

UNIT - IV

Carbonyl compound (Aldehyde & ketones)

→ Carbonyl group is $C=O$ bonded to C & H .

e.g. $R-CHO$, $R-C(=O)-R$

Physical property

(1) Smell $\rightarrow$ Lower aldehyde $\rightarrow$ unpleasant
 $\searrow$
 Increase size $\rightarrow$ fragrant
 & molecule

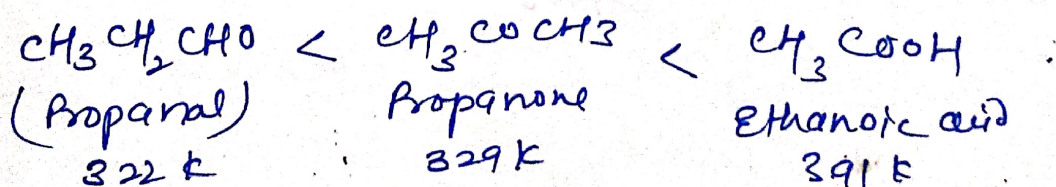
(2) Solubility

→ Aldehyde & ketone upto 4 C atom are soluble in H_2O .

→ As the size of alkyl group ↑, solubility decreases.

(3) B. P.

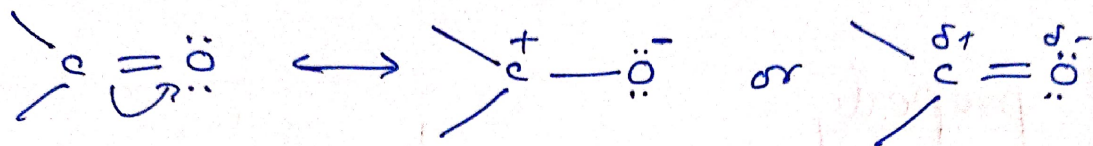
→ Aldehyde & ketone have weak intermolecular forces of attraction, so have low B.P.



⇒ Nature of Carbonyl group

→ C & O is sp^2 hybridized

→ C & O have one σ & one π bond.



→ Electronegativity is much higher of O so electron cloud shifted to O.

⇒ Nomenclature

① Aldehyde = suffix -al.

② Ketone = suffix -one

Ex. HCHO (formaldehyde) → Methanal

CH_3CHO (Acetaldehyde) → Ethanal

CH_3COCH_3 (Acetone) → Propanone

$\text{CH}_3\text{COC}_2\text{H}_5$ (ethyl methyl ketone) → Butanone

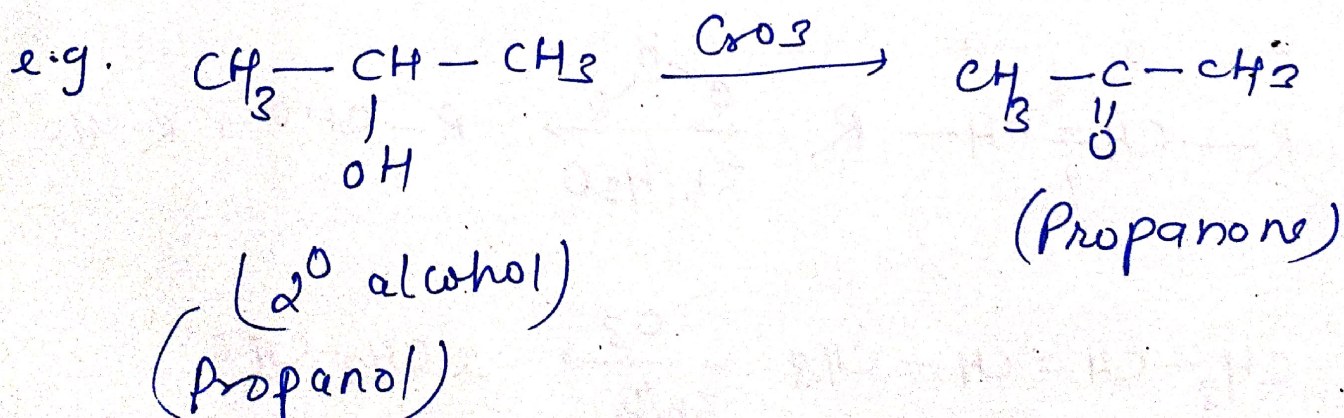
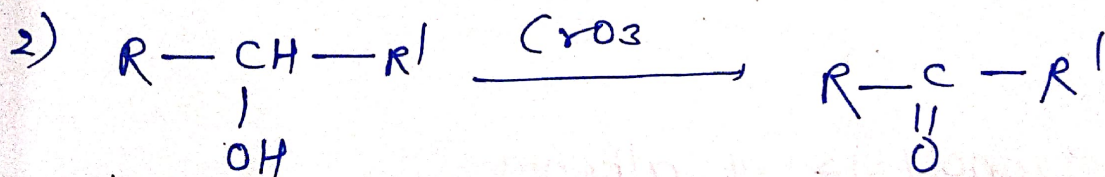
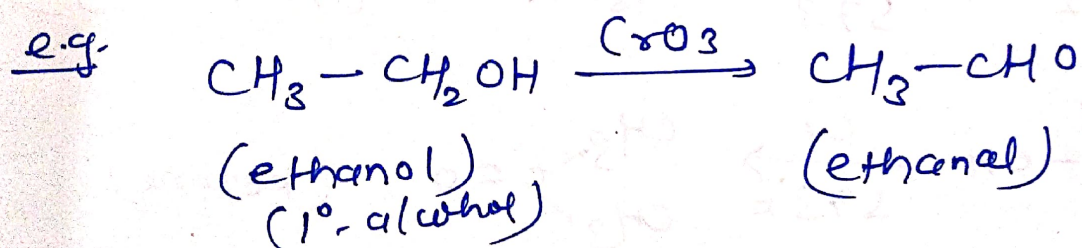
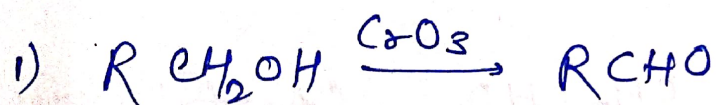
Preparation of aldehyde & ketone

(Aldehyde & ketone)

- (1) Oxidation of alcohol
- (2) Dehydrogenation of alcohol
- (3) Ozonolysis of alkenes.
- (4) Hydration of alkynes

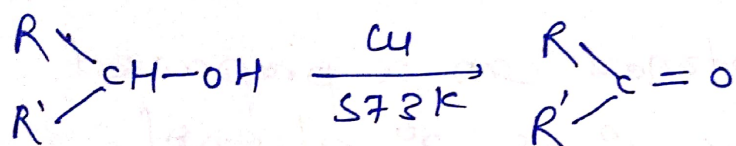
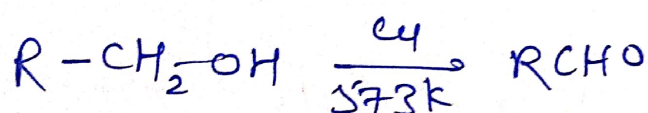
(1) Oxidation of alcohol

→ Aldehyde & ketones can be prepared by oxidation of 1° 2° 3° alcohol

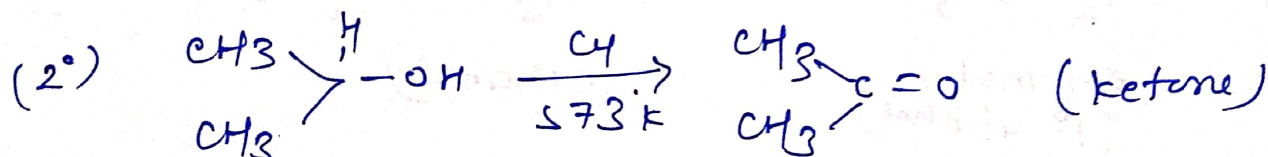
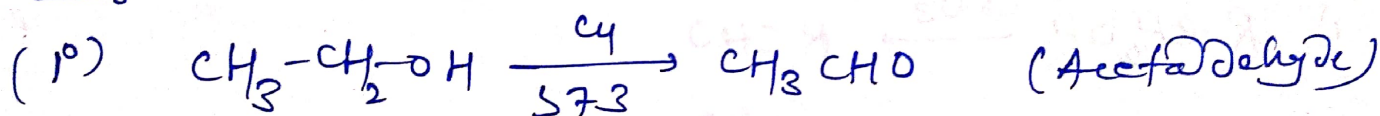


(II) Dehydrogenation of alcohol

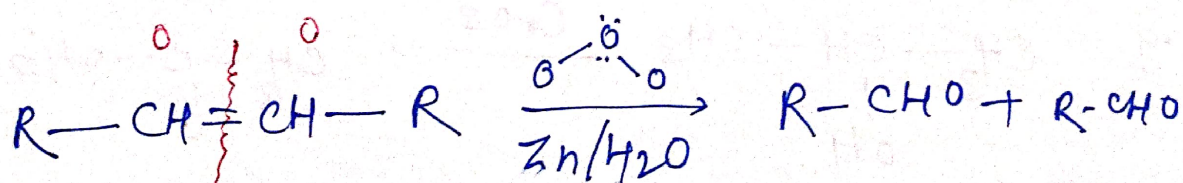
- Alcohol vapours are passed over heavy metal catalyst (Ag/cu).
- Primary and secondary alcohols give aldehyde & ketone.



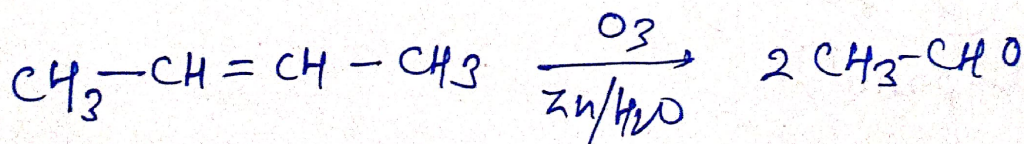
e.g.



(III) By Ozonolysis of alkenes

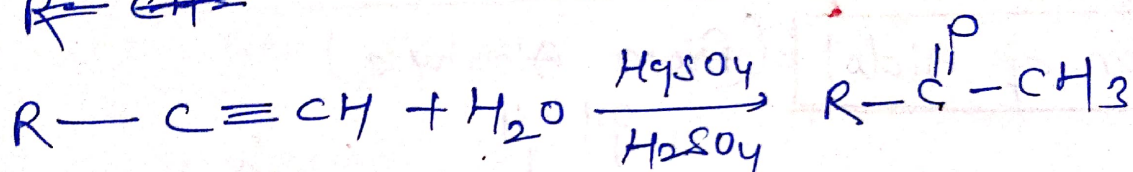
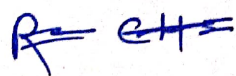
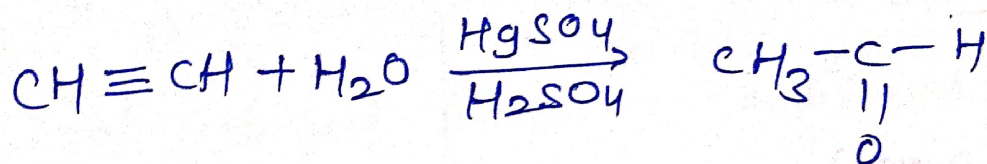


e.g.



(IV) Hydration of alkynes

Acetylene on hydration give acetaldehyde and other alkyne give ketone.



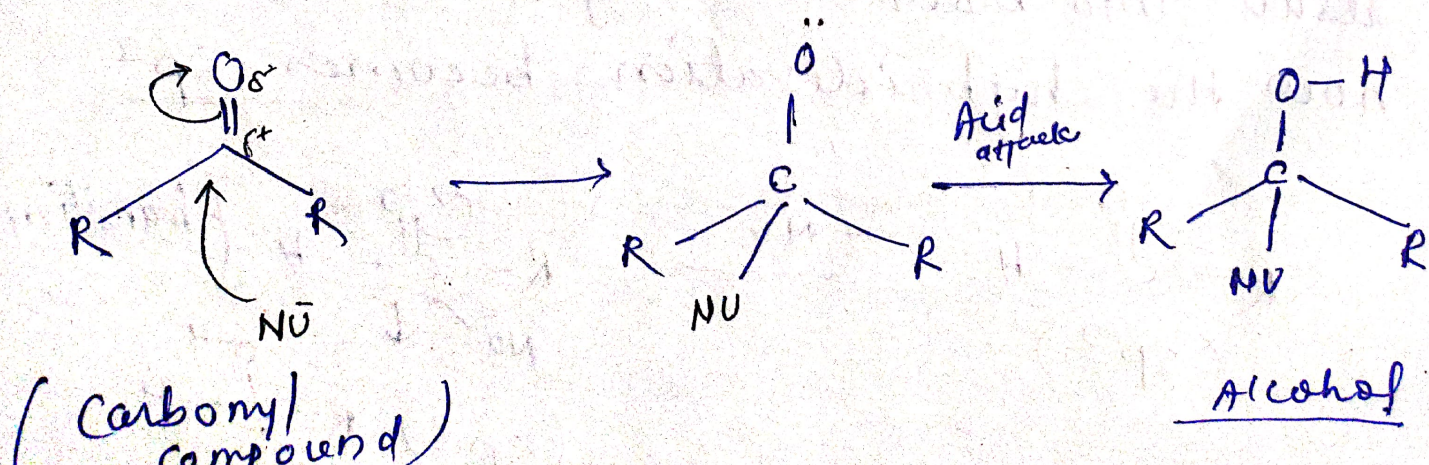
Nucleophilic addition

→ It is a chemical reaction in which a Nu forms a sigma (σ) bond with an electron deficient species.

⇒ Carbonyl compounds are: $\text{C}^{\text{O}}-\text{H}$, $-\text{C}^{\text{O}}-$

⇒ Steps

- 1) Electrophillic carbonyl compound 'C' forms a sigma bond with nucleophiles.
- 2) $\text{C}=\text{O}$, π bond broken down & forms a alkoxide intermediate (The bond pair electron is transferred to oxygen atom)
- 3) Protonation of alkoxide yields the alcohol derivatives.



Example of Nucleophiles

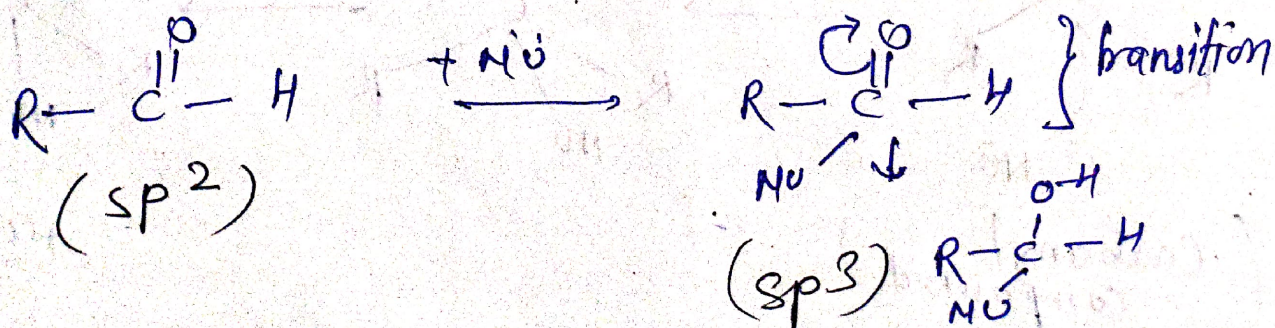
- 1) $\text{H} \ddot{\text{O}}:^- \rightarrow \text{hydroxide ion}$
 - 2) $\text{H}:^- \rightarrow \text{hydride ion}$
 - 3) $\text{R}_2\text{C}:^- \rightarrow \text{Carbanion}$
 - 4) $\text{R}-\ddot{\text{O}}:^- \rightarrow \text{alkoxide ion}$
 - 5) $\text{N} \equiv \text{C}:^- \rightarrow \text{cyanide ion}$
- } -vely charged

- 1) $\text{H}-\ddot{\text{O}}-\text{H} = \text{H}_2\text{O}$
 - 2) $\text{R}-\ddot{\text{O}}-\text{H} = \text{alcohol}$
 - 3) $\text{H}_3-\text{N}^+ = \text{ammonia}$
 - 4) $\text{R}-\ddot{\text{N}}\text{H}_2 = \text{amine}$
- } Neutral Nucleophiles

$\Rightarrow$ HYBRIDIZATION

$\rightarrow$ Carbonyl group is a co-planar structure and its carbon is sp^2 hybridized.

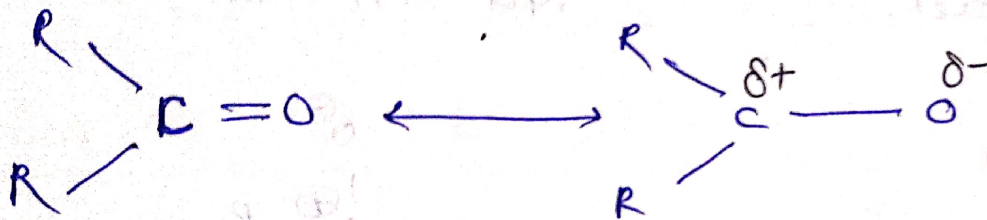
$\rightarrow$ The nucleophilic attack on $\text{C}=\text{O}$ group result into breakdown of π bond. so now the hybridisation becomes sp^3



Why Carbonyl Compound undergoes Nucleophilic addition Reaction.

→ In Carbonyl Compound, Carbon - oxygen bond is polar

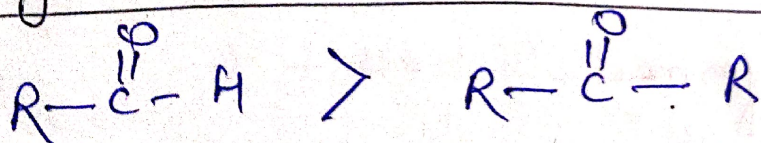
→ electron density is higher around O atom so partially -ve charge on 'O' generates along $\bar{e}$ partially +ve on 'C' atom.



→ carbon behaves as electrophile

→ Negative charge on oxygen is stabilized by protonation $\therefore$ neutralized the -ve charge.

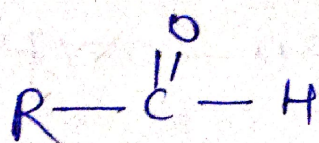
$\Rightarrow$ Aldehyde are more reactive than ketone



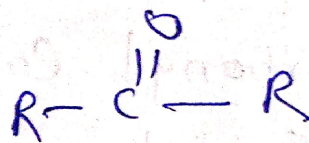
* ketone form 2° carbocation and are stabilized by adjacent 'R' group.

* while aldehyde forms 1° carbocation which are less stable than 2° carbocation formed by ketone, so it is more susceptible for

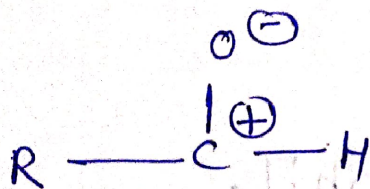
Nucleophilic attack.



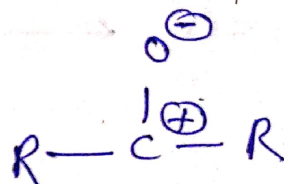
- forms less stable carbocation.
- less steric hindrance.
- more susceptible for HV Attack



- forms more stable carbocation
- more steric hindrance.
- less susceptible for Nu attack.



(1° carbocation)
(less stable)

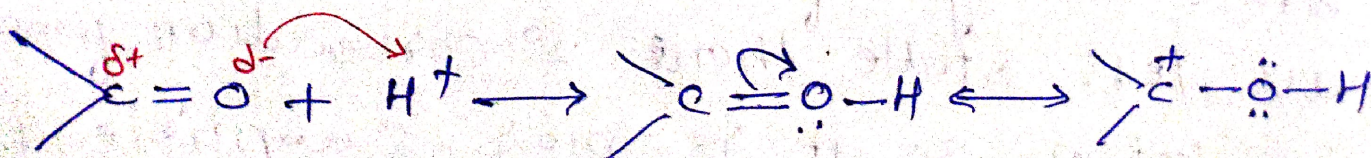


(2° carbocation)
(more stable)

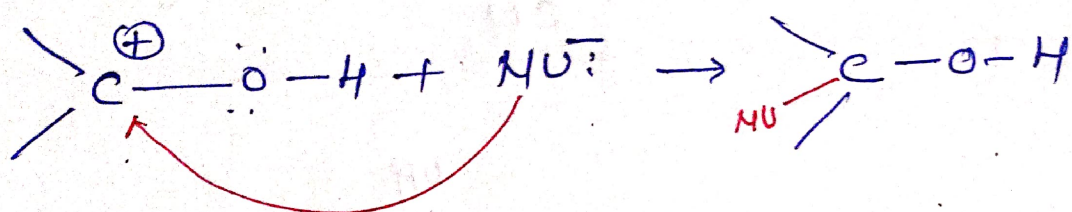
* If nucleophile is weak then acid catalysed reaction is performed.

Acid Catalysed addition

step 1: Hydrogen ion from an acid attacks on negatively charged carbonyl oxygen to give protonated carbonyl group

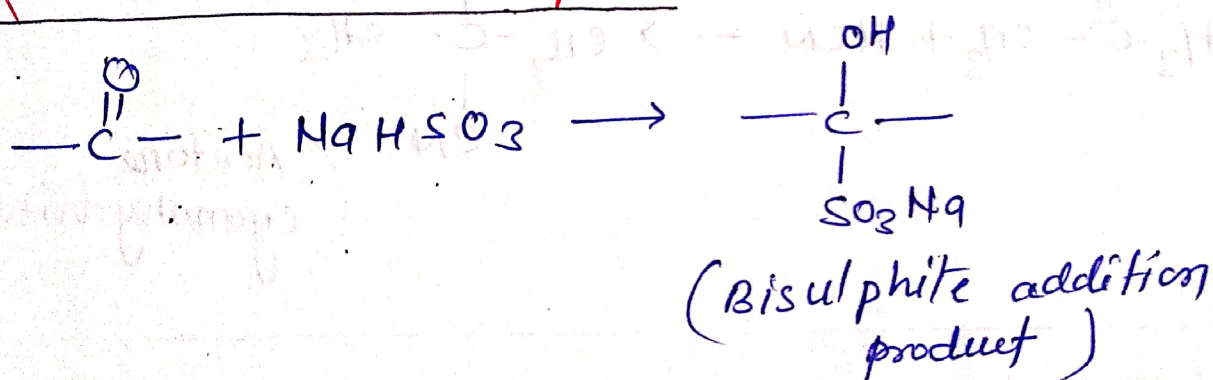


Step II : Nucleophilic attack on protonated carbonyl group to form an addition product

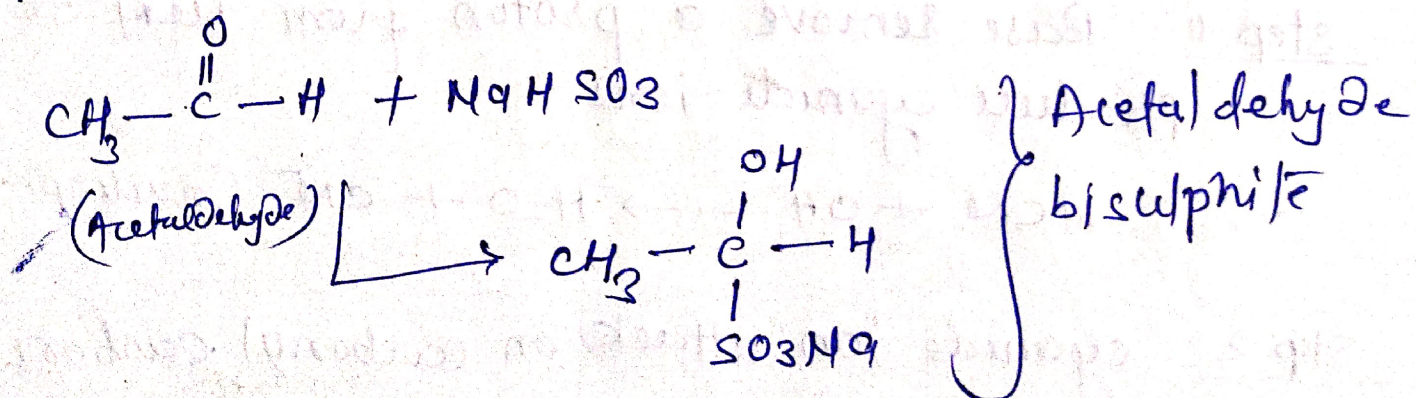


Addition Reactions of Carbonyl Compound

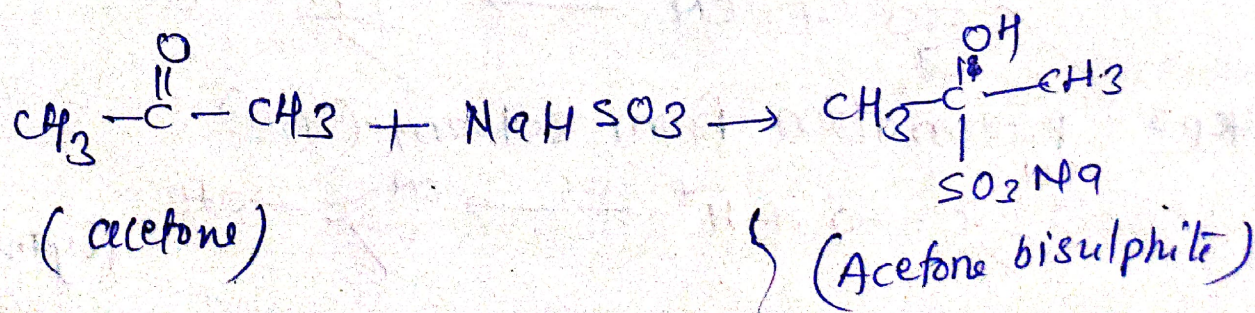
(1) Reaction with Sod. bisulphite



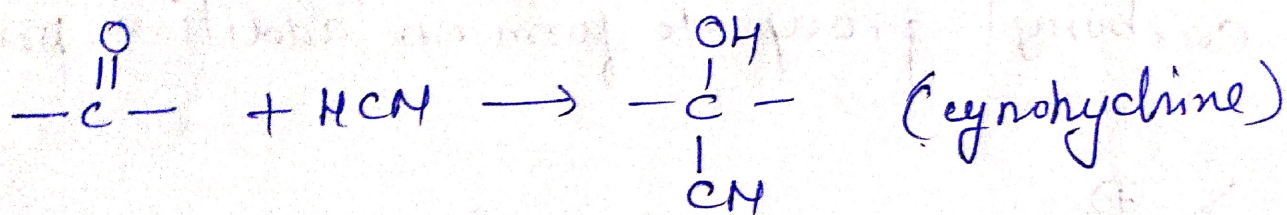
eg. 1



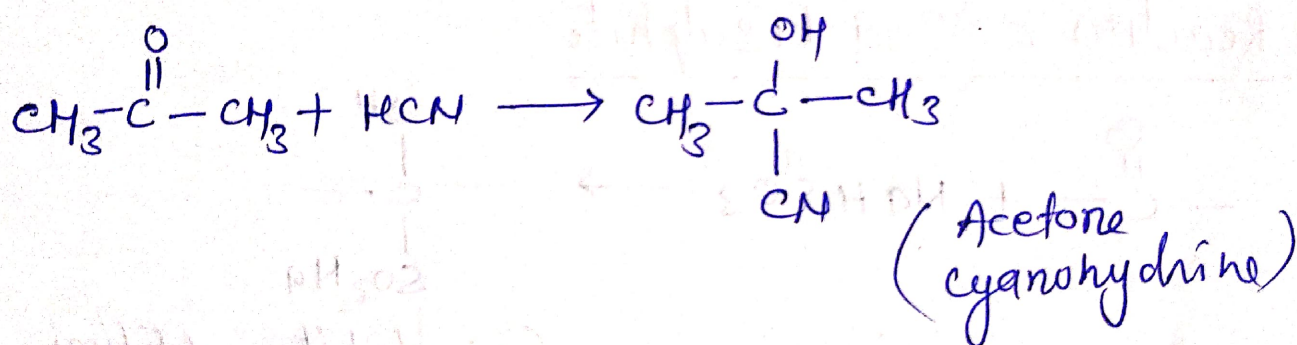
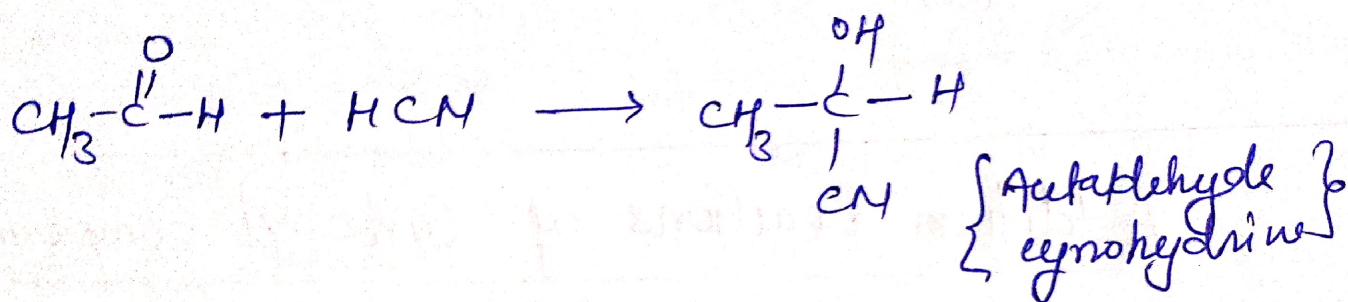
eg. 2



⑤ Addition of Hydrogen Cyanide (HCN)

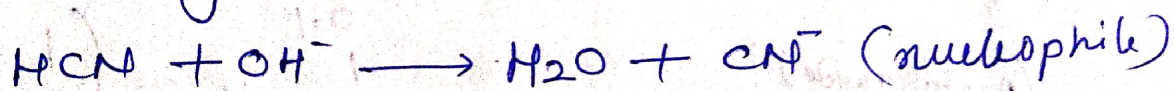


eg.

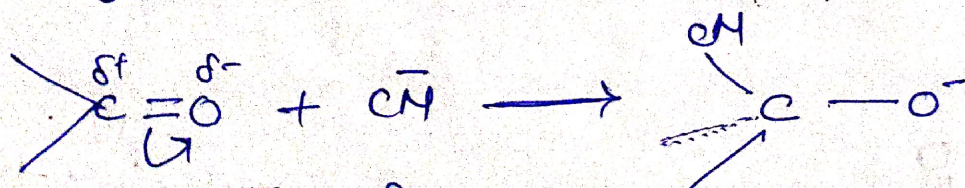


Mechanism

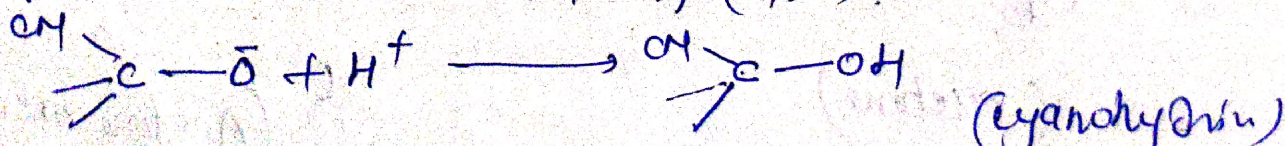
Step 1: Base remove a proton from HCN to produce cyanide ions.



Step 2: cyanide ion attack on carbonyl carbon.

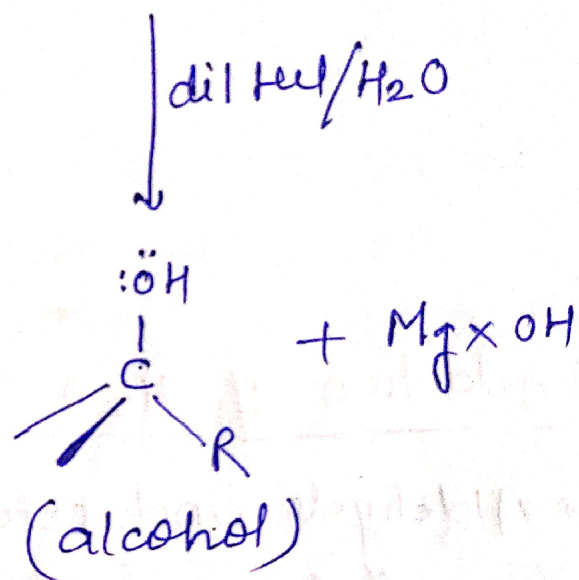
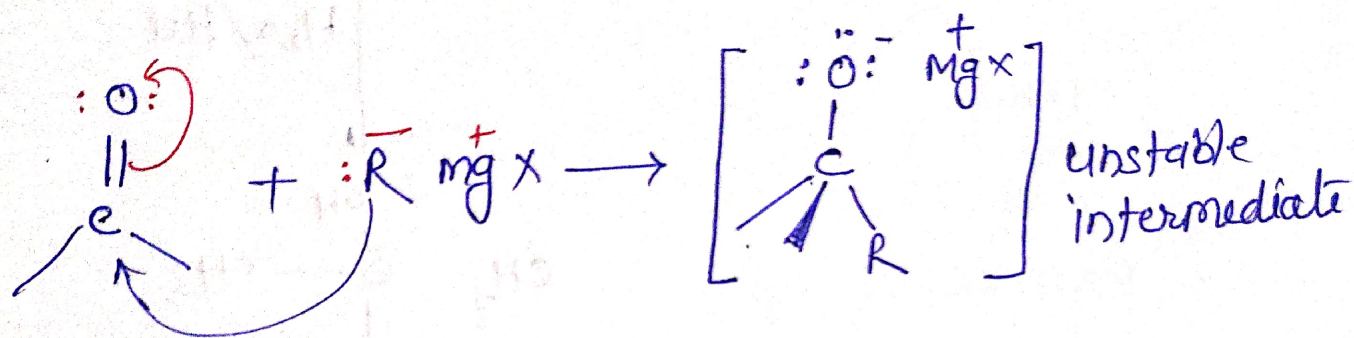


Step 3: Protonation from solvent (H_2O).

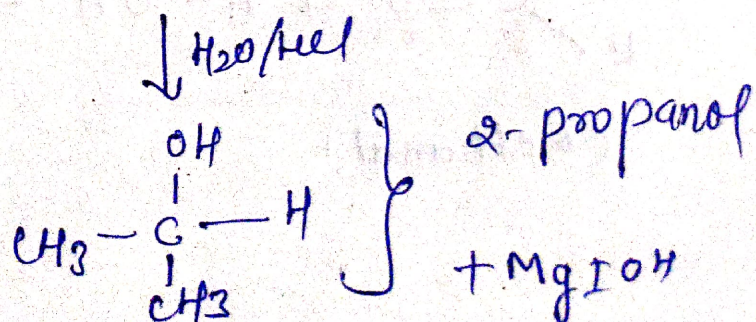
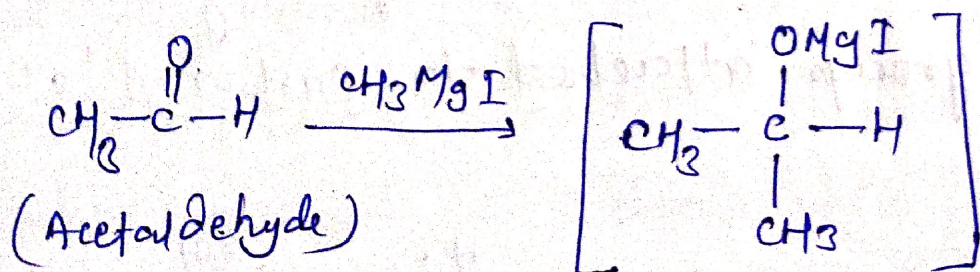


(3) Addition of Grignard Reagent ($R-MgX$)

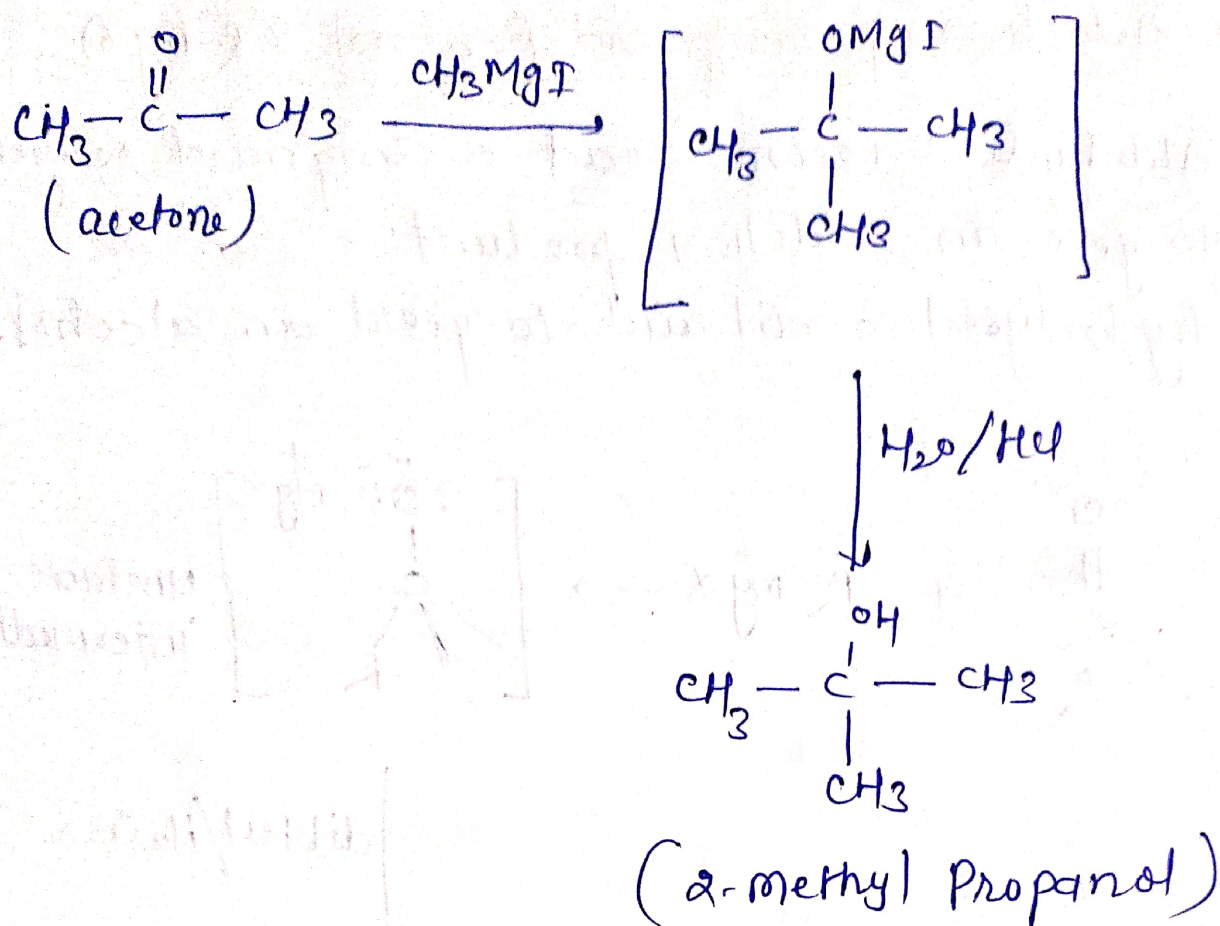
Aldehyde & ketone react w Grignard reagent to give an addition product & can be hydrolysed w dil acid to yield an alcohol.



ex.



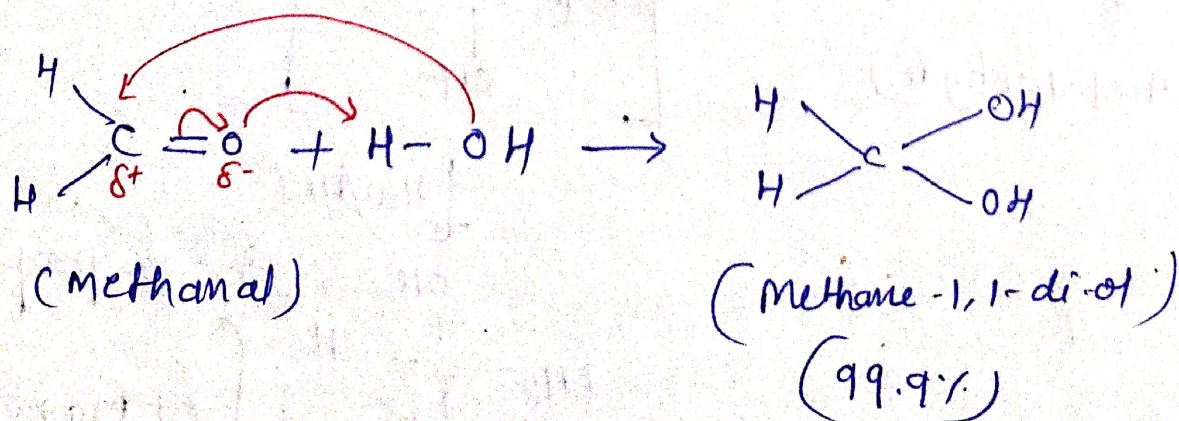
(2)

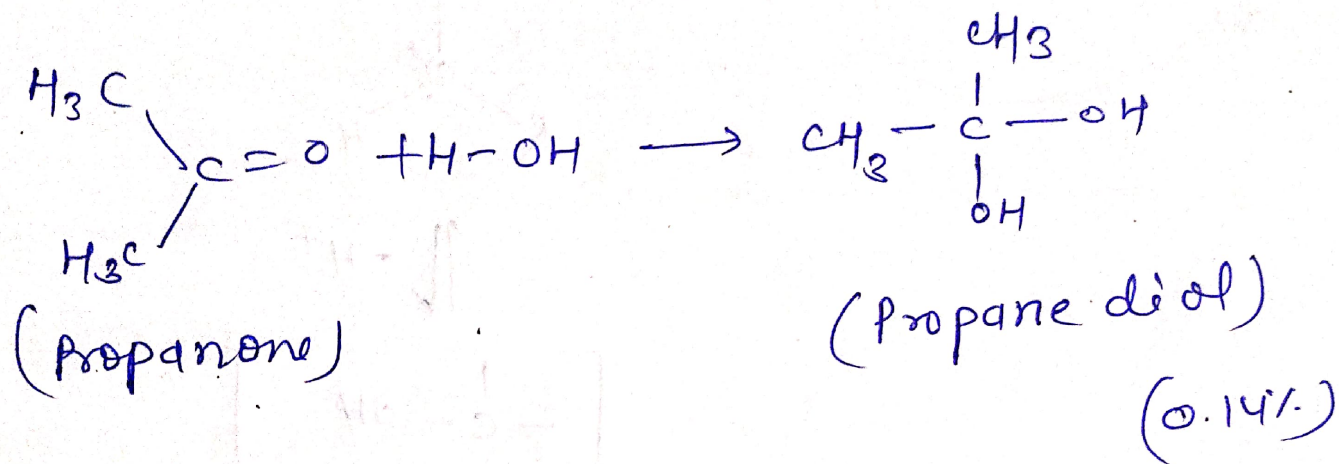
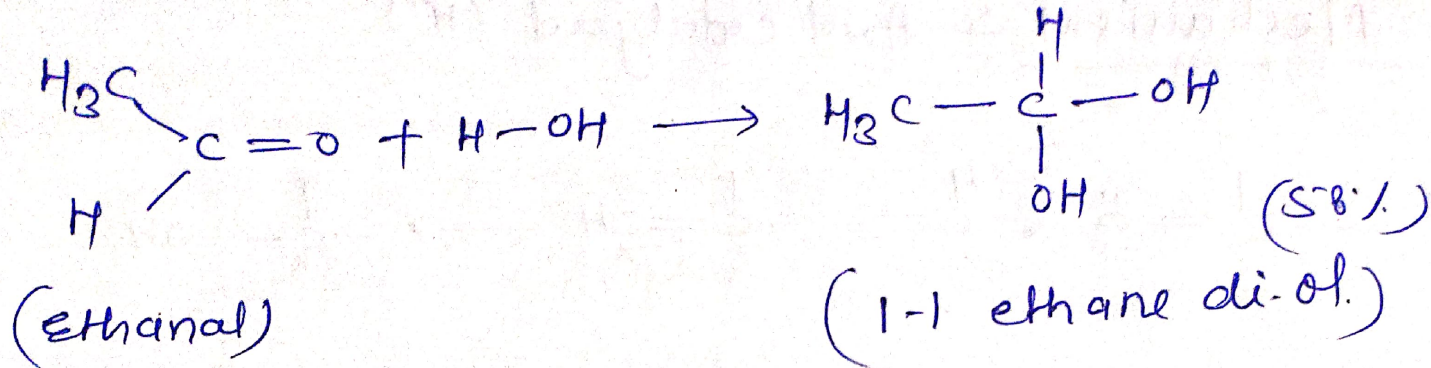


(4) Addition of H_2O ($\text{H}-\text{OH}$)

→ Aldehyde and ketone react w H_2O to form 1-1 diol or hydrates.

→ Hydrogen is attached to vely charged O_2 & hydroxy/ group attached to carbonyl 'C' atom.





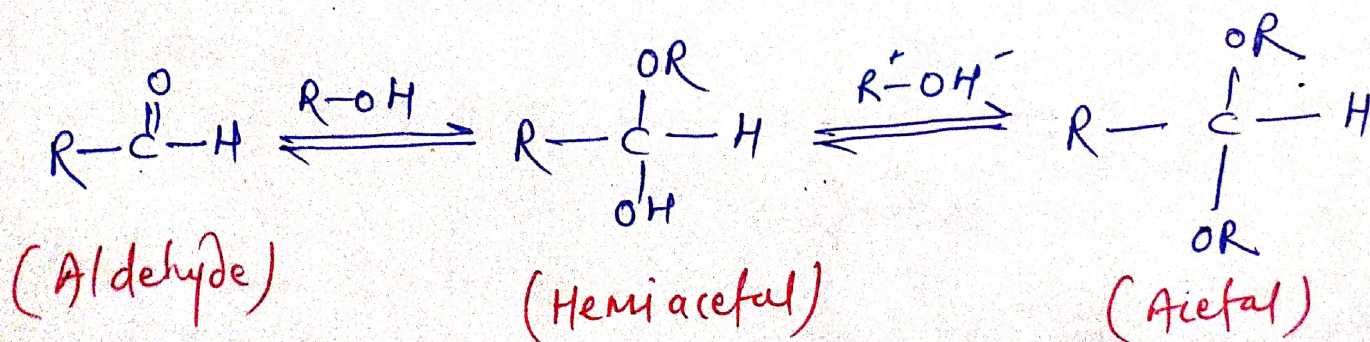
Note: Diol of Methanal is less crowded hence produce 99.96% while propanone forms much more crowded product, hence produce in less quantity.

(5) Addition of alcohol $\rightarrow$ forms Hemiacetal or Acetal.

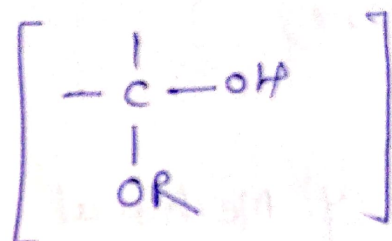
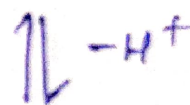
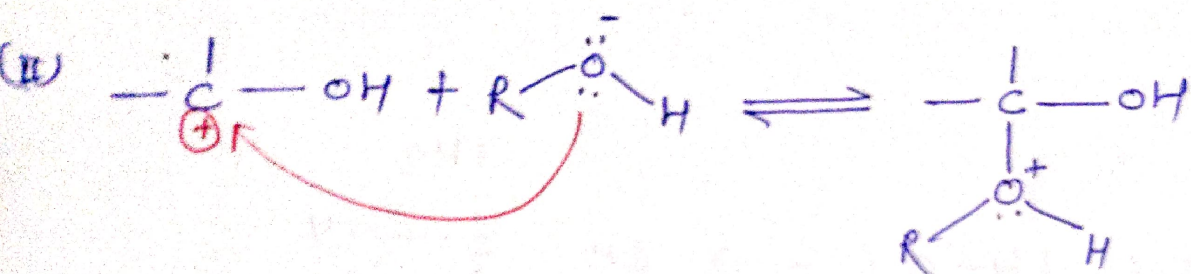
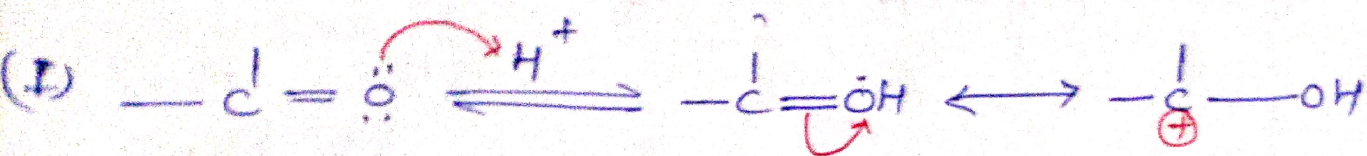
$\Rightarrow$ like H_2O , alcohol can also undergo addition reaction.

$\Rightarrow$ It is reversible reaction.

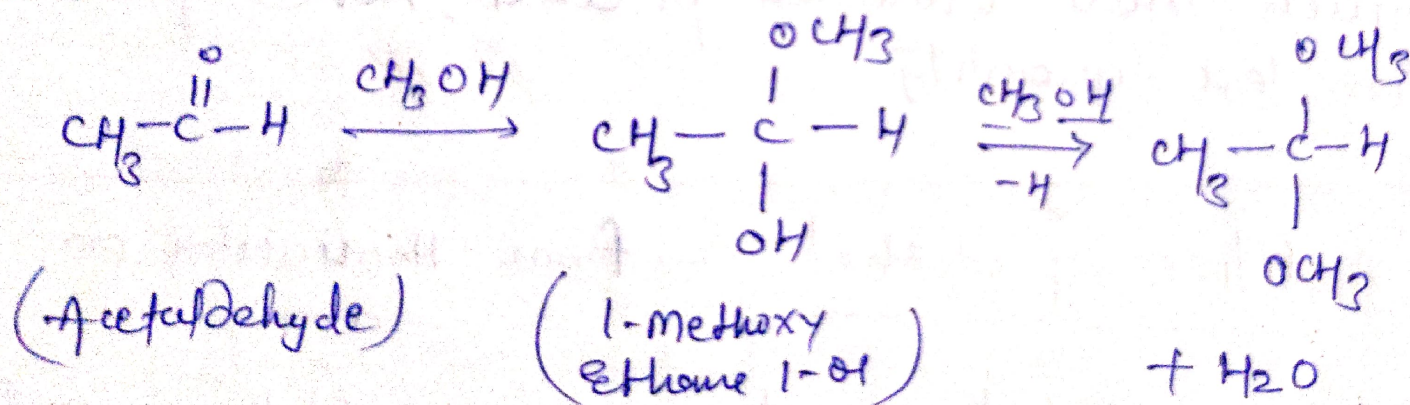
$\Rightarrow$ Product formed is Hemiacetal/Acetal.



Mechanism $\rightarrow$ Acid catalysed (H^+)



EX.

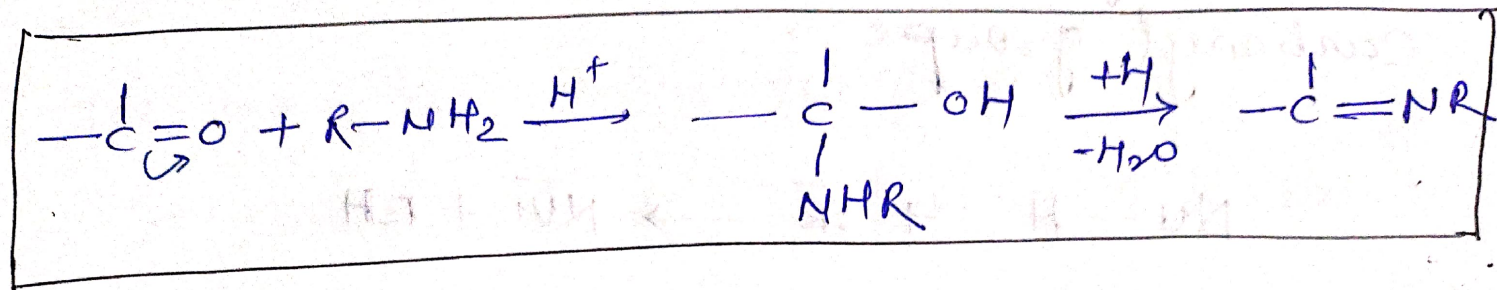


Reaction of Amine

⇒ Reaction of primary amine.

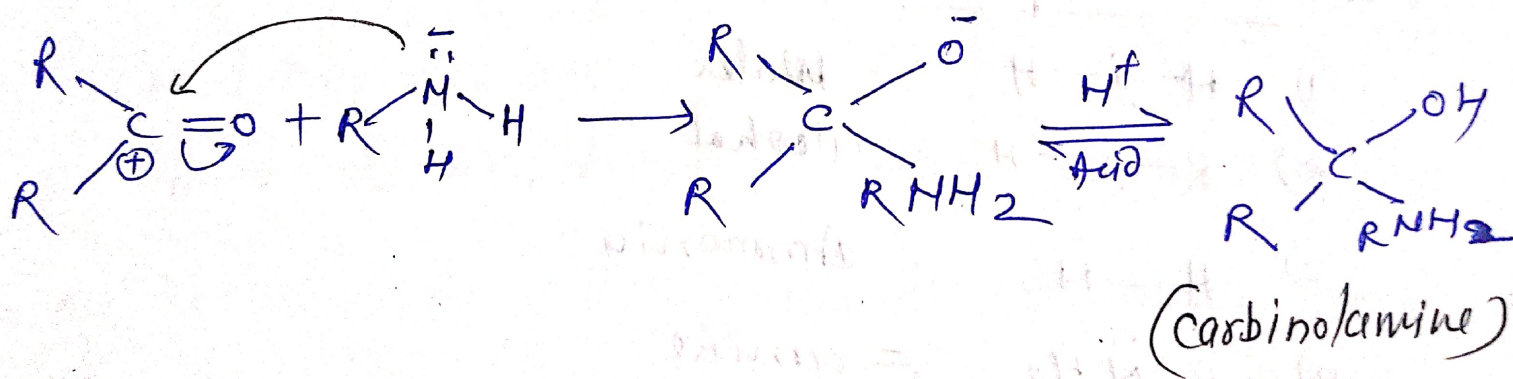
⇒ This reaction is catalysed by acid.

⇒ product is N-alkyl/N-aryl imine.



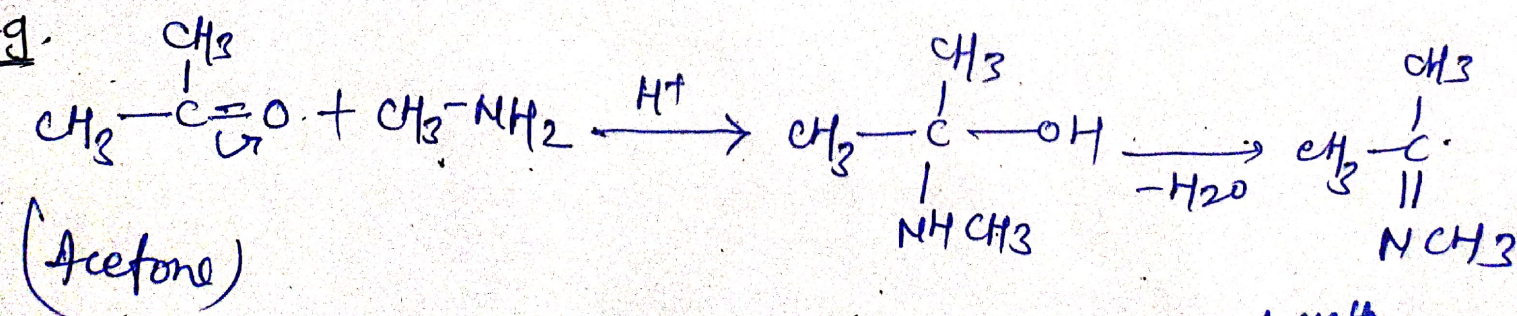
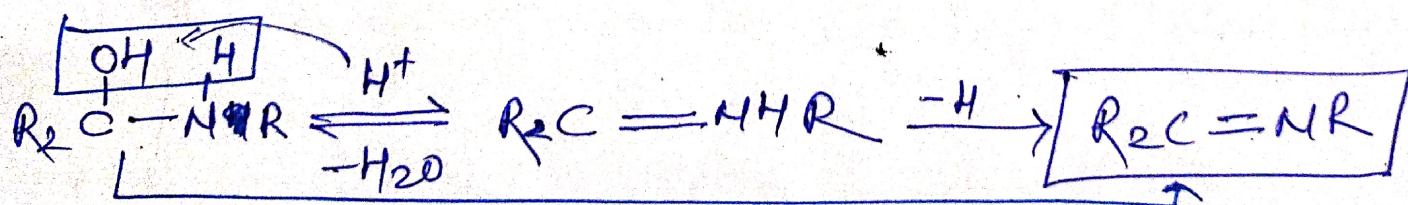
Mechanism

Step: 1 - formation of carbinolamine.



Step II

Carbinolamine eliminate H_2O to give imine.



1 methyl
2-2 dimethyl

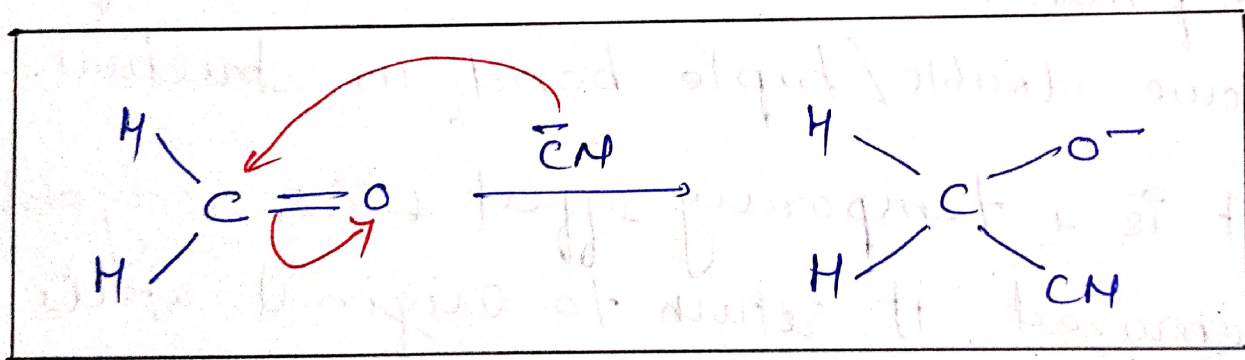
Electromeric Effect

Definition:

- It can be defined as a temporary effect produced, when a reagent attacks the multiple bonded compound.
- It causes a complete shift of π electron to either of two atom of bond.
- Due to which shared pair of electron causes polarity.
- This phenomenon is observed in compound c have double/triple bond in structure.
- As it is a temporary effect & as reagent is removed, it return to original state & become unpolarised.
- The reagent can be electrophil/nucleophiles.
- This effect is k/as E-effect.

Example

- ⇒ when aldehyde containing carbonyl carbon in $\text{C}=\text{O}$ carbon and oxygen is attached by double bond.
- ⇒ when a δ^- charged reagent attacks, the π e^- shift to the ' O_2 '.
- π e^- shift to oxygen as it is more electronegative.
- movement of electron from one atom to another is called electromeric effect.



TYPES OF ELECTROMERIC EFFECT

→ It is based on the direction in e^- electron transfer occurs.

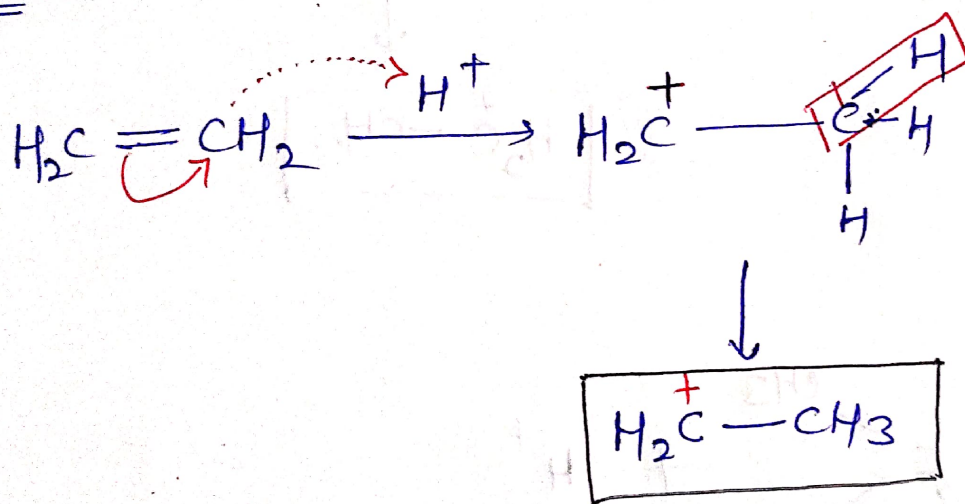
- ① $+E$ effect
- ② $-E$ effect

(1) +E-effect

condition : Attacking species have +ve charge.

- * shared pair of electron ~~from~~ directed towards positively charged reagent.
- * Reagent will form a bond π pair of electron.
- * Generally this reaction can be observed in reaction of addition of acid to alkenes.

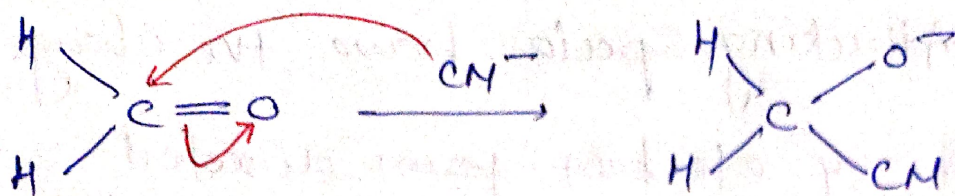
ex.



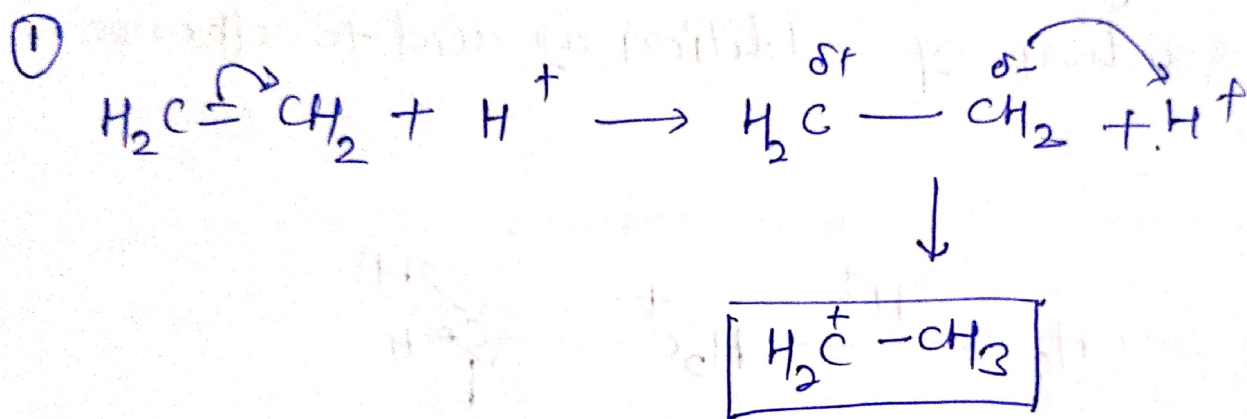
(2) -E-effect

- * It is observed when attacking reagent have -ve charge.
- * bond electron shifted away from attacking nucleophile.
- * Generally observed in Aldehyde & ketone.

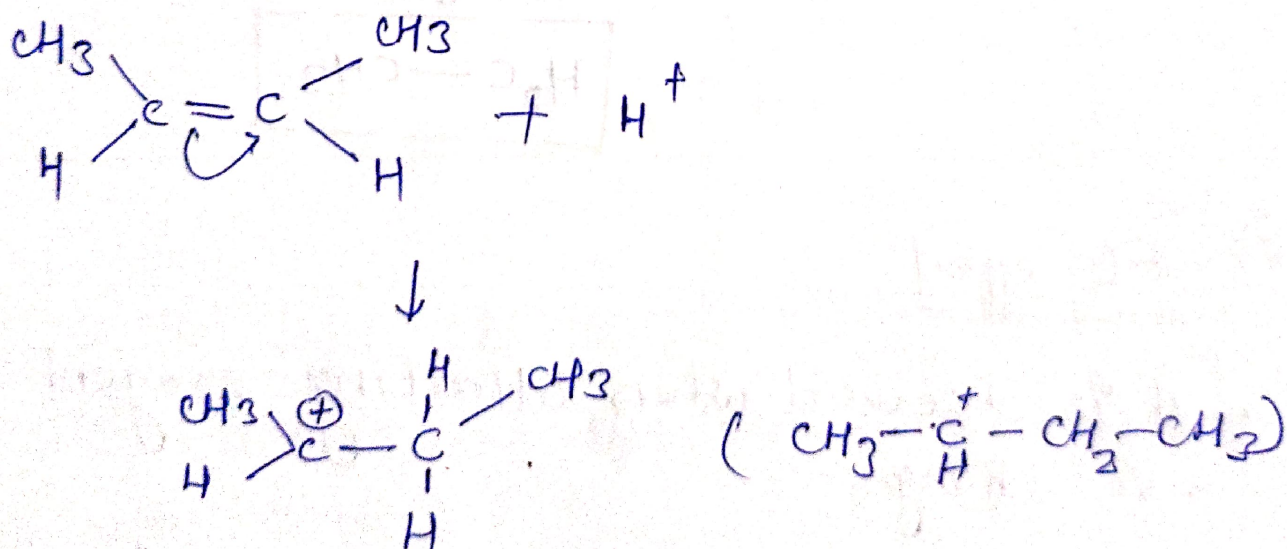
ex.

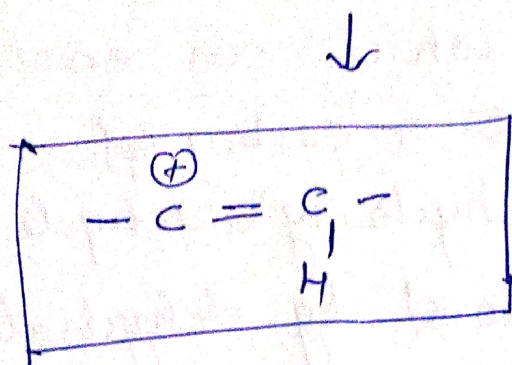
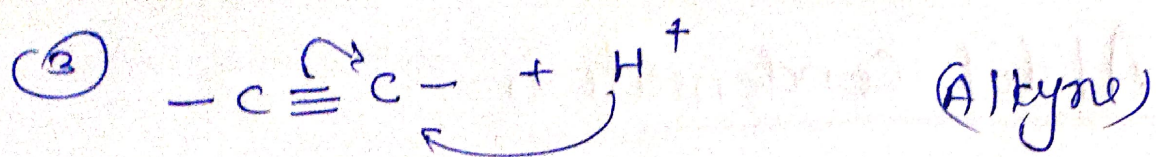


Examples of +E & -E effects



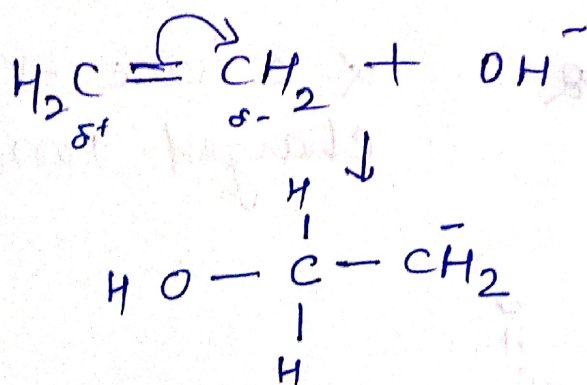
②



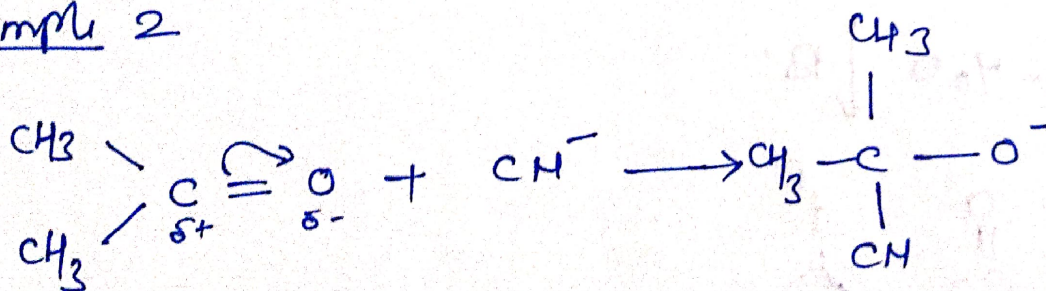


Inductive effect

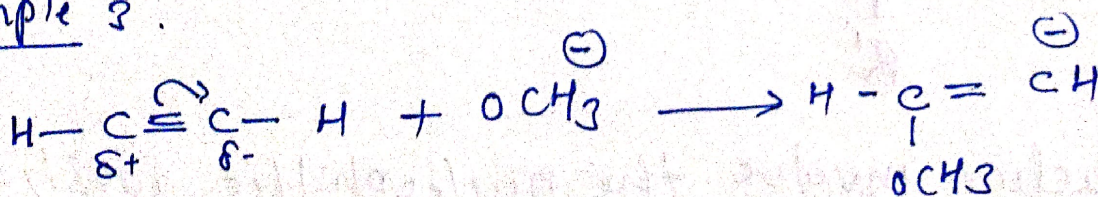
example 1



Example 2

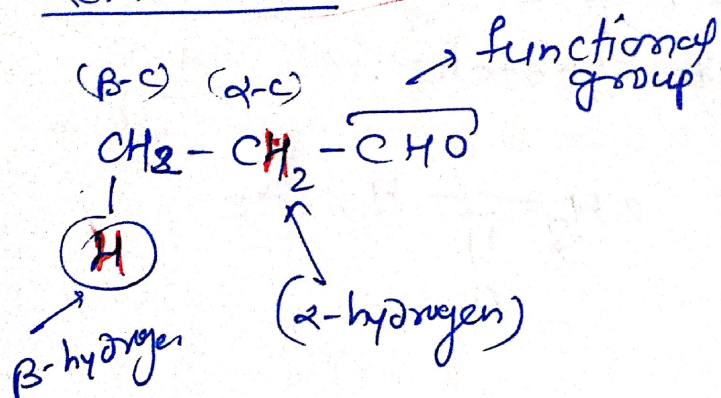


Example 3



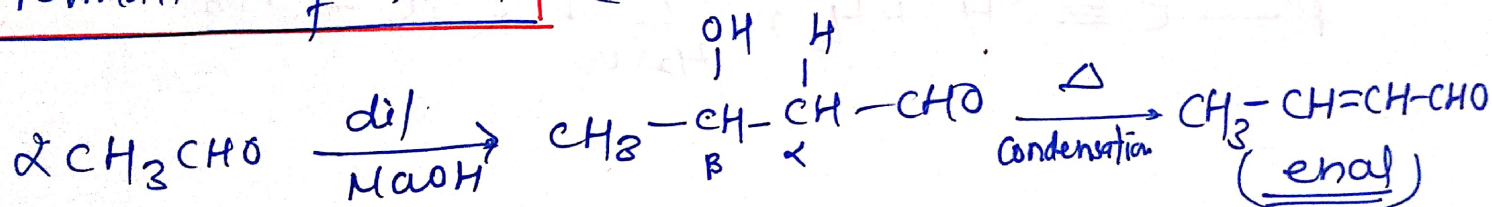
Aldol CONDENSATION

Remember



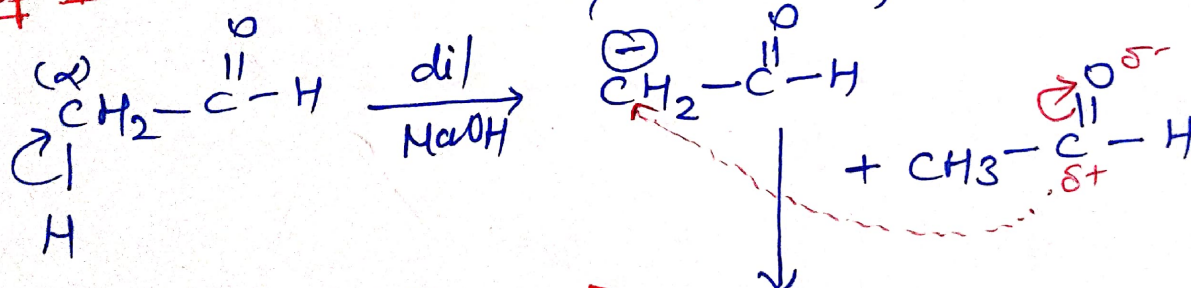
} dil NaOH
 Provides $\text{H}^+ \text{OH}^-$

formation of Aldol (from Aldehyde)

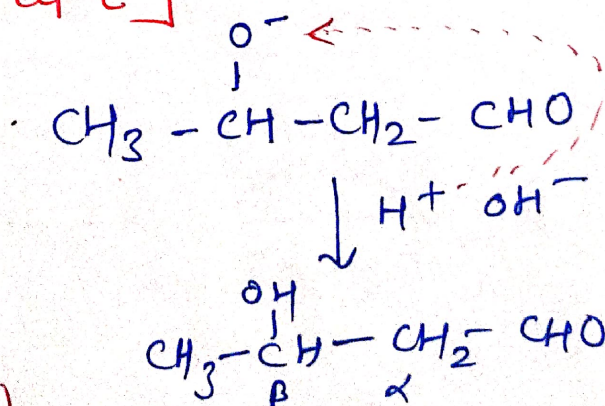


Mechanism

Step-I

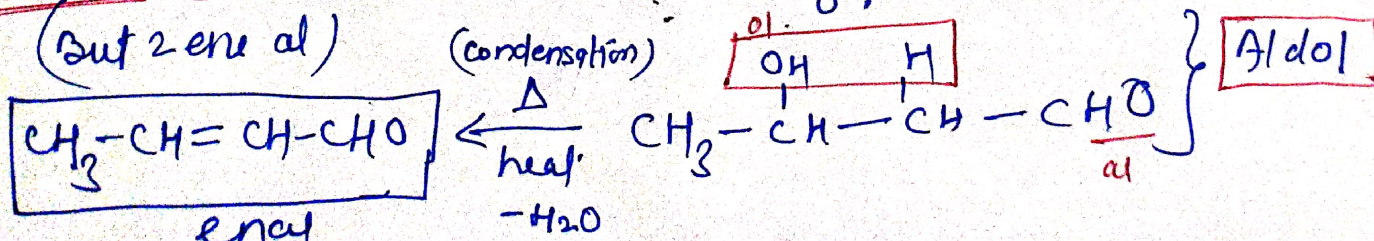


Step-II [Attack of $\text{N}^{\ominus}\text{O}$ at 'C']



Step-III (Removal of H_2O)

(But 2 enal)

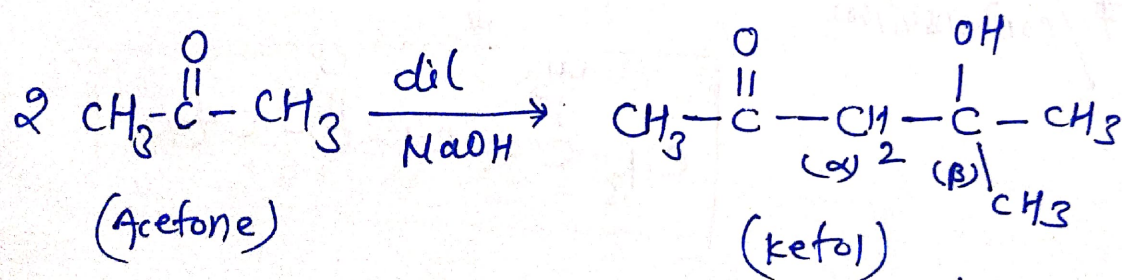


$\Rightarrow$ Aldehyde and ketone $\leq$ have at least one α -hydrogen undergoes an organic reaction in presence of dil NaOH to form β -hydroxy aldehyde (Aldol). Reacⁿ is Aldol_{rexn}.
 or Ketol.

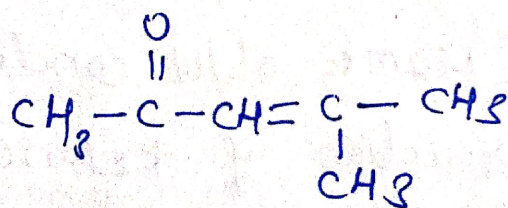
$\rightarrow$ final product have alcohol and aldehyde group so called Aldol.

$\Rightarrow$ finally after formation of aldol, on heating, H_2O molecule removed and the product formed is Enal. + Reaction is k/as Aldol condensation.

FORMATION OF KETOL

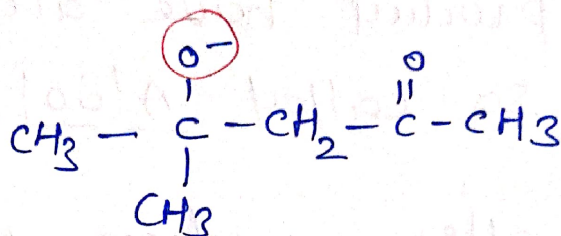
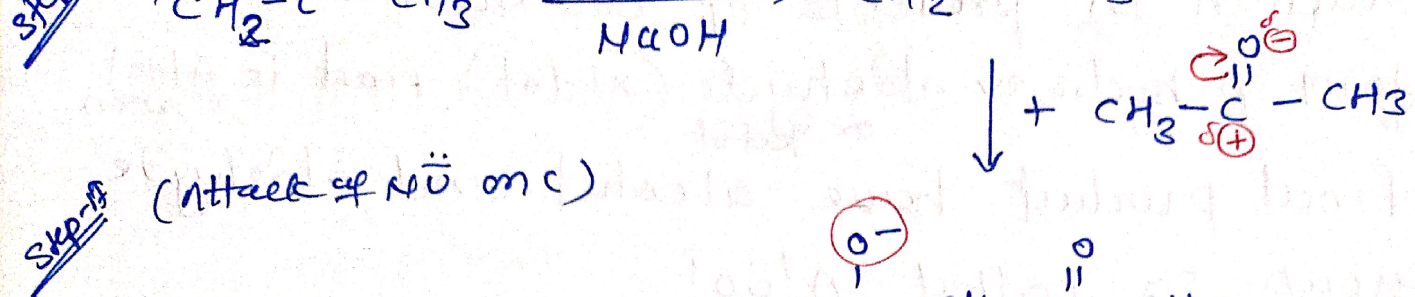
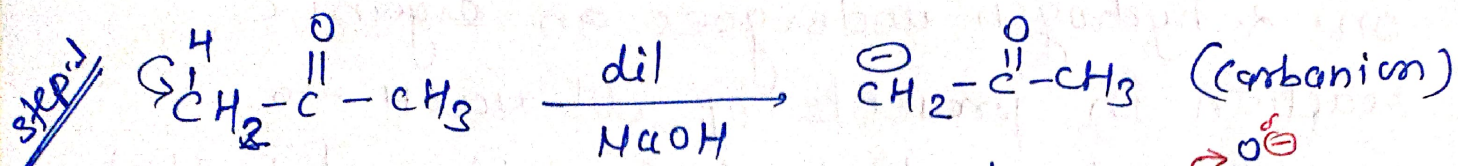


Condensation
 Δ

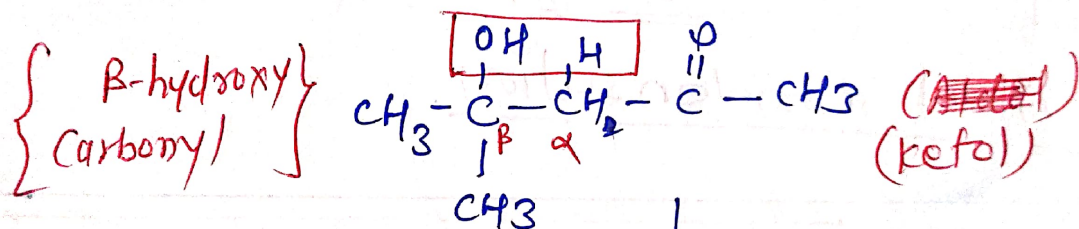
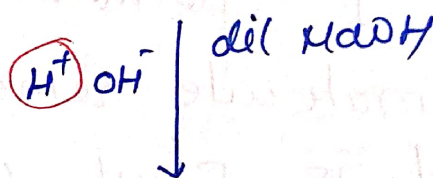


(α - β unsaturated carbonyl)

Mechanism (from ketone)

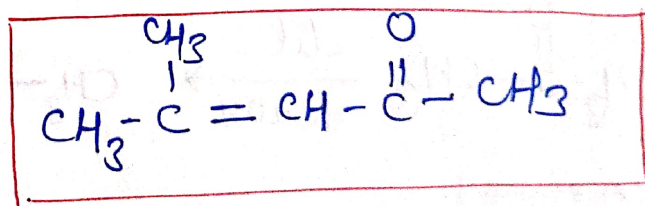
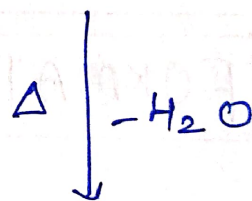


Step-III



Step-IV

Removal of H_2O / condensation



(4 methyl 3 Pentanone)

Note: General name aldol condensation still applies to the reaction of ketone due to similarity with aldehyde.

CROSS ALDOL CONDENSATION

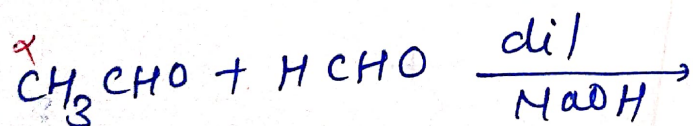
→ When Aldol condensation is carried out between two different aldehyde & ketone is called cross aldol condensation.

Condition

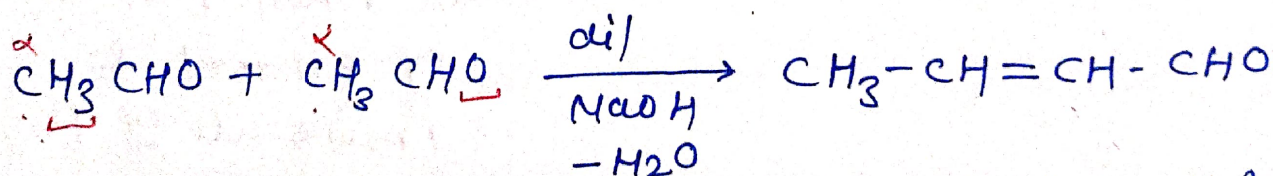
- 1) If only one species have α -hydrogen then two product will be formed.
- 2) If both species have α -hydrogen then four product will be formed.

Example

(i) Reaction b/w different aldehyde

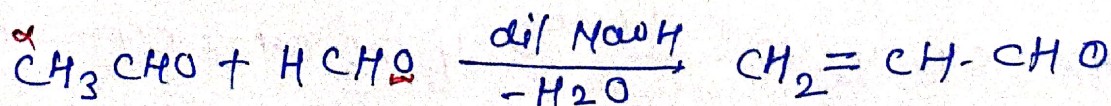


(i) Self aldol Product

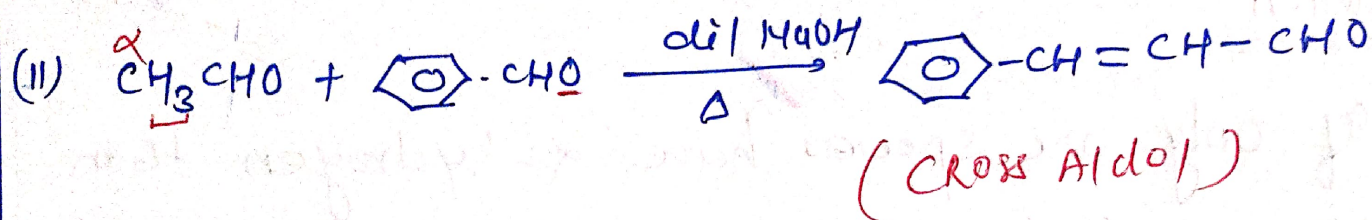
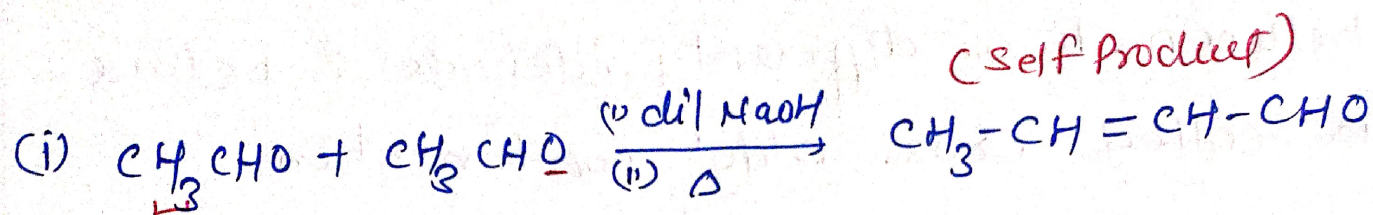
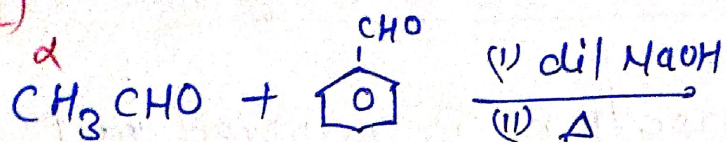


[one species will give 'O' & another one will give 2 Hydrogen]

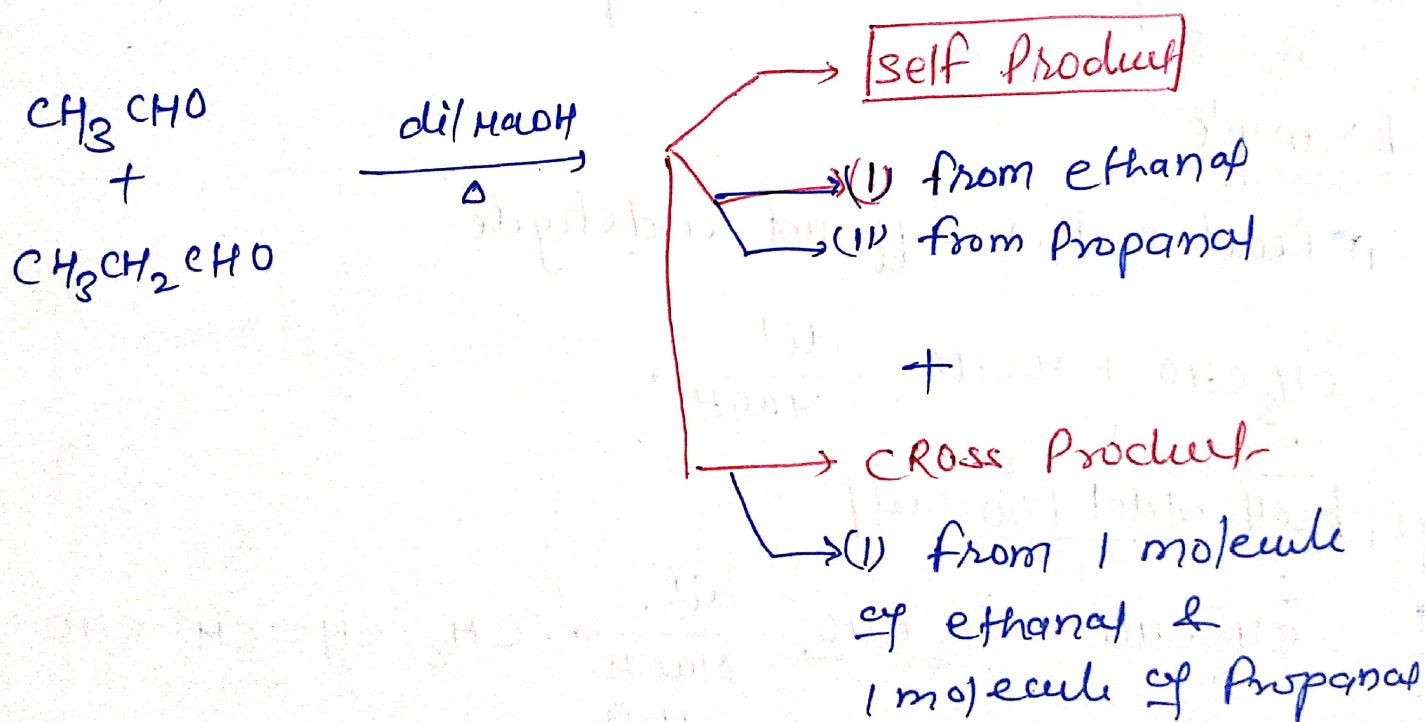
(ii) Cross Aldol Product



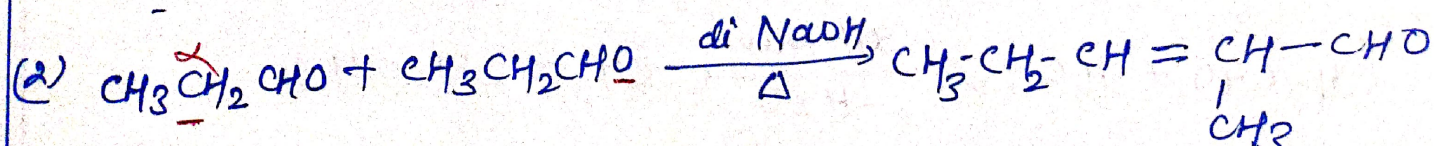
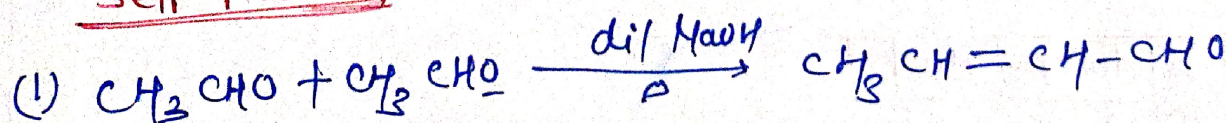
(II)



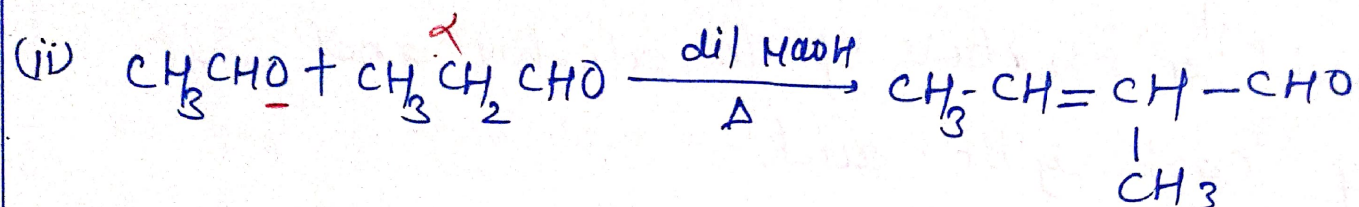
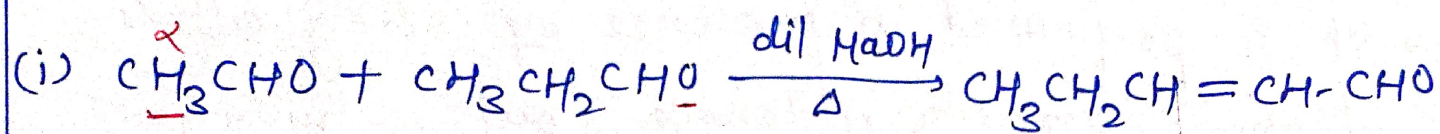
If Both species contain α -hydrogen, it give mixture of product.



Self Product



(II) CROSS Aldol Product



CANNIZARO REACTION

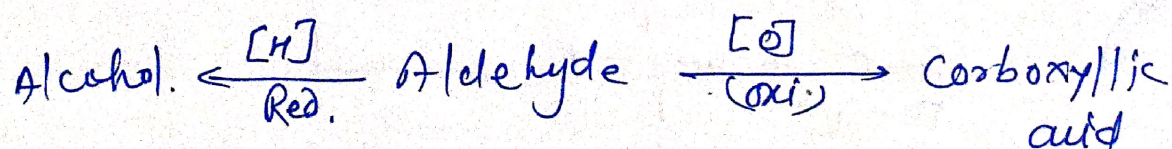
→ It is just opposite of aldol condensation.

→ It shown by species do not have α -hydrogen.

Ex. HCHO , -CHO.

→ Reaction takes place in highly basic medium.
conⁿ KOH + heat.

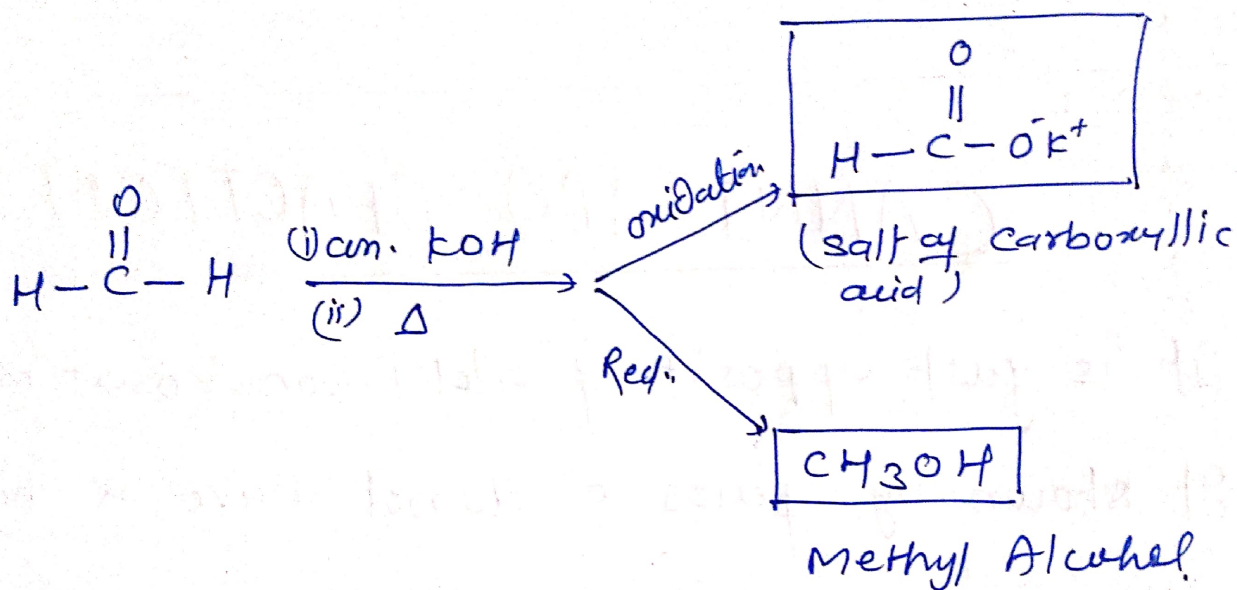
→ It is the disproportionation of aldehyde, means simultaneous oxidation + reduction of same compound.



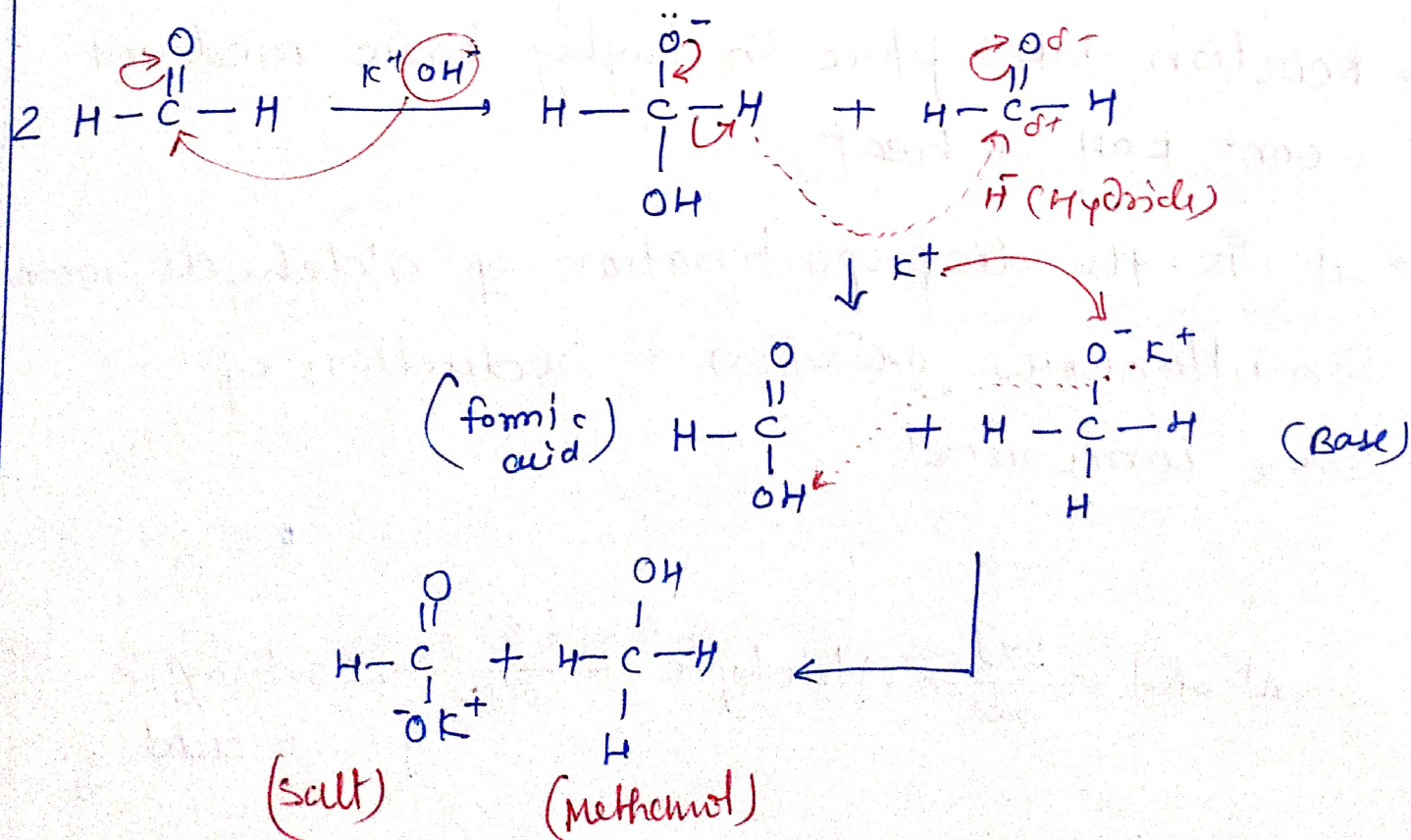
Chemical reaction

→ It is performed in presence of strong alkali, aliphatic/aromatic aldehyde $\pm$ out α -hydrogen undergoes self oxidation, self reduction to yield a mixture of an alcohol and salt of carboxylic acid.

ex.



Mechanism



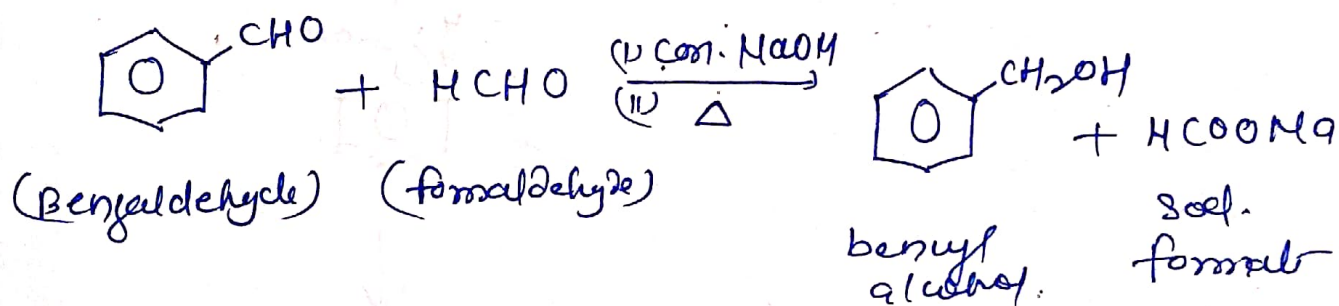
CROSS CANNIZARO REACTION

condition

- 1) There should be two different aldehyde.
- 2) Both shouldn't have α -hydrogen.
- 3) Out of two compound one must be HCHO.
- 4) HCHO always undergoes oxidation & other one will undergo reduction.

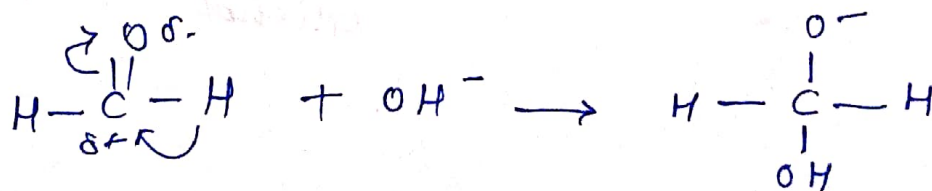
Ex.

- (1) Benzaldehyde React w/ formaldehyde in presence of NaOH/KOH & heat
→ Benzaldehyde goes for reduction & HCHO → oxidation.

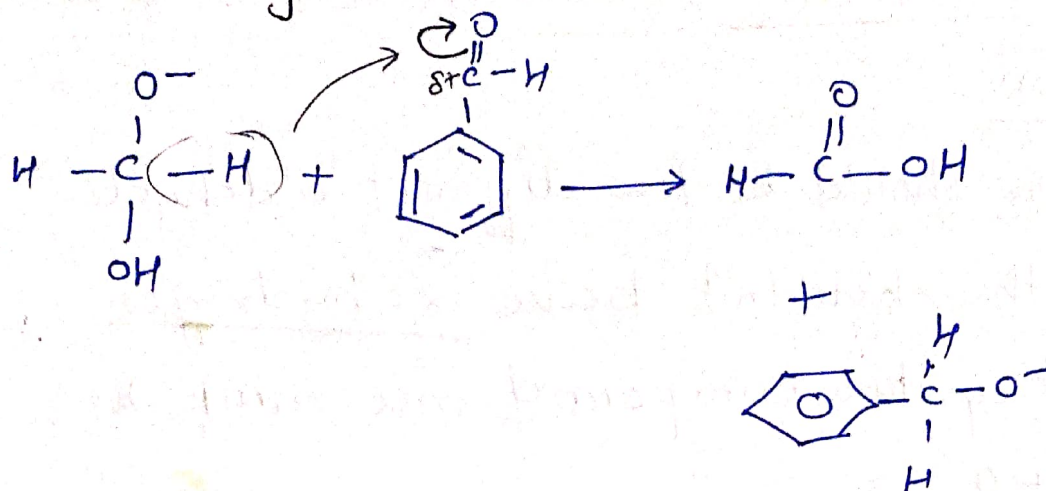


Mechanism

Step 1 Attack of OH^- on aldehyde

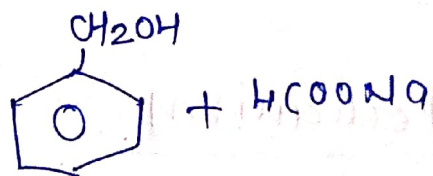
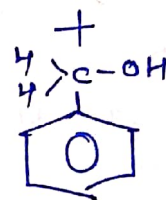
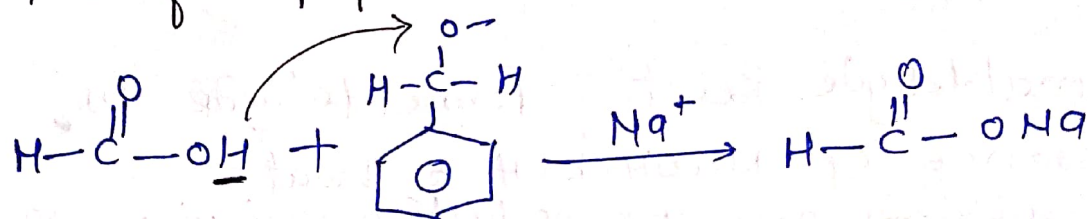


Step-I Hydride shift.



Step-II

Transfer of proton & Addition of Na^+



Benzyl
alcohol

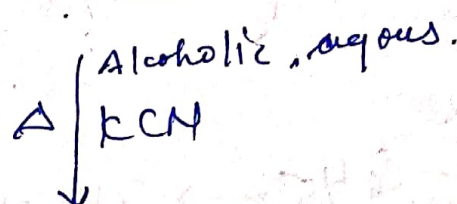
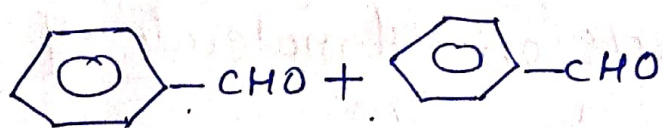
sod.
formate

Benzoin Condensation

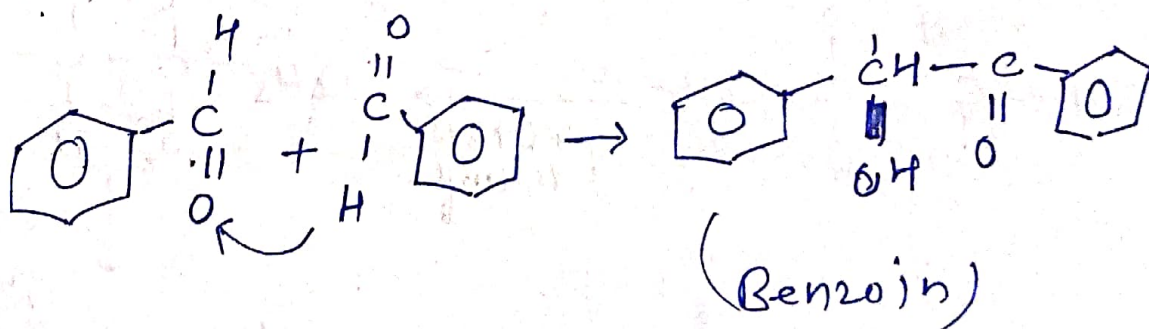
Benzoin condensation is a coupling reaction b/w two aldehyde molecules that further form α -hydroxy ketone.

Ex.

When benzaldehyde react $\bar{c}$ each other in presence of KCN to form benzoin.



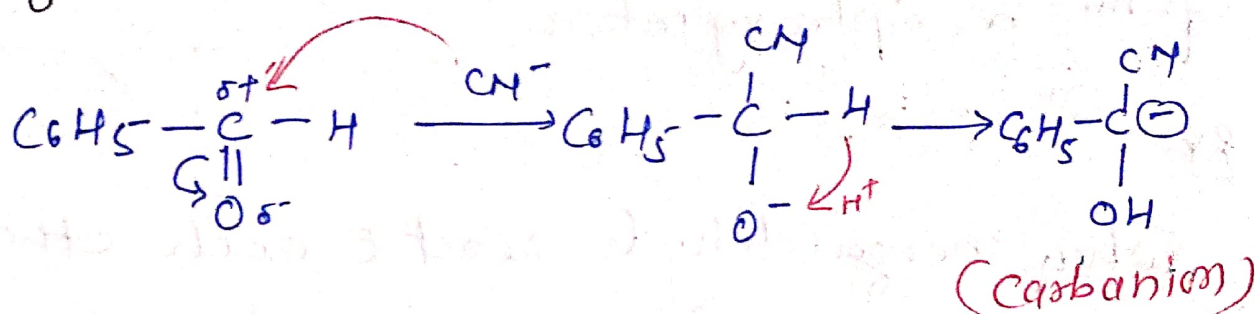
OR



Mechanism of Benzoin Condensation

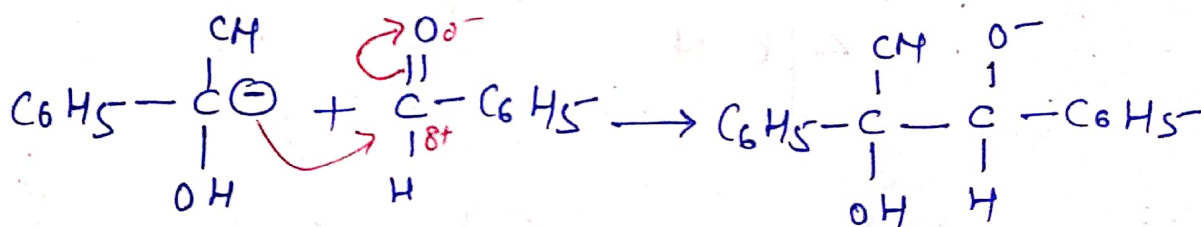
Step-I

cyanide ion attack on benzaldehyde to form Carbanion.



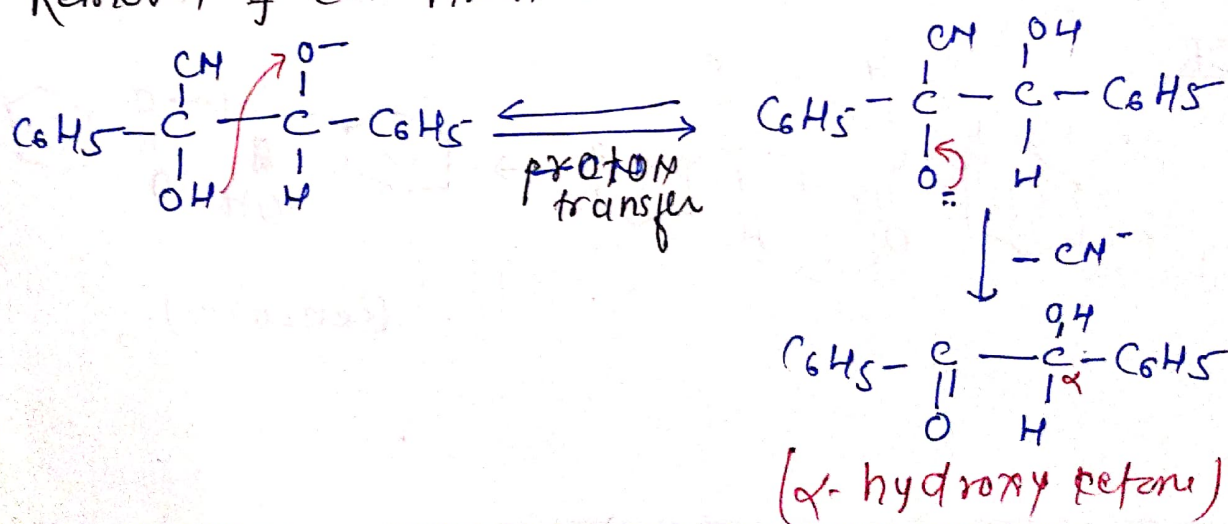
Step II

Carbanion ion attacks on 2nd molecule of Benzaldehyde



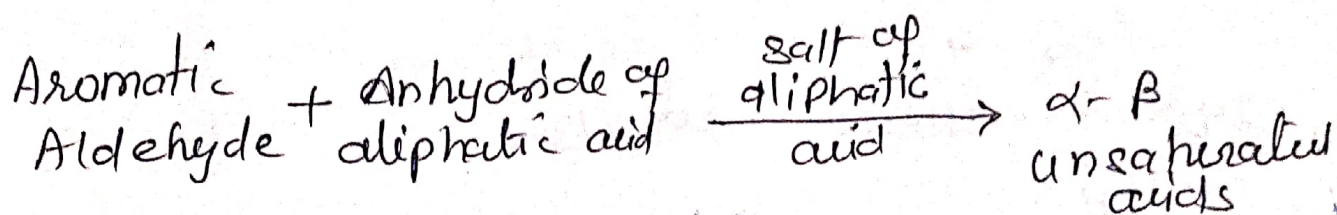
Step-III

Removal of CN^- from benzoin

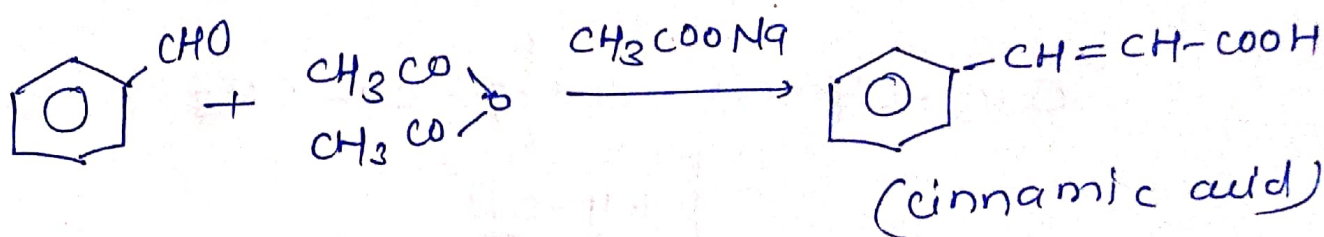


Perkin Condensation

In Perkin condensation aromatic aldehyde (Benzaldehyde) react with acetic anhydride in the presence of Carboxylic acid salt to form α, β unsaturated acid & acetic acid.

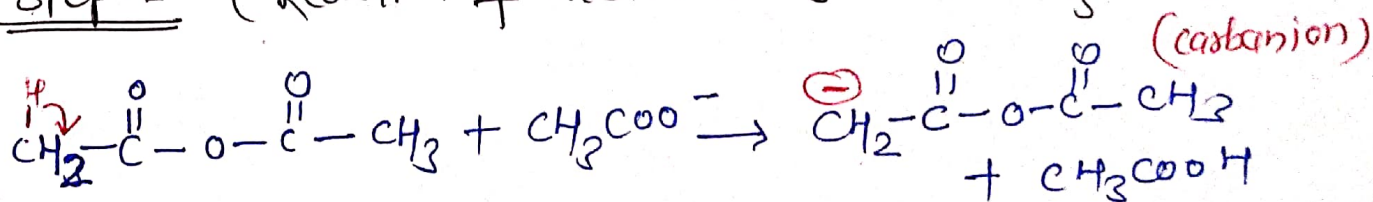


Ex-

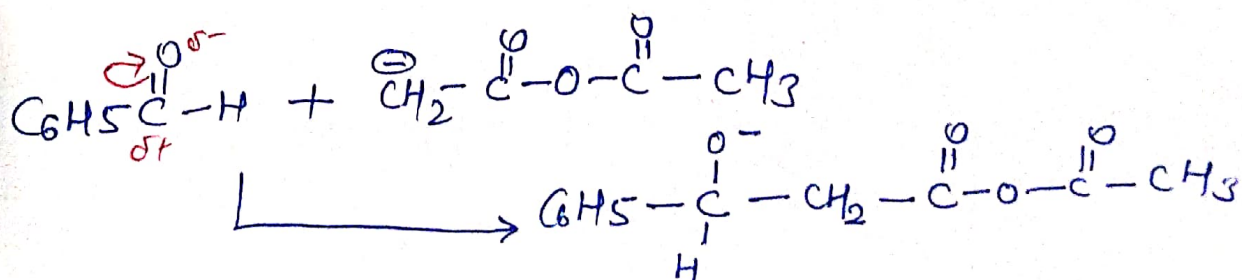


Mechanism

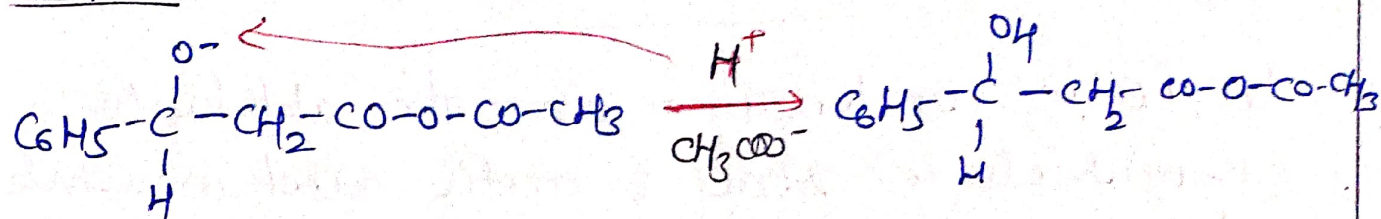
Step-I (Reaction of acetic anhydride & CH_3COO^-)



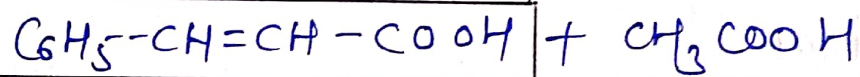
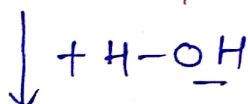
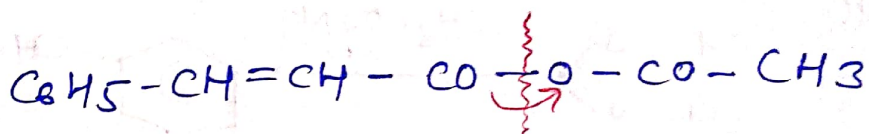
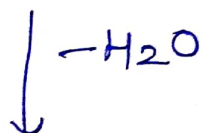
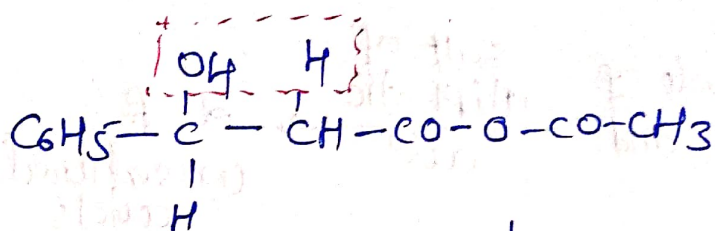
Step-II (Reaction of Benzaldehyde + Carbanion)



Step-III (Protonation)



Step-IV (Removal of H_2O)



(Cinnamic acid)

(Acetic acid)

STRUCTURE AND USES OF FORMALDEHYDE

- It is a simplest aldehyde made of C, H & O.
- Gen formula $\rightarrow \text{CH}_2\text{O}$
- It is a large family of volatile organic compound $\leq$ evaporate and become gaseous at room temperature.
- It is a reactive molecule.

→ Property

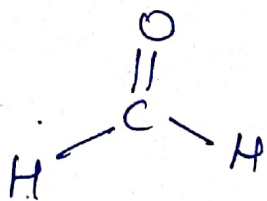
M. wt $\rightarrow 30.31 \text{ g/mol}$

B. P. $\rightarrow -19^\circ\text{C}$

M. P. $\rightarrow -92^\circ\text{C}$

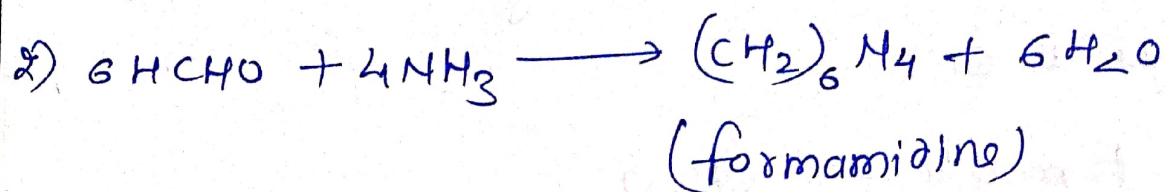
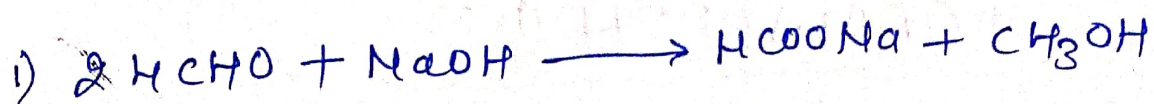
Chemical formula $\rightarrow \text{HCHO}$

Structure



DO PAC: Methanal

Chemical Property



Uses

- 1) Used in production of resins, usually urea-formaldehyde and phenol formaldehyde.
- 2) Used as disinfectant, fungicide, fumigant and preservatives.
- 3) Used to make building material also.

Benzaldehyde

- Simplest aromatic aldehyde having -CHO group
- m. formula $\rightarrow C_7H_6O$
- IUPAC $\rightarrow$ Benzene carbaldehyde
- $\Rightarrow$ Other name $\rightarrow$ Phenyl methanal, benzoic Ald.

Property

- $\rightarrow$ Smell $\rightarrow$ Almond like.
- $\rightarrow$ Solubility $\rightarrow$ miscible $\propto$ volatile oils, ether & alcohol
- $\rightarrow$ It is colourless to yellow in colour
- $\rightarrow$ m. weight $\rightarrow 106.12 \text{ g/mol}$
- $\rightarrow$ Highly reactive compound

Structure



USES

- 1) flavouring to items.
- 2) Precursor for additives & plastic
- 3) base repellent.
- 4) Some cosmetic product have this
- 5) Production of dyes.
- 6) Used as additive in antibacterial & antifungal preservative.