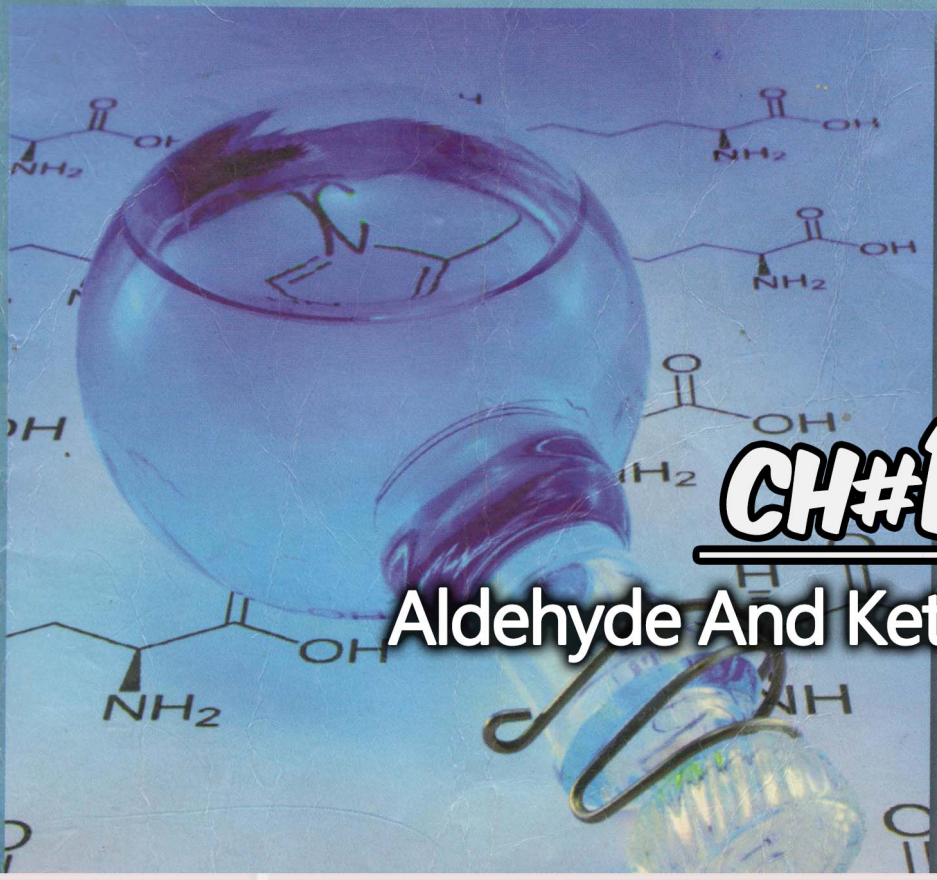
CHEMISTRY

12



CH#12

Aldehyde And Ketones

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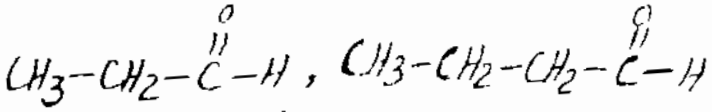
CHAPTER 12
ALDEHYDES AND KETONES

Organic Compounds Containing Carbonyl group ($>C=O$) are called Carbonyl Compounds. In aldehydes, the carbonyl group is bonded to at least one hydrogen atom. Its general formula is $R-\overset{O}{\overset{\|}{C}}-H$. e.g. $H-\overset{O}{\overset{\|}{C}}-H$, formaldehyde. In Ketones, the carbonyl group is bonded to two carbon atoms. Its general formula is $R-\overset{O}{\overset{\|}{C}}-R$ e.g. $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (acetone). The general molecular formula of aldehydes and ketones is $C_nH_{2n}O$

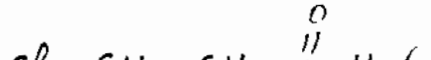
Nomenclature of Aldehydes

(a) Common Names:- The common name of an aldehyde is taken from its corresponding acid. The ending -ic acid is replaced by the word aldehyde. The position of substituents is indicated by Greek letters ($\alpha, \beta, \gamma, \delta$). The carbon adjacent to the carbonyl group is called α-carbon. Examples are given below

$H-\overset{O}{\overset{\|}{C}}-H$ (formaldehyde), $CH_3-\overset{O}{\overset{\|}{C}}-H$ (acetaldehyde)

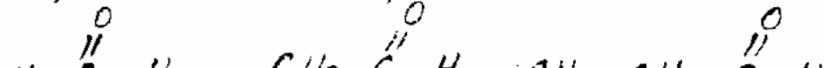


Propionaldehyde Butyraldehyde

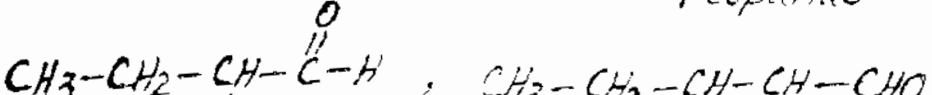


IUPAC Names:-

(i) The longest chain of carbon atoms containing $-\overset{O}{\overset{\|}{C}}-H$ group is selected.
(ii) Carbonyl Carbon is taken as Carbon No 1.
(iii) The ending -e of alkane is replaced with al
(iv) The position of side groups is indicated.

e.g 

Methanal Ethanal Propanal



2-Chlorobutanal 3-Hydroxy Pentanal

Ketones

(a) **Common Names:-** The word ketone is written after writing the names of two alkyl groups. The position of side groups is indicated by Greek letters (α, β, γ). The alkyl groups are written in alphabetical order.

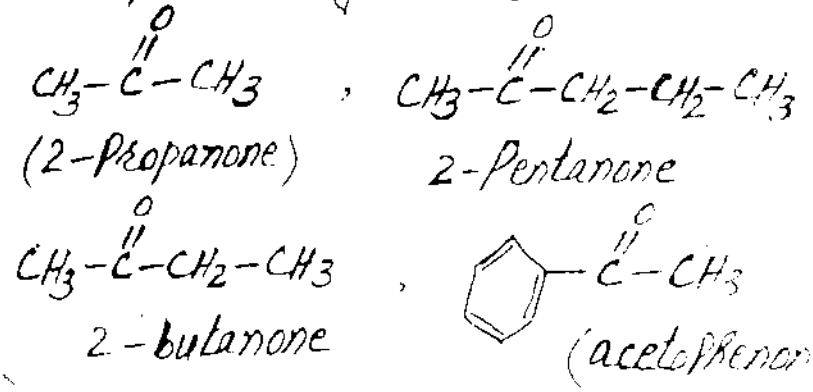
Dimethyl Ketone (Acetone) Ethyl methyl Ketone

If two alkyl groups in a ketone are same, the ketone is said to be **symmetrical**.
If two alkyl groups in a ketone are unlike, the ketone is said to be **un-symmetrical**.

IUPAC Names of Ketones:

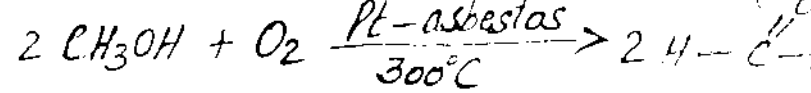
(i) The longest chain of carbon atoms containing Carbonyl group is choosen
(ii) Numbering is done from that end which is nearest to the Carbonyl group
(iii) The position of Carbonyl group and other side groups are indicated by numbers
(iv) The ending -e of alkane is replaced by "one"
(v) Aromatic ketones have no IUPAC names

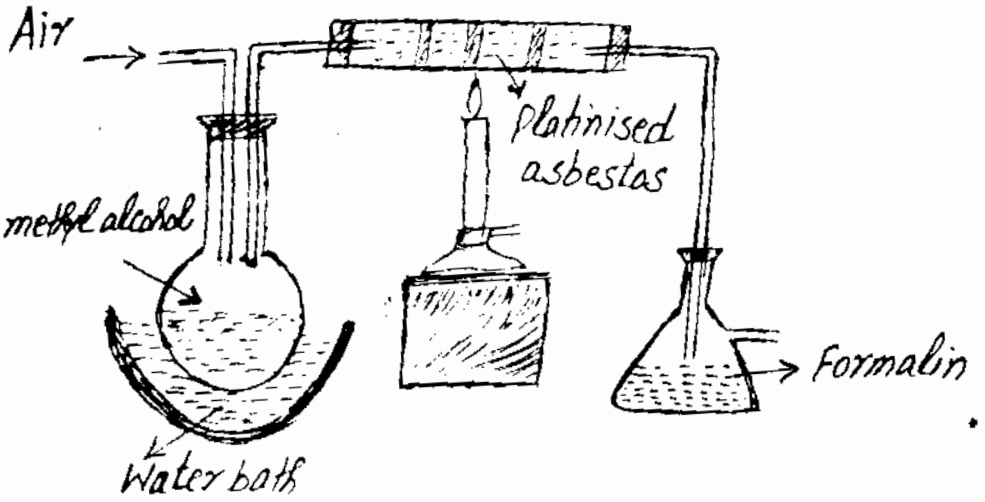
Examples are given below.



Formaldehyde

(i) Laboratory Preparation:- In the laboratory formaldehyde is prepared by following reaction





In this method methyl alcohol oxidises into formaldehyde which absorbs in water. The mixture of 40% formaldehyde, 8% methyl alcohol and 52% water is called **formalin**.

(iii) Industrial Preparation :- On industrial scale formaldehyde is prepared by passing mixture of methyl alcohol and air over a catalyst (Iron oxide - Molybdenum oxide or Silver)

$$2\,CH_3OH + O_2 \xrightarrow[500^\circ C]{FeO-MoO_3} 2\,H-\overset{O}{\overset{\|}{C}}-H + 2H_2O$$

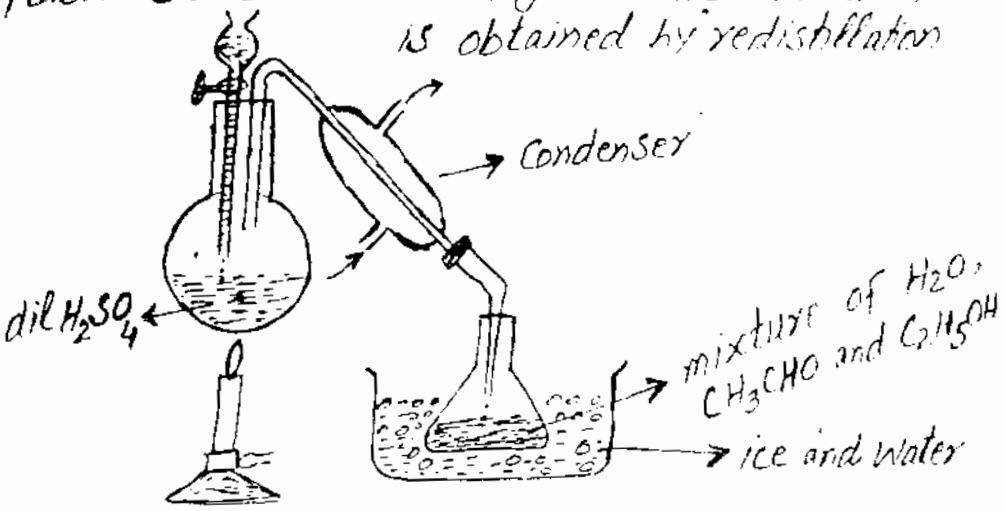
Acetaldehyde (CH_3CHO)

Laboratory Preparation:- In laboratory the acetaldehyde is prepared by following reaction

$$CH_3-CH_2OH + [O] \xrightarrow{Na_2Cr_2O_7+H_2SO_4} CH_3CHO + H_2O$$

The method is shown in figure. Dilute H_2SO_4 is taken in a flask. A mixture of ethyl alcohol and sodium dichromate is put in

the boiling H_2SO_4. A vigorous reaction takes place and acetaldehyde is formed. The mixture is distilled off. It is collected in a conical flask. It is shown in figure. Pure acetaldehyde is obtained by redistillation



Acetaldehyde is also prepared by dry distillation of mixture of Calcium formate and Calcium acetate.

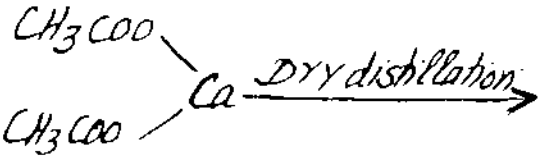
$$\begin{matrix} CH_3COO \\ | \\ Ca \\ | \\ CH_3COO \\ \text{Cal. Acetate} \end{matrix} + \begin{matrix} HCOO \\ | \\ Ca \\ | \\ HCOO \\ \text{Cal. formate} \end{matrix} \xrightarrow{\text{Heat}} 2CH_3CHO + 2CaCO_3$$

Industrial Preparation:- On industrial scale acetaldehyde is prepared by air oxidation of ethylene using Palladium Chloride as catalyst and Cupric Chloride as a Promoter

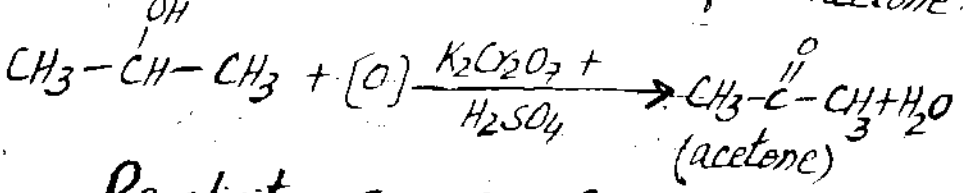
$$2CH_2=CH_2 + O_2 \xrightarrow[\text{Water}]{PdCl_2 + CuCl_2} 2CH_3CHO$$

Preparation of Acetone

(i) Dry distillation of Calcium acetate gives acetone

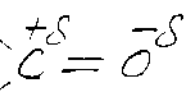


(ii) Oxidation of Sec-propyl alcohol gives acetone.



Reactivity of Carbonyl Group

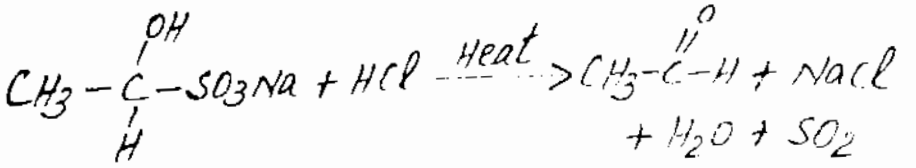
The Carbonyl group has a σ-bond and a π-bond. Thus it shows addition reactions. Because oxygen is more electronegative than Carbon. So oxygen has partial negative charge and Carbon has partial positive charge. Therefore Oxygen shows nucleophilic character and Carbon shows electrophilic character. It is shown as



Nucleophilic Addition Reactions of Aldehydes and Ketones.

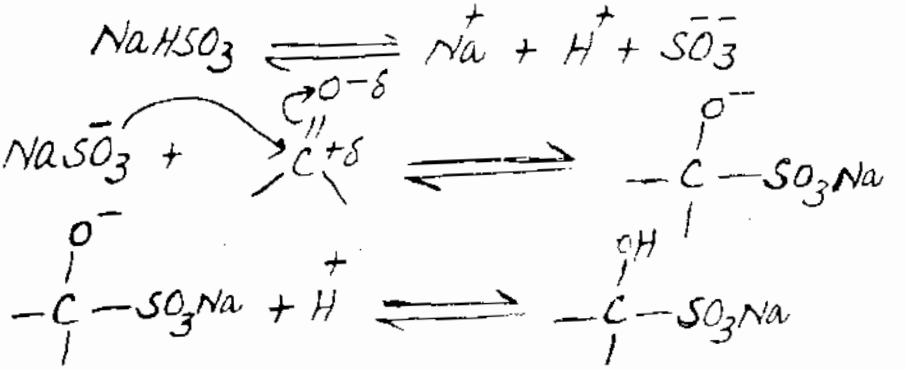
Carbonyl Compounds have Polarity. So they Can be attacked by a nucleophile or by an electrophile to give an addition Product.

This bisulphite adduct can regenerate the parent aldehyde or ketone



By this reaction we can separate and purify Carbonyl and non-Carbonyl compounds.

Mechanism:- Sodium bisulphite ionises in



Bisulphite adduct

Ketones without methyl group do not react with Sodium bisulphite.

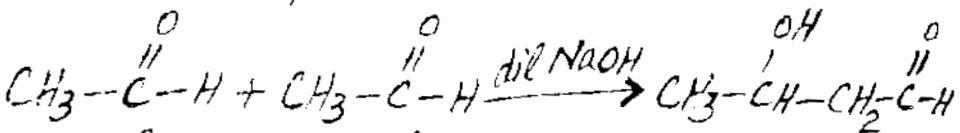
Condensation Reactions

The reaction in which two same or different molecules combine to form new compound with or without removal of water molecules is called Condensation Reaction.

e.g Aldol Condensation, Condensation of Carbonyl compounds with NH_3 and its derivatives

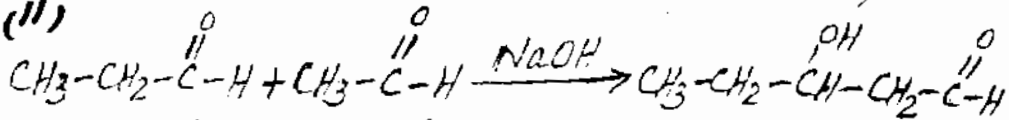
V. Imp **Aldol Condensation**

Two molecules of aldehydes or ketones having α – hydrogen condense together and form β-hydroxy aldehyde or ketone. It takes place in presence of a base. It is called Aldol condensation. The name "Aldol" is combination of words aldehyde and alcohol, the two functional groups present in the product. Examples are given below. (i) Two molecules of ethanal (acetaldehyde) give 3-hydroxybutanal



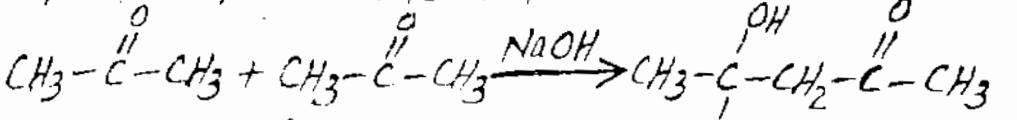
Ethanal Ethanal 3-hydroxybutanal (Aldol)

(ii)



Propanal Ethanal 3-hydroxy Pentanal (aldol)

(iii) Two molecules of propanone (acetone) give 4-Hydroxy-4-methyl-2-pentanone.



Propanone Propanone 4-hydroxy-4 methyl-2-pentanone

An aldol product loses water on heating to give an unsaturated aldehyde or ketone. e.g

$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[Heat]{dil\ HCl} CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H + H_2O$$

3-Hydroxybutanal — Crotonaldehyde

Mechanism:- The base $\bar{O}H$ ion removes a Proton from α-Carbon of aldehyde to form a Carbanion.

(i) $$\bar{O}H + H\text{-}CH_2-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons \bar{C}H_2-\overset{O}{\overset{\|}{C}}-H + H_2O$$

(Carbanion)

The Carbanion reacts another molecule of aldehyde to form an alkoxide ion

(ii) $$CH_3-\overset{O}{\overset{\|}{C}}-H + \bar{C}H_2-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons CH_3-\underset{O^-}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-$$

(An alkoxide ion

The alkoxide ion removes a Proton from Water

$$CH_3-\underset{O^-}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H + H_2O \longrightarrow CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H +$$

(aldol)

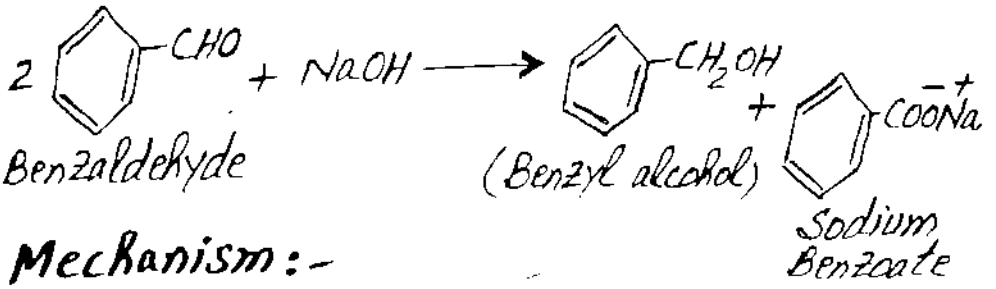
Cannizzaro's Reaction

Two molecules of aldehydes which do not Cont α-Hydrogen react with 50% NaOH and form a mixture of alcohol and acid. It is Called Cannizzaro's reaction. It is also Called Self oxidation-reduction of aldehyd

Examples are given below.

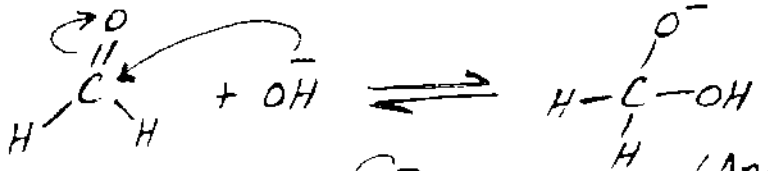
$$2\,HCHO + NaOH \longrightarrow CH_3OH + HCOO^-Na^+$$

Formaldehyde — Methanol — Sod. formate

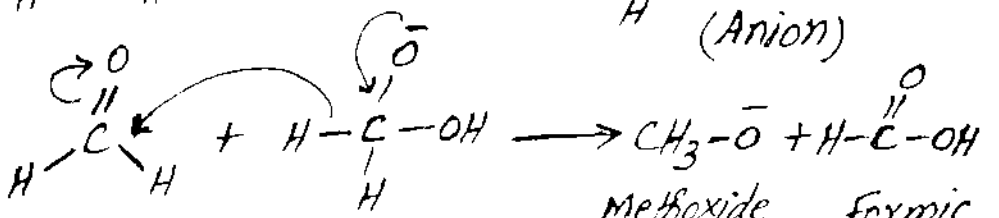


Benzaldehyde — (Benzyl alcohol) — Sodium Benzoate

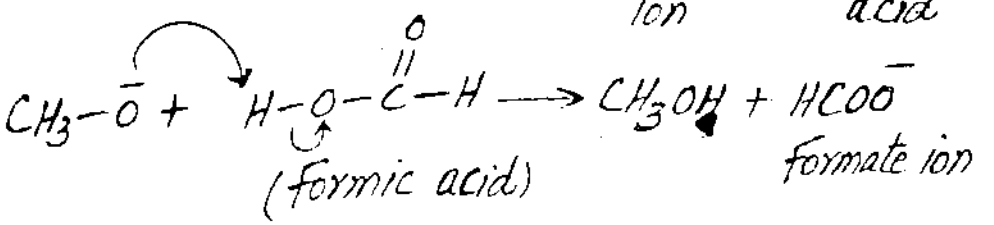
Mechanism:-



(Anion)



Methoxide ion — Formic acid



(formic acid) — Formate ion

$$HCOO^- + NaOH \longrightarrow HCOONa + OH^-$$

Sodium formate

Haloform Reaction:- Acetaldehyde or any methyl ketone reacts with halogens and aqueous NaOH to give haloform (CHX_3) It is called haloform reaction.

Examples are given below.

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3X_2 + 4NaOH \longrightarrow CHX_3 + RCOONa + 3NaX + 3H_2O$$

(Haloform) Sodium Carboxylate

$$CH_3-\overset{O}{\overset{\|}{C}}-H + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$$

acetaldehyde — Iodoform — Sod. Formate

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$$

acetone — Iodoform — Sod. acetate

A secondary alcohol also gives haloform reaction.

$$R-\overset{OH}{\underset{|}{C}}H-CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + RCOONa + 3NaI + 3H_2O$$

(Sod. Carboxylate)

Iodoform Test:- The haloform reaction using iodine and aqueous NaOH is called iodoform test. In iodoform test, Yellow Precipitates(ppt) of iodoform are formed. e.g

$$C_2H_5OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + HCOONa + 5H_2O + 5NaI$$

(Iodoform)

Iodoform test is very important.

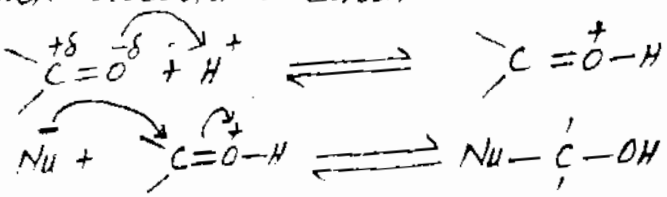
(i) By iodoform test we distinguish between methyl ketone and anyother ketone.

(ii) By iodoform test we distinguish between Ethyl alcohol and methyl alcohol.

(iii) By iodoform test we can distinguish between acetaldehyde and any other aldehyde

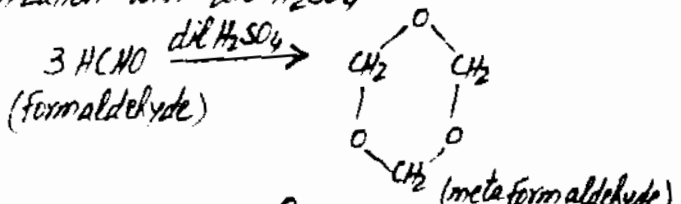
Acid Catalysed Addition Reactions

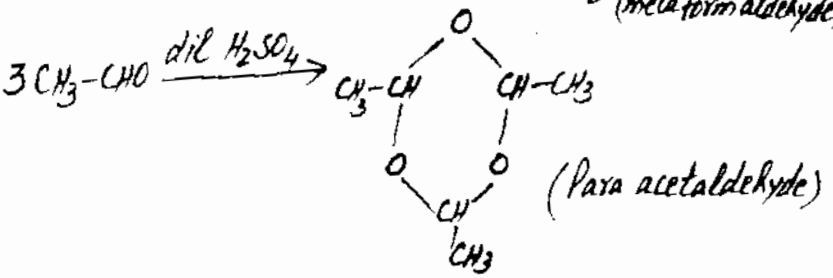
An acid catalysed addition reaction takes place with a weak nucleophile. The proton of an acid combines with Carbonyl oxygen and increases electrophillic Character of Carbonyl Carbon. Therefore a weak nucleophile can attack electrophilic Carbon.



Acid catalysed addition reactions of aldehydes and Ketones are given below.

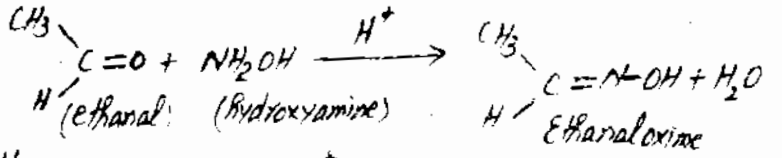
(1) **Polymerization** :- Formaldehyde and acetaldehyde show polymerization with dil H_2SO_4.

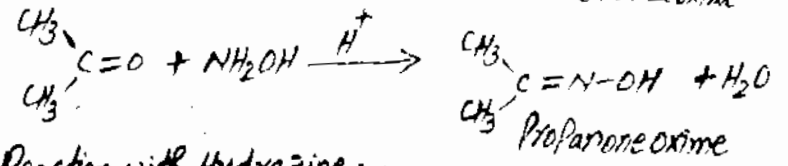




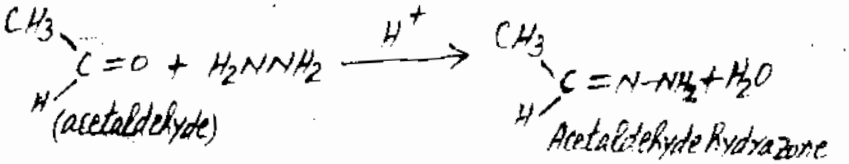
(2) **Addition of Ammonia derivatives** ($G-NH_2$)
The aldehydes and Ketones react with ammonia derivative ($G-NH_2$) to form an addition product with elimination of water molecule. The Product contains the group $>C=N-G$. It is called condensation or addition – elimination reaction

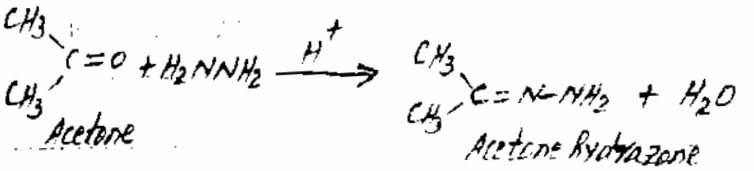
(i) Reaction with Hydroxylamine :- Aldehydes and Ketones react with Hydroxylamine to give Oxime in Presence of an acid.



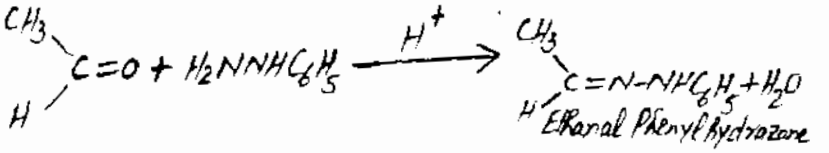


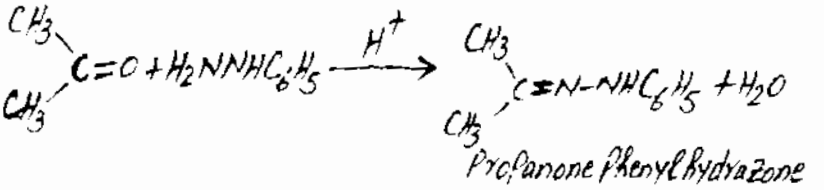
(ii) Reaction with Hydrazine :-
Aldehydes and Ketones react with Hydrazine (H_2NNH_2) to form Hydrazones in Presence of an acid.





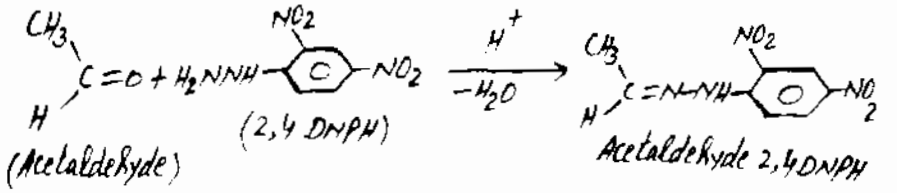
(iii) Reaction with Phenyl Hydrazine ($H_2NNHC_6H_5$)
Aldehydes and Ketones react with Phenyl Hydrazine to form Phenyl Hydrazones in the Presence of an acid.

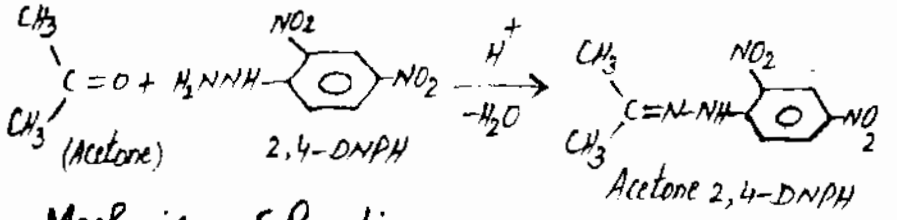




(iv) **Reaction with 2,4 dinitrophenyl hydrazine (2,4-DNPH)**

Aldehydes and ketones react with 2,4 dinitrophenylhydrazine to form 2,4 dinitrophenyl hydrazones in presence of an acid.

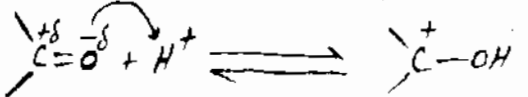




Mechanism of Reaction:-

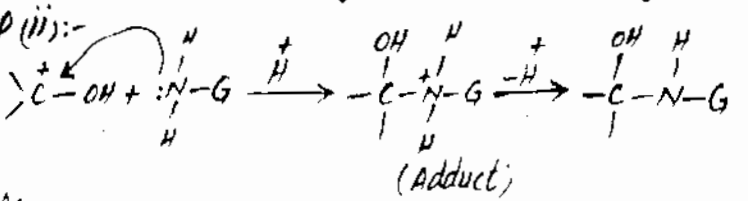
The mechanism of the reaction of Ammonia derivatives with aldehydes and ketones is given below.

Step (i)



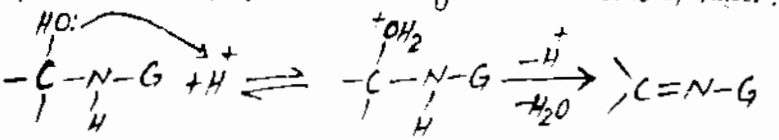
It is protonation of oxygen of carbonyl oxygen

Step (ii):-



It is formation of adduct and its deprotonation

Step (iii) It is protonation of oxygen and removal of water.



Reduction of Aldehydes and Ketones:-

Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols

(i) **Reduction with Sodium Borohydride ($NaBH_4$)**

Aqueous or alcoholic solution of aldehyde or ketone is reduced by $NaBH_4$.

$$H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaBH_4} CH_3OH$$
(Methanal) (Methanol)

$$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaBH_4} CH_3-CH_2-OH$$
(Ethanal) (Ethanol)

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NaBH_4} CH_3-\overset{OH}{\overset{|}{C}}H-CH_3$$
Propanone 2-Propanol

$NaBH_4$ reduces Carbon–oxygen double bond but not Carbon–Carbon multiple bond.

Mechanism:- $BH_4^- \longrightarrow BH_3 + H^-$ (hydride ion)

$$H^- + \overset{\delta+}{C}=\overset{\delta-}{O} \longrightarrow H-\overset{|}{\underset{|}{C}}-O^-$$

$$H-\overset{|}{\underset{|}{C}}-O^- + \overset{\delta+}{H}-\overset{\delta-}{O}H \longrightarrow H-\overset{|}{\underset{|}{C}}-OH + OH^-$$
(An alkoxide) (An alcohol)

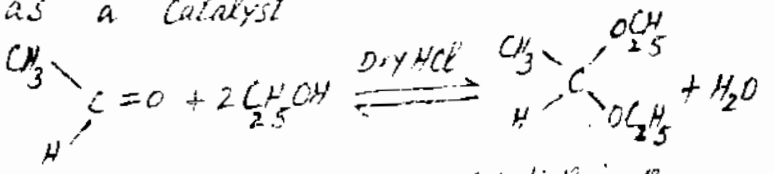
(ii) **Catalytic Reduction:-** Aldehydes and ketones show reduction with H_2 in presence of Pd, Pt or Ni.

$$H-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow{Pd,\ Pt\ or\ Ni} CH_3OH$$

$$CH_3-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow{Pd,\ Pt\ or\ Ni} CH_3-CH_2OH$$

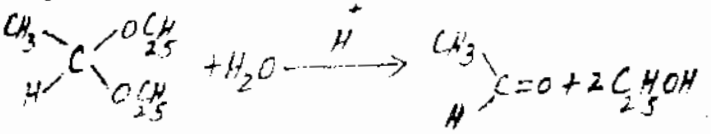
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2 \xrightarrow{Pd,\ Pt\ or\ Ni} CH_3-\overset{OH}{\overset{|}{C}}H-CH_3$$
2-Propanol

Addition of alcohols:- Aldehydes combine with alcohols to form acetals. Here dry HCl gas acts as a catalyst

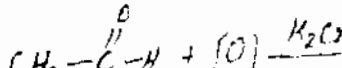


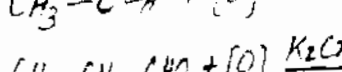
1,1 diethoxyethane (An acetal)

The hydrolysis of acetal regenerates aldehyde.



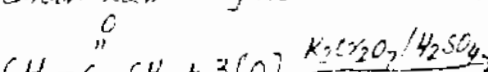
Oxidation of aldehydes:- Aldehydes are easily oxidised to carboxylic acids. Here H-atom attached to the carbonyl group is oxidised to OH group. Tollen's reagent, Fehling's solution and Benedict's solution are mild oxidising agents. The $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$ and Nitric acid are strong oxidising agents





Propanoic acid

Oxidation of Ketones:- Ketones are not oxidised by mild oxidising agent because their oxidation involves breaking of Carbon – Carbon bond. They are oxidised only by strong oxidising agents. In Ketones only Carbon atom adjacent to Carbonyl group is oxidised



(acetic acid) (formic acid)

In symmetrical ketones only one carbon atom adjacent to carbonyl group is oxidised and mixture of acids is obtained. In un-symmetrical ketones, the C-atom joined to smaller number of H-atoms is oxidised and carbonyl group remains with smaller alkyl group

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + 3[O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} 2CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Identification of Carbonyl Compounds
(Detection Tests for aldehydes and Ketones)

(i) 2,4-DNPH Test:- Aldehydes and ketones form yellow or red precipitates with 2,4 dinitrophenyl hydrazine solution.

(ii) Sodium Bisulphite Test:- Aldehydes and methyl ketones form white crystalline ppt with saturated $NaHSO_3$ solution

(iii) Tollen's Test:- Ammoniacal solution of silver nitrate is called Tollen's reagent. Add Tollen's reagent to an aldehyde in a test tube and warm. A silver mirror is formed on the inside of test tube. It is called **Silver Mirror Test**. High quality mirrors are manufactured by this principle. Ketones do not give this test.

$$AgNO_3 + 3NH_4OH \longrightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + H_2O$$

$$R-CHO + 2[Ag(NH_3)_2]OH \longrightarrow RCOONH_4 + 2NH_3 + 2Ag + H_2O$$

(An aldehyde) (Tollen's reagent)

(iv) Fehling Solution Test:- An alkaline solution which contains cupric tartarate complex ions is called Fehling's Solution. Aliphatic aldehydes form a brick-red precipitate with Fehling's solution. Add Fehling's solution

to an aldehyde solution and boil. A brick red precipitates of Cuprous Oxide are formed.

$$RCHO + 2\,Cu(OH)_2 + NaOH \longrightarrow RCOONa + Cu_2O + 3H_2O$$
(Brick red ppt)

Ketones do not give this test.

(V) **Benedict's Solution Test:-** An alkaline solution which contains Cupric Citrate complex ions is called Benedict's Solution. Aliphatic aldehydes form brick red precipitates with Benedict's solution. Add Benedict's Solution to an aldehyde solution and boil. A brick red ppt of Cuprous Oxide are formed. Ketones do not give this test.

$$RCHO + 2\,Cu(OH)_2 + NaOH \longrightarrow RCOONa + Cu_2O + 3H_2O$$
(Brick red ppt)

(Vi) **Sodium Nitroprusside test,** $Na_2[Fe(CN)_5NO]$

When Sodium nitroprusside solution is added to a ketone, then wine red or orange-red colour is produced. Aldehydes do not give this test.

Uses of formaldehyde:-

1:- Formaldehyde is used in Silvering of mirrors.
2:- It is used for Preparation of anti-polio vaccine
3:- It is used in tanning of hides
4:- It is used for Preparation of dyes e.g Indigo
5:- It is used for manufacture of Plastics and resins. e.g bakelite

6:- Formamint (formaldehyde + Lactose) is used as throat lozenges(گلے کی گولیاں).

7:- **Formalin** is mixture of 40% formaldehyde, 8% methyl alcohol and 52% water. It is used as an antiseptic, germicide, a fungicide, disinfectant It is also used for preserving (محفوظ کرنا) animal specimen and also as sterilizer.

Uses of Acetaldehyde:-

1:- It is used in Silvering of mirrors.

2:- It is used as an antiseptic in nasal infection

3:- It is used to prepare drugs and resins

4:- Acetaldehyde - ammonia complex is used as a rubber accelerator

5:- Acetaldehyde is used for the preparation of a large number of Chemicals e.g Acetic acid, Ethanol, n-butanol, Vinyl acetate, ethyl acetate acetic anhydride etc.

6:- Acetaldehyde is used to make Chloral hydrate, ethanal trimer and ethanal tetramer.

The Chloral hydrate and ethanal trimer are used as hypnotic drugs (نیند آور دوائیں). The ethanal tetramer is used as a slug poison (گھونگے مارنے کی دوا)

EXERCISE

Q1. *Fill in the Blanks.*

(i) Aldehydes are the first oxidation product of_____.
(ii) Ketones are the first oxidation product of_____.
(iii) Aldehydes and ketones undergo_____addition reactions.
(iv) Formaldehyde reacts with_____to give primary alcohol.
(v) Acetaldehyde reacts with_____to give 2-butanol.
(vi) Aldehydes are strong_____agents.
(vii) The oxidation of an_____always gives a carboxylic acid.
(viii) The reduction of a _____always gives a secondary alcohol.
(ix) Formaldehyde gives_____test with Tollen's reagent.
(x) Acetaldehyde gives a_____precipitate with Fehling's solution.

Answer:- (i) primary alcohol (ii) secondary alcohol (iii) nucleophilic
(iv) Grignard's reagent (v) C_2H_5-MgBr (vi) reducing
(vii) aldehyde (viii) ketones (ix) silver mirror (x)brick red

Q2. *Indicate True or false.*

(i) Formaldehyde is used in the silvering of mirrors.
(ii) Ketones combine with alcohols in the presence of HCl gas to form acetals.
(iii) Acetaldehyde undergoes cannizzaro's reaction.
(iv) Formaldehyde is used to prepare urotropine.
(v) Aldol condensation reaction is given by only those aldehydes and ketones which contain α-hydrogen atom.
(vi) Cannizzaro's reaction is given by only those aldehydes containing no α-hydrogen atom.
(vii) Propanal and propanone behave differently with Tollen's reagent.
(viii) Acetone reacts with sodium bisulphite to give a yellow crystalline product.
(ix) Acetone on reduction gives a primary alcohol.
(x) 40% aqueous solution of formaldehyde is called formalin.

Answer:- (i) true (ii) false (iii) false (iv) true (v) true
(vi) true (vii) true (viii) false (ix) false (x) true

Q3. Multiple Choice Questions. Encircle the correct answer.

(i) The carbon atom of a carbonyl group is.
(a) sp-hybridized (b) sp^2-hybridized
(c) sp^3 hybrizided (d) none of these.

(ii) Formalin is
(a) 10% solution of formaldehyde in water.
(b) 20% solution of formaldehyde in water.
(c) 40% solution of formaldehyde in water.
(d) 60% solution of formaldehyde in water.

(iii) Which of the following will have the highest boiling point?
(a) Mathanal (b) Ethanal (c) Propanal (d) 2-Hexanone

(iv) Ketones are prepared by the oxidation of
(a) Primary alcohol (b) Secondary alcohol
(c) Tertiary alcohol (d) None of these

(v) Acetone reacts with HCN to form a cyanohydrin. It is an example of.
(a) Electrophilic addition (b) Electrophilic substitution
(c) Nucleophilic addition (d) Nucleophilic substitution

(vi) Which of the following compounds will not give iodoform test on treatment with I_2/NaOH.
(a) Acetaldehyde (b) Acetone (c) Butanone (d) 3-Pentanone

(vii) Which of the following compounds will react with Tollen's reagent.

(a) $CH_3-\overset{O}{\overset{\|}{C}}-H$ (b) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(c) $CH_3-\overset{O}{\overset{\|}{C}}-OH$ (d) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

(viii) Cannizzaro's reaction is not given by
(a) Formaldehyde (b) Acetaldehyde
(c) Benzaldehyde (d) Trimethylacetaldehyde

(ix) Which of the following reagents will react with both aldehydes and ketones?
(a) Gringnard reagent (b) Tollen's reagent
(c) Fehling's reagent (d) Benedict's reagent

Answer:- (i) b (ii) c (iii) d (iv) b (v) c
(vi) d (vii) a (viii) b (ix) a

Q4. **Give one laboratory and one industrial method for the preparation of formaldehyde.**

Answer:- see page No. 173, 174

Q5. **How does formaldehyde react with the following reagents?**
(i) CH_3MgI (ii) HCN (iii) $NaHSO_3$
(iv) conc. NaOH (v) $NaBH_4/H_2O$ (vi) Tollen's reagent.
(vii) Fehling's reagent.

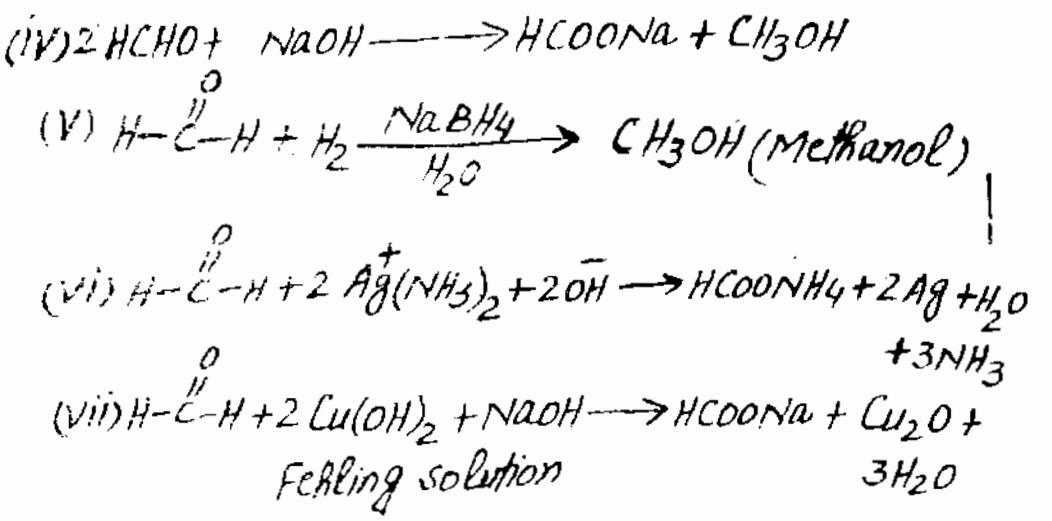
Answer:- (i) $CH_3-MgI + H-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\underset{H}{\overset{H}{C}}-\overset{-}{O}\overset{+}{M}gI$

$$CH_3-CH_2-\overset{-}{O}\overset{+}{M}gI + H_2O \xrightarrow{HCl} CH_3-CH_2OH + Mg\begin{smallmatrix} I \\ OH \end{smallmatrix}$$

(ii) $H-\overset{O}{\overset{\|}{C}}-H + HCN \longrightarrow H-\underset{CN}{\overset{OH}{C}}-H$

(formaldehyde) Cyanohydrin

(iii) $H-\overset{O}{\overset{\|}{C}}-H + NaHSO_3 \longrightarrow H-\underset{H}{\overset{OH}{C}}-SO_3Na$



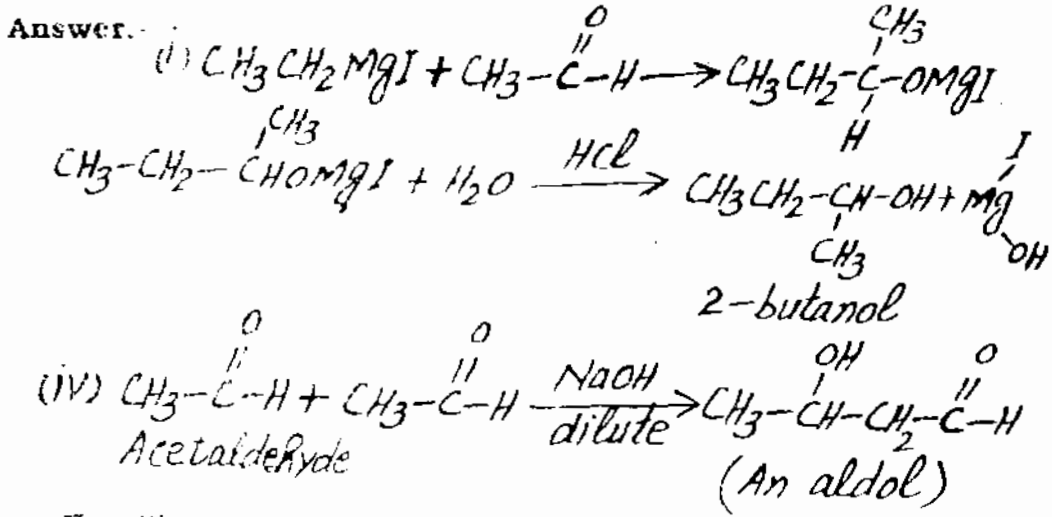
Q6. Give one laboratory and one industrial method for the preparation of acetaldehyde.

Answer:- see page No. 174, 175

Q7. How does acetaldehyde react with the following reagents?

(i) C_2H_5MgI (ii) HCN (iii) $NaHSO_3$
(iv) dilute NaOH (v) $I_2/NaOH$ (vi) $NaBH_4/H_2O$
(vii) NH_2OH (viii) $K_2Cr_2O_2/H_2SO_4$

Answer:-



For (iii), (v), (vi), (vii), (viii) see page No. 177, 178

Q8. Describe briefly the mechanism of nucleophilic addition to a carbonyl compound.

Answer:- see page No. 176, 177

Q9. Explain with mechanism the addition of ethylamagnesium bromide to acetaldehyde. What is the importance of this reaction?

Answer:- see page No. 135

Q10. Explain with mechanism the addition of sodium bisulphite to acetone. What is the utility of this reaction?

Answer:- see page No. 179

Q11. Describe with mechanism aldol condensation reaction. Why formaldehyde does not give this reaction?

Answer:- see page No. 180

Q12. What types of aldehydes give Cannizzaro's reaction? Give its mechanism

Answer:- see page No. 181

Q13. Explain the mechanism of the reaction of phenylhydrazine with acetone.

Answer:- see page No. 185

Q14. Using ethyne as a starting material how would you get acetaldehyde, acetone and ethyl alcohol?

Answer:-

(i) $CH \equiv CH + H_2O \xrightarrow[HgSO_4]{10\%\ H_2SO_4} CH_2=CHOH$ (vinyl alcohol)

$CH_2=CHOH \xrightarrow{Rearrange} CH_3-CHO$

(ii) $CH \equiv CH + H_2O \xrightarrow[HgSO_4]{10\%\ H_2SO_4} CH_2=CHOH$ (Acetylene)

$CH_2=CHOH \xrightarrow{rearrangement} CH_3-CHO$

$CH_3CHO + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$ (Acetic acid)

$2CH_3COOH + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca + 2H_2O$

$(CH_3COO)_2Ca \xrightarrow[Dry]{Distillation} CaCO_3 + CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (acetone)

(iii) $CH \equiv CH + H_2 \xrightarrow[BaSO_4]{Pd} CH_2 = CH_2$

$CH_2 = CH_2 + HBr \longrightarrow CH_3 - CH_2Br$

$CH_3 - CH_2Br + KOH \xrightarrow{Aq} CH_3 - CH_2OH + KBr$

Q15. Give the mechanism of addition of HCN to acetone.

Answer:- see page No. 178

Q16. How would you bring about the following conversion?

(i) Acetone into t-Butyl alcohol.
(ii) Propanal into 1-propanol
(iii) Propanone into 2-propanol
(iv) Methanal into ethanal
(v) Ethanal into propanone
(vi) Ethanal into 2 propanol
(vii) Ethyne into ethanal
(viii) Ethene into ethanal
(ix) Ethanal into ethanol
(x) Ethanol into 2-Butanone
(xi) Methanol into ethanal
(xii) Ethanol into ethanoic acid

Answer:- (i) Acetone into t-Butyl alcohol

$$CH_3MgBr + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O^{-}Mg^{+}Br$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OMgBr + H_2O \xrightarrow{HCl} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + Mg\begin{matrix}Br\\OH\end{matrix}$$

t-Butyl alcohol

(ii) Propanal into 1-Propanol:-

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}H + H_2 \xrightarrow{NaBH_4} CH_3-CH_2-CH_2OH$$

Propanal — 1-Propanol

(iii) Propanone into 2-Propanol

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2 \xrightarrow{NaBH_4} CH_3-\overset{OH}{\underset{H}{C}}-CH_3$$

2-Propanol

(iv) Methanal into Ethanal:-

$$CH_3MgBr + H-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-CH_2O^{-}Mg^{+}Br$$

$$CH_3-CH_2OMgBr + H_2O \xrightarrow{HCl} CH_3CH_2OH + Mg\begin{matrix}Br\\OH\end{matrix}$$

$$CH_3-CH_2-OH + [O] \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} CH_3-CHO + H_2O$$

(Ethanal)

(v) Ethanal into Propanone

$$CH_3CHO + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$$

$$2\,CH_3COOH + Ca(OH)_2 \longrightarrow \begin{matrix}CH_3COO\\CH_3COO\end{matrix}Ca + 2H_2O$$

$$\begin{matrix}CH_3COO\\CH_3COO\end{matrix}Ca \xrightarrow[Dry]{Distillation} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CaCO_3$$

Propanone

(vi) Ethanal into 2-Propanol

$$CH_3MgBr + CH_3-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{-}{O}\overset{+}{M}gBr$$

$$CH_3-\underset{CH_3}{\overset{|}{CH}}-OMgBr + H_2O \xrightarrow{HCl} CH_3-\underset{CH_3}{\overset{|}{CH}}-OH + Mg\begin{matrix}Br\\OH\end{matrix}$$

(2-Propanol)

(vii) Ethyne into Ethanal :-

$$CH\equiv CH + H_2O \xrightarrow[HgSO_4]{10\%\ H_2SO_4} CH_2=CHOH \text{ (vinyl alcohol)}$$

$$CH_2=CHOH \xrightarrow{Rearrange} CH_3-CHO \text{ (Ethanal)}$$

(viii) Ethene into Ethanal

$$CH_2=CH_2 + H_2O \xrightarrow[HgSO_4]{10\%\ H_2SO_4} CH_3-CH_2OH$$

$$CH_3-CH_2OH + [O] \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} CH_3-CHO + H_2O$$

(Ethanal)

(ix) Ethanal into Ethanol :-

$$CH_3-CHO + H_2 \xrightarrow{NaBH_4} CH_3-CH_2OH$$

(x) Ethanol into 2-Butanone

$$CH_3-CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O$$

$$CH_3-CH_2MgBr + CH_3-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H\bar{O}\overset{+}{M}gBr$$

$$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H\bar{O}\overset{+}{M}gBr + H_2O \xrightarrow{HCl} CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H-OH + Mg\overset{Br}{\underset{OH}{}}$$

$$CH_3-CH_2-\overset{OH}{\overset{|}{C}}H-CH_3 + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$$

2-butanol

(xi) Methanol into Ethanal.

$$CH_3OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} H-\overset{O}{\overset{\|}{C}}-H + H_2O$$

$$CH_3MgBr + H-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\overset{H}{\overset{|}{C}}-\bar{O}\overset{-+}{M}gBr$$

$$CH_3-CH_2-\bar{O}\overset{-+}{M}gBr + H_2O \xrightarrow{HCl} \overset{H}{CH_3CH_2OH} + Mg\overset{Br}{\underset{OH}{}}$$

$$CH_3-CH_2-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-CHO + H_2O$$

(Ethanal)

(xii) Ethanol into Ethanoic acid.

$$CH_3-CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-CHO + H_2O$$

$$CH_3CHO + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$$

(Ethanoic acid)

Q17. How will you distinguish between,.

(i) Methanal and ethanal
(ii) Ethanal and propanone
(iii) Ethanal and propanal
(iv) Acetone and ethyl alcohol
(v) Butanone and 3-pentanone
(vi) Acedaldehyde and benzaldehyde
(vii) 2-Pentanone and 3-pentanone

Answer:- (i) Ethanal gives iodoform test but methanal does not give iodoform test.

$$CH_3-CHO + 3I_2 + 4NaOH \longrightarrow \underset{\text{(Iodoform)}}{CHI_3} + HCOONa + 3NaI + 3H_2O$$

ethanal

$$HCHO + I_2 + NaOH \longrightarrow \text{No reaction}$$

(ii) Ethanal gives red ppt with Fehling solution but Propanone does not give this test.

$$CH_3-CHO + 2Cu(OH)_2 + NaOH \longrightarrow \underset{\text{(Fehling solution)}}{} CH_3COONa + \underset{\text{Red ppt}}{Cu_2O} + H_2O$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + \text{Fehling Solution} \longrightarrow \text{No Reaction}$$

(iii) Ethanal gives iodoform test but Propanal does not give iodoform test.

$$CH_3CHO + 3I_2 + 4NaOH \longrightarrow \underset{\text{(Iodoform)}}{CHI_3} + HCOONa + 3NaI + 3H_2O$$

$$CH_3CH_2CHO + 3I_2 + 4NaOH \longrightarrow \text{No reaction}$$

(iv) Acetone gives white ppt with $NaHSO_3$ and Ethanol does not give this test.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + NaHSO_3 \longrightarrow \underset{\text{White ppt}}{CH_3-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-SO_3Na}$$

$$CH_3CH_2OH + NaHSO_3 \longrightarrow \text{No reaction}$$

(v) Butanone gives iodoform test but 3-pentanone does not give iodoform test.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3CH_2COONa + 3NaI + 3H_2O$$

2-Butanone (iodoform)

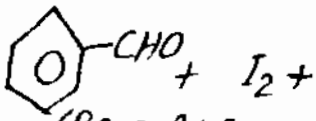
$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + I_2 + NaOH \longrightarrow \text{NO reaction}$$

3-Pentanone

(vi) Acetaldehyde gives iodoform test but benzaldehyde does not give iodoform test.

$$CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$$

(iodoform)



(Benzaldehyde)

(vii) 2-Pentanone (Methyl Ketone) gives iodoform test but 3-pentanone does not give iodoform test.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3CH_2CH_2COONa + 3NaI + 4H_2O$$

2-Pentanone

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + I_2 + NaOH \longrightarrow \text{NO Reaction}$$

3-Pentanone

Q18. Discuss oxidation of (a) aldehydes (b) ketones with:

(i) $K_2Cr_2O_7/H_2SO_4$ **(ii)** Tollen's reagent

(iii) Fehling's solution

Answer:- see page No. 188, 189

Q19. Discuss reduction of (a) aldehydes (b) ketones with

(a) $NaBH_4/H_2O$ (ii) H_2/Pd

Answer:-

Q20. Give three uses for each of formaldehyde and acetaldehyde.

Answer:- see page No. 190, 191

$CH_3-CH_2-CH_2-O-CH_2-CH_3$

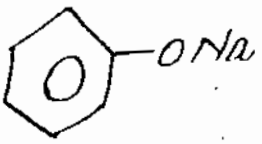
Ethyl, n-Propyl ether.

(b) Methoxy ethane $CH_3-O-CH_2-CH_3$

(ii) ethoxybenzene $CH_3-CH_2-O-C_6H_5$

(iii) Sodium Ethoxide $CH_3-CH_2-\bar{O}\overset{+}{N}a$

(iv) Sodium Phenoxide

$C_6H_5\bar{O}\overset{+}{N}a$ OR 

(v) Propoxy Propane

$CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$

گلدستہ ڈاٹ پی کے کی جانب سے خوش آمدید

السلام علیکم ورحمتہ اللہ وبرکاتہ

مختصر تعارف

کافی عرصہ سے خواہش تھی کہ ایک ایسی ویب سائٹ بناؤں جس پر طالب العلموں کیلئے کچھ تعلیمی مواد جمع کر سکوں۔ اللہ تعالیٰ نے توفیق دی اور میں نے ایک سال کی محنت کے بعد ایک سائٹ "گلدستہ ڈاٹ پی کے" کے نام سے بنائی جو کہ قرآن و حدیث، اصلاحی، دلچسپ، تاریخی قصے واقعات، اُردو انگلش تحریریں، شاعری و اقوال زریں، F.Sc اور B.Sc کے مضامین کے آن لائن نوٹس، اسلامک، تفریحی، معلوماتی وال پیپرز، حمد و نعت، فرقہ واریت سے پاک اسلامی بیانات، پنجابی نظمیں و ترانے اور کمپیوٹر و انٹرنیٹ کی دنیا کے بارے میں ٹپس، آن لائن کمائی کرنے کے مستند طریقہ کار۔ کے ساتھ ساتھ اور بھی بہت سی چیزوں پر مشتمل ہے۔ اور انشاء اللہ میں مزید وقت کے ساتھ ساتھ اضافہ کرتا جاؤں گا۔ آپ کی قیمتی رائے کی ضرورت ہے۔ عرنان شفیق

اہم نوٹ

ذیل میں جو نوٹس مہیا کیے گئے ہیں وہ کئی گھنٹوں کی لگاتار محنت کے مرتب ہوئے ہیں۔ اور آپ کو بالکل مفت مہیا کر رہے کیے جارہے ہیں۔ آپ سے ان کی قیمت صرف اتنی سی متوقع ہے کہ ایک بار **درودّ ابراھیمی** اپنی زبان سے ادا کر دیں۔

درود شریف

بسم اللہ الرحمٰن الرحیم

اَللّٰھُمَّ صَلِّ عَلٰی مُحَمَّدٍ وَّ عَلٰٓی اٰلِ مُحَمَّدٍ کَمَا

اے اللہ! رحمت بھیج حضرت محمد پر اور حضرت محمدؐ کی آل پر

صَلَّیْتَ عَلٰٓی اِبْرَاھِیْمَ وَ عَلٰٓی اٰلِ اِبْرَاھِیْمَ

جس طرح تو نے رحمت بھیجی حضرت ابراھیم پر اور حضرت ابراہیمؑ کی آل پر

اِنَّکَ حَمِیْدٌ مَّجِیْدٌ

بے شک تو تعریف کیا گیا بزرگ ہے۔

اَللّٰھُمَّ بَارِکْ عَلٰی مُحَمَّدٍ وَّ عَلٰٓی اٰلِ مُحَمَّدٍ کَمَا

اے اللہ! برکت دے حضرت محمد کو اور حضرت محمدؐ کی آل کو جس

بَارَکْتَ عَلٰٓی اِبْرَاھِیْمَ وَ عَلٰٓی اٰلِ اِبْرَاھِیْمَ

طرح برکت دی تو نے حضرت ابراھیم کو اور حضرت ابراہیمؑ کی آل کو

اِنَّکَ حَمِیْدٌ مَّجِیْدٌ

بے شک تو تعریف کیا گیا بزرگ ہے۔