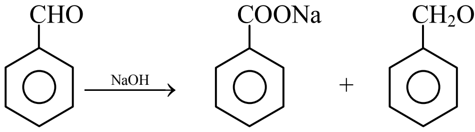
$CH_3-CO-CH_3+NH_3+Mg\!<\!\begin{matrix}Br\\OH\end{matrix}$

5. **(b)** 2

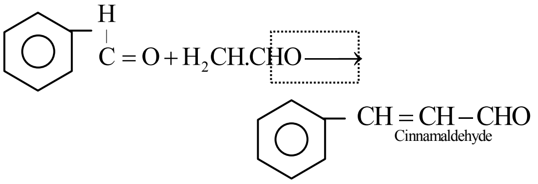


This reaction is called as Cannizzaro's reaction.

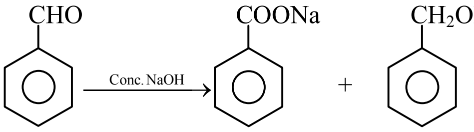
6. **(b)**



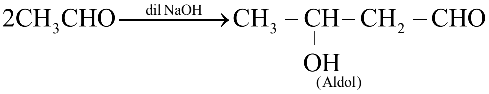
7. **(b)**



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



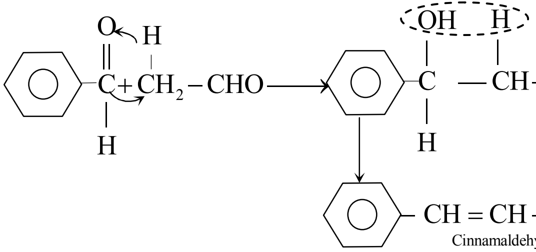
Cannizaro reaction



$2CH_3CHO\xrightarrow{\text{dil NaOH}}CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$

(Aldol)

9. **(d)**



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

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

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

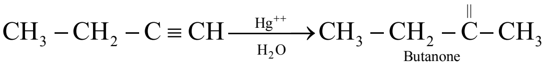
12. **(c)** Ketonic hydrolysis: $CH_3-CO-CH_2COOC_2H_5$

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

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

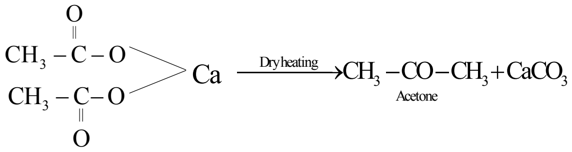
14. **(c)** $\underset{\text{Acetone}}{CH_3COCH_3}\xrightarrow{CH_3MgI}\underset{\text{tert-Butyl alcohol}}{(CH_3)_3COH}$

15. **(a)** It is hydration of alkynes.



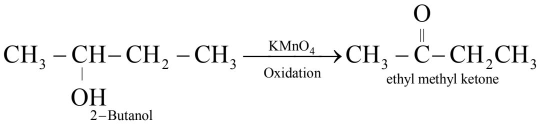
$CH_3-CH_2-C\equiv CH\xrightarrow[H_2O]{Hg^{++}}\underset{\text{Butanone}}{CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_3}$

16. **(d)**



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

17. **(c)**



$\underset{\text{2-Butanol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3}\xrightarrow[\text{Oxidation}]{KMnO_4}\underset{\text{ethyl methyl ketone}}{CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_3}$

18. **(b)** $HC \equiv CH + H_2O \xrightarrow{HgSO_4/H_2SO_4} CH_3CHO$

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

$C_6H_6 + CH_3COCl \xrightarrow[\text{reaction}]{\text{Friedel craft's}} C_6H_5COCH_3 + HCl$

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

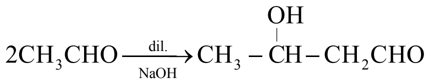
21. **(c)** Although both $CH_3CH_2COCH_3$ and $(CH_3)_3CCOCH_3$ contain α-hydrogen, yet $(CH_3)_3CCOCH_3$ does not undergo Aldol condensation due to steric hindrance.

22. **(a)** $\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow[H^+/H_2O]{CH_3MgBr} \underset{2°\text{Alcohol}}{C_6H_5CH(OH)CH_3}$

23. **(a)** Chloral $CCl_3CHO,$ has no α-hydrogen atom and hence does not undergo aldol condensation.

24. **(b)** Among the given compounds only acetone gives crystalline coloured derivative with 2, 4 DNP.

25. **(d)** Ethanal among the given compounds gives positive iodoform test.

26. **(c)**


$2CH_3CHO \xrightarrow[NaOH]{dil.} CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2CHO$

27. **(c)** $C_2H_5CHO + 2Cu^{+2} + 5OH^- \longrightarrow \underset{\text{Red ppt}}{Cu_2O} + 3H_2O$

$+C_2H_5COO^-$

$CH_3COCH_3 + 2Cu^{+2} + 5OH^- \longrightarrow \text{No reaction}$

28. **(a,b,d)** Deuterium behaves like H and hence trideuteroacetaldehyde also undergoes aldol condensation but benzaldehyde does not since it has no α-hydrogen.

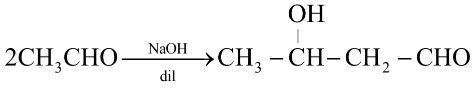
29. **(b)** $1°$ Primary alcohol $\xrightarrow{ZnCl_2/HCl}$ White turbidity only heating $2°$ Alcohol $\xrightarrow{ZnCl_2/HCl}$ White turbidity after 5 min heating $3°$ Alcohol $\xrightarrow{ZnCl_2/HCl}$ easily in seconds

30. **(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.

$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$

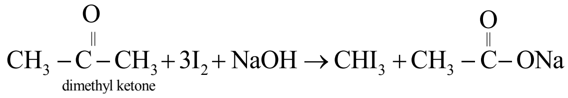
31. **(d)** $2HCHO \xrightarrow[Conc.]{NaOH} CH_3OH + HCOONa$

It is a Cannizzaro's reaction.



$2CH_3CHO \xrightarrow[dil]{NaOH} CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-CHO$

It is aldol condensation reaction.

32. **(b)**


$\underset{\text{dimethyl ketone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + 3I_2 + NaOH \rightarrow CHI_3 + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONa$

33. **(c)** CHI_3 is yellow compound when iodine reacts with NaOH and ketone.

34. **(c)** $HCHO + HCHO \xrightarrow{KOH} HCOOK + CH_3OH$

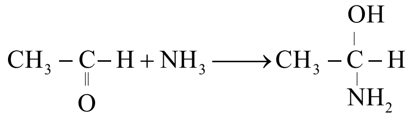
35. **(d)** The solution represented is fehling's and it has no tendency to oxidise benzaldehyde.

36. **(a)** Increasing alkyl group the reactivity decreases.

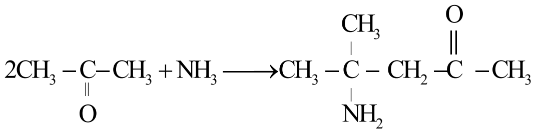
37. **(d)** $RCHO + \frac{1}{2}O_2 \longrightarrow RCOOH$

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

$2[Ag(NH_3)_2]^+ + RCHO \longrightarrow RCOOH + 2Ag + 4NH_3 + H_2O$

39. **(b)**


$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-H + NH_3 \longrightarrow CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{C}}-H$



$2CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3 + NH_3 \longrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{C}}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

40. **(b)** $CH_3CH_2CHO + 4H \xrightarrow[HCl]{Zn/Hg} CH_3CH_2CH_3 + H_2O$

This reaction is called clemmenson's reduction.

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

$HCHO + HCHO \xrightarrow{KOH} CH_3OH + HCOOK$

42. **(a)** Acetone forms sodium bisulphate adduct but acetophenone does not. Aromatic ketones do not gives addition product with $NaHSO_3$.

43. **(c)** $CH_3 \rightarrow O \leftarrow CH_3$. The electron density of oxygen is highly increased therefore resistant its nucleophilic attack.

44. **(b)** $C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3CO_2Na}$

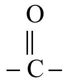
$C_6H_5CH = CHCO_2H$

It is Perkin's reaction.

45. **(a)** Crossed aldol reaction gives benzyl alcohol and sodium formate.

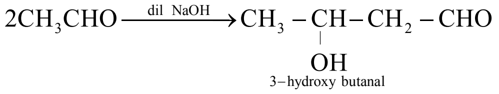
$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{NaOH(aq)} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. formate}}{HCOONa}$

46. **(d)** HI/P/,Zn/Hg/conc. HCl and NH_2–NH_2/OH–/C_2H_5ONa

Used to the reduction of  $-\overset{\overset{\displaystyle O}{\|}}{C}-$ group into –CH_2–group.

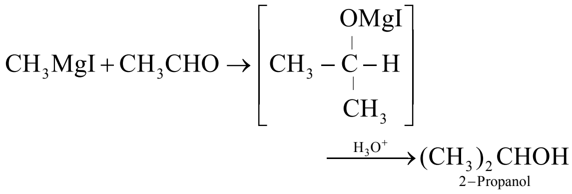
47. **(a)** Because acetone require stronger oxidising agent and hence not oxidized with Fehling solution to give brick red *ppt.*

48. **(a)** This reaction is aldol condensation



$$2CH_3CHO \xrightarrow{\text{dil NaOH}} \underset{\text{3-hydroxy butanal}}{CH_3-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_2-CHO}$$

49. **(c)**



$$CH_3MgI + CH_3CHO \rightarrow \left[\begin{array}{c} OMgI \\ | \\ CH_3-C-H \\ | \\ CH_3 \end{array}\right] \xrightarrow{H_3O^+} \underset{\text{2-Propanol}}{(CH_3)_2CHOH}$$

50. **(e)** Fehling solution⇒ Alkaline $CuSO_4 + Na-K$ tartarate

Tollen's reagent ⇒ $NH_4OH + AgNO_3$

Schiff's reagent ⇒ *P*-rosaniline hydrochloride or magneta

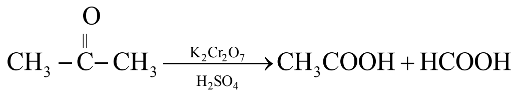
Benedict's solution ⇒ Alkaline $CuSO_4$ + Citrate ions

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

51. **(c)** $\overset{\beta}{CH_3}-\overset{\alpha}{CH_2}-CHO$ aldehydes having α-H atom can participate in aldol condensation. The H–atom attached to α carbon atom is called α -hydrogen.

52. **(c)** Cannizzaro's reaction is shown by aldehydes in which α-H atom is absent. CH_3CHO contains 3,α-H atoms thus, does not show this reaction.

53. **(a)**



$$CH_3-\overset{\displaystyle O}{\overset{||}{C}}-CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH + HCOOH$$

One carbon atom is less in the ketone group

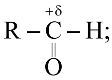
54. **(a)** $\underset{\text{(Colourless)}}{\text{Aldehyde} + \text{Schiff's reagent}} \rightarrow \text{Pink colour}$

Ketone do not give this test.

55. **(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.

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

57. **(b)**



$R-\underset{\displaystyle O}{\underset{||}{\overset{+\delta}{C}}}-H$; 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.

58. **(d)** Fehling's solution is the solution of $CuSO_4 + NaOH$ + Roschel salt (Sodium potassium tartarate). Aldehyde give red precipitate with Fehling's solution.

59. **(a)** Molecular weight of the compound
= 2 × Vapour density; = 2 × 29 = 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.

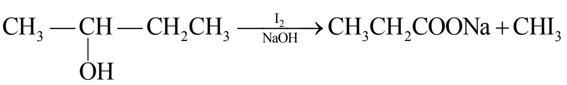
60. **(d)** Acetaldehyde have CH_3CO–group so it give positive iodoform test with I_2 and NaOH while formaldehyde does not have $–CH_3CO$ group so it will not give the positive haloform test.

NCERT Exemplar Problems

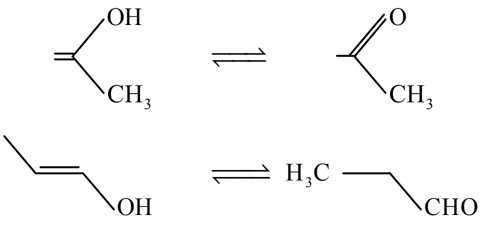
More than One Answer

61. **(a,b,d)** Deuterium behaves like H and hence trideuteroacetaldehyde also undergoes aldol condensation but benzaldehyde does not since it has no α-hydrogen.

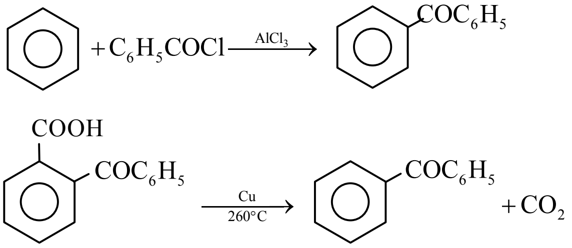
62. **(a, d)** $ICH_2COCH_2CH_3 \xrightarrow{I_2/NaOH} CHI_3 + CH_3CH_2COONa$



$$CH_3-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_2CH_3 \xrightarrow[NaOH]{I_2} CH_3CH_2COONa + CHI_3$$

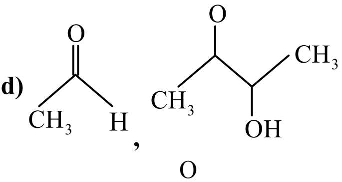


63. **(b)**

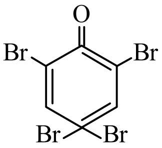


64. **(a,b)** Aldol condensation is the condensation of carbonyl having α-hydrogen.

65. **(c,d)**

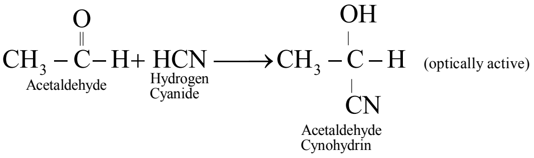


66. **(a,c)** HOBr,

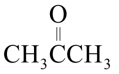


67. **(a,b,c,d)** SeO_2 oxidizes $—CH_2-\alpha$ w.r.t. keto group

68. **(a)**

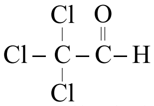


$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\displaystyle O}{\overset{||}{C}}-H} + \underset{\substack{\text{Hydrogen}\\\text{Cyanide}}}{HCN} \longrightarrow \underset{\substack{\text{Acetaldehyde}\\\text{Cynohydrin}}}{CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CN}{\underset{|}{C}}}}-H}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

69. **(b)** 

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

2 propanone

70. **(d)** 

$Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-\overset{\overset{O}{||}}{C}-H$

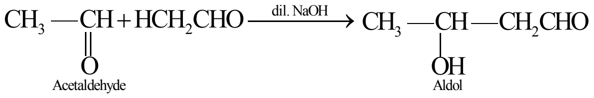
2, 2, 2, trichloroethanal

71. **(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 $HCHO > CH_3CHO > C_6H_5CHO$

Assertion and Reason

72. **(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.

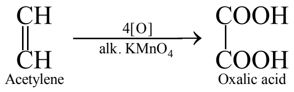
73. **(a)** Carbonyl compounds having α-hydrogen atom condenses to produce aldol in presence of alkali.



$CH_3-\underset{\underset{O}{||}}{CH}+HCH_2CHO\xrightarrow{\text{dil. NaOH}}CH_3-\underset{\underset{OH}{|}}{CH}-CH_2CHO$

Acetaldehyde Aldol

74. **(d)** Acetylene, on treatment with alkaline $KMnO_4$ is oxidised to produce oxalic acid.

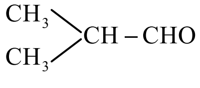


$\begin{matrix}CH\\||\\CH\end{matrix}\xrightarrow[\text{alk. }KMnO_4]{4[O]}\begin{matrix}COOH\\|\\COOH\end{matrix}$

Acetylene Oxalic acid

Therefore, both assertion and reason are false.

75. **(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.

76. **(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.

77. **(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.

78. **(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.

79. **(e)** Oximes are more acidic because, there is a delocalization 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^-)

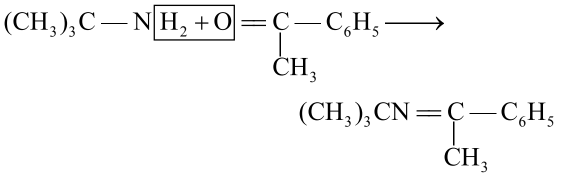
80. **(b)** HCHO cannot be prepared by Rosenmund's reduction because formyl chloride is unstable at room temperature.

81. **(e)** HCHO reacts with NH_3 to form urotropine

$6HCHO+4NH_3\longrightarrow(CH_2)_6N_4+6H_2O$

Comprehension Based

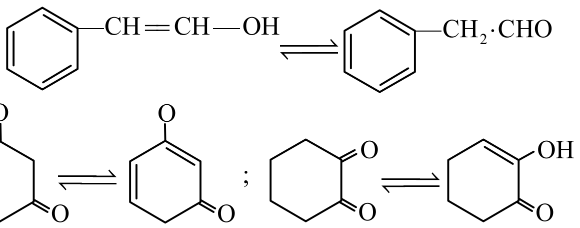
82. **(a)** Rest all do not have α- H-atom.

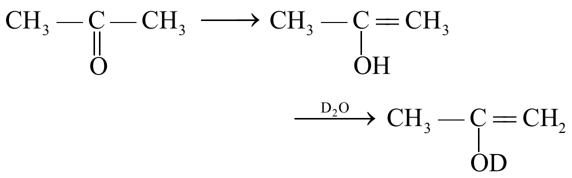
83. **(c)** 

$(CH_3)_3C-N\boxed{H_2+O}=\underset{\underset{CH_3}{|}}{C}-C_6H_5\longrightarrow$

$(CH_3)_3CN=\underset{\underset{CH_3}{|}}{C}-C_6H_5$

84. **(a)** C_6H_5 give rise to –I effect and thus nucleophilic addition is favoured.

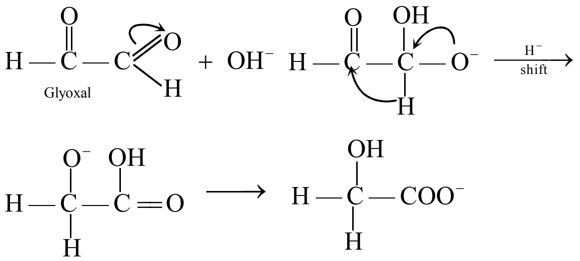
85. **(b)** 

86. **(a)** 

$CH_3-\underset{\underset{O}{||}}{C}-CH_3\longrightarrow CH_3-\underset{\underset{OH}{|}}{C}=CH_3$

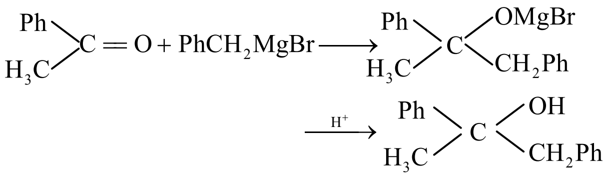
$\xrightarrow{D_2O}CH_3-\underset{\underset{OD}{|}}{C}=CH_2$

87. **(d)** Rest all show intermolecular Cannizzaro reaction.

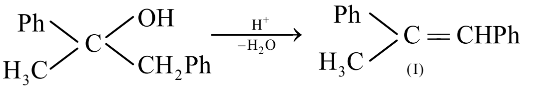


88. **(d)** It is Cannizzaro reaction.

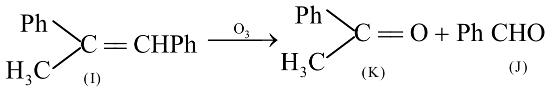
89. **(b)** A tertiary alcohol (H) which can undergo acid catalysed dehydration will be formed when the ketone $PhCOCH_3$ reacts with $PhCH_2MgBr$. The reaction is



90. **(a)** The acid catalysed dehydration reaction is



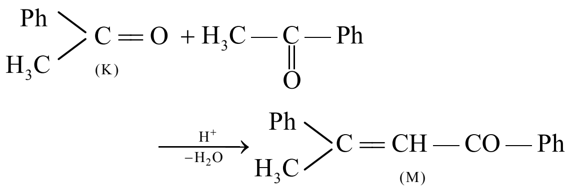
91. **(d)**



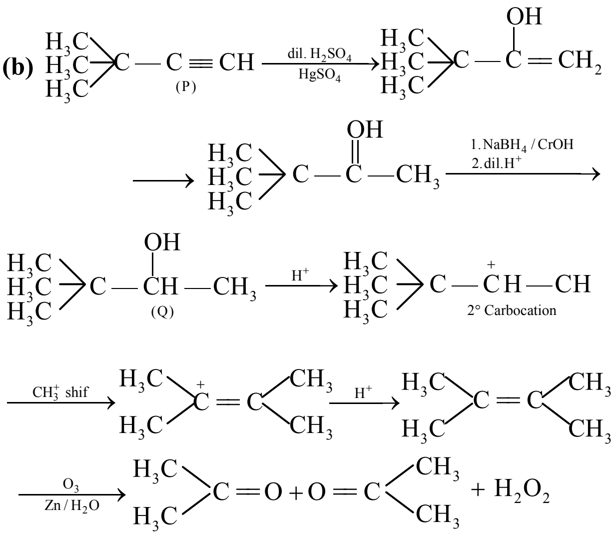
The compound J is PhCHO. It undergoes Cannizzaro reaction.

$$2PhCHO \xrightarrow[H_2O]{KOH} PhCH_2OH + \underset{(L)}{PhCOO^-K^+}$$

The compound K undergoes aldol condensation.



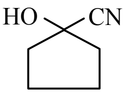
92. **(b)**



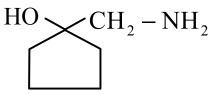
Match the Column

93. **(d)** A→2,3,4; B→1,4; C→2,4; D→4

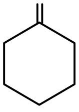
(a)



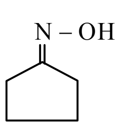
(b)

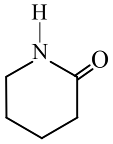


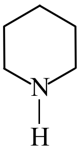
(c)



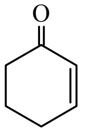
94. **(b)** A→3,4; B→2,3,4; C→1,2,4; D→1,4



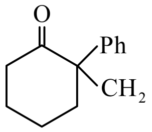




95. **(a)** A→1,2,4; B→1,2,3,4; C→1; D→2,3,4

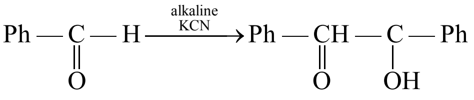


96. **(b)** A→1,2,4; B→1; C→1,2,4; D→1,2,4



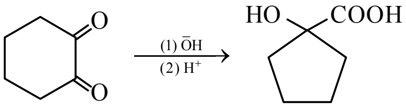
(Pinacol-Pinacolone rerrangement)

97. **(d)** A→1,2,4; B→3,4; C→2; D→3,4

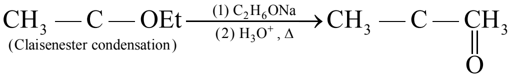


$$Ph—\underset{\underset{O}{\|}}{C}—H \xrightarrow[KCN]{\text{alkaline}} Ph—\underset{\underset{O}{\|}}{CH}—\underset{\underset{OH}{|}}{C}—Ph$$

(Benzoincondensation)



(Benzil benzylic acid rearrangement)



$$CH_3—C—OEt \xrightarrow[(2)\ H_3O^+,\ \Delta]{(1)\ C_2H_6ONa} CH_3—\underset{\underset{O}{\|}}{C}—CH_3$$

(Claisenester condensation)

$$Ph—CH=O \xrightarrow[(2)\ H^+]{(1)\ KOH} Ph—COOH + Ph—CH_2—OH$$

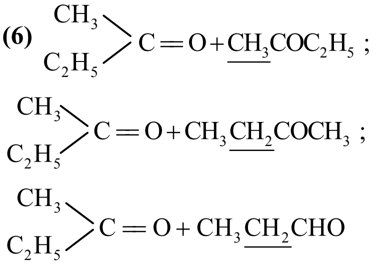
(Cannizzaro reaction)

Integer

98. **(1)**

99. **(5)**

100. **(6)**



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>C=O+\underline{CH_3}COC_2H_5\ ;$$

$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>C=O+CH_3\underline{CH_2}COCH_3\ ;$$

$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>C=O+CH_3\underline{CH_2}CHO$$

$CH_3CH_2CH=O\ +\ CH_3\underline{CH_2}CHO$

$CH_3CH_2CH=O\ +\underline{CH_3}COC_2H_5\ ;$

$CH_3CH_2CH=O\ +CH_3\underline{CH_2}COCH_3$

* * *