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Study Notes On Aldol Condensation Reaction

ALDOL CONDENSATION

Aldol condensation reaction is a Carbon-Carbon bond forming reaction in which an enolate ion reacts with a carbonyl compound in presence of suitable acid or a base to form a β-hydroxy aldehyde or β-hydroxy ketone. This further undergoes dehydration to give conjugated enone. Dehydration may be accompanied by decarboxylation when an activated carboxyl group is present.

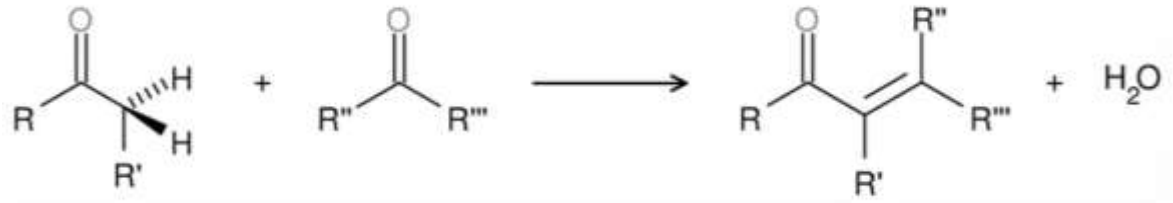
It involves the nucleophilic addition of a ketone enolate to an aldehyde to form a β-hydroxy ketone, or β-hydroxy aldehyde (aldol).

Aldol is a structural unit which is a union of an aldehyde and alcohol, i.e., Aldol = aldehyde + alcohol.

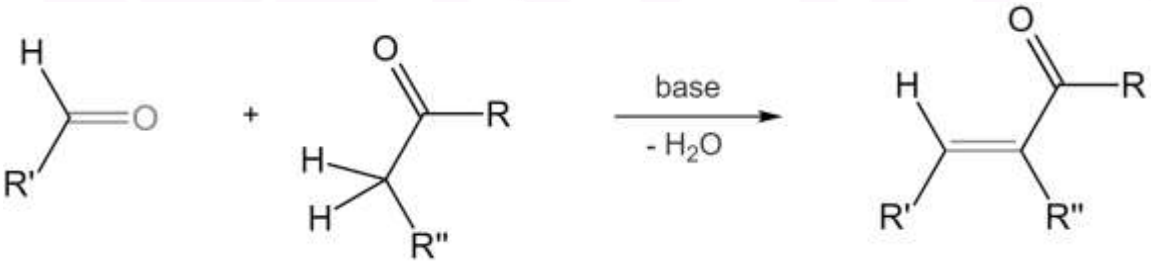
The fundamental steps of the aldol condensation reaction are:

1. Aldol (aldehyde + alcohol) reaction
2. Dehydration/Elimination reaction

General reaction-

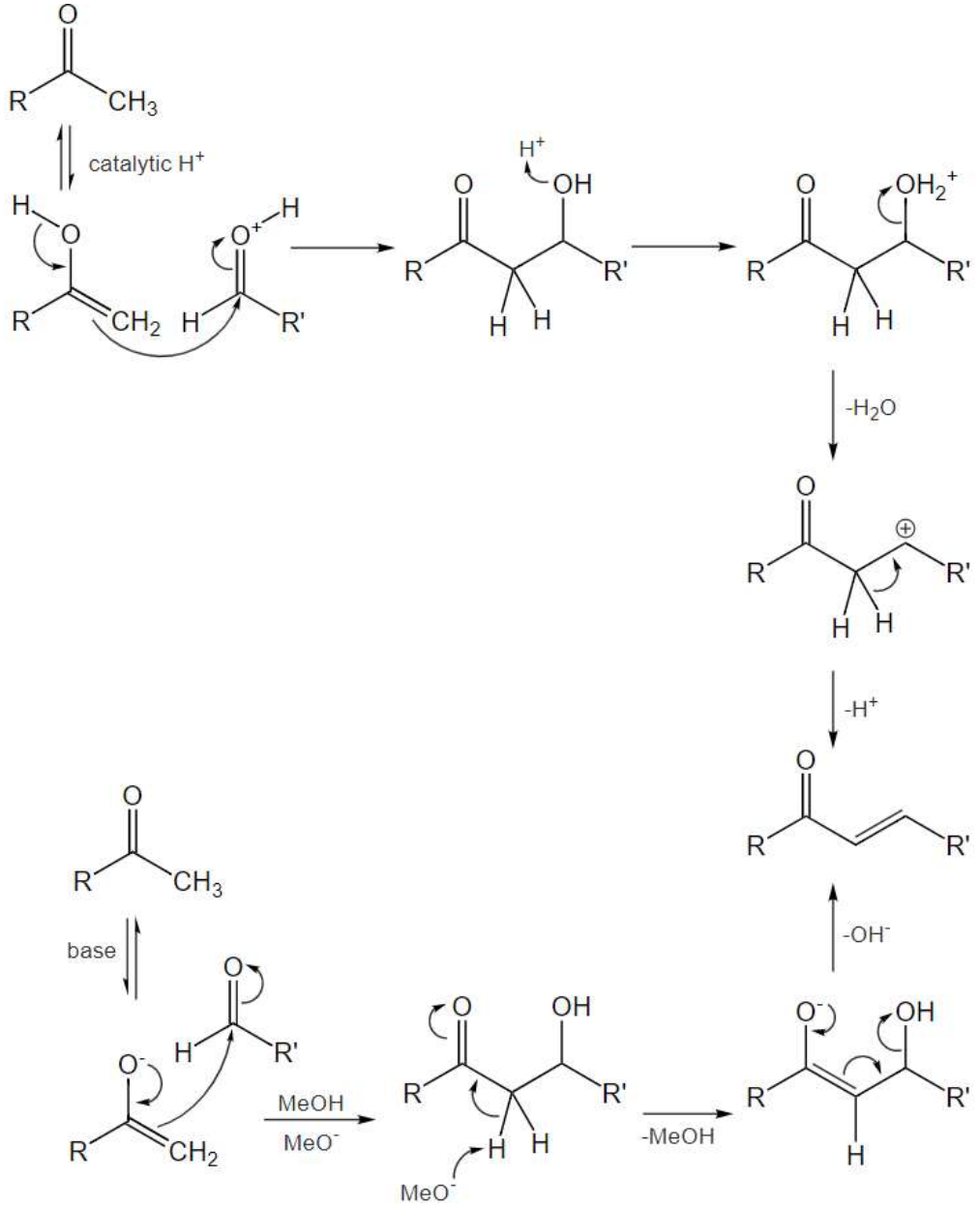


Or,



Reaction Mechanism-

We can summarize acid and base catalyzed reaction in this manner-



The aldol addition product can be dehydrated through any of these two mechanisms-

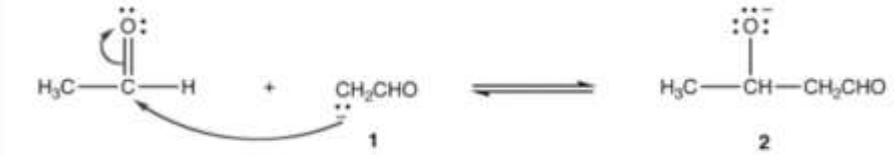
(i) In presence of strong base like- potassium t-butoxide, potassium hydroxide or sodium hydride; which deprotonates the product to an enolate.
Here, elimination occurs via the E1cB mechanism.

(ii) In presence of acid, dehydration proceeds via E1 mechanism.
Depending on the nature of the desired product, the aldol condensation may be carried out under two types of conditions: *kinetic control* or *thermodynamic control*.

The reaction mechanism of Aldol condensation can also be explained step by step as follows-

Step 01: The hydroxide ion deprotonates the aldehyde.

Step 02: Enolate ion formed above adds to the unreacted aldehyde.



Step 03: Alkoxide ion formed above is protonated by water.

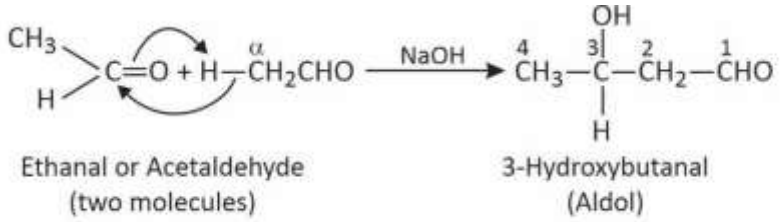
Step 04: Hydroxide ion converts some amount of aldol into enolate ion.

Step 05: Enolate ion further loses a hydroxide ion.

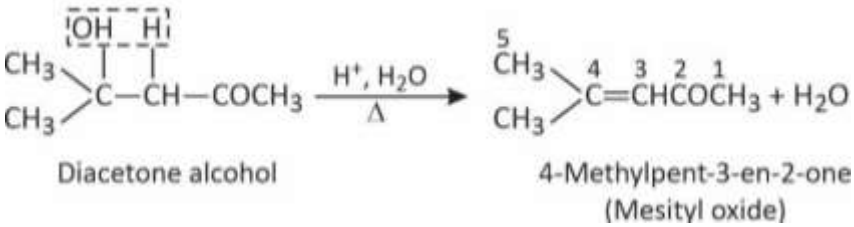
Note:

- The addition products formed from the Aldol Addition reaction can easily be converted (in situ) to α,β-unsaturated carbonyl compounds, either thermally or under acidic or basic catalysis. For spontaneous dehydration, the driving force is the formation of the conjugated system.
- In an aldol condensation between an aldehyde and a ketone, the ketone acts as the nucleophile as its carbonyl carbon does not possess high electrophilic character due to the +I effect and steric hindrance.

Example-

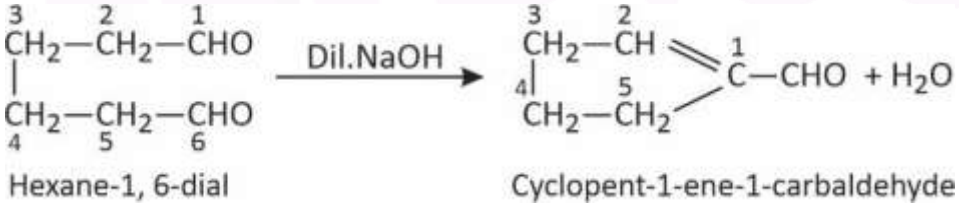


Note: The products of aldol condensation when heated with dilute acids undergo dehydration which further yields α, β-unsaturated aldehydes or ketones. Example-



Intramolecular Aldol Condensation:

If a compound contains two aldehydes/ketones or one aldehyde and one ketone group at 1,6 or 1,7-positions with respect to to each other, intramolecular aldol condensation occurs to yield α, β-unsaturated aldehyde/ketone.



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