UNIT VI

Aldehyde and Ketone

→ General formula: $C_nH_{2n}O$

→ Representative formula: $R-\overset{O}{\overset{\|}{C}}-H$ aldehyde, $R-\overset{O}{\overset{\|}{C}}-R$ Symmetric Ketone

$R-\overset{O}{\overset{\|}{C}}-R_1$ Unsymmetric Ketone.

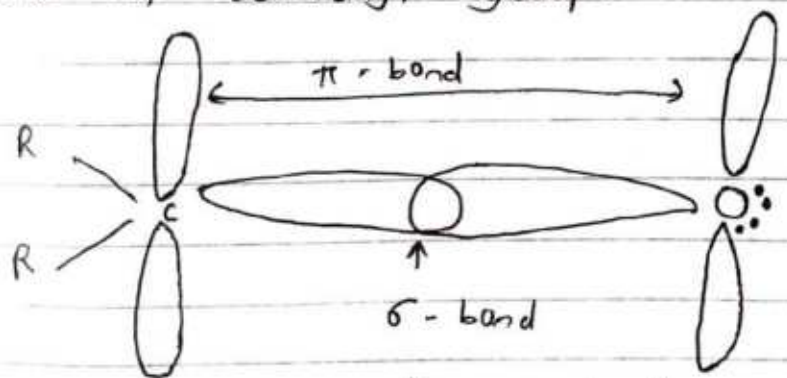
Aldehyde and Ketone are commonly called carbonyl compound because may contains carbonyl group.

Aldehyde and Ketone are functional isomer of each other.

Eg C_3H_6O

CH_3-CH_2-CHO $CH_3-CO-CH_3$ Ketone.

* Structure of carbonyl group:



In carbonyl group the central carbonyl carbon is sp^2 - hybridised with trigonal planar geometry having bond 120°.

carbon forms three sigma bond with it's three sp^2 - hybrid orbital by axial overlapping of atomic orbitals of oxygen and other two atoms.

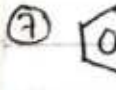
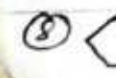
It has still one half filled p-orbital with which it forms π-bond by side ways overlapping with p-orbital of oxygen.

* Nomenclature of aldehyde :-

* Common System :-

Common Name of aldehyde is derived from the common name of corresponding carboxylic acid by replacing ic acid or oic acid with aldehyde. The position of ~~indicated~~ substituent is indicated by Greek letter α, β, γ etc as shown below :-

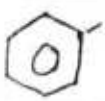
→ IUPAC Name :- prefix + word root + pri. suffix + al
If aldehyde group is attached to carbon of a ring then secondry suffix carbal-dehyde is used

Eg	Formula	Common Name	IUPAC NAME
①	HCHO	~~Meth~~ · Formaldehyde	Methanal
②	CH_3-CHO	Acetaldehyde	ethanal
③	CH_3-CH_2-CHO	propionaldehyde	propanal.
④	$CH_3-CH_2-CH_2-CHO$	n-Butyraldehyde	Butanal
⑤	$CH_3-\underset{\beta}{CH}(CH_3)-CHO$	iso-Butyraldehyde	2-Methylpropanal
⑥	$CH_3-\underset{\alpha}{CH}(Br)-CHO$	α-Bromopropionaldehyde	2-Bromopropanal.
⑦		Benzaldehyde	Benzaldehyde (Benzene carbaldehyde)
⑧		—	Cyclopentane carbaldehyde

* Nomenclature of Ketone :-

- Common Name :- Symmetric Ketones are named as dialkyl Ketone. Unsymmetric Ketones are named by writing name of alkyl group in alphabetical order before the word Ketone.

- * IUPAC System: prefix + word root + position + suffix + one.

Formula	Common Name	IUPAC Name.
(1) $CH_3-\overset{O}{\overset{\|\|}{C}}-CH_3$ or $CH_3-CO-CH_3$ or CH_3COCH_3	Dimethyl Ketone. (Acetone)	propanone.
(2) $CH_3-CH_2-\overset{O}{\overset{\|\|}{C}}-CH_2-CH_3$	Diethyl Ketone.	pentan-3-one.
(3) $CH_3-CH_2-\overset{O}{\overset{\|\|}{C}}-CH_3$	Ethylmethyl Ketone.	Butanone.
(4) $CH_3-CH_2-CH_2-\overset{O}{\overset{\|\|}{C}}-CH_3$	Methyl-n-propyl Ketone	Pentan-2-one
(5) $CH_3-\underset{CH_3}{CH}-\overset{O}{\overset{\|\|}{C}}-CH_3$	iso-~~ethyl~~propyl methyl Ketone.	3-Methylbutan-2-one
(6)  $CO\,CH_3$	Methylphenyl Ketone (Acetophenone)	Acetophenone. (~~methylphe~~ phenylethanone)
(7)  $CO-CH_2-CH_3$	Ethylphenyl Ketone.	1-phenylpropan-1-one

* General Method of preparation of aldehyde and Ketone.

(I) From alcohol

(i) By oxidation

$CH_3-CH_2-OH \xrightarrow[A.]{KMnO_4/H^+} CH_3-CHO$

$CH_3-\underset{OH}{CH}-CH_3 \xrightarrow[A]{KMnO_4/H^+} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(ii) By Dehydrogenation reaction:-

$CH_3-CH_2-OH \xrightarrow[300^\circ C]{Cu/Red\ hot} CH_3-CHO+H_2$

$CH_3-\underset{OH}{CH}-CH_3 \xrightarrow[\quad]{\quad} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(2) From acid Halide :-

When acid halide is treated of palladium deposited on Barium sulphate aldehyde is formed. This rxn is called Rosenmund reduction

$R-\overset{O}{\overset{\|}{C}}-X + H_2 \xrightarrow{Pd/BaSO_4} R-\overset{O}{\overset{\|}{C}}-H + HX$

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd/BaSO_4} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + HCl$

propanal

$R-\overset{O}{\overset{\|}{C}}-X + R_2-Cd \xrightarrow[\Delta]{\text{Dry ether}} 2\,R-\overset{O}{\overset{\|}{C}}-R + CdCl_2$

$CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3-Cd \xrightarrow[\Delta]{\text{dry ether}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CdCl_2$

Propanone

(3) By distillation

(i) $(R-COO)_2Ca + H_2O \xrightarrow[\text{distillation}]{\Delta} R-CHO + CaCO_3$

Methanal

(ii) $(R-COO)_2Ca + H_2O \xrightarrow[\text{distillation}]{\Delta} R-\overset{O}{\overset{\|}{C}}-R + CaCO_3$

(iii) $(R-COO)_2Ca + (HCOO)_2Ca \xrightarrow[\text{distillation}]{\Delta} R-CHO + 2CaCO_3$

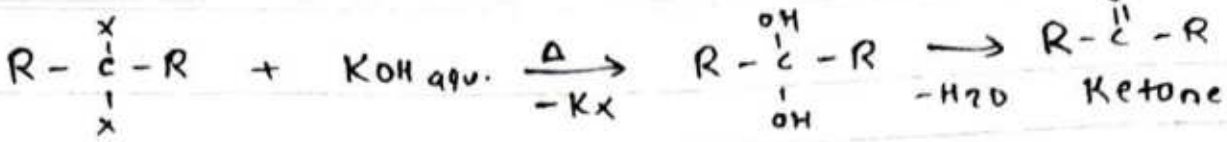
(iv) $(CH_3-CH_2-CH_2-COO)_2Ca + (HCOO)_2Ca \xrightarrow[\text{distillation}]{\Delta} CH_3-CH_2-CH_2-CHO$

Butanal

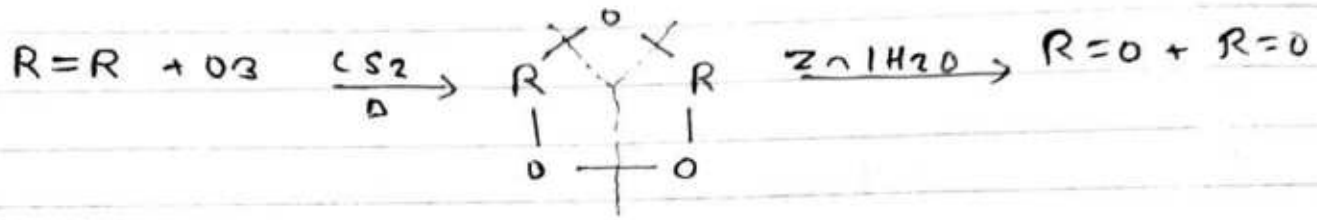
where R = alkyl group (R = CH_3, CH_3-CH_2 etc)

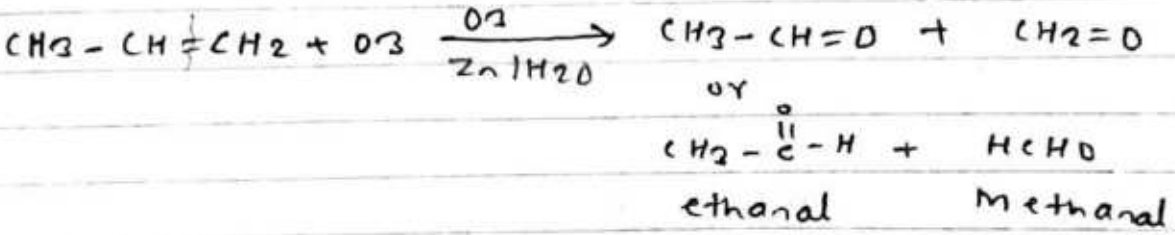
(4) By hydrolysis of gem-halides

$R-\overset{X}{\underset{X}{\overset{|}{\underset{|}{C}}}}-H + KOH(aqu.) \xrightarrow[-KX]{\Delta} R-\overset{OH}{\underset{OH}{\overset{|}{\underset{|}{C}}}}-H \xrightarrow{-H_2O} R-\overset{O}{\overset{\|}{C}}-H$ or $R-CHO$


R - C(X)(X) - R + KOH aqu.
Δ
- KX
R - C(OH)(OH) - R
- H2O
R - C(=O) - R
Ketone

⑤ Ozonlysis :-


R=R + O3
CS2
Δ
R
R
O
O
O
Zn/H2O
R=O + R=O


CH3 - CH=CH2 + O3
O3
Zn/H2O
CH3 - CH=O + CH2=O
or
CH2 - C(=O) - H + HCHO
ethanal
Methanal

⑥ By using Grignard reagent:-

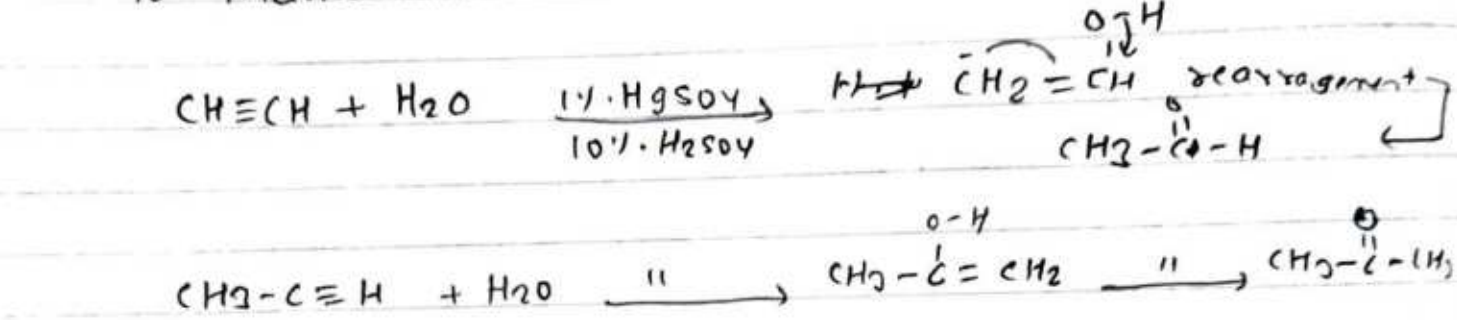
$$R\text{-}MgX + HCN \longrightarrow R\text{-}CH{=}N\text{-}MgX \xrightarrow[A]{H_3O^+} R\text{-}CHO$$

$$R\text{-}MgX + R'\text{-}CN \rightarrow R\text{-}\underset{R'}{C}{=}N\text{-}MgX \xrightarrow{H_3O^+} R\text{-}\underset{R'}{C}{=}O$$

⑦ From alkyne:-

When alkyne is added which water in presence of 10% H_2SO_4 and 1% $HgSO_4$, Carbonyl compound is formed.

acetylene is the only alkyne which gives aldehyde. All other alkynes give Ketone because addition of water takes place according to Markovnikov's rule.

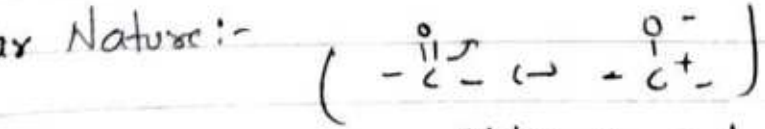


physical property

(i) physical state:-

Formaldehyde is gas. All other aldehyde and Ketones upto C11 are colourless volatile liquid and more higher members are solid.

(ii) polar Nature:-



Aldehyde and Ketones are highly polar compound due to presence of polar carbonyl group.

(iii) Odour:-

Lower member of aldehyde have unpleased smell. Higher member of aldehyde and all Ketones have pleasant smell

(iv) Solubility:-

lower member of aldehyde and ketone upto C_4 carbon are miscible in water due to formation of inter molecular H-bond with water.

But as carbon chain increases miscibility decrease due to increase in Hydrophobic interaction.

(v) Boiling point:-

Aldehyde and Ketones are highly polar compound so, they have high boiling point than known polar compound like alkane, ether etc.

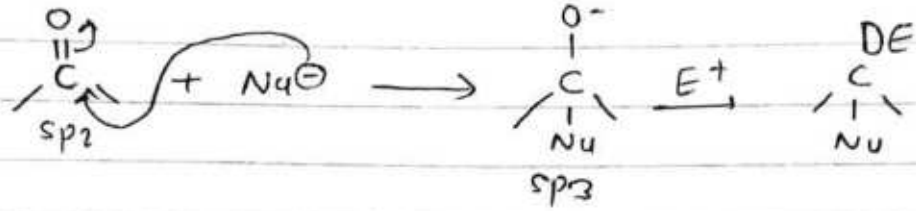
Aldehyde and Ketones have less boiling point than alcohol, carboxylic acid etc having comparable molecular mass because they can form inter molecular H-bond but aldehyde and ketone cannot form inter-molecular H-bond.

Chemical properties of aldehyde and Ketone:-

(1) Both aldehyde and Ketone containe carbonyl group so they show similar chemical property but aldehyde reacts faster than Ketone due to positive inductive effect shown by alkyl group and also steric hindrance shown by alkyl group.
(दोनों)

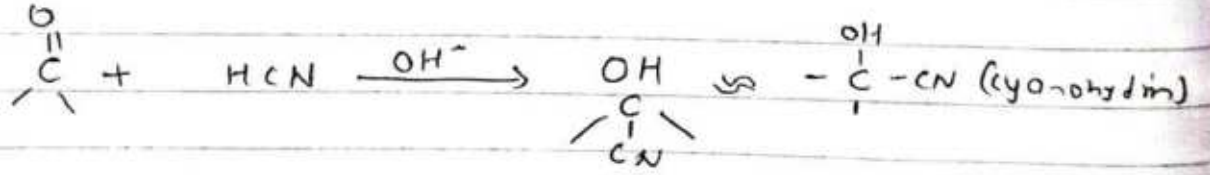
Some common chemical reaction shown by aldehyde and Ketones are

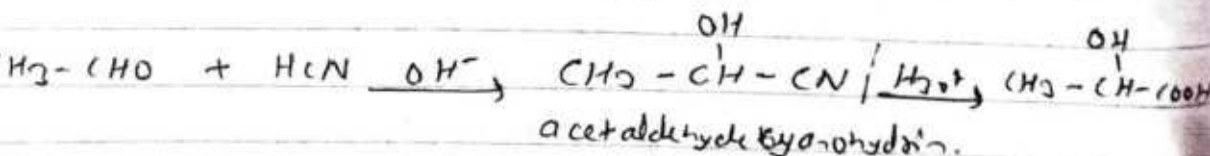
(1) Nucleophilic addition reaction :-



(i) Addition of hydrogen cyanide (HCN) :-

Aldehyde and Ketone reacts with hydrogen cyanide in slightly alkaline medium producing cyano hydrin.



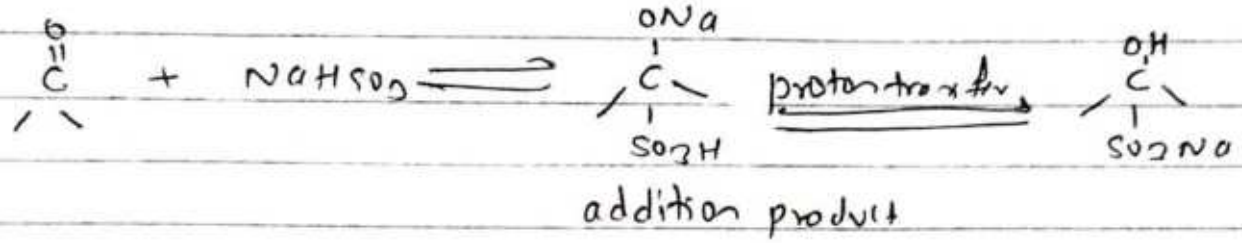


acetaldehyde cyanohydrin.
2-Hydroxypropanitrile.

(ii) Addition of Sodium hydrogen sulphite ($NaHSO_3$) :-

Aldehyde gives good yield (Product) with sodium hydrogen sulphite but Ketone gives less yield with sodium hydrogen sulphite due to electronic factor and steric hindrance. The sodium hydrogen

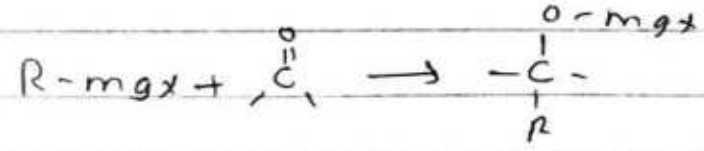
Sulphide addition product formed is crystalline solid and gives the original aldehyde or Ketone on treatment with alkali or minerals acid so this reaction is used for purification of aldehyde and ketone.



addition product

(ii) ~~Nucleophilic addition reaction with el~~

(iii) Addition of Grignard Reagent.



(2) Nucleophilic addition reaction with elimination of water molecule.

→ Reaction with ammonia and its derivative

NH_2-Z where $Z = -H, -R, -OH, -NH_2$ etc.

$(=C=O + NH_2-Z \longrightarrow =C=N-Z + H_2O)$

① Reaction with ammonia (NH_3) :-

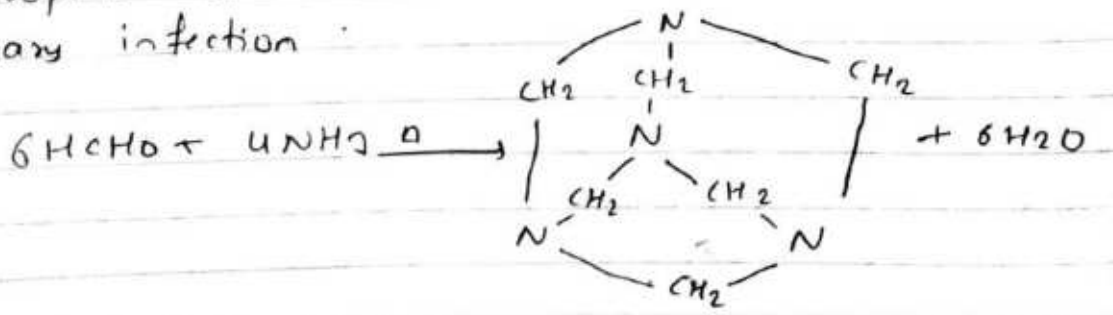
Aldehyde (except formaldehyde) and Ketone (except acetone) reacts with ammonia producing imine on heating.

$$=C=O + NH_3 \xrightarrow{\Delta} =C=N-H + H_2O.$$

$$CH_3-CHO + NH_3 \xrightarrow{\Delta} CH_3-CH=N-H + H_2O$$

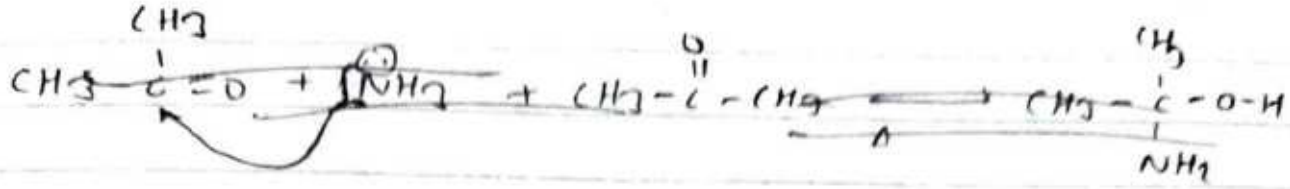
Ethanal — ethanal imine (ethanimine)

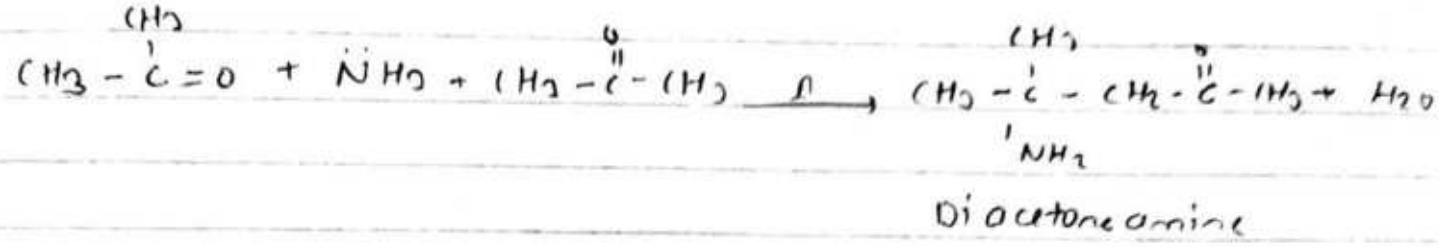
* Formaldehyde reacts with ammonia producing hexamethylenetetramine which is commonly called urotropine. It is used in medicine for treatment of urinary infection.



Hexamethylenetetramine (Urotropine)

Acetone reacts with ammonia in molar ratio 2:1, producing diacetone amine





Diacetone amine

IUPAC Name:

ii) Reaction with amine ($R-NH_2$)

$$=C=O + R-NH_2 \xrightarrow{\Delta} =C=N-R + H_2O$$

substituted imine

$$CH_3-CHO + CH_3-NH_2 \xrightarrow{\Delta} CH_3-CH=N-CH_3 + H_2O$$

N-methyl ethanimine

(N-methyl ethanimine)

(iii) Reaction with hydroxylamine (NH_2-OH)

$$>C=O + NH_2-OH \xrightarrow{\Delta} =C=N-OH + H_2O$$

oxime

(IV) Reaction with hydrazine (NH_2-NH_2)

$$=C=O + NH_2-NH_2 \xrightarrow[\Delta]{H^+} =C=N-NH_2 + H_2O$$

Hydrazone

$$CH_3-CHO + NH_2-NH_2 \rightarrow CH_3-CH=N-NH_2 + H_2O$$

Ethanal hydrazone

(v) Reaction with phenylhydrazine ($NH_2-NH-C_6H_5$)

$$>C=O + NH_2-NH-C_6H_5 \xrightarrow[\Delta]{H^+} >C=N-NH-C_6H_5 + H_2O$$

phenylhydrazone

(vi) Reaction with 2,4-Dinitro phenylhydrazine ($NH_2-NH-C_6H_3(NO_2)_2$) or 2-4-DNPH or 2,4-DNP or DNP test)

$$>C=O + NH_2-NH-C_6H_3(NO_2)_2 \xrightarrow[\Delta]{H^+} >C=N-NH-C_6H_3(NO_2)_2 + H_2O$$

2,4-Dinitrophenylhydrazone.

(yellow, red precipitate)

→ (It is used as test reaction for carbonyl group.)

(vii) Reaction with semi carbazide ($NH_2-NH-\overset{O}{\overset{\|}{C}}-NH_2$)

$$>C=O + NH_2-NH-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\Delta]{H^+} >C=N-NH-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

semicarbazone.

③ Reduction:-

① Reduction to alcohol:-

$$R-CHO + H_2 \xrightarrow[\Delta]{Ni} R-CH_2-OH$$

$$R-CO-R + H_2 \xrightarrow[\Delta]{Ni} R-\overset{OH}{\underset{|}{C}}H-R$$

UV

(ii) clemmensen reduction:-

When aldehyde or ketone is reduced with zinc-almalgum and conc. HCl, alkane is formed. This reaction is called clemmesen reduction.

$$>C=O + 4[H] \xrightarrow{Zn-Hg + conc.HCl} >C<_{H}^{H} + H_2O$$

$$CH_3-CHO + 4[H] \xrightarrow{Zn-Hg + conc.HCl} CH_3-CH_3 + H_2O$$

$$CH_3-CO-CH_3 + 4[H] \xrightarrow[\text{reagent}]{\text{clemmenson}} CH_3-CH_2-CH_3 + H_2O$$

iii) wolf Kishner's reduction:-

Aldehyde or ketone reacts with hydrogin to form Hydrazone which on treatment with alkali like KOH, at high temperature in presence of high boiling liquid like glycerol or ethylene glycerol gives alkane. This reaction is called wolf Kishner's reduction.

① $>C=O + NH_2-NH_2 \xrightarrow[\Delta - H_2O]{H^+} >C=N-NH_2 \xrightarrow[200^\circ C]{KOH\ glycol} =C<_{H}^{H}$

$CH_3-CHO + NH_2-NH_2 \xrightarrow[\Delta - H_2O]{H^+} CH_3-CH=N-NH_2 \xrightarrow[200^\circ C]{KOH\ glycol} CH_3-CH_3 + N_2$

(4) Oxidation:

① Oxidation with Tollen's reagent:-

Ammonical silver nitrate solution is called Tollen's reagent.

Tollen's reagent oxidize aldehyde itself being reduce to silver which deposit on inner wall of the vessel and appears as silver mirror.

It cannot oxidise Ketone so it is used as test reaction for aldehyde and is called silver mirror test reaction

$$R-CHO + 2[Ag(NH_3)_2]OH \xrightarrow{warm} R-COONH_4 + 2Ag\downarrow + 3NH_3 + H_2O$$
(silver mirror)

$$CH_3-CHO + 2[Ag(NH_3)_2]OH \longrightarrow CH_3-COONH_4 + 2Ag\downarrow + 3NH_3 + H_2O$$
(silver mirror)

ii Oxidation with fehling's solution:-

Mixture of equivalent amount of copper sulphate solution and alkaline sodium-potassium tartrate which is deep blue in colour is called fehling's solution.

Fehling's solution

oxidise aliphatic aldehyde itself being reduced to reddish brown precipitate of cuprous oxide. It cannot oxidize aeromatic aldehyde and all Ketone so it is used as test reaction for aliphatic aldehyde.

$$R-CHO + [4\cdot Cu^{++} + OH^-] \xrightarrow{\Delta} R-COO^- + Cu_2O\downarrow + H_2O$$

from fehling's solution — reddish colour

(iii) Haloform oxidation (Iodoform test reaction) :-

Aldehyde or Ketone containing methyl group directly attached to carbonyl carbon or alcohol which on oxidation gives such aldehyde or Ketone, when heated with alkali like NaOH and Iodine yellow coloured compound having hospital smell (Iodoform) is formed.

Formation of Iodoform shows the presence of $CH_3-\overset{\overset{O}{\|}}{C}-$ or $CH_3-\overset{\overset{OH}{|}}{CH}-$ group so it is used to test the presence of these group and is called Iodoform test reaction.

Iodoform.

① $CH_3-\overset{\overset{O}{\|}}{C}-Z + 4NaOH + 3I_2 \xrightarrow{\Delta} CHI_3 + Z-COONa + 3NaI + 3H_2O$
where $Z = -H, -R$

② $CH_3-\overset{\overset{O}{\|}}{C}-H + 4NaOH + 3I_2 \xrightarrow{\Delta} CHI_3 + H-COONa + 3NaI + 3H_2O$

③ $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 4NaOH + 3I_2 \xrightarrow{\Delta} CHI_3 + CH_3\cdot COONa + 3NaI + 3H_2O$

④ $CH_3-\underset{\underset{OH}{|}}{CH}-H + 6\,NaOH + 4I_2 \longrightarrow CHI_3 + H-COONa + 5NaI + 5H_2O$.

⑤ $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 + 6NaOH + 4I_2 \longrightarrow CHI_3 + CH_2-CH_2-COONa + 5NaI + 5H_2O$.

Note:- Ethanal is the only aldehyde which gives positive Iodoform test

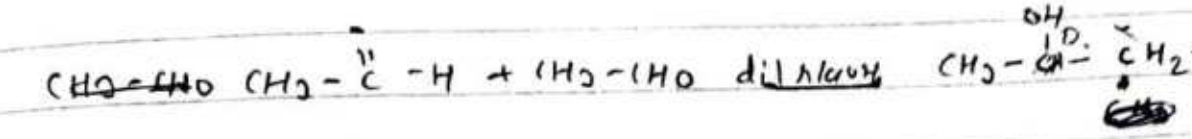
2.) Note:- Ethanol is the only only primary alcohol which gives positive Iodoform test.

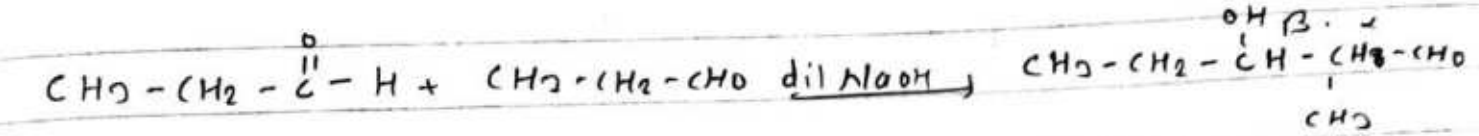
⑤ Some other reaction.

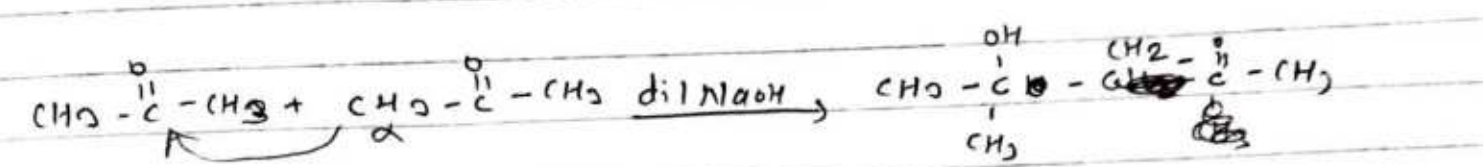
① Aldol condensation reaction:-

When aldehyde or Ketone containing α-hydrogen is treated with dilute NaOH, it under goes condensation reaction producing β-hydroxy aldehyde or β-hydroxy Ketone. This reaction is called Aldol condensation reaction.

$$R-CH_2-\overset{\overset{O}{\|}}{C}-H + R-CH_2-CHO \xrightarrow{\text{dil. NaOH}} R-CH_2-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}H-CH-CHO \xrightarrow{\Delta} R-CH_2-CH=\underset{\underset{R}{|}}{C}-CHO$$



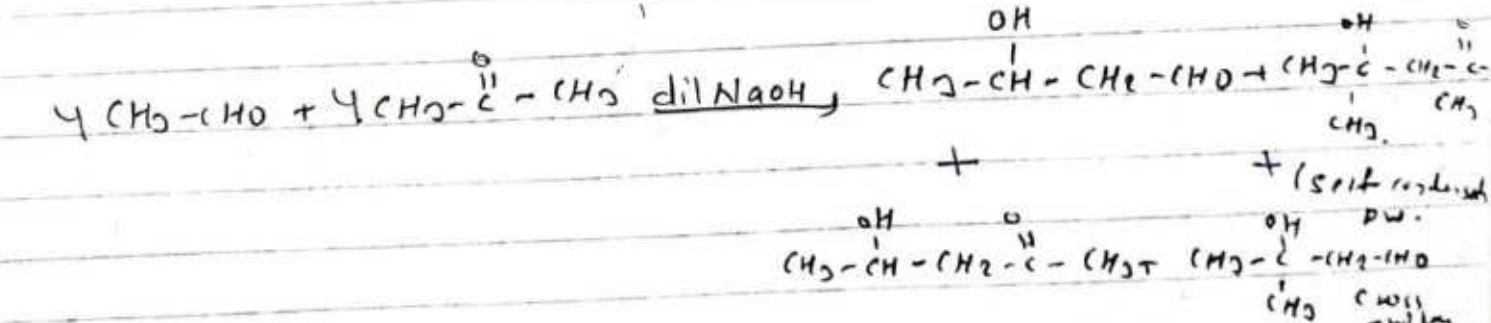




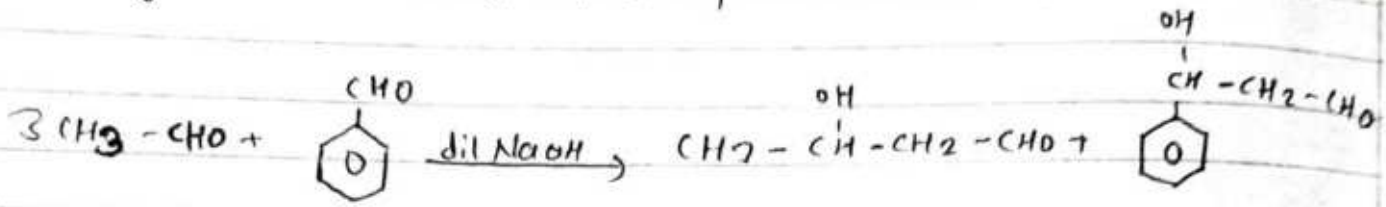
Sub!-

(a) cross aldol condensation reaction:-

The aldol condensation reaction in which two different aldehyde or ketones are used is called cross aldol condensation reaction. if both reactant contain α-hydrogen then four different products are formed.



if Only one reactant contains α-hydrogen then only two products are form

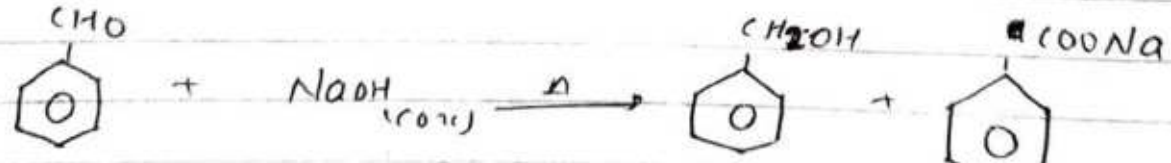


3-Hydroxy-3-phenyl propanal

(ii) Cannizzaro's Reaction :-

Aldehyde not containing α-hydrogen when treated with conc. NaOH, it under goes disproportionation reaction (some molecule undergoes oxidation and reduction) producing alcohol and sodium salt of carboxylic acid.

$$2\,HCHO + NaOH_{(conc.)} \xrightarrow{\Delta} CH_3OH + HCOONa.$$



Phenylmethanol Sodium benzoate.

(iii) Reaction with PCl_5 :-

$$=C=O + PCl_5 \xrightarrow{\Delta} =C(Cl)(Cl) + POCl_3.$$

gem dichloride.

$$CH_3-CHO + PCl_5 \xrightarrow{\Delta} CH_3-CHCl_2 + POCl_3.$$

1,1,-Dichloroethane.

$$CH_3COCH_3 + PCl_5 \xrightarrow{\Delta} CH_3-\underset{Cl}{\overset{Cl}{C}}-CH_3 + POCl_3.$$

2,2 Dichloropropane.

(iv) polymerization:-

40% aqu. solution of formaldehyde is called formaline which on evaporation polymerize to give paraformaldehyde.

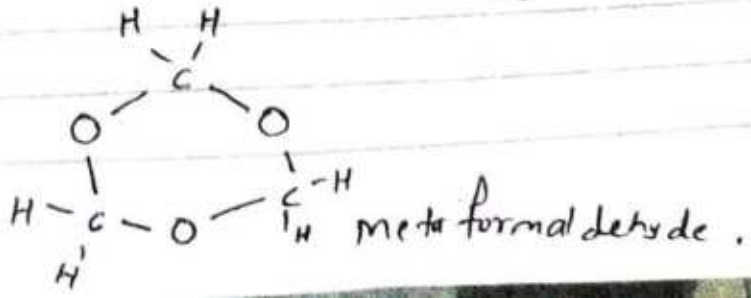
$$n\,HCHO \xrightarrow{\text{evaporation}} \left(-\underset{H}{\overset{H}{C}}-O-\right)_n \quad n = 6 \text{ to } 50.$$

or $H-C(=O)-H$

paraformaldehyde.

Formaldehyde on long standing gives meta formaldehyde

$$3\,HCHO \xrightarrow{\text{on long standing}}$$



meta formaldehyde.

polymrization of formaldehyde
and phenol gives bakelite