



GOVERNMENT OF ANDHRA PRADESH
COMMISSIONERATE OF COLLEGIATE EDUCATION



**Named Reactions in Carbonyl
Compounds-
Aldol, Cannizzaro reactions**
Subject: Chemistry

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Learning Outcomes

At the end of this presentation, student will be able to,

1. Write down the Aldol and Cannizzaro reactions.
2. Describe the mechanism of Aldol condensation in base.
3. Describe the crossed Aldol condensation.
4. Describe the intramolecular Aldol condensation.
5. Describe the mechanism of Cannizzaro reaction.

Aldol and Cannizzaro reactions

1. Introduction
2. Aldol reaction
 - 2.1 Characteristics of Aldol reaction
 - 2.2 Mechanism of Aldol reaction
 - 2.3 Dehydration of Aldol product
 - 2.4 Crossed- Aldol condensation
 - 2.5 Intramolecular Aldol reactions
3. Cannizzaro reaction
 - 3.1 Mechanism of Cannizzaro reaction

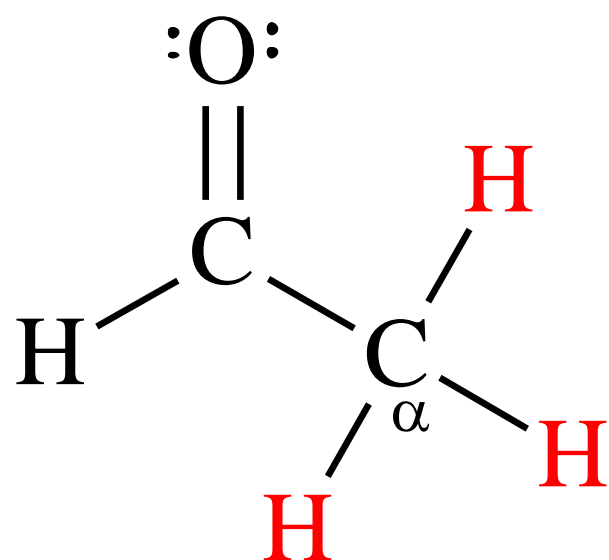
1. Introduction

- ❖ An aldehyde or a ketone having α -hydrogens undergoes self condensation in the presence of dilute base to obtain β -hydroxy aldehyde (*Aldol*) or β -hydroxy ketone which upon dehydration generates α , β -unsaturated aldehyde or ketone. This reaction is called ***Aldol Condensation reaction***.
- ❖ An aromatic or aliphatic aldehyde having no α -hydrogens undergoes disproportionation reaction in the presence of concentrated base to obtain salt of carboxylic acid (oxidised product) and a primary alcohol (reduced product). This reaction is called ***Cannizzaro reaction***.

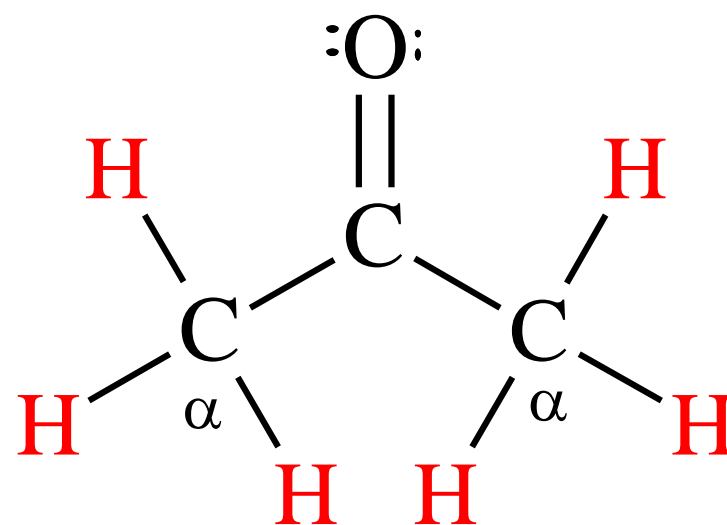
2. Aldol Reaction

2. Aldol Reaction

❖ Aldehydes and ketones with α -hydrogens undergo an aldol reaction.



Acetaldehyde



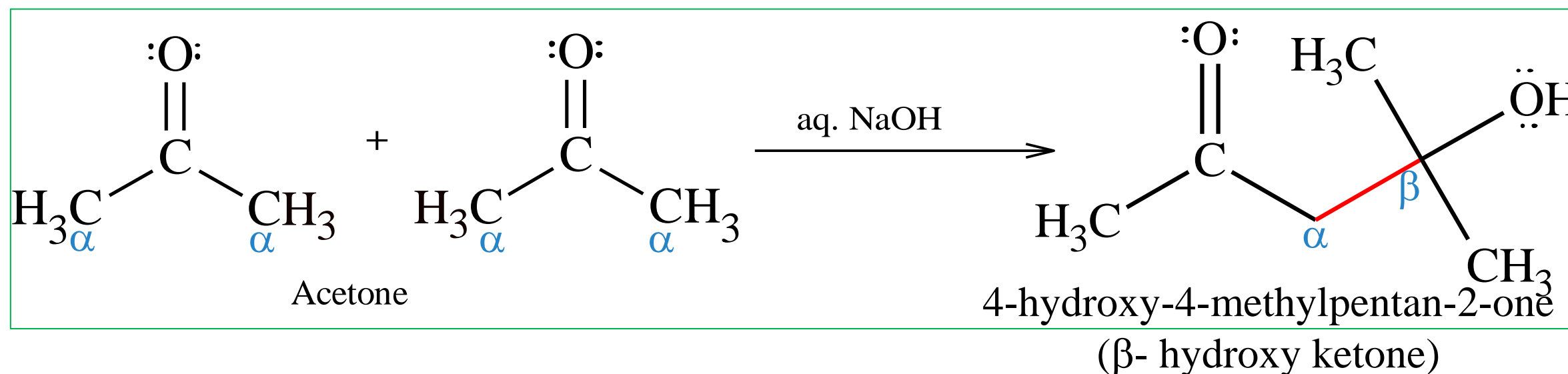
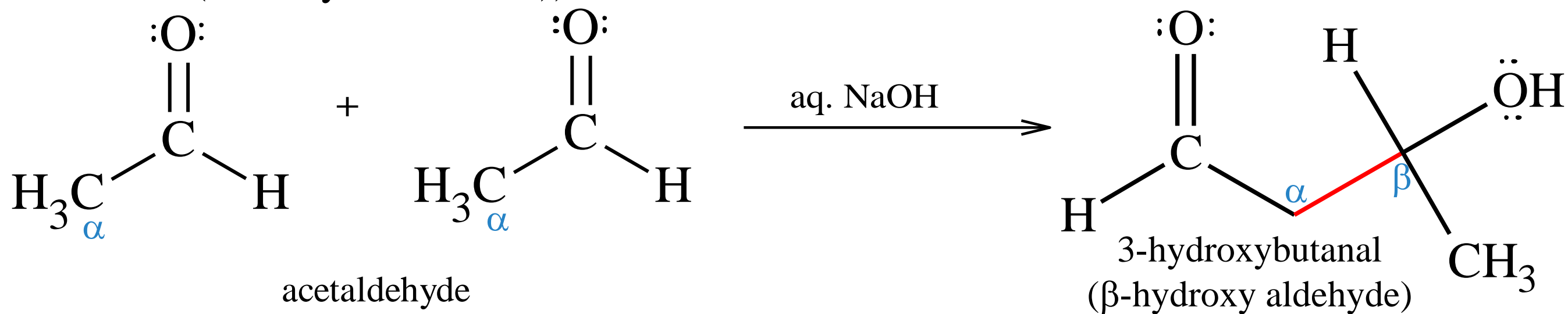
Acetone

The carbon atom adjacent to the carbonyl carbon is referred to as α -carbon & the H-atoms on it are called α -Hydrogens



2. Aldol Reaction

❖ It is an addition reaction between two aldehydes, two ketones, or an aldehyde and a ketone in presence of aqueous base gives **β - Hydroxy aldehyde** or a **β -hydroxy ketone** (commonly known as **Aldol** ("*aldehyde alcohol*")).



2. Aldol Reaction

- ❖ The successive loss of water from β - Hydroxy aldehyde or a β - Hydroxy ketone produces an α, β - unsaturated aldehyde or ketone.
- ❖ Both the aldol reaction and dehydration steps are catalysed by base or acid.

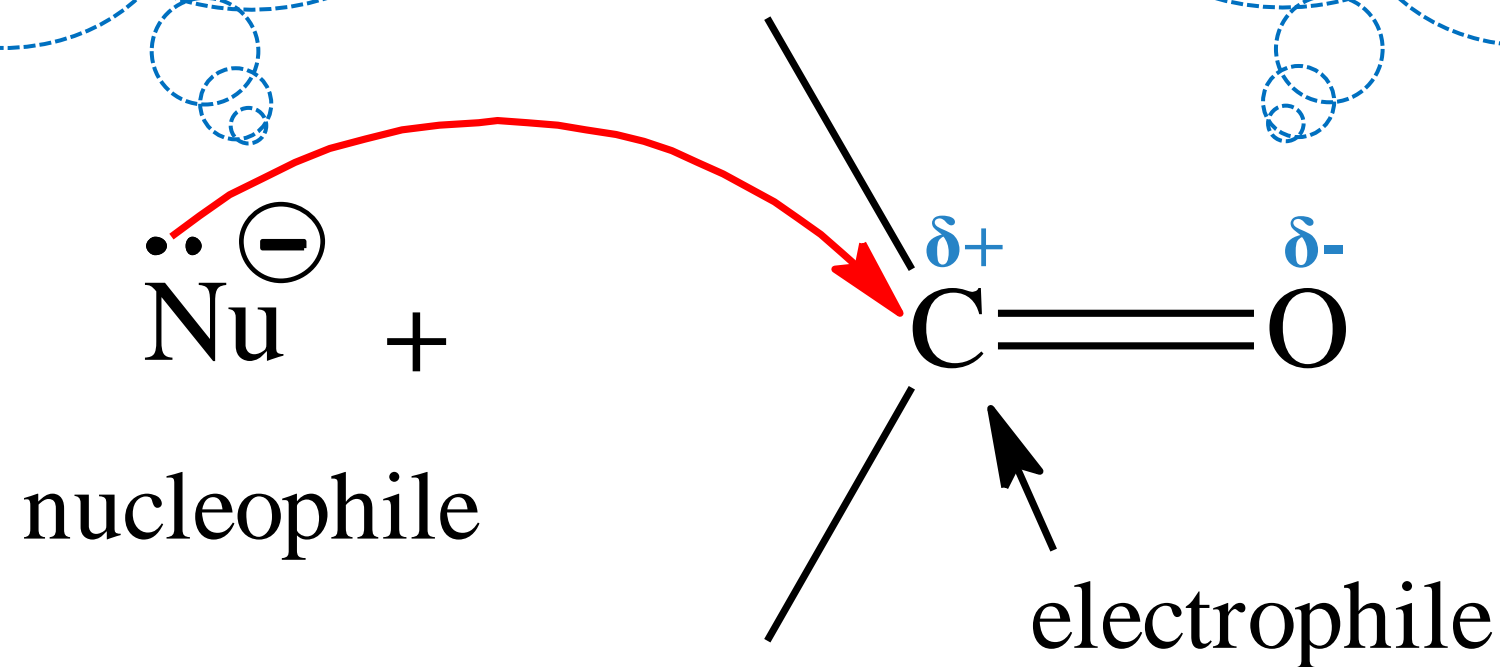
2.1. Characteristics of Aldol Reaction

- ❖ An Aldol reaction is a nucleophilic addition in which a carbanion is the nucleophile.
- ❖ One molecule of aldehyde or ketone becomes a carbanion.
- ❖ Another molecule serves as the electrophile because its carbonyl carbon is electron deficient.
- ❖ Presence of α -hydrogen in aldehyde or ketone is the essential condition for aldol reaction

2.1. Characteristics of Aldol Reaction

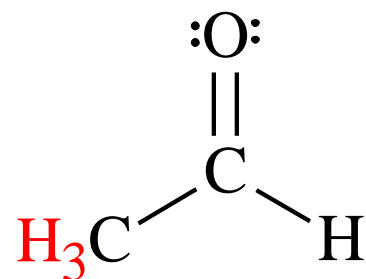
A **nucleophile** is a chemical species that donates an electron pair to form a chemical bond in relation to a reaction.

An **electrophile** is an electron pair acceptor. Electrophiles are positively charged or neutral species having vacant orbitals that are attracted to an electron rich center.

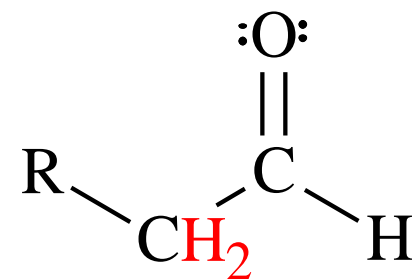


2.1. Characteristics of Aldol Reaction

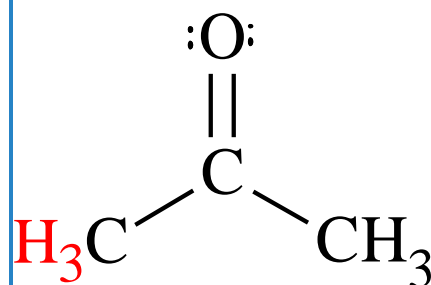
Some examples of the aldehydes and ketones that undergo aldol reaction are given below:



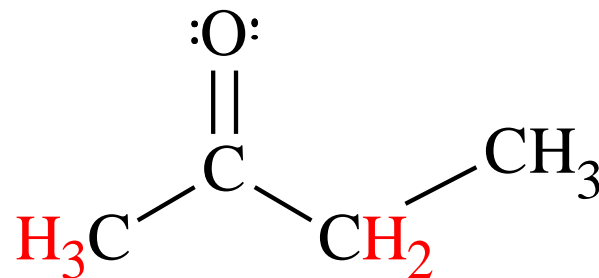
Acetaldehyde



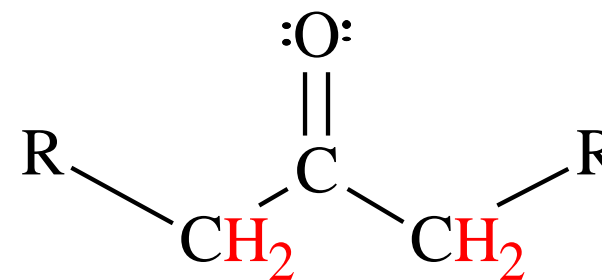
Where R = -H or -CH₃ or -phenyl group



Acetone



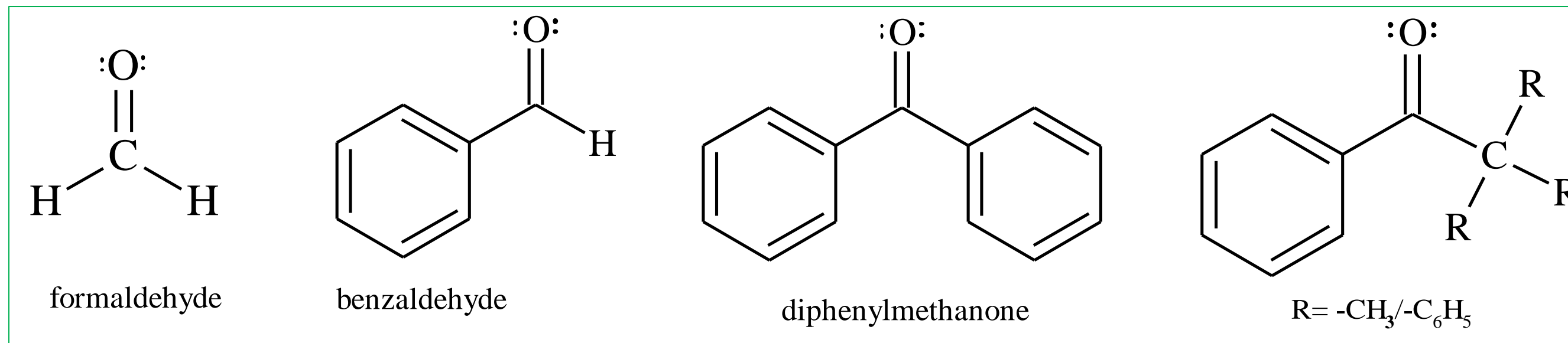
butan-2-one



Where R = -H or -CH₃ or -phenyl group

2.1. Characteristics of Aldol Reaction

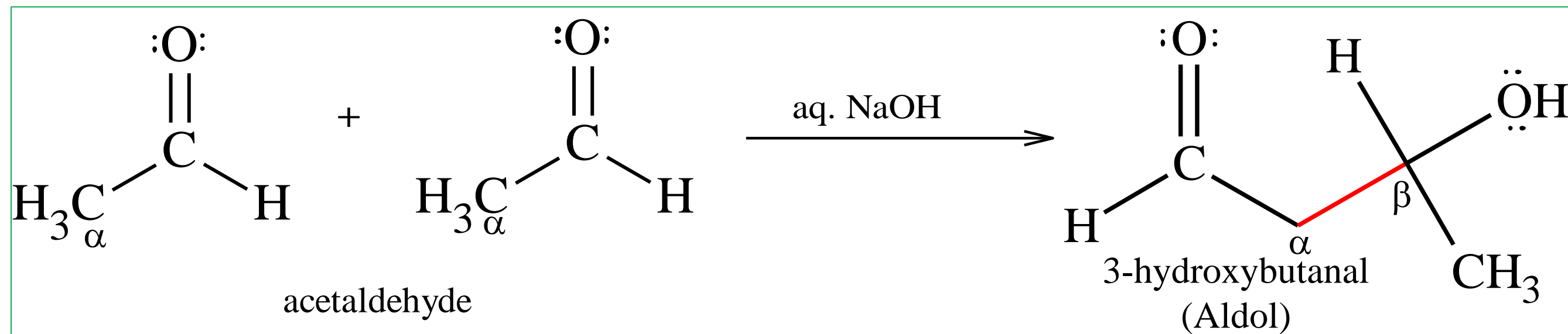
Aldehydes or ketones, not having α -hydrogen atom, do not undergo aldol reaction.



- Since there is no availability of α -hydrogen atoms in the above compounds, these do not undergo aldol reaction.
- However, in the presence of concentrated base, they undergo Cannizzaro reaction.

2.2. Mechanism of Aldol Reaction

Treatment of acetaldehyde with an aqueous base produces 3-hydroxybutanal.

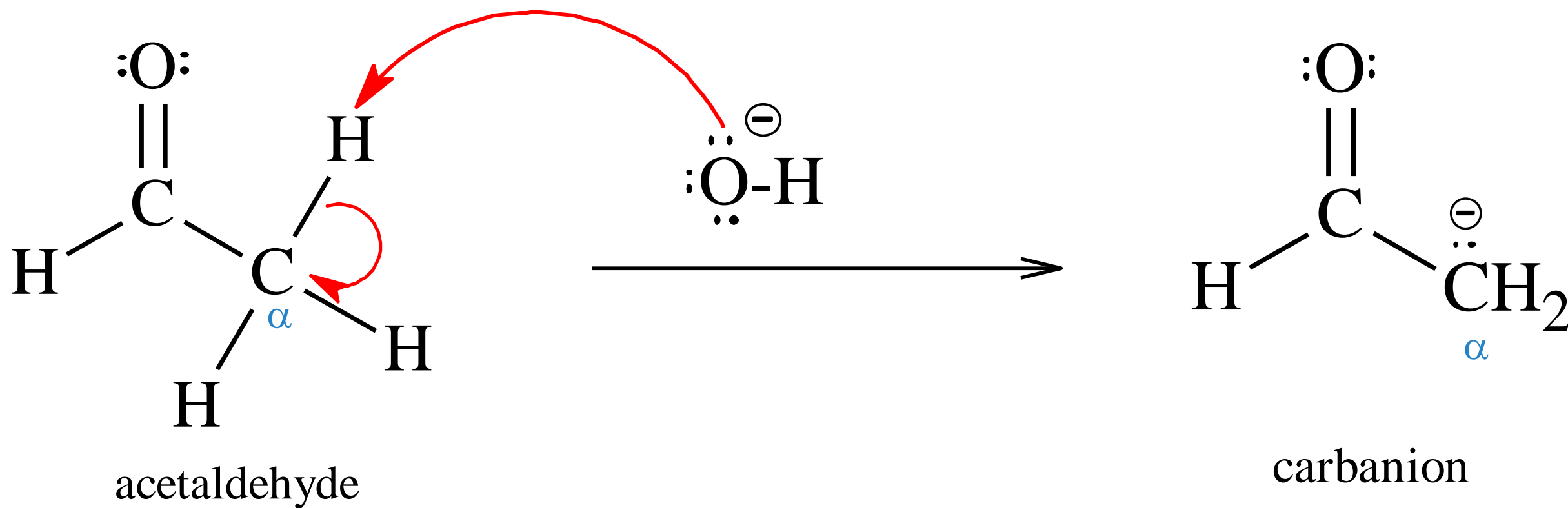


➤ The Mechanism occurs in three steps.

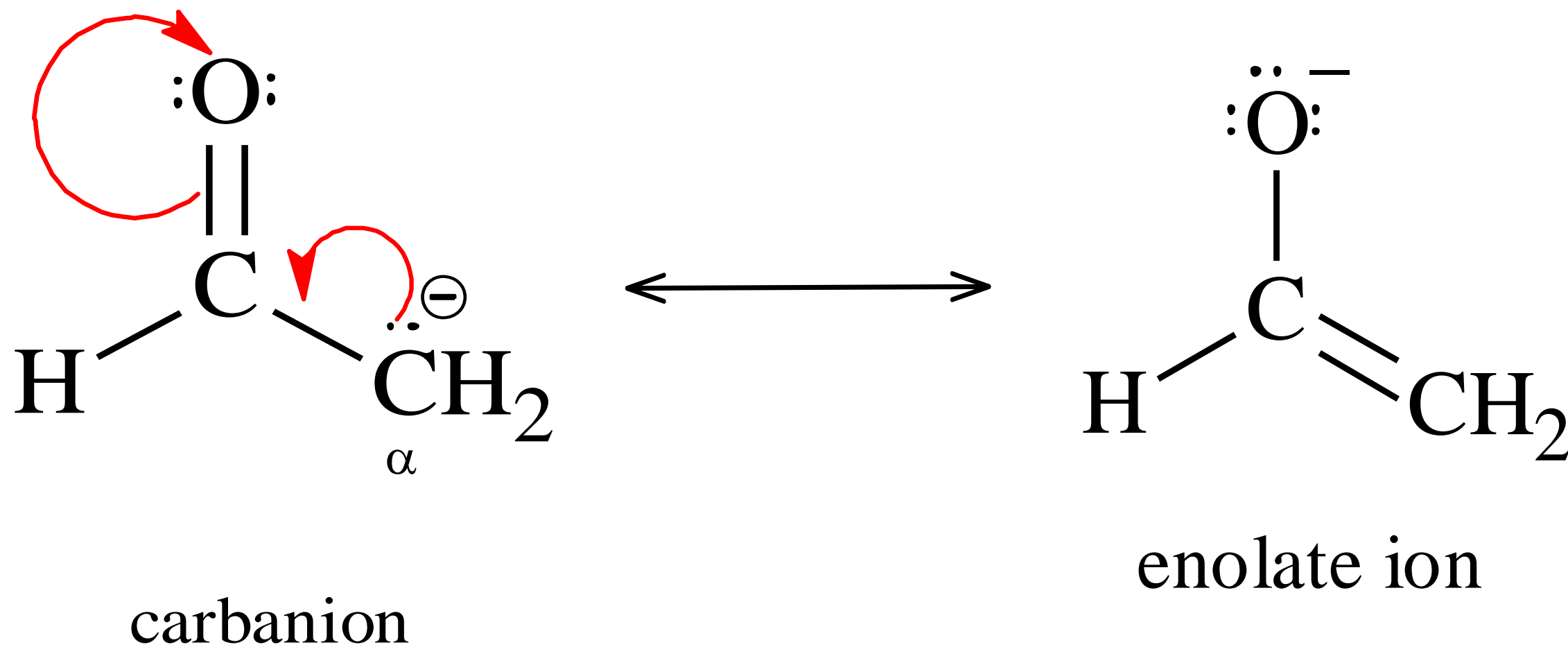
1. **Generation of carbanion**
2. **Nucleophilic attack of carbanion**
3. **Protonation**

2.2. Mechanism of Aldol Reaction

Step 1: Attack of a base to remove a proton from the α -carbon ($C\alpha$) of the aldehyde or ketone to generate resonance stabilized carbanion.



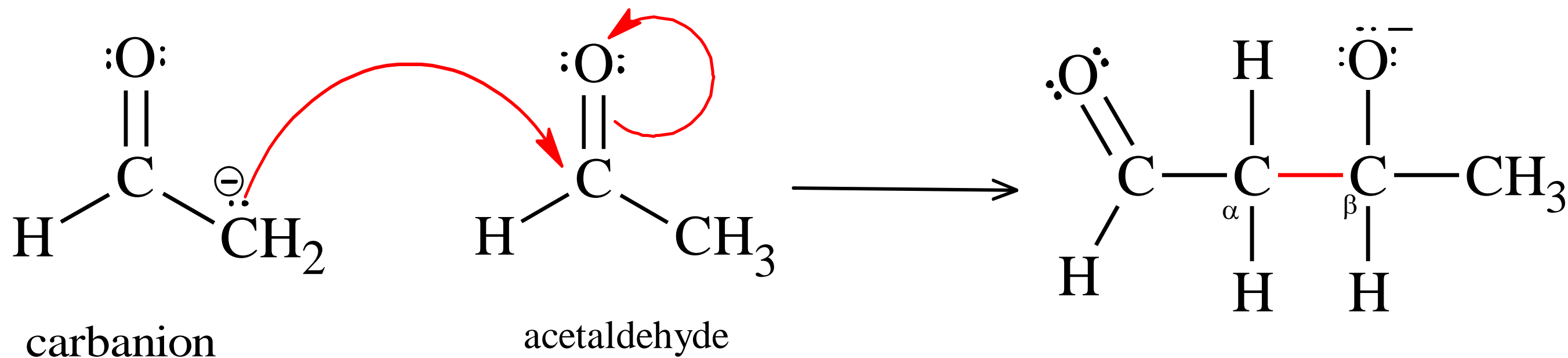
2.2. Mechanism of Aldol Reaction



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

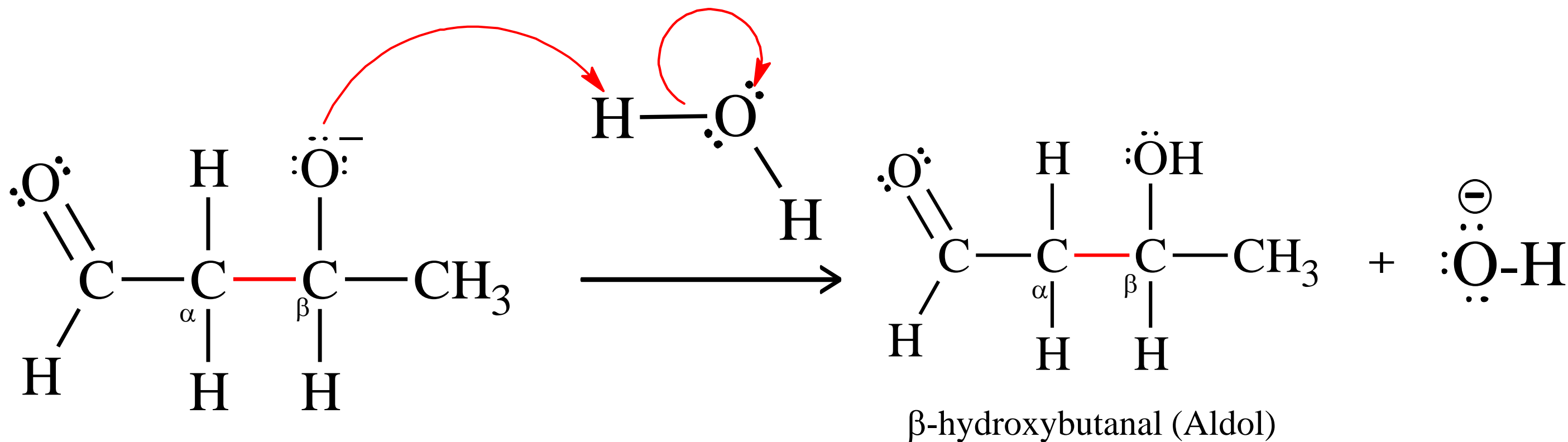
2.2. Mechanism of Aldol Reaction

Step 2: Nucleophilic carbanion attacks the electrophilic carbonyl carbon of a second molecule of aldehyde, thus forming a new carbon-carbon bond.



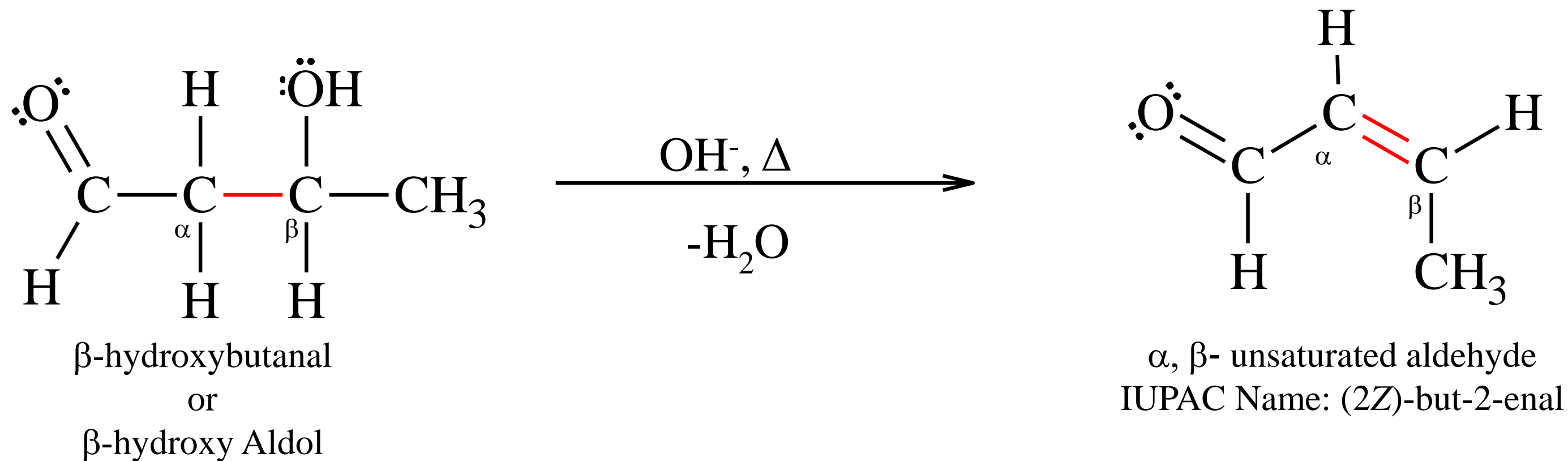
2.2. Mechanism of Aldol Reaction

Step 3: Protonation of the product formed in step 2 gives the β -hydroxy aldehyde.



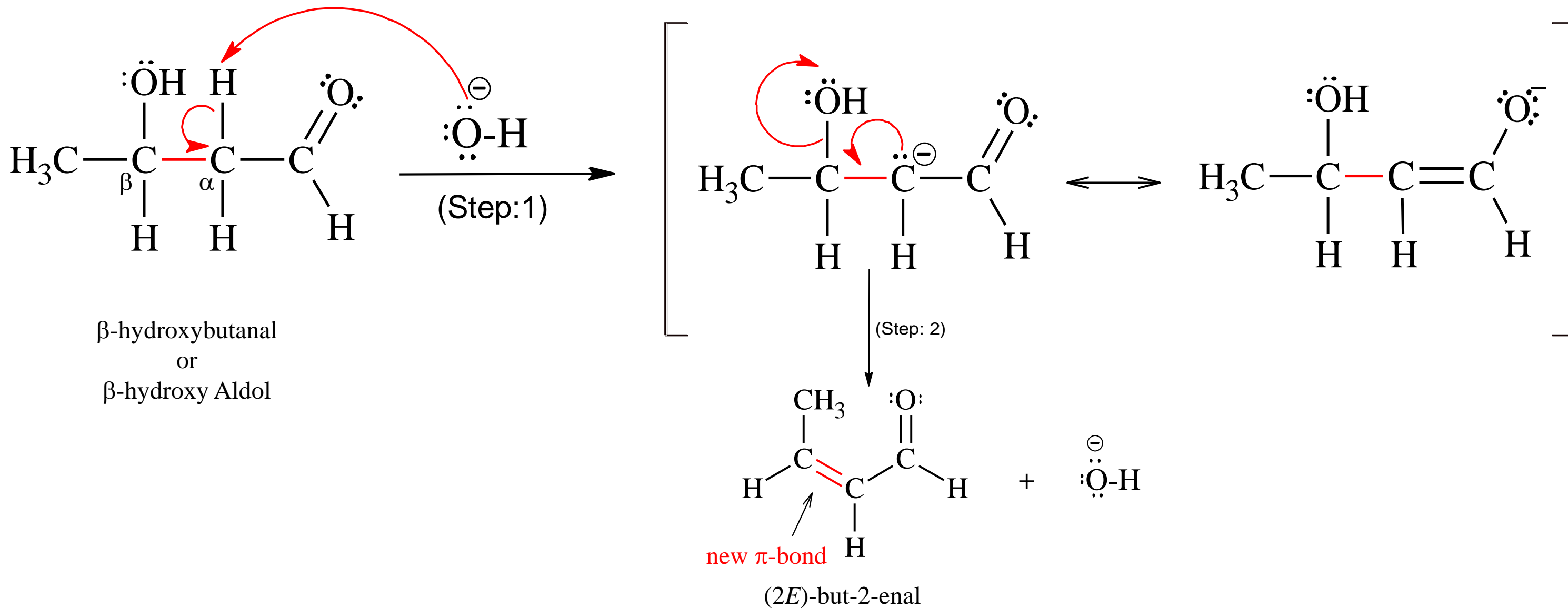
2.3. Dehydration of Aldol Reaction

The β -hydroxy carbonyl compound formed in the aldol reaction dehydrate more readily in the presence of base.



2.3. Dehydration of Aldol Reaction

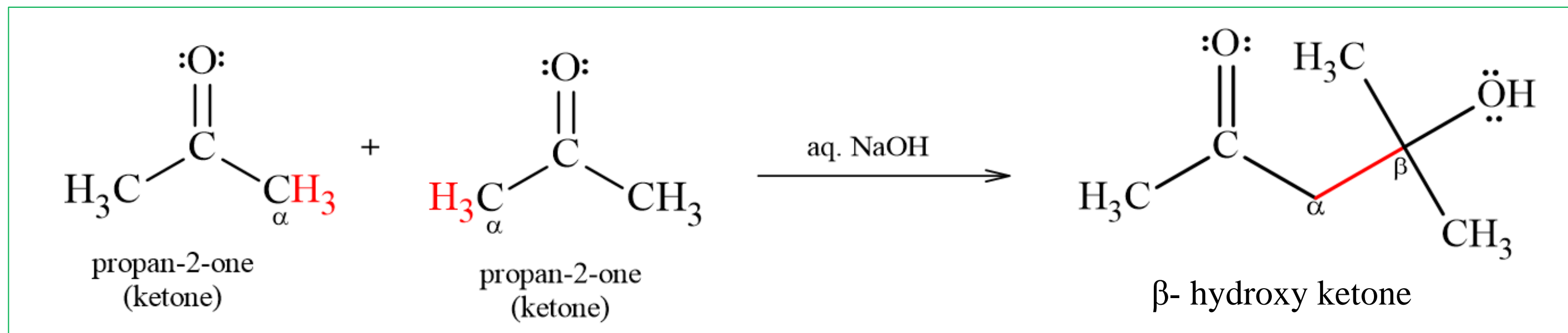
➤ Mechanism of dehydration with base completes in two steps.



Mechanism of Aldol Reaction

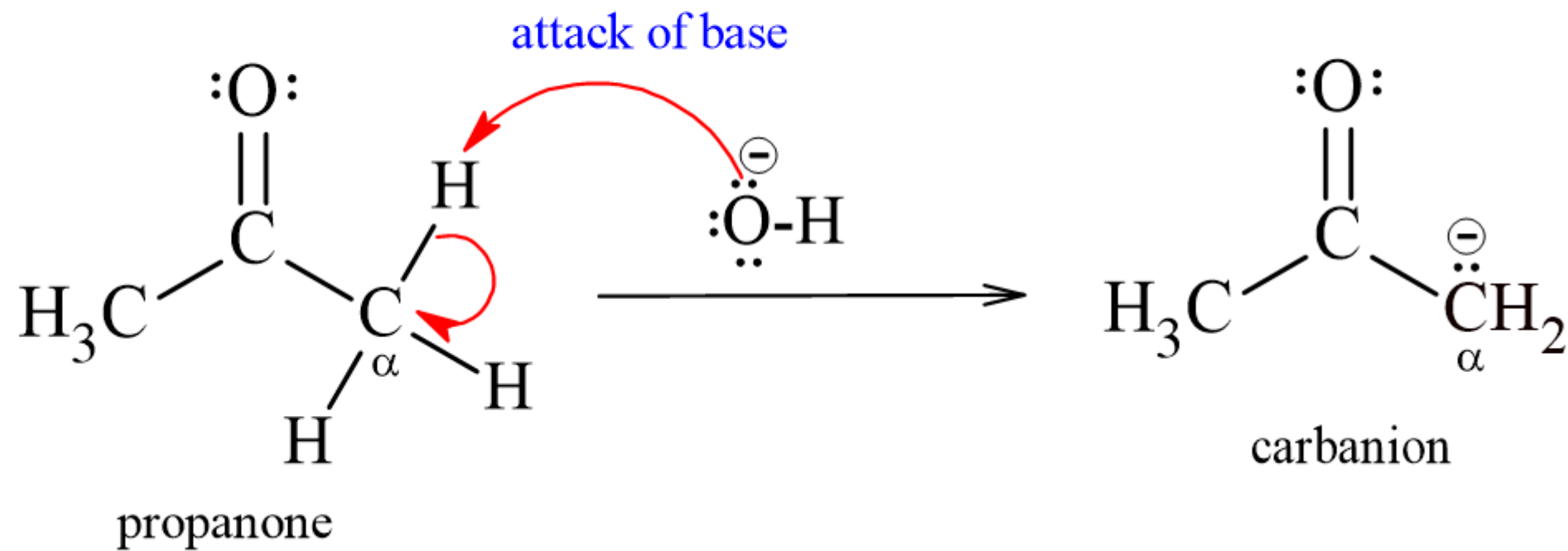
In case of Ketones the reaction mechanism follows as shown below:

Example: Formation of β -hydroxy ketone from acetone

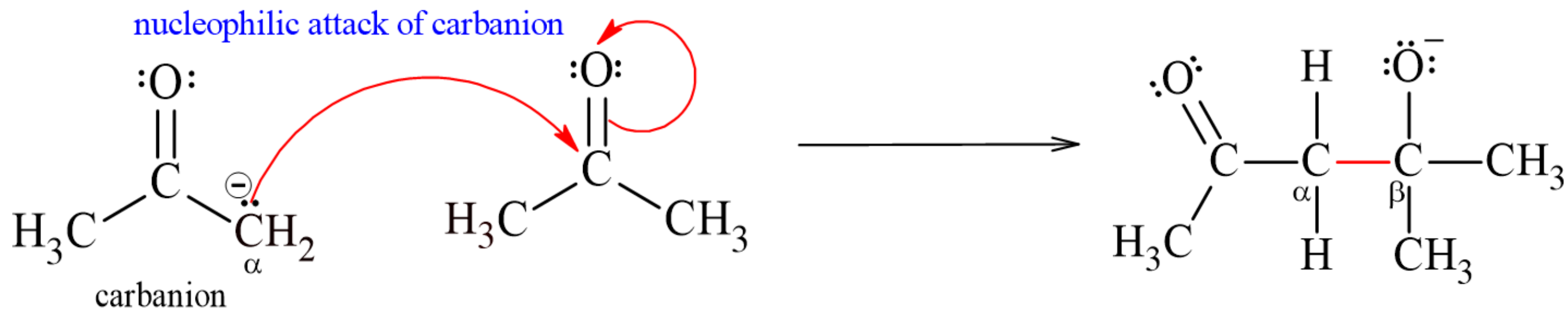


In case of Ketones the reaction mechanism follows as shown below:

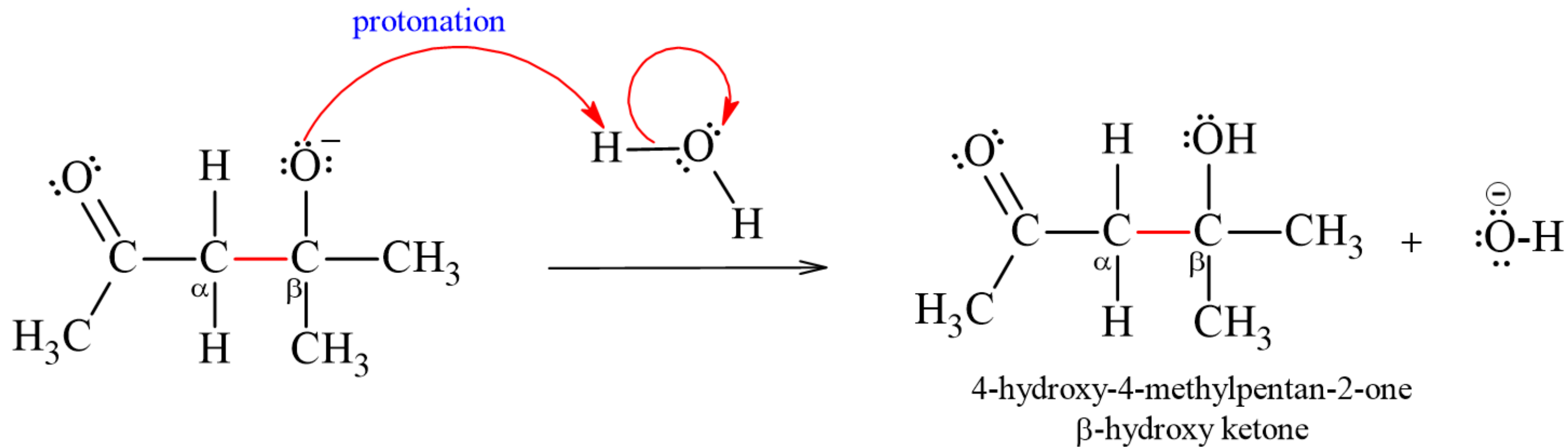
Step 1



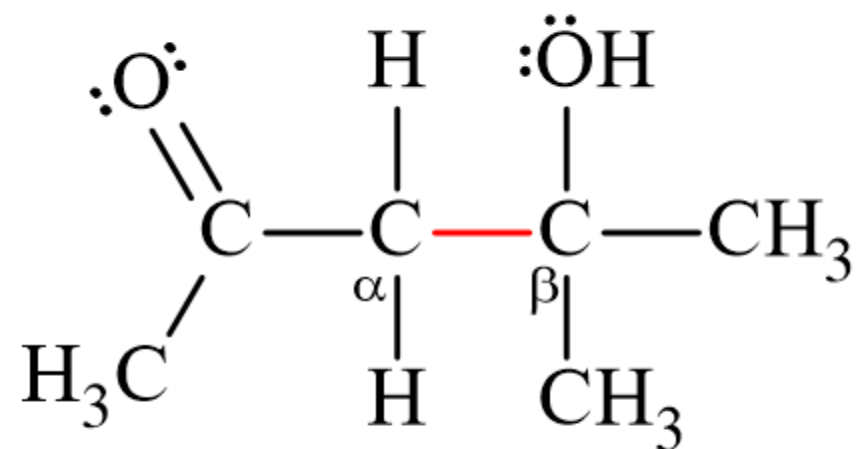
Step 2



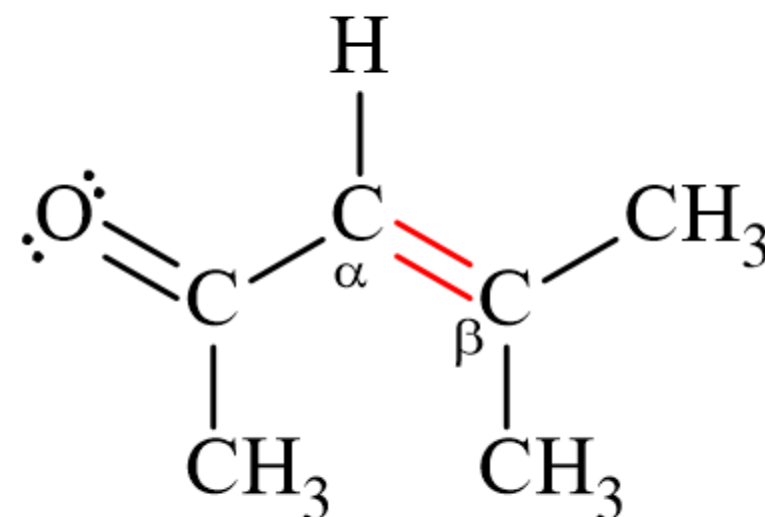
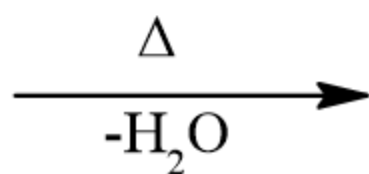
Step 3



Step 4: A dehydration step to yield a α , β -unsaturated ketone.



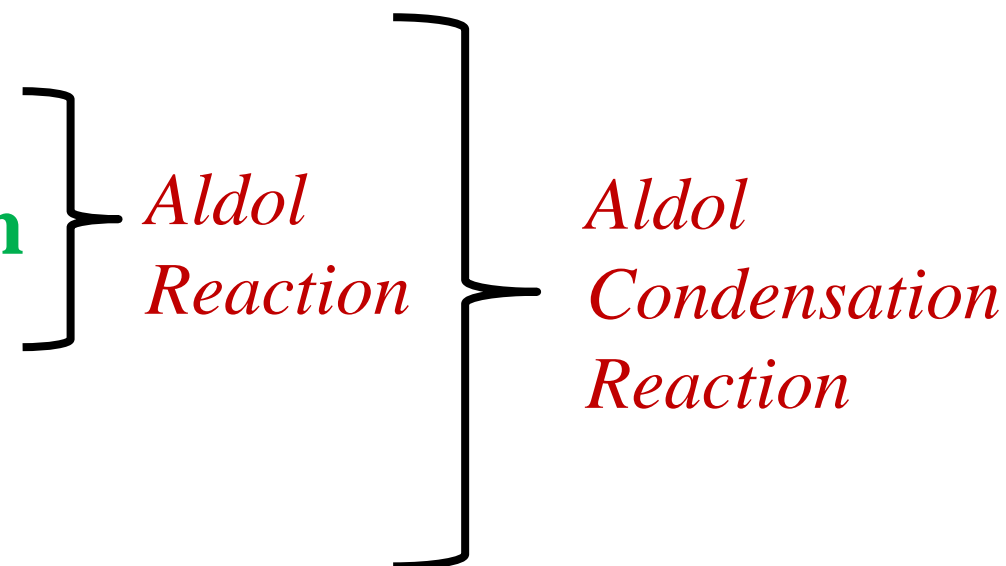
4-hydroxy-4-methylpentan-2-one
 β -hydroxy ketone



α,β -unsaturated ketone
IUPAC Name: 4-methylpent-3-en-2-one

If the mechanism involves steps 1 to 3 only, then it is termed as an ***Aldol addition reaction*** (or simply ***an Aldol reaction***). But if dehydration step takes place, then it becomes an ***aldol condensation reaction*** (because a water molecule is lost in the event).

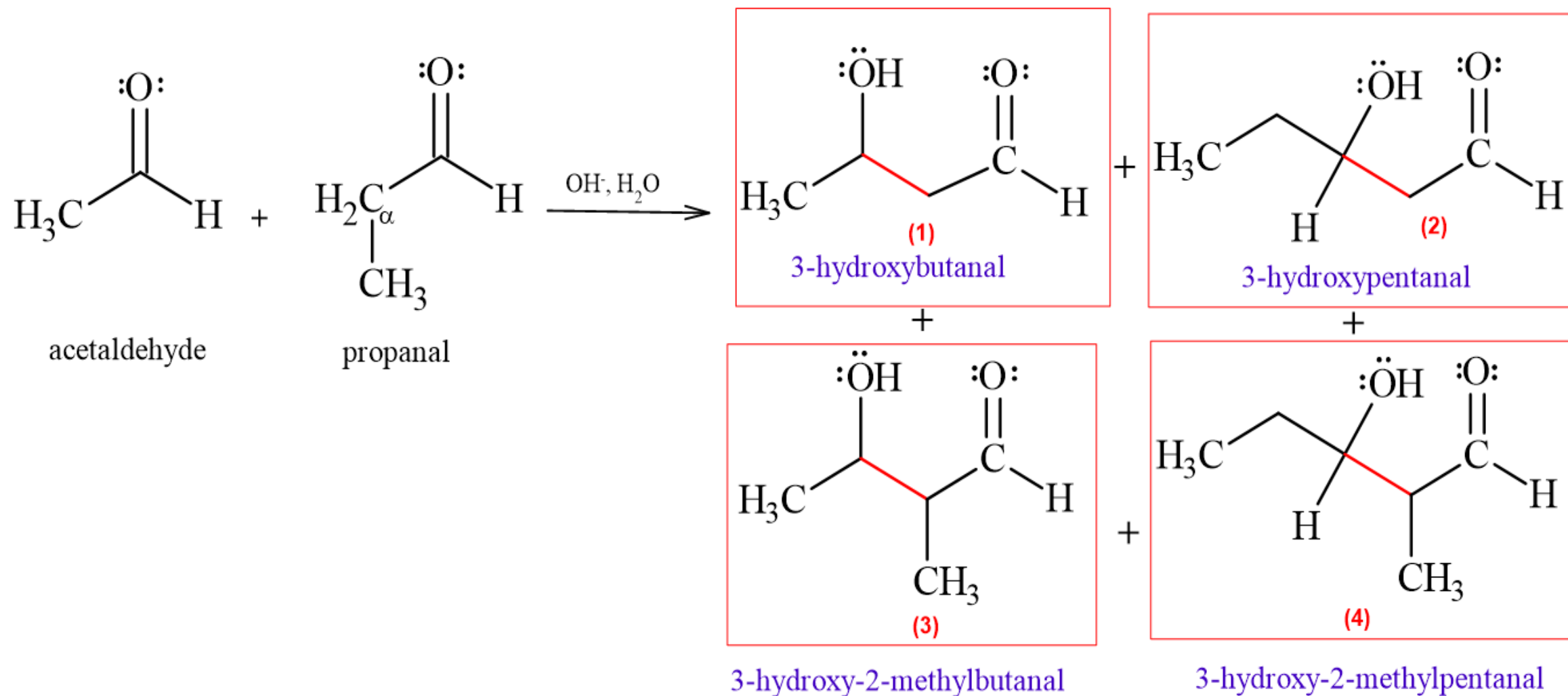
- 1. Generation of carbanion**
- 2. Nucleophilic attack of carbanion**
- 3. Protonation**
- 4. Dehydration of Aldol product**



2.4. Crossed Aldol Reaction

- Aldol reaction between two different carbonyl compounds is called a *crossed aldol* or *mixed aldol reaction*.

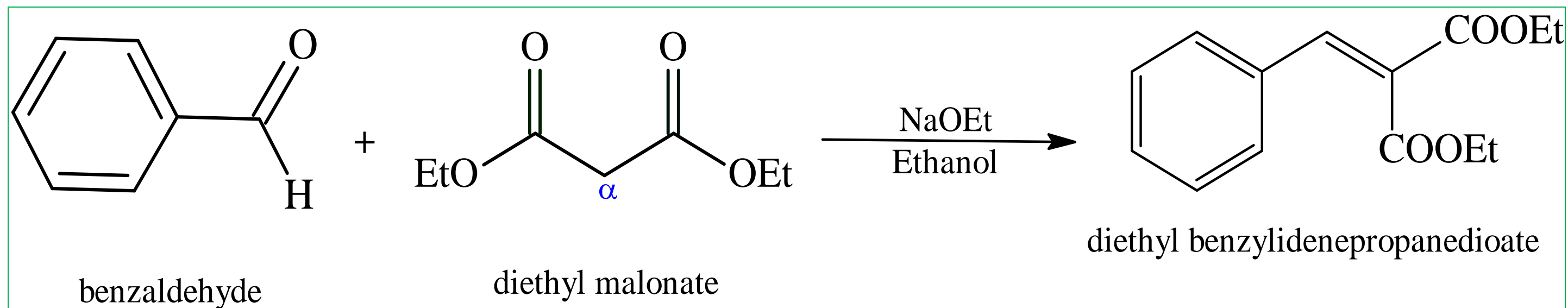
For example, Reaction between an acetaldehyde and a propanal



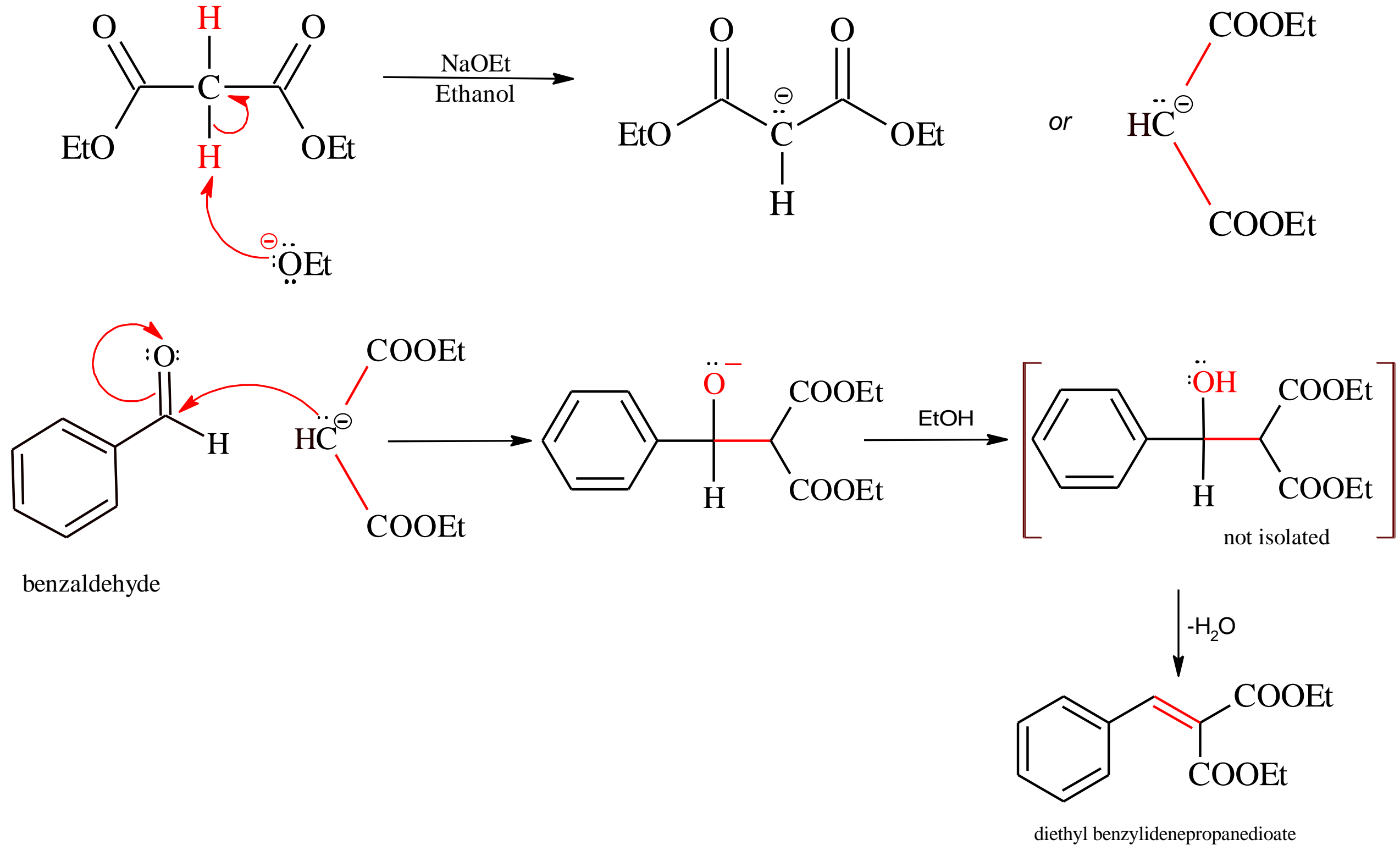
2.4. Crossed Aldol Reaction

- A crossed aldol reaction occurs readily when one carbonyl component has specifically acidic α -hydrogen atoms.

For example: Crossed aldol reaction between an aldehyde or ketone and a β -dicarbonyl (or similar) compound.

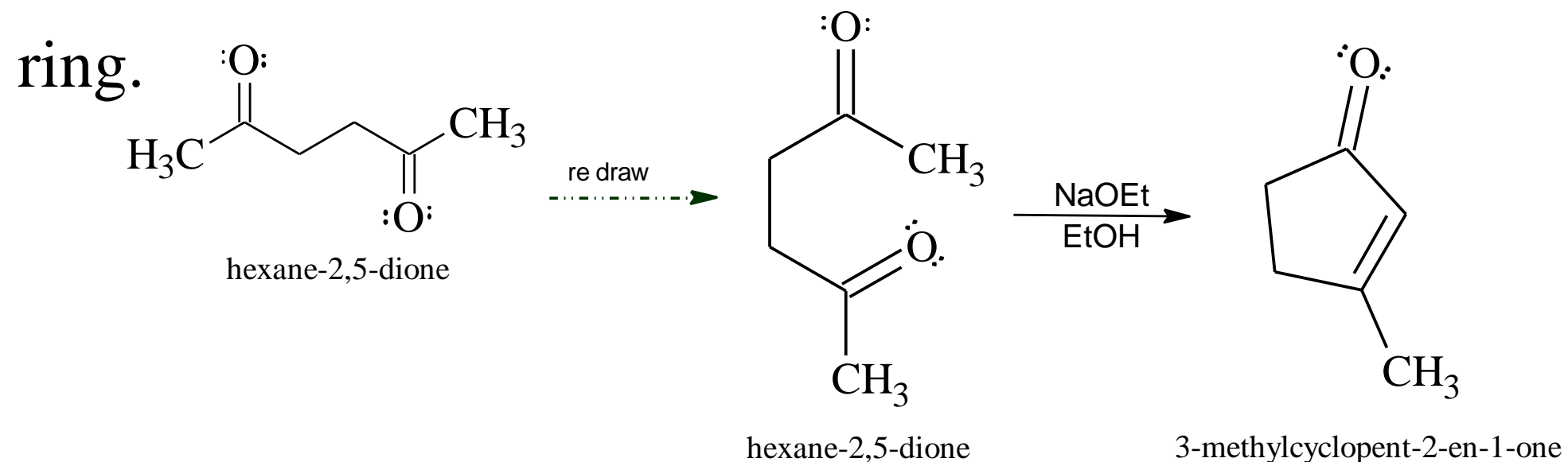


2.4. Crossed Aldol Reaction



2.5. Intramolecular Aldol Reaction

- ❖ Di carbonyl compounds undergo aldol reactions to make five and six member rings.
- ❖ The carbanion formed from one carbonyl group is the nucleophile and the carbonyl carbon of another carbonyl group is the electrophile.
- ❖ For example, treatment of 2,5 hexadione with base forms a five membered ring.



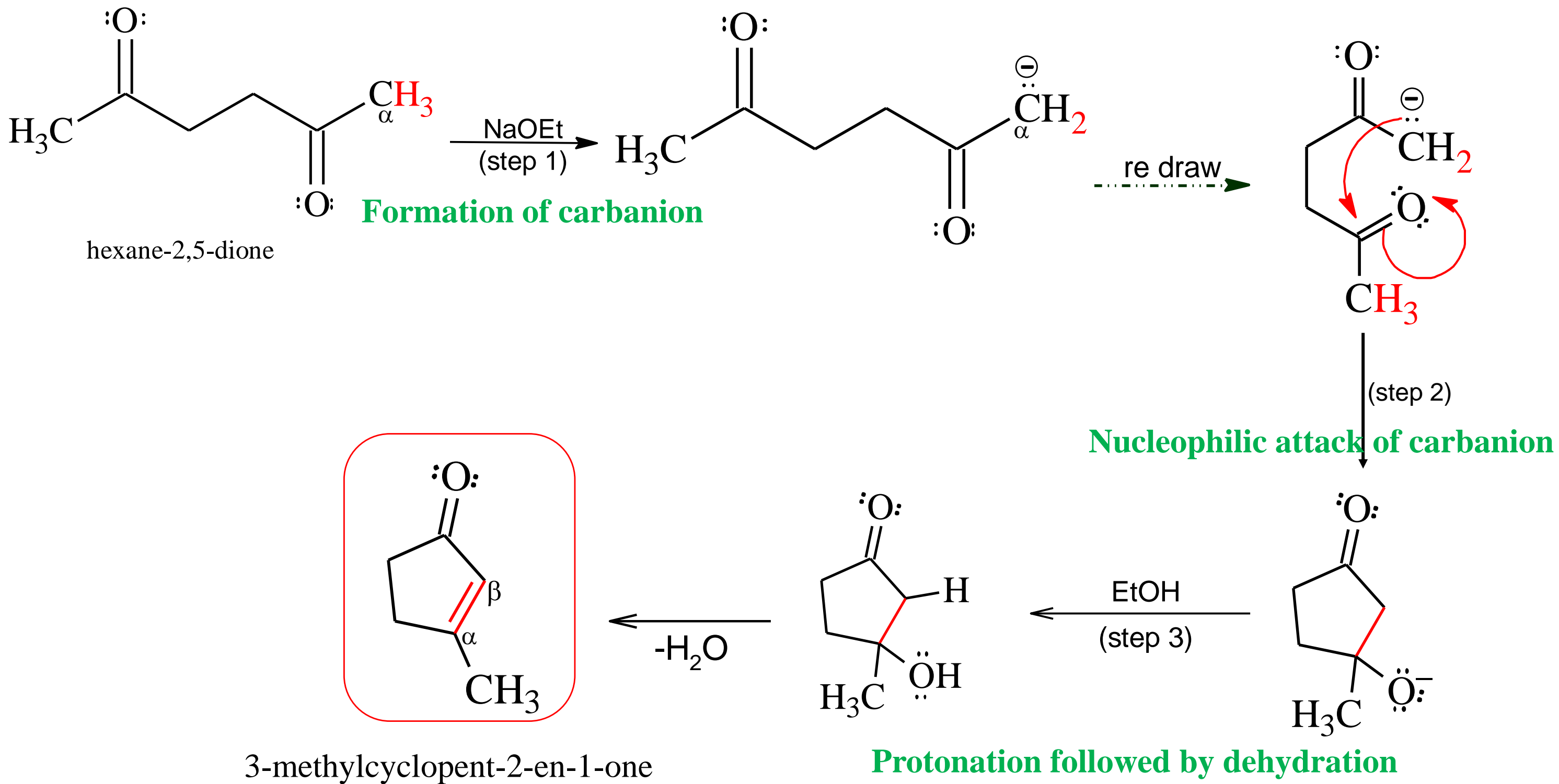
2.5. Intramolecular Aldol Reaction

Step 1: Formation of carbanion

Step 2: Nucleophilic attack of carbanion

Step 3: Protonation followed by dehydration

2.5. Intramolecular Aldol Reaction



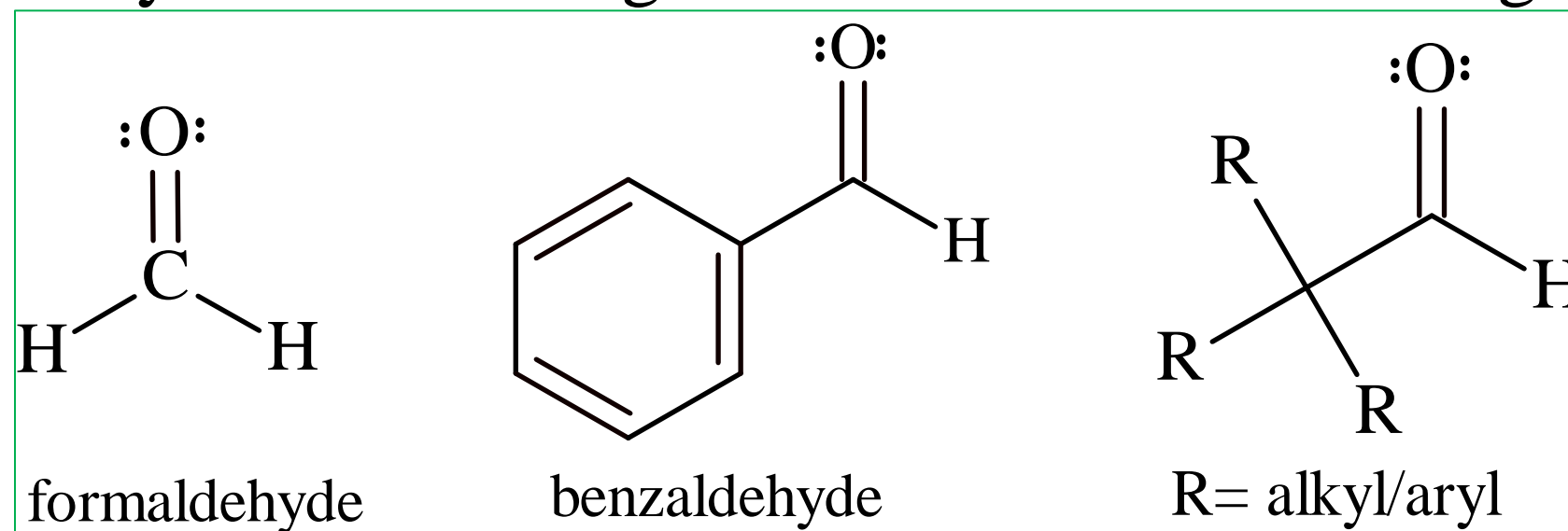
3. Cannizzaro Reaction

3. Cannizzaro Reaction

- ❖ Named after its discoverer **Stanislao Cannizzaro**.
- ❖ Aromatic and aliphatic aldehydes with no α -hydrogen atom gives the Cannizzaro reaction when treated with concentrated NaOH or other strong bases.
- ❖ One molecule of aldehyde oxidises to form salt of carboxylic acid and another aldehyde is reduced to the primary alcohol.
- ❖ This simultaneous oxidation and reduction (Disproportionation) of aldehyde is known as **Cannizzaro reaction**.

3. Cannizzaro Reaction

The aldehydes that undergo Cannizzaro reaction are given below:

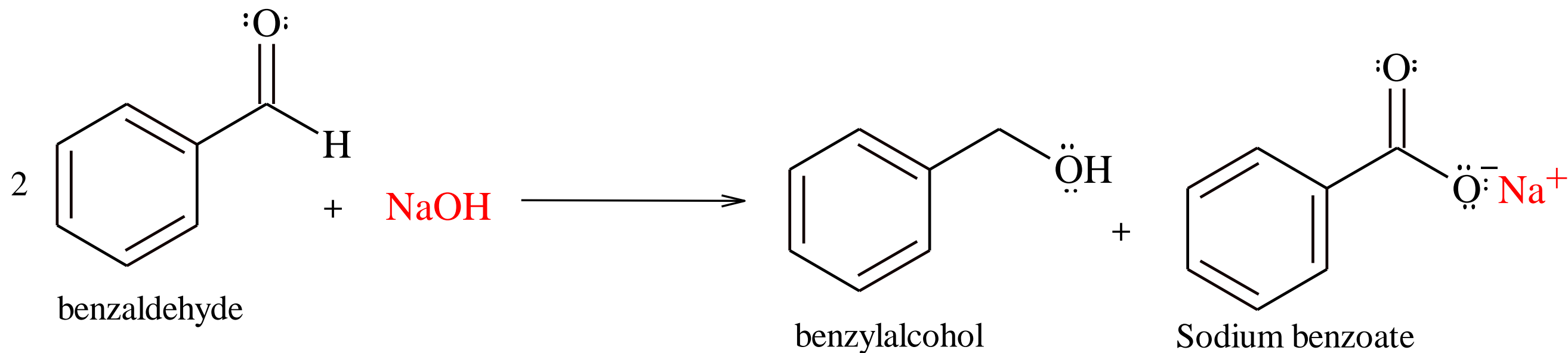
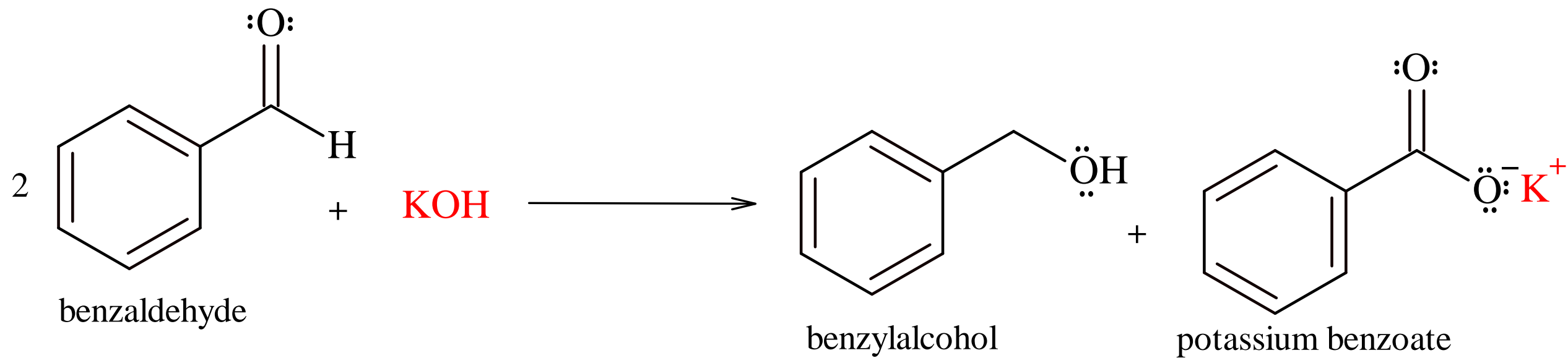


The reaction takes place with sodium or potassium hydroxide.

The oxidation product is a salt of a carboxylic acid and the reduction product is an alcohol.

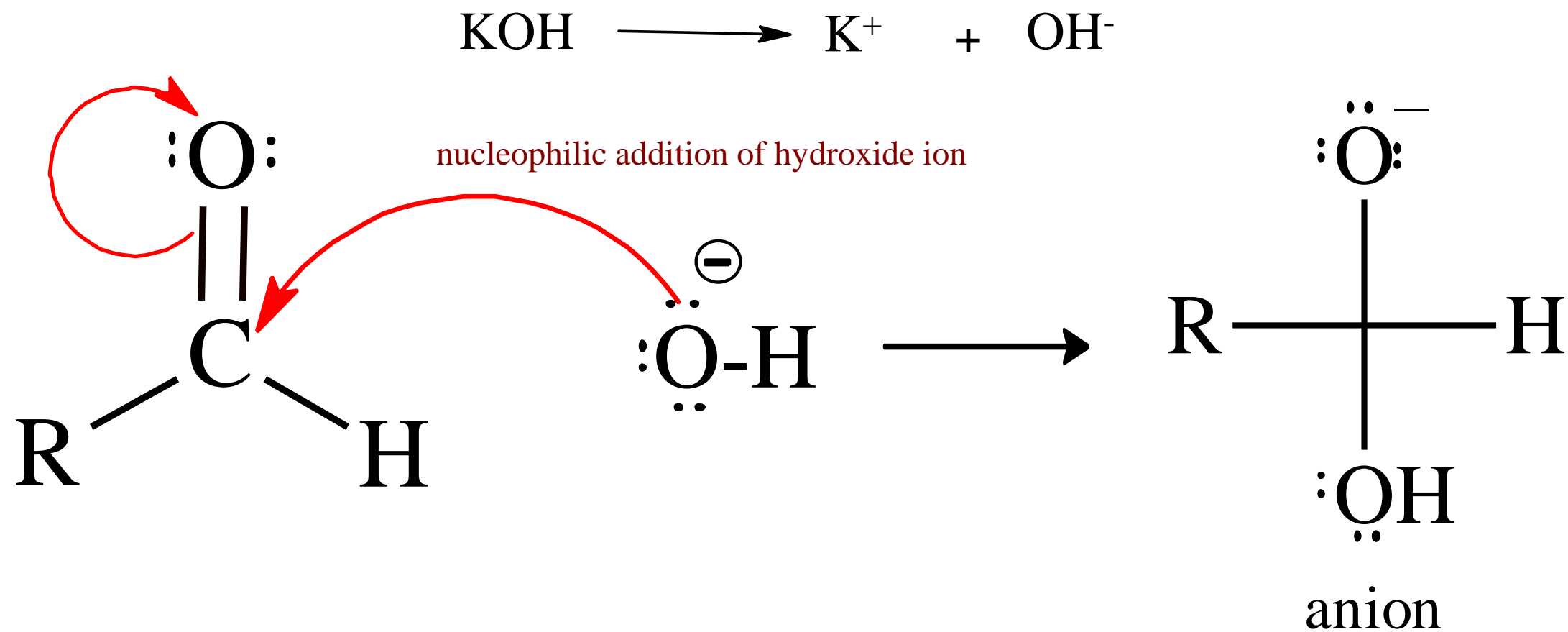


3. Cannizzaro Reaction



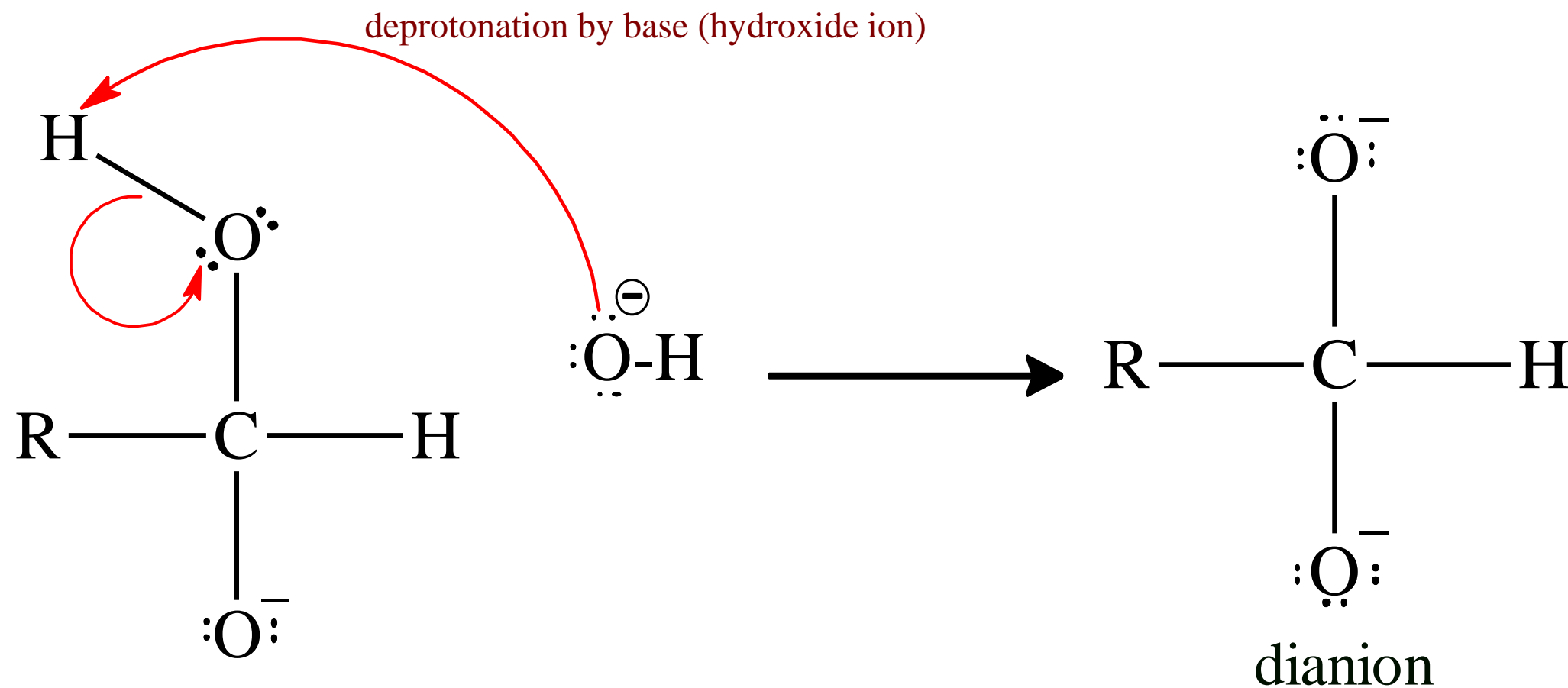
3.1. Mechanism of Cannizzaro Reaction

The reaction is initiated by the nucleophilic addition of hydroxide ion to the carbonyl group of an aldehyde molecule to give the anion (**Step-1**).



3.1. Mechanism of Cannizzaro Reaction

In a strongly basic medium, the anion formed in step-1 can be deprotonated to give the di anionic species. (**Step-2**).

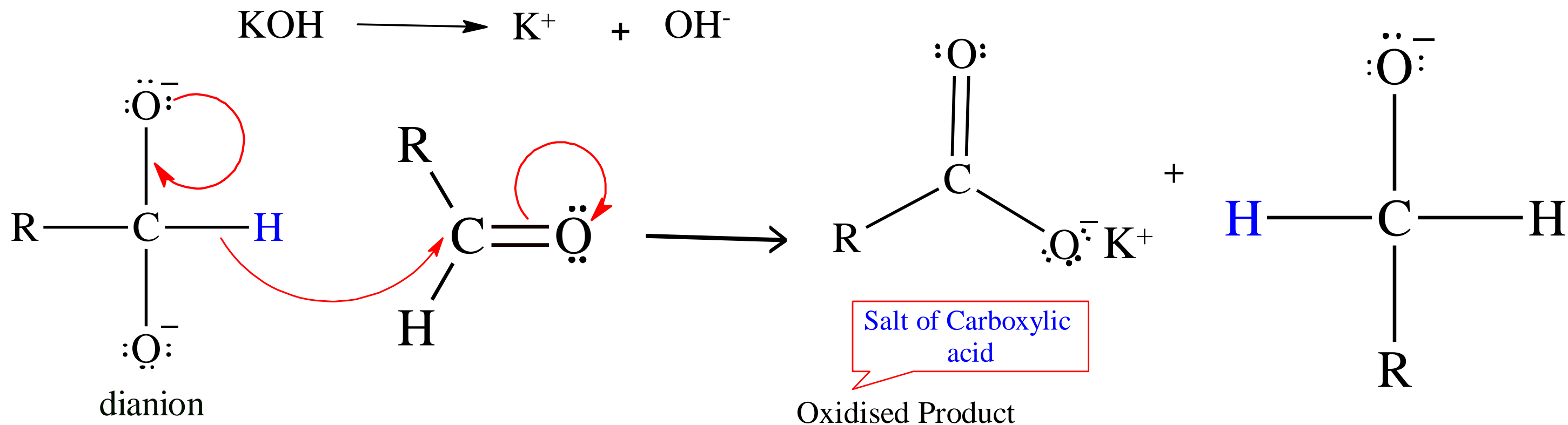


3.1. Mechanism of Cannizzaro Reaction

- ❖ The dianionic species is unstable.
- ❖ It attains stability by transferring a hydride ion to the other aldehyde and gets oxidized to the corresponding salt of a carboxylic acid.
- ❖ The second molecule of aldehyde is there by reduced to alcohol.

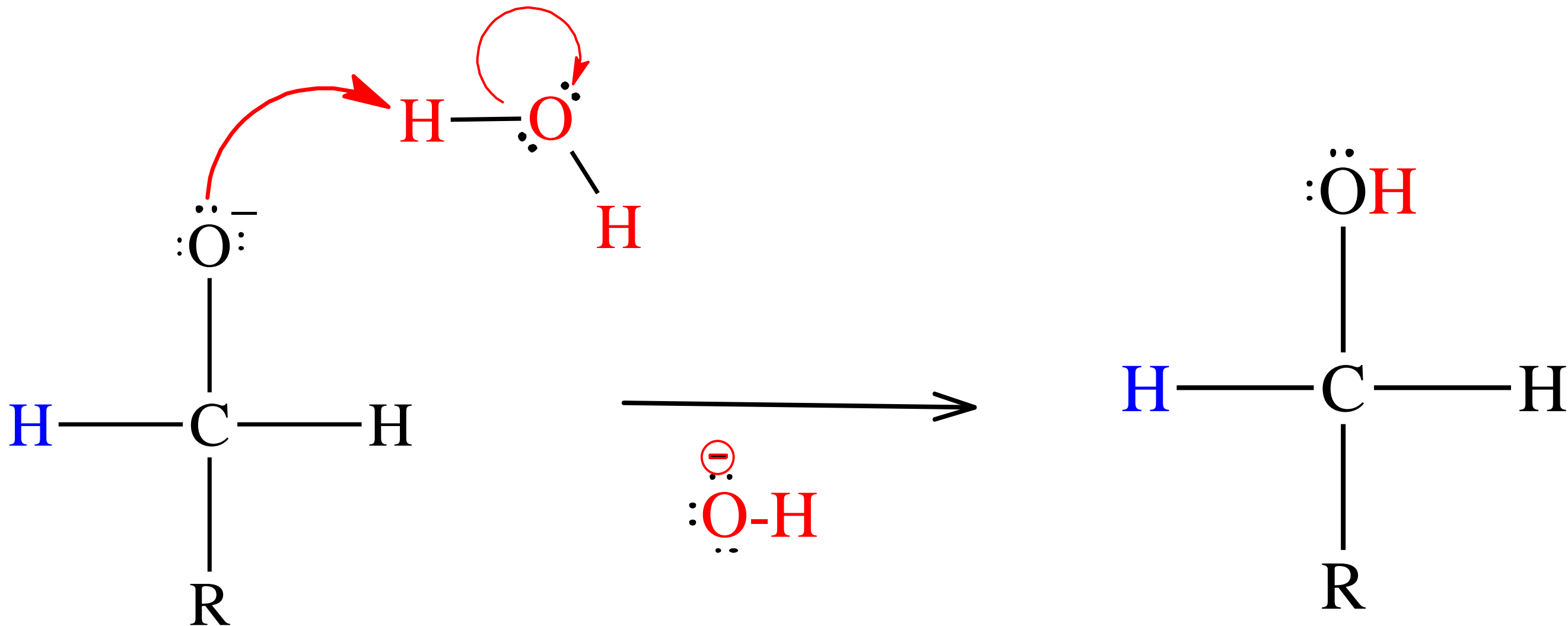
3.1. Mechanism of Cannizzaro Reaction

The key step of the Cannizzaro reaction is a hydride transfer.



Hydride ion transfer
from dianionic species

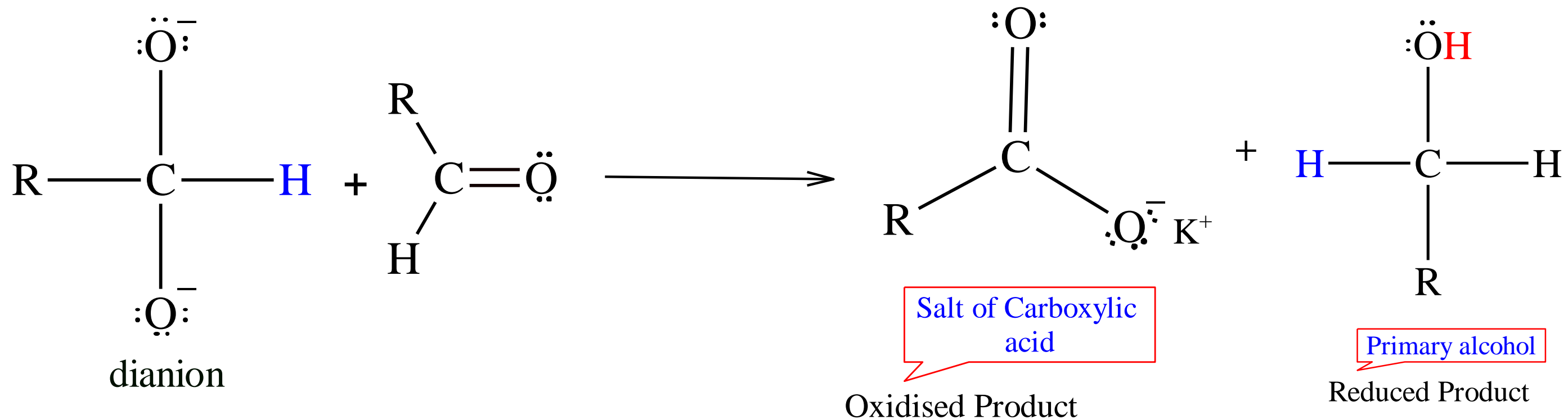
3.1. Mechanism of Cannizzaro Reaction



Primary alcohol

Reduced Product

3.1. Mechanism of Cannizzaro Reaction



4. Summary

- ❖ Aldol reaction is an addition reaction between two carbonyl compounds in presence of aqueous base forms β - Hydroxy carbonyl compounds.
- ❖ Reaction between two different carbonyl compounds in the presence of base is called “*crossed aldol reaction*”.
- ❖ Intramolecular aldol reaction leads to the product having five or six membered rings.
- ❖ Aromatic and aliphatic aldehydes with no α -hydrogens react with concentrated NaOH or other strong alkalis to give Cannizzaro reaction (disproportionate reaction).

THANK YOU

References:

1. Advanced Organic Chemistry: Reactions, Mechanisms, by Michael B. Smith; Jerry March, Fourth edition, John Wiley & Sons.
2. Writing Reaction Mechanisms in Organic Chemistry by Audrey Miller, Philippa H. Solomon, Third edition, Elsevier Science & Technology Books.
3. Organic Chemistry by Jonathan Clayden, Nick Greeves, Stuart Warren, Second edition, Oxford University press.
4. Advanced Organic Chemistry: Part B: Reactions and Synthesis by Francis A Carey, Richard J. Sundberg, Fifth edition, Springer.
5. Organic Chemistry by T. W. Graham Solomons, Craig B. Fryhle, Tenth edition, John Wiley & Sons.