



GOVERNMENT OF ANDHRA PRADESH
COMMISSIONERATE OF COLLEGIATE EDUCATION



**Named Reactions in Carbonyl
Compounds-
Perkin, Benzoin reactions**
Subject: Chemistry



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Learning Outcomes

At the end of the presentation, Student will be able to,

1. Write Perkin and Benzoin Condensation reactions.
2. Describe the mechanism of Perkin Reaction.
3. Describe the importance of role of CN^- in Benzoin Condensation.
5. Describe the mechanism of Benzoin Condensation.

Named reactions in carbonyl compounds-

Perkin and Benzoin reactions

1. Introduction
2. Perkin reaction
 - 2.1 Reactivity of anhydride
 - 2.2 Mechanism of Perkin reaction
3. Benzoin reaction
 - 3.1 Role of Cyanide ion in Benzoin reaction
 - 3.2 Mechanism of Benzoin reaction

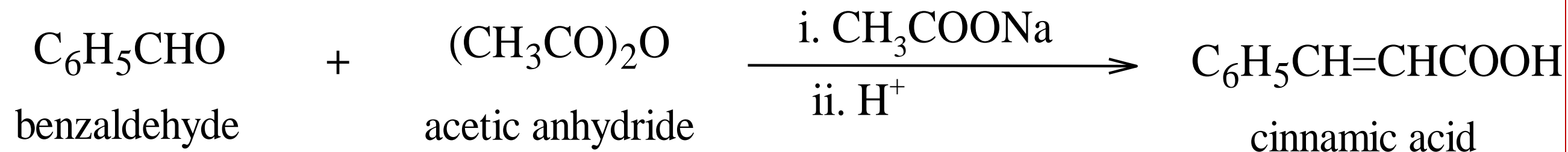
1. Introduction

- ❖ Perkin reaction is the modification of aldol condensation.
- ❖ If aromatic carbonyl compound undergoes condensation reaction with acid anhydride in presence of a weak base, it is called *Perkin condensation reaction*.
- ❖ In *Benzoin Condensation reaction*, aromatic aldehydes (with no α -hydrogens) condense in the presence of cyanide ion to form α -hydroxy ketone, commonly known as Benzoin.

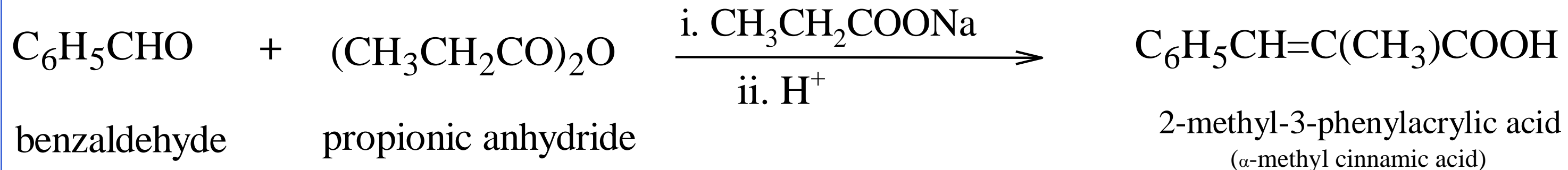
2. Perkin Reaction

2. Perkin Reaction

- ❖ Developed by William Henry Perkin.
- ❖ **Aromatic aldehydes** participate in Perkin reaction.
- ❖ Condensation of an aromatic aldehyde with an aliphatic acid anhydride in the presence of a weak base (usually sodium or potassium salt of the same acid), to form α, β - unsaturated aromatic acids.



2. Perkin Reaction



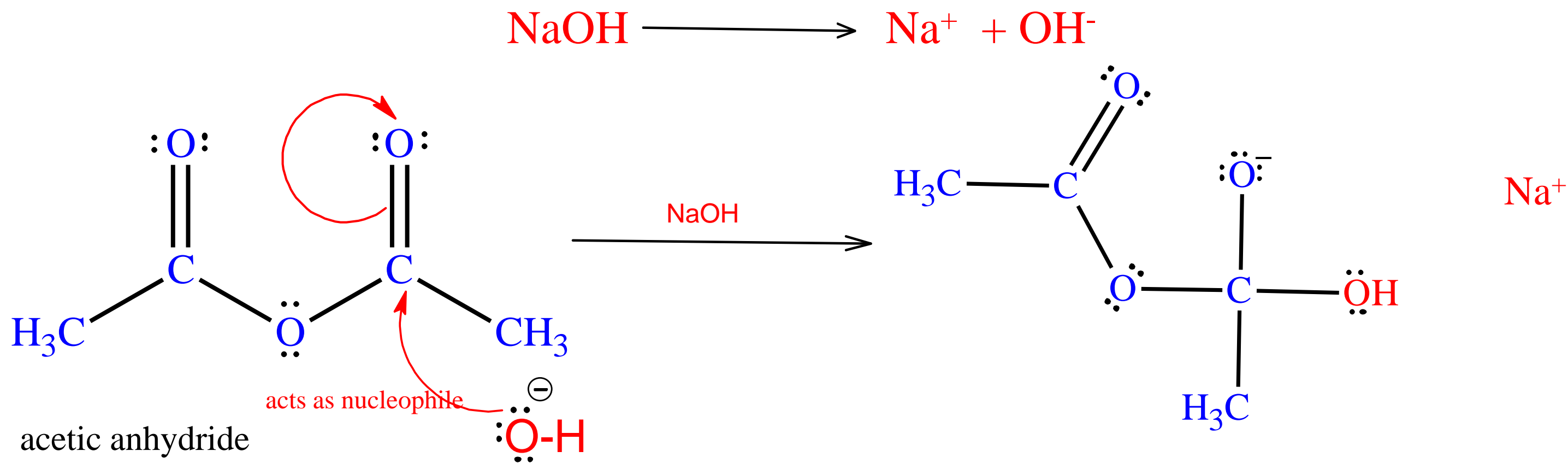
- ❖ The alkali salt of the carboxylic acid (acts as base) abstracts the proton from anhydride to generate α - carbanion.
- ❖ Hence, it is the α - carbon atom of the anhydride that reacts with the aromatic aldehyde group.

2.1. Reactivity of Anhydride

- ❖ In the aldol condensation, NaOH or KOH is used as the base to generate the enolate ion.
- ❖ But these bases cannot be used to generate enolate ions from acid anhydrides.
- ❖ For acid anhydrides, the order of reactivity for enolization is same as the order of reactivity towards nucleophilic attack.

2.1. Reactivity of Anhydride

If the strong bases like NaOH are used, they hydrolyse the anhydride giving rise to salt of carboxylic acid (**Scheme-1**)

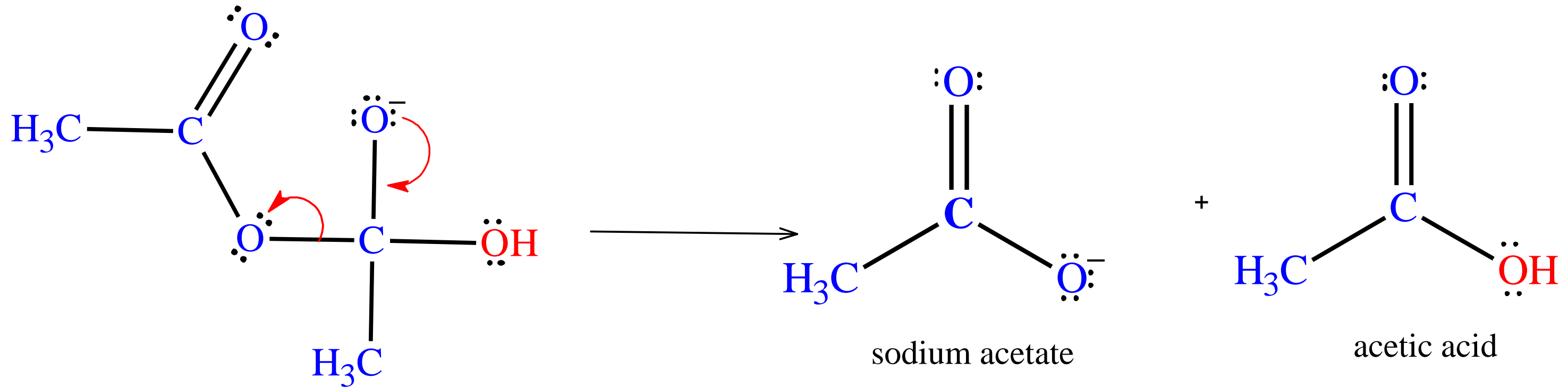


(Scheme-1)

2.1. Reactivity of Anhydride

Na⁺

(Scheme-1)

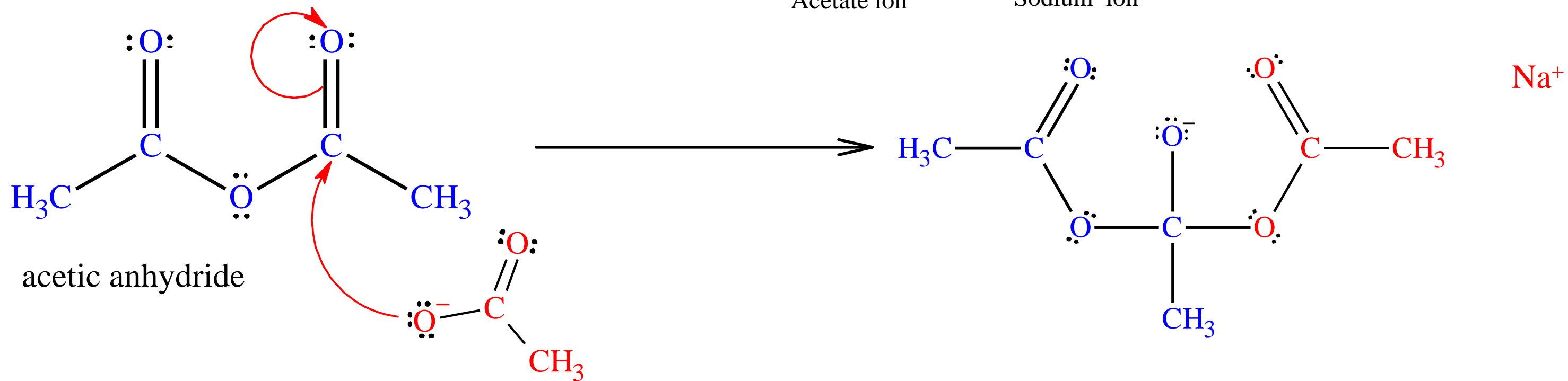
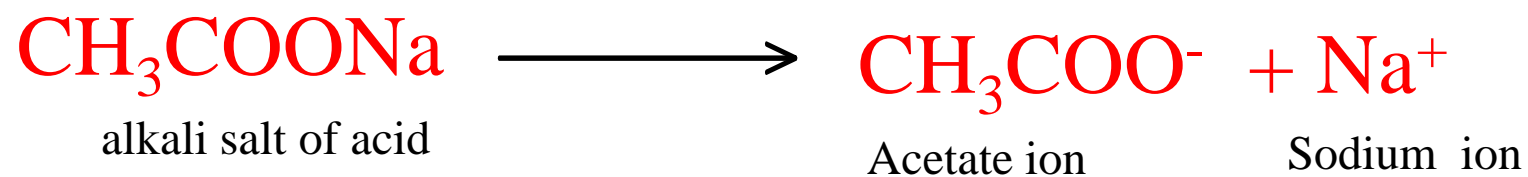


Use of strong bases like NaOH to generate carbanions from acid anhydrides is restricted.

Since no Perkin reaction possible.

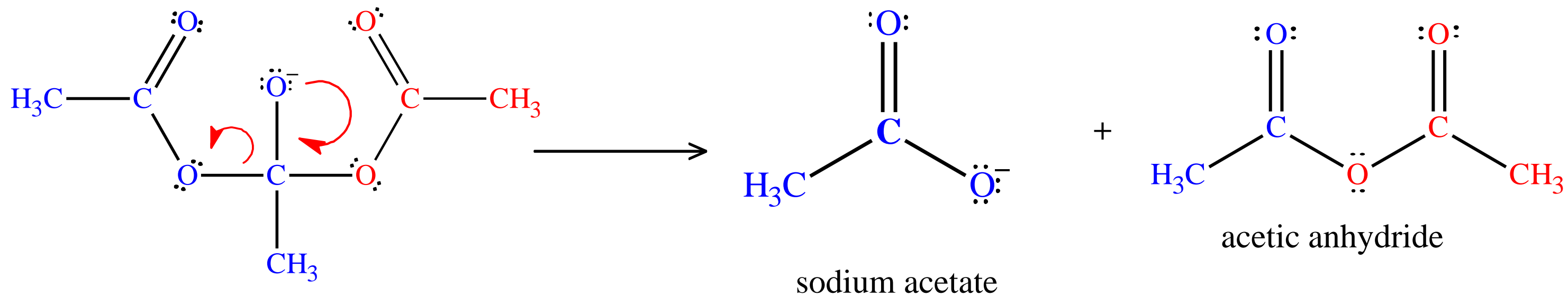
2.1. Reactivity of Anhydride

If mild base like alkali salt of acid (ex: sodium acetate (CH_3COONa)) is used they does not show any impact on the anhydride functional group.



2.1. Reactivity of Anhydride

Na⁺

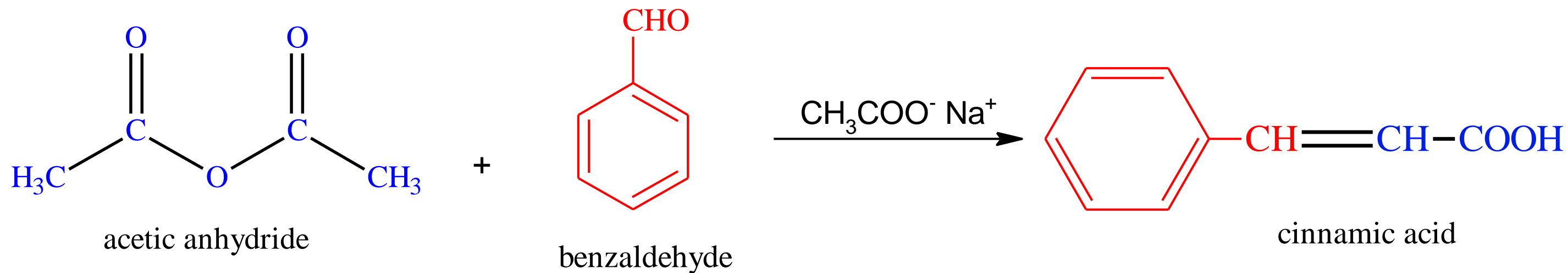


When **Sodium acetate attacks as a nucleophile** on acid anhydride, there is **no destruction on the anhydride functional group**.

Thus, use of alkali salt of same acid as that of anhydride is **suitable to generate the carbanion**.

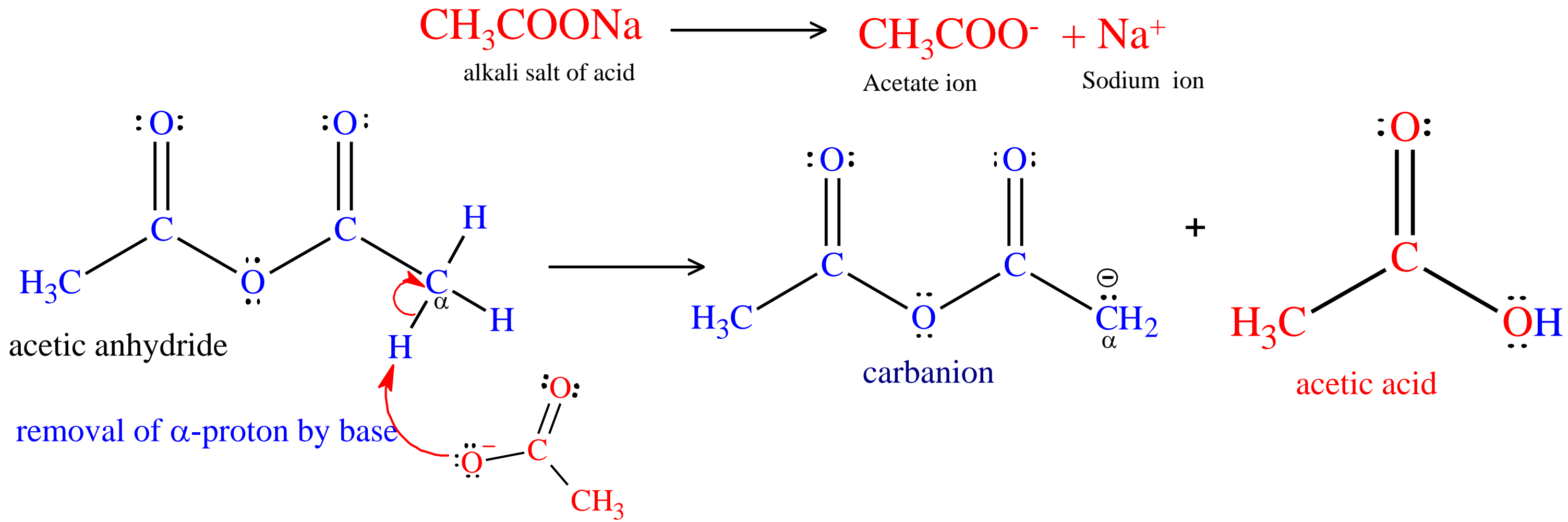
2.2. Mechanism of Perkin Reaction

Example: Reaction of acetic anhydride with benzaldehyde in the presence of sodium acetate to produce cinnamic acid.

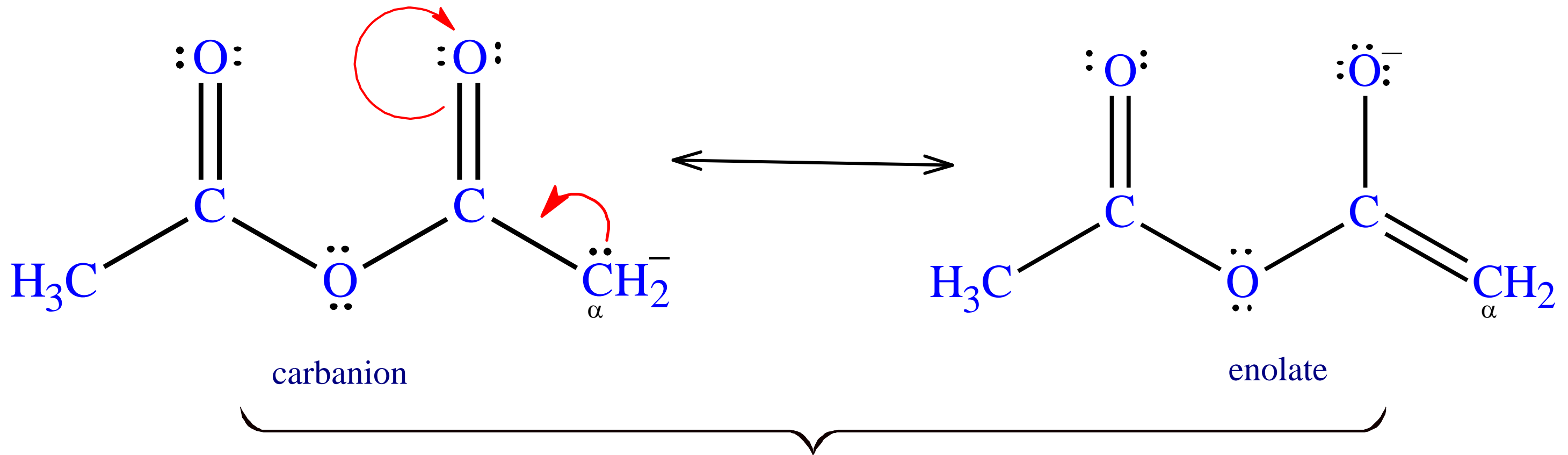


2.2. Mechanism of Perkin Reaction

Step 1: Sodium acetate acts as a base and acetate ion abstracts the alpha hydrogen of the acetic anhydride molecule giving rise to carbanion which is resonance stabilised with its enolate ion.



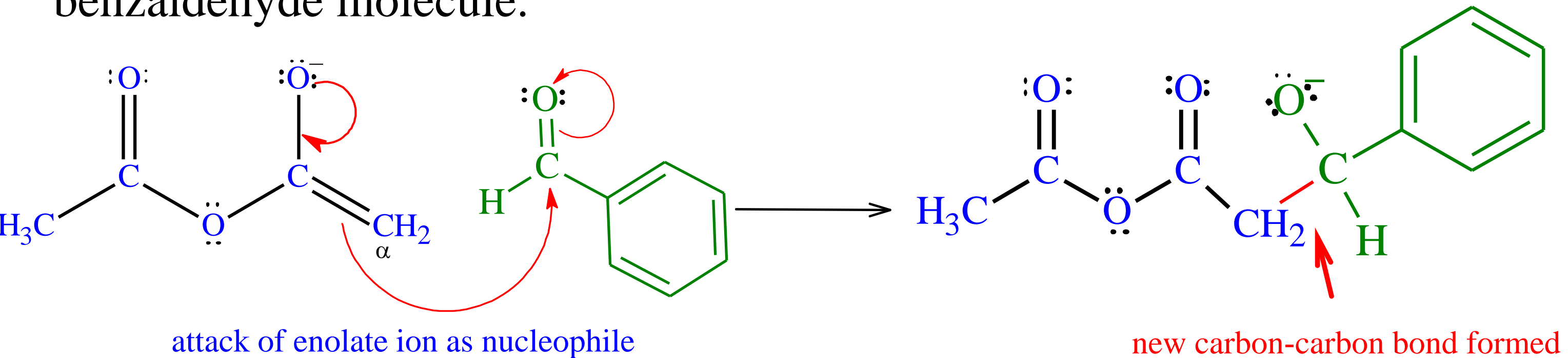
2.2. Mechanism of Perkin Reaction



The carbanion formed in step-1 is resonance stabilized with an enolate ion

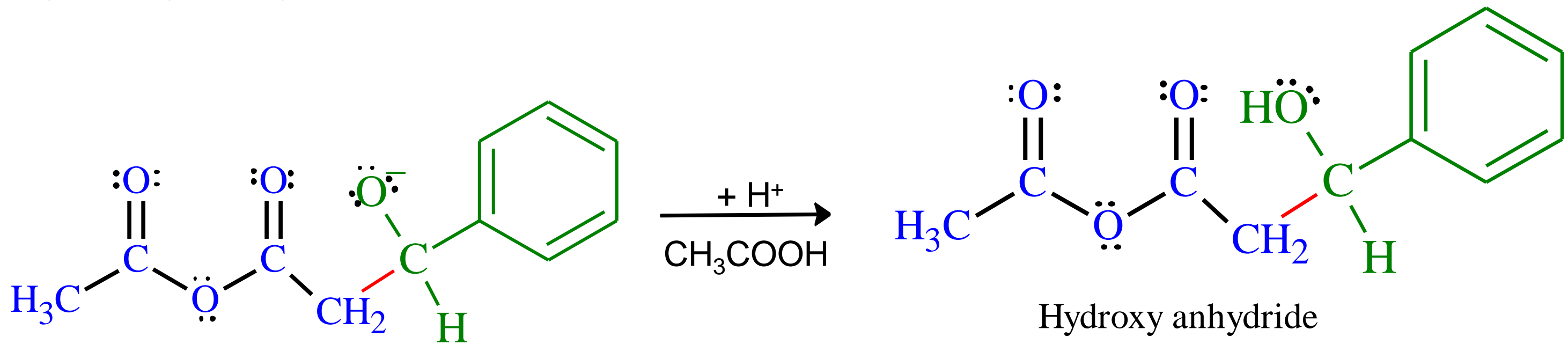
2.2. Mechanism of Perkin Reaction

Step 2: The enolate ion attacks the electrophilic carbonyl carbon of the benzaldehyde molecule.



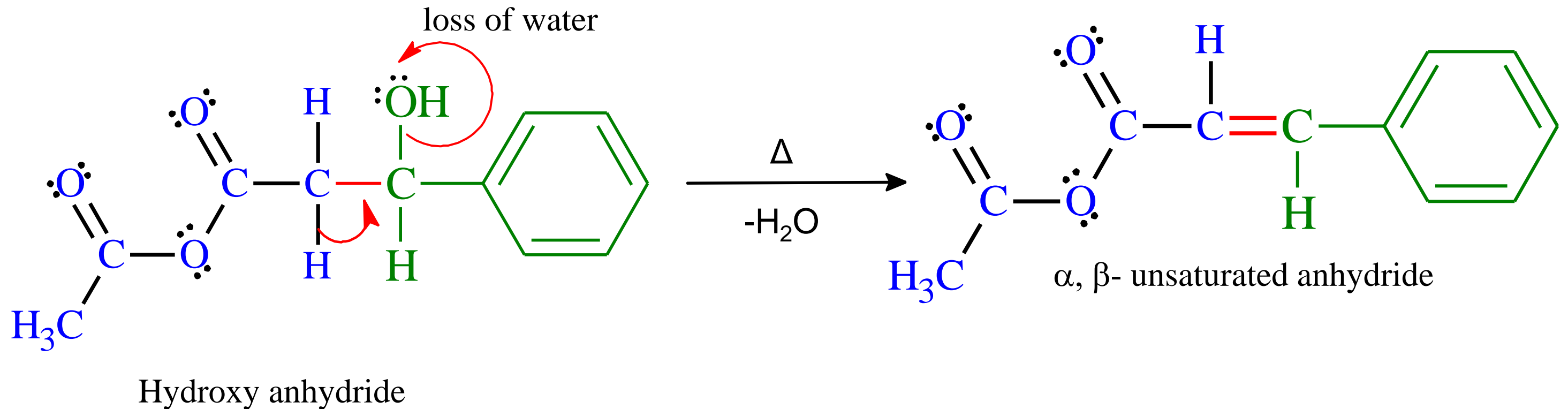
2.2. Mechanism of Perkin Reaction

Step 3: The intermediate obtained in step 2 abstracts a proton and forms a hydroxy anhydride molecule.



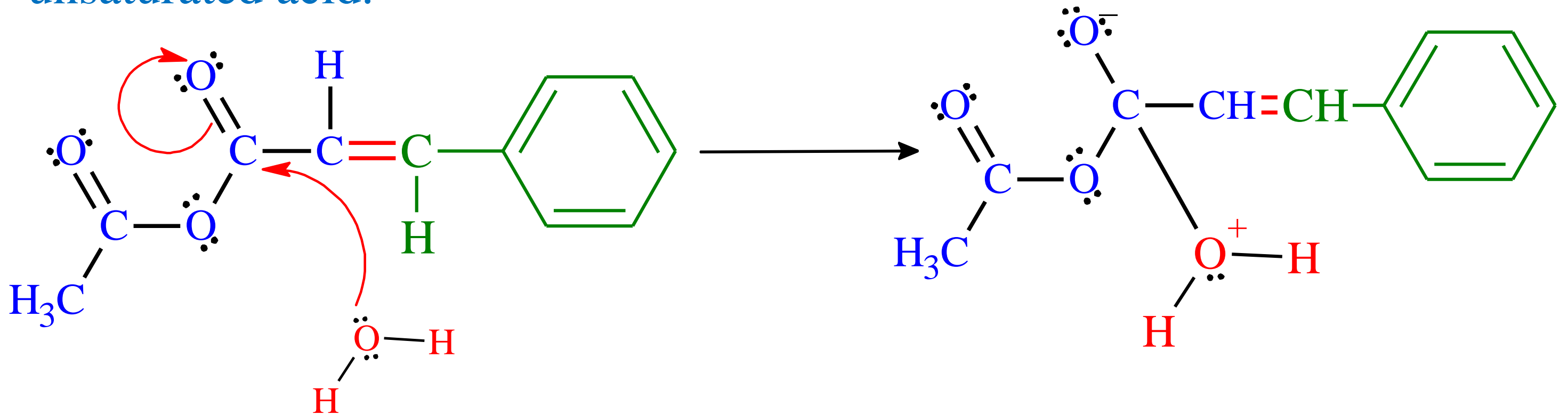
2.2. Mechanism of Perkin Reaction

Step 4: Hydroxy anhydride undergoes **dehydration** (loss of water) on heating to form α, β -unsaturated anhydride.



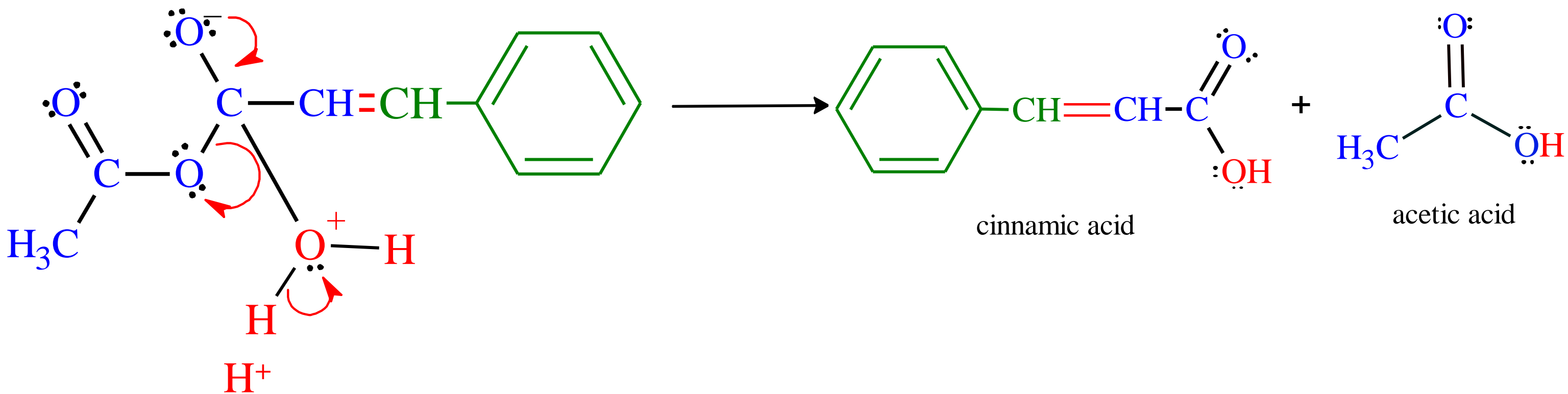
2.2. Mechanism of Perkin Reaction

Step 5: α , β -unsaturated anhydride undergoes hydrolysis to form α , β -unsaturated acid.



2.2. Mechanism of Perkin Reaction

Step 5: α , β -unsaturated anhydride undergoes Hydrolysis to form α , β -unsaturated acid.

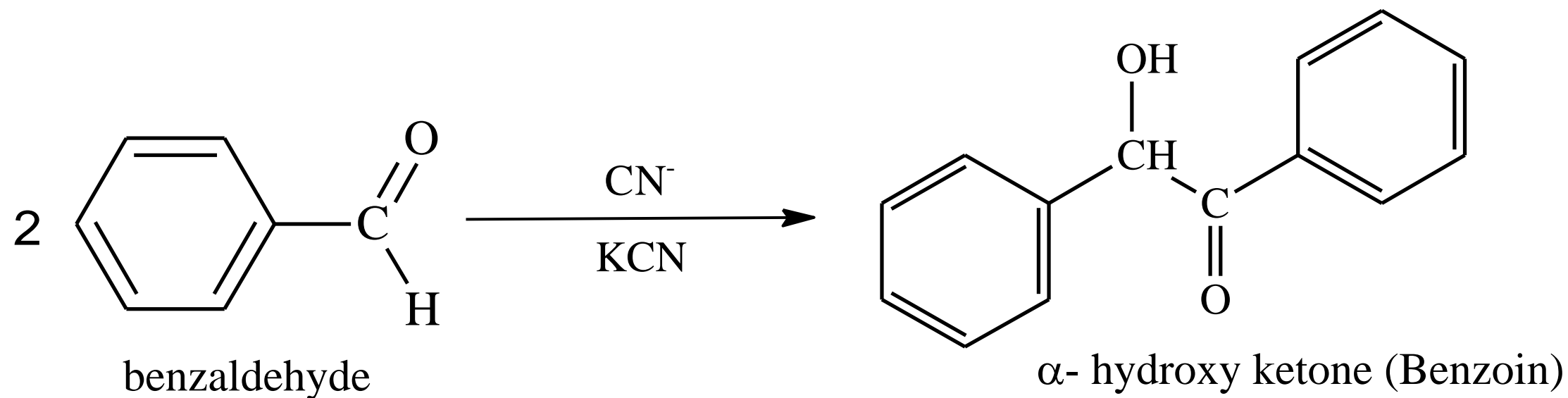


3. Benzoin Condensation Reaction

3. Benzoin Condensation Reaction

- ❖ The benzoin condensation was first reported in 1832 by Justus von Liebig and Friedrich Wohler.
- ❖ The catalytic version of the reaction involving cyanide ion was developed by Nikolay Zinin.
- ❖ It is a reaction between two aromatic aldehydes, particularly benzaldehyde in the presence of cyanide ion to result an α - hydroxy ketone commonly known as benzoin.

3. Benzoin Condensation Reaction



➤ In this reaction, the two aldehydes serve different purposes; **one aldehyde donates** a proton and the **other aldehyde accepts** a proton.

3.1. Role of Cyanide ion in Benzoin Reaction

Cyanide ion (CN^- ion) catalyses the reaction because:

- (i) It is good nucleophile
- (ii) It is good leaving group
- (iii) It increases the acidity of the C-H bond and stabilizes the carbanion that results from the loss of proton from Carbon

3.2. Mechanism of Benzoin Reaction

Step-1: Formation of a Cyanohydrin

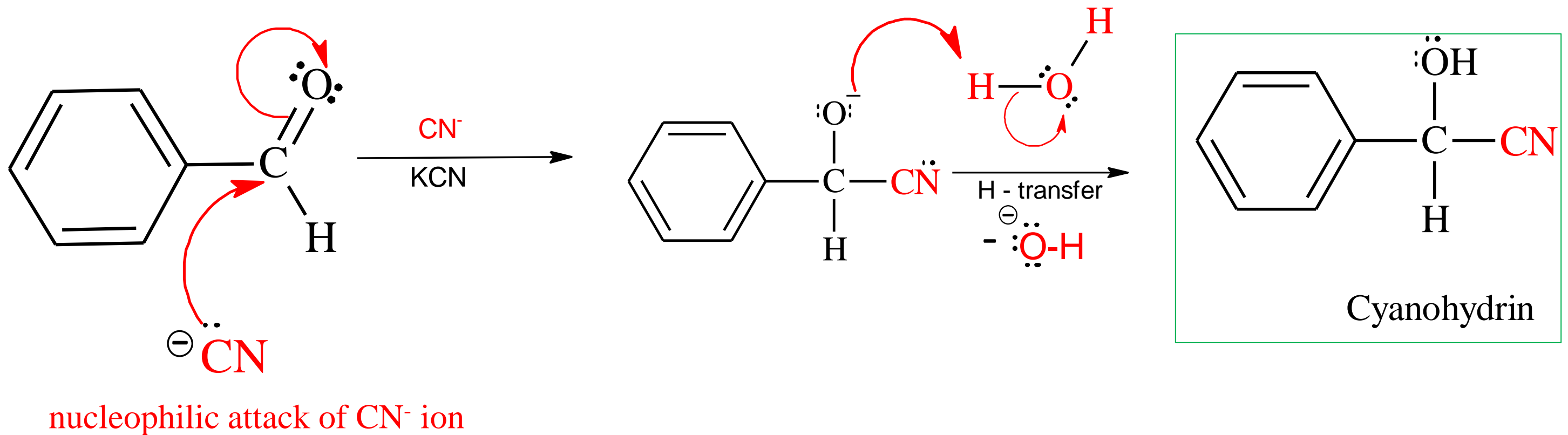
Step-2: Formation of a nucleophile from cyanohydrin

Step-3: Formation of a new C-C bond via the nucleophilic attack

Step-4: Formation of benzoin and regeneration of catalyst

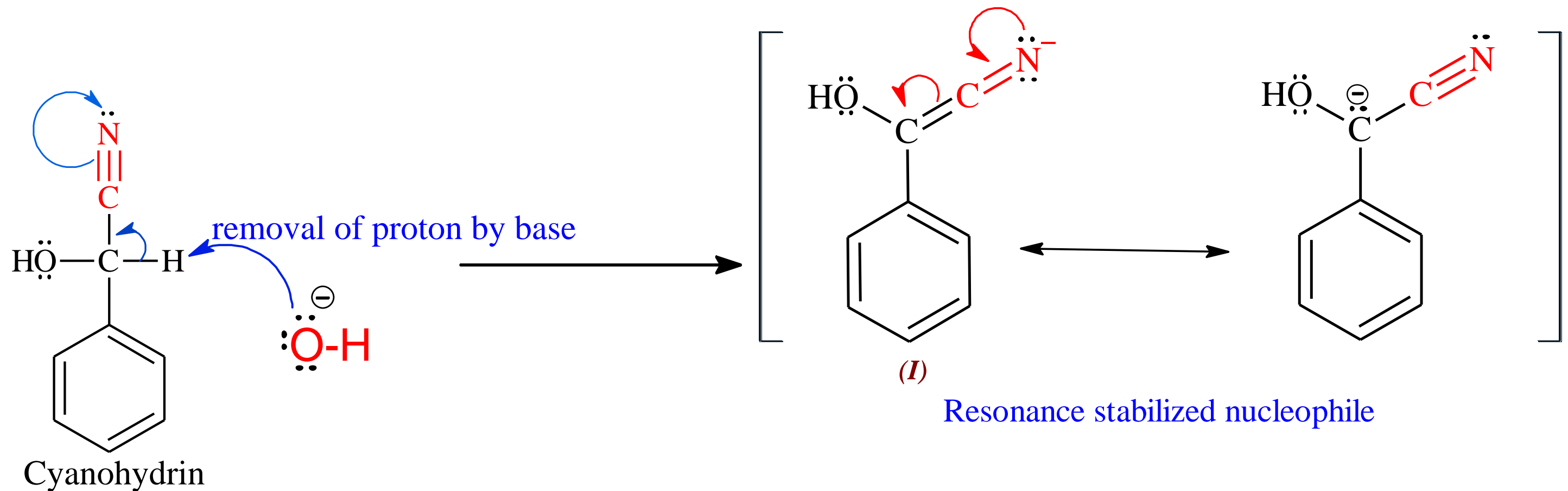
3.2. Mechanism of Benzoin Reaction

Step-1: Formation of a Cyanohydrin: Nucleophilic attack of cyanide ion on the carbonyl carbon (electrophile) of benzaldehyde to form a cyanohydrin.



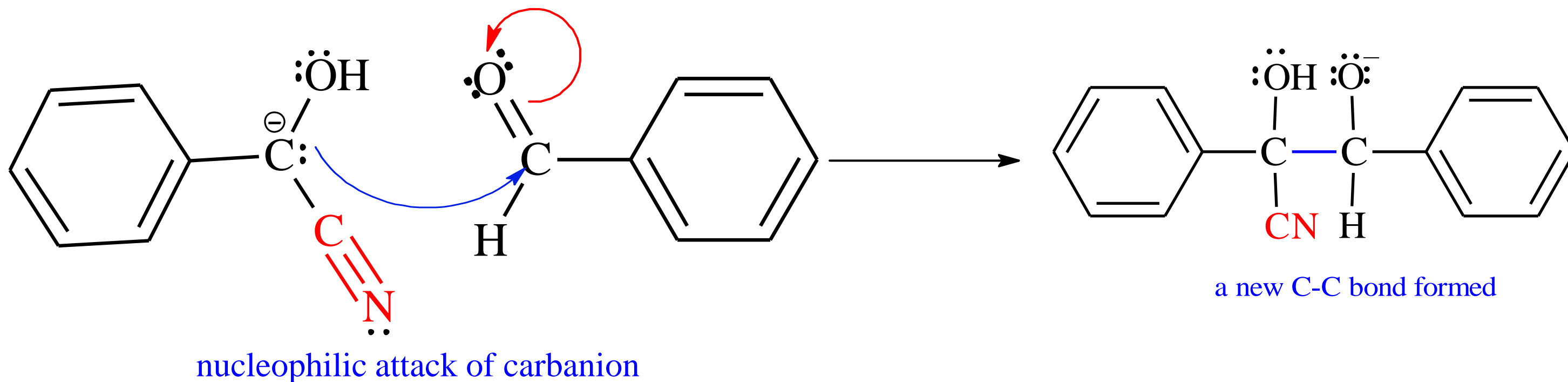
3.2. Mechanism of Benzoin Reaction

Step-2: Formation of a nucleophile from cyanohydrin: The base (OH^- ion) formed in the first step deprotonates the cyanohydrin and form a resonance stabilized nucleophilic species(I).



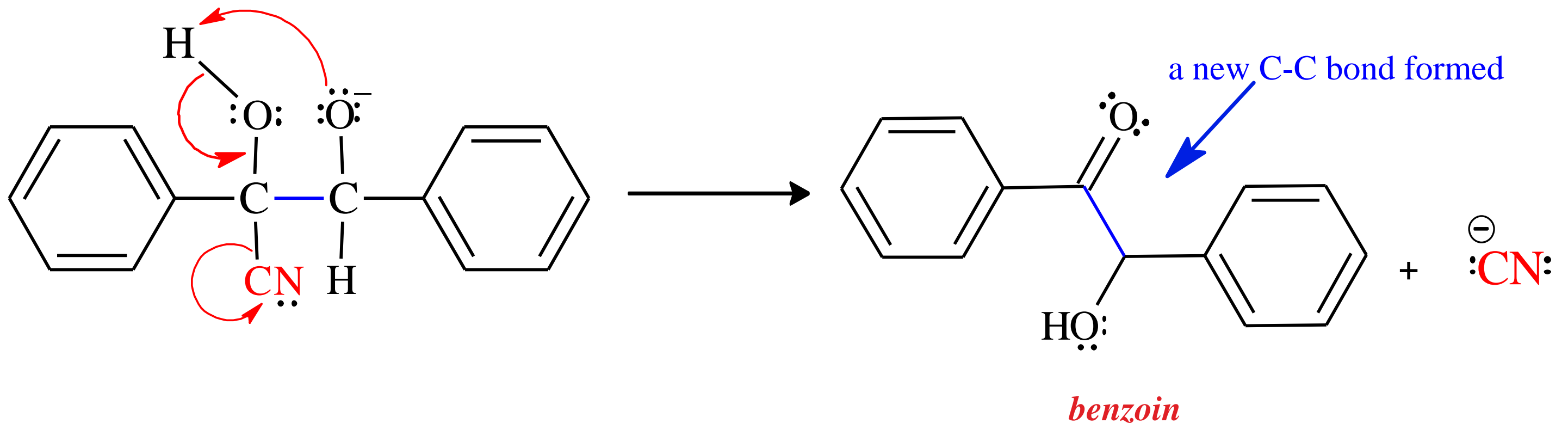
3.2. Mechanism of Benzoin Reaction

Step-3: Formation of a new c-c bond via the nucleophilic attack: The attack of nucleophilic species (I) formed in step 2 on the carbonyl carbon of another benzaldehyde molecule leads to the formation of a new carbon-carbon bond.



3.2. Mechanism of Benzoin Reaction

Step-4: Formation of benzoin and regeneration of catalyst: Transfer of Proton and elimination of the cyanide ion results in benzoin as the product.



4. Summary

1. Perkin condensation is modification to aldol condensation.
2. In Perkin reaction α , β -unsaturated acids are formed due to reaction of aldehydes (having no α -hydrogens) with acid anhydrides in presence of base.
3. Benzoin condensation involves dimerization of two aromatic aldehydes in the presence of CN^- to form benzoin.
4. Benzoin condensation is catalyzed by cyanide ion, because it acts as a good nucleophile as well as good leaving group. It also increases the acidity of the C-H bond.

THANK YOU

References:

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