ORGANIC CHEMISTRY – I

IMPORTANT QUESTIONS

UNIT 4

Rx Pharma Education

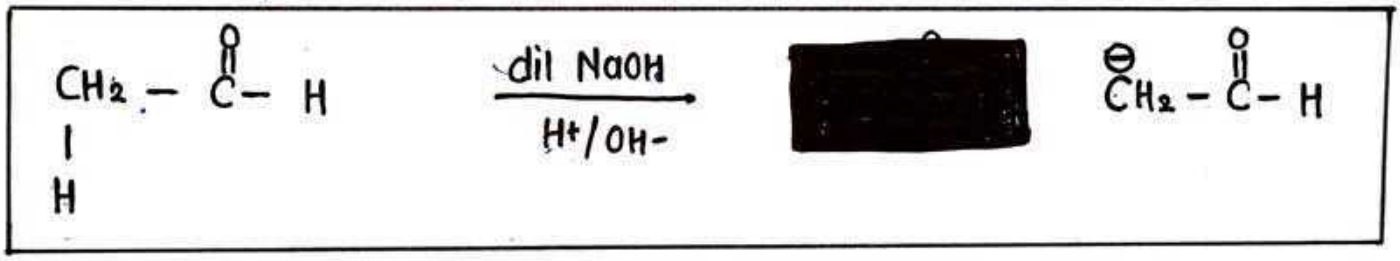
ALDOL CONDENSATION

- Aldehydes or ketones having at least one α - hydrogen undergoes an organic reaction in presence of dilute base (generally dilute NaOH) to form β - hydroxyaldehyde (also known as Aldol) & the reaction is known as **Aldol Reaction**.
- Finally after the formation of Aldol by removing a water molecule a new product form known as Enal & the reaction is known as Aldol Condensation.

Mechanism

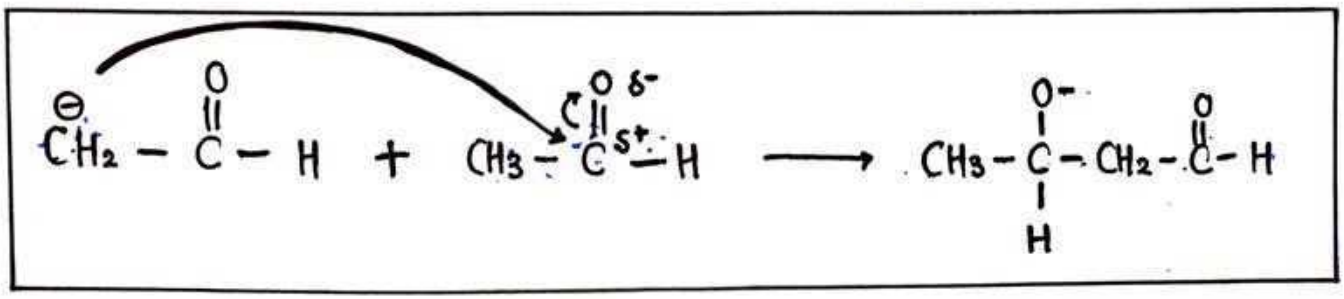
STEP-I

Hydroxide acts as a base & removes the acidic α - hydrogen from aldehyde.



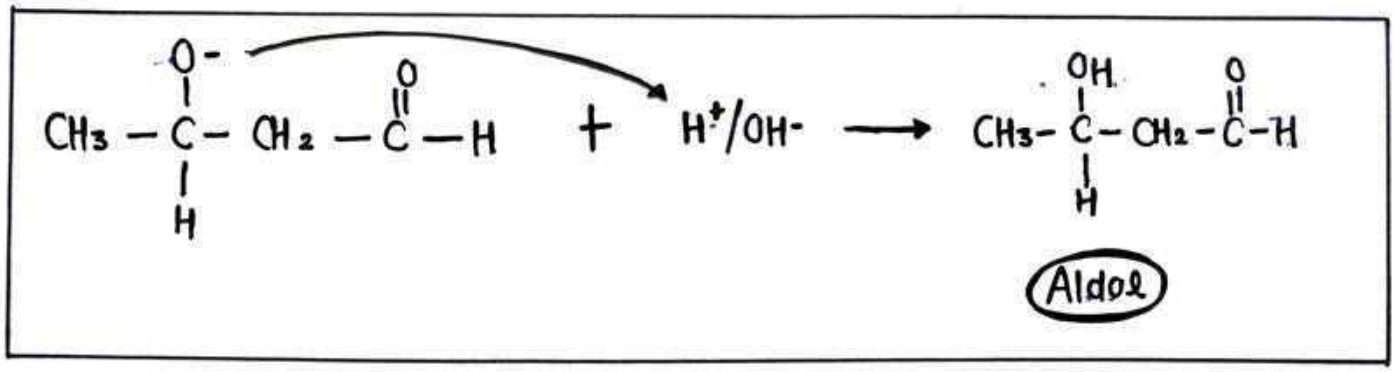
STEP-II

Nucleophile attacks on aldehyde at electrophilic carbon atom.



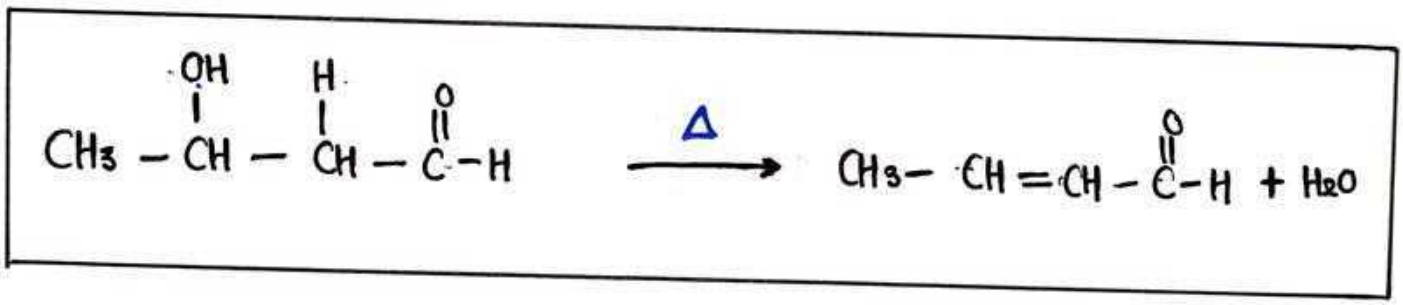
STEP - III

Removal of H^+ from water to form Aldol



FINAL STEP

Removal of water molecule from Aldol compound

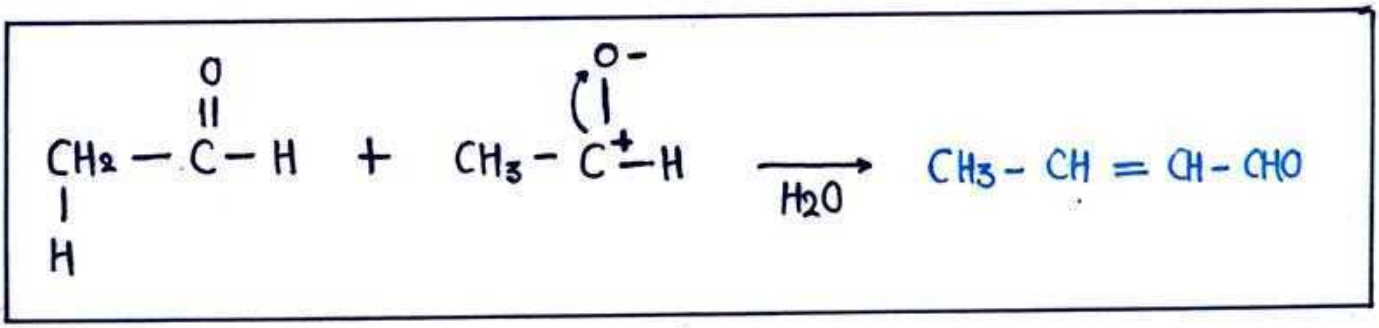


CROSSED ALDOL CONDENSATION

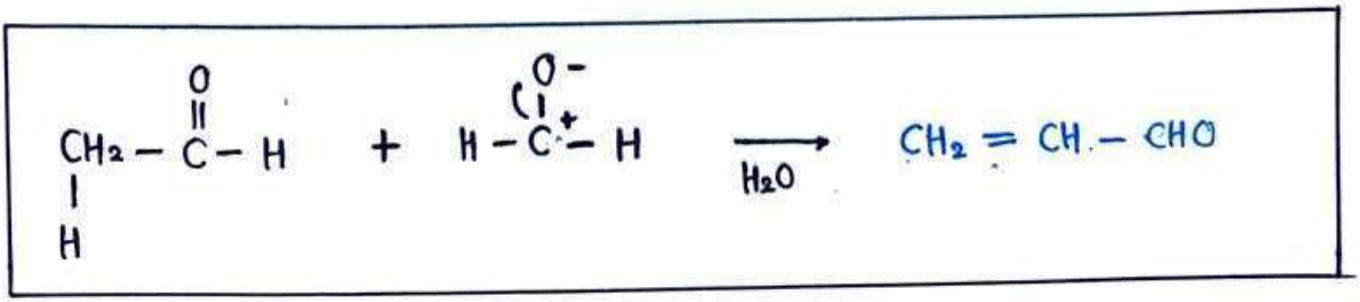
- When aldol condensation is carried out between two different aldehydes or ketones, then it is known as Crossed Aldol Condensation.
- Now if only one species will contain α - hydrogen then two products will be formed, while.
- If both the species contain α- hydrogen then 4 products will be formed.

- Lets assume we carried out our reaction b/w Formaldehyde (Methanal) & Acetaldehyde (ethanal), Now here acetaldehyde contains α hydrogen while formaldehyde don't so we get two products by the following reactions:

Reaction - I



Reaction - II



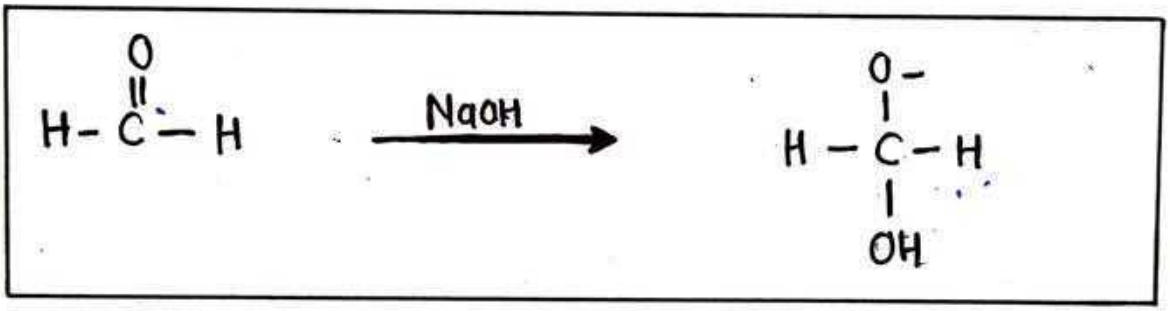
CANNIZARO REACTION

- Cannizaro reaction is a type of organic reaction in which reaction takes place between those aldehydes that do not contain α - hydrogen
- Reaction takes place only in the presence of concentrated base.

Mechanism

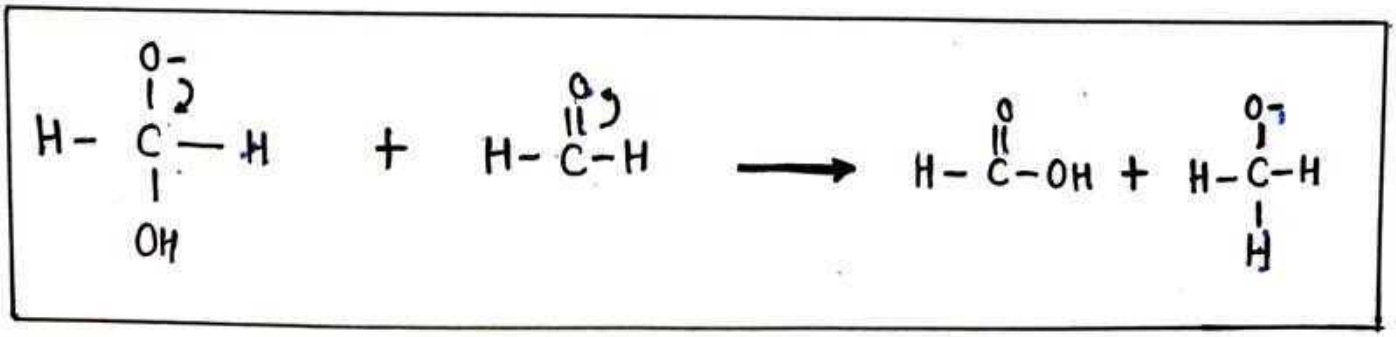
STEP-I

Attack of Hydroxide ion (OH^-) on aldehyde ~~group~~ compound.



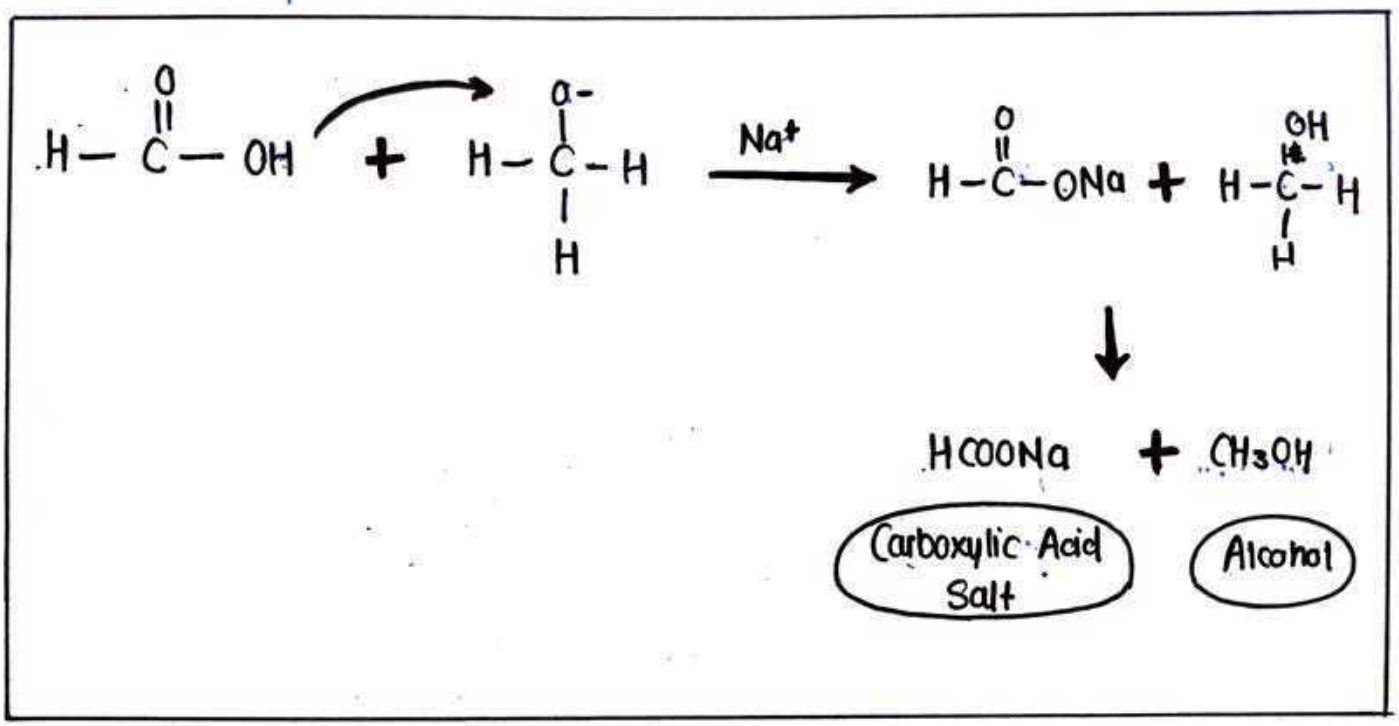
STEP-II

Hydride Shift



STEP - III

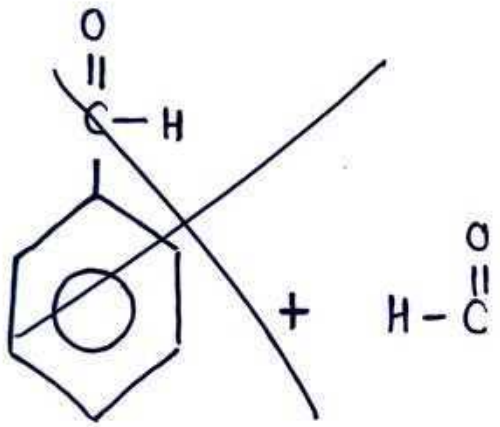
Transfer of proton & addition of Na^+



CROSSED CANNIZARO REACTION

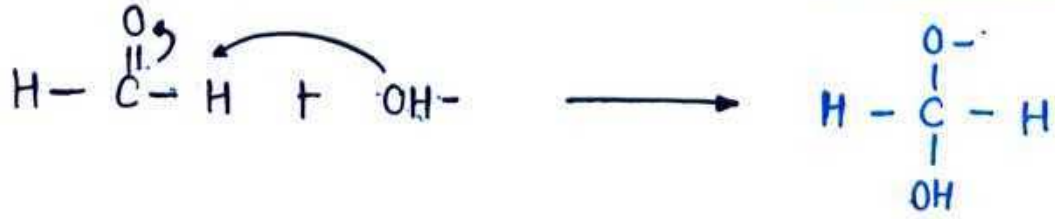
- Crossed cannizaro is also same as cannizaro reaction the main difference is here the reaction takes place blw two different aldehyde group not having α - hydrogen atom.
- Reaction takes place in the presence of concentrated base.
- The reaction mainly takes place blw formaldehyde & Benzaldehyde

STEP-I



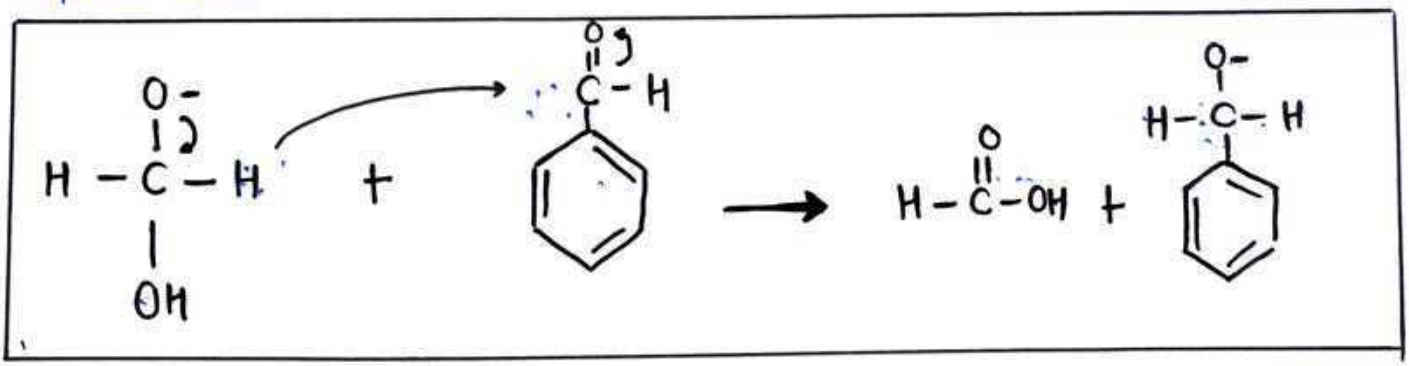
STEP-I

Attack of OH- on aldehyde



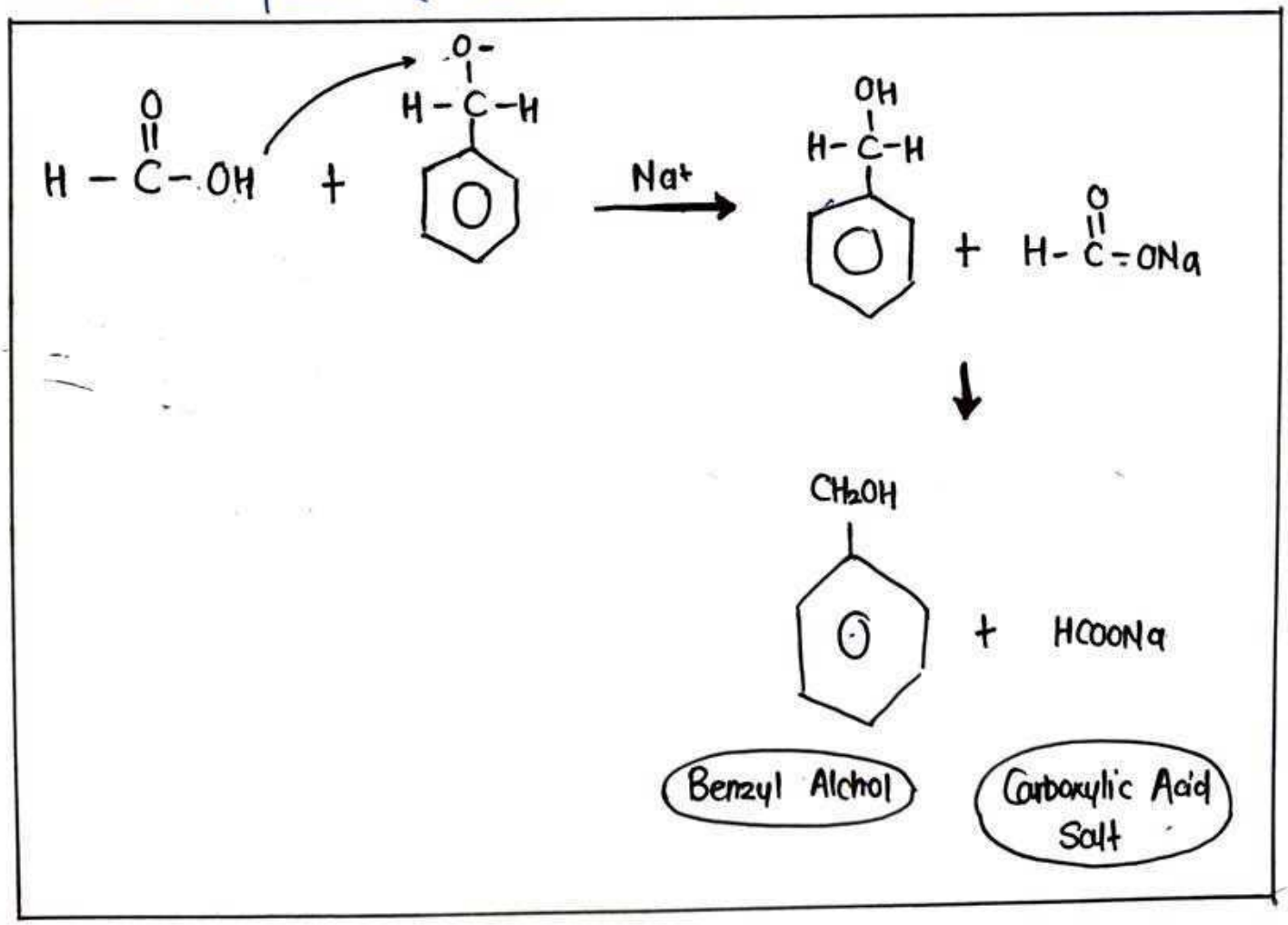
STEP-II

Hydride shift



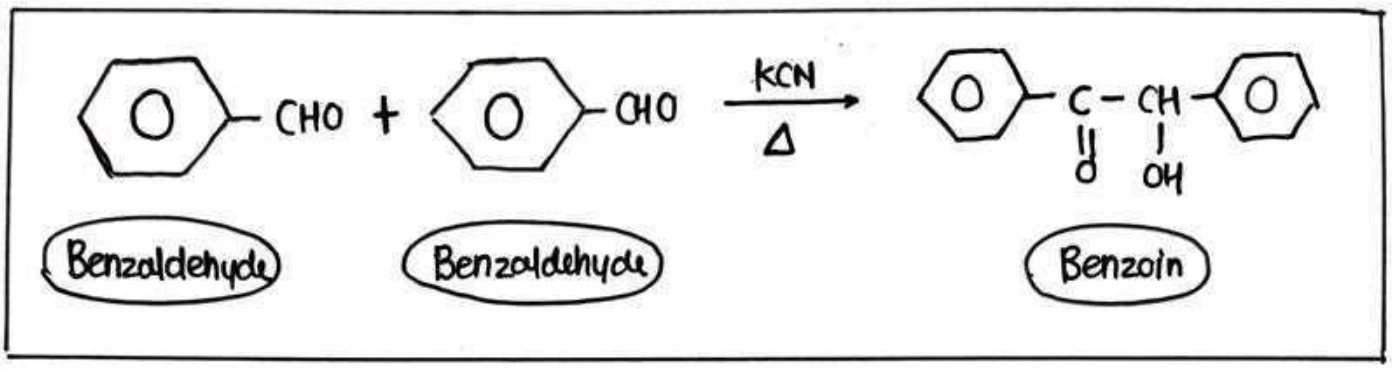
STEP-III

Transfer of proton & addition of Na^+



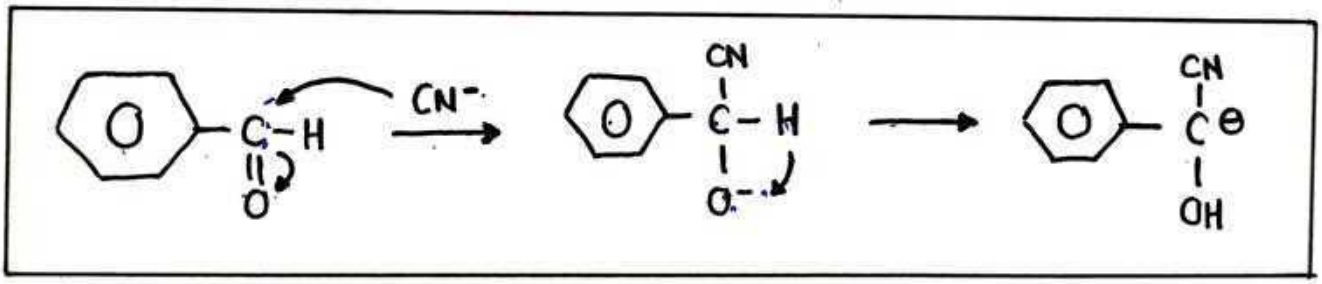
Benzoin Condensation

In benzoin condensation two moles of aromatic aldehydes (mainly benzaldehydes) reacts with each other in the presence of KCN (potassium cyanide) to form benzoin



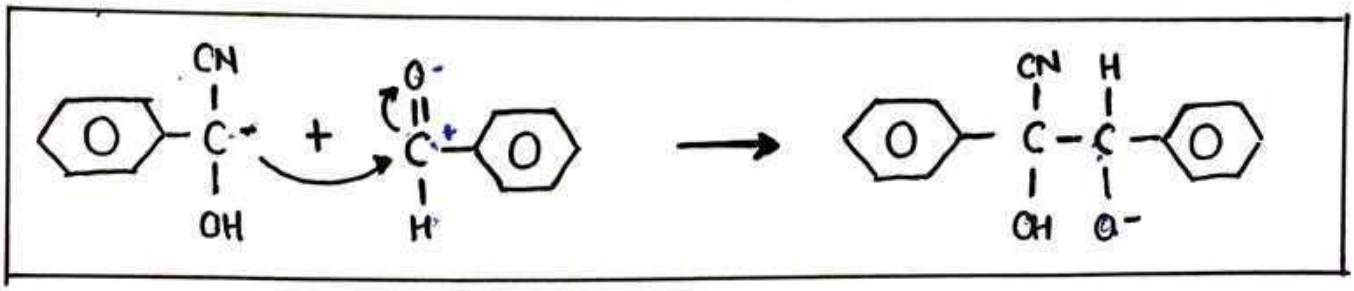
STEP-I

Cyanide ion attacks on benzaldehyde to form carbanion



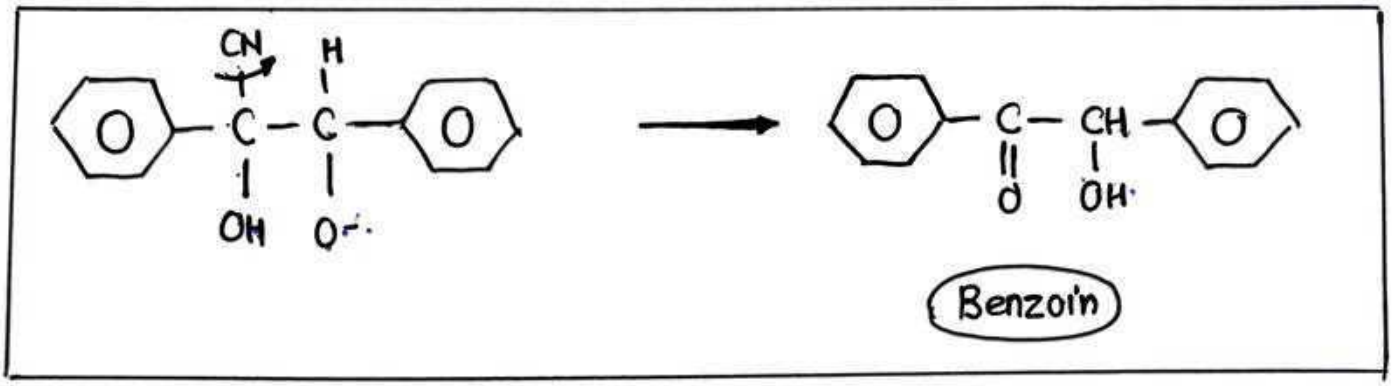
STEP-II

Carbanion attacks on second benzaldehyde to form intermediate.



STEP - III

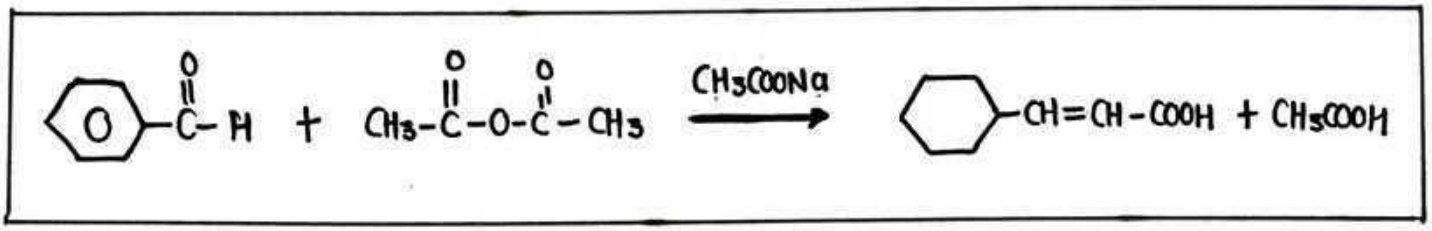
Removal of cyanide ion to form benzoin



Benzoin

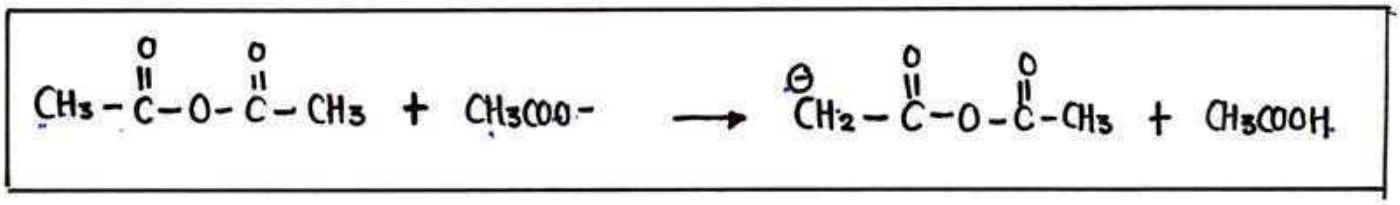
PERKIN CONDENSATION

In perkin condensation aromatic aldehyde (mainly benzaldehyde) reacts with acetic anhydride in the presence of carboxylic acid salt to form α, β unsaturated acid & acetic acid.

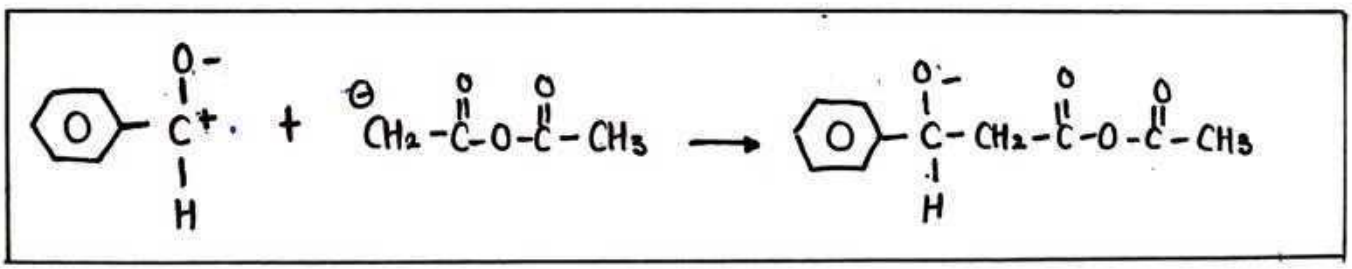


Mechanism

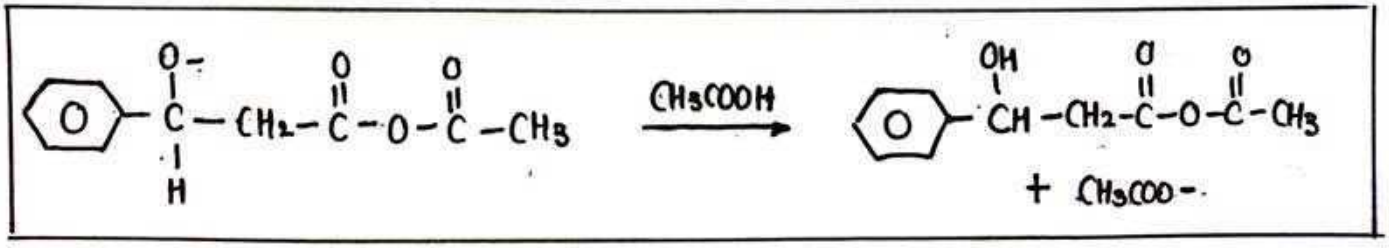
STEP-I



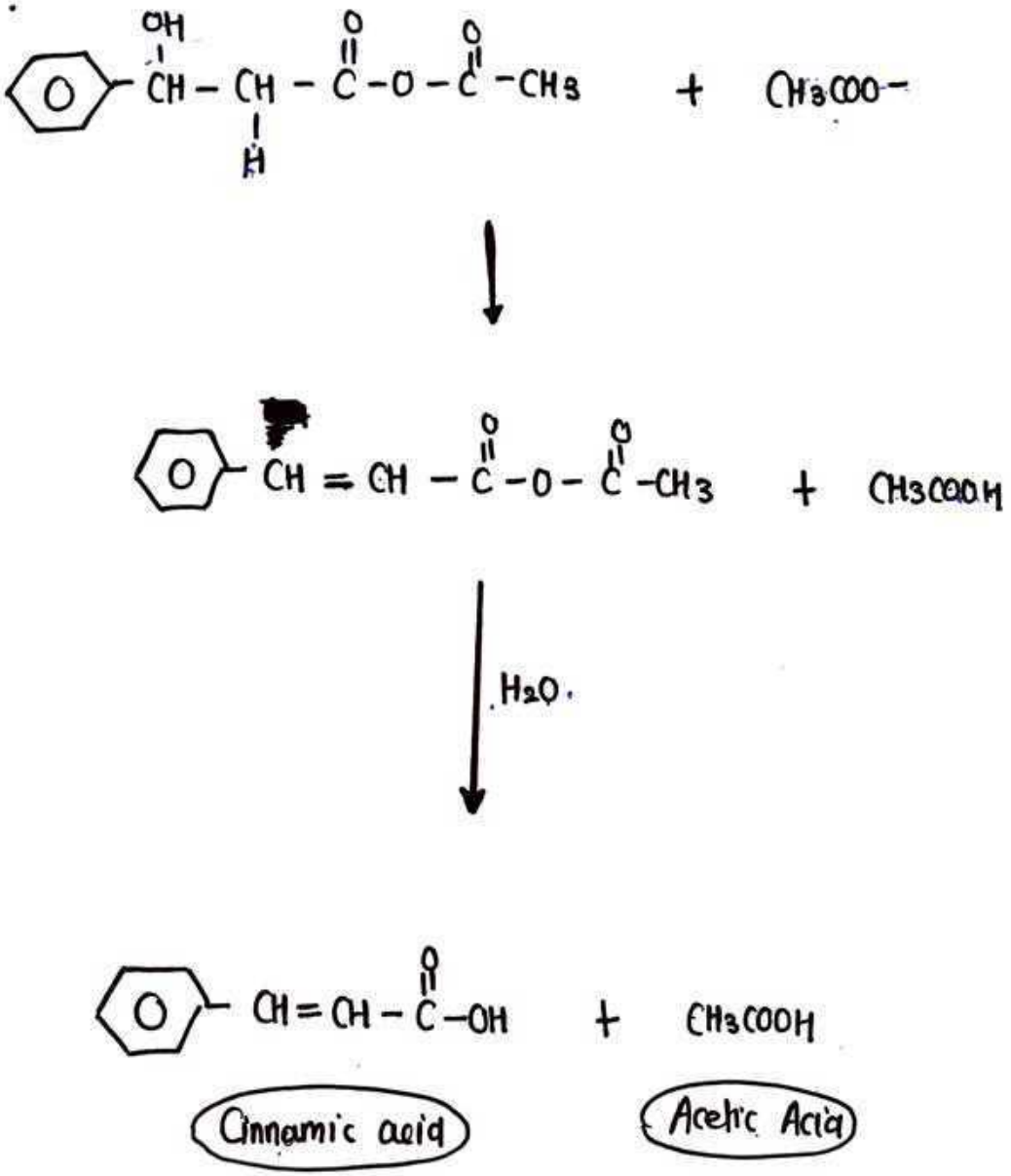
STEP-II



STEP-III



STEP-4


OH
CH – CH – C – O – C – CH3
H
+ CH3COO–
CH = CH – C – O – C – CH3
+ CH3COOH
H2O.
CH = CH – C – OH
+ CH3COOH
Cinnamic acid
Acetic Acid

UNIT- 5 NOTES

① Discuss the acidity of Carboxylic Acid.

- Carboxylic acids are acidic in nature.
- They dissociate in water according to following equilibrium to give a proton and carboxylate ion

$$R\text{-}COOH \rightleftharpoons R\text{-}COO^- + H^+$$

Carboxylic Acid — Carboxylate Ion — Proton

- Carboxylic acids as well as carboxylate ion both are stabilized by resonance.
- However, carboxylate ion is more stabilized by resonance because its contributing structures are exactly identical.
- On the other hand, the contributing structures of carboxylic acid involve charge separation.
- Since carboxylate ion is more stabilized by resonance than carboxylic acid, therefore equilibrium lies very much in forward direction.
- Hence, Carboxylic acids behaves as strong acids.
- Both carboxylic acid and carboxylate ion are resonance stabilized but stabilization is far greater for the carboxylate ion than for the acid.
- Thus, carboxylic acids get ionized due to gain in the stability in going from carboxylic acid to more stable carboxylate ion.
- Hence greater the stability of carboxylate ~~ion~~ anion, greater its acid strength

$$RCOOH > HOH > ROH > CH \equiv CH > NH_3 > RH$$

Effect of Electron Withdrawing Substituents

- The electron withdrawing substituents decrease the electron density on the O-H bond thus facilitating the release of H^+ ions and also stabilize the carboxylate anion by dispersal of negative charge.
- Electron Withdrawing Group stabilized the carboxylate anion by dispersing the negative charge & therefore increase the acidity.
- Thus, an electron withdrawing group increases the strength of the acid.

EFFECT OF ELECTRON RELEASING SUBSTITUENTS

- The presence of electron releasing substituent intensifies the electron density in O-H bond.
- Electron Releasing Group intensify the negative charge on the anion which leads to decrease in the stability of carboxylic acids and a decrease in the acidity of acid.
- As a result, it adversely affect the release of H^+ ions & hence decreases the acidic character.