Condensation Reaction

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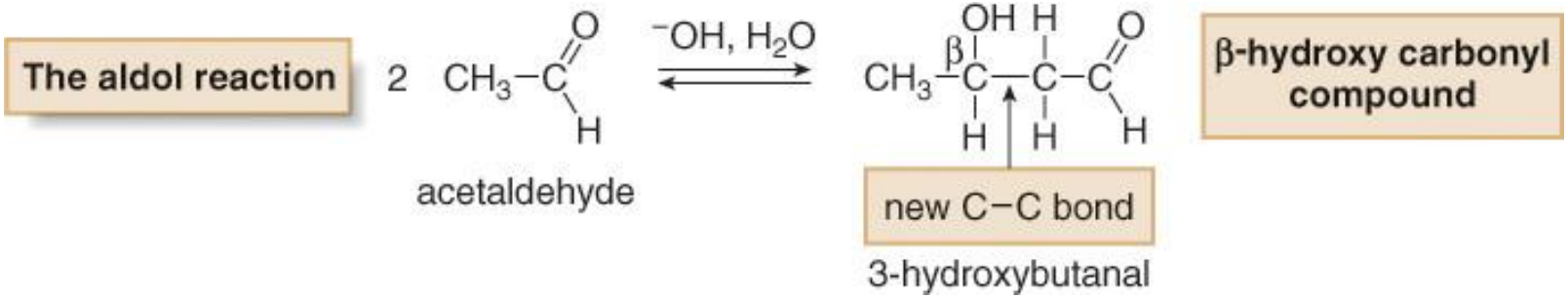
Selective Organic Name Reaction

Msc Ist & IInd

Carbonyl Condensation Reactions

The Aldol Reaction

- **In the aldol reaction, two molecules of an aldehyde or ketone react with each other in the presence of a base to form a β-hydroxy carbonyl compound.**



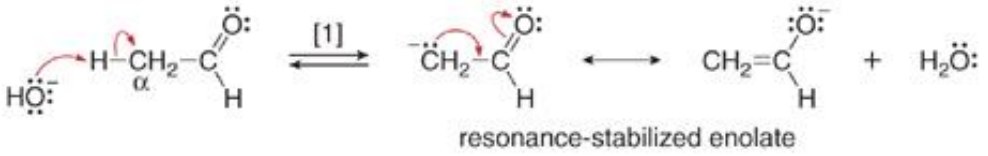
Carbonyl Condensation Reactions

The Aldol Reaction

- **The mechanism of the aldol reaction occurs in three steps.**

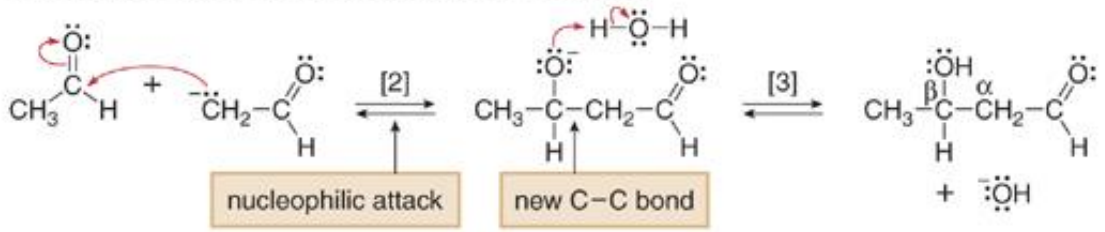
Mechanism 24.1 The Aldol Reaction

Step [1] Formation of a nucleophilic enolate



- In Step [1], the base removes a proton from the α carbon to form a **resonance-stabilized enolate.**

Steps [2]–[3] Nucleophilic addition and protonation



- In Step [2], the nucleophilic enolate attacks the electrophilic carbonyl carbon of another molecule of aldehyde, thus forming a new carbon–carbon bond. **This joins the α carbon of one aldehyde to the carbonyl carbon of a second aldehyde.**
- Protonation of the alkoxide in Step [3] forms the **β-hydroxy aldehyde.**

Carbonyl Condensation Reactions

The Aldol Reaction

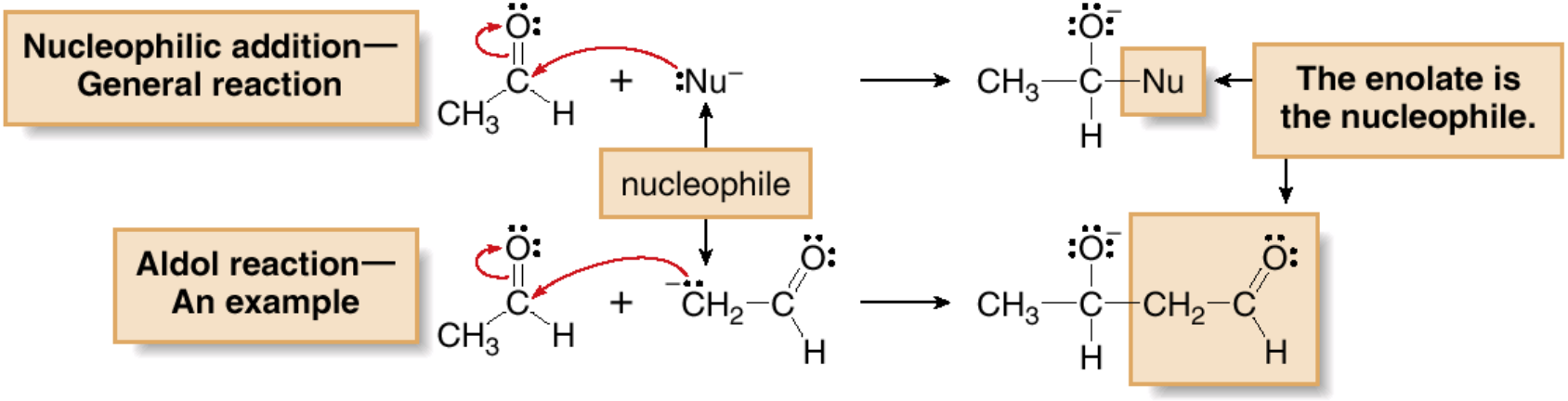
- The aldol reaction is a reversible equilibrium, so the position of the equilibrium depends on the base and the carbonyl compound.
- $^{-}$OH Is the base typically used in an aldol reaction. Although with $^{-}$OH only a small amount of enolate is formed, this is appropriate because the starting aldehyde is needed to react with the enolate in the second step of the reaction.
- Aldol reactions can be carried out with either aldehydes or ketones. With aldehydes, the equilibrium usually favors products, but with ketones the equilibrium favors the starting materials. However, there are ways of driving the equilibrium to the right.

Carbonyl Condensation Reactions

The Aldol Reaction

- **Recall that the characteristic reaction of aldehydes and ketones is nucleophilic addition. An aldol reaction is a nucleophilic addition in which an enolate is the nucleophile.**

Figure 24.1
The aldol reaction—An example of nucleophilic addition



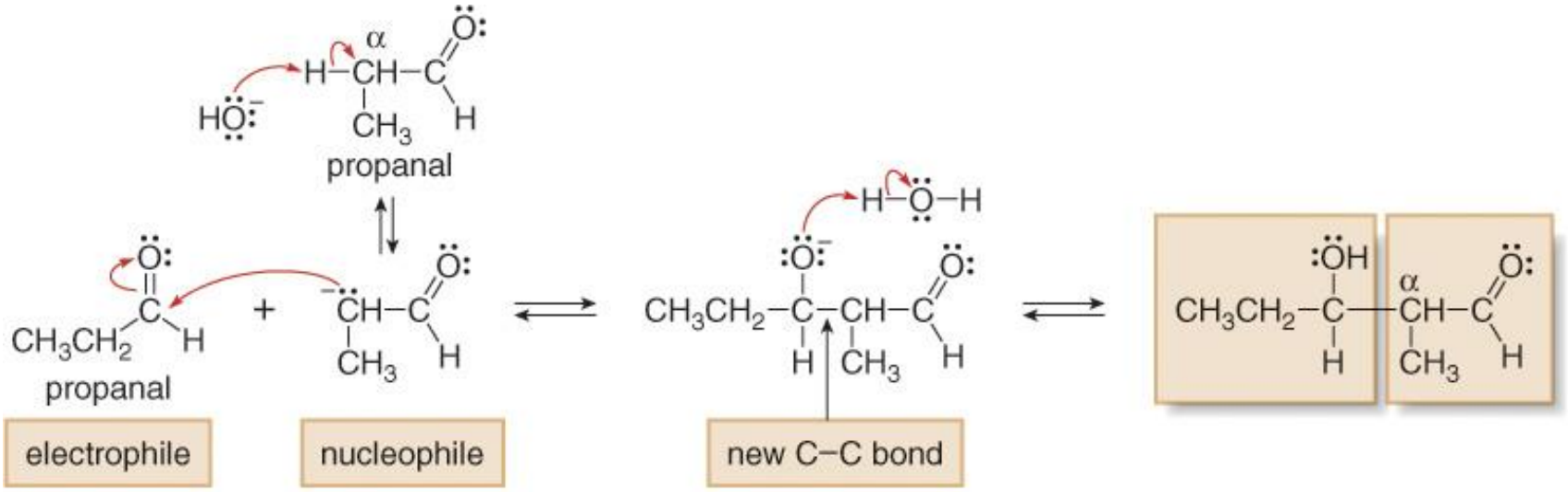
- Aldehydes and ketones react by nucleophilic addition. In an aldol reaction, an enolate is the nucleophile that adds to the carbonyl group.

Carbonyl Condensation Reactions

The Aldol Reaction

- **A second example of an aldol reaction is shown with propanal as the starting material. The two molecules of the aldehyde that participate in the aldol reaction react in opposite ways.**

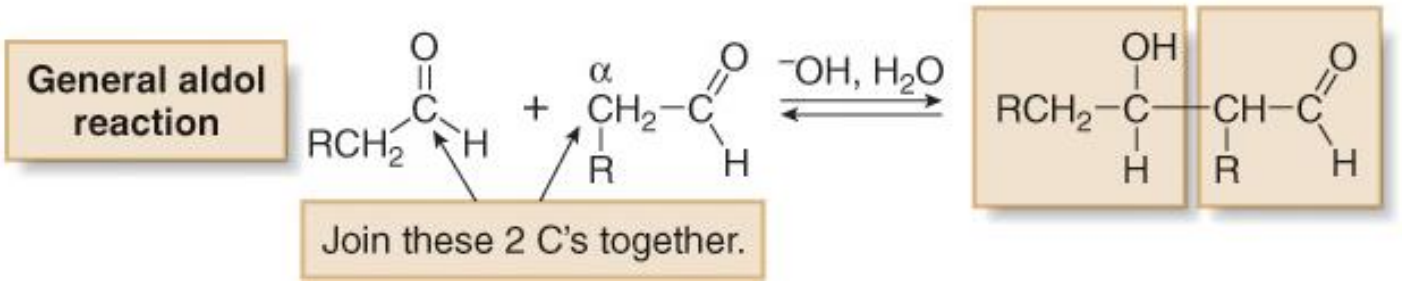
  - One molecule of propanal becomes an enolate—an electron-rich *nucleophile.*
  - One molecule of propanal serves as the *electrophile* because its carbonyl carbon is electron deficient.



Carbonyl Condensation Reactions

The Aldol Reaction

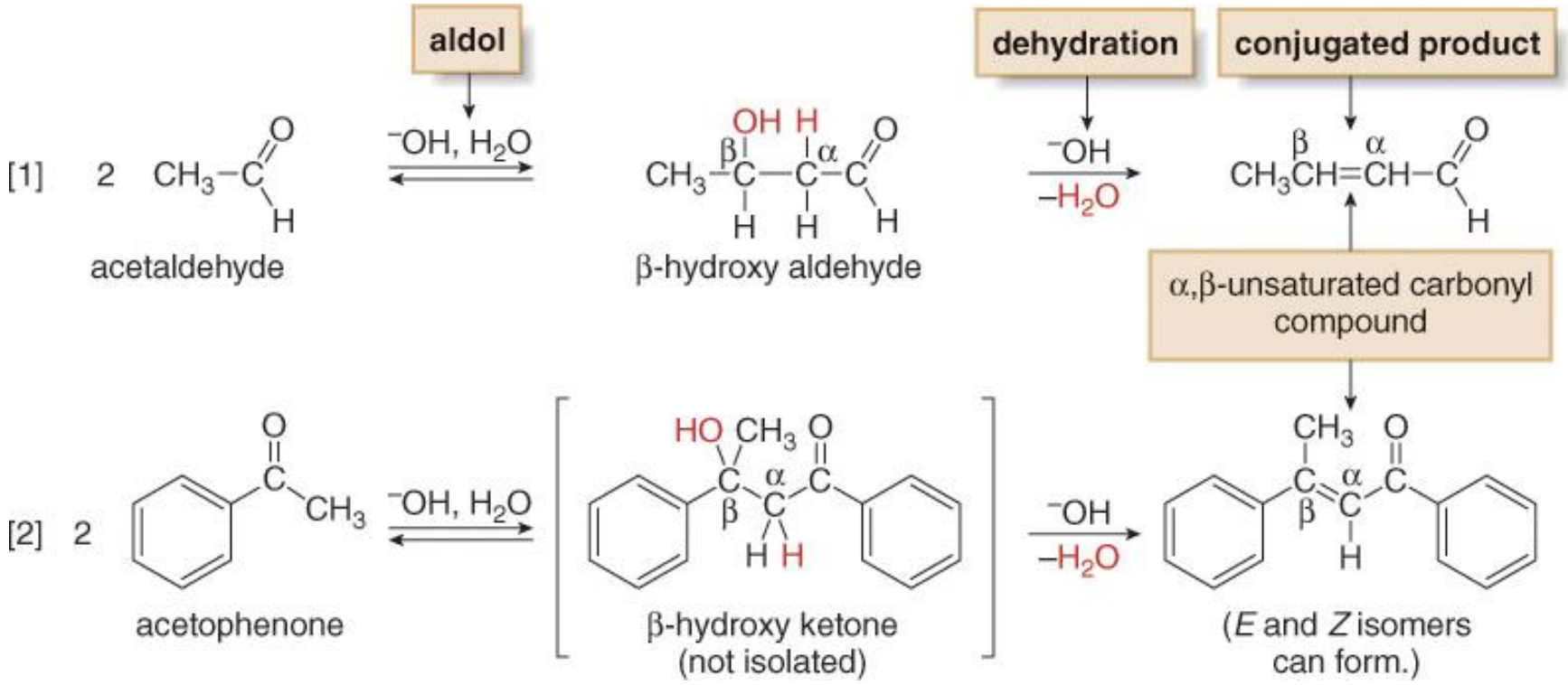
- These examples illustrate the general features of the aldol reaction. The α carbon of one carbonyl component becomes bonded to the carbonyl carbon of the other component.



Carbonyl Condensation Reactions

The Aldol Reaction—Dehydration of the Aldol Product

- Under the basic reaction conditions, the initial aldol product is often not isolated. Instead, it loses the elements of H_2O from the α and β carbons to form an α,β-unsaturated carbonyl compound.



Carbonyl Condensation Reactions

The Aldol Reaction

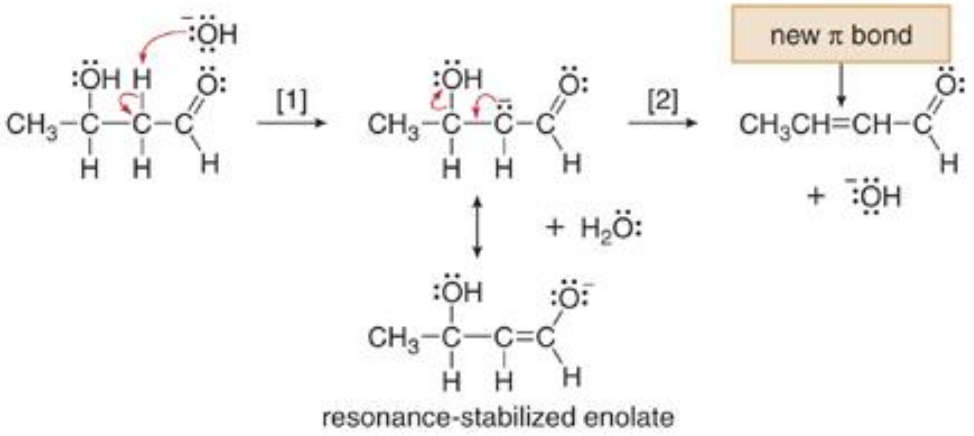
- An aldol reaction is often called an aldol condensation because the β-hydroxy carbonyl compound that is initially formed loses H_2O by dehydration. A condensation reaction is one in which a small molecule, in this case, H_2O, is eliminated during the reaction.
- It may or may not be possible to isolate the β-hydroxy carbonyl compound under the conditions of the aldol reaction. When the α,β-unsaturated carbonyl compound is further conjugated with a carbon-carbon double bond or a benzene ring (as is the case in reaction 2), elimination of H_2O is spontaneous and the β-hydroxy carbonyl compound cannot be isolated.

Carbonyl Condensation Reactions

The Aldol Reaction

- **The mechanism of dehydration consists of two steps: deprotonation followed by loss of ^{-}OH.**

Mechanism 24.2 **Dehydration of β-Hydroxy Carbonyl Compounds with Base**

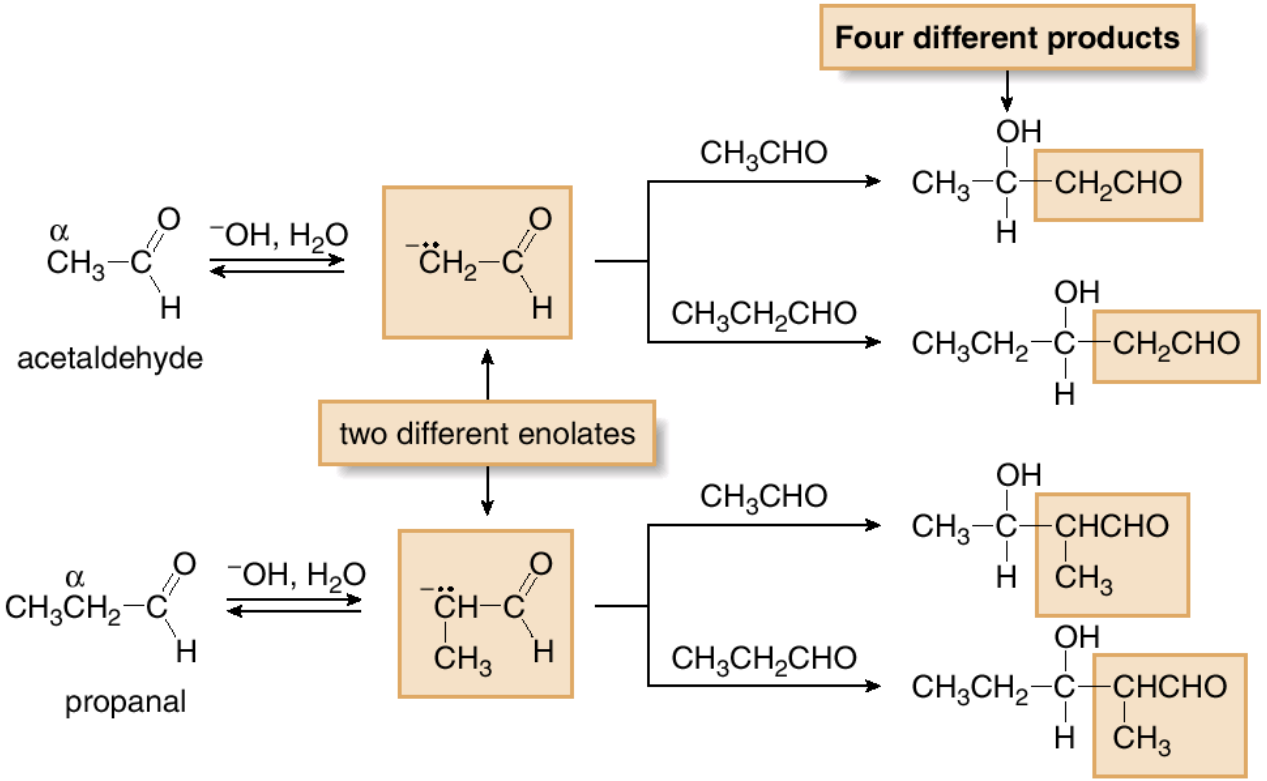


- In Step [1], base removes a proton from the α carbon, thus forming a resonance-stabilized enolate.
- In Step [2], the electron pair of the enolate forms the π bond as ^{-}OH is eliminated.

Carbonyl Condensation Reactions

Crossed Aldol Reactions

- **Sometimes it is possible to carry out an aldol reaction between two different carbonyl compounds. Such reactions are called crossed or mixed aldol reactions.**



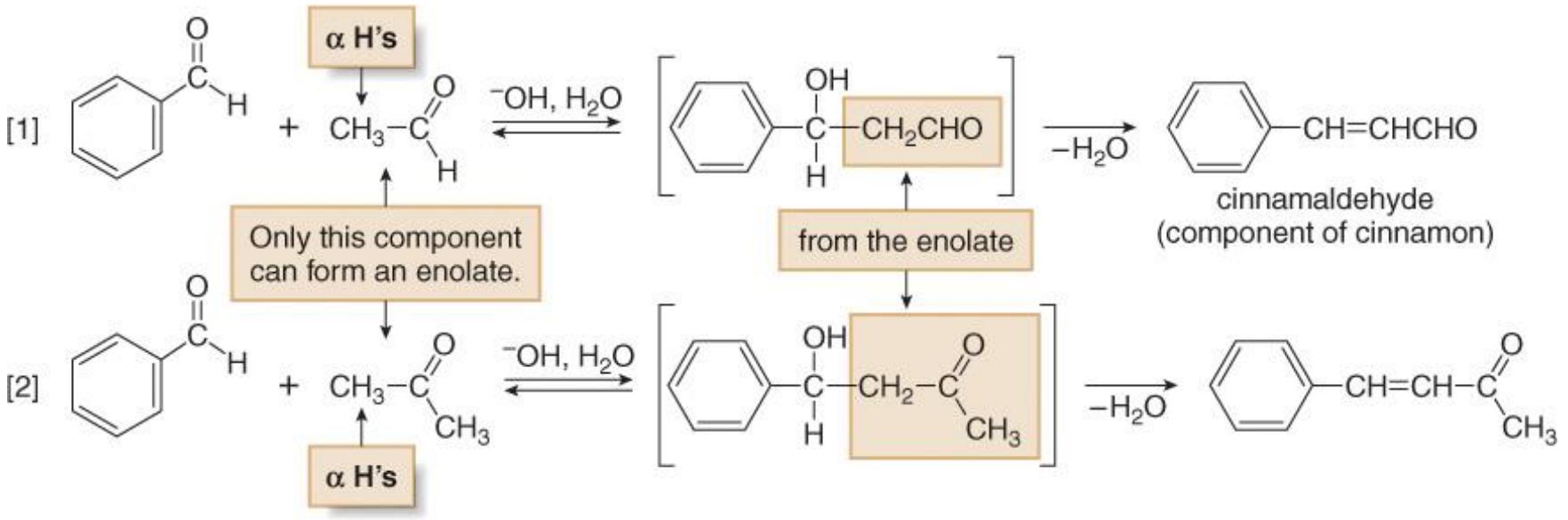
- Conclusion: When two different aldehydes have α hydrogens, a crossed aldol reaction is *not* synthetically useful.

Carbonyl Condensation Reactions

Crossed Aldol Reactions

Crossed aldols are synthetically useful in two different situations:

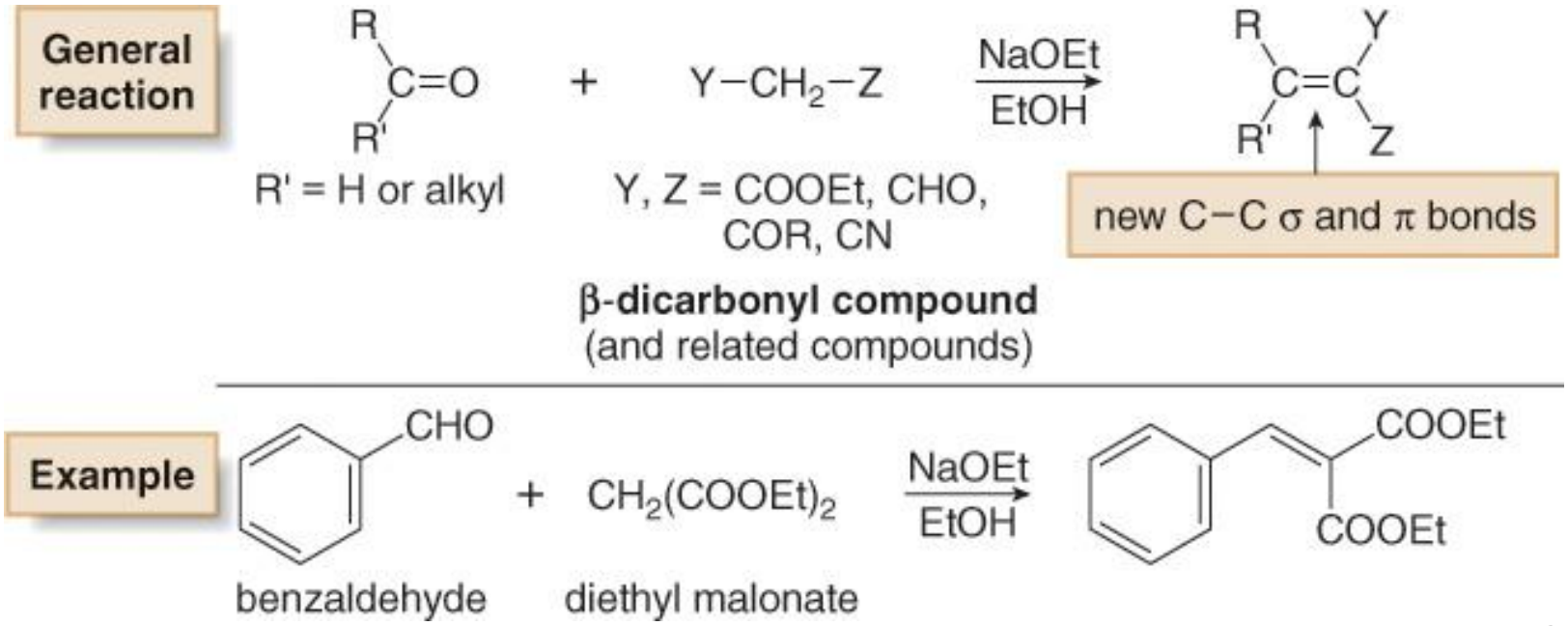
[1] When only one carbonyl component has α hydrogens—such cases often lead to the formation of only one product.



Carbonyl Condensation Reactions

Crossed Aldol Reactions

[2] When one carbonyl component has especially acidic α hydrogens, these hydrogens are more readily removed than the other α H atoms. As a result, the β-dicarbonyl compound always becomes the enolate component of the aldol reaction.



Carbonyl Condensation Reactions

Crossed Aldol Reactions

Figure 24.2 below shows the steps for the crossed aldol reaction between diethylmalonate and benzaldehyde. In this type of crossed aldol reaction, the initial β-hydroxy compound always loses water to form the highly conjugated product.

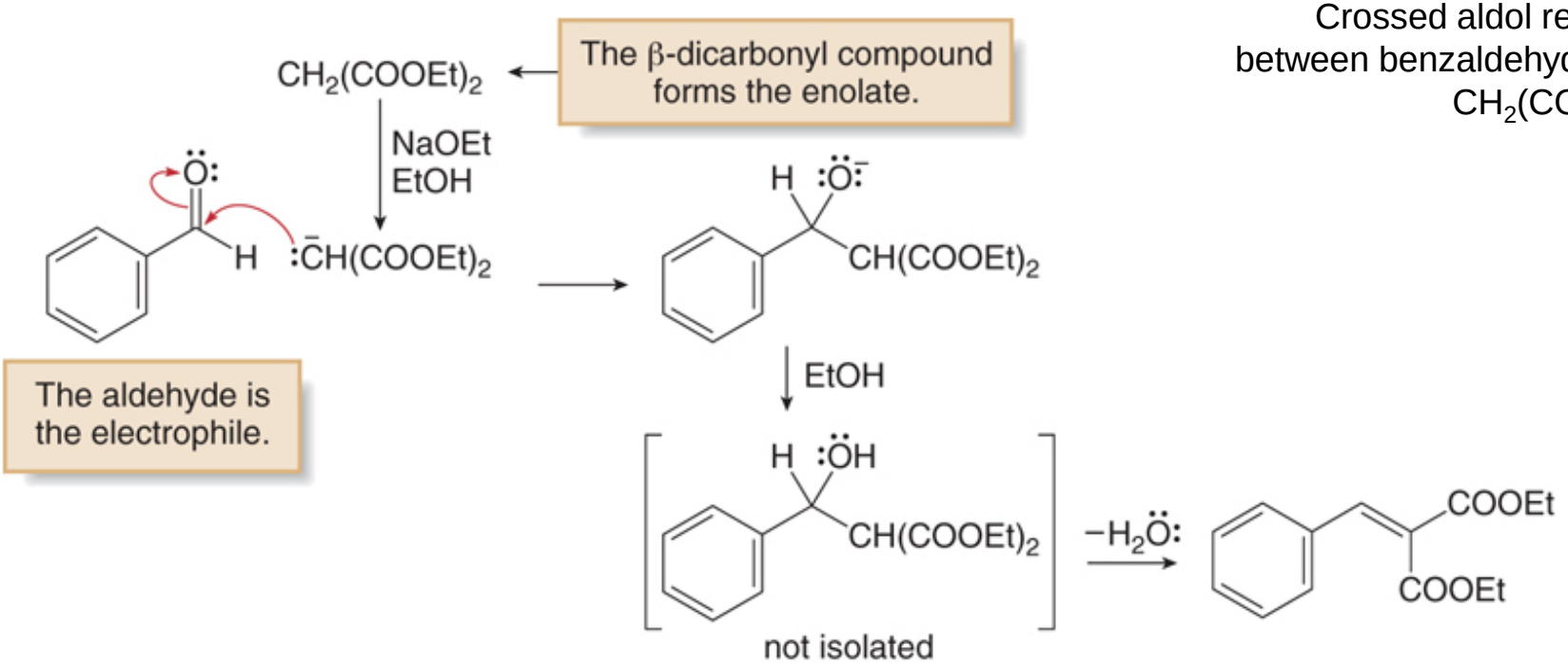


Figure 24.2
Crossed aldol reaction between benzaldehyde and $CH_2(COOEt)_2$


Thank
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