2 Perkin reaction proceeds more rapidly when the aromatic aldehyde contains halogen atom or a nitro group in the ring.

Methyl substituents present in the ortho position slow down the

reaction.

Benzaldehyde reacts with acetic anhydride in presence of sodium acetate to give cinnamic acid.

C<sub>H</sub>CHO + CH<sub>3</sub>COOCOCH<sub>3</sub> 
$$\longrightarrow$$
 C<sub>6</sub>H<sub>5</sub>CH=CHCOOCOCH<sub>3</sub>

Benzaldehyde Acetic
anhydride
$$\longrightarrow$$
 CH<sub>3</sub>COOH + C<sub>6</sub>H<sub>5</sub>CH=CHCOOH
Cinnamic acid

### Mechanism

- 1) The CH<sub>3</sub>COO<sup>-</sup> ion produced by sodium acetate acts as a basic catalyst. It removes the α hydrogen from the aliphatic anhydride to form the carbanion I.
- 2) The carbanion I adds to the carbonyl group of the aromatic aldehyde to form an intermediate II.
- 3) The intermediate II after protonation forms an aldol like product III (a hydroxy acid anhydride).
- 4) In this product III, internal proton transfer occurs leading to the elimination of a water molecule to form an α, β - unsaturated mixed anhydride IV.
- 5) Hydrolysis of the unsaturated mixed anhydride gives cinnamic acid V.

$$CH_{3}-C-O - CO-CO-CO-CH_{3} \longrightarrow CH_{3}COOCOCH_{3}$$

$$CH_{3}COOH + CH_{2}COOCOCH_{3}$$

$$I$$

$$CH_{3}-CO \longrightarrow H$$

$$CH = CH - CO - O + CH_3$$

$$CH = CH - CO - O + CO - CH_3$$

$$CH = CH - CO - O + CH_3$$

$$CH = CH - CO - O + CH_3$$

$$CH = CH - CO - O + CH_3$$

$$CH = CH - CO - O + CH_3$$

$$CH = CH - CO - O + CH_3$$

$$CH = CH - CO - O + CH_3$$

KNOEVENAGEL REACTION I LEGY TOP A Analy 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, cyonoacetic 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 Konevenagel 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 from the carbanion I.
- The carbanion I attacks the carbonyl carbon of the aldehyde to from an anion II.
- 3) The protonated base reacts with the anion II to from 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.

$$CH_2(COOC_2H_5)_2 + B \rightleftharpoons CH(COOC_2H_5)_2 + BH^+$$

$$R - C + CH(COOC_2H_5)_2 \rightleftharpoons R - C - CH(COOC_2H_5)_2$$

$$I$$

$$I$$

$$I$$

$$R - C - CH(COOC_2H_5)_2 + BH \longrightarrow R - C - CH(COOC_2H_5)_2 + B$$

$$II$$

$$III$$

$$III$$

$$R - C - CH(COOC_2H_5)_2 \longrightarrow RCH = C(COOC_2H_5)_2 + H_2O$$

$$H$$
III

$$RCH = C(COOC_2H_5)_2 \xrightarrow{H_2O} RCH = CHCOOH_V$$

F A

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 CN anion as catalyst, is referred to as benzoin condensation.

Mechanism

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from

roxy

: the

. V.

Nucleophilic addition of a cyanide anion to the carbonyl carbon.

$$C_6H_5 - C_6H_5 - C_6H_5 - C_6H_5 - C_6H_5$$

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

$$C_6H_5$$
— $C$ — $C$ 0:

 $C_6H_5$ — $C$ — $C$ 0H

 $CN$ 

Resonance stabilised carbanion

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

THE PART OF THE TOTAL TO SELECT THE SECOND S

$$C_6H_5$$
 $C_6H_5$ 
 $C_6H_5$ 

The migration of the proton of OH to the oxygen accompanied by abstraction of cyanide anion, forms benzion.

$$C_6H_5 - C - C - C_6H_5 \longrightarrow C_6H_5 - C - C_6H_5$$

$$CN H \longrightarrow C_6H_5 - C - C_6H_5$$

$$CN GH_5 - C - C_6H_5$$

$$Benzoin$$

Benzoin can be readily oxidised to a diketone, benzil and reduced to a number of substances such as desoxybenzoin, hydrobenzion, stilbene and dibenzyl.

$$C_{0}SO_{4}$$

$$Pyridinc, H_{1}O$$

$$C_{2}H_{3}-CO-CO-C_{6}H_{3}+H_{2}O$$

$$Benzil$$

$$C_{4}H_{1}-CO-CH_{2}-C_{4}H_{3}+H_{2}O$$

$$Desoxybenzoin$$

$$Desoxybenzoin$$

$$+2[H] \xrightarrow{Na/Hg/EzOH} C_{4}H_{3}-CHOH-CHOH-C_{6}H_{5}$$

$$Hydrobenzoin$$

$$+6[H] \xrightarrow{Zn/Hg/HCl} C_{4}H_{3}-CH+CH-C_{4}H_{5}+2H_{2}O$$

$$Stilbene$$

$$+4H_{2} \xrightarrow{H_{2}/Raney Ni} C_{4}H_{5}-CH_{2}-CH_{2}-C_{6}H_{5}+2H_{2}O$$

$$Dibenzyl$$

# S CLAISEN REACTION

(also known a 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 and  $\alpha$ ,  $\beta$  - unsaturated compounds.

Eg.

Mechanism

13

$$C_{e}H_{3}$$
  $C_{e}$   $C_{e}H_{4}$   $C_{e}$   $C_{e}H_{5}$   $C_{e}$   $C_{e}H_{5}$   $C_{e}$   $C_{e}H_{5}$   $C_{e}$   $C_{$ 

## REFORMATSKY CONDENSATION \*

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