DATE: Aldol Condensation

Aldehyde having α-hydrogen undergo self condensation on warming with dilute or mild base to give β-hydroxy aldehyde called aldol (aldehyde + alcohol). This reaction is known as aldol condensation. e.g. The reaction of acetaldehyde with base under mild condition

$$CH_3CHO + CH_3CHO \underset{}{\overset{OH^-}{\rightleftharpoons}} CH_3CH(OH)CH_2CHO \text{ (Acetaldol)}$$

Various basic reagents such as dil NaOH, aq alkali carbonate, alkali metal alkoxide etc. may be used. The reaction is not favourable for ketones. It can occur between

(a) Two identical or different aldehyde
(b) Two identical or different ketone
(c) An aldehyde and a ketone

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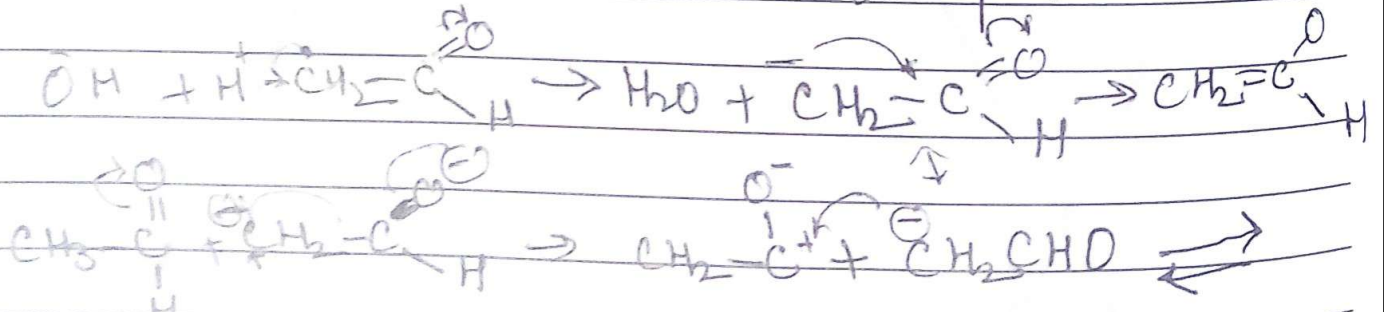
When the condensation between two different carbonyl compounds, it is called cross condensation. Mechanism :-

The first step involve the formation of a resonance stabilized enolate anion by the removal α-hydrogen from the aldehyde by the base. In the second step the enolate anion attack the carbonyl carbon of the second ~~no~~ ~~mole~~ molecule of the aldehyde to form alkoxide ion, the latter then takes up a proton from the solvent to yield aldol in the third step.



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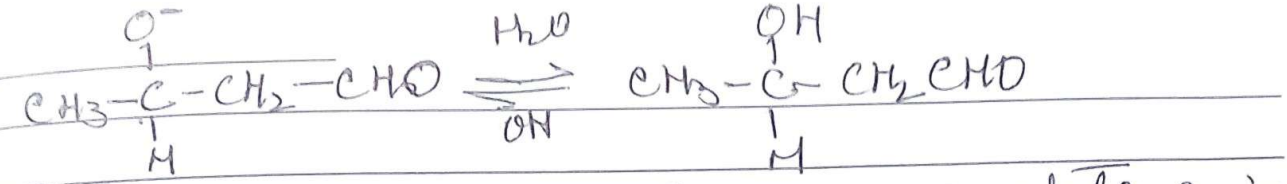
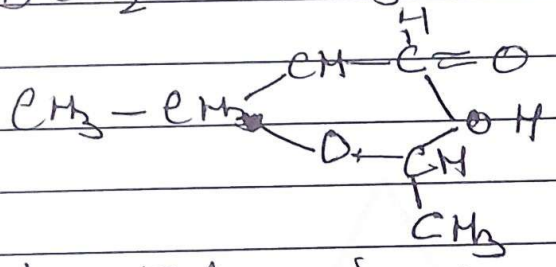


Thus the overall reaction of enolate anion to the carbonyl double bond. Acetaldol is isolated as a cyclic hemiacetal.

$CH_3CH(OH)CH_2CHO + CH_3CHO \longrightarrow$



cyclic Hemiacetal.

Aldol is isolated in the mild condition using K_2CO_3 as base. The reaction between two ketones is not very successful. The equilibrium is not favorable.

$2CH_3COCH_3 \xrightleftharpoons{OH^\ominus} CH_3-C(CH_3)(OH)-CH_2-CO-CH_3$

This is because the carbonyl carbon of ketone bears positive (due to +I effect) the more sterically hindered relative to

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aldehyde. This reduces the nucleophilic attack on the carbonyl carbon. However it is possible to prepare diacetone alcohol in reasonable good yield by boiling acetone with solid $Ba(OH)_2$ in specially designed apparatus.

Silent features of aldol condensation —

(a) Aldol are easily dehydrated to α, β-unsaturated compound on heating alone or with acid or base

$$CH_3CH(OH)CH_2-CHO \xrightarrow[\Delta]{H^+ \text{ or } OH^-} CH_3-CH=CH-CHO$$

but-2-enal aldehyde

(b) When aldol condensation is carried out in the presence of strong alkali repeated condensation and dehydration results in the formation of resin.

$$CH_3-CH=CH-CHO \xrightarrow[OH^-]{CH_3CHO} CH_3-CH=CH-CH=CH-CH=CH-CHO$$

Resin

(c) The condensation is promoted by $-I$ effect and reduces the $+I$ effect.

(d) The reaction equilibrium is favourable for aldehyde but much less favourable for ketones.