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Name of Unit	Carbonyl Compounds (Aldehydes, Ketones)
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Learning Outcome of Module 04

LO	Learning Outcome	Course Outcome Code
LO1	To gain knowledge about carbonyl compounds.	BP202.3
LO2	To understand different nomenclature system.	BP202.1
LO3	To gain knowledge of Synthesis methods of carbonyl compounds and its properties.	BP202.4
LO4	To get the knowledge about structure and medicinal uses of some organic compounds.	BP202.4, BP202.1
LO5	To get the knowledge about some important naming reactions.	BP202.2

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INTRODUCTION OF CARBONYL COMPOUNDS

Aldehyde are the compounds with have general formula $C_nH2_{n+1}CHO$ or C_nH2_nO and ketones are compounds with have general formula Cn H₂nO. It may be aliphatic or aromatic group. Aldehyde and Ketone, both have C=O (carbonyl group). These are also called **carbonyl compounds**. Example,



Structure of Carbonyl Compound:- The carbonyl group is composed of one sigma and one π bond.



Both C and O are sp² hybridized. The α bond is formed by the overlap of an sp² orbital Of carbon and an sp-orbital of oxygen. The π bond is formed by the overlap of unhybridized p orbital of two atoms. Two unshared pair of electrons occupies the sp² hybrid orbitals of oxygen. Because the carbonyl carbon is sp² hybridized, three atoms attached to it lie in same plane. The bond angle is 120°. The electrons in π bond are not shared. They are pulled more toward electronegative oxygen atom. As a result the bond is polarized with oxygen atom having slight negative chargeand having slight positive charge.



Nomenclature of Aldehyde:- There are two system for naming aldehydes:-

1.Common Name System:- Common name for aldehyde is derived from name of corresponding carboxylic acid. The ending -ic acid of acid name is replaced with aldehyde. Example,



While naming substituted aldehyde, the position of substituent on parent chain is indicated by Greek letter α , β etc. The α -carbon, next along chain is β and so on.



In this system ,names for aldehyde are obtained by replacing the ending letter -'e' of



corresponding alkane with –'al' .since the aldehyde functional gp. Is always at the end of chain, there is no need to specify is position. But when other substituents are present, the carbonyl C is assigned as no.1.



Nomenclature of Ketone:- There are two system for naming of ketones:-

(1) **Common name system:-** Having of ketone is done by simply naming two alkyl groups attached to carbonyl group and adding the word ketone .The simplest ketone i.e. dimethyl ketone is also calledacetone.



(2) IUPAC System:- IUPAC NAMING is done by replacing the ending -'e' of corresponding alkane carbon '-one'. The longest chain is numbered to give carbonyl carbon the lowest possible no. The position of carbonyl group and the substituent is indicated carbon no.



Isomerism of Aldehyde and Ketone:-

Aldehyde and Ketone show

1.Chain Isomerism:-Higher aldehyde (containing 4or more carbon atoms) and ketone (containing 5 or more carbon) show chain isomerism in which isomer differ in chain of carbon





Butanal



Pentan-2-one







2.Position Isomerism :- Higher ketone and aromatic aldehydes exhibit position isomerism in which the isomer differ in the position of carbonyl group.



Aliphatic aldehyde do not show position isomerism .Because -CHO group is always present at the endof carbon chain .

3.Functional Isomerism :- Aliphatic aldehyde and ketone are functional isomers of each other. Because they have same molecular formulae but different functional groups .example :-



Methods of Preparation of Aldehyde:-

1.Oxidation of Aldehydes:-- Primary alcohol on oxidation gives aldehydes.

$$\begin{array}{cccc} R & & (O) \\ R & - CH_2OH & & (O) \\ p\text{-alcohol} & & K_2Cr_2O_2/H_2SO_4 & Aldehyde \\ (O) \\ e.g. & CH_3 & - CH_2OH & & (O) \\ Ethanol & & K_2Cr_2O_2/H_2SO_4 & CH_3 & - CHO \\ Ethanal \end{array}$$

Mild oxidizing agents are required for this reaction.

Limitation:- Aldehyde ,formed gets further oxidized to carboxylic acid . So, aldehyde formed should be removed as early as possible.

COREY'S reagent: it is a solution of pyridinium chlorochromate.

PYRIDINIUM DICHROMATE (PDC) :- complex of pyridine with chromic acid are used Advantage of using these special oxidizing agents is that they restrict the oxidation of primary alcohols to aldehyde stage This is because these reagents are used in non-aqueous medium and therefore do not allow the formation of aldehyde hydrate RCH(OH)2 to take place during oxidation .Another advantage of using these reagents is that C-C double bonds .if present in starting alcohol, are not oxidized.

(2) **Dehydrogenation of Primary Alcohol :-** It involves direct removal of hydrogen by passing vapours of alcohol over heated copper.

$$\begin{array}{ccc} R & \xrightarrow{Cu/573 \text{ K}} & RCHO + H_2 \\ p\text{-alcohol} & \xrightarrow{P\text{-alcohol}} & RCHO + H_2 \\ e.g. & CH_3CH_2OH & \xrightarrow{Cu/573 \text{ K}} & CH_3CHO \\ & & \text{Ethanol} & & \text{Ethanal} \end{array}$$

Advantage: there is no risk of further oxidation of aldehyde formed.

(3) **Rosenmund Reaction:-** Aldehydes can be prepared by hydrogenation of acid chloride in presence of palladium supported over barium sulphate.



Normally aldehydes are further reduced to primary alcohol. Therefore, in order to prevent the further reduction of aldehyde, the catalytic mixture is poisoned or deactivated by addition of sulphur or quinoline.

(4)Oxidation of Alkenes:-(OZONOLYSIS):- It involves reaction of alkene with ozone and there is intermediate formation of ozonide which on reduction (Zn + CH3COOH or H2,Pd) gives aldehydes.



(5)Gattermann-Koch Reaction:- It is a useful method for the preparation of aromatic aldehydes. This reaction uses Lewis acid and Copper (I) chloride.



(6)Reimer-Tiemann Reaction:-Phenolic aldehyde are obtained by treating phenol with CHCl3 in aq.NaOH solution at 340K.



Methods of Preparation pf Ketone:-

(1) Oxidation of Secondary Alcohol:-:-Oxidation of secondary alcohols by using acidified sodium or potassium dichromate or potassium permanganate produces ketones.

 $\begin{array}{c} \mathsf{OH} & \mathsf{O}\\ \mathsf{I} & \mathsf{H}\\ \mathsf{CH}_3\mathsf{CHCH}_3 & \xrightarrow{K_2\mathsf{Cr}_2\mathsf{O}_7} & \mathsf{CH}_3 & \mathsf{CH}_3 \end{array}$

Isopropyl alcohol (a secondary alcohol)

Acetone (a ketone)

Ketones produced does not get easily oxidized.

(2) **Dehydrogenation of Secondary Alcohol:-:-** This is done by passing alcoholvapours over heated copper.



(3) From Grignard Reagent:- Ketone can be prepared by the reaction of Grignard reagent on alkane nitrile or arene nitriles followed by acid hydrolysis of the addition product.



(4) Friedel- Craft Reaction:- Aromatic ketones can be prepared by this reaction bytreating aromatic hydrocarbons with acid chloride in presence of AlCl3.



Physical properties of Aldehydes And Ketones:-

1.Formaldehyde is a gas. Aldehydes and ketones up-to 11 carbon are colorless liquid while highermembers are solid.

2.Lower aldehydes have pungent, unpleasant smell while higher members of aldehydes and ketonesare having pleasant and fragrant odor.

3. Density of aldehyde and ketone is less than that of water'

4.BOILING POINT OF ALDEHYDE AND KETONE:- Because of polarity of the carbonyl group, aldehyde and ketone are polar compounds. The polar character of molecule gives rise to intermolecularinteraction. These attractive forces called dipole- dipole attractions occur between the partial negative charge on the carbonyl oxygen of one molecule and the partial the charge on the carbonyl carbon of another molecule.

Dipole-dipole attraction are not strong as hydrogen bonding.



As a result, the boiling point of aldehyde and ketone are higher than those of non -polar alkanes, butlower than those of alcohols of comparable molecular weight.



Among the carbonyl compounds ketones have slightly higher boiling point than isomeric aldehydes. This is due to presence of two electron releasing group around the carbonyl carbon makes them more polar.



(5)Solubility in water:- The lower aldehydes and ketones are soluble in H2O .Because aldehydes and ketones form hydrogen bond with water molecule even though they are incapable of intermolecular hydrogen bonding with themselves.



As the hydrocarbon portion of molecule increases, the solubility in H2O decreases rapidly. However the higher and lower aldehyde and ketones are soluble in organic solvent such as benzene, ether and CCl4.

Chemical Reactions of Aldehyde and Ketones:-

(1)Nucleophilic Addition Reaction:- The carbonyl group of aldehyde and ketone is a highly polar group.

The -vely charged carbon is readily attached by electron rich nucleophiles. The +ve charged Oxygen isattached by electron deficient electrophiles.



General Mechanism of Nucleophilic Addition Reaction:-

STEP 1:- The nucleophiles attacks the +vely charged carbon to form a new bond. As a new bond is formed π bond by C and O is broken. The electron pair goes to oxygen acquires -ve charge.



STEP 2:- The electrophile eg. (H^+) attacks -ve charged oxygen to form addition product.



Relative Reactivity of Aldehyde and Ketones:-Ketones are less reactive than aldehyde .This is due to

(1) Inductive Effect:- Ketones have two alkyl group while aldehyde have one alkyl group attached to carbonyl group. The +I effect of alkyl group leads to dispersal of +ve charge present on carbonyl carbon more stable and less reactive. The reduced +ve charge on carbon in case of ketone discourged the attack of nucleophile. Hence ketone are less reactive than aldehydes.



(2) Steric Effect:- In aldehydes, there one alkyl group ,but in ketones there are two alkyl groups attached to carbonyl carbon .The alkyl group larger than H atom and causes steric hindrance to attacking group. As the no. and size of alkyl group increases, hindrances to attack of nucleophile also increases and reactivity decreases.

Aromatic Aldehydes and Ketones:- In general, aromatic aldehydes and ketones are less reactive than corresponding aliphatic analogues. Eg. Benzaldehyde is less reactive than aliphatic aldehydes. This can be explained on basis of resonating structure of benzaldehyde.



Due to +I effect (electron releasing) effect of benzene, the magnitude of +ve charge on carbonyl carbondecreases and it becomes less susceptible to nucleophilic attack.

Acidity of α -Hydrogen:- The α - hydrogen of aldehyde and ketone in acidic in nature. This is due to the fact that the anion formed by removal of α - hydrogen by a base :B⁻ is stabilized by resonance. This resonance stabilized anion is called *ENOLATE ION*.



The α -carbon of enolate ion is -vely charged. It can act as a nucleophile. The formation of enolate ion is followed by its addition to carbonyl gp. Is the process involved in all condensation reaction of aldehydes and ketones.

(A) Nucleophilic Addition Reaction:-

(a)Addition of Sodium Bisulphite:- Aldehyde and ketone reacts with saturated solution of sodium bisulphite in which carbonyl carbon gets bonded to the sulphur atom of the nucleophile .At the end of the reaction addition product gets precipitated out.

For example. Aldehyde react with sodium bisulphite.



Ketone react with sodium bisulphite.



MECHANISM :-



(b)Addition of Hydrogen Cyanide:- Aldehydes and ketones react with HCN to form cyanohydrins. The reaction is carried out in basic catalyst.



HCN is a very poisonous gas. It is produced in situ by the action of dilute sulphuric acid and KCN.

MECHANISM:- Three steps are involved in this mechanism .



(C)Addition of Grignard Reagent:- Aldehyde and ketone reacts with Grignard reagent to give

addition product which can be hydrolyzed with dil. HCl acid to give alcohol.



(B)Addition Reaction Followed By Loss of Water:-

(a)Addition of alcohols:- Alcohols react with aldehyde in presence of anhydrous HCl to form unstable addition products known as hemiacetals. These hemiacetals react further with alcohol to form stable compounds known as acetals. Acetals are gem dialkoxy.



This reaction is reversible. So a large quantity of alcohol is used to shift the equilibrium in favour ofacetal formation.

(b)Reaction with Ammonia derivatives:- Some ammonia derivatives (NH2-Z) reacts with aldehyde and ketone to form compounds containing C=N, together with elimination of H2O molecule.

$$>C = 0 + H_2 N - Z \iff \left[>C < OH \\ NHZ \right] \longrightarrow >C = N - Z + H_2 O$$

Where Z = Alkyl, aryl, OH, NH₂, C₆H₅NH, NHCONH₂, etc.

MECHANISM:-

(1) Ammonia derivatives (NH2-Z) behave as a nucleophile reagent .They have an unshared pair of electron on N .They add to carbonyl group in aldehyde and ketone .

(2) Addition product rapidly loses a molecule of H2O to give final product.



(C)Reduction Reaction:-

Aldehydes and ketones can be reduced to alcohols or alkanes.

(a)Reduction to alcohols:-Aldehydes and ketones can be reduced to alcohols by hydrogen and Ni orPt catalyst .Aldehyde give 1° and ketone give 2° alcohols.

Eg.,

 $\begin{array}{ll} R & -- \text{CHO} + 2[H] \xrightarrow{\text{Ni},\text{Pt or Pd}} R & -- \text{CH}_2\text{OH} \\ \text{Aldehyde} & \text{Primary alcohol}(1^\circ) \end{array}$



Reduction alkanes:- Aldehyde and ketones can be reduced to alkanes by either Clemmensen or wolff-kishner reduction.

(1)Clemmensen reduction:- This involves the use of Zn-Hg amalgam in HCl as reducing agents.



(2)Wolff-Kishner reduction:- This involves the use of basic solution of hydrazine as a reducing agent.



(D)Oxidation Reaction:- Although behaviour of aldehyde and ketone are very similar, the behaviour towards oxidizing agent is quite different .Aldehydes are easily oxidized while

ketones areoxidized in drastic conditions.

(a)Oxidation of aldehydes:- Aldehydes can be oxidized with Sodium or Potassium Dichromate inacidic medium to form carboxylic acid containing same no. of carbon atoms.



QUALITATIVE TESTS:-Aldehydes can be oxidized by much milder oxidizing agents such as Tollen's reagent ,Fehling'ssolution and Benedict's solution.

(1)Oxidation with Tollen's Reagent:- Tollens's reagent is an ammoniacal solution of silver oxide. It is obtained by adding ammonia to precipitate of silver oxide present in a solution of silver nitrate and NaOH.

Step 1: Sodium hydroxide is added to silver nitrate until a light brown precipitate of silver oxide is formed.										
2AgNO ₃	+	2NaO	н·	\rightarrow	Ag₂O	+	2NaNO ₃	+	H₂O	
Silver nitrat	e	Sodiun hydroxi	lium Silver oxide oxide (brown ppt.)		le t.)	Sodium nitrate		Water		
Step 2: Concentrated ammonia solution is added to the silver oxide until the latter completely dissolves forming a diaminesilver (I) complex.										
Ag₂O	+	$4NH_3$	+	$H_{2}O$	\longrightarrow		2[Ag(NH ₃) ₂	,] [⊕]	он [⊝]	
Silver oxide		Ammonia		Water		c	diaminesilver(l) hydroxide (Tollens' reagent)			

When Tollen's reagent is used to oxidized an aldehyde, the silver ion is reduced to metal form anddeposits as a mirror. The silver mirror formed indicates presence of aldehyde group.



(2) Oxidation with Fehling solution:- Fehling solution is an alkaline solution of Cupric ion complexed with Sodium Potassium Tartrate ions.



When Fehling solution is used to oxidized an aldehyde, the complexed cupric ion (deep blue is reduced to cuprous oxide (red). The presence of red precipitate of cuprous oxide serves as an indication of an aldehyde group in molecule.

$$\begin{array}{rcl} CH_{3}-C < \begin{matrix} 0 \\ H \\ acetaldehyde \end{matrix} + 2Cu^{++} + 4OH^{-} & \stackrel{\Delta}{\longrightarrow} \\ & & \\ Fehling's \ solution \\ & \\ CH_{3}-C < \begin{matrix} 0 \\ OH \end{matrix} + Cu_{2}O\downarrow + 3H_{2}O \\ & \\ acetic \ acid \end{matrix} + Cu_{2}O\downarrow + 3H_{2}O \\ & \\ \end{array}$$

(3)Benedict's solution:- It is an alkaline solution of cupric ion complexed with citrate ions. It reacts in the same way as Fehling 's solution.

(b) Oxidation of Ketones:- Ketones can be oxidized by strong oxidizing agents such as alkaline KMnO4 or hot conc. HNO3 to form two carboxylic acid with fewer carbon atoms than the original ketone .This is because ketone is broken into two fragments by attack on either side of carbonyl group.

$$CH_3 - C - CH_3 \xrightarrow{[0]} HCOOH + CH_3COOH \\ Conc \\ HNO_3 Formic Acetic \\ acid acid \\ Conc \\ HNO_3 COOH \\ Conc \\ Co$$

Electromeric Effect:-

The instantaneous formation of a dipole in the molecule of an organic compound due to the complete transfer of shared pi electron pairs to one of the atoms under the influence of an attacking reagent is referred to as the **Electromeric effect.**

The electromeric effect is a temporary effect that remains as long as the attacking reagent is present and exposed to the organic compound. Once this attacking reagent is removed from the system, the molecule that was polarized goes back to its original state.

Types of Electromeric Effects

The electromeric effect can be broken down into two types, namely the +E effect and the -E effect. This classification is done based on the direction in which the electron pair is transferred.

+E Effect

This effect occurs when the electron pair of the pi bond is moved towards the attacking reagent. The +E effect can be observed in the addition of acid to alkenes. The attacking reagent attaches itself to the atom which obtained an electron pair in the transfer.

The +E effect is generally observed when the attacking reagent is an electrophile and the pi electrons are transferred towards the positively charged atom. An example where the +E effect occurs is the protonation of ethene which is illustrated below.



Positive Electromeric Effect

-E Effect

This effect occurs when the electron pair of the pi bond is moved away from the attacking reagent. The attacking reagent attaches itself to the positively charged atom in the molecule, i.e. the atom which lost the electron pair in the transfer.

The -E effect is generally observed when the attacking reagent is a nucleophile and the pi electrons are transferred to the atom which the attacking reagent will not bond with. An example

where the -E effect occurs would be the addition of nucleophiles to carbonyl compounds as illustrated below.



Negative Electromeric Effect

Aldol Condensation:-

Aldol condensation is an organic reaction in which an enolate ion reacts with carboxyl compound in order to form a β - hydroxy aldehyde or β - hydroxy ketone.



Mechanism of Aldol Condensation:-The mechanism of aldol condensation initiates with the formation of carbanion intermediate. Refer to the steps below to observe the mechanism of aldol condensation in the presence of a base as a catalyst. Aldol Condensation in Aldehydes with Base as a Catalyst

Step 1: Removal of α-hydrogen from the base.



Removal of α-hydrogen, Formation of Carbanion

Step 2: The first step results in the formation of carbanion which undergoes a nucleophilic addition reaction with the carbonyl group present in the second molecule of the aldehyde (in this case ethanal). The second step results in the formation of the condensation product.



Step 3: Protonation of alkoxide ion will occur due to reaction with water.

$$\begin{array}{ccccccc} H & :\ddot{O}: & H & H & OH & H \\ | & | & | & | & | & | & | \\ H - C - C - C - CH_2 - C = O + HOH & \longrightarrow H - C - C - CH_2 - C = O + OH \\ | & | & | & | \\ H & H & H & H \end{array}$$

Step 4: Heating of the aldol compound in the basic solution will help in dehydrating the product to form $\alpha \beta$ -unsaturated aldehyde compound.

$$CH_{3} - \begin{array}{c} OH \\ - \\ CH_{2} - C \\ - \\ H \end{array} \xrightarrow{I} OH \\ - \\ OH \\ -$$

Application of Aldol Condensation

- ✓ The reaction is commonly used to produce solvents such as alcohol isophorone and diacetone.
- ✓ It works as an intermediate for perfume production.
- ✓ It is also used in pharmaceutical manufacturing, unsaturated ketones and chalcones known as aromatic ketones.
- ✓ Usually, it is used to create plasticizers as well.
- ✓ The enone product of an aldol condensation is versatile because it contains two functional groups (alkene & carbonyl) which can be subject to further reactions. Among many possible

reactions, an enone can undergo hydrogenation to produce an aldehyde or ketone. Also, the carbonyl group can undergo hydride reduction to produce a beta-hydroxy alkene.



These additional reactions can be applied with the consideration of using an aldol reaction in the synthesis of a target molecule. A similar analysis can be extrapolated to the other reactions possible with the alkene and carbonyl present in an enone.

Cross Aldol Condensation Reaction:-

Crossed aldol condensation is a variation of aldol condensation in which two dissimilar carbonyl compounds (each containing alpha hydrogens) undergo the condensation reaction together. For example,



Mechanism:-



Cannizaro Reaction:- Cannizzaro reaction is a chemical reaction named after **Stanislao Cannizzaro** that involves the base-induced disproportionation of two molecules of a nonenolizable aldehyde to yield a carboxylic acid and a primary alcohol. Example,



Cannizzaro Reaction Mechanism details the method to get one molecule of alcohol and one molecule of carboxylic acid from two molecules of a given aldehyde. Scientist Stanislao Cannizzaro, in 1853 succeeded in obtaining benzyl alcohol and sodium benzoate from benzaldehyde.

Mechanism of Cannizzaro Reaction

Step 1:-A nucleophile such as a hydroxide ion is used to attack the carbonyl group of the given aldehyde, causing a disproportionation reaction and giving rise to an anion carrying 2 negative charges.



Step 2:-This resulting intermediate can now function as a hydride reducing agent. Due to its unstable nature, the intermediate releases a hydride anion. This hydride anion proceeds to attack another aldehyde molecule. Now, the doubly charged anion is converted into a carboxylate anion and the aldehyde is converted into an alkoxide anion.



Step 3:-In this final step, water offers a proton to the alkoxide anion which gives rise to the final alcohol product. The reaction can proceed since the alkoxide is more basic than water. Now, the carboxylate ion gives rise to the final carboxylic acid product when acid workup is used (the acid workup is required since carboxylate is less basic than water and therefore cannot obtain a proton from water).



Cross Cannizzaro Reaction:-When a mixture of formaldehyde and other aldehyde which has no α-hydrogen atom is treated with conc. alkali, formaldehyde is oxidized to carboxylic acid and another aldehyde is reduced to alcohol. This reaction **is Crossed Cannizzaro's Reaction**. For example, benzyl alcohol and sodium formate is formed when a mixture of benzaldehyde and formaldehyde is treated with conc. NaOH.



Mechanism of crossed Cannizzaro's reaction:-

Step-I: In first step, there is nucleophilic addition of the hydroxide ion on the carbonyl group of formaldehyde to give anion.



Step II : In this step, the anion transfers a hydride ion to the electron deficient carbonyl carbon of benzaldehyde molecule to give carboxylic acid and alkoxide ion.



Step III : In this step, there is proton exchange between the carboxylic acid and the alkoxide ion to give salt of carboxylic acid (sod. formate) and alcohol (benzyl alcohol).



Advantage of crossed- Cannizzaro's reaction:

In this reaction an aldehyde is treated with formaldehyde. Here, formaldehyde is oxidized to sodium formate and required alcohol is obtained from the reduction of the other aldehyde. Since both the aldehydes used are completely converted into the required products, there is no wastage of the valuable chemicals.

Why does methyl alcohol is not formed instead of sodium formate in Crossed Cannizzaro's reaction?

The initial nucleophilic addition of hydroxide ion is faster on formaldehyde than on other aldehyde as there is no electron donating groups on formaldehyde. Hence, formic acid (sodium formate) is formed but not methyl alcohol.

Benzoin Condensation:- Benzoin condensation reaction can be defined as the reaction between two kinds of aromatic aldehydes especially benzaldehyde, in the presence of some catalyst (either nucleophile or heterocyclic) to form an aromatic parent compound.

The benzoin condensation reaction is nothing but the coupling reaction that occurs between aldehydes for the formation of parent benzoin. In this case, the benzaldehyde is involved in this homocoupling process.



Mechanism:-

Step 1: Nucleophilic addition of a cyanide with benzaldehyde to form cyanohydrin



Benzaldehyde

Cyanohydrin

Step 2: Condensation reaction between the cyanohydrin and a second benzaldehyde



Step 3: Rearrangement reaction removing the cyanide group resulting in a benzoin



Perkin Condensation:- Perkin's reaction is an organic reaction proposed by **William Henry Perkin**, an **English Chemist, in the year 1868**. When an acid anhydride and aromatic aldehyde react with each other in the presence of a weak base, they condense to give the desired product.



Perkin Reaction Mechanism

The generally accepted mechanism of the Perkin reaction is represented by the following steps:

1. Involves the abstraction of proton by the carboxylate ion to form the resonance stabilized carbanion, which is a species containing carbon with a negative charge.

- **2.** Involves the nucleophilic addition of the carbanion to the carbonyl carbon atom of the aldehyde to form a tetrahedral intermediate.
- **3.** The tetrahedral intermediate is protonated by the acetic acid formed in the process.
- **4.** Involves the elimination of water molecule from the hydroxy derivative.
- **5. Hydrolysis**, which is the addition of water, of the unsaturated compound to the unsaturated acid occurs.



Structure and uses of Formaldehyde



Formaldehyde (systematic name - methanal) is an organic compound with the formula CH2O (H–CHO). It is the simplest of the aldehydes (R–CHO). It is an organic chemical which contains hydrogen, oxygen and carbon atoms.

Physical Properties

- It is colorless liquid.
- At room temperature it is a flammable liquid.

• It has a strong pungent odor.

Chemical Properties

Formaldehyde reacts with a base like sodium hydroxide forms sodium formate and methanol. The chemical equation is given below.

2 HCHO + NaOH \rightarrow HCOONa + CH₃OH

Formaldehyde sodium hydroxide

sodium formate methanol

Formaldehyde react with ammonia to produce hexamethylene tetra ammine and water. The chemical equation is given below.

 $6\text{HCHO} + 4\text{NH}_3 \rightarrow (\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O}$

Formaldehyde ammonia hexamethylenetetraammine

Method of Preparation

Methanol and oxygen react at 450 °C in presence of silver as catalyst to form formaldehyde.

 $\begin{array}{ccc} 2 \ CH_3OH + O_2 & \rightarrow & 2 \ CH_2O + 2 \ H_2O \\ \text{Methanol} & & \text{formaldehyde} \end{array}$

Formaldehyde Uses:-

Because it is highly chemically reactive, formaldehyde has many uses in science and industry. These uses include:

Formaldehyde Uses in Biology

Formaldehyde is often used in biology to preserve tissue specimens. Formaldehyde is useful for this purpose as it kills all bacteria and fungi, and can preserve the shape of a specimen by bonding with proteins and DNA.

Formaldehyde Uses in Medicine

- Used as an antiseptic, as it kills most bacteria and fungi.
- Used in the treatment of warts and some parasites.
- Used in the production and sterilization of some vaccines.

- A formaldehyde precursor is sometimes used as an alternative to antibiotics in the treatment of urinary tract infections. The kidneys turn this precursor into formaldehyde, which is then excreted into the urinary tract instead of circulating in the blood.
- Used in some personal hygiene products to prevent bacterial growth.

Formaldehyde Uses in Industry

- ✓ Used as a reactant to produce many artificial materials such as resins, plastics, and other industrial chemicals.
- ✓ Used to treat clothes to make fabrics crease-resistant
- ✓ Used to produce materials used in numerous parts of car manufacture.
- ✓ Used in the production of plywood, carpeting, and building insulation.
- ✓ Used in the production of sanitary paper products such as napkins, paper towels, and tissues.
- ✓ Used to make chemicals used in paints and explosives.
- ✓ Used to prevent bacterial and fungal growth in animal feed for commercial farming.
- ✓ Used in the development of some types of photography film

Structure and uses of Paraldehyde



Paraldehyde is the cyclic trimer of acetaldehyde molecules and belongs to the family of aldehydes. Chemical Formula is $C_6H_{12}O_3$. IUPAC name of paraldehyde 2,4,6-trimethyl-1,3,5-trioxane.

Properties

- A colorless liquid, with sweet odor and boiling point is 128 °C.
- It is sparingly soluble in water and highly soluble in ethanol.

- Paraldehyde slowly oxidizes in air, turning brown and producing an odor of acetic acid.
- It quickly reacts with most plastics and rubber.
- It regenerates acetaldehyde on distilling with conc. Sulphuric acid.

 $C_6H_{12}O_3 \rightarrow 3CH_3CHO$

Paraldehyde Acetaldehyde

Method of Preparation

Acetaldehyde treated with conc. Sulphuric acid at room temperature give Paraldehyde.



Uses of Paraldehyde

- Paraldehyde is used in resin manufacture.
- It is used as a preservative.
- It has been used in the treatment of epilepsy.
- It is used as an effective central nervous system depressant.
- It is used in the preparation of aldehyde fuchisn dye.
- It is also used as solvent in industries.

Structure and uses of Benzaldehyde



Benzaldehyde (C6H5CHO) is an organic compound consisting of a benzene ring with a formyl substituent. It is the simplest aromatic aldehyde and one of the most industrially useful. Systematic IUPAC name is Benzene carbaldehyde.

Properties

- It is a colorless liquid with a characteristic almond-like odor.
- Boiling point is 179 °C.
- It is soluble in ethanol and diethyl ether.
- Benzaldehyde react with formaldehyde to give benzyl alcohol.



Method of Preparation

By oxidation of Toluene

Oxidation of toluene is done with air and diluted with nitrogen (to prevent complete oxidation) at 3500 C in the presence of Vanadium pentoxide as catalyst.



Uses of Benzaldehyde

- Benzaldehyde is commonly employed to confer almond flavor to foods and scented products.
- It is sometimes used in cosmetics products.
- Benzaldehyde is used chiefly as a precursor to other organic compounds, ranging from pharmaceuticals to plastic additives.
- Benzaldehyde is also a precursor to certain acridine dyes.
- Benzaldehyde is used in the preparation of cinnamaldehyde, mandelic acid and styrene.

- Benzaldehyde is used in the preparation of aniline dye malachite green.
- Benzaldehyde is used as a bee repellent.

Structure and uses of Cinnamaldehyde



Cinnamaldehyde is an organic compound with the formula C6H5CH=CHCHO. IUPAC name 3phenylpropenal. Occurring naturally as predominantly the trans (E) isomer, it gives cinnamon its flavor and odor. This pale yellow, viscous liquid occurs in the bark of cinnamon trees and other species of the genus Cinnamomum.

Properties

- Cinnamaldehyde (C9H8O) is pale yellow, viscous liquid with boiling point 252° C.
- It has cinnamon-like odor.
- Soluble in ether, chloroform.
- Insoluble in petroleum ether, miscible with alcohol, oils.

Method of Preparation

Benzaldehyde react with acetaldehyde to give Cinnamaldehyde.



Uses of Cinnamaldehyde

- The most obvious application for cinnamaldehyde is as flavoring in chewing gum, ice cream, candy,liquid and beverages.
- It is also used in some perfumes of natural, sweet, or fruity scents.

- Cinnamaldehyde has been tested as a safe and effective insecticide against mosquito larvae.
- Trans-cinnamaldehyde works as a potent fumigant.
- Cinnamaldehyde is also known as a corrosion inhibitor for steel and other ferrous alloys in corrosive fluids such as hydrochloric acid
- The compound is also added to a number of cosmetics and home care products to improve their odor. Such products include deodorants, detergents, mouthwashes, perfumes, soaps, and toothpastes.

Structure and medicinal uses of Acetone:-



Acetone, propanone or dimethylketone,isan organiccompound withthe formula $(CH_3)_2CO$. It is the simplest and smallest ketone.

Physical Properties:-

- It is a colorless, highly volatile and flammable liquid with a characteristic pungent odor.
- Acetone is miscible with water and serves as an important organic solvent in its own right, in industry, home, and laboratory.
- Acetone is a highly flammable organic compound. It is also found in the human body usually present in urine and blood.

Preparation Method of Acetone:-

Currently, acetone is produced by propylene either by the direct or indirect method. Almost 83% of acetone is produced during the cumene process. Also, there are other older methods to produce acetone.



Uses :-

- It is used as a solvent for synthetic fibres and plastics.
- It is used as a precursor for methyl methacrylate.
- It is used to prepare metal before painting.
- It is used in pharmaceutical industries in some drugs.
- It is volatile and hence used in the laboratory to rinse lab glassware.
- It is used as a drying agent.
- It is used in the defatting process.
- It is used in cosmetics such as nail polish remover.
- It is used in the treatment of acne.
- In the pharmaceutical industry, acetone is often used as a solvent in fillers and active ingredients to ensure accurate dosage of medicine.
- Acetone is also commonly used in the medical field to clean and sterilize medical tools and equipment.

Structure and medicinal uses of Chloral hydrate :-

Chloral hydrate is a geminal diol with the formula C₂H₃Cl₃O₂. Its structure is



Physical Properties:-

- It is a colorless solid.
- It is soluble in both water and alcohol and it readily forms concentrated solutions solutions. On heating it gets decomposed and gives toxic fumes having hydrogen chloride gas. It readily reacts with strong bases to form chloroform.

Preparation method of chloral hydrate:-

Chloral hydrate, 2,2,2-trichloro-1,1-ethandiol is synthesized either by chlorination of ethanol or chlorination of acetaldehyde and the subsequent addition of water molecules to the resulting trichloroacetic aldehyde.

Uses of chloral hydrate

- Chloral hydrate, a sedative, is used in the short-term treatment of insomnia (to help you fall asleep and stay asleep for a proper rest).
- Relieve anxiety and induce sleep before surgery. It is also used after surgery for pain and to treat alcohol withdrawal.
- It is useful ingredient for microscopic investigation of seeds, ferns, small mites etc.

Hexamine:-

 $C_6H_{12}N_4$ is a heterocyclic organic compound with a chemical name Hexamine. It is also called Methenamine or Hexamethylenetetramine or Urotropin.

Structure:-



Method of preparation:- It is prepared industrially by combining formaldehyde and ammonia. The reaction can be conducted in gas phase and in solution.

Physical Properties :-

 It is white crystalline compound, highly soluble in water and other polar organic solvents. It has cage like structure. It gets sublimed in vacuum at 280°c.

Hexamine Uses (C₆H₁₂N₄)

- Hexamine is used in the production of liquid or powdery preparations of phenolic resins.
- Used as binders in clutch and brake linings.
- Used in the form of spray and cream to treat concomitant odor and excessive sweating.
- Used in Grocott's methenamine silver stain.
- Used as a solid fuel.
- Used as a food preservative.
- Used as a primary ingredient in making RDX.
- Used to prevent vulcanized rubber.
- Used as a corrosion inhibitor for steel.
- Used for the prophylaxis (prevention) of urinary tract infections, where it is hydrolyzed in the acidic pH of the urine to form formaldehyde. Formaldehyde is an effective antiseptic against bacteria and fungi.

Vanillin:-

Vanillin is an organic compound with the molecular formula $C_8H_8O_3$. It is a phenolic aldehyde. Its functional groups include aldehyde, hydroxyl, and ether. It is the primary component of the extract of the vanilla bean.



Physical Properties :-

- It is white crystalline powder having sweet, pleasant and balsamic taste and odor.
- Crystalls of vanillin occurs as monoclinic. Natural vanilla extract is a mixture of various hundred different compounds including vanillin.

Uses:-

- Vanillin is used in perfumes and fragrances in both cleaning products and candles, in the food industry to flavor chocolate, baked goods, and ice cream, and in medicines to mask unpleasant flavors.
- It also used to mask the bitter taste of medicines.
- Vanillin- hydrochloride staining is used for visualizing tannins present in plant cells.

Questions carrying 2 marks

1. Why do aldehydes have lower boiling point than corresponding alcohol?

2. Why does methanal not give aldol condensation while ethanol gives?

3. Why are aldehydes are more reactive than ketones when undergo nucleophilic addition reaction?

4. Give structure and medicinal uses of Formaldehyde.

- 5. Give structure and medicinal uses of chloral hydrate.
- 6. Give structure and medicinal uses of Benzaldehyde.
- 7. Give structure and medicinal uses of Hexamine, Vanillin.
- 8. Give structure and medicinal uses of Cinnamaldehyde.
- 9. Define Aldol Condensation.
- 10. Give qualitative test for aldehydes and ketones.
- 11.Define Cannizzaro reaction with suitable example.
- 12.Define Electromeric effect.
- 13.Explain Molecular orbital structure of carbonyl compounds.

- 14.Write Rosenmund Reaction.
- 15.Write Gattermannn- Koch Reaction.
- 16.Write Reimer-Tiemann Reaction.

Questions carrying 5 marks

- 1. Give methods of preparation of Aldehydes.
- 2. Give methods of preparation of Ketone.
- 3.Differentiate between Aldehyde and Ketone.
- 4. Discuss the mechanism of Benzoin Condensation and Cannizzaro Reaction.
- 5.Write Chemical properties of Carbonyl compounds.
- 6. Discuss the mechanism of Perkin Condensation.

Questions carrying 10 marks

1. What are carbonyl compounds? Discuss the reactivity of carbonyl group towards nucleophilic attack.

2.Explain following reaction with mechanism

Aldol Condensation Crossed Cannizzaro Reaction. Benzoin Condensation

3.Discuss the behaviour of aldehydes and ketones towards Tollen's reagent and Fehling solution.4.What is Aldol Condensation? What are its limitations? What is Cross Aldol Condensation? Explain.