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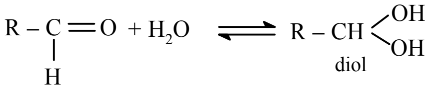
CHAPTER

aldehydes and ketones

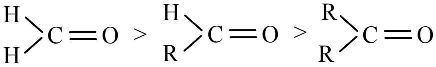
- Aldehydes are compounds of the general formula **RCHO** and ketones are compounds of the general formula **RR′CO**.
- Both aldehydes and ketones contain the carbonyl group $>C=O$ and are called **carbonyl compounds**.

  The carbonyl group is polar in nature and carbonyl carbon is sp^2 hybridised.
- Aldehydes are prepared by the controlled oxidation of 1° alcohols using acidified potassium permanganate or acidified potassium dichromate.
- **Oppenauer oxidation** of 2° alcohols (saturated or unsaturated) with aluminium tert-butoxide in presence of excess of acetone gives ketones in good yields without the danger of being further oxidised to carboxylic acids.
- **Collin's reagent** ($CrO_3 \cdot 2C_5H_5N$) and pyridinium chlorochromate (PCC, $CrO_3 \cdot C_5H_5N$) are better oxidising agents than $K_2Cr_2O_7/H_2SO_4$ or $KMnO_4/KOH$ for converting 1° alcohols to aldehydes since these reagents oxidise 1° alcohols to the corresponding aldehydes and the aldehydes formed are not further oxidised to the carboxylic acids.
- Reduction of acid chlorides with H_2 in presence of Lindlar's catalyst (Pd deposited over $BaSO_4$ and partially poisoned by addition of S or quinoline) gives aldehydes - **Rosenmund reduction**.
- The reaction of acid chloride with dialkyl cadmium gives ketones.
- **Friedel-Craft's reaction** involves the treatment of an aromatic hydrocarbon with an acid chloride or acid anhydride in the presence of a Lewis acid such as anhydrous aluminium chloride in dry ether.
- **Etard's reaction** involves the oxidation of toluene with CrO_2Cl_2/CS_2 followed by decomposition of the complex thus formed with water.
- Friedel Craft's acylation of arenes with acid chlorides and anhydrides give ketones.
- **Reductive ozonolysis of alkenes** give aldehydes or ketones depending upon the structure of alkene.
- **Lithium organocuprates** react readily with acid chlorides to yield ketones.
- The boiling points of aldehydes and ketones are higher than those of hydrocarbons of comparable molecular masses.
- Among isomeric aldehydes and ketones, ketones have higher boiling points.
- **Benzaldehyde** has a smell of bitter almonds.
- Solubility of aldehydes and ketones in water decreases with the increase in molecular mass.

- Diol formation of aldehydes with water also helps in solubility in water.



- Boiling points of ketones are slightly higher than those of isomeric aldehydes because ketones are relatively more polar than their corresponding isomeric aldehydes due to the presence of two electron repelling alkyl groups around the carbonyl carbon.
- Aldehydes and ketones can be reduced to hydrocarbons by the action of amalgamated zinc and concentrated hydrochloric acid - the Clemmensen reduction and of hydrazine NH_2NH_2, and a strong base like KOH or potassium tert-butoxide, the **Wolf Kishner reduction**.
- Aldehyde are more reactive than ketones and the order of reactivity is based upon the +I effect of the alkyl group as follows.



- As the size of the alkyl group increases, the reactivity decreases. The order of reactivity of various ketones is as follows.
  $CH_3COCH_3 > CH_3CH_2COCH_3 > CH_3CH_2COCH_2CH_3$
- Presence of electron attracting group on carbonyl compounds increases positive charge on carbonyl carbon due to –I effect and increases the reactivity. The order of reactivity of substituted aldehydes is as follows:

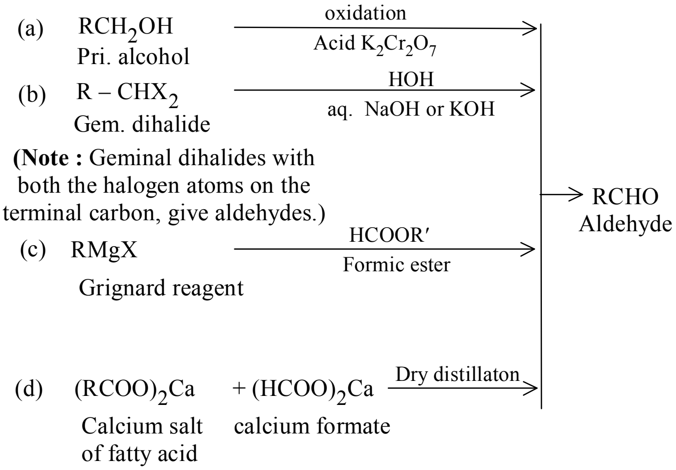
$$NO_2CH_2CHO > ClCH_2CHO > CH_3CHO$$

- Aromatic aldehydes are more reactive than alkyl-aryl ketones which in turn are more reactive than diaryl ketones.
- The elements of HCN add to the carbonyl group of aldehydes and ketones to yield compounds known as **cyanohydrins**.
- Alcohols add to the carbonyl group of aldehydes in presence of anhydrous acids to yield **acetals**.
- In the presence of concentrated alkali, aldehydes containing no α-hydrogen undergo self-oxidation and reduction to yield a mixture of an alcohol and a salt of carboxylic acid.
- Aldehydes and ketones react with hydroxyl amine to form **oximes**.
- Aldehydes and ketones react with hydrazine forming **hydrazones**.
- Aldehydes and ketones react with semicarbazide to form **semicarbazones**.
- Aldehyde reduce Tollen's reagent and Fehling's solution.
- **Tollen's reagent** is an ammoniacal solution of silver nitrate and Fehling's solution is an alkaline solution of $CuSO_4$ containing some **Rochelle salt** *i.e.* sodium potassium tartarate.
- Ketones cannot be oxidised by weak oxidising agents such as Tollen's reagent, Fehling solution and these reagents are used for distinguishing aldehydes from ketones.
- Ketones are oxidised by strong oxidising agents like conc. HNO_3, $KMnO_4/H_2SO_4$, $K_2Cr_2O_7/H_2SO_4$.
- During oxidation of unsymmetrical ketones, the point of cleavage is such that keto group stays preferentially with the smaller alkyl group (**Popoff's rule**).

- Two molecules of an aldehyde or a ketone having atleast one α-hydrogen atom condense in the presence of dilute alkali to form a β-hydroxy aldehyde or a β-hydroxy ketone. The reaction is called **aldol condensation**.
- Aldehydes and ketones containing α-hydrogen atoms undergo halogenation when treated with halogens in the presence of an acid or a base.
- Aldehydes and ketones like formaldehyde, benzaldehyde and benzophenone do not undergo aldol condensation since they do not have any α-hydrogen.
- In general a mixture of two aldehydes undergoes a Cannizzaro reaction to yield all possible products. If one of the aldehyde is formaldehyde, the reaction yields almost exclusively sodium formate and the alcohol corresponding to the other aldehyde such a reaction is called a crossed **Cannizzaro reaction**.
- The reaction between an aldehyde or a ketone with a phosphorus ylide to give a substituted alkene is called the **Wittig reaction** and the phosphorus ylide is commonly called the **Wittig reagent**.
- On heating with an ethanolic solution of KCN, two molecules of an aromatic aldehyde condense to form **benzoin**.
- Aromatic ketones do not form addition products with sodium bisulphite due to **steric hindrance**.
- Aldol condensation can also take place between two different aldehydes or ketones or between one aldehyde and one ketone.
- When aldehydes are treated with **Schiff's reagent**, its pink or magenta colour is restored and this reaction is used as a test for aldehydes because ketones do not restore the pink colour of Schiff's reagent.
- **Schiff's reagent** is an aqueous solution of magenta or pink coloured rosaniline hydrochloride which has been decolourised by passing SO_2.
- Formaldehyde reacts with ammonia to form **hexamethylene tetraamine**.
- Hexamethylene tetraamine is used as a urinary antiseptic under the name **urotropine**.
- Aldehydes and ketones react with primary amines in the presence of trace amount of an acid to form **azomethines** or **Schiff's bases**.
- **Perkin's reaction** involves heating of an aromatic aldehyde with an acid anhydride and its corresponding sodium salt.
- **Benzaldehyde** is prepared by the dry distillation of a mixture of calcium benzoate and calcium formate.
- Benzaldehyde on oxidation with alkaline potassium permanganate gives benzoic acid.
- Nitration of benzaldehyde with a mixture of conc. nitric acid and sulphuric acid gives *m*-nitrobenzaldehyde.
- **Paraldehyde** is used in medicine as hypnotic.
- When a few drops of conc. H_2SO_4 are added to acetaldehyde at room temperature, a rapid exothermic reaction occurs and a cyclic trimer called paraldehyde is formed.
- **Formaldehyde** is used in leather industry for tanning hides and as a reducing agent in silvering of mirrors and decolourising vat dyes.
- A 40% solution of formaldehyde in water is called **formalin** and is used for the preservation of biological or anatomical specimens.

- Formaldehyde is used in the manufacture of bakelite, resins and other polymers.
- When gaseous formaldehyde is allowed to stand it gives trioxane or **metaformaldehyde**.
- Nitration of hexamethylene tetraamine under controlled conditions gives the well known explosive **RDX (research and development explosive)**.
- Benzaldehyde reacts with ammonia to form a complex products called **hydrobenzamide**.
- A base-catalysed crossed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or a ketone is called **Claisen-Schmidt condensation** or simply **Claisen reaction**.
- Even aliphatic esters containing α-hydrogen atoms undergo Claisen-Schmidt condensation on treatment with an aromatic aldehyde in presence of a base.
- Ketones on reduction with magnesium amalgam and water form pinacole.
- All aldehydes and ketones having CH_3CO – group (attached either to H or to C) on treatment with an excess of halogen in presence of alkali (i.e. sodium hypohalite, NaOX) give haloform ($CHCl_3$, $CHBr_3$, CHI_3) and the salt of a carboxylic acid having one carbon atom less than the original aldehyde or ketone. This reaction is known as **haloform reaction**.
- When I_2 is used as the halogen in haloform reaction, yellow ppt. of iodoform are formed and the test is called **iodoform test**.
- **$LiAlH_4$** reduces aldehydes, ketones, acids, esters, amides and nitriles.
- Chain isomerism is exhibited by aldehydes containing four or more carbon atoms and ketones having five or more carbon atoms.
- Higher ketones and aromatic aldehydes show position isomerism.
- Aldehydes and ketones show functional isomerism among themselves but also with alcohols and ethers which may be either cyclic or acyclic.
- Aldehydes and ketones with a methyl or methylene group adjacent to $\rangle C = O$ group on oxidation with selenium dioxide (SeO_2) at room temperature, give α-dicarbonyl compounds.
- Ketones can be reduced to corresponding secondary alcohols with aluminium isopropoxide in isopropyl alcohol.
- Formaldehyde does not give iodoform test.
- The acidity of α-hydrogens is partly due to the –I-effect of the carbonyl group which weakens the $C^{\alpha} – H$ bond and partly due to the resonance stabilisation of the resulting carbanion.
- The β^-, γ^-, δ^- ... etc. hydrogens are not acidic because the inductive effect decreases with distance and the resulting carbanions are not stabilised by resonance.
- Electrophilic substitution reactions in aromatic aldehydes and ketones occur at the *m*-position.
- Acetaldehyde readily dissolves in water, alcohol and ether in all proportions.
- **Acetaldehyde** is used in silvering of mirrors.
- When distilled with conc. H_2SO_4, acetone gives mesitylene *i.e.* 1,3,5-trimethyl benzene.
- **Acetone** is used as one of the constituents of liquid nail polish.
- **Mesityl oxide** (4-methylpent-3-en-2-one) is formed when two molecules of acetone in the presence of HCl combine with the elimination of one molecule of water.

- Benzaldehyde is used as a flavouring agent in perfume industry.
- Benzaldehyde is used in the manufacture of dyes like malachite green.
- In **Gattermann-Koch aldehyde synthesis** a mixture of CO and HCl gas is passed through benzene at 323 K in presence of a catalyst consisting of anhydrous $AlCl_3$ and a small amount of CuCl to give benzaldehyde.
- Acetone is used as a solvent for acetylene, cellulose acetate, cellulose nitrate, celluloid, lacquers and varnishers.
- With phosphorus pentachloride, aldehydes and ketones gives **gem-dihalides**.
- Because of the small size of oxygen as compared to carbon, $>C=O$ bond length is shorter (1.23 Å) than that of $C=C$ bond length (1.34 Å).
- Carbon-oxygen double bond is polar but carbon-carbon double bond is non-polar.
- Aliphatic aldehydes do not show position isomerism since aldehyde group being monovalent is always present at the end of the carbon chain.
- Formaldehyde cannot be prepared by **Rosenmund reduction** since formyl chloride HCOCl, is unstable at room temperature.
- In presence of hot dilute H_2SO_4 and $HgSO_4$ alkynes add up a molecule of water to form aldehydes and ketones.
- Aromatic aldehydes can be prepared by the oxidation of methyl benzenes with chromium trioxide in acetic anhydride.
- **Benzophenones** can also be prepared by Friedel-Craft's reaction of carbonyl chloride (phosgene) with excess of benzene.
- Acetone is a highly inflammable liquid and rapidly catches fire.
- Lower member of carbonyl compounds are miscible in water due to hydrogen bonding between oxygen of polar carbonyl group and hydrogen of water molecules.
- Cannizzaro reaction is a disproportionation reaction in which one molecule of an aldehyde is reduced while the other is oxidised.
- **Preparation of Aldehydes**
  They can be summarized as follows.



(a) $$\underset{\text{Pri. alcohol}}{RCH_2OH} \xrightarrow[\text{Acid } K_2Cr_2O_7]{\text{oxidation}} RCHO$$

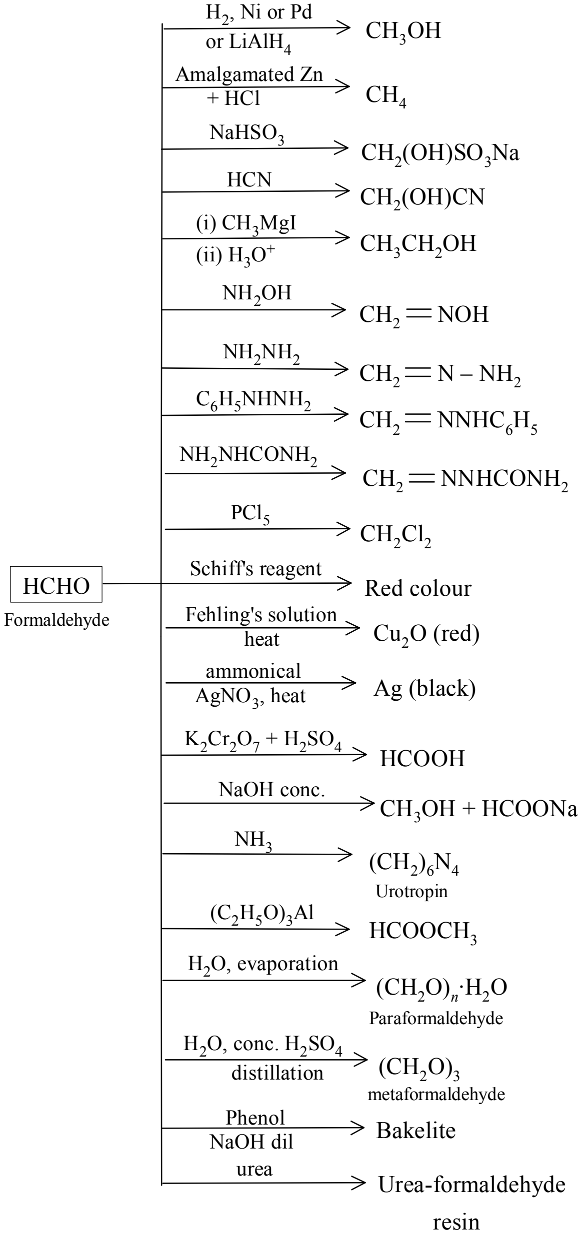
(b) $$\underset{\text{Gem. dihalide}}{R-CHX_2} \xrightarrow[\text{aq. NaOH or KOH}]{HOH} RCHO$$

(Note : Geminal dihalides with both the halogen atoms on the terminal carbon, give aldehydes.)

(c) $$\underset{\text{Grignard reagent}}{RMgX} \xrightarrow[\text{Formic ester}]{HCOOR'} RCHO$$

(d) $$\underset{\text{Calcium salt of fatty acid}}{(RCOO)_2Ca} + \underset{\text{calcium formate}}{(HCOO)_2Ca} \xrightarrow{\text{Dry distillaton}} \underset{\text{Aldehyde}}{RCHO}$$

- **Properties of formaldehyde**



- **Preparation of Ketones**

  They can be summarized as follows.

(a) $R_2CHOH \xrightarrow[\text{Acid } K_2Cr_2O_7]{\text{oxidation}}$

Sec. alcohol

(b) $R.CX_2.R \xrightarrow[\text{aq. NaOH or KOH}]{\text{HOH}}$

Gem. dihalide

(Note : Geminal dihalides with both the halogen atoms on the middle carbon only gives ketones)

(c) $RMgX \xrightarrow[\text{Alkyl cyanide or alkyl nitrile}]{\text{RCN}}$

Grignard reagent

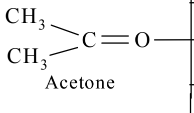
(d) $(RCOO)_2\,Ca \xrightarrow{\text{Dry distillaton}}$

Calcium salt of fatty acid

$\longrightarrow$ RCOR

Ketone

- **Properties of acetone**



Acetone

$$\xrightarrow[\text{or } LiAlH_4]{H_2\text{, Ni or Pd}} (CH_3)_2CH(OH)$$

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

$$\xrightarrow{NaHSO_3} (CH_3)_2C(OH)SO_3Na$$

$$\xrightarrow{HCN} (CH_3)_2C(OH)CN$$

$$\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgI} (CH_3)_3COH$$

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

$$\xrightarrow{NH_2NH_2} (CH_3)_2C=NNH_2$$

$$\xrightarrow{C_6H_5NHNH_2} (CH_3)_2C=NNHC_6H_5$$

$$\xrightarrow{NH_2NHCONH_2} (CH_3)_2C=NNHCONH_2$$

$$\xrightarrow{PCl_5} (CH_3)_2CCl_2$$

$$\xrightarrow{Cl_2} CCl_3COCH_3$$

$$\xrightarrow{I_2 + NaOH} CHI_3$$

$$\xrightarrow[\text{heat}]{\text{bleaching powder}} CHCl_3$$

$$\xrightarrow{HCl} \underset{\text{phorone}}{(CH_3)_2C=CHCOCH=C(CH_3)_2}$$

$$\xrightarrow{(BaOH)_2} \underset{\text{diacetone alcohol}}{(CH_3)_2C(OH)CH_2COCH_3}$$

$$\xrightarrow{\text{Schiff's reagent}} \text{No red colour}$$

$$\xrightarrow[\text{heat}]{\text{Fehling's solution}} \text{No reduction}$$

$$\xrightarrow[\text{silver nitrate}]{\text{ammonical}} \text{No reduction}$$

$$\xrightarrow[+ H_2SO_4 \text{ conc.}]{K_2Cr_2O_7} CH_3COOH + CO_2 + H_2O$$

$$\xrightarrow{NH_3} \text{Complex products}$$

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

$$\xrightarrow[\text{distill}]{\text{conc. } H_2SO_4} \underset{\text{Mesitylene}}{C_6H_3(CH_3)_3}$$

Condensation reactions

(a) Condensation with hydroxylamine (NH_2OH)

$$CH_3CH=O \xrightarrow{NH_2OH} \underset{\text{Acetaldoxime}}{CH_3CH=NOH}$$

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

(b) Condensation with phenylhydrazine ($C_6H_5NHNH_2$)

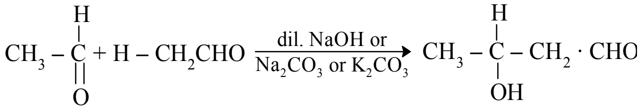
$$CH_3CH=O \xrightarrow{C_6H_5NHNH_2} \underset{\text{Acetaldehyde phenylhydrazone}}{CH_3CH=N\cdot NH\cdot C_6H_5}$$

$$(CH_3)_2C=O \xrightarrow{C_6H_5NHNH_2} \underset{\text{Acetone phenylhydrazone}}{(CH_3)_2C=N\cdot NH\cdot C_6H_5}$$

Note : Oximes and phenylhydrazones, being crystalline solids, are used to identify aldehydes and ketones

- **Aldol Condensation**

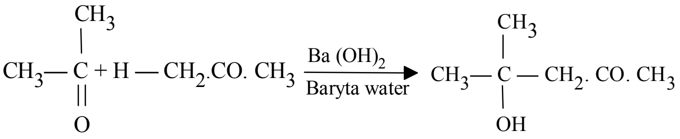
  This reaction is given only by aldehydes and ketones which contain α-hydrogen atom. When such aldehydes or ketones are treated with dil. alkali, two molecules undergo addition to give an aldol or a ketol respectively.



$$CH_3-\underset{\underset{O}{||}}{\overset{\overset{H}{|}}{C}}+H-CH_2CHO \xrightarrow[Na_2CO_3 \text{ or } K_2CO_3]{\text{dil. NaOH or}} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_2\cdot CHO$$

Two molecules of acetaldehyde

acetaldol or β-hydroxy butyraldehyde



$$CH_3-\underset{\underset{O}{||}}{\overset{\overset{CH_3}{|}}{C}}+H-CH_2.CO.\,CH_3 \xrightarrow[\text{Baryta water}]{Ba(OH)_2} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2.\,CO.\,CH_3$$

Two molecules of acetone

diacetone alcohol or β – hydroxy ketone

Note : Aldol condensation may occur between

(i) Two aldehyde molecules (same or different)

(ii) Two ketone molecules (same or different)

(iii) An aldehyde and a ketone

- **Cannizzaro's Reaction**

  Aldehydes which do not contain α-hydrogen atom can only give this reaction. Other aldehydes as well as ketones do not give this reaction. *e.g.* formaldehyde (HCHO) and benzaldehyde (C_6H_5CHO) give this reaction.

  The reaction is brought about by 50% aqueous or alcoholic alkali (NaOH or KOH). The reaction involves two molecules of aldehyde, one of them is reduced to a primary alcohol while the other is oxidized to an acid. In this case, reduction and oxidation take place simultaneously and called **base catalysed auto-redox reaction.**

$$\underset{\substack{\text{Formaldehye}\\ \text{(2 molecules)}}}{2HCHO} \xrightarrow[\text{50\% NaOH}]{\text{Warm}} \underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Formic acid}}{HCOOH}$$

Formic acid actually comes out in the form of its salt, *i.e.* sodium formate (HCOONa) due to the presence of alkali in the reaction mixture.

- **Reduction**

  Aldehydes and ketones on reduction give primary and secondary alcohols respectively. The common reducing agents used are

  (1) Hydrogen in the presence of finely divided Ni, Pt or Pd as catalyst.
  (2) Raney Nickel
  (3) Amalgams of Na, Mg or Zn and water or dil. acid.

$$RCHO \xrightarrow{\text{Redn.}} RCH_2OH \text{ (primary alcohol)}$$

$$R_2CO \xrightarrow{\text{Redn.}} R_2CHOH \text{ (secondary alcohol)}$$

Clemmensen's Reduction : Ketones on reduction with Zn amalgam and conc. HCl give alkanes, when $>C=O$ group is reduced to a —CH_2 — group

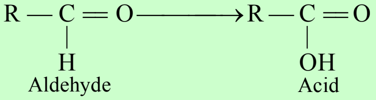
$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow[\text{conc. HCl}]{\text{Zn (Hg)}} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

Tests of aldehydes and ketones

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

Reducing properties of Aldehydes (Not given by ketones)

The H–atom on carbonyl group in aldehydes is readily oxidized to –OH group, hence aldehydes act as reducing agents.



$$\underset{\text{Aldehyde}}{R-\underset{\underset{\displaystyle H}{|}}{C}=O} \longrightarrow \underset{\text{Acid}}{R-\underset{\underset{\displaystyle OH}{|}}{C}=O}$$

In these reactions aldehyde is oxidized to a carboxylic acid. Aldehydes readily reduce

(a) Fehling's solution (b) Tollen's reagent and (c) Schiff's reagent

(a) With Fehling's Solution : It is an alkaline $CuSO_4$ solution containing Rochelle salt (sodium potassium tartarate). Aldehyde reduces it to give a red ppt. of cuprous oxide, (Cu_2O)

(b) With Tollen's Reagent : It is an ammoniacal $AgNO_3$ solution. It contains the complex ion, $[Ag(NH_3)_2]^+$. Aldehyde reduces it to give silver mirror, hence called as silver mirror test.

$$CH_3CHO + 2[Ag(NH_3)_2]OH \xrightarrow{\text{warm}} CH_3COONH_4 + 2Ag\downarrow + 3NH_3 + H_2O$$

(c) With Schiff's Reagent : It is *p*–rosaniline hydrochloride (Magenta dye) solution decolourized by passing SO_2 gas. Aldehyde restores the original pink colour of the reagent.