Organic Chemistry

Condensation Reaction

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Selective Organic Name Reaction

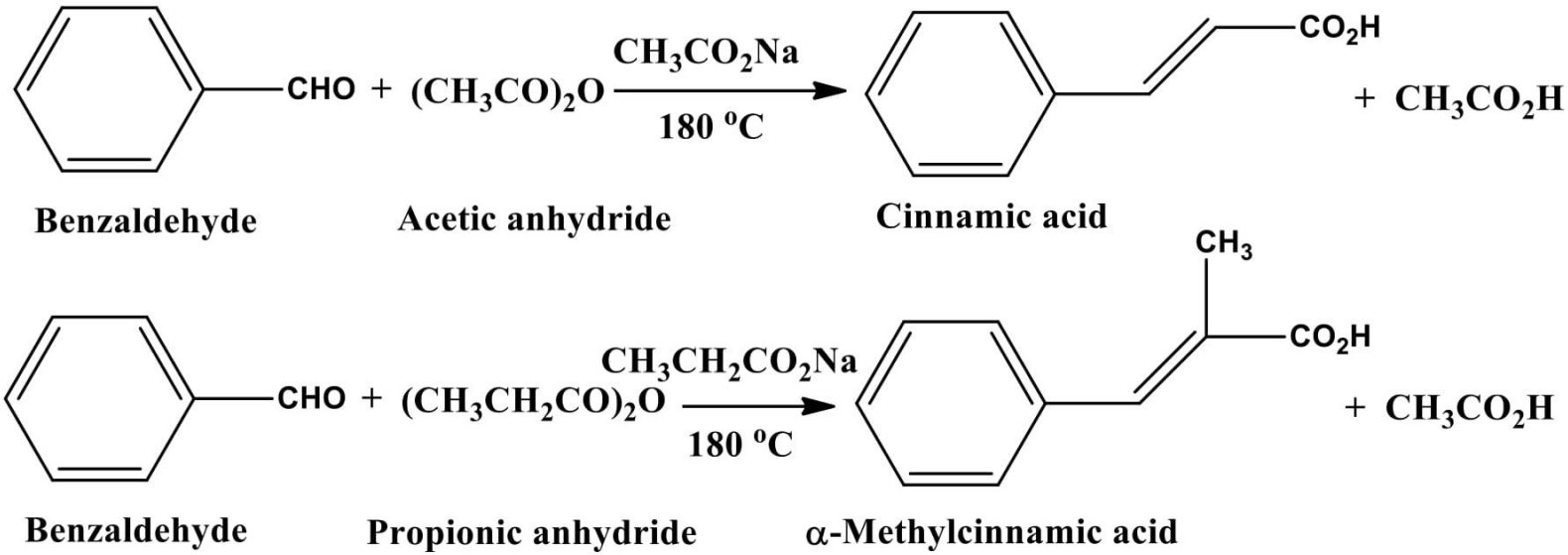
Msc Ist & IInd

CONDENSATION

- **PERKIN REACTION**

PERKIN REACTION

- When an aromatic aldehyde is heated with the anhydride of an aliphatic acid containing at least two α-hydrogen atoms in the presence of its anhydrous sodium salt, condensation takes place to form a β-arylacrylic acid. The reaction is known as Perkin reaction.
- Only the α-hydrogen atoms of the anhydride are involved in the reaction. The acetoxyl ion acts as the base, and in some cases triethylamine as base gives better yield.



GENERAL FEATURES

- The base in the Perkin reaction is always the sodium or potassium salt of the acid corresponding to the anhydride.

- Although reaction is best carried out with aromatic aldehydes, aliphatic aldehydes with no α-hydrogen atoms as well as certain α,β-unsaturated aldehydes also take part in this reaction.

- Aromatic aldehydes having one or more electron withdrawing groups give better yield and the reaction is found to be more facile, when the substituent is at the *p*-position. Electron donating groups like –OH or $–OCH_3$ slows down the reaction.

- The stereochemistry of the newly formed double bond is typically (*E*) because the last step of the reaction is dehydration through E2 mechanism.

MECHANISM

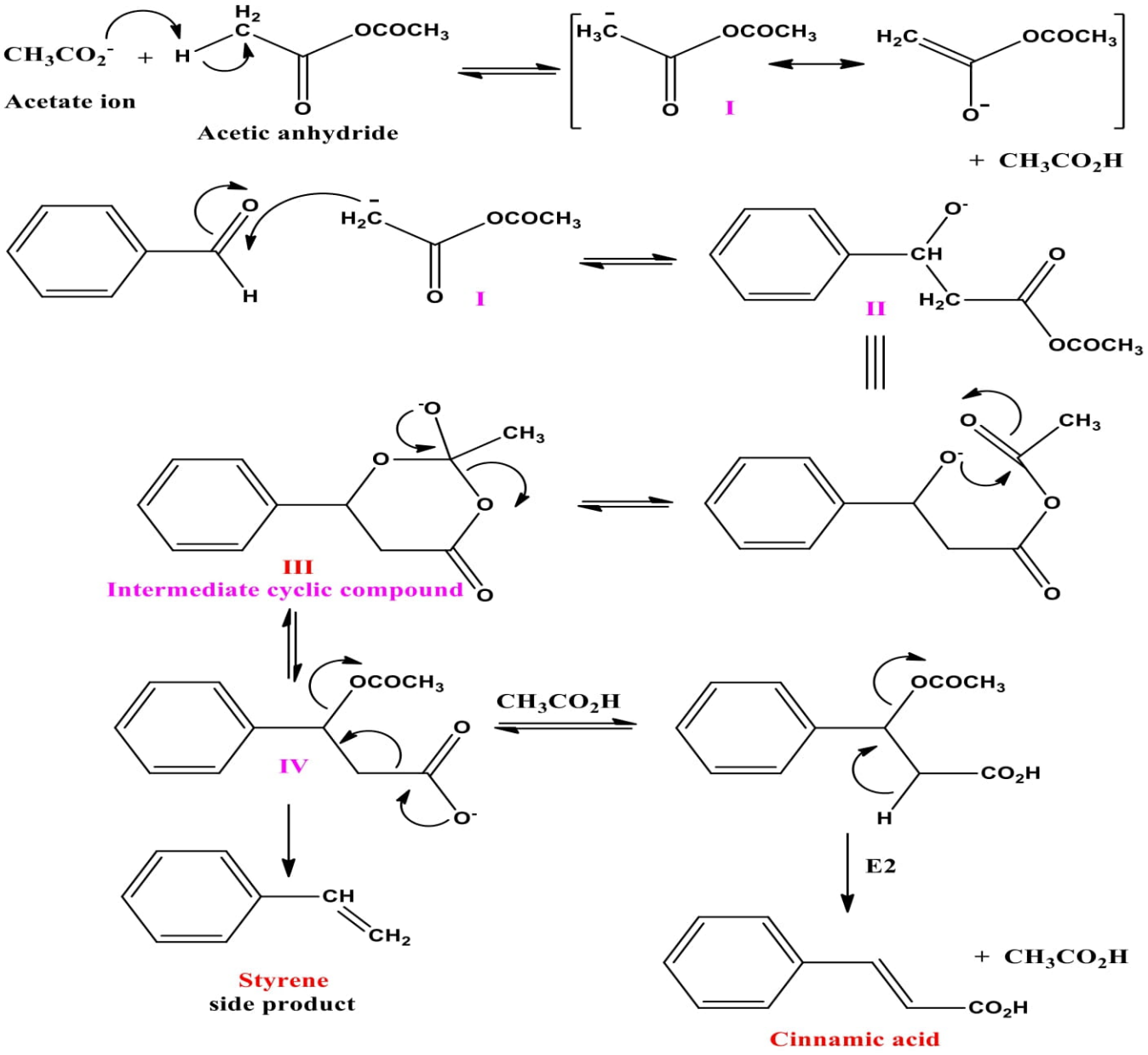
- Acetate ion, $CH_3CO_2^-$ (from the anhydrous sodium acetate), acting as basic catalyst, abstracts α-H atom from acetic anhydride to form a carbanion (I).

- The carbanion (I) combines with the partially positively charged carbon atom of the carbonyl group of the aldehyde and forms the oxyanion (II), which forms a cyclic intermediate (III).

- An intramolecular acylation reaction takes place.

- A molecule of acetic acid is then lost from (III) by E2 mechanism to give αβ-unsaturated acid.

MECHANISM


Acetate ion
Acetic anhydride
I
+ CH3CO2H
I
II
III
Intermediate cyclic compound
IV
CH3CO2H
Styrene
side product
E2
+ CH3CO2H
Cinnamic acid

FORMATION OF SIDE PRODUCT

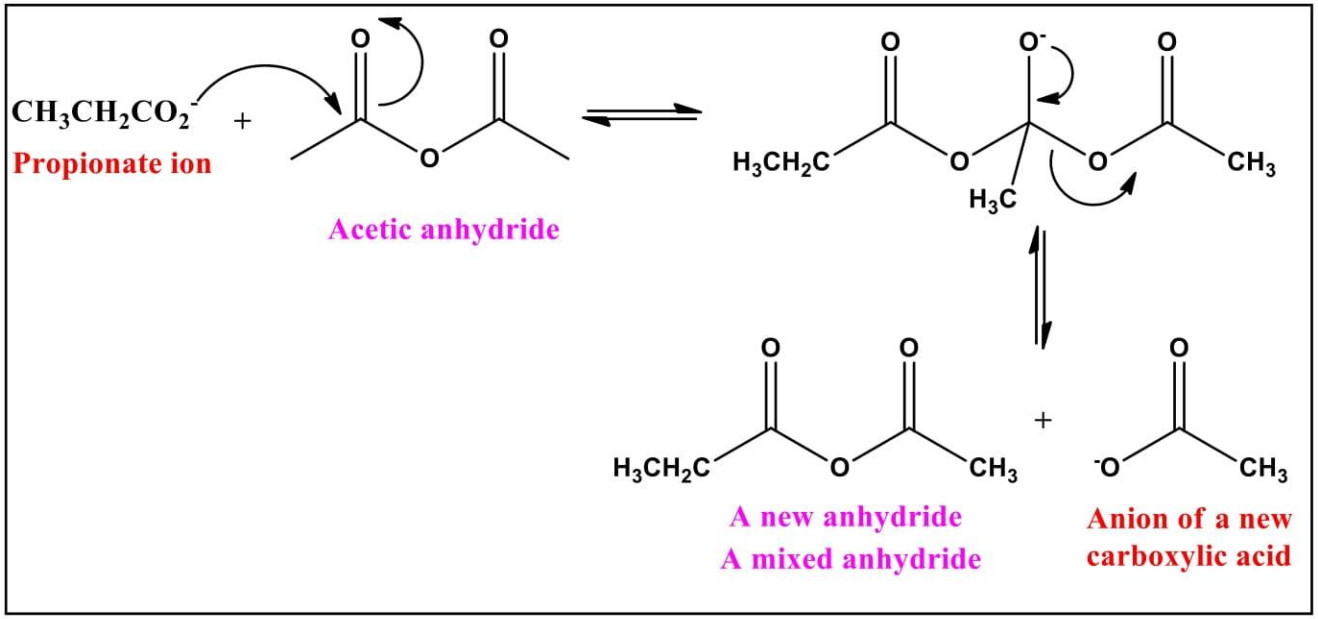
- In the Perkin reaction between benzaldehyde, acetic anhydride and sodium acetate, some amount of styrene is obtained. Its formation can be explained from the intermediate IV obtained from the cyclic anhydride III as shown in the mechanism.

- It is important to note that in the Perkin reaction, the anhydride and the sodium salt should be from the same carboxylic acid; otherwise a mixture of α,β-unsaturated acids would be formed. This is because of the fact that when anhydride of one carboxylic acid and sodium salt of another carboxylic acid are taken then a possible side reaction can produce a second set of reagent leading to the formation of another product.

- If sodium salt and the anhydride of the same acid is used then side reaction, if occurs, produces the same original set of reagents and consequently only one product is obtained.

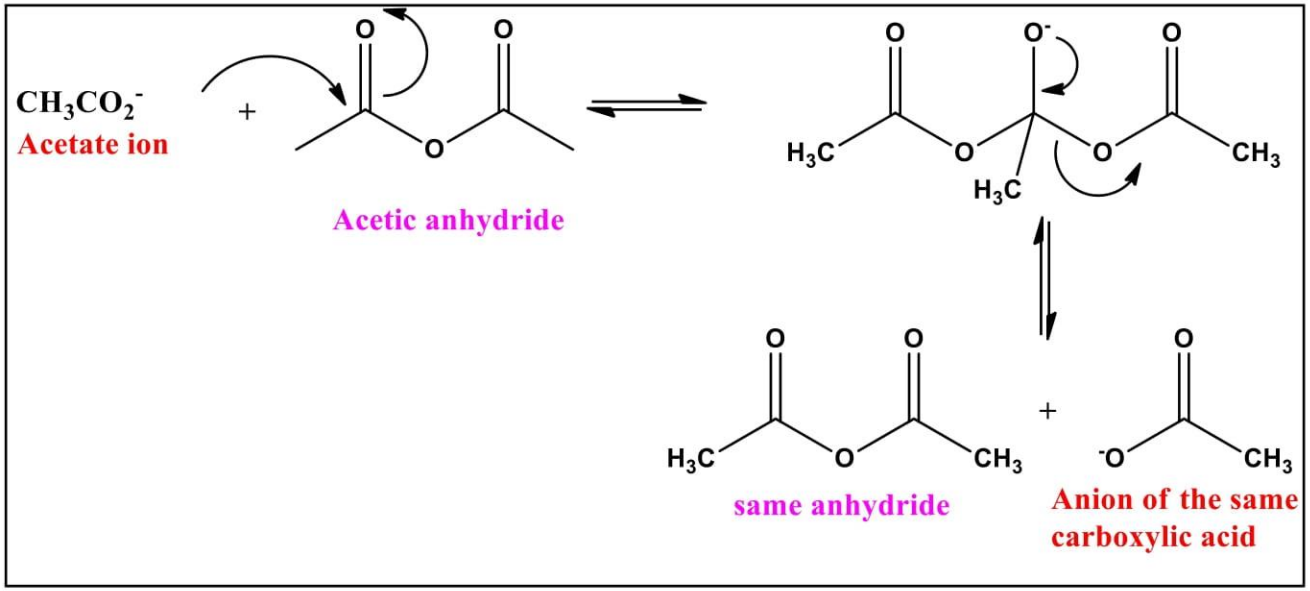
CASE-I

The sodium salt and the anhydride from the different carboxylic acid



CASE-II

The sodium salt and the anhydride from the same carboxylic acid




Thank
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