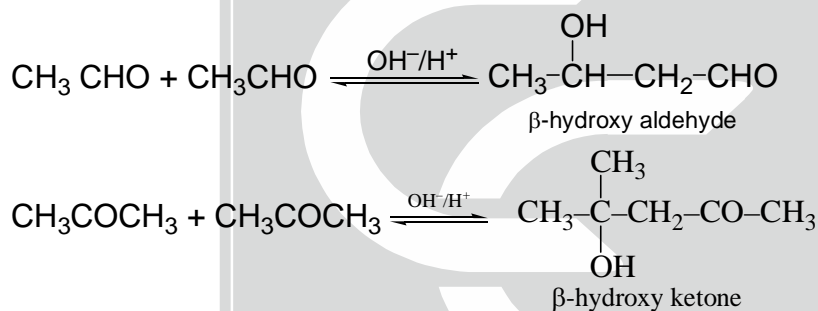


Named Reactions

6.1. Aldol Condensation

Aldehyde containing an α -hydrogen atom undergoes a reversible self addition in presence of acid or usually in dil. alkali to give condensation product β -hydroxy aldehyde or ketone. In every case the addition occurs in such a way that α -carbon of the first carbonyl compound get attached to the carbonyl carbon of the second.



Note: If an aldehyde and ketone do not contain α -H, the self condensation reaction donot occur.

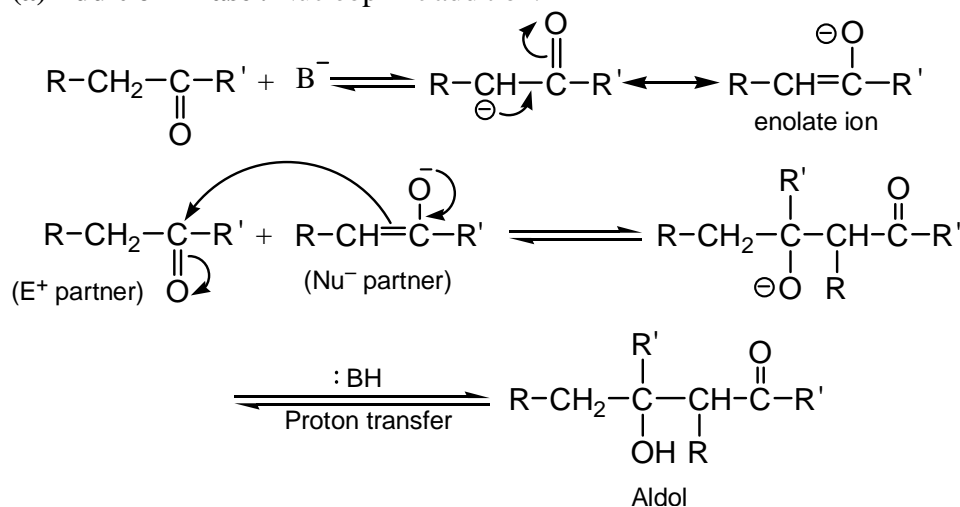
e.g. ArCHO, HCHO, $(\text{CH}_3)_3\text{C-CHO}$, Ar-CO-Ar,

Ar-C(=O)-CR₃ can't undergo self condensation due to absence of α H-atom.

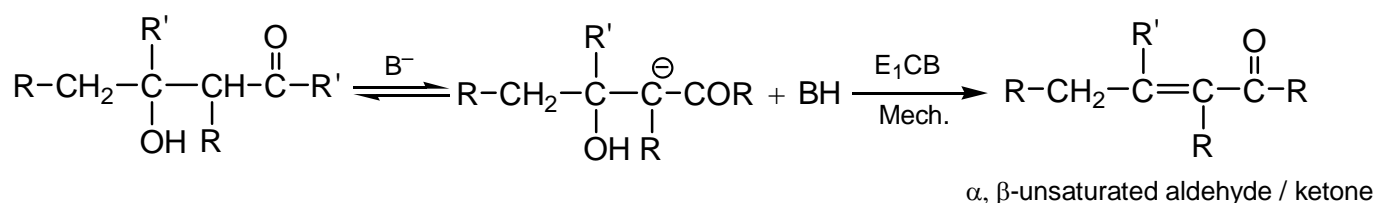
Mechanism:

(1) Base - Catalysed mechanism

(a) Addition Phase : Nucleophilic addition.



Proton transfer reactions are always reversible reaction.

(b) Dehydration Phase :


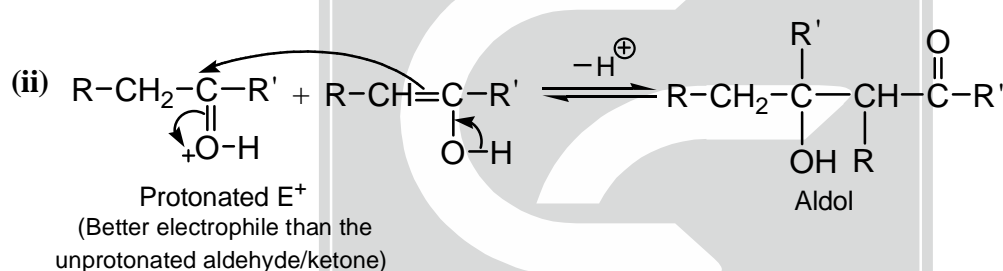
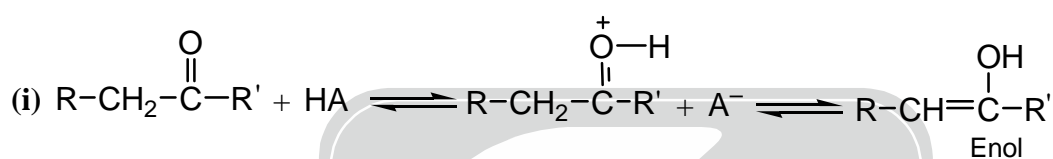
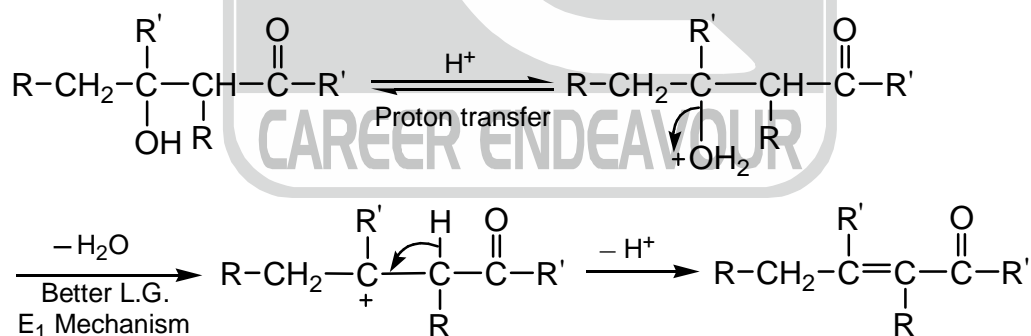
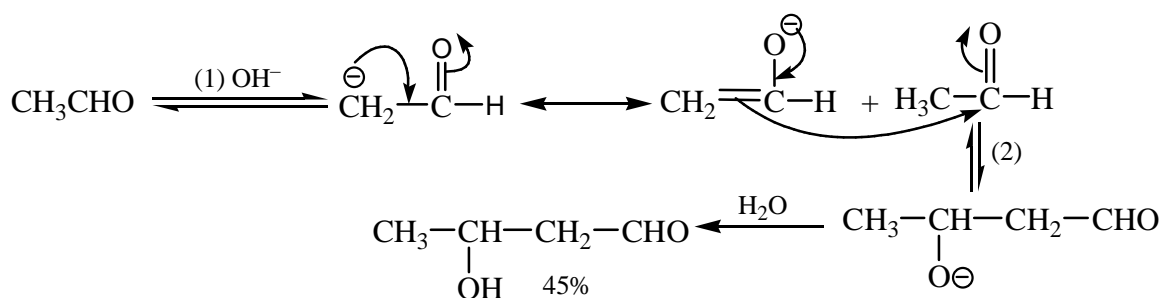
In general the aldol reaction is reversible in both acidic and basic condition, but when reaction conditions are favourable to cause dehydration, predominantly in acidic medium the reaction goes to completion.

The reaction is unfavourable usually for acyclic ketones this is because -

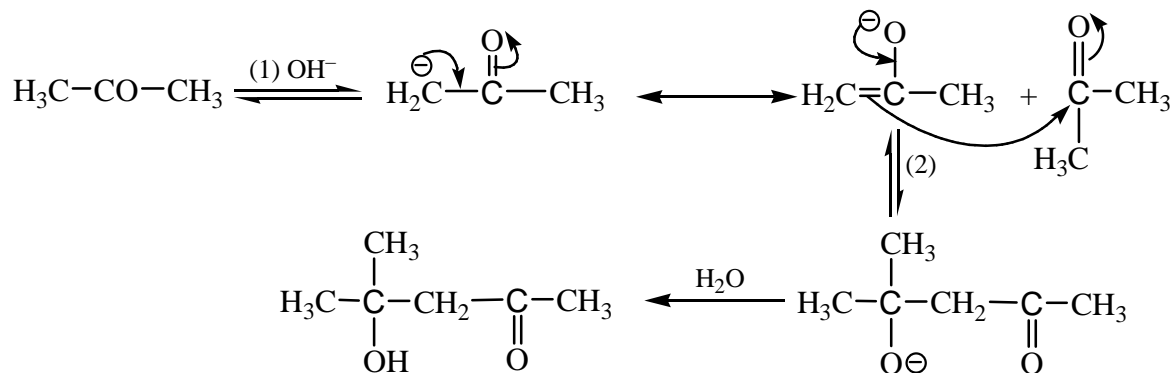
1. Carbonyl carbon of the ketone is less electrophilic because of the +I effect of the alkyl groups.
2. Due to steric hindrance the probability of nucleophilic attack by enolate or enol is decreased.

(2) Acid Catalysed Mechanism :

Enol is less nucleophilic than enolate.

(a) Addition Phase :

(b) Dehydration Phase :

Experimental Evidence :
Aldehyde :


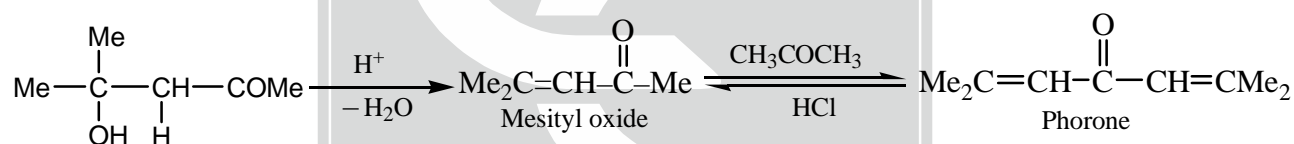
Ketone :



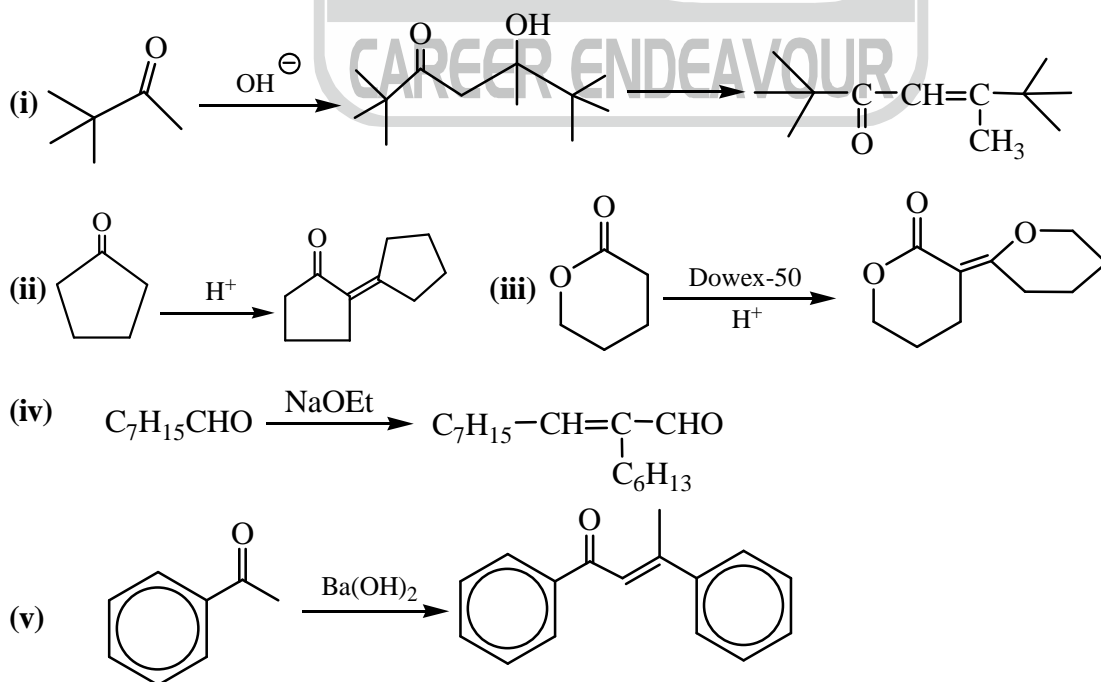
Carrying out a reaction with D₂O fails to result in the incorporation of any deuterium to the CH₃ group of aldehyde to produce D-CH₂-CHO but it produces D-CH₂-COCH₃ in case of ketone. This indicates that the step two is faster than reversal of state one in case of aldehyde and slower in case of ketone.

The reaction can be made of synthetic importance by :

- (1) Continuous distillation of the products in a Soxhlet Apparatus (Reaction move forward following Le - Chatelier Principle) using Ba(OH)₂ base.
- (2) Using acid catalysis tendency of dehydration of aldol products is increased producing more stable α-β unsaturated aldehyde / ketone
- (3) To stop at the aldol stage the best catalyst are *basic ion exchange resin*.
- (4) A 3° alcohol always undergoes dehydration through E₁ mechanism. E₁ (3° > 2° > 1°)

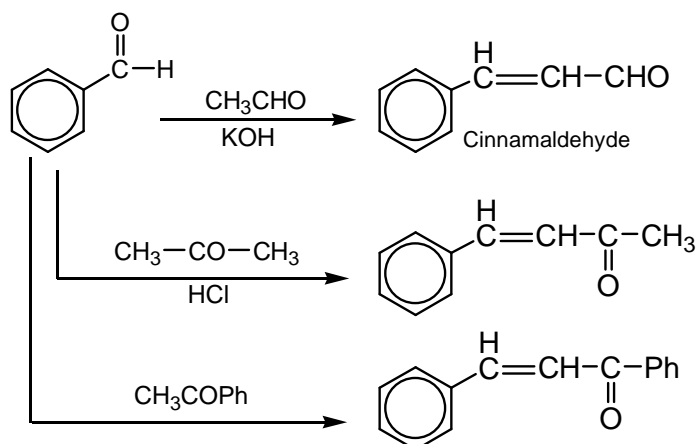


Example:

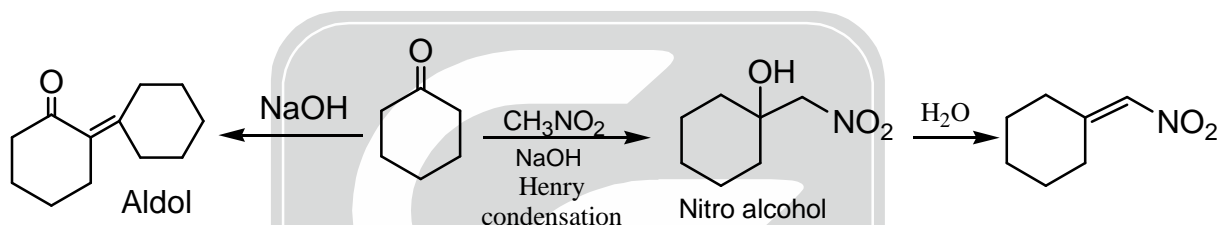


Crossed-Aldol / Mixed Aldol : (Claisen-Schmidt Condensation)

When one of the partner in a crossed aldol condensation is benzaldehyde which can only act as a E⁺ and any other aldehyde or ketone which can form either enol or enolate then this type of mixed condensation is known as Claisen - Schmidt Condensation.



Electron donating groups in benzaldehyde will make the reaction slower and e⁻ withdrawing groups make the reaction faster.



Conditions For Crossed Aldol :

- (i) Only one enolizable component (aldehyde / ketone having $\alpha\text{-H}$)
- (ii) No other compound containing more acidic hydrogens than aldehyde/ketone eg. CH_3NO_2
- (iii) The carbonyl E⁺ should be more reactive than the compound being enolised)

Example:

