



**GOVERNMENT OF ANDHRA PRADESH**  
**COMMISSIONERATE OF COLLEGIATE EDUCATION**



# Named reactions in Carbonyl Compounds- Perkin and Benzoin Condensation reactions

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## 1. Learning Outcomes

After studying this topic, student will be able to

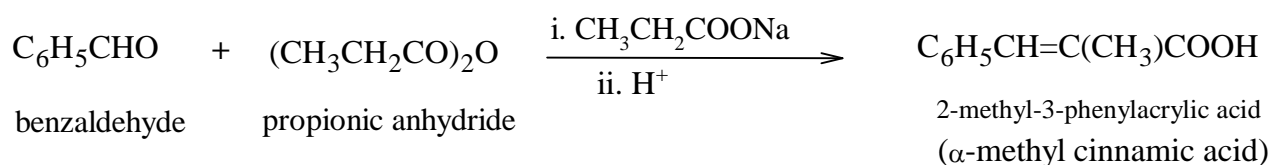
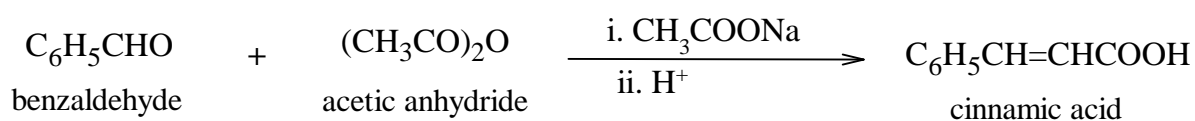
1. Write Perkin and Benzoin Condensation reactions.
2. Describe the mechanism of Perkin Reaction.
3. Describe the similarities between Aldol Condensation and Perkin reaction.
4. Describe the importance of role of  $\text{CN}^-$  in Benzoin Condensation.
5. Describe the mechanism of Benzoin Condensation.

## 2. Introduction

Perkin reaction is the modification of aldol condensation. In aldol condensation, two carbonyl compounds are condensed. If aromatic carbonyl compound condenses with acid anhydride, it is called Perkin condensation reaction. Another significant reaction for C-C bond formation is Benzoin condensation, in which aromatic aldehydes (with no  $\alpha$ -hydrogens) in the presence of cyanide ion condensed to form benzoin. As a result of this reaction, number of carbon atoms are present in the final product become doubled as compared to the starting molecule.

## 3. Perkin Reaction

- Perkin reaction was developed by William Henry Perkin and it is used to make  $\alpha$ ,  $\beta$ -unsaturated aromatic acids, commonly known as cinnamic acids.
- 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  $\alpha$ ,  $\beta$  - unsaturated aromatic acids.

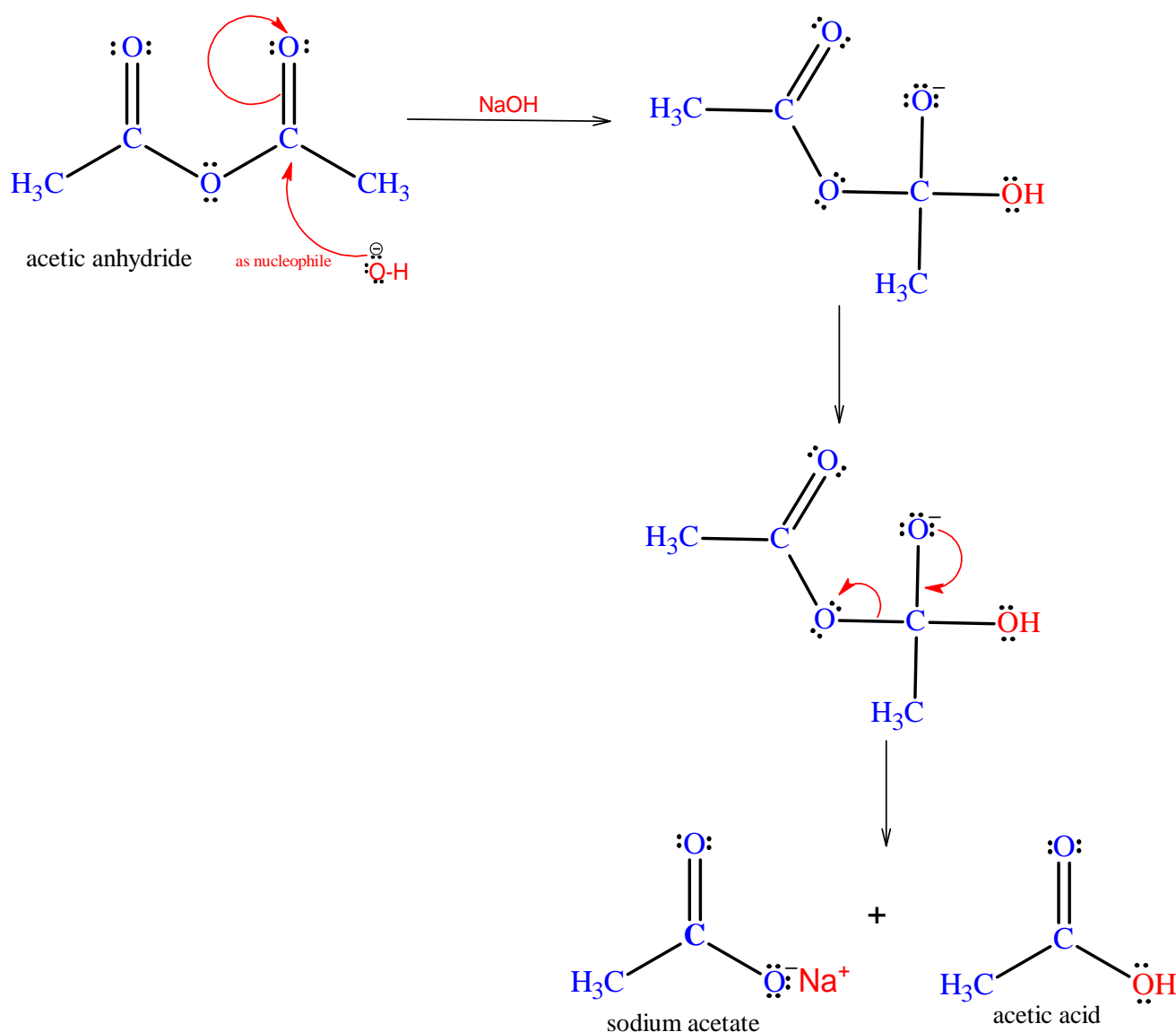


- The alkali salt of the carboxylic acid (acts as base) abstracts the proton from anhydride to generate  $\alpha$ -carbanion.
- Hence, it is the  $\alpha$  - carbon atom of the anhydride that reacts with the aromatic aldehyde group.

### 3.1 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. If mild base like alkali salt of acid (ex: sodium acetate ( $\text{CH}_3\text{COONa}$ )) is used they does not show any impact on the anhydride functional group (**see in scheme-3**). But if the strong bases like NaOH are used, they hydrolyse the anhydride giving rise to salt of carboxylic acid (**scheme-1**) and thus it is not possible to generate the enolate ion from it, thereby no Perkin reaction possible.

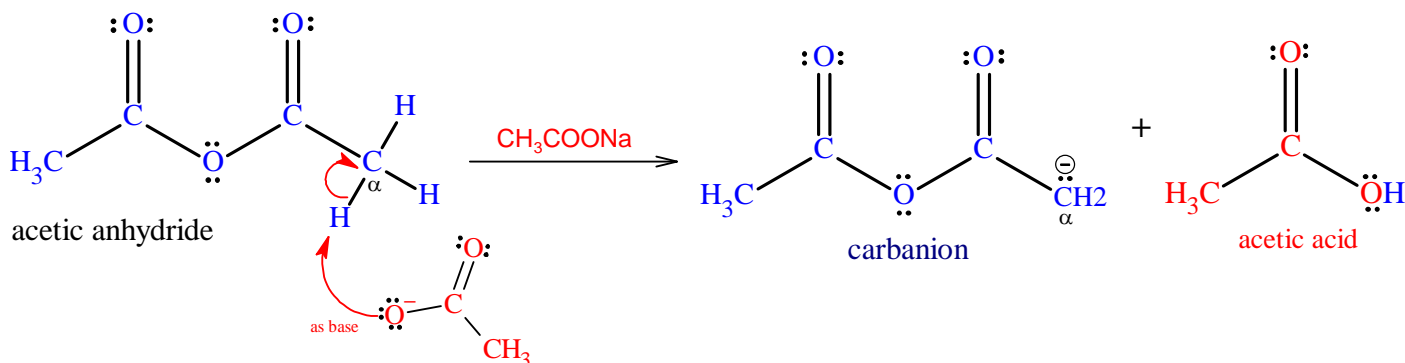
**Scheme-1:** Sodium Hydroxide (NaOH) as nucleophile.



Hence use of strong bases like NaOH to generate enolate ions from acid anhydrides is restricted.

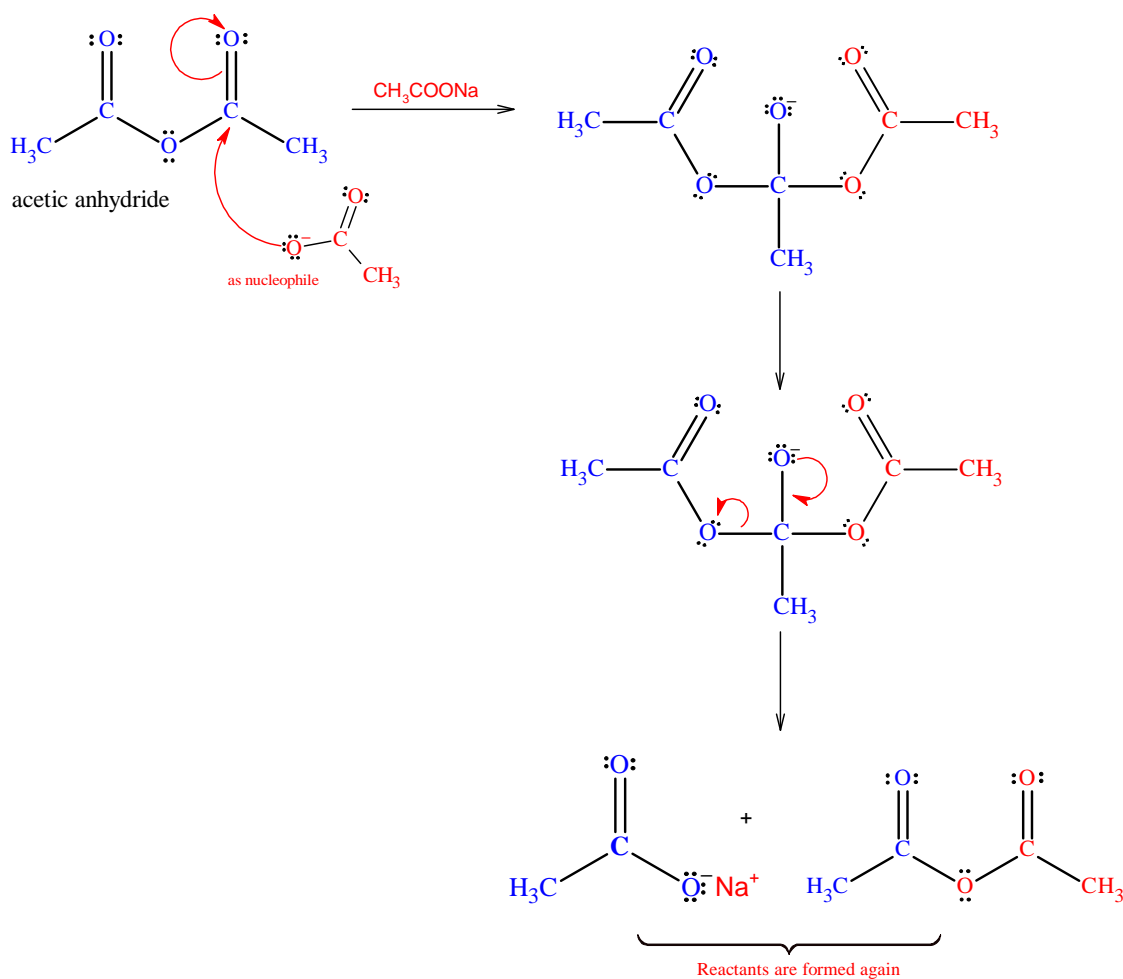
**Scheme-2:** Sodium salt of acid (ex: Sodium acetate ( $\text{CH}_3\text{COONa}$ )) as base.

When it attacks as a base on acid anhydride, it abstracts acidic hydrogen at alpha position. Note that the alpha hydrogen atoms are acidic due to electron withdrawing nature of anhydride group.



**Scheme-3:** Sodium salt of acid (ex: Sodium acetate ( $\text{CH}_3\text{COONa}$ )) as nucleophile.

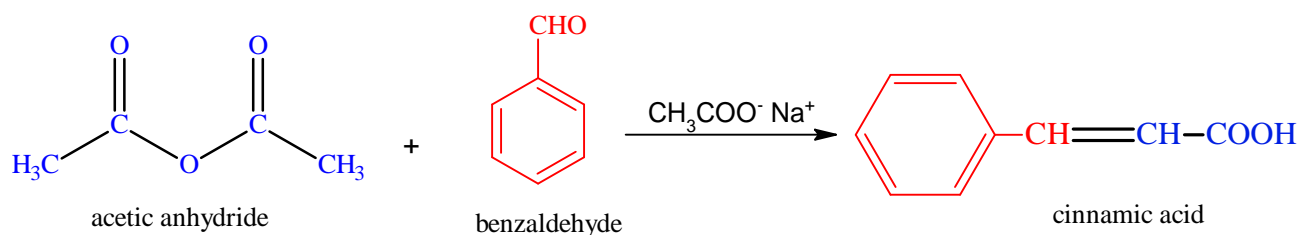
When it attacks as a nucleophile on electrophilic carbon of the acid anhydride, there is no destruction on the anhydride functional group.



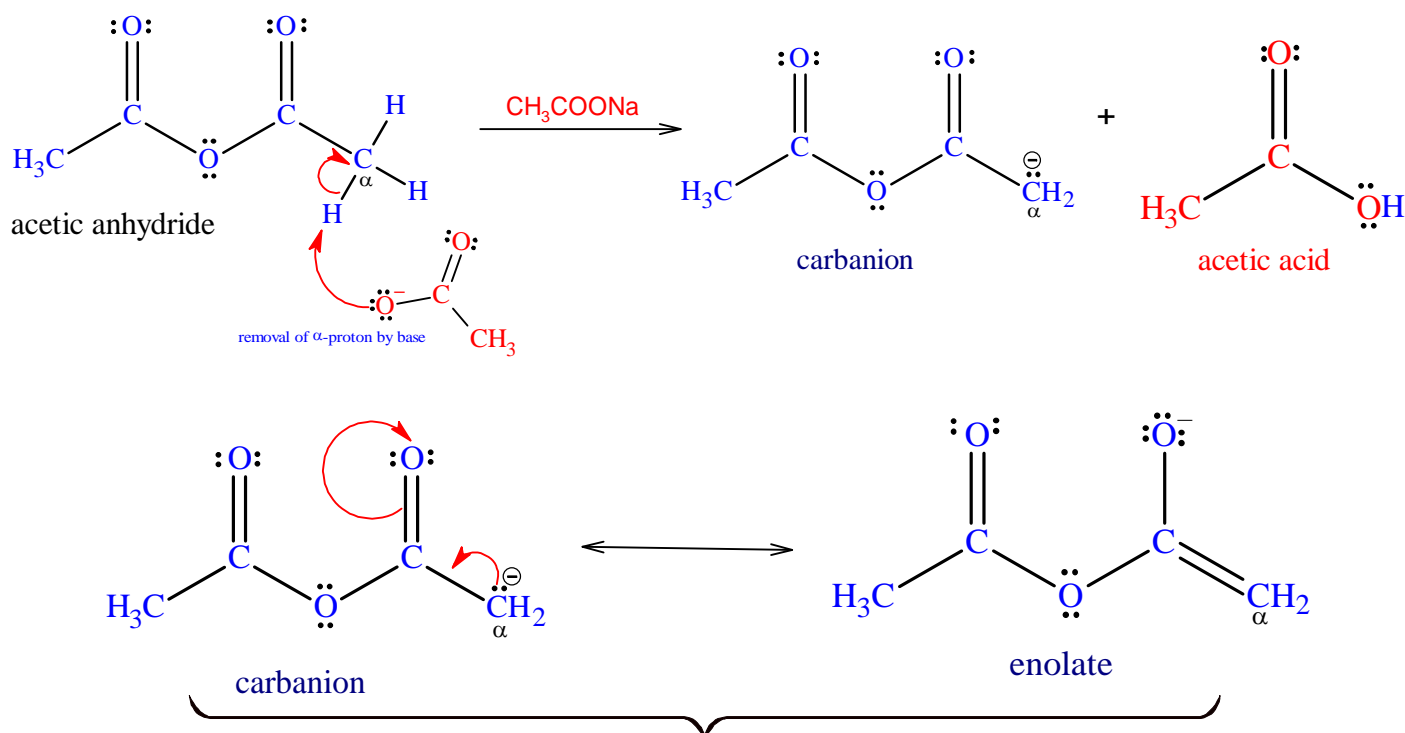
Thus, using alkali salt of same acid as that of anhydride is suitable to generate the enolate ion with no harm on the anhydride.

## 3.2 Mechanism of Perkin Reaction:

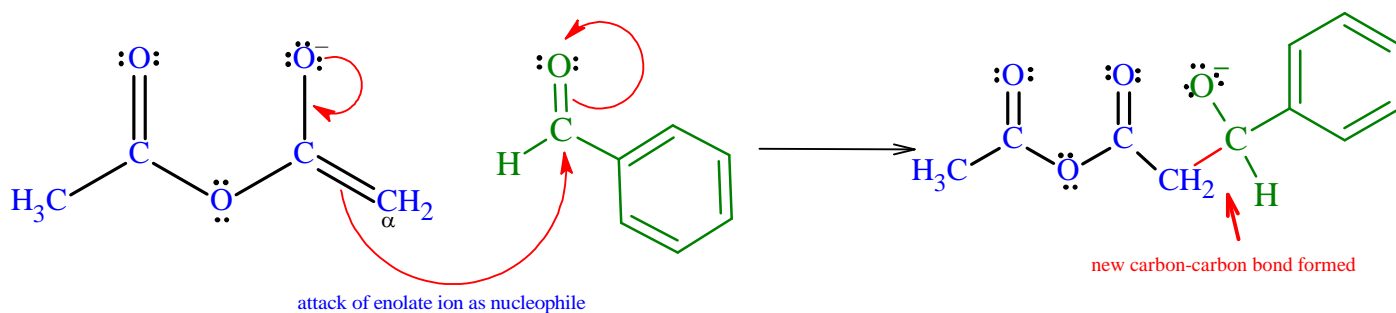
Let us consider the reaction of acetic anhydride with benzaldehyde in the presence of sodium acetate to produce cinnamic acid.



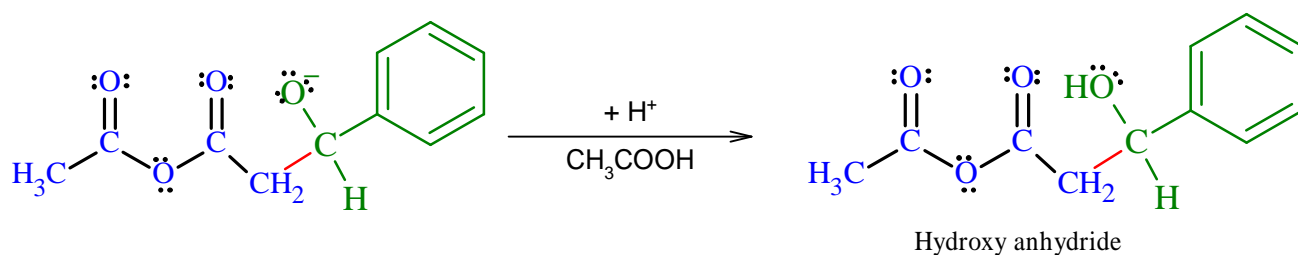
**Step 1:** Sodium acetate acts as a base and acetate ion abstracts the alpha hydrogen of the acetic anhydride molecule giving rise to carbanion which is resonance stabilised with its enolate ion.



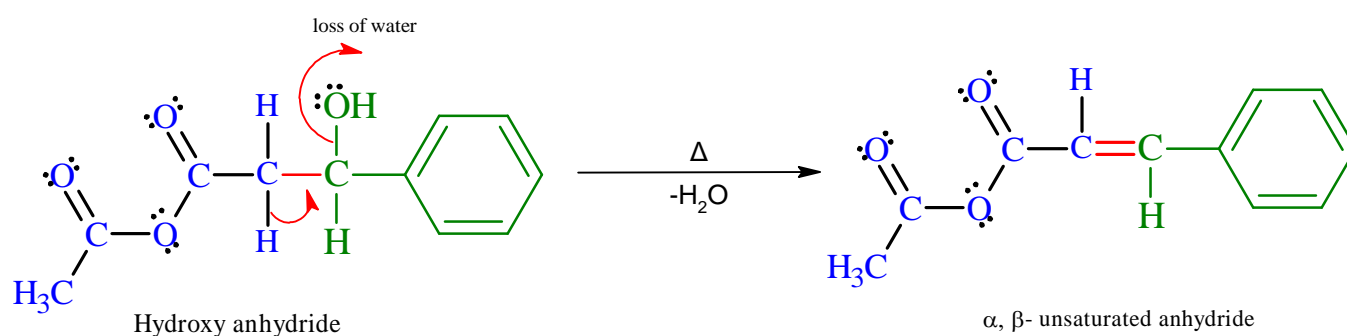
**Step 2:** The enolate ion attacks the electrophilic carbonyl carbon of the benzaldehyde molecule. This results in the formation of a new carbon-carbon bond between the two molecules.



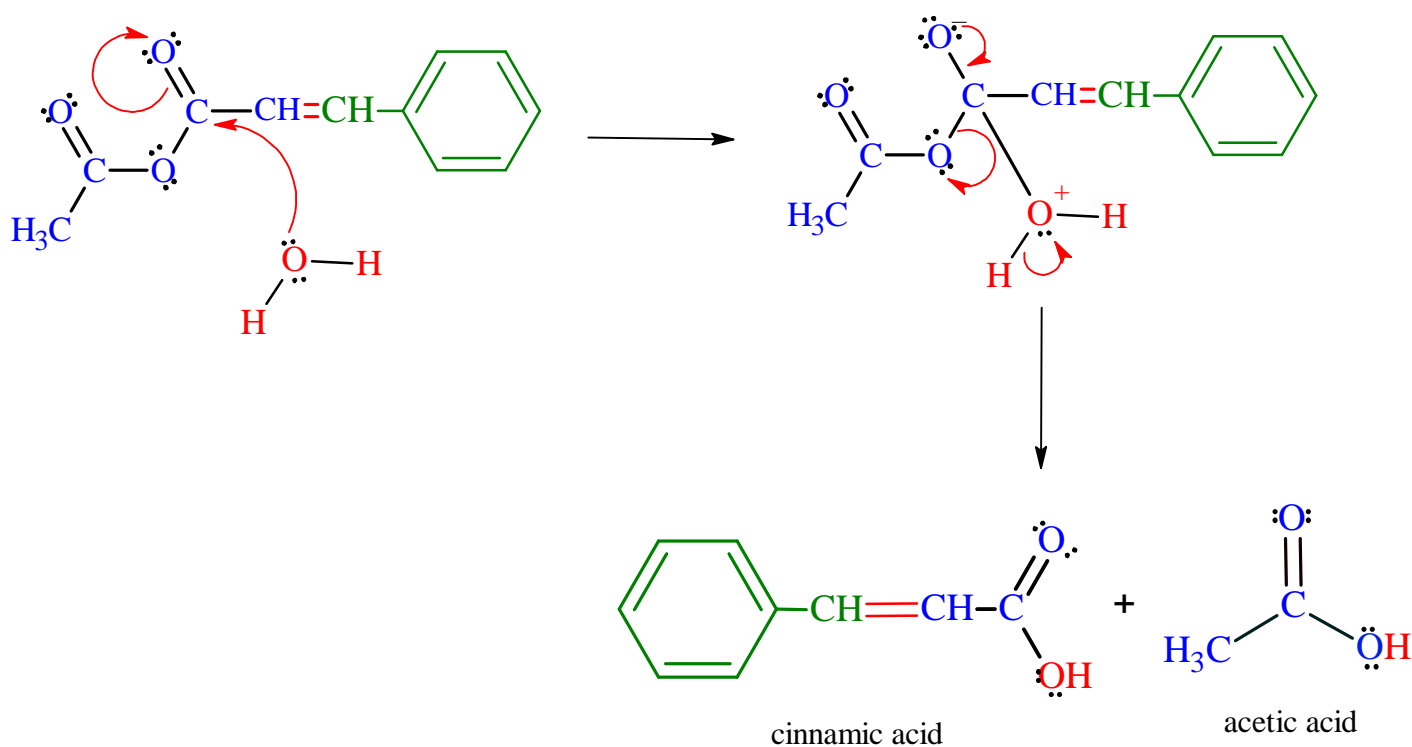
**Step 3:** The intermediate obtained in step 2 abstracts a proton and forms a hydroxy anhydride molecule



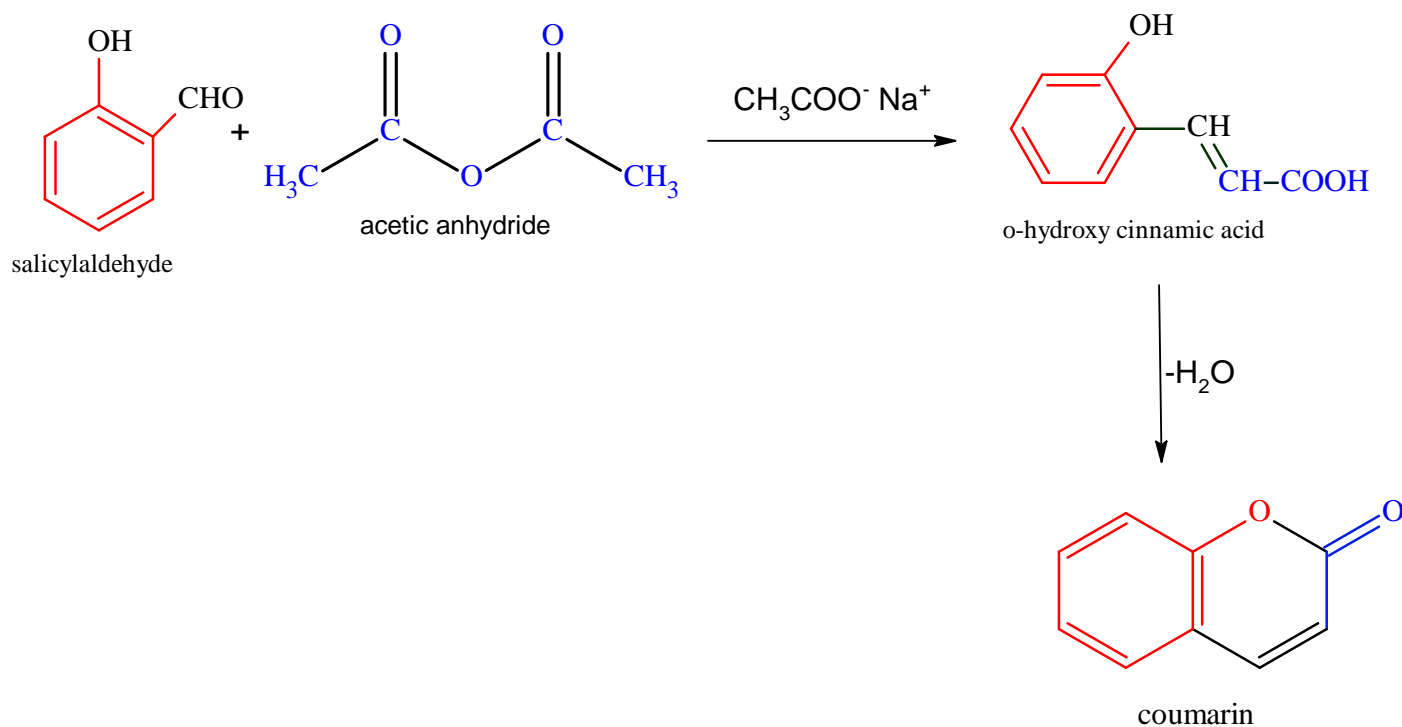
**Step 4:** Hydroxy anhydride undergoes dehydration (loss of water) on heating to form  $\alpha$ ,  $\beta$ - unsaturated anhydride.



**Step 5:**  $\alpha$ ,  $\beta$ - unsaturated anhydride undergoes Hydrolysis to form  $\alpha$ ,  $\beta$ - unsaturated acid.



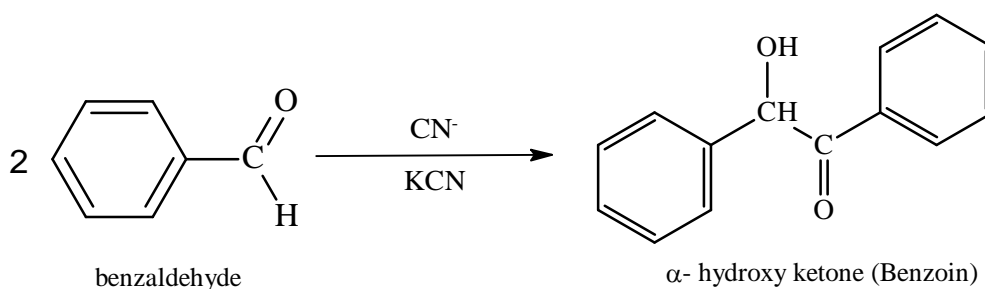
In Perkin reaction, instead of Benzaldehyde, if salicylaldehyde is taken **coumarins** are formed as the final product.



#### 4. Benzoin condensation reaction

The benzoin condensation was first reported in 1832 by *Justus von Liebig* and *Friedrich Wohler* during their research on bitter almond oil. The catalytic version of the reaction involving cyanide ion was developed by *Nikolay Zinin* in the late 1830s.

The benzoin condensation is a reaction between two aromatic aldehydes, particularly benzaldehyde in the presence of cyanide ion to result an  $\alpha$ -hydroxy ketone (aromatic acyloin), commonly known as **benzoin**.



When a solution of benzaldehyde dissolved in alcohol is refluxed with sodium cyanide or potassium cyanide, the two molecules of benzaldehyde dimerizes to give benzoin in high yields. In this reaction, the two aldehydes serve different purposes; one aldehyde donates a proton and the other aldehyde accepts a proton.

## 4.1. Role of cyanide ion in benzoin reaction

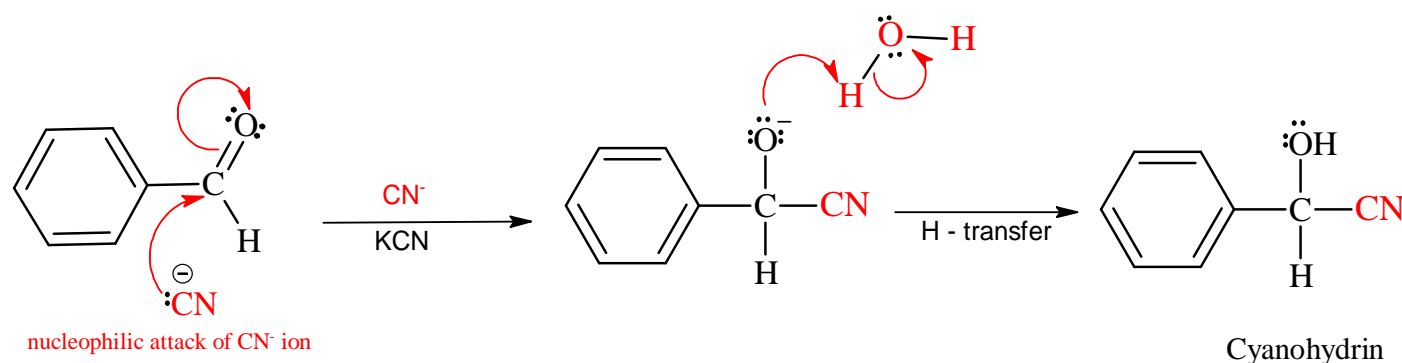
Cyanide ion ( $\text{CN}^-$  ion) catalyses the reaction because:

- (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.

## 4.1. Mechanism of Benzoin condensation reaction

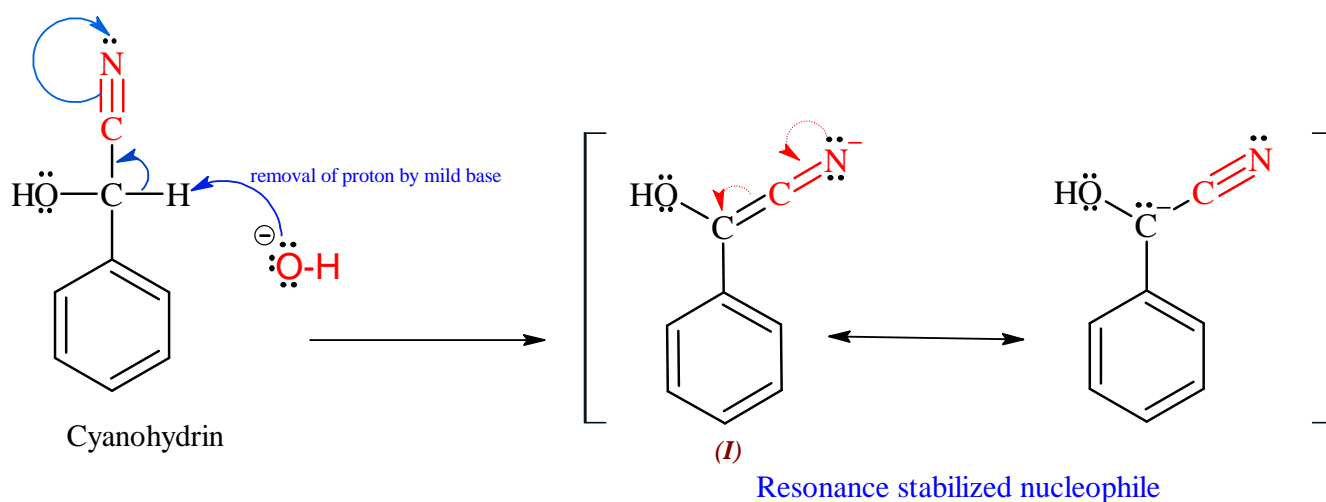
### Step-1: Formation of a Cyanohydrin

The reaction gets started by the attack of cyanide ion (nucleophilic catalyst) on the carbonyl carbon (electrophile) of benzaldehyde to form a cyanohydrin.



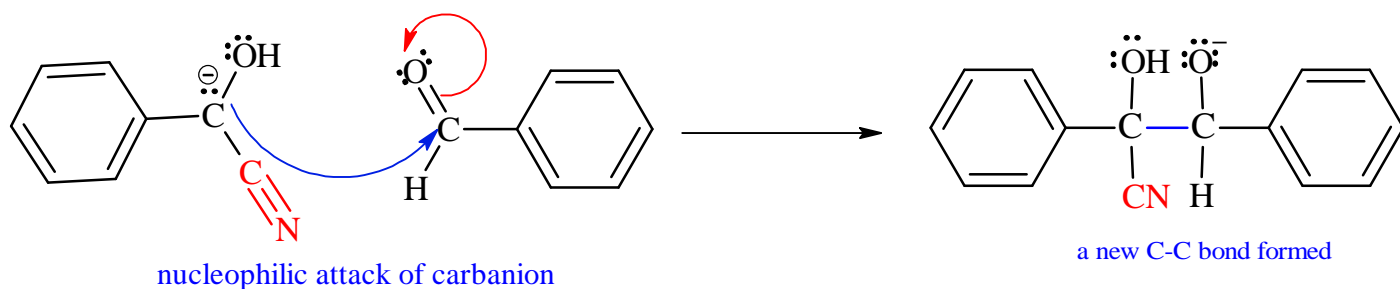
### Step-2: Formation of a nucleophile from cyanohydrin

The base ( $\text{OH}^-$  ion) formed in the first step deprotonates the cyanohydrin and form a resonance stabilized nucleophilic species (**I**). The electron-withdrawing nature of cyanide makes the hydrogen more acidic and thus easily deprotonated. Without cyanide, the proton is not sufficiently acidic and no deprotonation possible in the presence of mild base like  $\text{OH}^-$



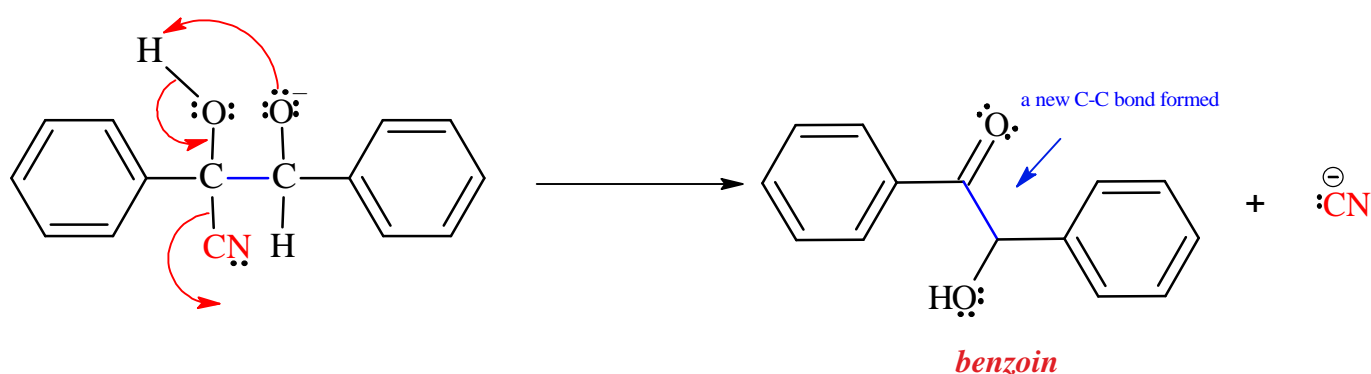
### Step-3: Formation of a new c-c bond via the nucleophilic attack

The attack of nucleophilic species (I) formed in step 2 on the carbonyl carbon (electrophile) of another benzaldehyde molecule leads to the formation of a new carbon-carbon bond.



### Step-4: Formation of benzoin and regeneration of catalyst

Transfer of Proton and elimination of the cyanide ion results in benzoin as the product.



## 5. Summary

1. Perkin condensation is modification to aldol condensation.
2. In Perkin reaction an  $\alpha$ ,  $\beta$ -unsaturated acids are formed due to reaction of aldehydes (having no  $\alpha$ -hydrogens) with acid anhydrides in presence of base.
3. Benzoin condensation involves dimerization of two aromatic aldehydes (with no  $\alpha$ -hydrogens) in the presence of  $\text{CN}^-$  to form  $\alpha$ -hydroxy ketone (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 and stabilizes the carbanion that results from the loss of H-atom

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