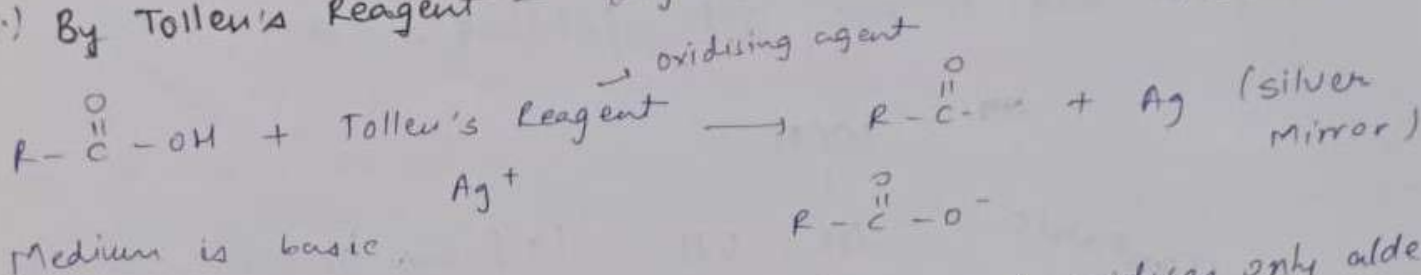


## Oxidation to Aldehydes and Ketones

Aldehydes can be oxidised easily and this is used to distinguish aldehydes from ketones.

(1) By Tollen's Reagent -  $(AgNO_3 + NH_4OH)$  Ammonical silver nitrate.



Medium is basic.

Tollen's reagent is a selective oxidising agent oxidises only aldehydes.  $\rightarrow$  does not attack alkenes.

If not done in perfect conditions in spite of silver mirror we can get black ppt. also.

**Silver mirror test** - If we heat Ag in a test tube then when it will be cooled it may deposited on the walls of the test tube or it may lie down if very low concentration of  $AgNO_3$  was taken then black ppt. will appear.

$\rightarrow$  Formic acid also gives Tollen's Test

$\rightarrow$   $\alpha$  hydroxy ketones give a positive Tollen's test (Imp.)

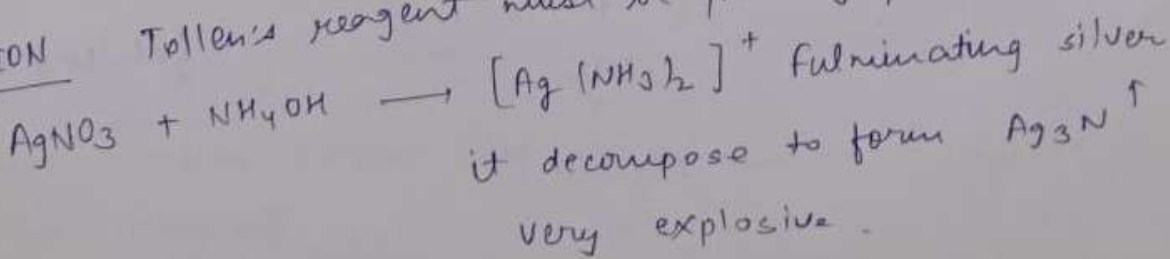
ex Fructose, Benzoin

$\rightarrow$  This rxn is used for making mirrors

In making mirror an oxide of lead is used because it restricts the contact of silver and air because when silver contacts with air it turns black.

Take a piece of silver and add  $AgNO_3 + NH_4OH$  with lukewarm water and take HCHO or glucose (cheaper). here a film will be formed to protect it lead paste is used.

PRECAUTION Tollen's reagent must be freshly prepared



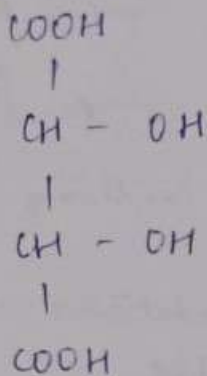
## Fehling's Test

A  
 $\text{CuSO}_4$   
sol<sup>n</sup>

B  
Sodium Potassium Tartarate  
(Roschelle's Salt)

By mixing A and B we get Fehling's sol<sup>n</sup>

Tartaric acid



(If we remove one H from one and the other carboxylic acid and give Na<sup>+</sup>

and K<sup>+</sup> we will get Sodium Potassium Tartarate)

This is a redox rxn here aldehyde is oxidised Cu is reduced from +2 to +1



⚠ Aromatic aldehydes do not give this test.

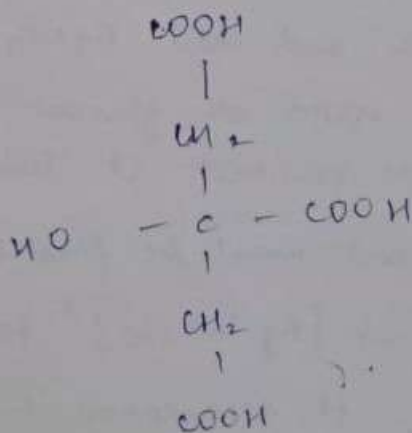
Reason: They give Cannizzaro rxn.

## Benedict's Test

A  
 $\text{CuSO}_4$  sol<sup>n</sup>

B  
Sodium Citrate

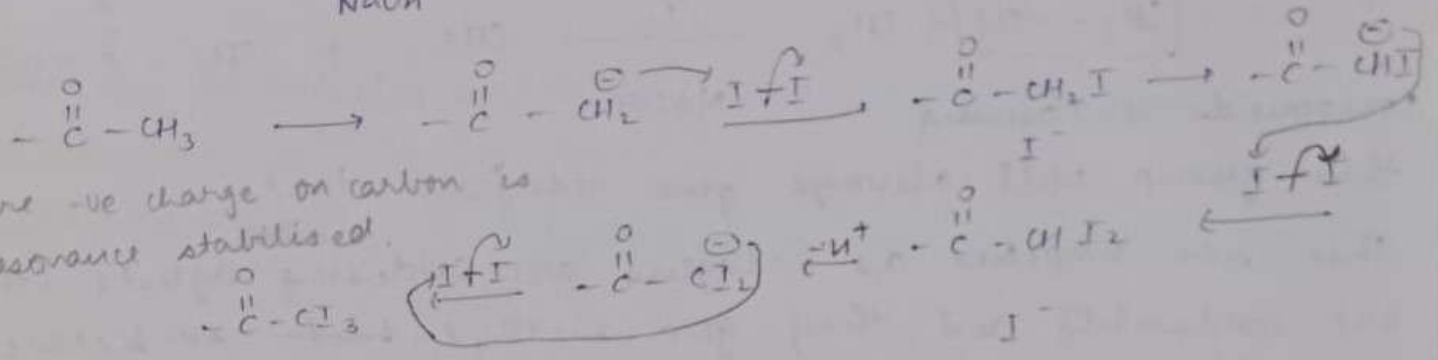
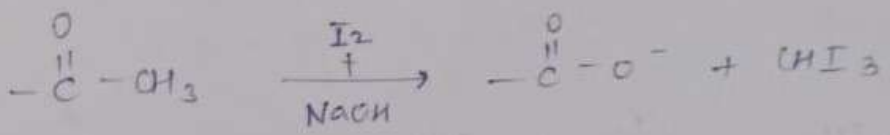
By mixing A and B we will get Benedict's Test



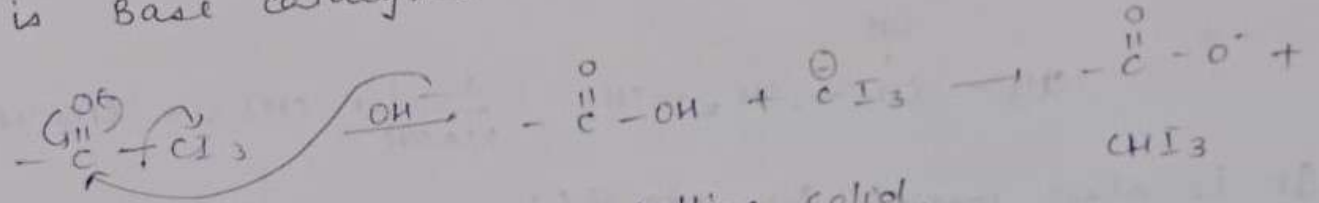
Rest everything is like Fehling's test

# # OXIDATION OF METHYL KETONES (The Iodoform reaction)

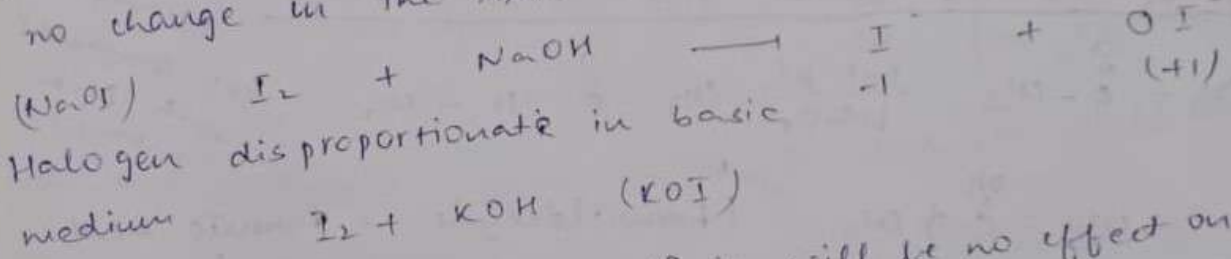
(All 2-ol give iodoform test)



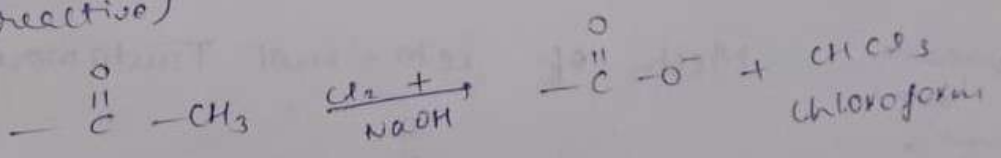
This is Base catalysed α Halogenation



Iodoform is a yellow-crystalline solid. Here we can write NaOI instead of I<sub>2</sub> + NaOH it will make no change in the rxn.

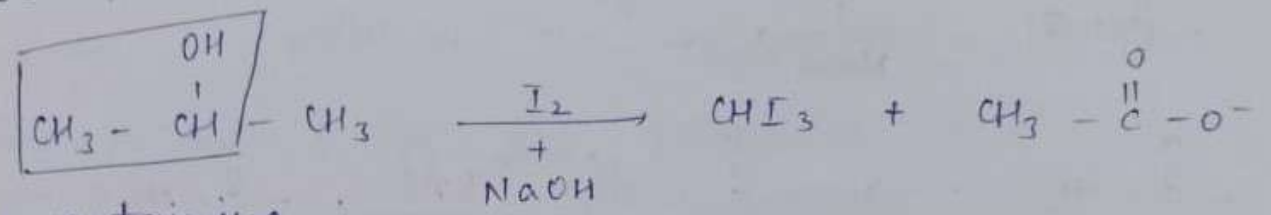


By changing the halogen there will be no effect on rxn but fluorine cannot be disproportionated we cannot make F<sup>+</sup> (it will do rxn instantly with NaOH being very reactive)



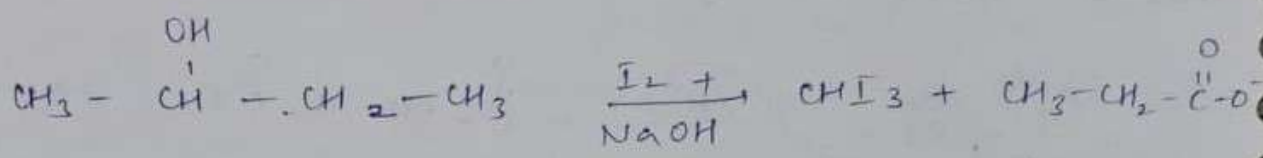
Carbon-Carbon double bonds are not affected by this reagent.

Acetaldehyde gives +ve iodoform test (it means yellow ppt. has occurred)



Compounds containing this group will always give iodoform test

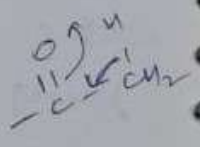
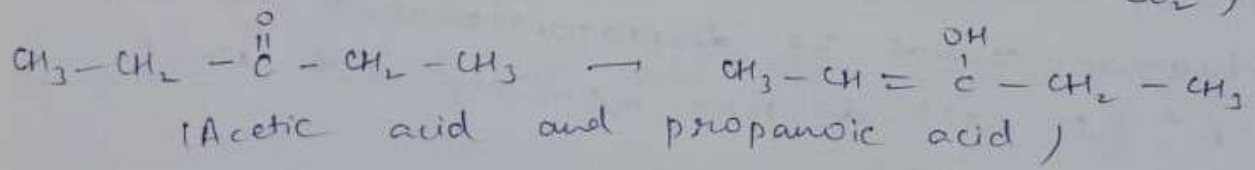
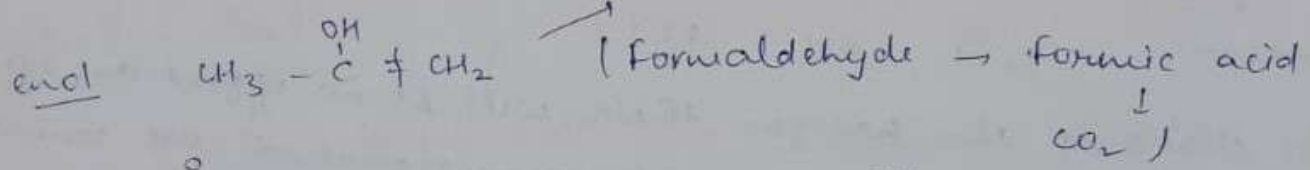
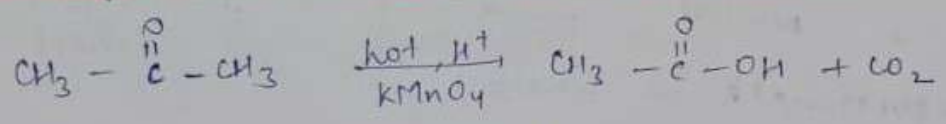
This rxn happens as halogens are oxidising agents (they are oxidisable and they give methyl test to ketone so methyl ketone finally give test result)



It is also used for identifying  $\text{CH}_3\text{CH}(\text{OH})$  gp and produces  $\text{CH}_3\text{CO}$  group on oxidation

★★ Oxidation of ketones under vigorous conditions

(C-C bond cleavage get compounds with lesser carbons)

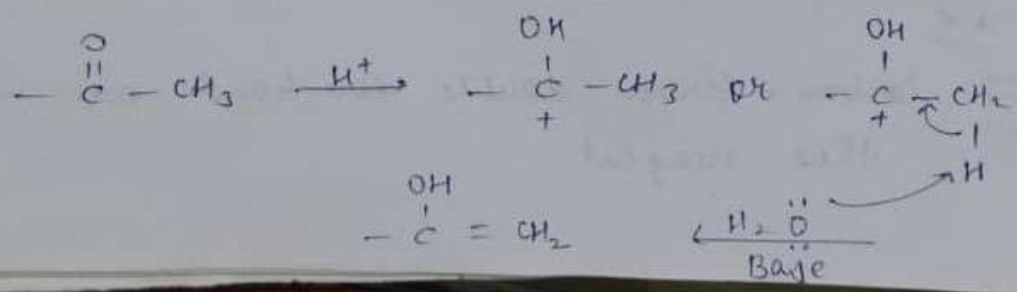


Carbocation  
acid  
solvent  
base

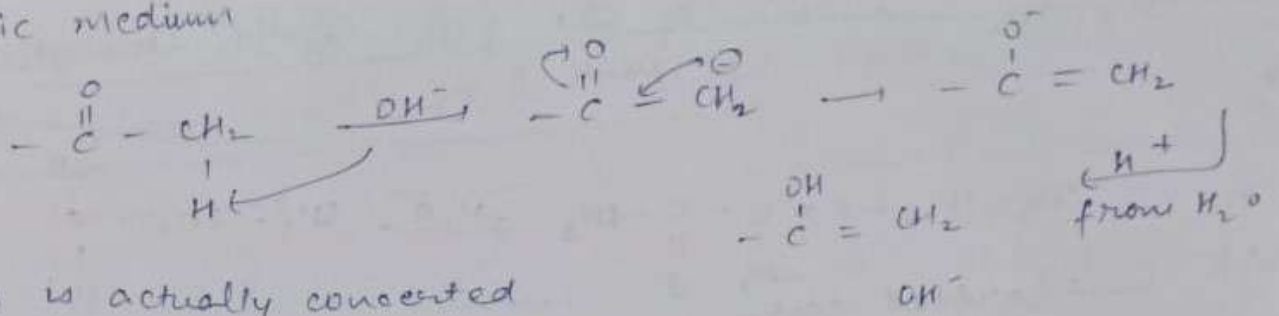
Mech of keto-enol Tautomerism



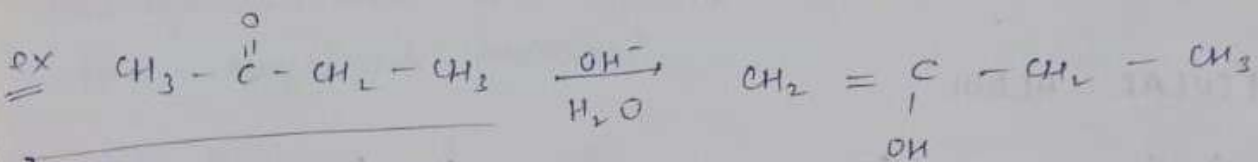
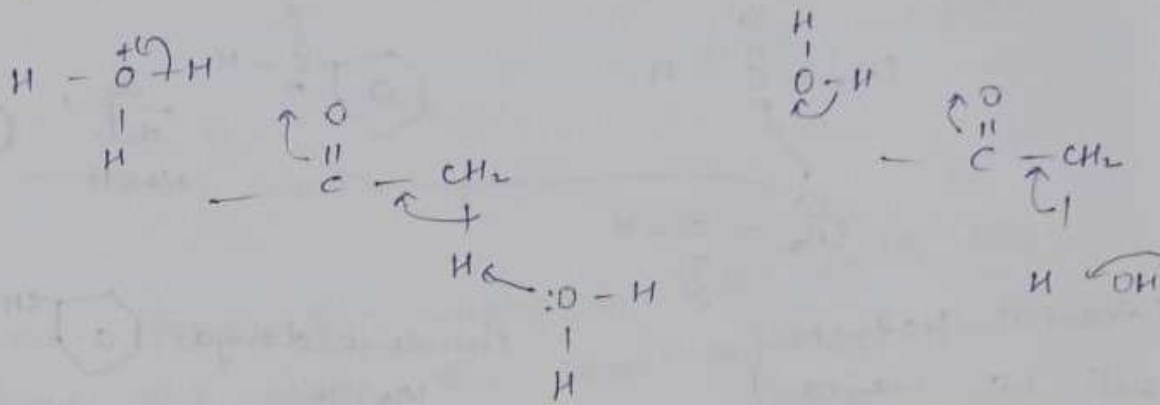
In acidic medium



In Basic medium



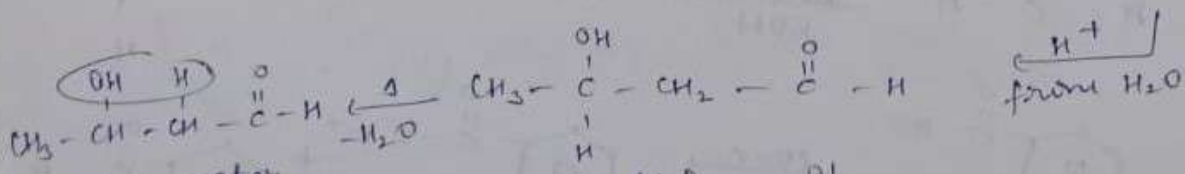
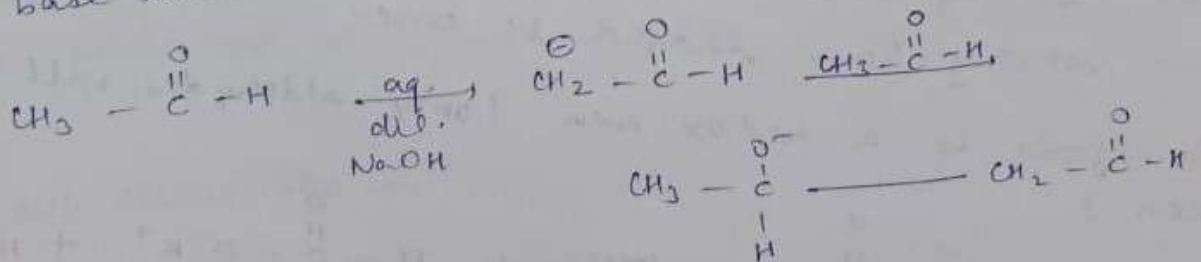
This rxn is actually concerted  
it follows 3<sup>rd</sup> order kinetics  
molecularity is 3



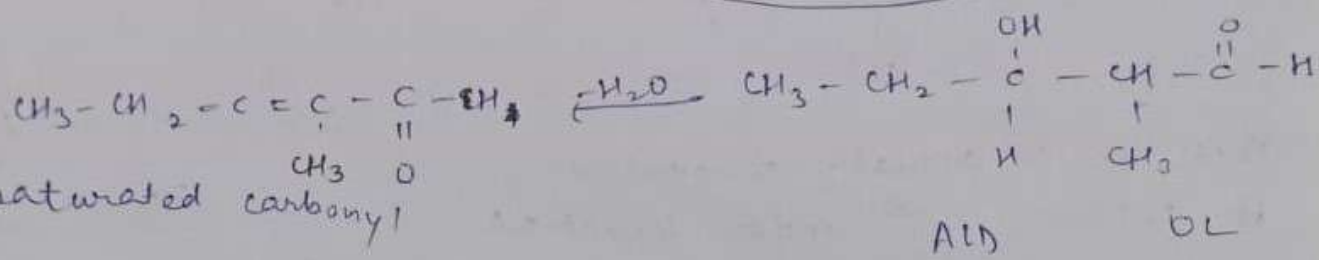
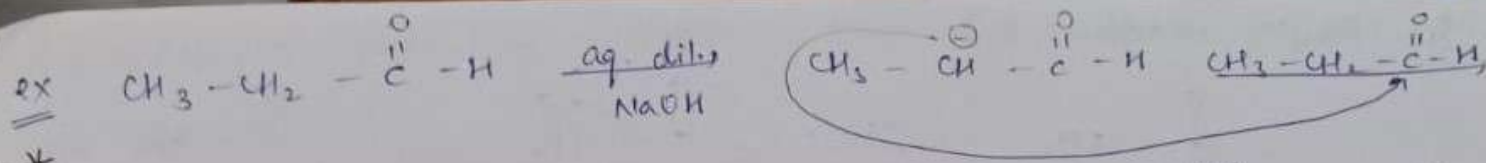
(In basic medium this is the major product)  
 $\xrightarrow{\text{H}^+, \text{H}_2\text{O}}$   $\text{CH}_3-\overset{\text{OH}}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}_3$  (on reaction with hot and acidified & alkaline  $\text{KMnO}_4$  different products will be formed)

Aldol condensation 3<sup>rd</sup> conditions for aldol condensation

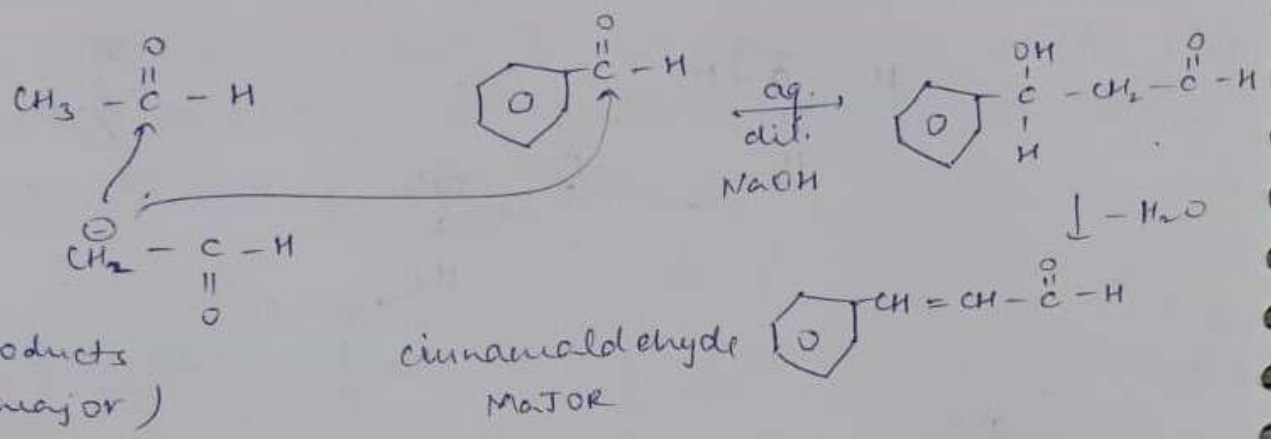
- $\alpha$  H
- Weaker Base
- The base should be dilute



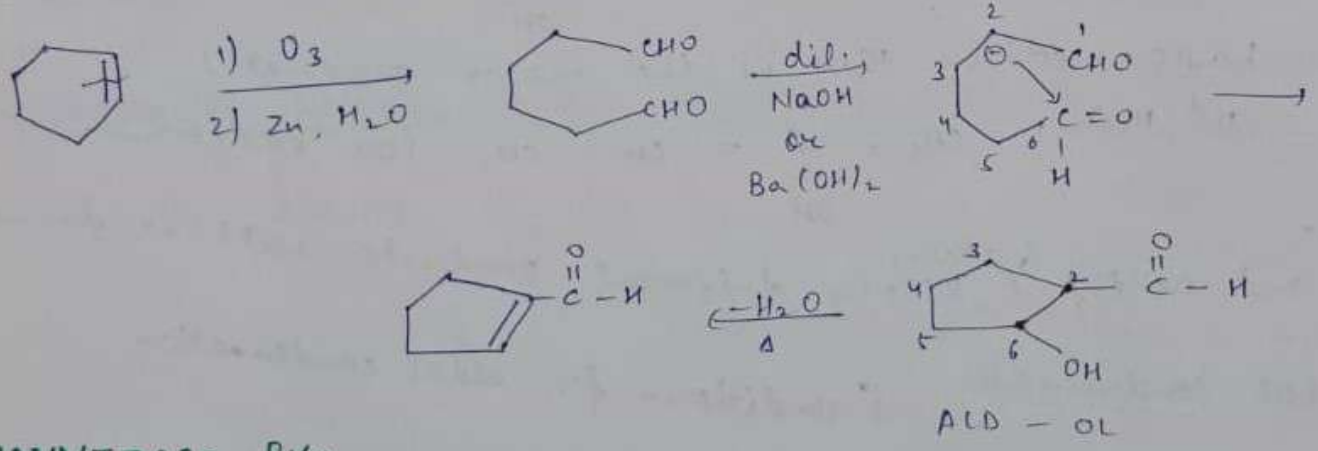
(When water will be separated resonance will occur  $\alpha, \beta$  unsaturated carbonyls)



CROSSED ALDOL



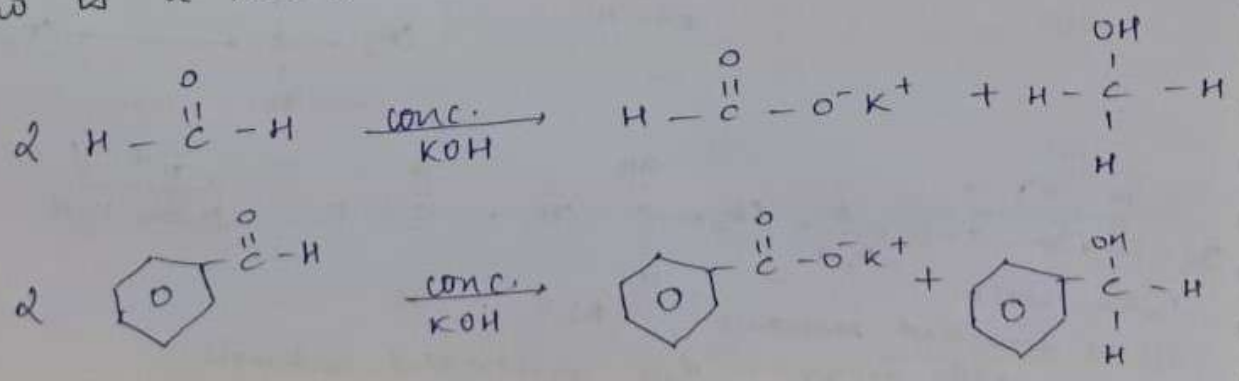
INTRAMOLECULAR ALDOL



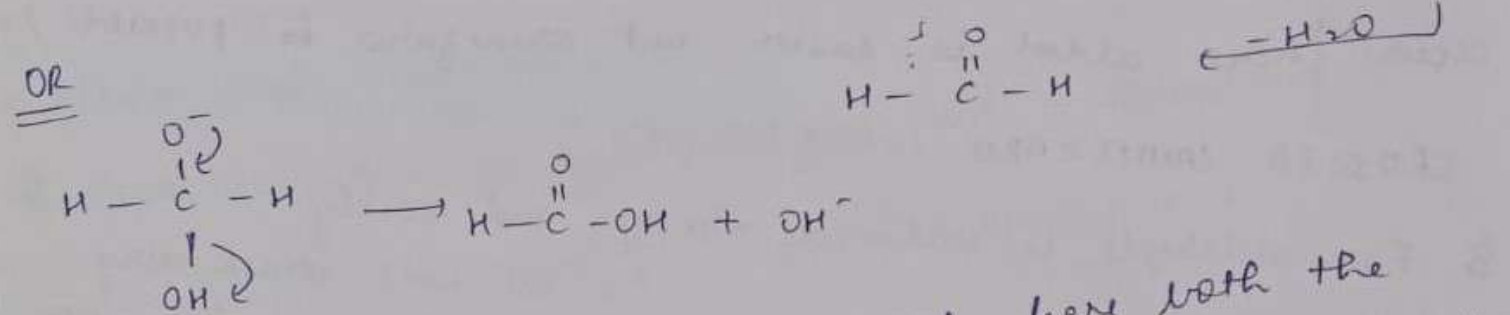
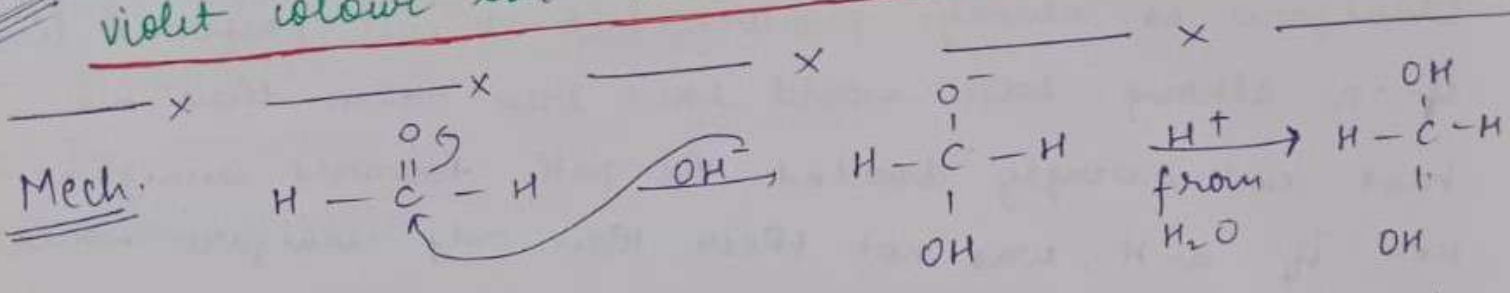
CANNIZARO RXN

- No  $\alpha$  H
- strong base
- strong Base should be conc.

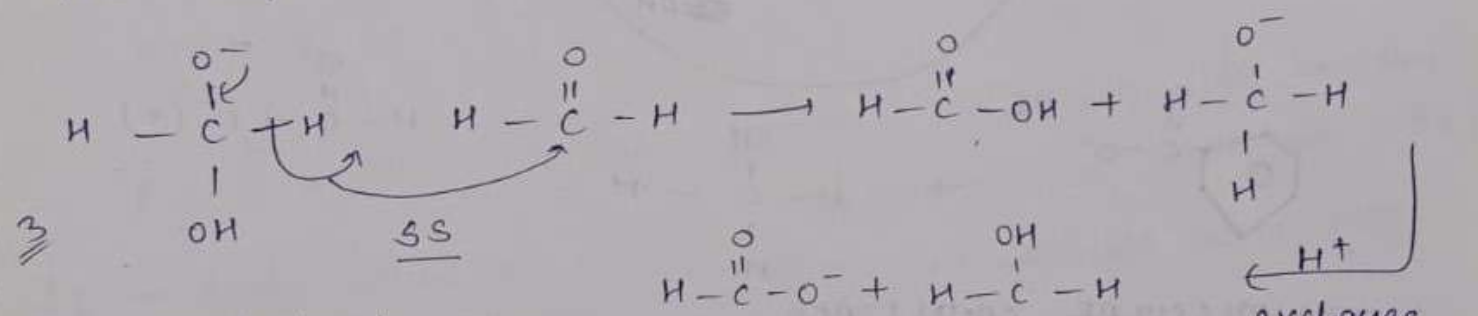
Cannizaro is a redox rxn (only aldehydes will do this rxn)



All compounds which have enol in high content give violet colour sol<sup>n</sup> with neutral FeCl<sub>3</sub> sol<sup>n</sup>.



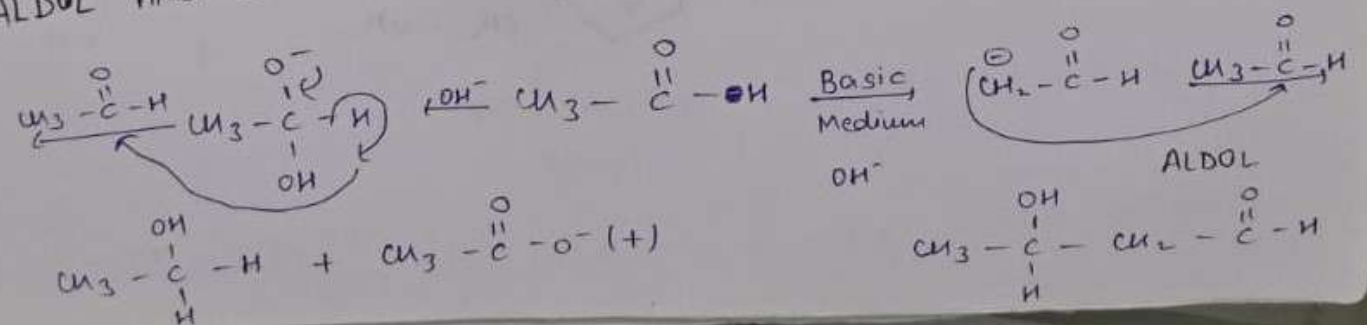
This is a non-productive approach here both the transformations are giving the same product but not the required product.



Here hydride is very unstable so it do not have time it will go and react with formaldehyde so this will be our slow step O<sup>-</sup> is making H<sup>-</sup>

Proof of strong Base - 3<sup>rd</sup> step will occur more if OH<sup>-</sup> is more and it is more when strong base is more.

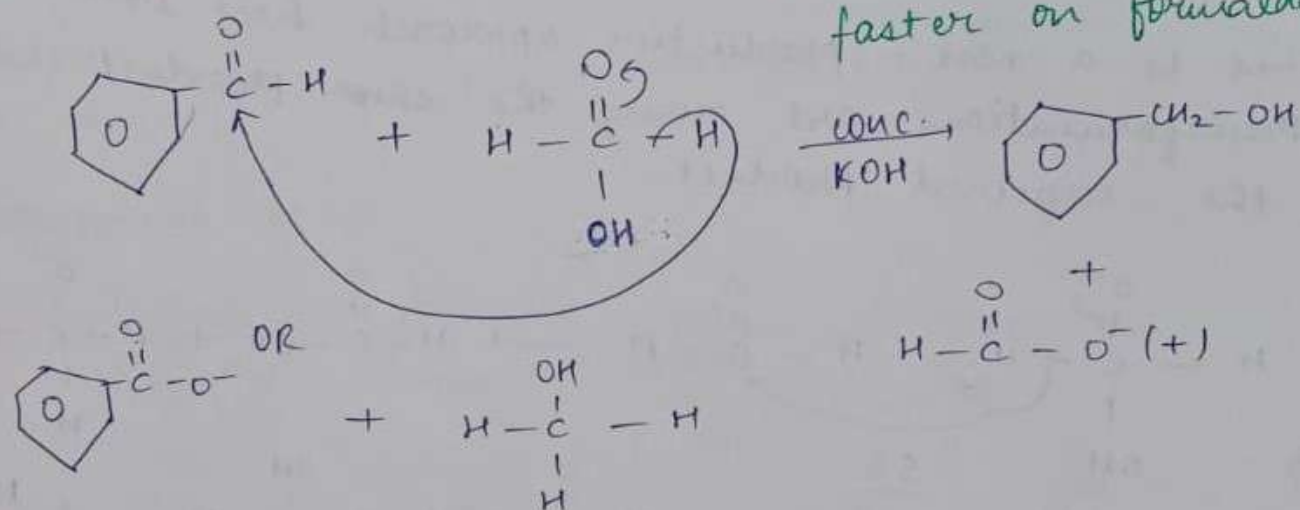
ALDOL AND CANNIZARO →



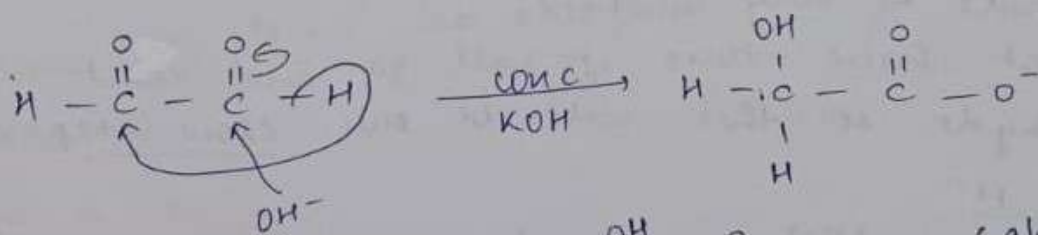
Here we have to take weak base because it will make the way easier for aldol, wherever aldol is possible Cannizaro is always possible but it will preferred less if a strong base would have been taken then we have unknowingly diverted the path towards cannizaro rxn if  $\alpha$ -H was not there then only cannizaro would occur (here aldol is easier but cannizaro is possible)

CROSSED CANNIZARO (redox rxn not disproportionation or both)

Formaldehyde is oxidised always and easily  
 $\text{OH}^-$  will attack very faster on formaldehyde



INTRAMOLECULAR CANNIZARO



glyoxal

