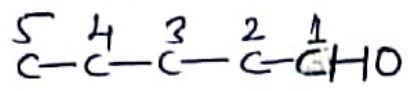
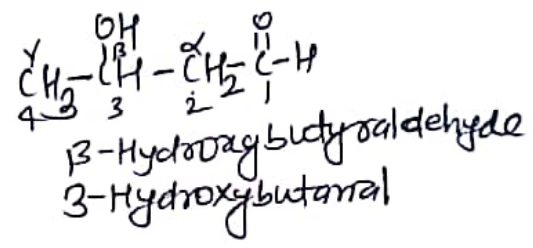
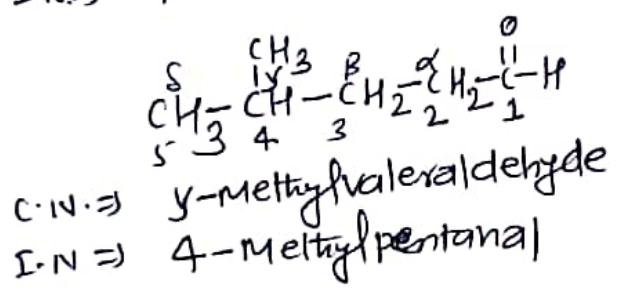
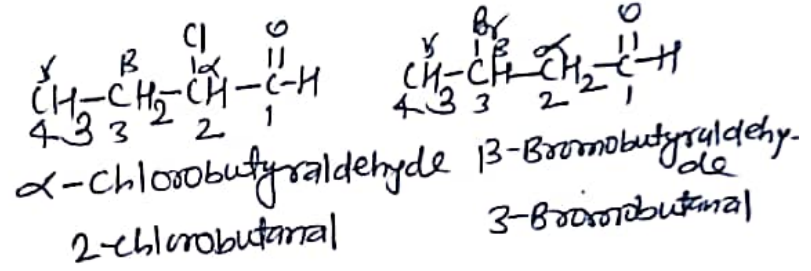
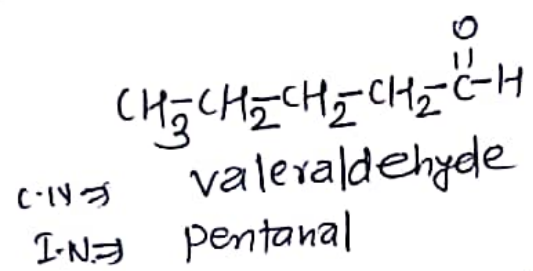
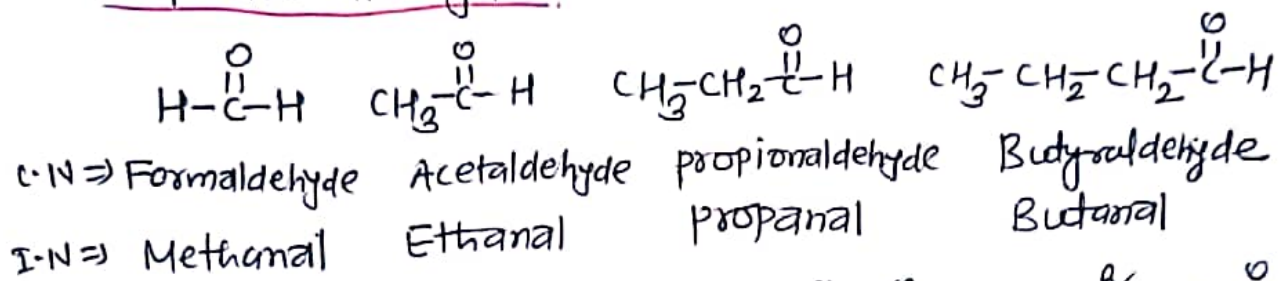


IUPAC system ⇒ IUPAC name of aldehyde is obtained by replacing 'e' (terminal) of parent alkane by 'al'. The carbonyl carbon of aldehyde is numbered as '1' while counting the carbon atoms.

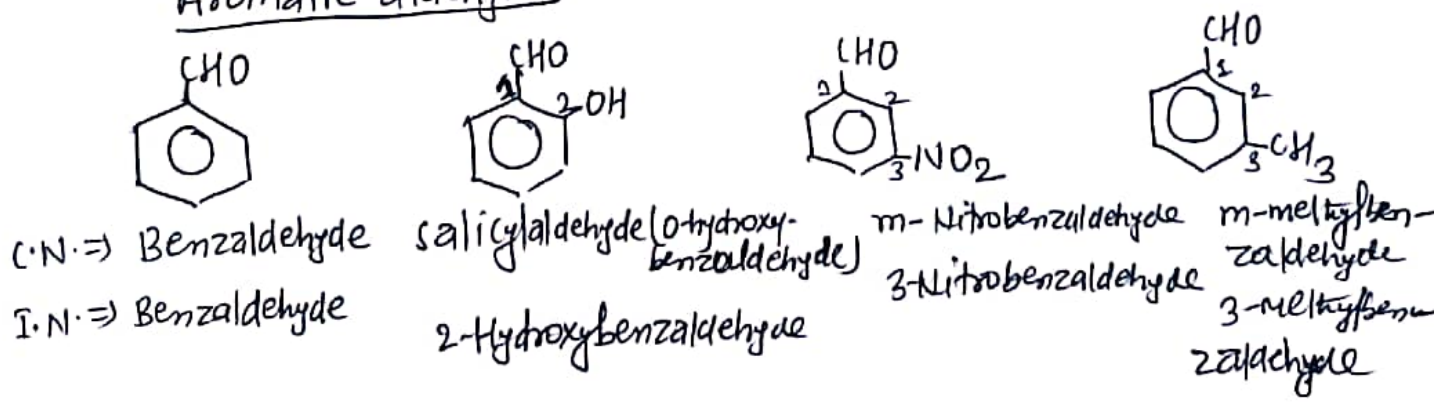
Alkane - e + al ⇒ Alkanal.



Aliphatic aldehydes:



Aromatic aldehyde ⇒



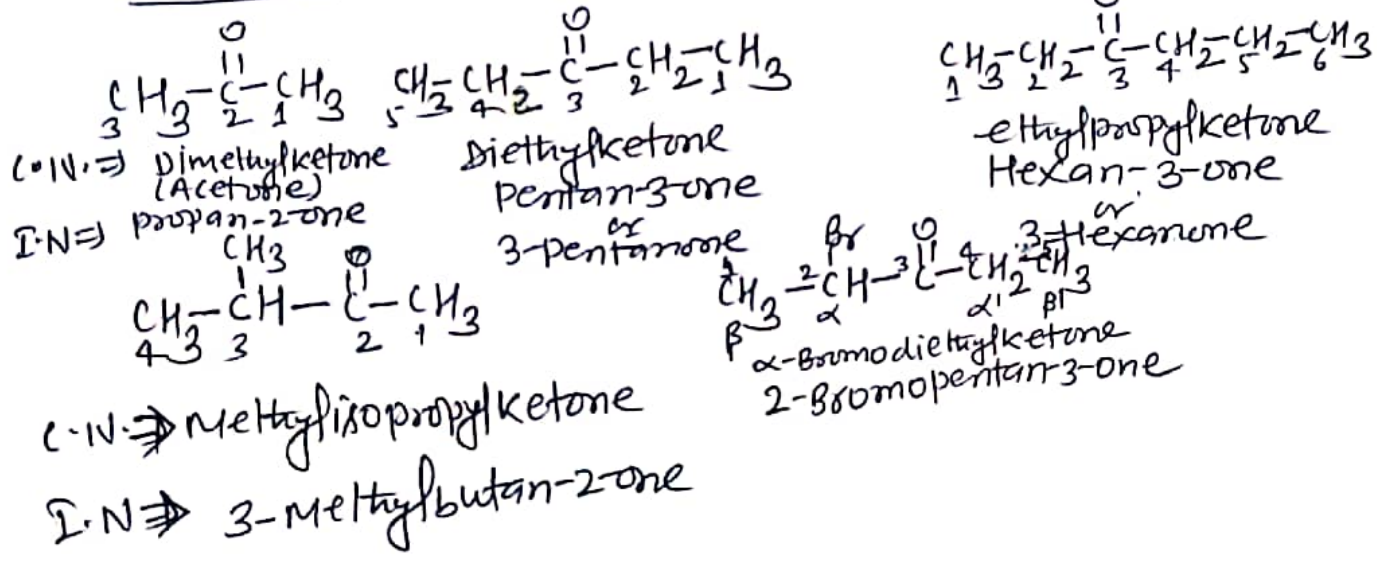
Ketone ⇒

Common system ⇒ common name of ketone is written by writing the names of alkyl or aryl groups attached to the carbonyl carbon atom in the alphabetical order before the word 'ketone'.

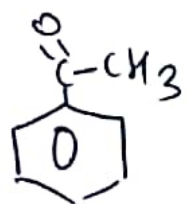
IUPAC system ⇒ IUPAC name of ketone is obtained by replacing 'e' (terminal) of parent alkane by 'one'.

Alkane-~~e~~one → Alkanone.

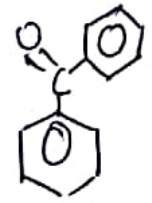
Aliphatic ketones ⇒



Aromatic ketones



C.N. ⇒ Acetophenone (Methylphenylketone)
I.N. ⇒ Acetophenone (Phenylethanone)



Benzophenone (Diphenylketone)
Benzophenone (Diphenylmethanone)

A ketone in which the carbonyl group is attached to a benzene ring is named as 'phenone'.

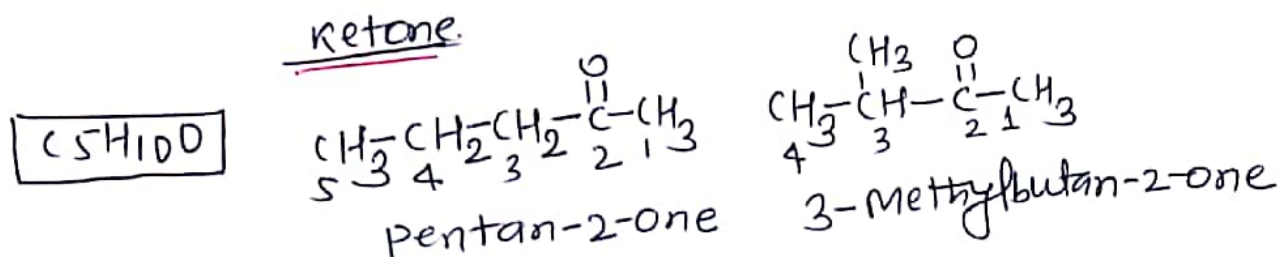
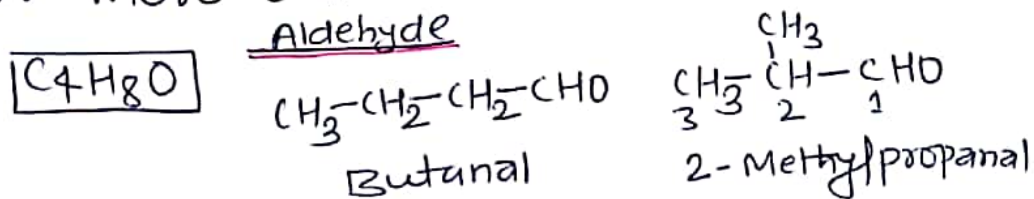
Aliphatic aldehydes and ketones

Page-5

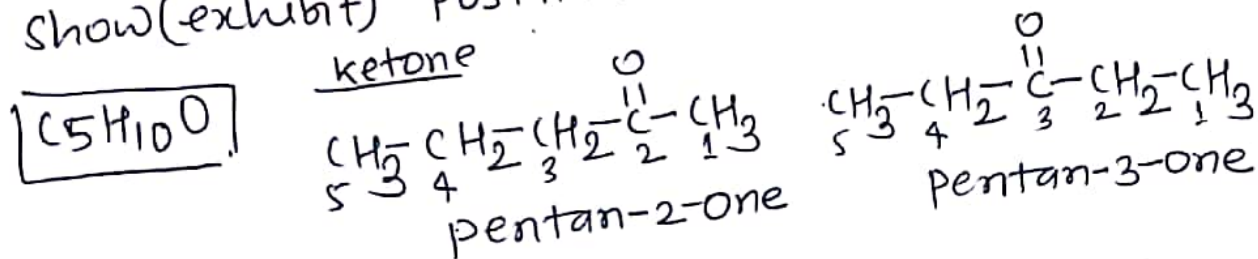
Isomerism in aldehydes and ketones:

They (aldehydes and ketones) show the following types of structural isomerisms.

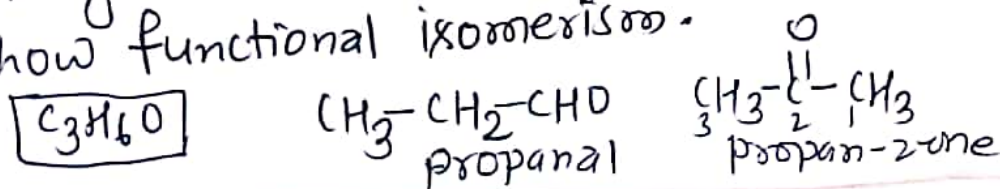
① chain isomerism: Aldehydes containing four or more C-atoms and ketones containing five or more C-atoms show chain isomerism.



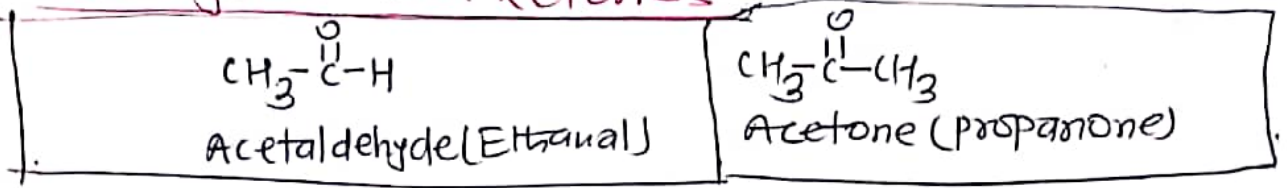
② position isomerism ⇒ Aldehydes generally do not show position isomerism because -CHO group in aldehyde is present at the end of the chain. Ketones containing five or more C-atoms show (exhibit) position isomerism.



③ Functional isomerism ⇒ Aldehydes and ketones having same no. of C-atoms (at least three C-atoms) show functional isomerism.



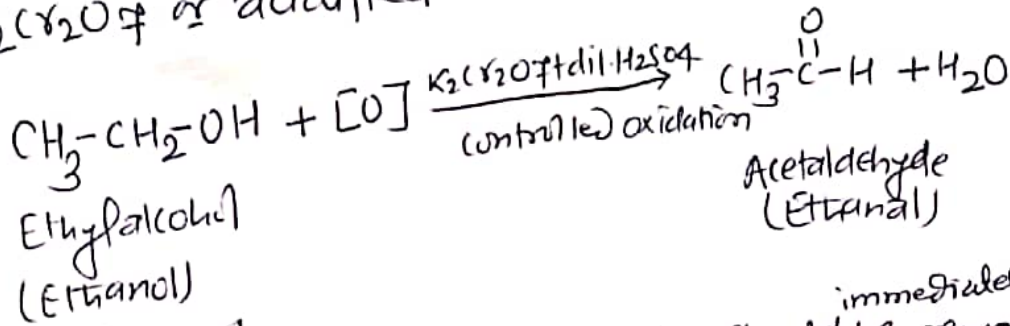
General methods of preparation of aliphatic aldehydes and ketones



1. From alcohols ⇒

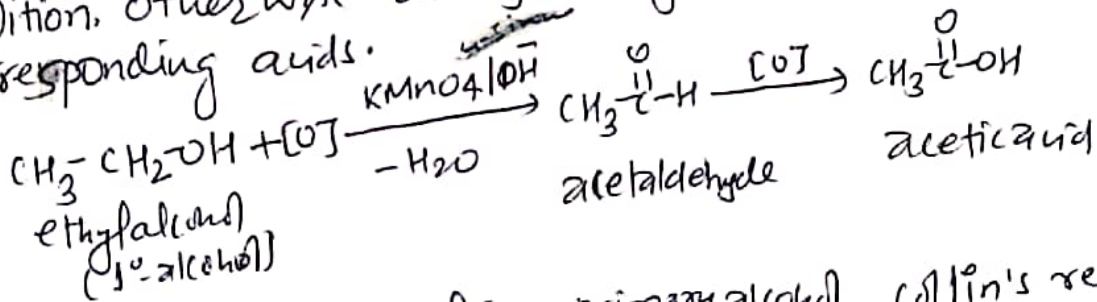
a) By oxidation of alcohols ⇒

Aldehyde ⇒ Aldehyde is obtained by the oxidation (controlled oxidation) of primary alcohol with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or acidified or alkaline KMnO_4 .



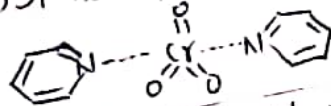
1° alcohol so the formed aldehyde in this reaction should be removed immediately by distillation.

Note: In this method, oxidation should be done under controlled condition, otherwise aldehyde may be further oxidised to corresponding acids.

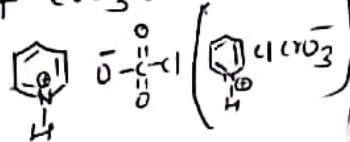


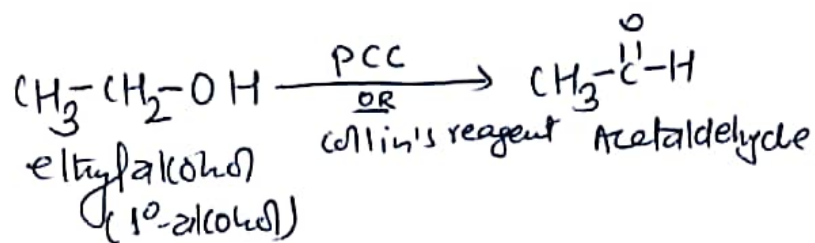
To get aldehyde from primary alcohol, Collin's reagent or pyridinium chlorochromate (PCC) can be used.

Collin's reagent ⇒ It is a solution of $\text{CrO}_3 \cdot 2\text{Pyridine}$ (Sarett reagent) in CH_2Cl_2 .

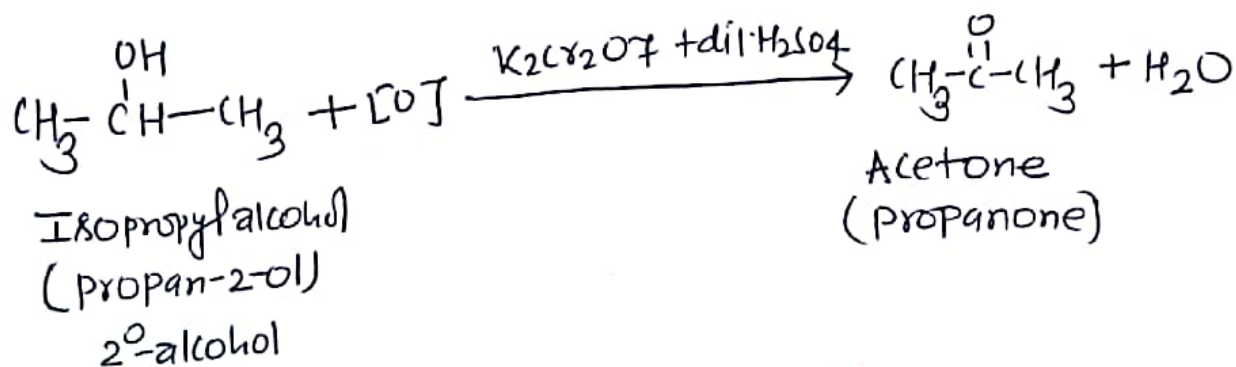


Pyridinium chlorochromate (PCC) ⇒ It is a solution of CrO_3 (chromium trioxide) and HCl in CH_2Cl_2 (dichloromethane):



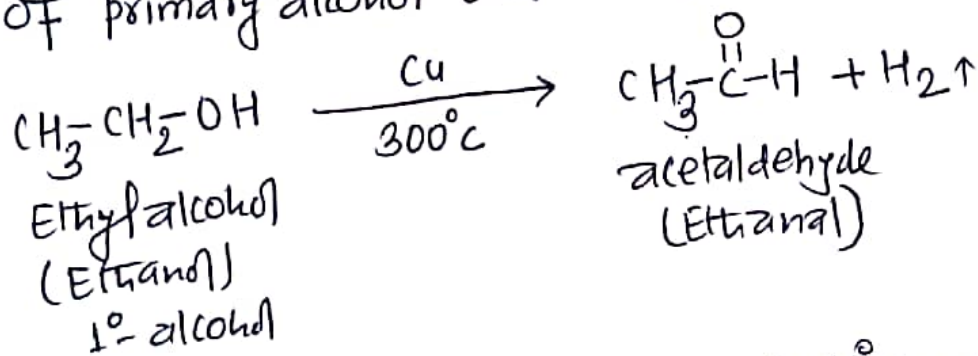


Ketone: ketone is obtained by the oxidation of secondary alcohol with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or acidified or alkaline KMnO_4 .

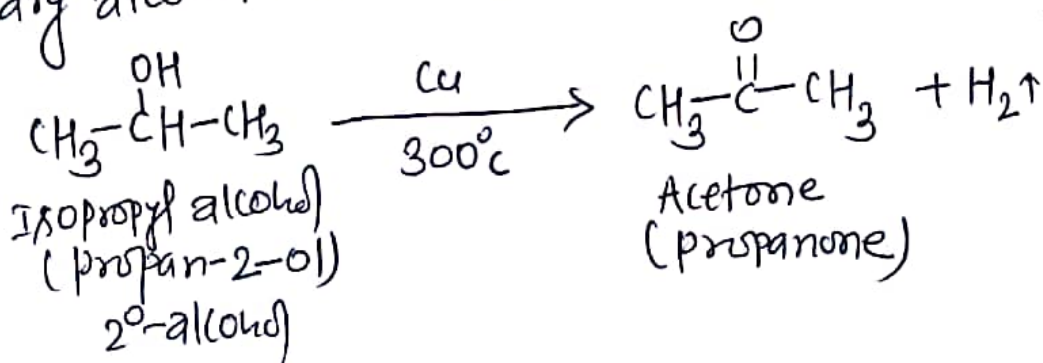


b. By catalytic dehydrogenation of alcohols \Rightarrow

Aldehyde \Rightarrow Aldehyde is obtained by passing vapours of primary alcohol over heated copper at 300°C .

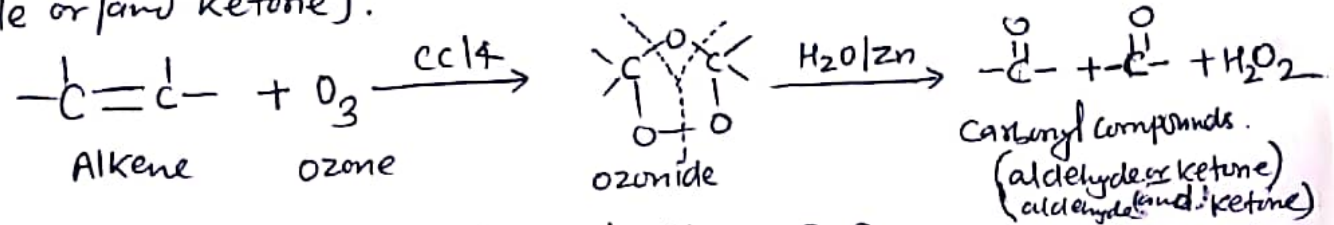


Ketone: Ketone is obtained by passing vapours of secondary alcohol over heated copper at 300°C .



2. From alkenes :- By ozonolysis of alkenes:

Alkene reacts with ozone (O₃) in presence of CCl₄ to form ozonide (unstable) which on hydrolysis with H₂O (water) in presence of zinc gives carbonyl compound (aldehyde or/and ketone).

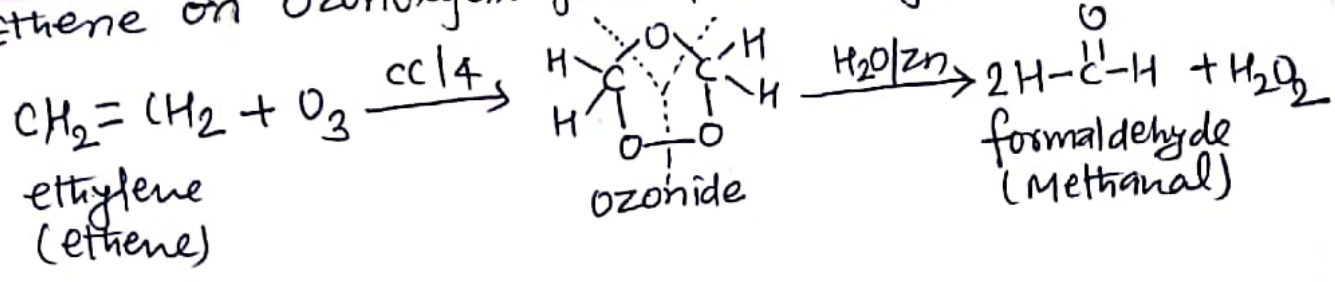


⇒ In this reaction, if the doubly bonded carbon has a H-atom, then aldehydes are formed. on the other hand, if there is no H-atom on doubly bonded carbon atom, then ketone are formed.

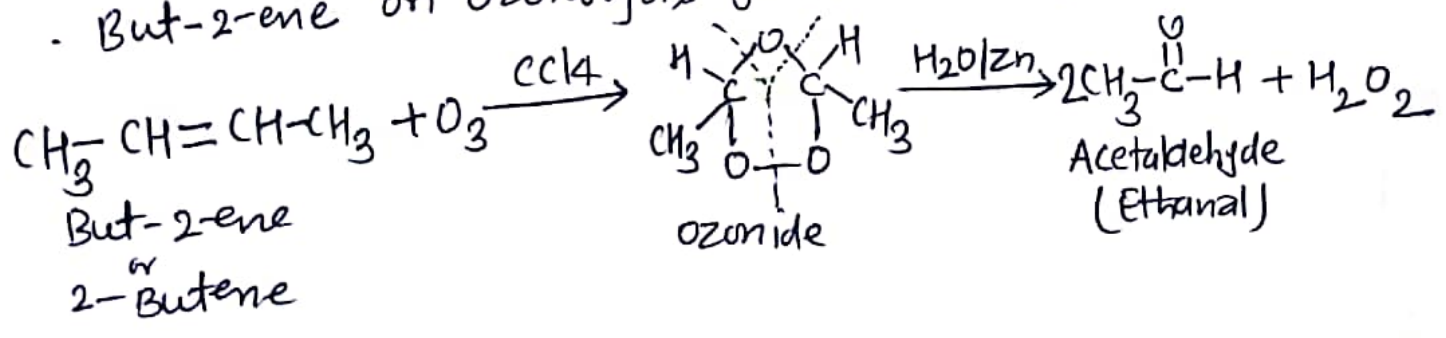
⇒ In case of symmetrical alkene, two same molecules of carbonyl compounds (aldehyde or ketone) are formed but in case of unsymmetrical alkene, mixture of carbonyl compounds (aldehyde and ketone or aldehyde and ketone or ketone and ketone) is formed (i.e. nature of products formed depend upon the nature of alkene)

Aldehyde ⇒

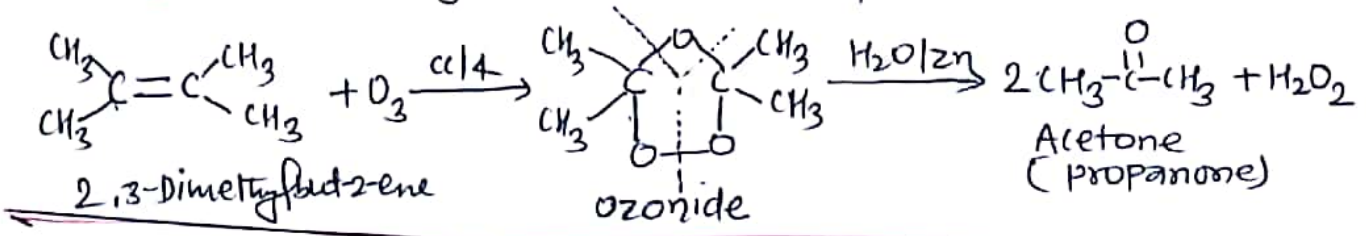
Ethene on ozonolysis gives formaldehyde



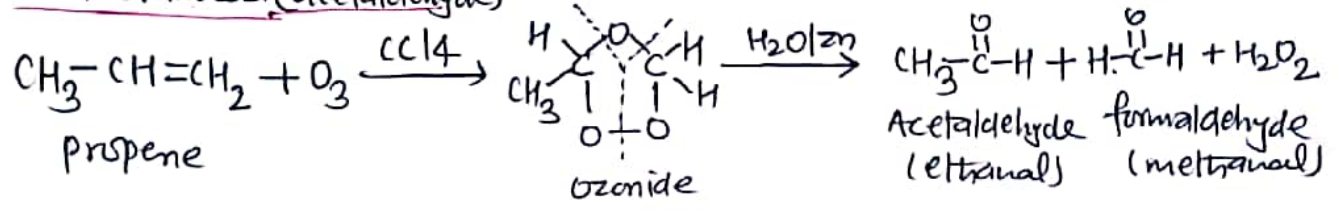
But-2-ene on ozonolysis gives acetaldehyde



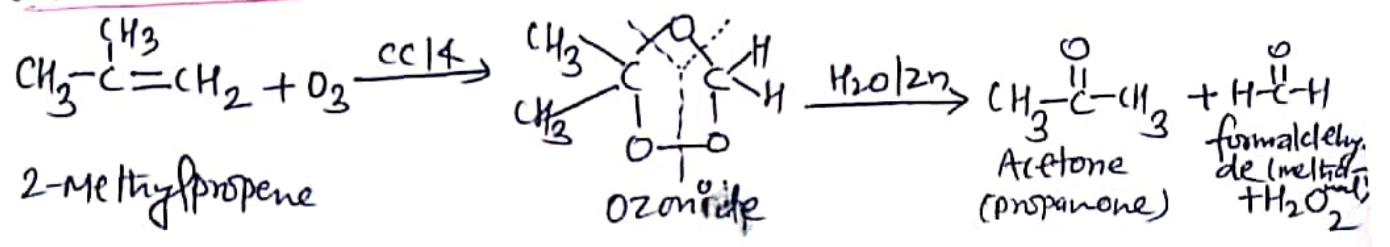
Ketone: 2,3-Dimethylbut-2-ene on ozonolysis gives acetone.



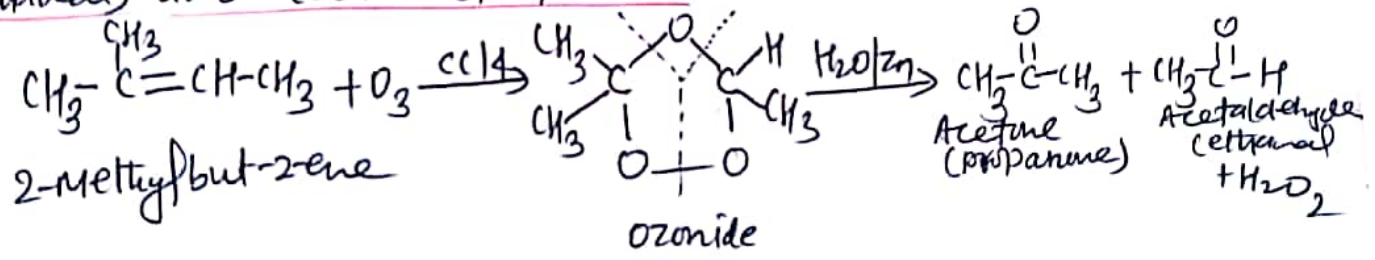
⇒ propene on ozonolysis gives a mixture of methanal (formaldehyde) and ethanal (acetaldehyde)



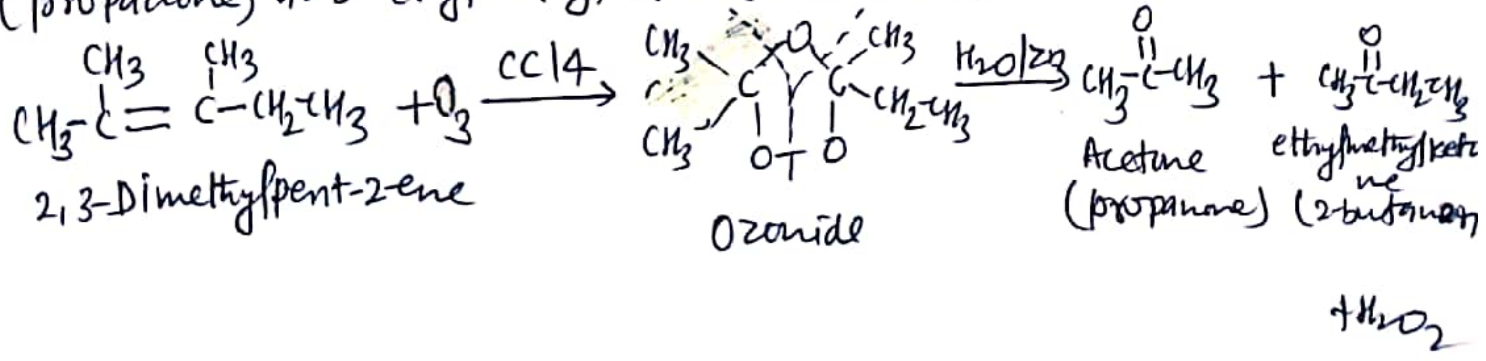
⇒ 2-Methylpropene on ozonolysis gives a mixture of acetaldehyde (ethanal) and acetone (propanone).



⇒ 2-methylbut-2-ene on ozonolysis gives a mixture of acetaldehyde (ethanal) and acetone (propanone)

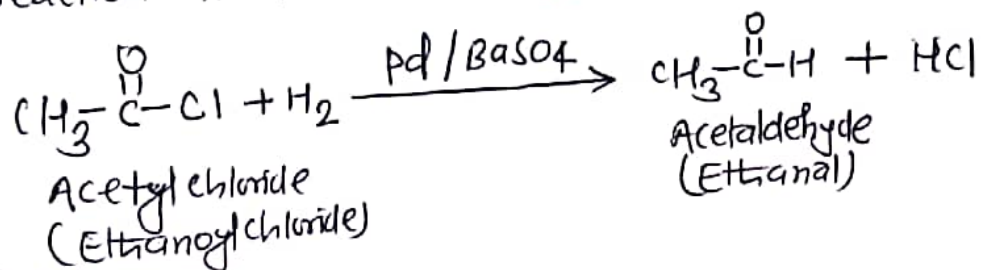


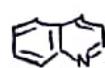
⇒ 2,3-Dimethylpent-2-ene on ozonolysis gives a mixture of acetone (propanone) and ethylmethylketone (2-butanone).



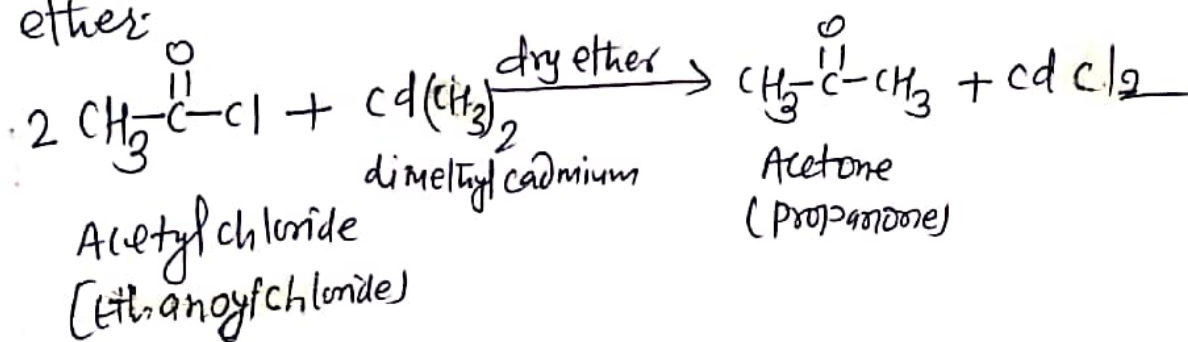
3. From acid chloride (acyl chloride) :-

Aldehyde :- ^{(By Rosenmund's reduction) :-} Aldehyde is prepared by the reduction of acid chloride with H_2 (hydrogen) in the presence of palladium catalyst suspended in $BaSO_4$ (barium sulphate). This reaction is known as Rosenmund's reduction reaction.



Note :- Lindler's catalyst: $Pd/BaSO_4$ is poisoned by sulphur or quinoline () to prevent the reduction of aldehyde to alcohol. Ketones can not be prepared by this method. Formaldehyde cannot be prepared because formyl chloride ($HCOCl$) is unstable at room temperature.

Ketone :- Ketone is prepared by treating acid chloride with dialkyl cadmium $[Cd(CH_3)_2]$ in the presence of dry ether:

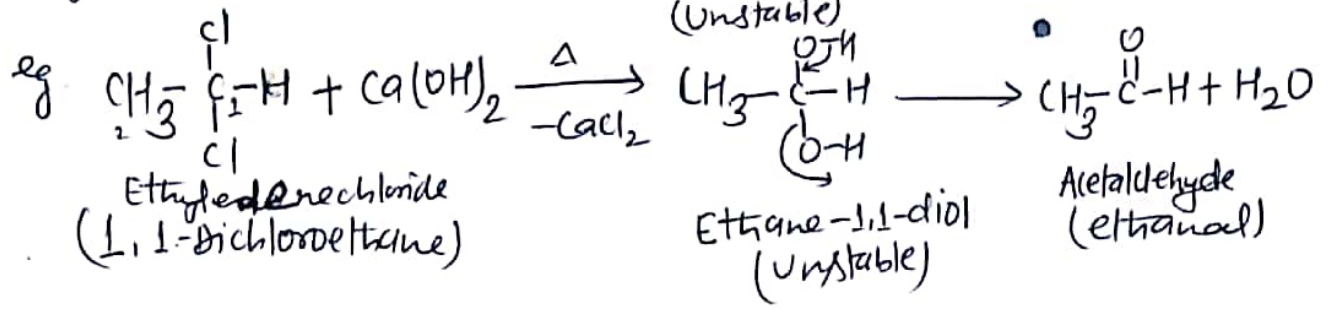
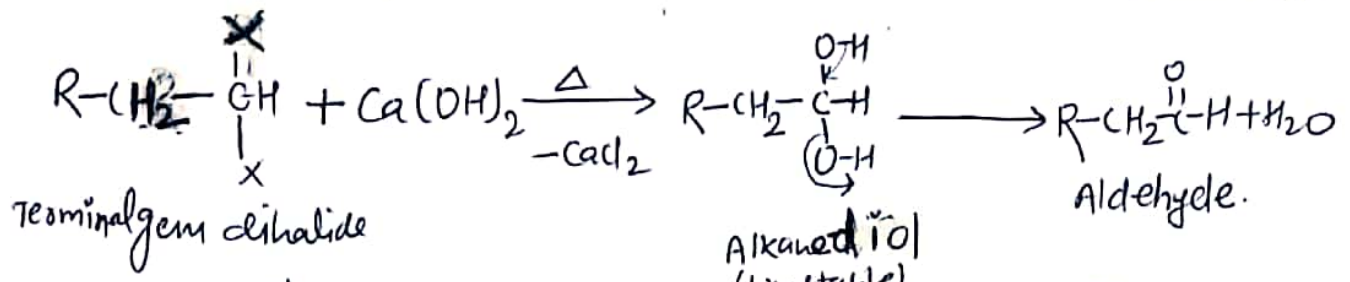


4. From gem-dihaloalkane (gem dihalide) :- By the hydrolysis

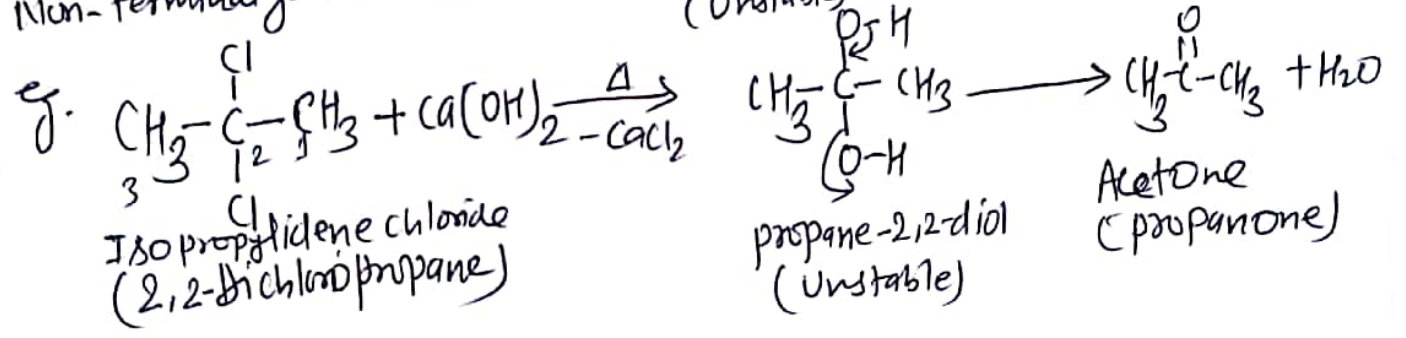
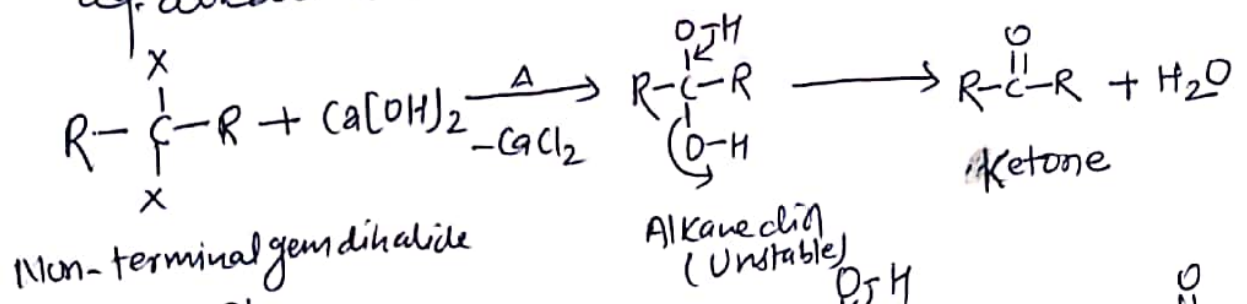
of gem dihalides:

Aldehyde :- Aldehyde is prepared by the hydrolysis ^(boiling) of gem dihalide (two halogen atoms attached to terminal

(Carbon atom) with aq. alkali like KOH, NaOH, Ca(OH)₂ or Ba(OH)₂

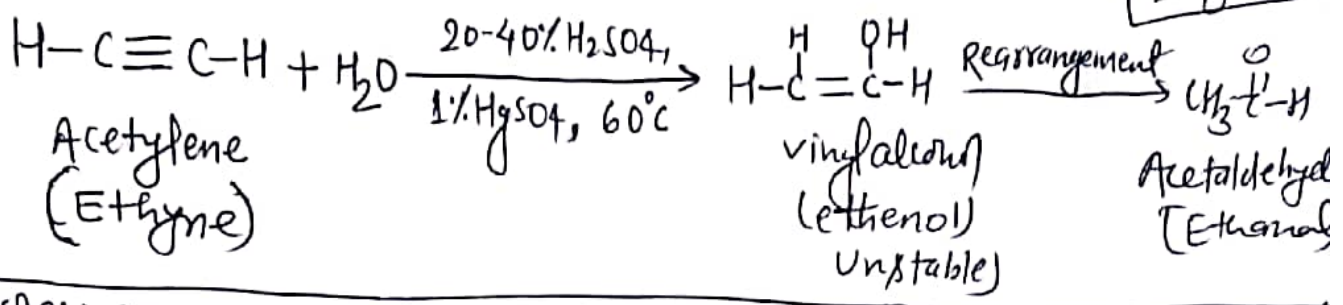


ketone ⇒ ketone is prepared by the hydrolysis (boiling) of gem dihalide (two halogen atoms attached to carbon-atom other than terminal carbon atom) with aq. alkali KOH, NaOH, Ca(OH)₂, Ba(OH)₂.



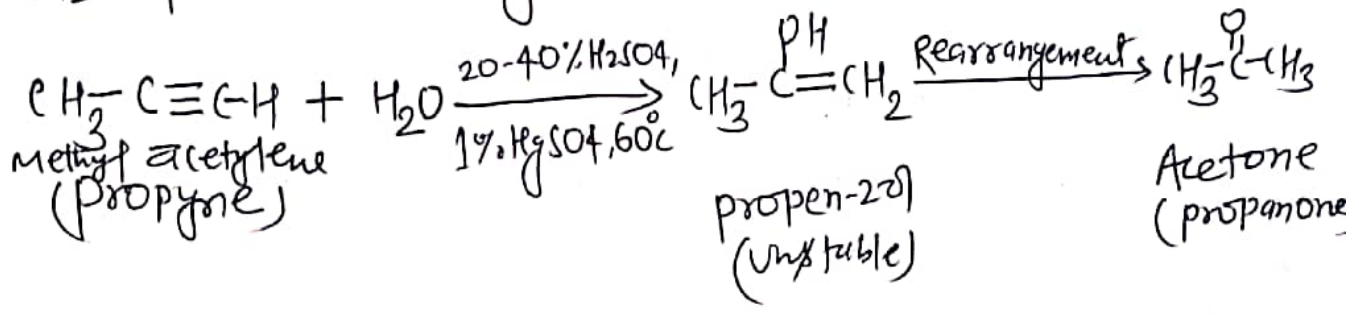
5. From alkynes ⇒ By catalytic hydration of alkynes ⇒

Aldehyde ⇒ Acetaldehyde is obtained by the catalytic hydration of acetylene (ethyne) with 20-40% H₂SO₄ and 1% HgSO₄ as catalyst at 60°C.



Note: Besides acetylene (ethyne) all alkynes give ketones in presence of 20-40% H₂SO₄ and 1% HgSO₄ at 60°C.

Ketone :- Ketone is prepared by the catalytic hydration of alkyne [except: acetylene (ethyne)] with 20-40% H₂SO₄ and 1% HgSO₄ at 60°C. It follows Markovnikov's



Properties of aldehydes and ketones page-13

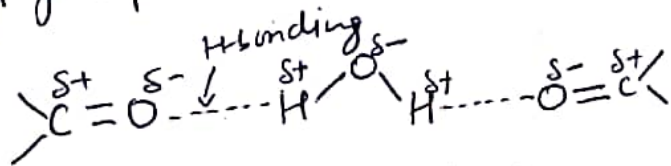
Physical properties:

1. Physical State: ⇒ Formaldehyde is a gas and acetaldehyde is volatile liquid. Lower aldehydes and ketones (upto C11) are colourless liquids. but higher members are solids.

(40% aqueous solution of formaldehyde is called formalin, which is used as preservative of anatomic specimens).

2. Smell: Lower aldehydes have unpleasant irritating odours while higher aldehydes and ketones possess pleasant odours.

3. Solubility: ⇒ Aldehydes and ketones containing four carbon atoms are soluble due to the formation of intermolecular hydrogen bonding between carbonyl group and water molecules



But higher aldehydes and ketones are insoluble due to the increase in the size of alkyl groups and their hydrophobic nature.

4. Boiling point: ⇒ Aldehydes and ketones have higher boiling points than those of ^{comparable weights of} alkanes ~~but~~ lower boiling points than those of comparable weights

of alcohols and carboxylic acids. Their higher boiling points than the alkanes are due to intermolecular δ dipole-dipole interaction between opposite ends of dipoles.

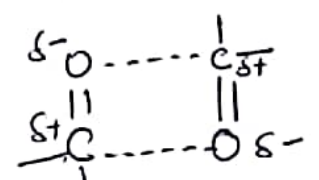
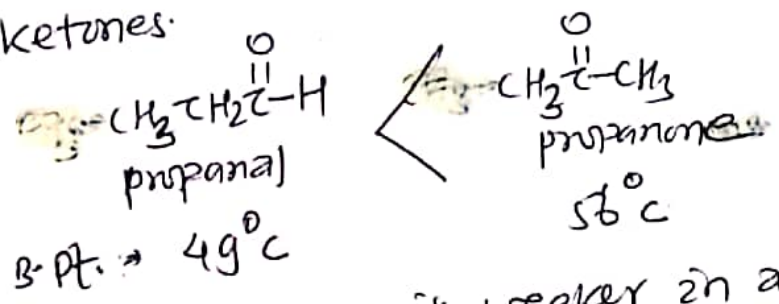


Fig. Dipole-dipole interaction.

However, these dipole-dipole interactions are weaker than the intermolecular hydrogen bonding in alcohols and carboxylic acids.

Isomeric aldehydes possess less boiling point than isomeric ketones.



Dipole-dipole interaction is weaker in aldehyde than in ketone.

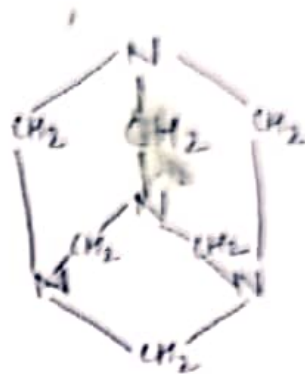
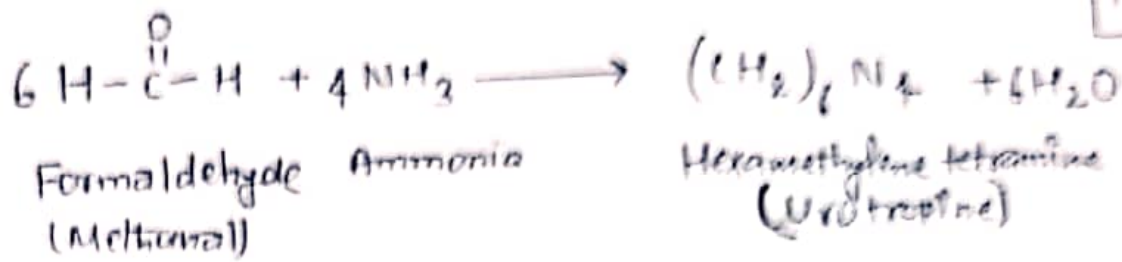
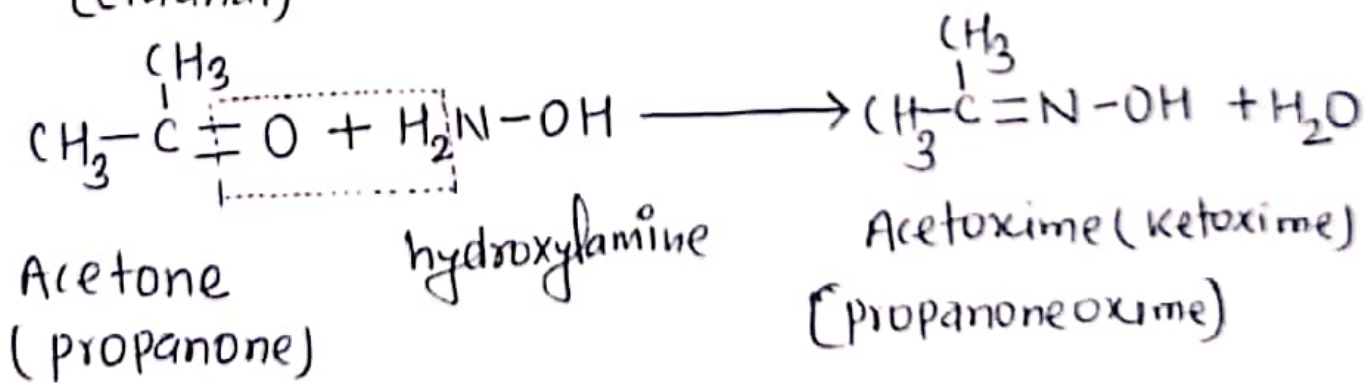
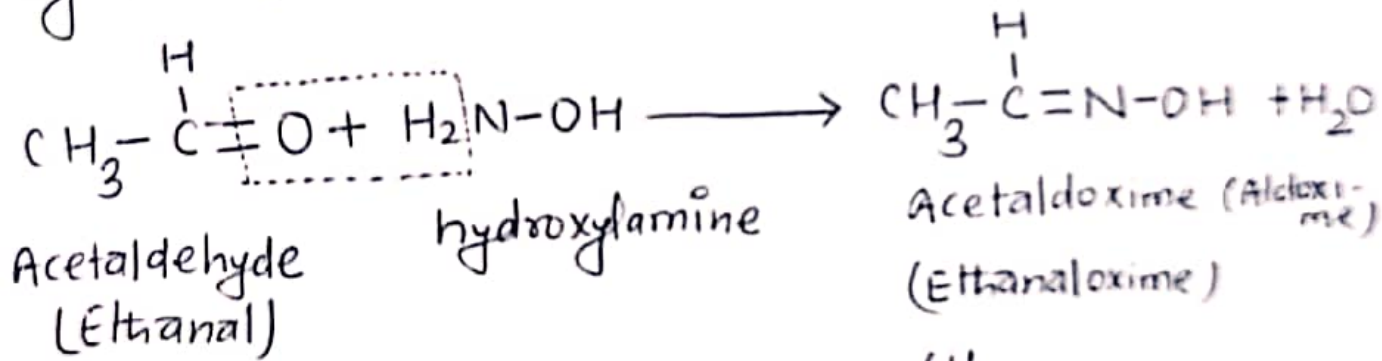
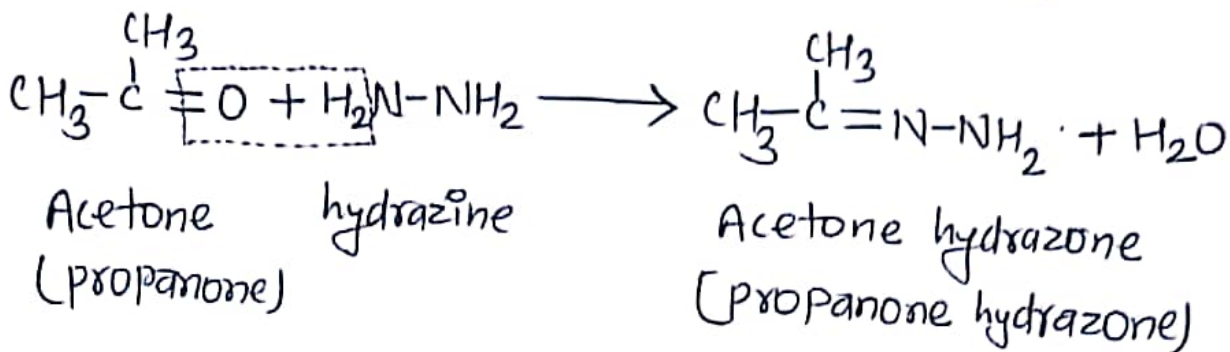
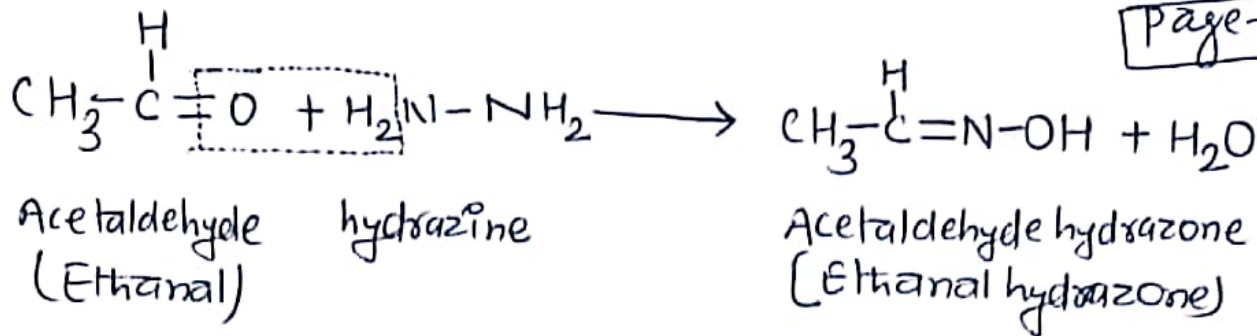


fig. structure of Urotropine

b) With NH_2OH (hydroxylamine) \Rightarrow to form oxime
Aldehyde or ketone reacts with hydroxylamine to form aldoxime or ketoxime.

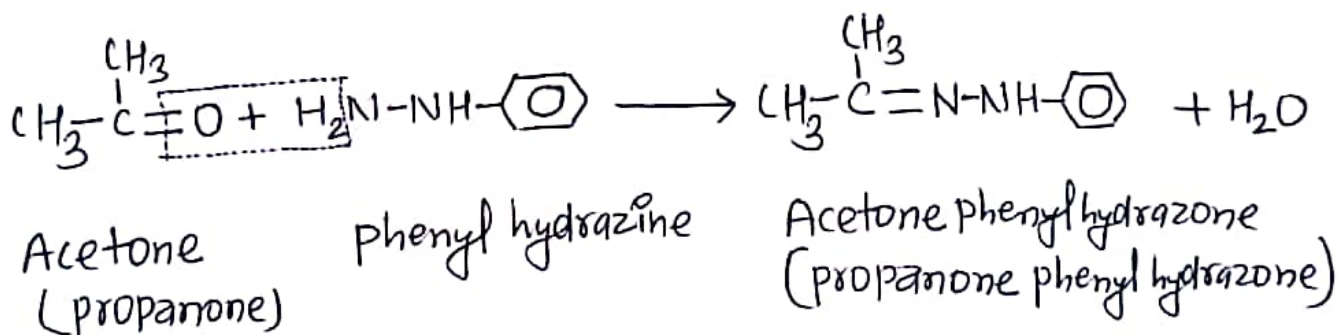
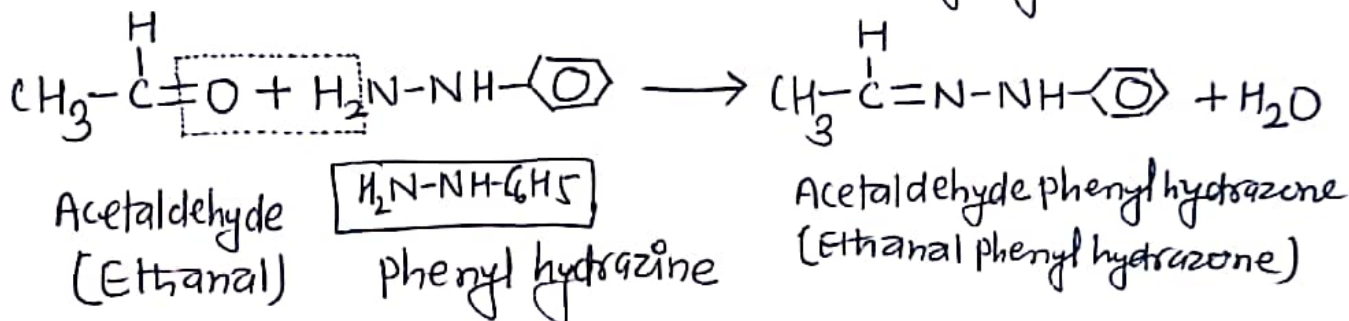


c) With NH_2-NH_2 (hydrazine) \Rightarrow to form hydrazone.
Aldehyde or ketone reacts with hydrazine (N_2H_4) to form aldehyde or ketone hydrazone.



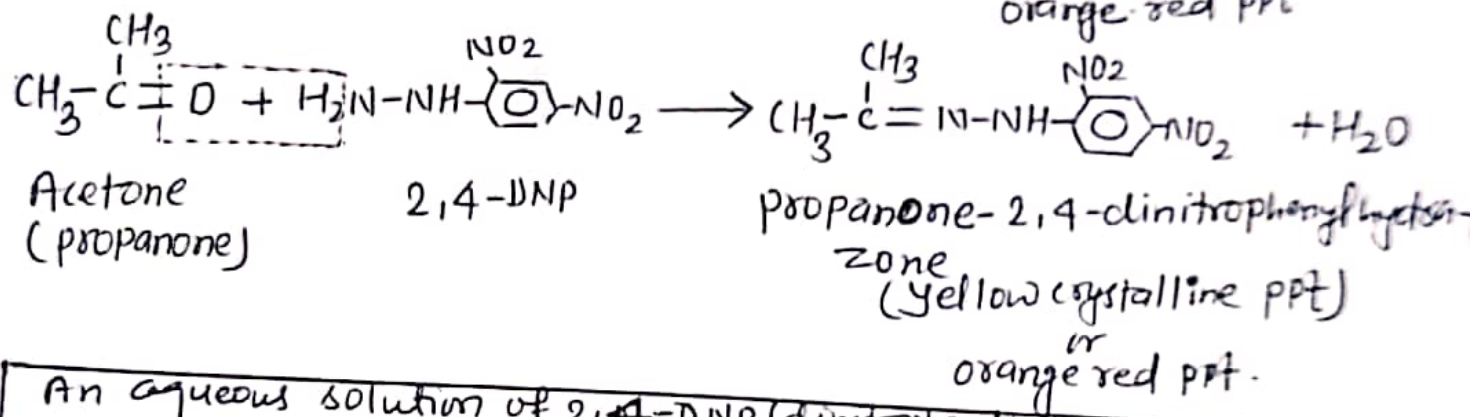
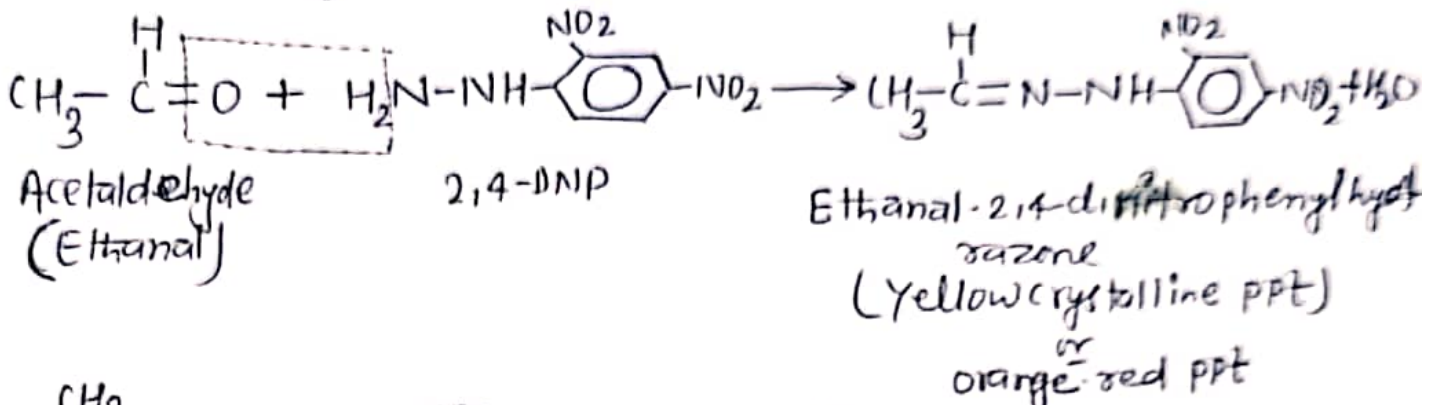
d) With $\text{H}_2\text{N}-\text{NH}-\langle\bigcirc\rangle$ (Phenyl hydrazine) \Rightarrow to form phenyl hydrazone.

Aldehyde or ketone reacts with phenyl hydrazine to form aldehyde or ketone phenyl hydrazone.



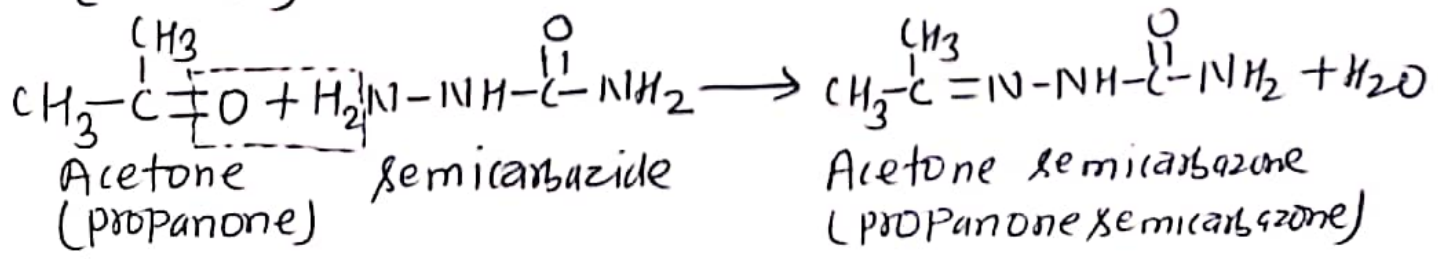
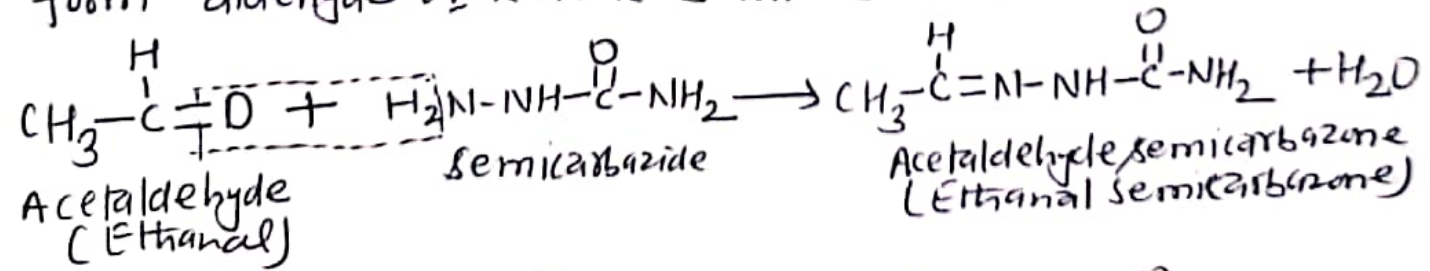
gmp e) With 2,4-DNP or 2,4-DNPH (2,4-dinitrophenyl hydrazine):
 $(\text{H}_2\text{N}-\text{NH}-\langle\bigcirc\rangle_{2,4-\text{NO}_2}) \Rightarrow$ to form yellow crystalline ppt. of 2,4-dinitrophenyl hydrazone.

Aldehyde or ketone reacts with 2,4-DNP to form yellow crystalline precipitate of aldehyde or ketone-2,4-dinitrophenylhydrazone. This reaction is used to identify the carbonyl group (aldehyde and ketone) from other categories of organic compounds in the laboratory.



An aqueous solution of 2,4-DNP (dinitrophenylhydrazine) is called Brady's reagent.

f) With $\text{H}_2\text{N}-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$ (semicarbazide); to form semicarbazone
 Aldehyde or ketone reacts with semicarbazide to form aldehyde or ketone semicarbazone.



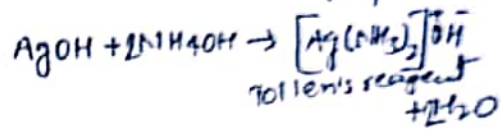
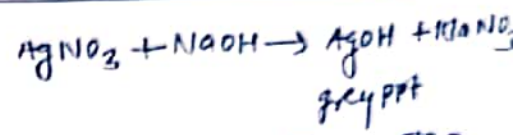
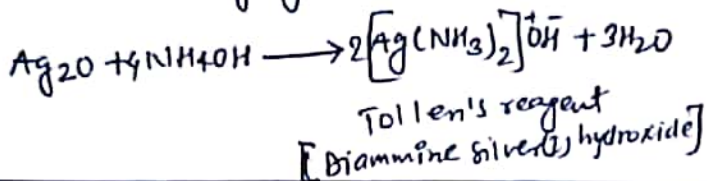
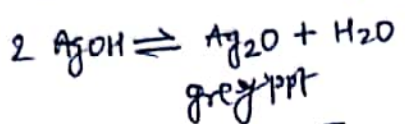
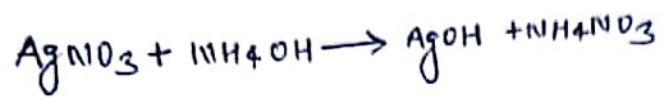
3. Oxidation reactions of aldehydes
 (Distinction between aldehyde and ketone.)

a) With Tollen's reagent (Ammonical silver nitrate solution):

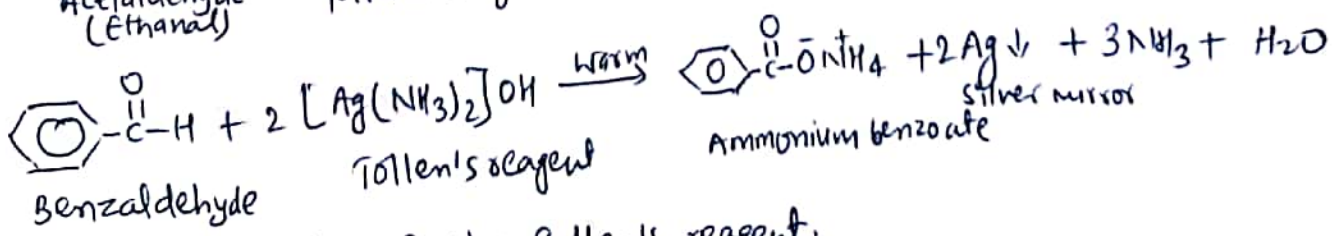
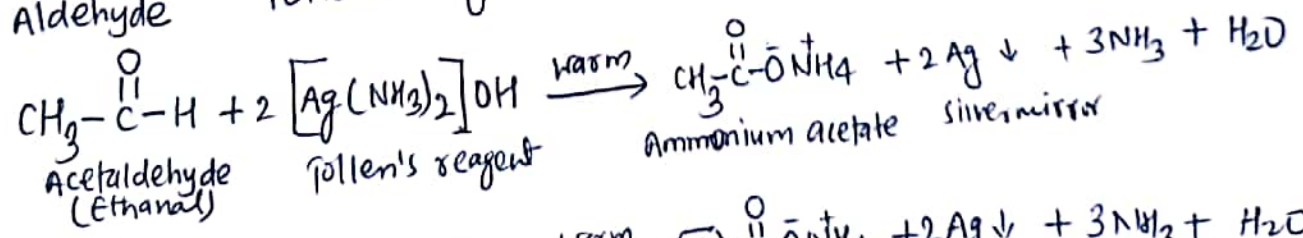
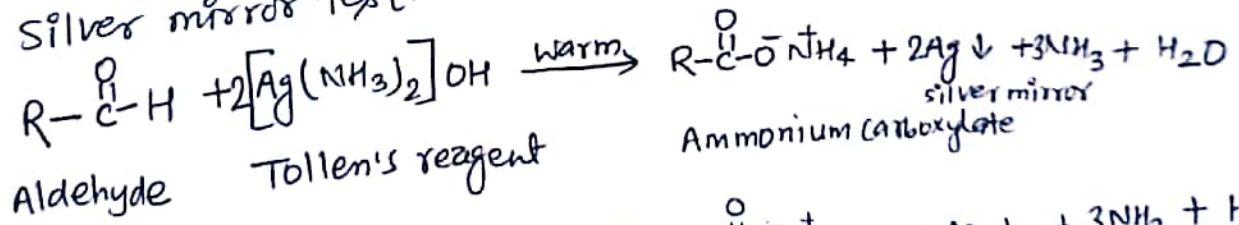
Ammonical silver nitrate (AgNO_3) solution is called

Tollen's reagent.

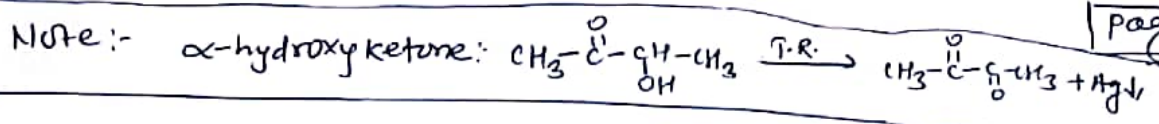
Tollen's reagent is prepared by adding ammonium hydroxide (NH_4OH) to AgNO_3 solution till the grey ppt of AgOH (formed by adding few drops of dil. NaOH with AgNO_3) just formed first gets dissolved.



When an aldehyde is warmed with Tollen's reagent, it (aldehyde) gets oxidized to ammonium carboxylate and silver ions get reduced to metallic silver. This metallic silver gets deposited on the inner wall of the test tube to form a silver mirror. Therefore, this reaction is also known as silver mirror test.



But ketone does not give Tollen's reagent.

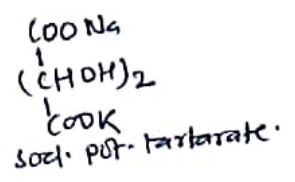


b) With Fehling's solution (Fehling test)

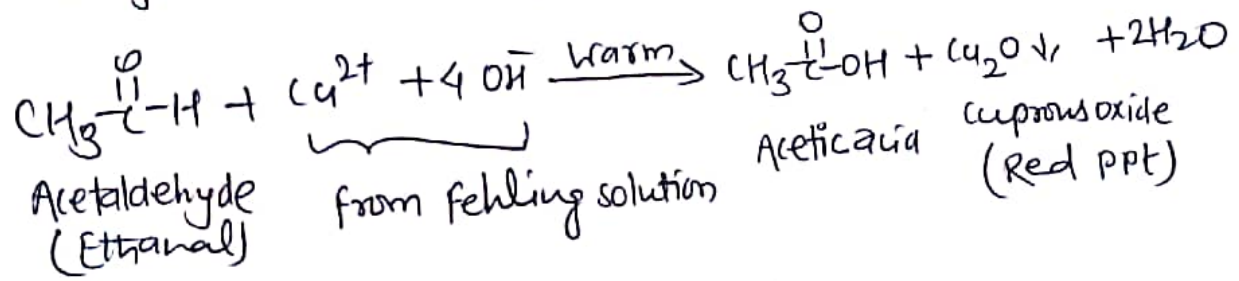
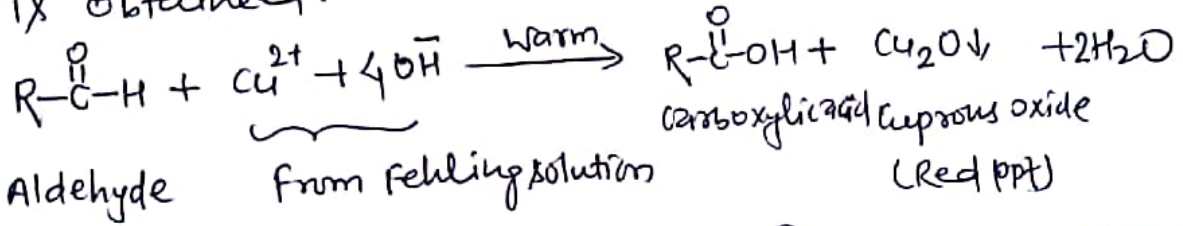
Fehling solution is a mixture of Fehling-A and Fehling B.

Fehling-A \Rightarrow CuSO_4 solution.

Fehling-B \Rightarrow sodium potassium tartarate (Rochelle salt) in NaOH solution.



When an aldehyde is warmed with Fehling's solution, it (aldehyde) oxidises to carboxylic acid and a red ppt of Cu_2O (cuprous oxide) is obtained.



But ketone doesnot give this test.

Benzaldehyde also doesnot give this test.

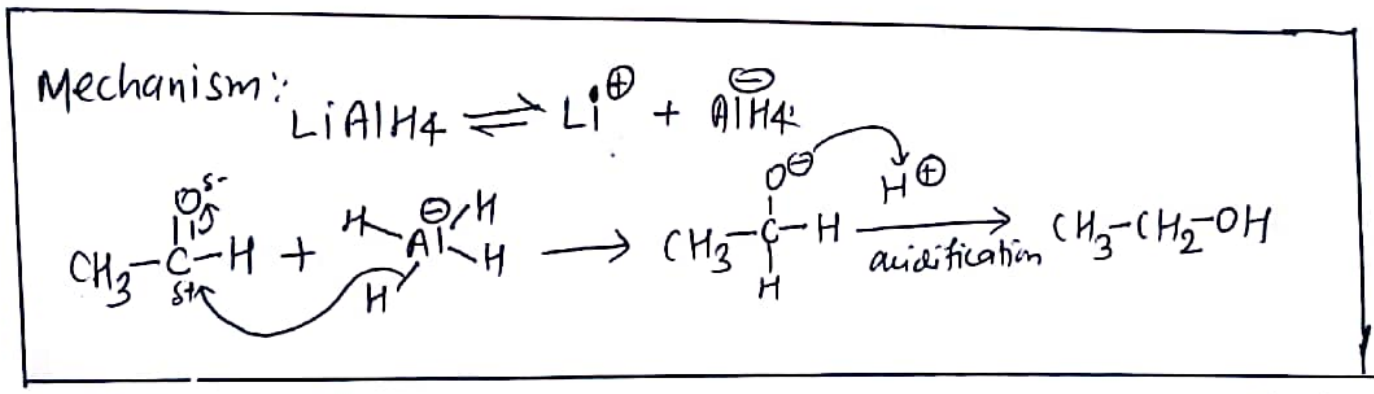
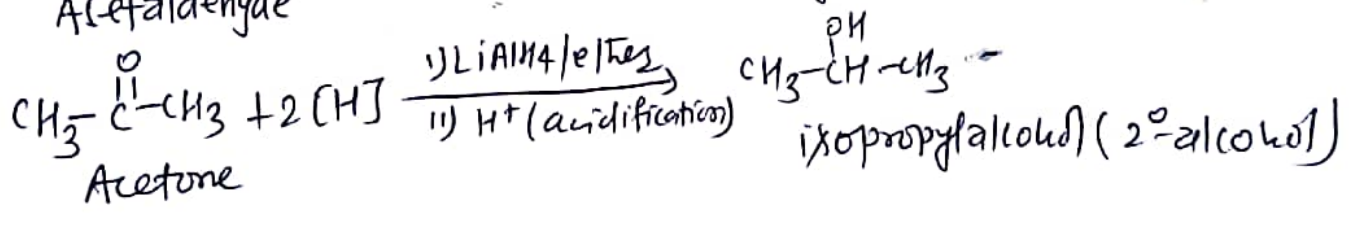
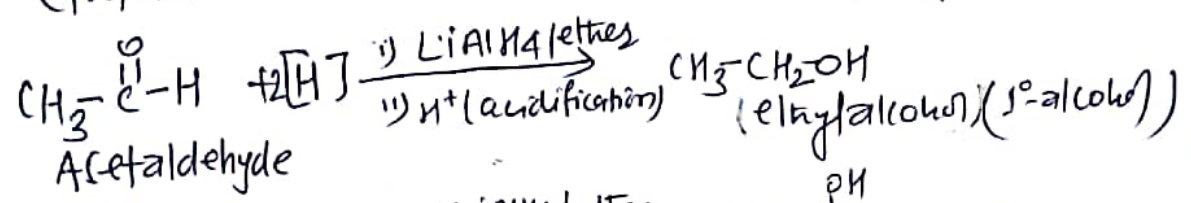
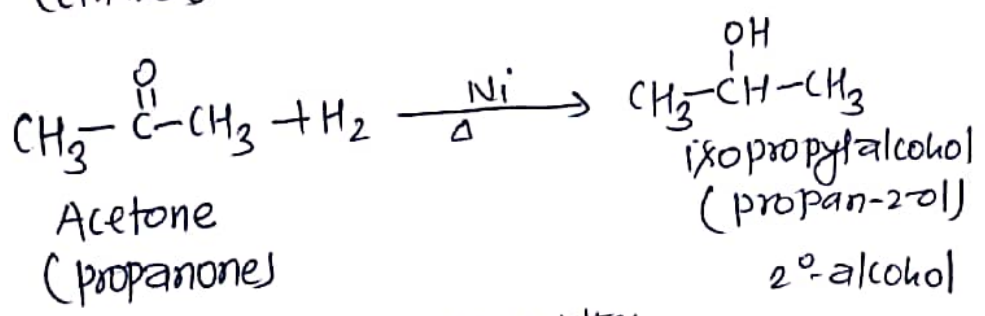
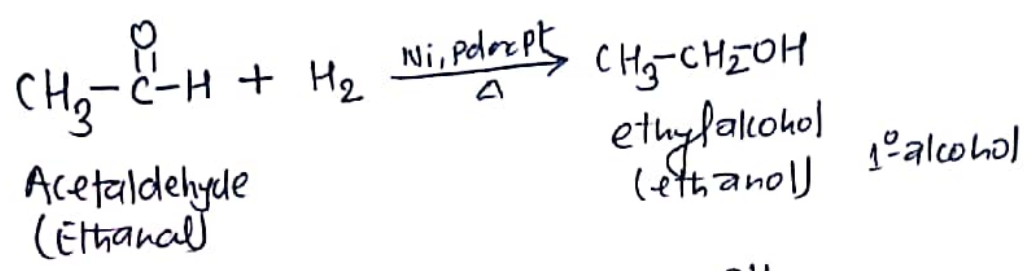
Reason: \Rightarrow due to lack of α -hydrogen in benzaldehyde it cannot form an enolate and thus donot give a positive test with Fehling's solution which is comparatively a weaker oxidizing agent than Tollens' reagent, under usual conditions.

This test is used to identify aliphatic aldehydes from aromatic aldehyde and ketone.

4. Reduction reactions ⇒

a) With H₂ in presence of Ni, Pd or Pt or LiAlH₄ (or NaBH₄) used for selective reduction of C=O group

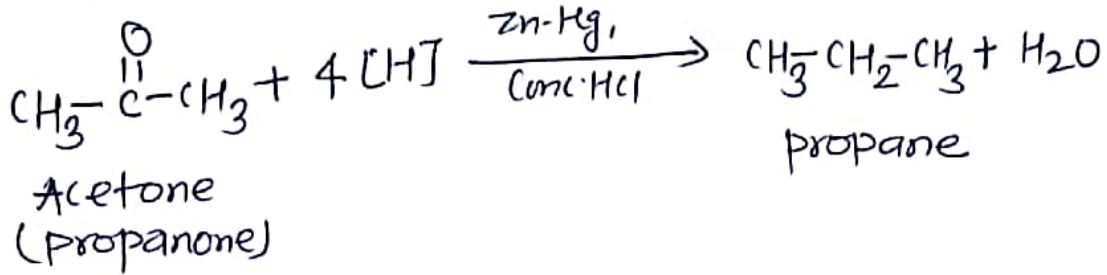
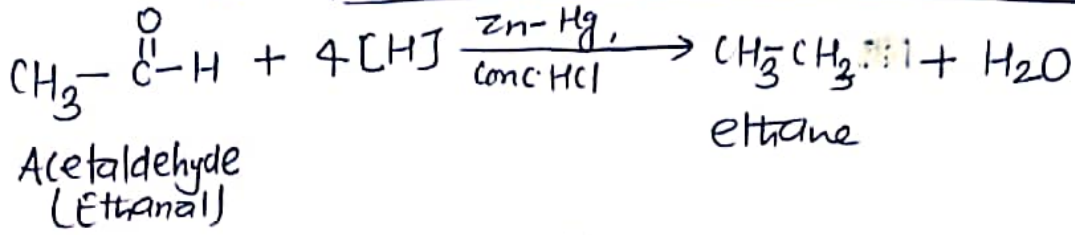
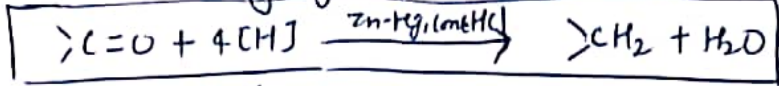
Aldehyde and ketone can be reduced to primary and secondary alcohols respectively by using reducing agents like H₂/Ni or Pd or Pt or LiAlH₄ or NaBH₄ (sodium borohydride).
(Lithium aluminium hydride)



b) With Zn-Hg (zinc amalgam) / conc. HCl (Clemmensen's reduction) ⇒

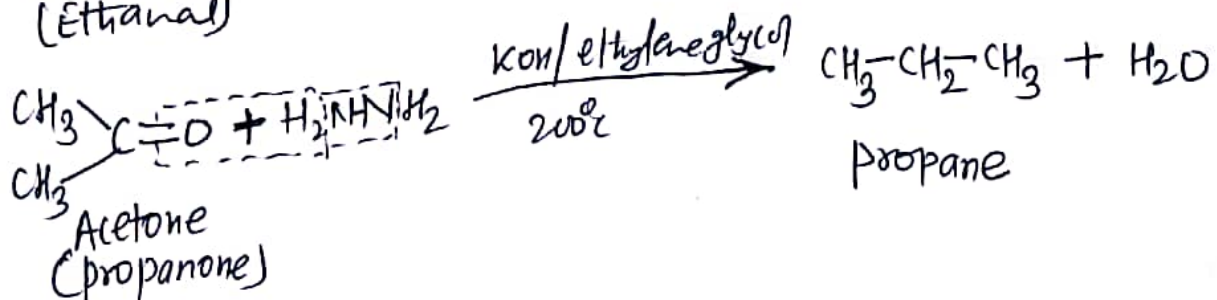
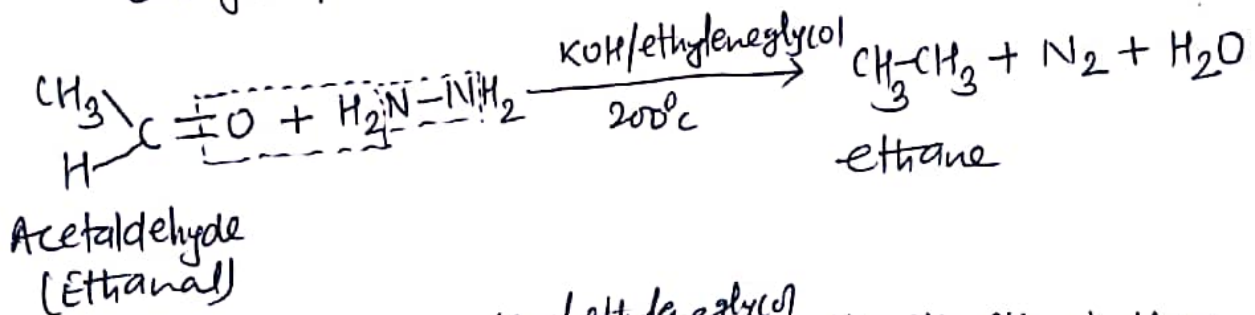
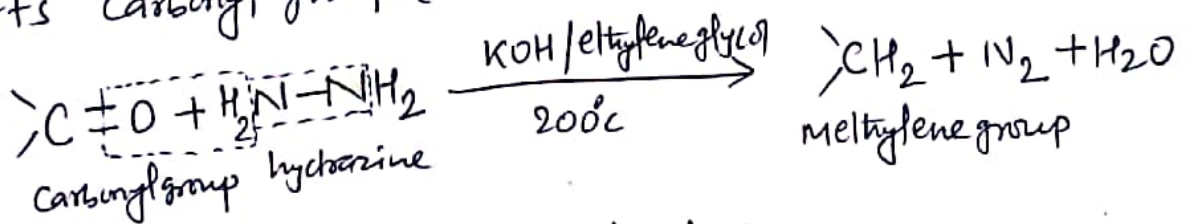
Carbonyl compound (aldehyde or ketone) reacts with zinc amalgam (Zn/Hg) in presence of conc. HCl to form an alkane. This

reaction is known as Clemmensen's reduction; This reaction converts the carbonyl group ($>C=O$) into methylene group ($>CH_2$).



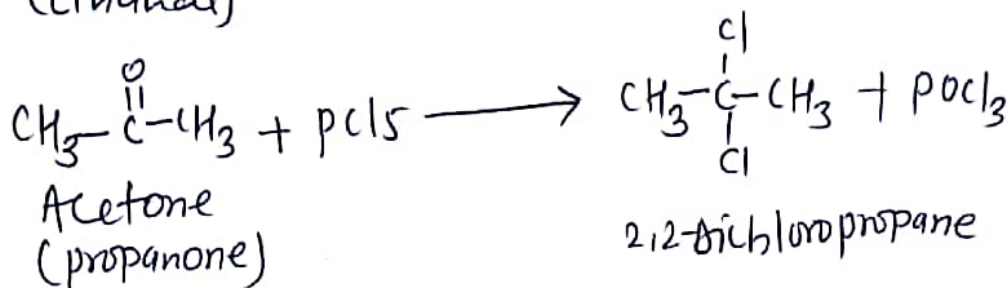
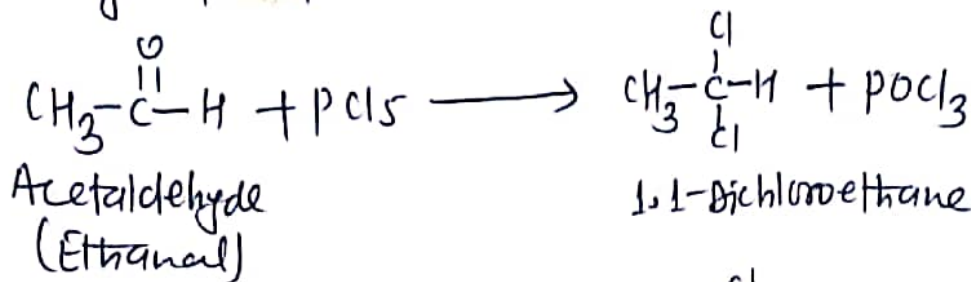
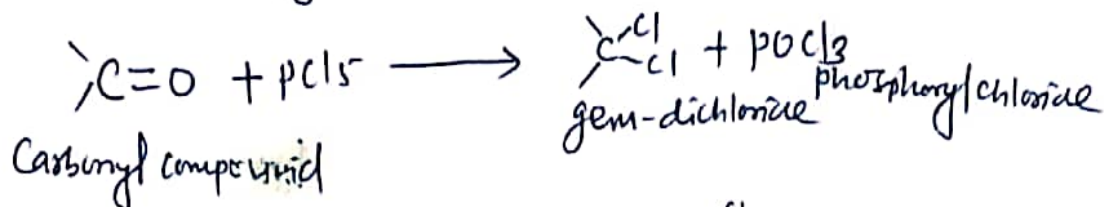
c) With ^{alkaline} N_2H_4 (hydrazine) in presence of ethylene glycol (Wolff-Kishner reduction).

Carbonyl compound (aldehyde or ketone) reacts with alkaline hydrazine (N_2H_4 or NH_2NH_2 and $NaOH$ or KOH) in presence of ethylene glycol ($HO-CH_2-CH_2-OH$) at $200^\circ C$ to form an alkane. This reaction is known as Wolff-Kishner reduction. This reaction converts carbonyl group ($>C=O$) into methylene group ($>CH_2$).



d) With PCl₅ (Phosphorus pentachloride)

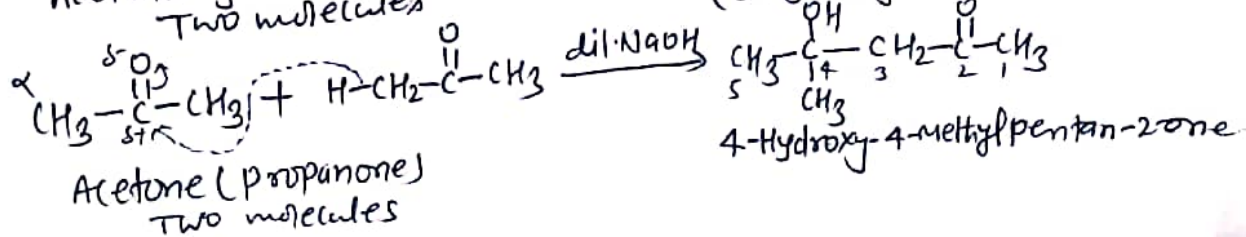
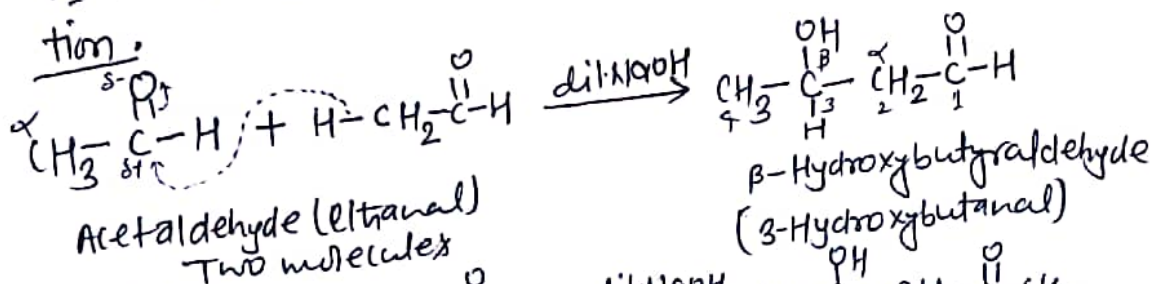
Aldehyde or ketone reacts with PCl₅ to form gem-dichloride (gem-dichloroalkane).



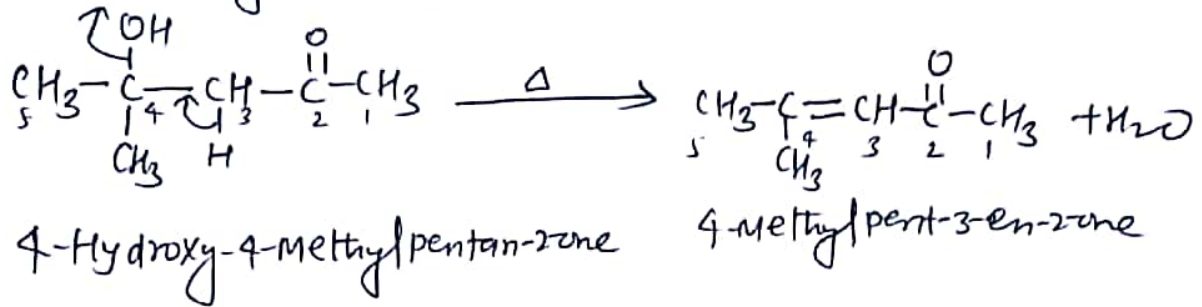
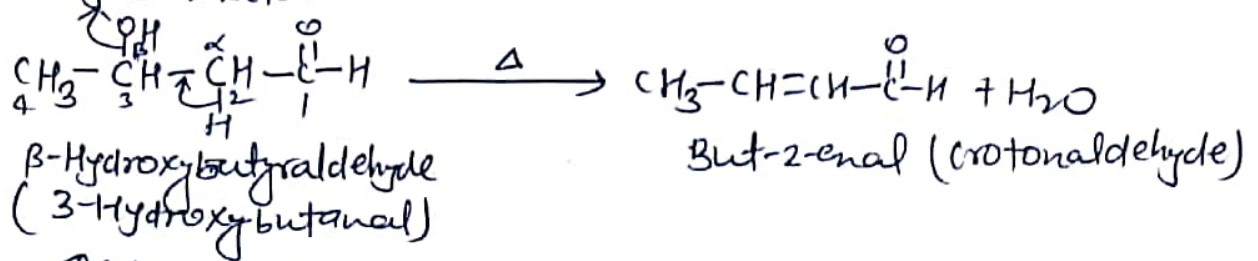
5. Reactions due to alkyl group

⇒ With dil. alkali (dil. NaOH) ⇒ Aldol condensation :

Two molecules of aldehyde or ketone containing α-hydrogen undergo self condensation in the presence of dil. alkali like dil. NaOH to give β-hydroxyaldehyde (called aldol) or β-hydroxyketone. This reaction is known as aldol condensation.



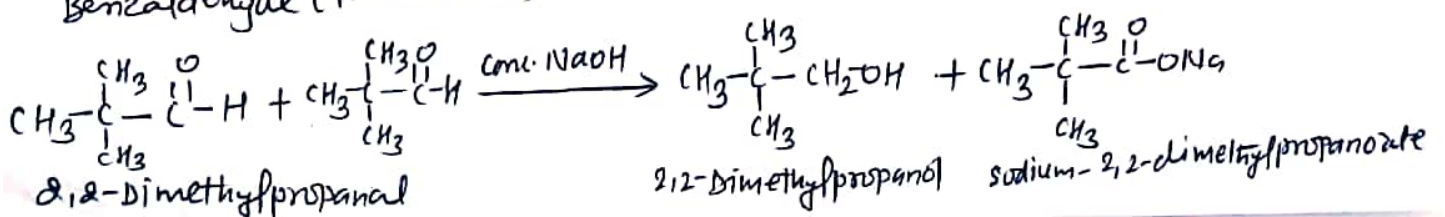
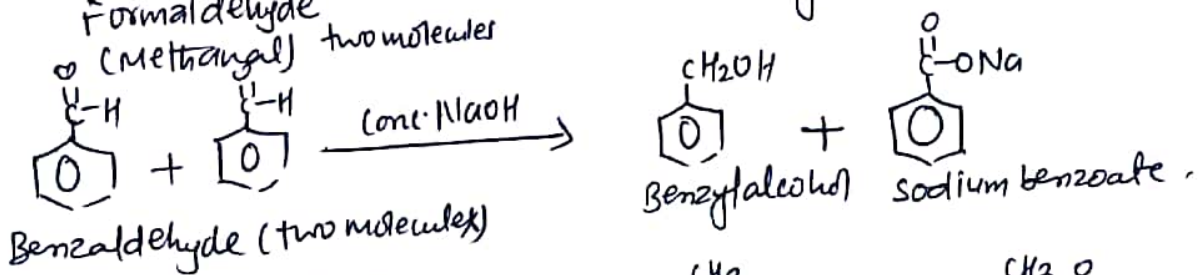
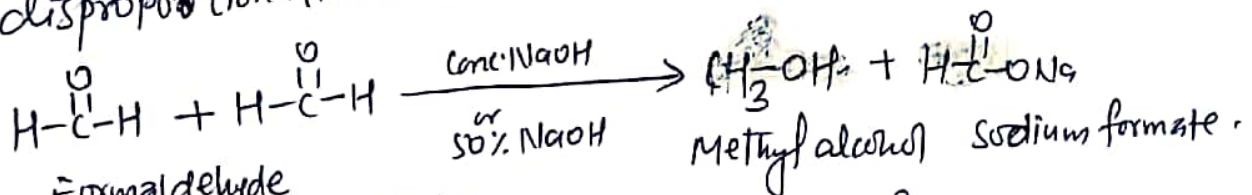
So the formed β -hydroxyaldehyde or β -hydroxyketone Page-28
 on heating (warming) undergoes dehydration to form unsaturated
 aldehyde or ketone.



6. Miscellaneous reactions :-

9) With conc. NaOH or 50% NaOH (Cannizzaro's reaction):

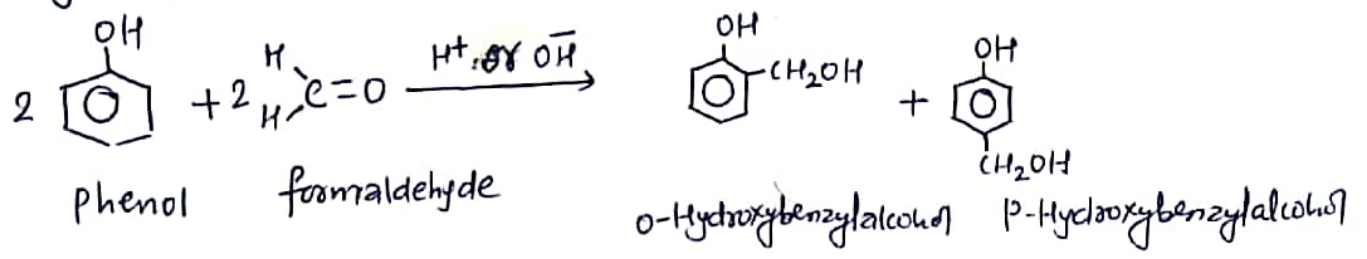
Aldehydes having no α -hydrogen (eg. HCHO , $\text{C}_6\text{H}_5\text{CHO}$, R_3CCHO etc) undergo self oxidation and reduction in the presence of conc. NaOH or 50% NaOH to form sodium salt of carboxylic acid and alcohol respectively. This reaction is known as Cannizzaro's reaction. This reaction is also known as disproportionation reaction.



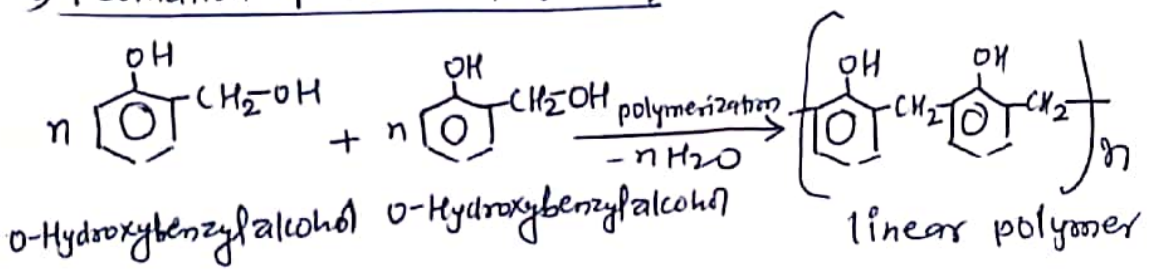
b) Reaction methanal (formaldehyde) with phenol:

Formaldehyde (Methanal) condenses with phenol in the presence of acid or base as catalyst to bakelite (phenol-formaldehyde resin). This reaction is known as Lader-Manase's reaction.

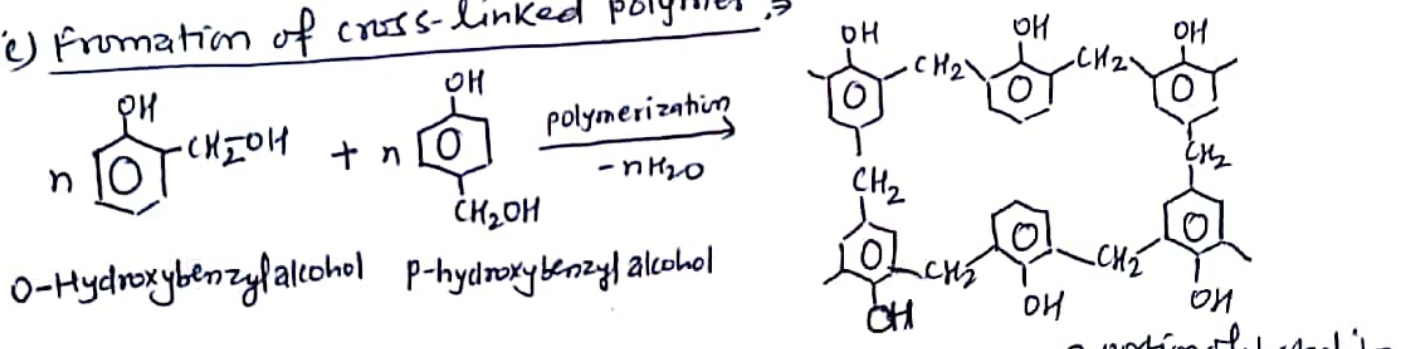
9) Formation of intermediates i.e. o-hydroxybenzyl alcohol and p-hydroxybenzyl alcohol.



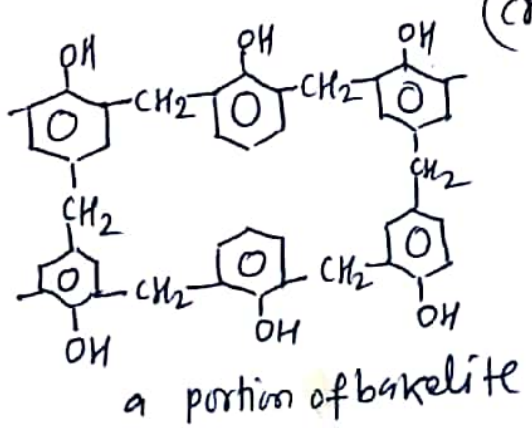
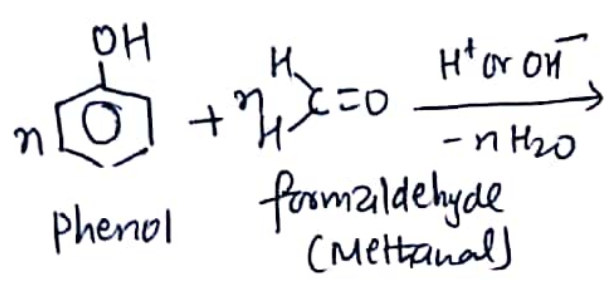
b) Formation of linear polymer :-



e) Formation of cross-linked polymer :-

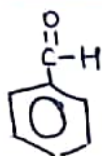


OR



Aromatic aldehydes and ketones:

Aromatic aldehyde:



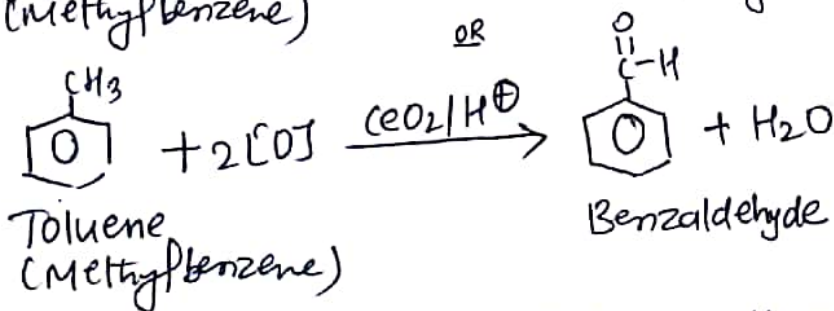
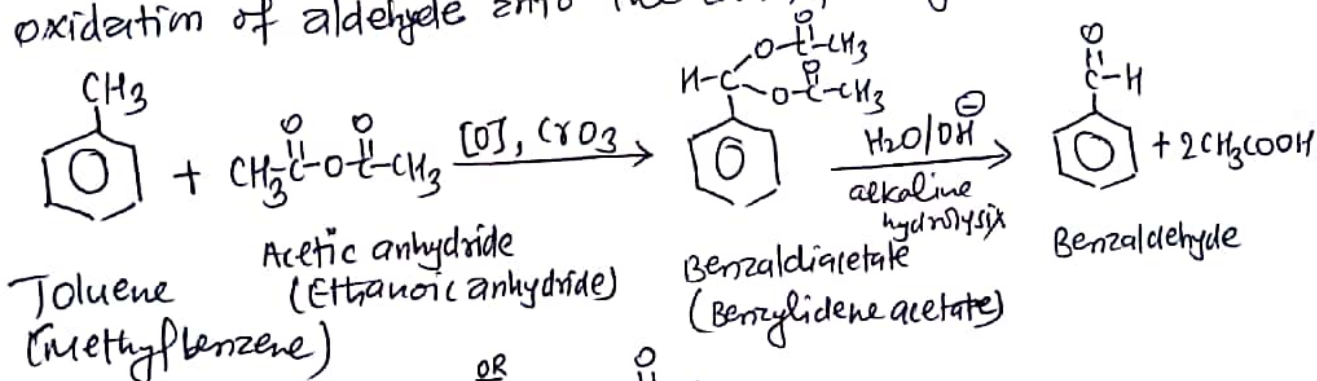
Benzaldehyde

General method of preparation of benzaldehyde

1. From toluene (methylbenzene):

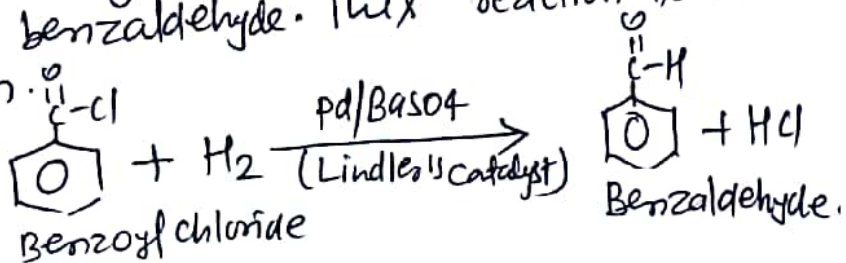
Benzaldehyde is prepared by the oxidation of toluene (methylbenzene) with chromic anhydride i.e. chromium trioxide (CrO_3) in acetic anhydride [or acidified cerium oxide (CeO_2/H^+)] followed by hydrolysis in the presence of alkali.

The function of acetic anhydride is to prevent the further oxidation of aldehyde into the corresponding acid.



2. From benzoyl chloride: (Rosenmund's reduction):

Benzoyl chloride reacts with H_2 in presence of $Pd/BaSO_4$ to form benzaldehyde. This reaction is known as Rosenmund's reduction.

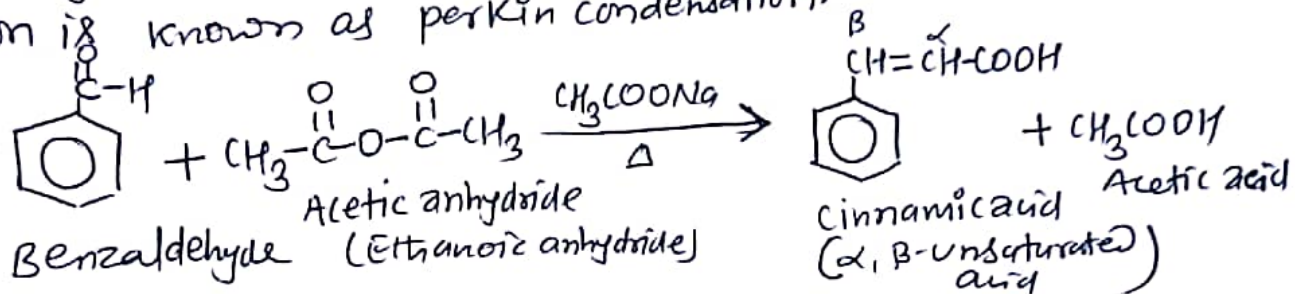


properties of benzaldehyde :-

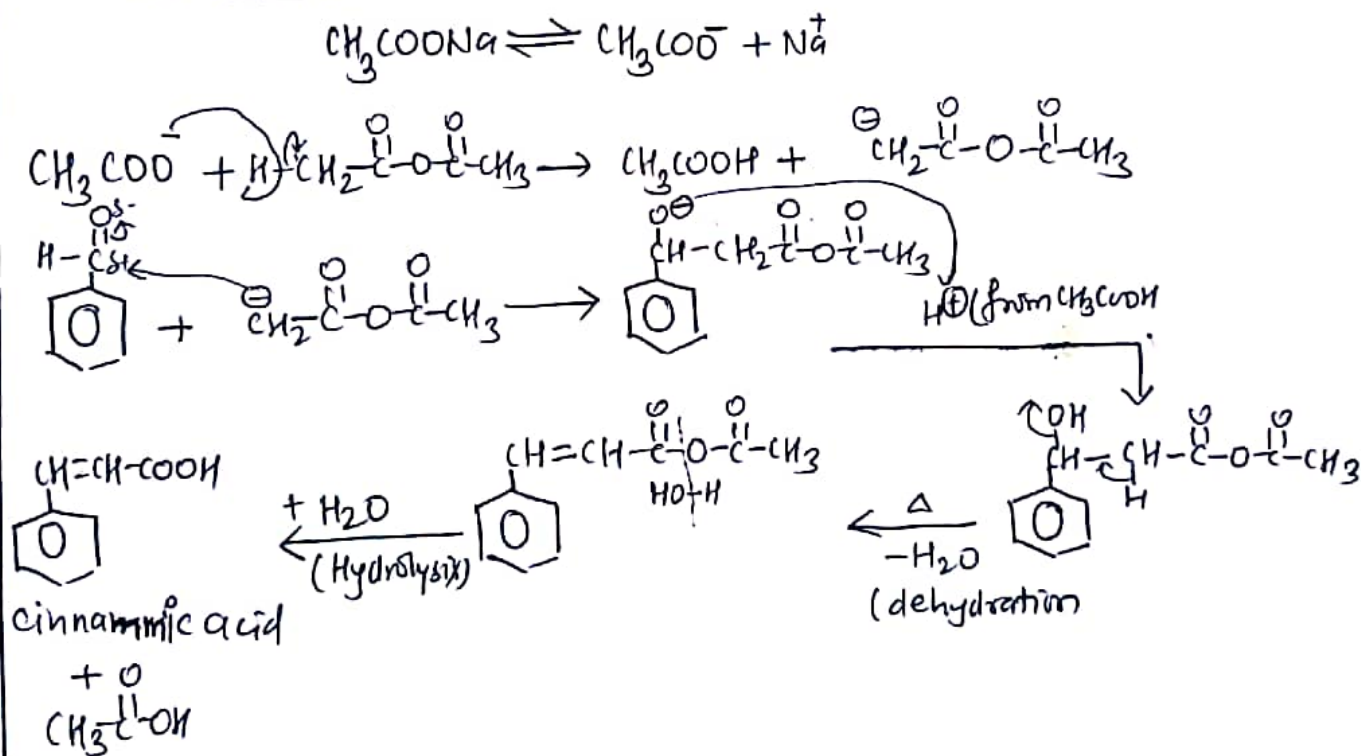
Important reactions of benzaldehyde different from aliphatic aldehydes :

1. Perkin condensation (perkin reaction)

Benzaldehyde (aromatic aldehyde) reacts with acetic anhydride (aliphatic anhydride having at least two α -hydrogen atoms) in the presence of sodium acetate (sodium salt of aliphatic acid) to give α, β -unsaturated acid. This reaction is known as perkin condensation.



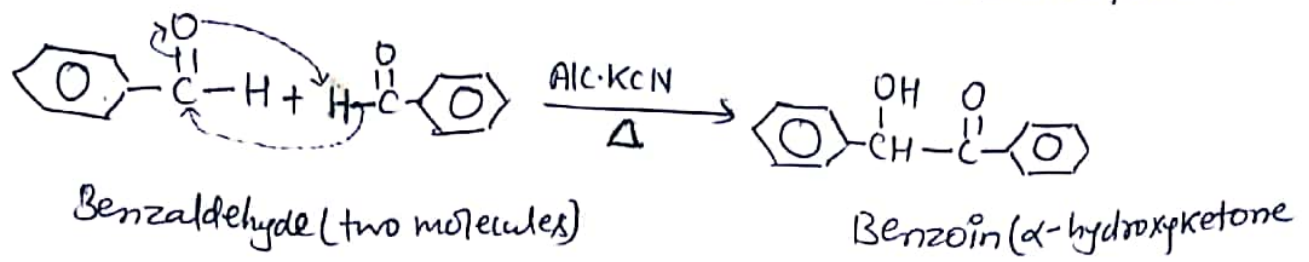
Mechanism :-



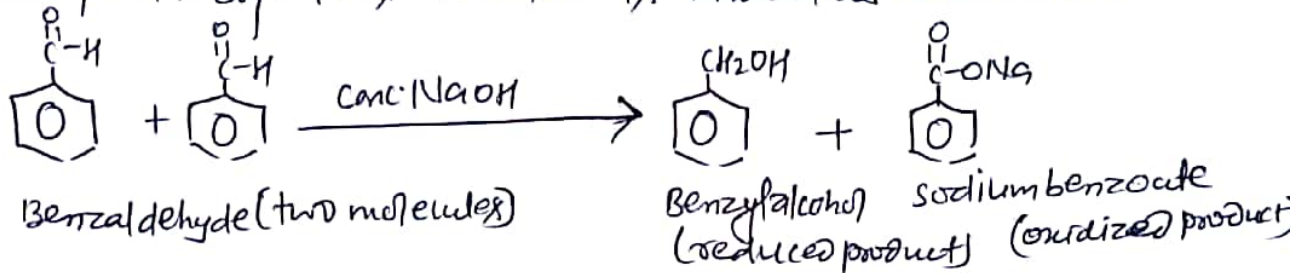
2. Benzoin condensation :- Benzaldehyde (aromatic aldehyde) is heated (refluxed) with an alcoholic solution of KCN (potassium cyanide) to form benzoin (α -hydroxyketone). This reaction is known

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as benzoin condensation. In this reaction, two molecules of benzaldehyde undergo condensation to form a molecule of benzoin.



3. Cannizzaro's reaction \Rightarrow Benzaldehyde (having no α -hydrogen) undergoes oxidation and reduction in presence of conc. NaOH or 50% NaOH to form sodium benzoate and benzyl alcohol respectively. This reaction is known as Cannizzaro's reaction.



4. Electrophilic substitution reactions (Reactions due to benzene ring)

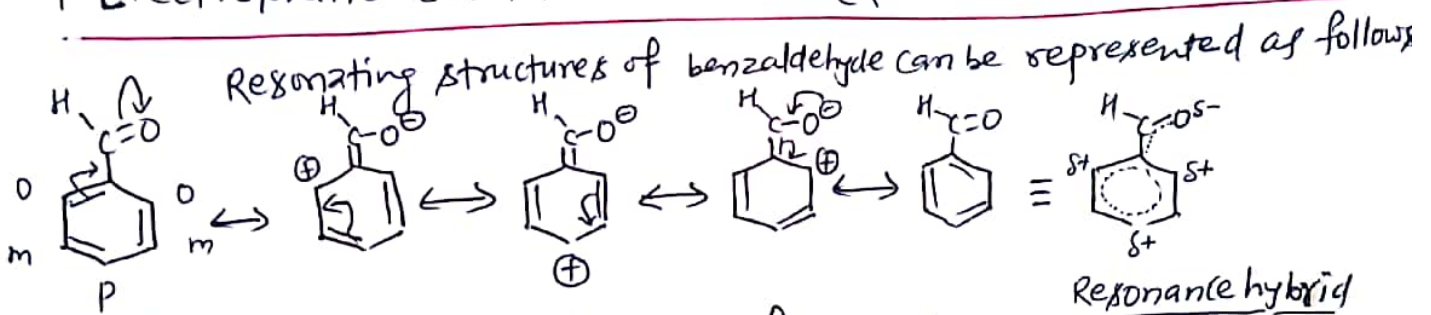
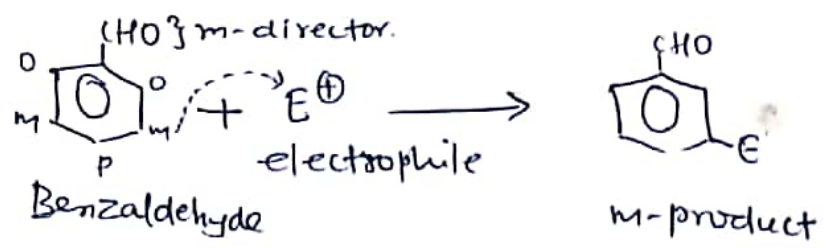


Fig. Resonating structures of benzaldehyde

Here, $-CHO$ group in benzaldehyde is electron withdrawing group (EWG). It decreases electron density at o- and p- positions in the benzene ring of benzaldehyde. Because of this, the electron density is relatively higher at meta position than at ortho and para positions. Therefore, electrophile can attack at meta-positions. Hence, electrophilic substitution reaction in benzaldehyde takes place at meta-position i.e. $-CHO$ group in benzaldehyde is m-directing.



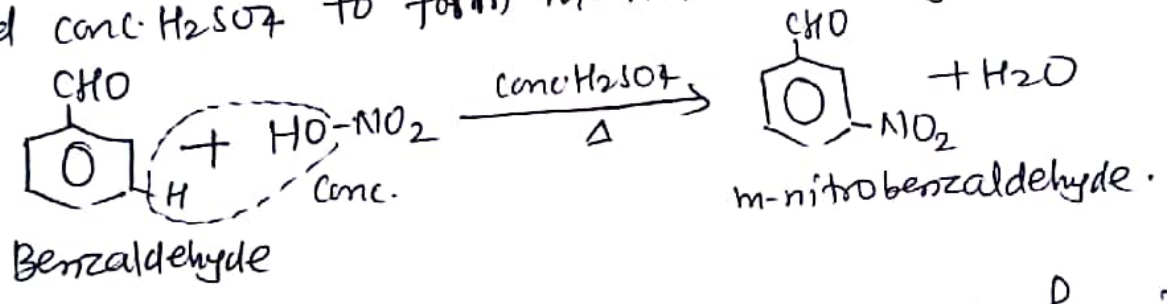
Some electrophilic substitution reactions in benzaldehyde are given below:

i. Chlorination (Halogenation):

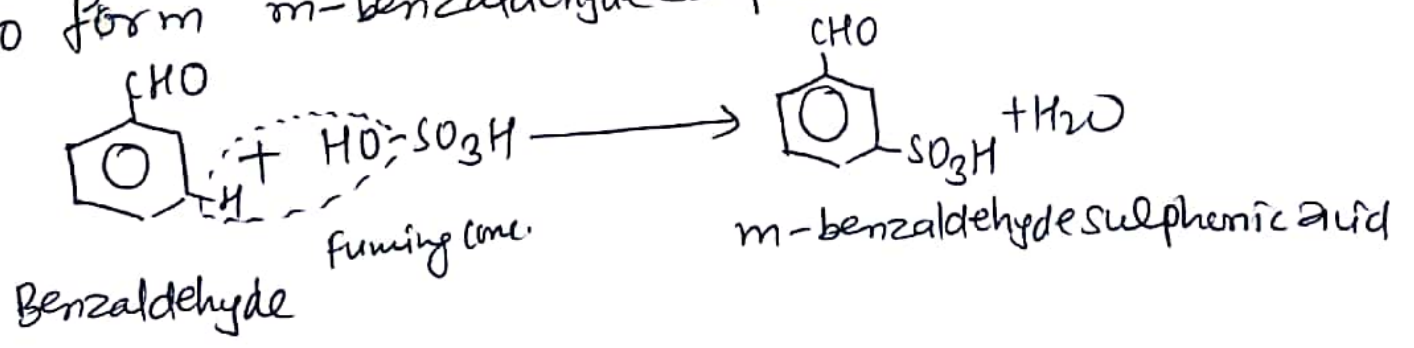
Benzaldehyde reacts with chlorine in presence of FeCl_3 to form m-chlorobenzaldehyde.

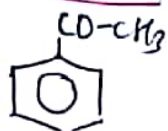


ii. Nitration: Benzaldehyde is heated (at 40°C) with conc. HNO_3 and conc. H_2SO_4 to form m-nitrobenzaldehyde.



(iii) Sulphonation: Benzaldehyde reacts with fuming conc. H_2SO_4 to form m-benzaldehyde sulphonie acid.

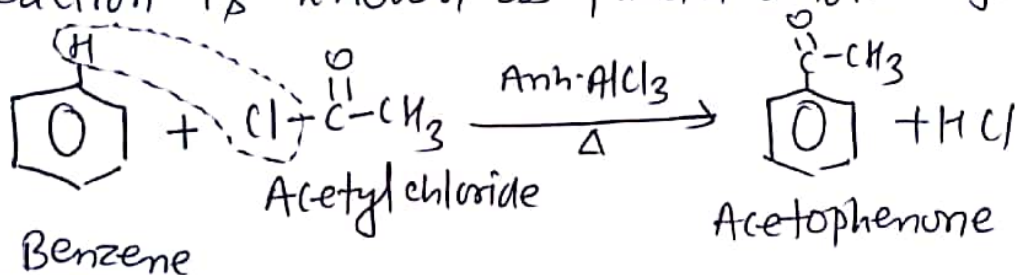




Acetophenone

Preparation of Acetophenone from benzene by Friedel-Crafts acylation :-

When benzene is heated with acetylchloride in the presence of anhydrous $AlCl_3$, Acetophenone is obtained. This reaction is known as Friedel-Crafts acylation.



Mechanism;

