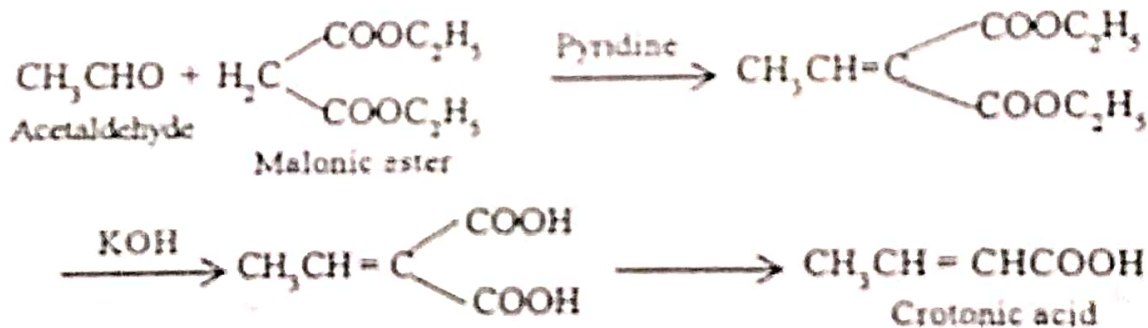


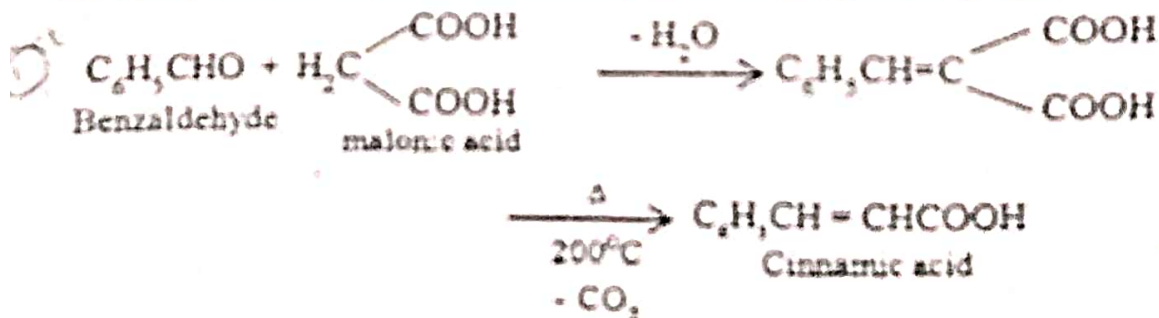
### 5. KNOEVENAGEL REACTION

This is the reaction between an aldehyde and compound with active methylene groups in the presence of an organic base. This is an aldol type of condensation reaction. Compounds like acetoacetic ester, cyanoacetic ester, malonic ester and 1,3-carbonyl compounds containing reactive methylene group react with aldehydes. Pyridine is usually used as the catalyst.

Acetaldehyde reacts with malonic ester to give crotonic acid.



Benzaldehyde undergoes Knoevenagel condensation. It condense with malonic acid in ethanolic ammonia to form cinnamic acid.

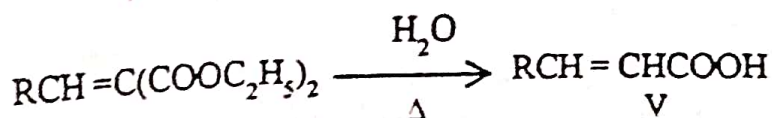
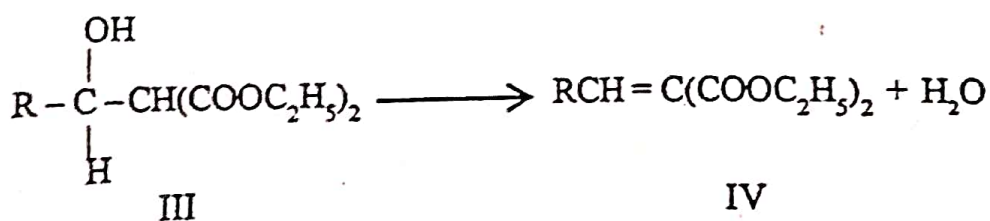
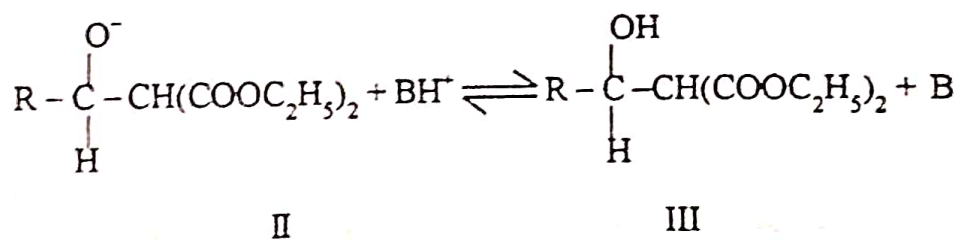
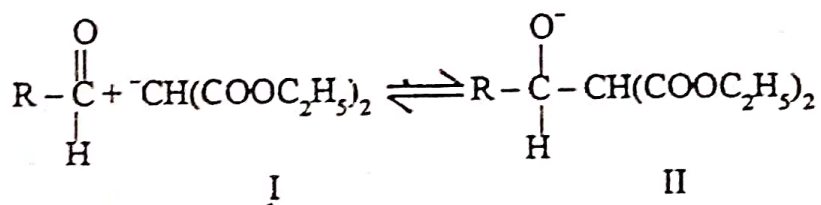
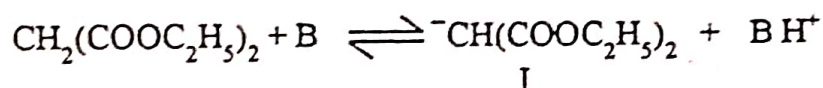


This reaction is also known as Knoevenagel condensation.

**Mechanism**

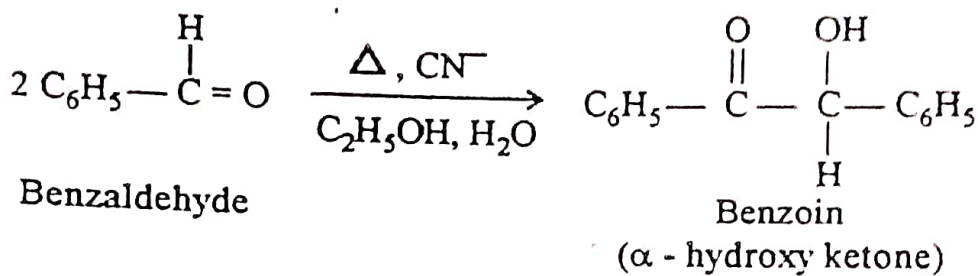
The mechanism is similar to that of aldol condensation.

- 1) The base removes a proton from the reactive methylene group to form the carbanion I.
- 2) The carbanion I attacks the carbonyl carbon of the aldehyde to form an anion II.
- 3) The protonated base reacts with the anion II to form hydroxy compound III.
- 4) The hydroxy compound eliminates a water molecule to give the unsaturated ester IV.
- 5) The unsaturated ester on hydrolysis gives the unsaturated acid V.



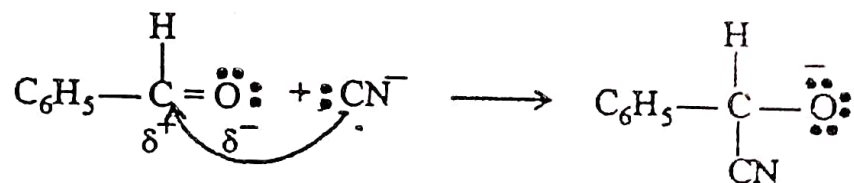
### \* 4. BENZOIN CONDENSATION :

When benzaldehyde is heated with aqueous - ethanolic NaCN or KCN, it dimerizes to form an  $\alpha$  - hydroxy ketone called *benzoin*. This reaction involving self - condensation of an aromatic aldehyde in the presence of  $\text{CN}^-$  anion as catalyst, is referred to as *benzoin condensation*.

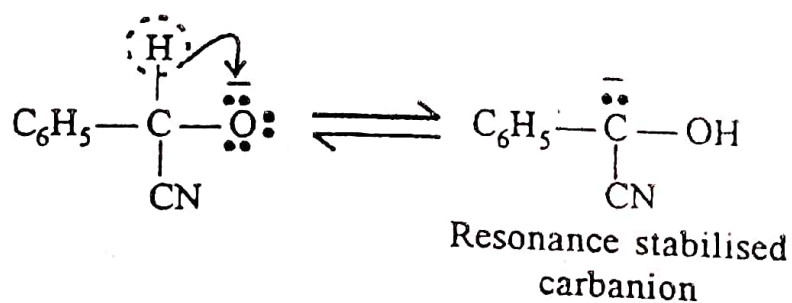


#### Mechanism

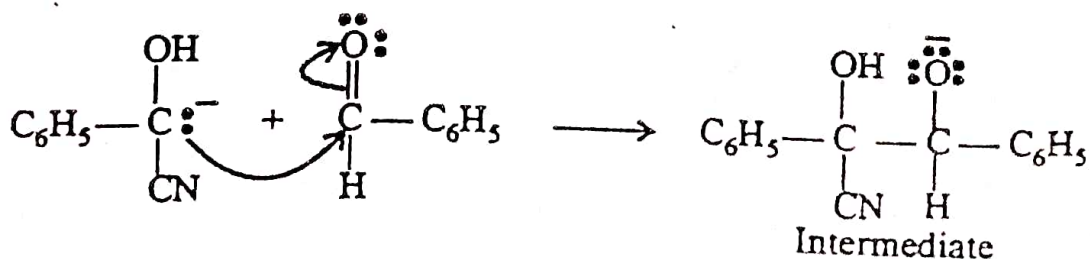
i. Nucleophilic addition of a cyanide anion to the carbonyl carbon.



ii. The CN group acidifies the former aldehyde H atom which migrates to the former carbonyl group.



iii. The resonance - stabilised carbanion adds to the carbonyl carbon of another molecule of benzaldehyde.





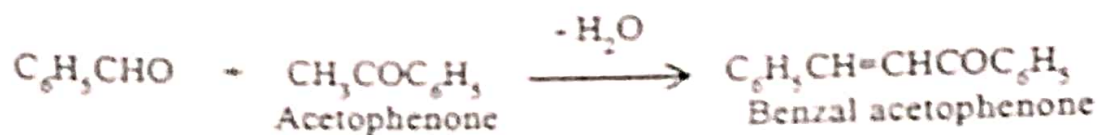
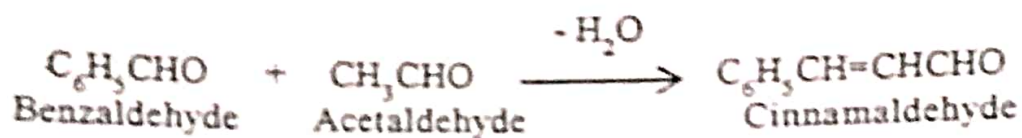


## 5. CLAISEN REACTION

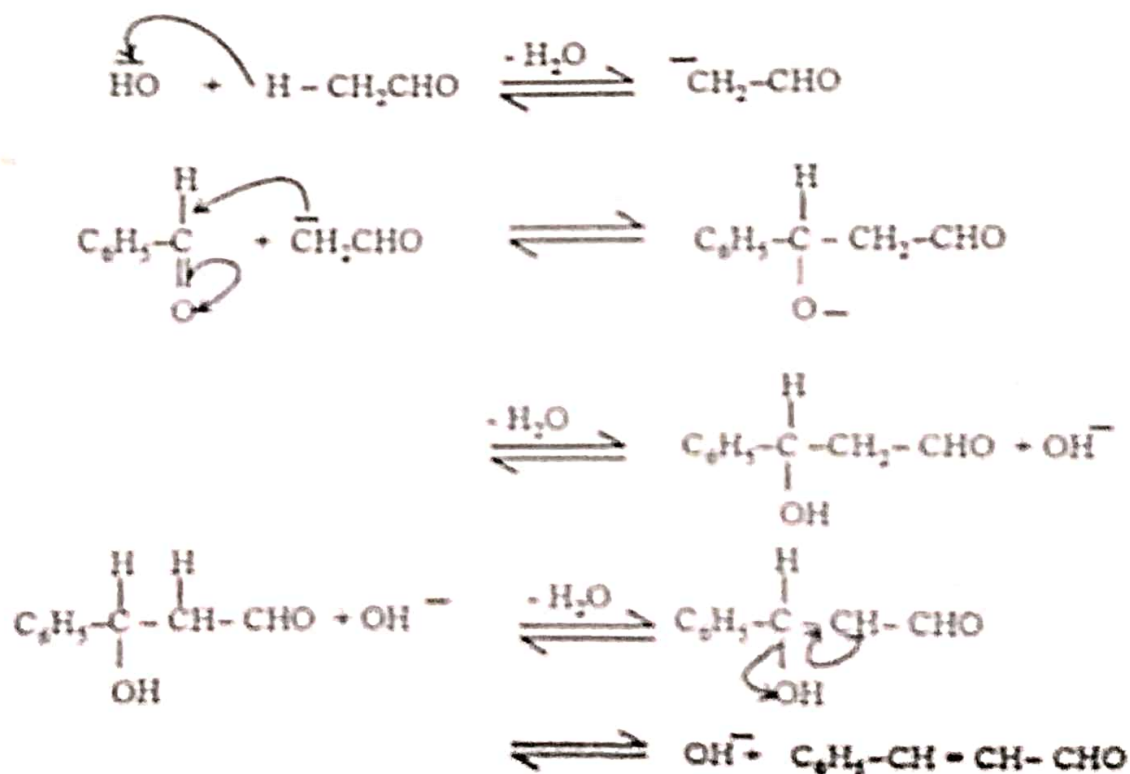
(also known as *Claisen - Schmidt reaction*).

It is the condensation between an aromatic aldehyde (or ketone) and an aldehyde or ketone in the presence of dilute alkali to form  $\alpha, \beta$  - unsaturated compounds.

E.g.,



### Mechanism



## REFORMATSKY CONDENSATION

This is the reaction between an aldehyde or a ketone and an  $\alpha$  - bromoester in presence of metallic zinc in dry ether or benzene. The