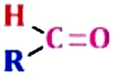
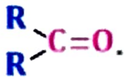
CARBONYL COMPOUND

Points to be covered in this topic

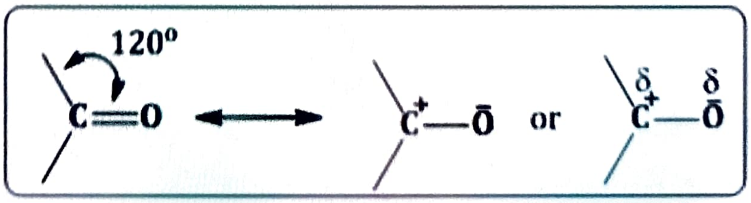
- 1. INTRODUCTION
- 2. NATURE OF CARBONYL GROUP
- 3. NOMENCLATURE
- 4. METHOD OF PREPARATION
- 5. CHEMICAL PROPERTIES

INTRODUCTION

- Carbonyl compounds are of two types, **aldehydes and ketones.**
- Both have a **carbon-oxygen double bond** often called as carbonyl group.
- Aldehydes and Ketones are characterized by the presence of **Carbonyl group >C = O** in their molecules
- Aldehydes contain group  $\overset{H}{\underset{R}{}}>C=O$ and ketones the  $\overset{R}{\underset{R}{}}>C=O$.

NATURE OF CARBONYL GROUP

- The **carbon and oxygen** of the carbonyl group are **sp^2-hybridised** and the carbonyl double bond contains **one σ-bond and one π-bond.**
- The carbon-oxygen double bond is different than carbon-carbon double bond.
- Since, **oxygen is more electronegative**, the electrons of the bond are attracted towards oxygen.



❑ NOMENCLATURE OF ALDEHYDE

Common system: The suffix **"-ic acid"** is replaced by the suffix **"-aldehyde"**
IUPAC system: The suffix **"-e"** of alkane is replaced by the suffix **"-al"**.

Compound	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
CH_3-CH=CH-CHO	Crotonldehyde	But-2-enal

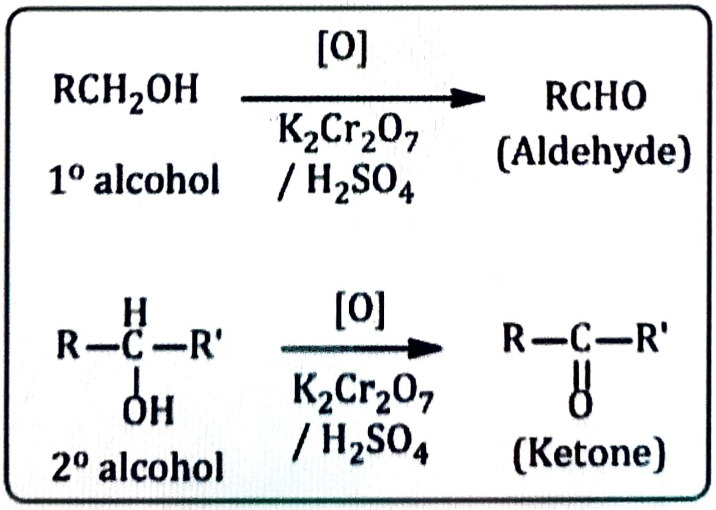
❑ NOMENCLATURE OF KETONE

Common system : **Symmetrical ketones** are named as **dialkyl ketone** and name of **unsymmetrical ketone** is obtained by naming the **alkyl groups** alphabetically and adding the **third word ketone.**
IUPAC system : The **suffix "-e"** of corresponding alkane is **replaced by "-one"**

Compound	Common name	IUPAC name
CH_3COCH_3	Dimethyl ketone (Acetone)	Propanone
$CH_3COC_2H_5$	Ethyl methyl ketone	Butanone

❑ METHOD OF PREPARATION

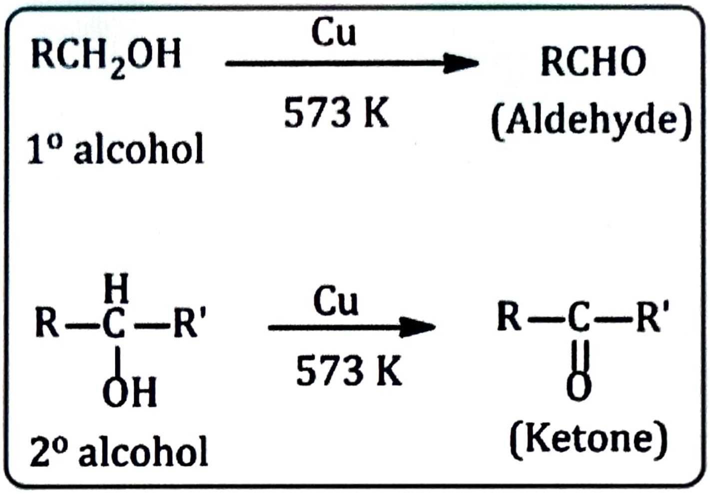
1. By oxidation of alcohols: Aldehydes and ketones are generally prepared by **oxidation of primary and secondary alcohols**, respectively.



$$\underset{1^\circ \text{ alcohol}}{RCH_2OH} \xrightarrow[K_2Cr_2O_7 / H_2SO_4]{[O]} \underset{\text{(Aldehyde)}}{RCHO}$$

$$\underset{2^\circ \text{ alcohol}}{R-\overset{H}{\underset{OH}{C}}-R'} \xrightarrow[K_2Cr_2O_7 / H_2SO_4]{[O]} \underset{\text{(Ketone)}}{R-\underset{O}{\overset{}{\underset{\|}{C}}}-R'}$$

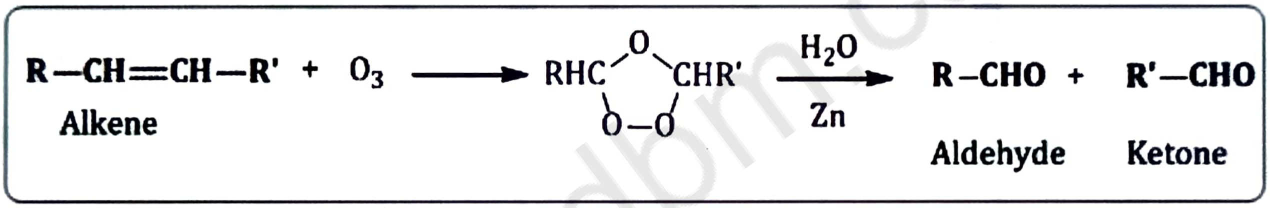
2. By dehydrogenation of alcohols: In this method, **alcohol vapours** are passed over heavy metal catalysts **(Ag or Cu).**



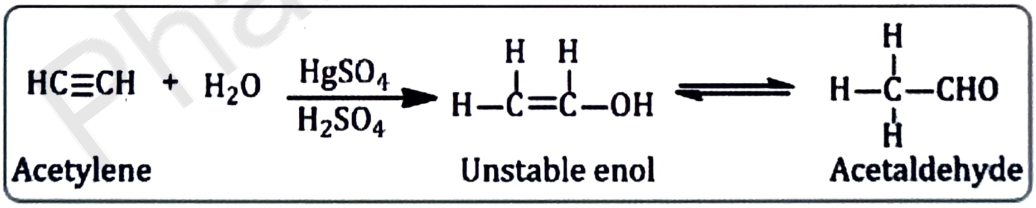
$$\underset{\text{1° alcohol}}{RCH_2OH} \xrightarrow[573\ K]{Cu} \underset{\text{(Aldehyde)}}{RCHO}$$

$$\underset{\text{2° alcohol}}{R{-}\overset{H}{\underset{OH}{C}}{-}R'} \xrightarrow[573\ K]{Cu} \underset{\text{(Ketone)}}{R{-}\underset{O}{\overset{}{\underset{\|}{C}}}{-}R'}$$

3. Ozonolysis of alkenes: This reaction is used to determine the **position of double bond in alkene**



4. Hydration of alkyne: Acetylene on hydration **gives acetaldehyde** and other **alkynes on hydration give ketones.**

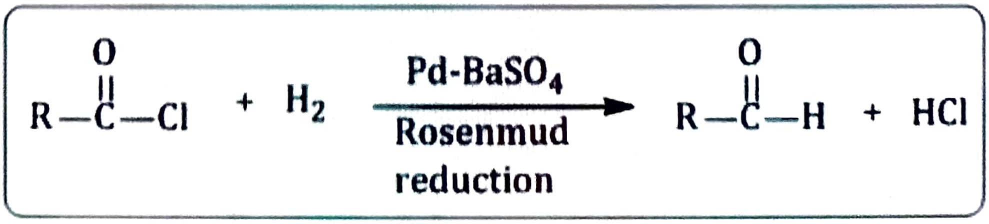


$$\underset{\text{Acetylene}}{HC{\equiv}CH} + H_2O \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{Unstable enol}}{H{-}\overset{H}{C}{=}\overset{H}{C}{-}OH} \rightleftharpoons \underset{\text{Acetaldehyde}}{H{-}\overset{H}{\underset{H}{C}}{-}CHO}$$

❑ METHOD OF PREPARATION FOR ALDEHYDE ONLY

5. From acyl chloride (Rosenmund's reduction)

- **Acyl chlorides** are selectively reduced into **aldehydes.**
- **Formaldehyde** can not be prepared by this method.



$$R{-}\overset{O}{\overset{\|}{C}}{-}Cl + H_2 \xrightarrow[\text{Rosenmud reduction}]{Pd\text{-}BaSO_4} R{-}\overset{O}{\overset{\|}{C}}{-}H + HCl$$

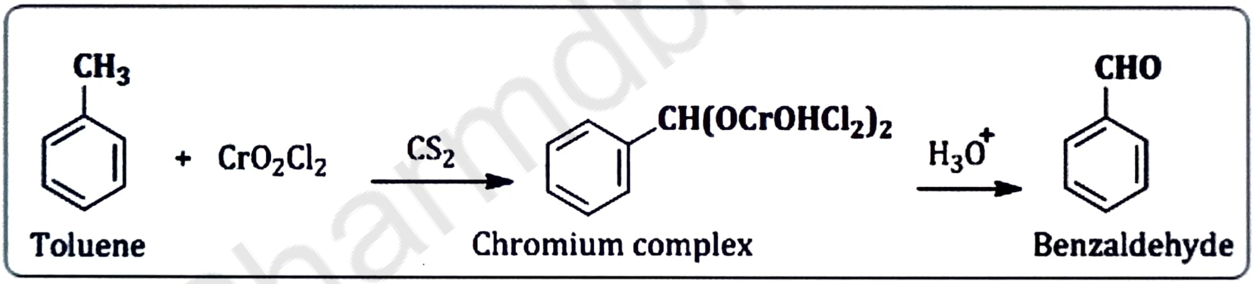
6. Stephen's reduction: Alkyl cynides or alkyl nitriles are reduced with stannous chloride and hydrochloride acid in presence of ether to yield iminochloride which on futher hydrolysis yields aldehyde

$$\underset{\text{Alkyl nitrile}}{R-C\equiv N} \xrightarrow[HCl]{SnCl_2} \underset{\text{Imino-chloride}}{R-CH=NH.HCl} \xrightarrow{H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_4Cl$$

Alternatively, **nitriles** are selectively reduced by **di isobutyl aluminium hydride, [DiBAL-H]** to imines which on **hydrolysis give aldehydes.**

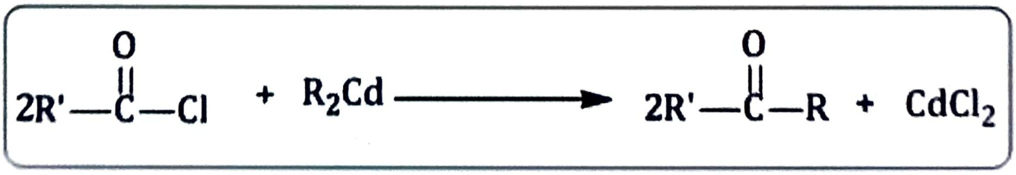
$$RCN \xrightarrow[H_2O]{AlH(iBu)_2} RCHO$$

7. Etard reaction: In Etard reaction, **chromyl chloride oxidises methyl group to a chromium complex,** which on hydrolysis gives corresponding benzaldehyde.



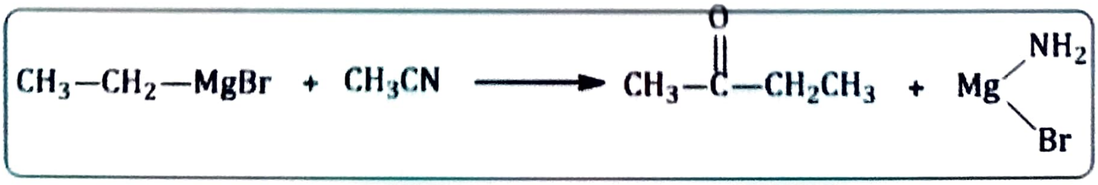
❑ METHOD OF PREPARATION FOR KETONE ONLY

8. Acyl chloride



$$2R'-\overset{O}{\overset{\|}{C}}-Cl + R_2Cd \longrightarrow 2R'-\overset{O}{\overset{\|}{C}}-R + CdCl_2$$

9. From nitriles



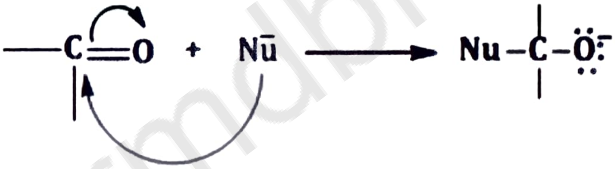
$$CH_3-CH_2-MgBr + CH_3CN \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3 + Mg\begin{smallmatrix} NH_2 \\ Br \end{smallmatrix}$$

❑ CHEMICAL PROPERTIES

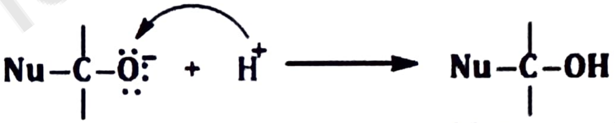
General mechanism of Nucleophilic addition reaction

- Aldehydes and ketones are highly reactive compounds.
- Both aldehydes and ketones undergo nucleophilic addition reactions.
- Reactive nature of aldehydes and ketones is because of the **presence of a polar carbonyl group.**
- As the oxygen atom is **more electronegative**, therefore, it pulls the electron around itself acquiring **partial negative charge (δ–)** whereas a partial positive charge (δ+) is developed on the carbon atom.
- The positively charged **carbon atom of carbonyl group** is then readily attacked by the nucleophilic species for initiation of the reaction.
- This leads to the **formation of an intermediate anion** which further undergoes the attack of (H^+) ion or other positively charged species to form the **final product.**

1. Addition of the nucleophile



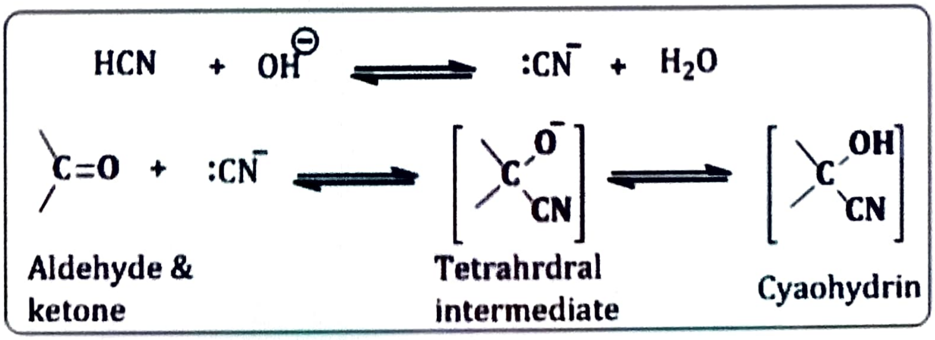
2. Protonation



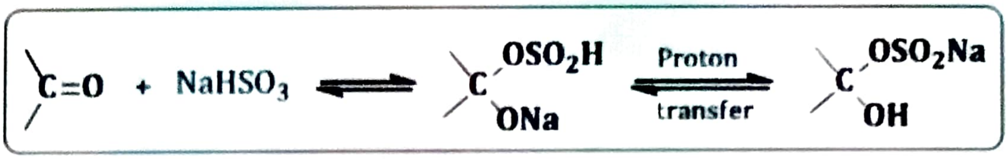
Addition product

Addition Reactions

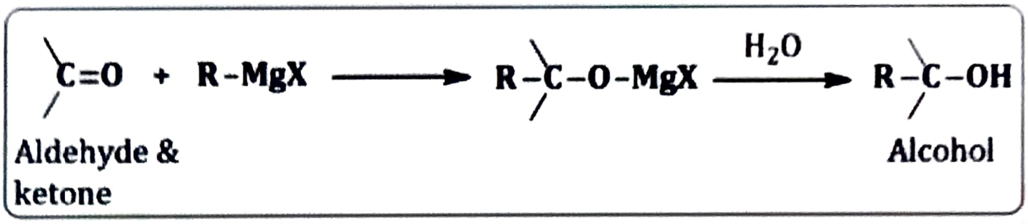
1. Addition of hydrogen cyanide (HCN)



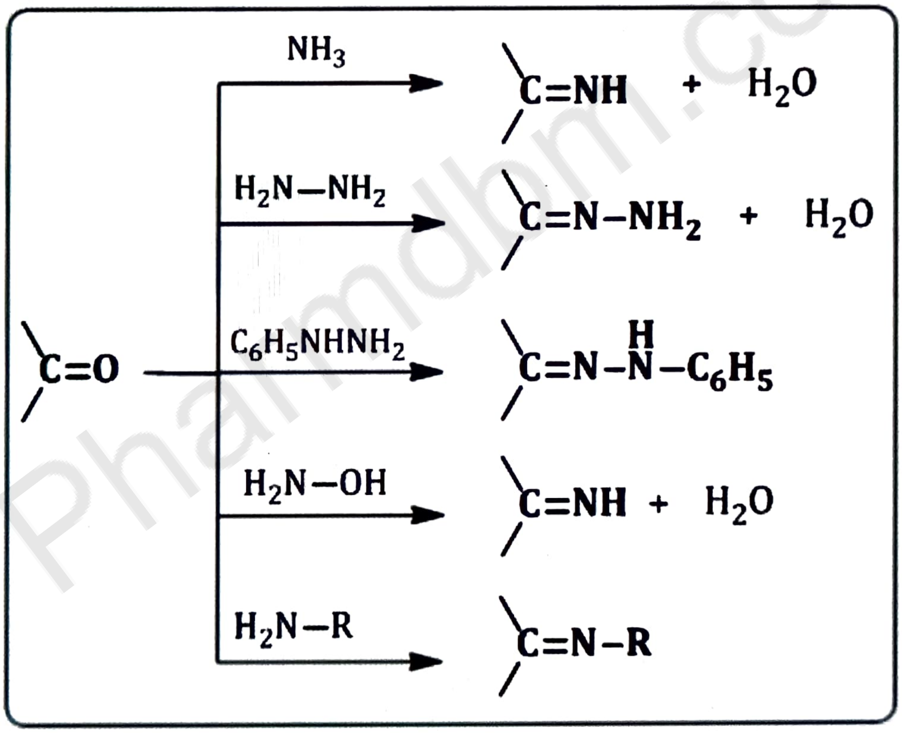
2. Addition of sodium hydrogen sulphite ($NaHSO_3$)



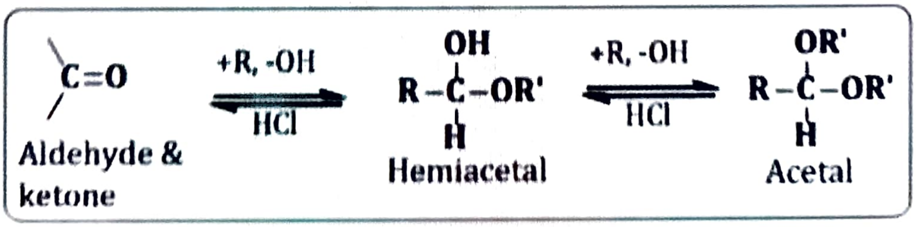
3. Addition of Grignard reagent



4. Addition of Ammonia and its derivatives



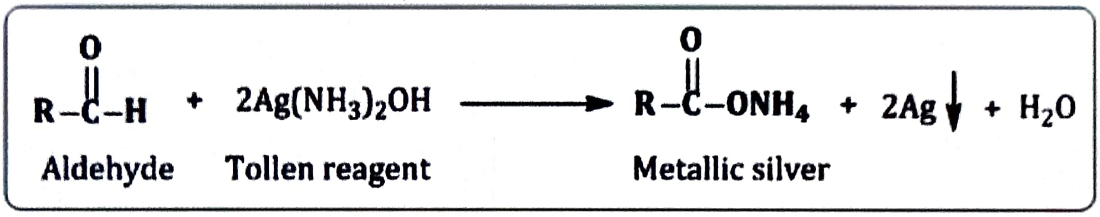
5. Addition of Alcohol



Oxidation reaction of Aldehyde: Aldehydes are easily **oxidised to carboxylic acids** on treatment with **common oxidising agents** or mild oxidizing agent like **Tollens' reagent or Fehling's solution.**

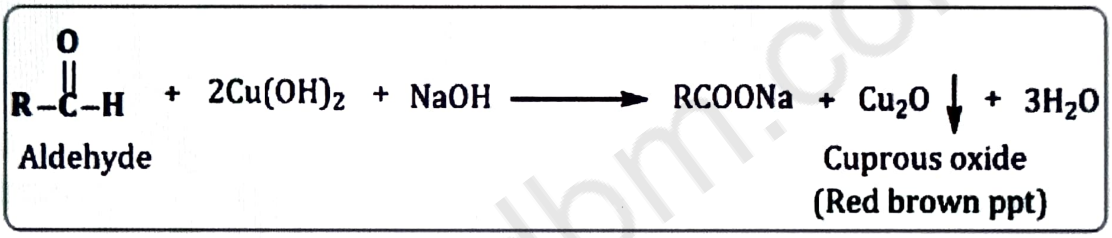
$$\underset{\text{Aldehyde}}{R{-}CHO} + [O] \longrightarrow \underset{\text{Carboxylic acid}}{R{-}COOH}$$

Reaction with tollen's reagent



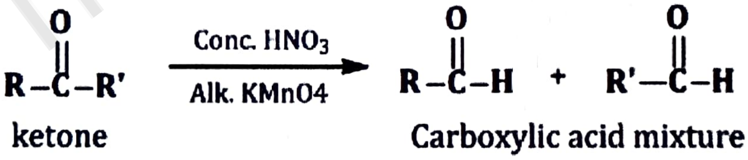
$$\underset{\text{Aldehyde}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H} + \underset{\text{Tollen reagent}}{2Ag(NH_3)_2OH} \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}ONH_4 + \underset{\text{Metallic silver}}{2Ag\downarrow} + H_2O$$

Reaction with Fehling's reagent



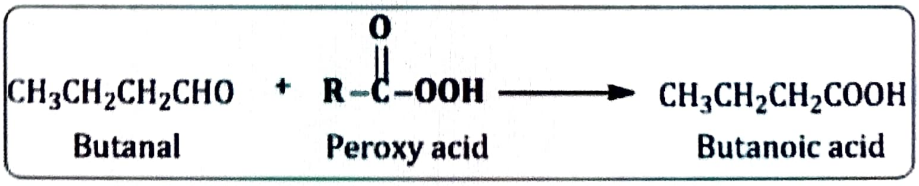
$$\underset{\text{Aldehyde}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H} + 2Cu(OH)_2 + NaOH \longrightarrow RCOONa + \underset{\substack{\text{Cuprous oxide}\\ \text{(Red brown ppt)}}}{Cu_2O\downarrow} + 3H_2O$$

Oxidation reaction of Ketone: Ketones are **oxidized** by strong oxidizing agents such as hot concentrated **HNO_3 or alkali $KMnO_4$** to give **carboxylic acid** with **fewer carbon atom less than** that of the **original ketone.**



$$\underset{\text{ketone}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'} \xrightarrow[\text{Alk. KMnO4}]{\text{Conc. }HNO_3} \underbrace{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H}_{\text{Carboxylic acid mixture}}$$

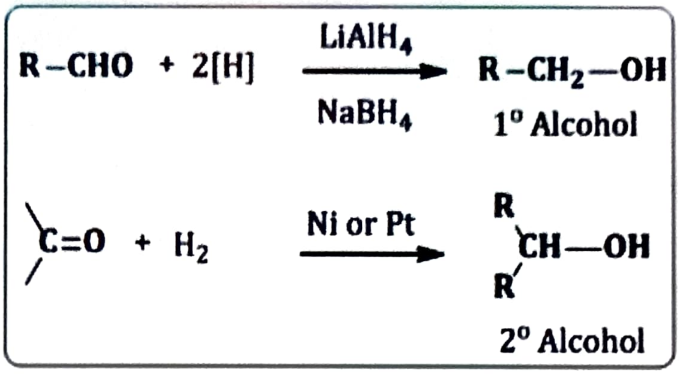
Oxidation by peroxy acid (Bayer–Villiger oxidation): Aldehyde give carboxylic acid and **ketones give esters**. A peroxy acid contains **one more oxygen atom that of carboxylic acid** and this atom is inserted **between the carbonyl carbon and the hydrogen of an aldehyde or the R group of a ketone**



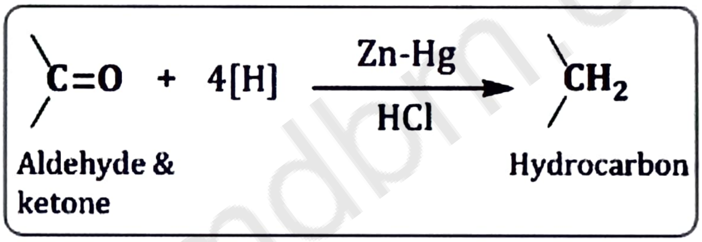
$$\underset{\text{Butanal}}{CH_3CH_2CH_2CHO} + \underset{\text{Peroxy acid}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OOH} \longrightarrow \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

Reduction reaction

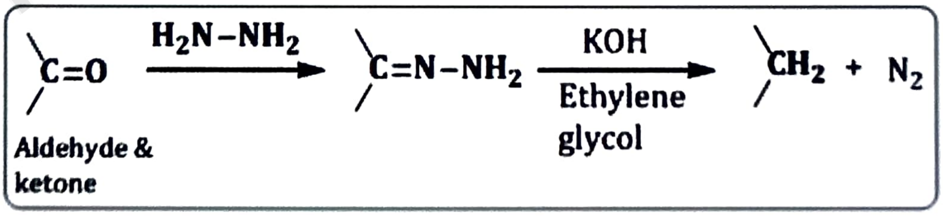
1. Reduction: Aldehyde and ketone are reduced to primary and secondary alcohol respectively by $LiAlH_4$ or $NaBH_4$ or H_2 in presence of Ni and Pt



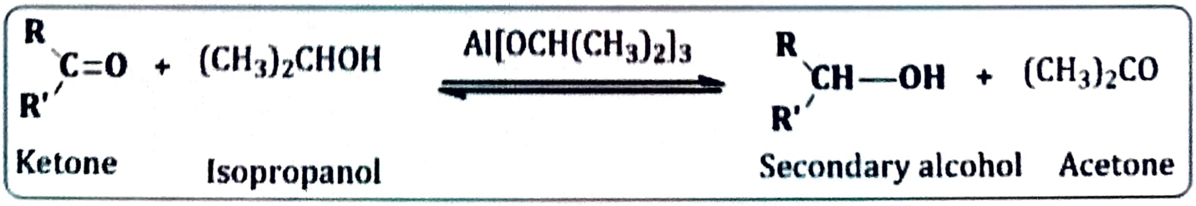
2. Clemmenson reduction: Clemmensen reduction is a reaction that is used to reduce aldehydes or ketones to alkanes using hydrochloric acid and zinc amalgam.



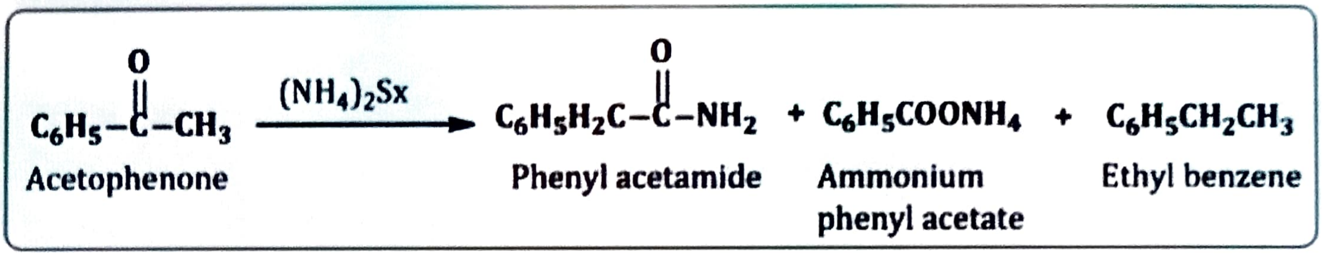
3. Wolff–Kishner reduction: Clemmensen reduction is a reaction that is used to reduce aldehydes or ketones to alkanes using hydrochloric acid and zinc amalgam.



4. Meerwein pondorf – Varley reduction: Aldehyde and ketone are reduced to the corresponding alcohol by treating with aluminum isopropoxide in isopropoxide solution



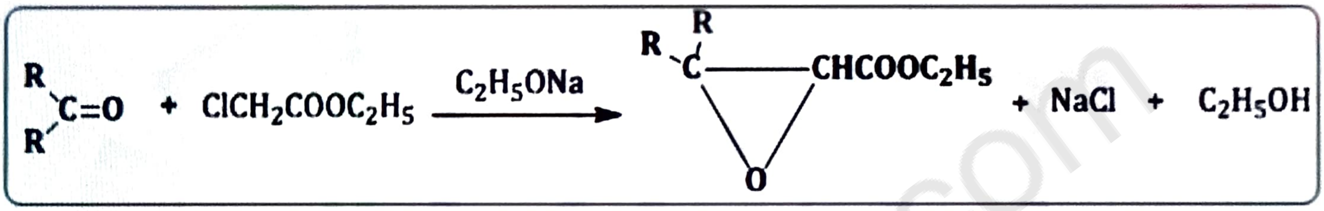
5. Willgerodt reaction: The conversion of aryl ketones into an amide by using yellow ammonium polysulphide is called willegerodt reaction.



$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{(NH_4)_2Sx} C_6H_5H_2C-\overset{O}{\overset{\|}{C}}-NH_2 + C_6H_5COONH_4 + C_6H_5CH_2CH_3$$

Acetophenone — Phenyl acetamide — Ammonium phenyl acetate — Ethyl benzene

6. Darzein condensation: Condensation of an aldehyde or a ketone with an alpha halogen ester in the presence of sodium ethoxide or sodamide to yield an α, β-epoxy ester



Condensation reaction

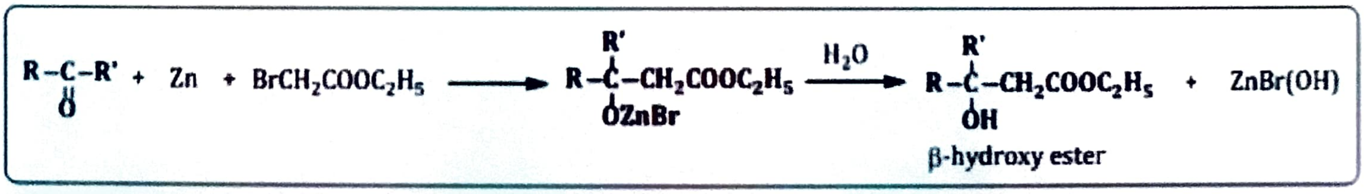
Cannizaro reaction: Aldehyde which **lack of α-hydrogen atom** gives this reaction, Aldehyde **heated with concentrated NaOH** undergoes self redox reaction **to form primary alcohol** and a salt of an acid.

$$\underset{\text{Formaldehyde}}{2\,HCHO} + NaOH \longrightarrow \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Sodium formate}}{HCOONa}$$

Cross cannizaro reaction: Cannizaro reaction occurring between two different aldehyde is as crossed cannizaro reaction.

$$\underset{\text{Formaldehyde}}{HCHO} + \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{NaOH} HCOONa + C_6H_5CH_2OH$$

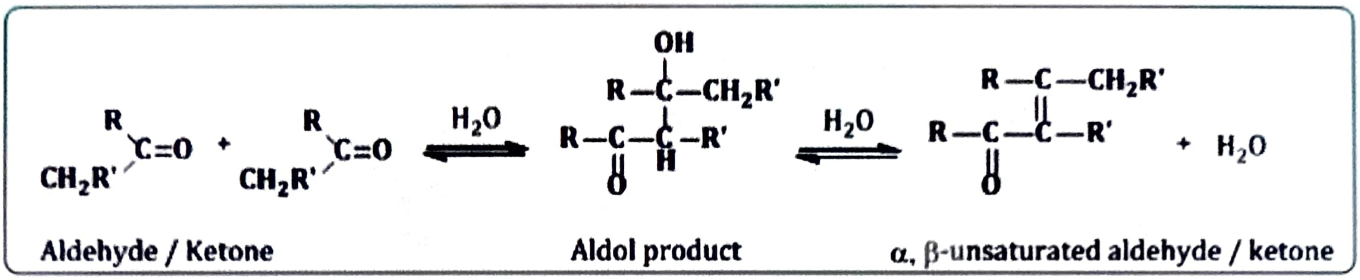
Reformatsky reaction: It involves the reaction of aldehyde and ketones **with α–bromoester** in the presence of **zinc metal** to give **β-hydroxyl ester** after hydrolysis



$$R-\underset{O}{\underset{\|}{C}}-R' + Zn + BrCH_2COOC_2H_5 \longrightarrow R-\overset{R'}{\underset{OZnBr}{C}}-CH_2COOC_2H_5 \xrightarrow{H_2O} R-\overset{R'}{\underset{OH}{C}}-CH_2COOC_2H_5 + ZnBr(OH)$$

β-hydroxy ester

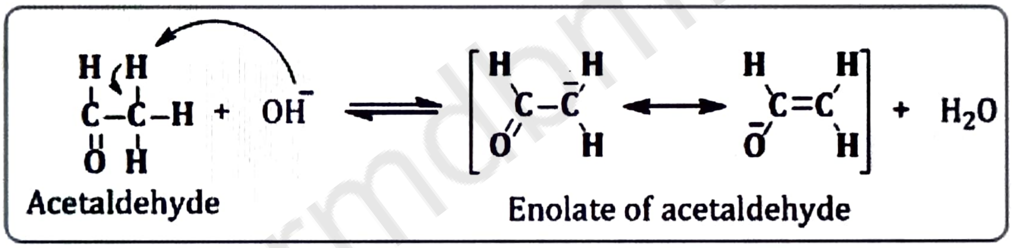
Aldol condensation:. Aldehydes possessing **α-hydrogen atoms** undergo this reaction in the **presence of base** to yield the product known as aldols. The product obtained **is β-hydroxy aldehyde or ketone** as it contains both **aldehyde/ketone and alcohol.**



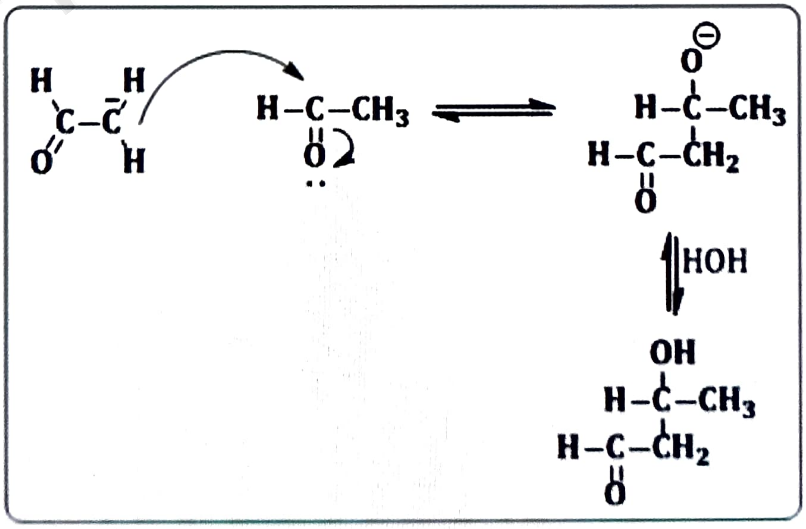
Base catalyzed aldol condensation

Two molecule of acetaldehyde condense in the presence of dilute alkali like potassium carbonate to give a syrupy liquid aldol

Step – 1: Formation of enolate carbanion form one molecule of acetaldehyde



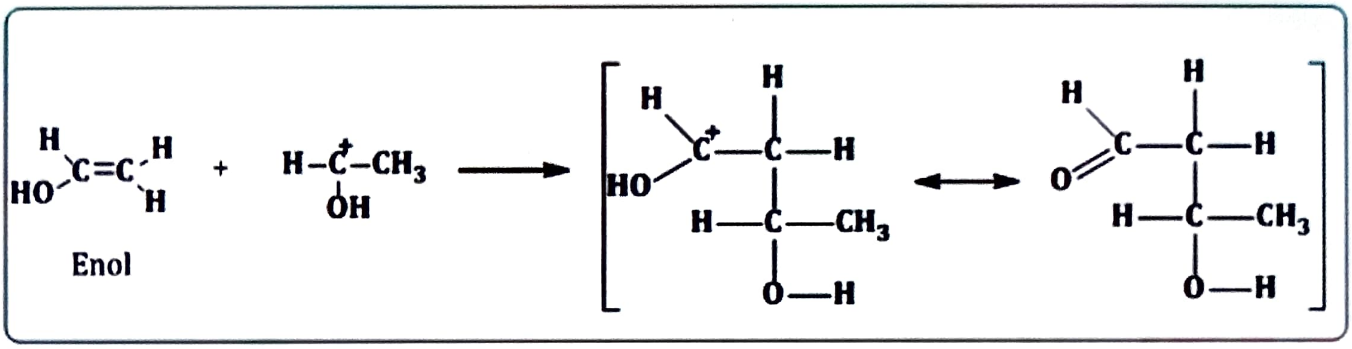
Step – 2: Attack of nucleophile to carbonyl carbon of the 2nd molecule of acetaldehyde



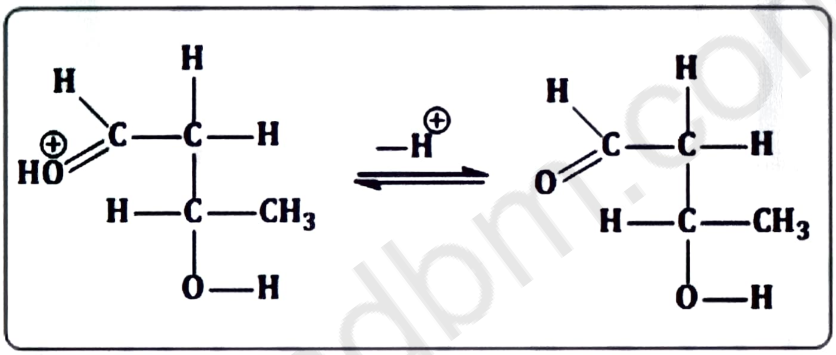
Acid catalyzed aldol condensation

Enol act as a weak nucleophile and attacks the carbonyl carbon

Step – 1: Condensation of enol to the protonated carbonyl

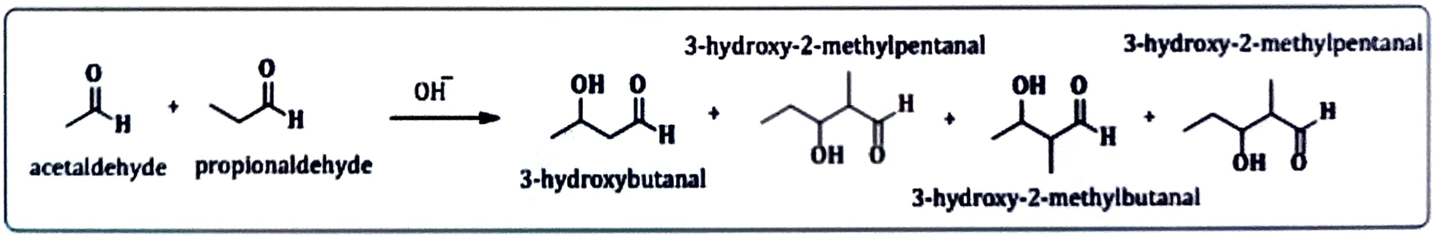


Step – 2: Deprotonation

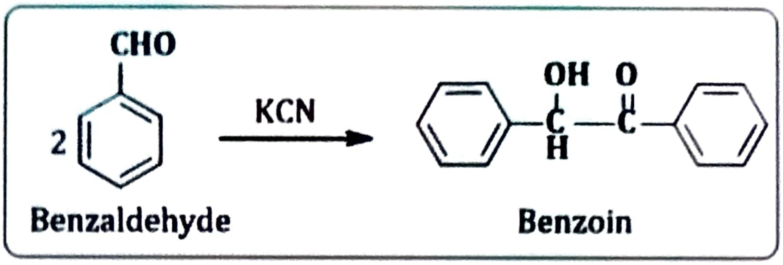


Cross aldol condensation:. When condensation is between **two different carbonyl compounds,** it is called cross aldol condensation. If both contain the **atoms of α-hydrogen**, then it will give out a **mixture of four products.** It is because both can **form carbanions** and can also act as carbanion acceptors.

If one of the aldehydes **does not have alpha hydrogen**, it can only act as a carbanion acceptor. In this case, **only two products are formed.**



Benzoin condensation:. When two moles of benzaldehyde are condensed in the presence of potassium cyanide then they gives benzoin



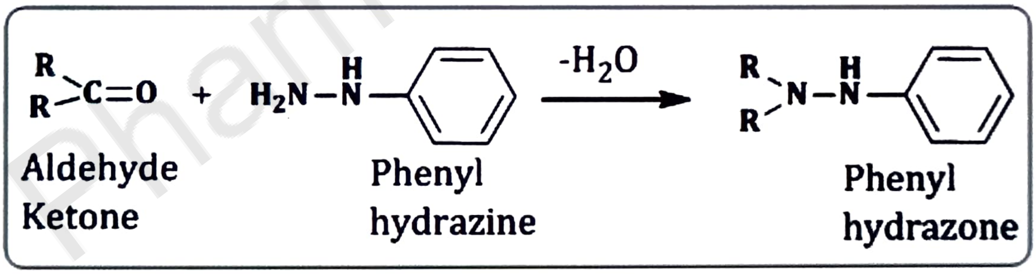
Perkin condensation:. The condensation between **aromatic aldehydes and acid anhydride** having at **least two α-hydrogen** in the presence of weak base like **sodium or potassium acetate** with formation of α, β unsaturated acid is known as perkin reaction

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH{=}CHCOOH + CH_3COOH$$

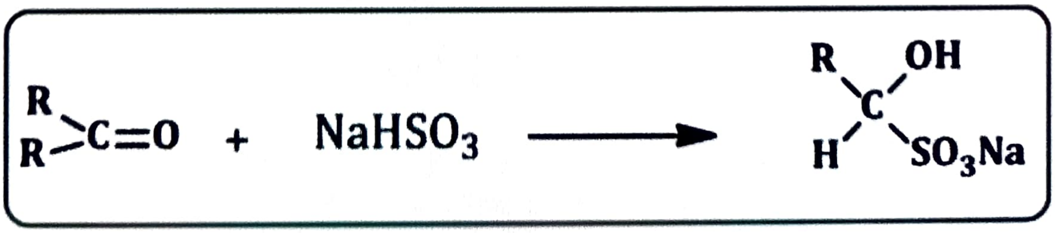
Benzaldehyde; Acetic anhydride; Cinamic acid; Acetic acid

❑ QUALITATIVE TEST

2,4-dinitrophenylhydrazine test: Aldehydes and ketones react with 2,4-dinitrophenylhydrazine to give an orange-yellow precipitate.



Sodium Bisulphite ($NaHSO_3$)Test: Aldehydes and ketones combine with sodium bisulphite to for well-crystallized water-soluble products known as "aldehyde bisulphite" and "ketone bisulphite".



DISTINGUISHING TESTS BETWEEN ALDEHYDES AND KETONE

1. Schiff test: Schiff's reagent is prepared by **passing sulphur dioxide** into a solution of the **dye fuchsin**. The solution **becomes colourless** due to the formation of an additional product. Aldehydes abstract sulphurous acid from Schiff's reagent and **restore the pink colour.** The colouration is due to the **formation of complex compound**. Ketones, in general, do not respond to this reaction.

2. Fehling test: Fehling's solution is a complex compound of Cu^{2+}. When the **aldehyde compound** is treated with Fehling's solution **Cu^{2+} is reduced** to **Cu^{+} and the aldehyde** is **reduced to acids**. During the reaction, **a red precipitate** is formed.

3. Tollen's Test (Silver Mirror Test): Aldehydes react with Tollens reagent **giving a grey-black precipitate** or a silver mirror. Aldehydes are **oxidized to the corresponding acids,** and silver in Tollens reagent is reduced from +1 oxidation state to its elemental form. Generally, ketones do not respond to this test.

4. Test with Chromic Acid: A **green to blue precipitate** is given by aldehydes reacting with chromic acid. With chromic acid, ketones do not react

5. Sodium Nitroprusside Test: Ketones only give this test and not aldehyde. An anion is formed **when ketone reacts with an alkali,** further this anion **reacts with sodium nitroprusside** to form **a coloured complex**. **The red colour shows the presence of ketones.**

6. Iodoform Test: Methyl ketones can be distinguished from other ketones by their reaction with iodine in basic solution to yield iodoform CH_3I as a yellow coloured precipitate

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3I_2 + 4NaOH \longrightarrow 3NaI + RCOO^{\ominus}\,Na^{\oplus} + CH_3I$$

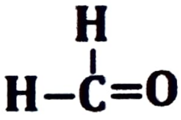
ALDEHYDE & KETONE

Points to be covered in this topic

- FORMALDEHYDE
- PARALDEHYDE
- ACETONE
- CHLORAL HYDRATE
- HEXAMINE
- BENZALDEHYDE
- VANILIN
- CINNAMALDEHYDE

❑ FORMALDEHYDE

STRUCTURE



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

USES:

1. As a general anaesthetics
2. Used as germicide, fungicides for plant and vegetable
3. As a local anaesthetics
4. Urinary antiseptic
5. Preservation of biological specimens
6. Manufacturing of synthetic plastics

❑ PARALDEHYDE

STRUCTURE

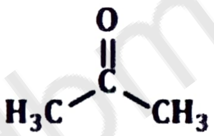
$3CH_3CHO$

USES:

1. Manufacturing of resin
2. Used as solvent and preservatives
3. Used as CNS depressant, Anticonvulsant, hypnotic and sedative
4. As an expectorant

❑ ACETONE

STRUCTURE

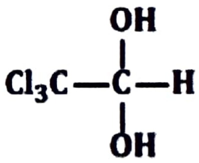


USES:

1. Solvent for acetylene, Cellulose derivatives, Varnish, lacquers
2. Production of chloroform and diacetone alcohol
3. Manufacturing of thermosetting plastic

❑ CHLORAL HYDRATES

STRUCTURE



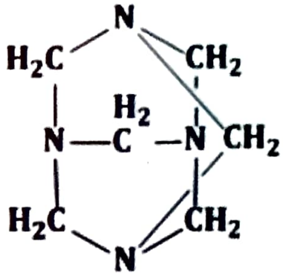
$$Cl_3C-\underset{OH}{\overset{OH}{C}}-H$$

USES:

1. For preparation of DDT
2. As a hypnotic
3. As a insecticide

❑ HEXAMINE

STRUCTURE

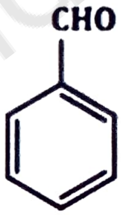


USES:

1. Used as urinary antiseptic
2. Absorbent for absorbing poisonous gas
3. As a disinfectant and antibacterial agent
4. Explosive
5. Used in vulcanizing rubber and as anticorrosive agent.

❑ BENZALDEHYDE

STRUCTURE

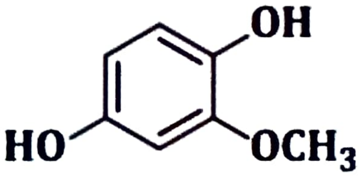


USES:

1. Benzaldehyde is used as flavouring agent
2. Used as production of cinnamic acid
3. Manufacturing of malachite green

❑ VANILINE

STRUCTURE

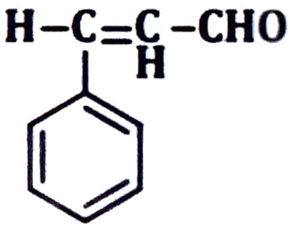


USES:

1. Vaniline is used as flavouring agent
2. Used as fragrance industry, in perfume
3. Used as flavour industry

❑ CINNAMALDEHYDE

STRUCTURE



USES:

1. Used as flavouring agent
2. Cinnamaldehyde used as fungicide
3. Corrosion inhibitor for steel and other ferrous alloy