

Experiment 9

Aldol Condensation

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Aldol Condensation:

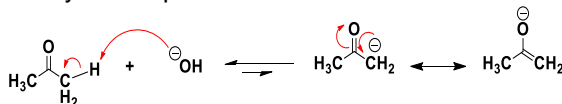
Aldol: (Aldehyde and alcohol): The reaction between an **aldehyde/ketone** and an **aromatic carbonyl compound** lacking an α -hydrogen (cross aldol condensation)

The **purpose** of this experiment is to synthesis dibenzalacetone (trans, trans-1,5-diphenyl-1,4-pentadien-3-one) through the aldol condensation of acetone with benzaldehyde. (**Claisen-Schmidt** condensation).

Why **sp^3 hydrogens** alpha (α) to carbonyl group are acidic?

The synthesis begins by using **strong base** to generate the acetone **enolate** ion. Water (not shown) is formed as a byproduct.

The equilibrium position of this reaction strongly favors the starting acetone, and the amount of acetone enolate formed is quite small; however the enolate is extremely nucleophilic



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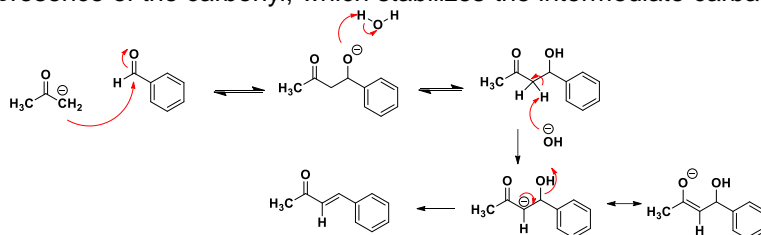
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Aldol Condensation:

Being a very strong **nucleophile**, this enolate attacks the carbonyl of benzaldehyde and forms a **β -carbonyl alkoxide** ion.

This **alkoxide** ion abstracts a proton from **water** to form a beta hydroxy ketone. Sodium hydroxide abstracts **another acidic** alpha H to form a stabilized carbanion. The electron pair on carbon is used to eliminate the hydroxide ion, forming an alpha-beta unsaturated ketone in an **irreversible** step.

This is an example of an **$E1_{CB}$ (Elimination Unimolecular Conjugate Base)** mechanism. Note that in this reaction, the intermediate alcohol is dehydrated under basic conditions, unlike most alcohol dehydrations, which are generally **$E1$** mechanisms under **acid conditions**. The $E1_{CB}$ mechanism is made possible by the presence of the carbonyl, which stabilizes the intermediate carbanion.

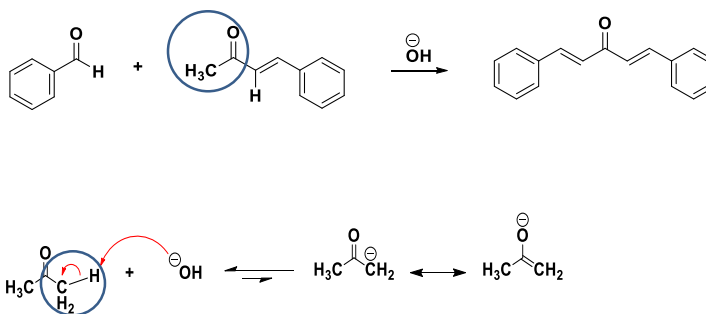


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Aldol Condensation:

Since this newly formed ketone still possesses alpha hydrogens, it too can undergo the same enolate condensation reaction with a second mole of benzaldehyde to form the final product:



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Aldol Condensation:

Procedure:

1- Place into a 500-mL Erlenmeyer flask the following quantities: **1.6g acetone**(2.0 ml, 0.028 mole) and **6.3g benzaldehyde** (6.0 ml, 0.059 mole) and 50 ml. of ethanol.

Note: it is important to maintain a **1:2 molar ratio** of acetone to benzaldehyde.

2-Add 60 ml. of 10% sodium hydroxide and shake the flask for 15-20 minutes. Note any color changes that may occur.

3-The reaction mixture should be first clear, then it becomes milky and a precipitate forms a bit later.

4- Isolate the yellow precipitate by suction filtration using water to transfer and wash the product.

5- Press the solid onto the filter paper to remove as much water as possible, then turn off the suction and break up lumps of crystals with a spatula.

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Aldol Condensation:

Procedure-Continued

6- Add to the solid on the filter paper an ice-cold solution of ethanol and acetic acid (1 ml. of acetic acid in 25 ml of ethanol). Let it stand for 1 minute, then apply the suction filtration for an additional 5-10 minutes to allow the product to air dry.

(The **acid** treatment removes traces of the remaining base)

7-Recrystallize the crude product place it in an Erlenmeyer flask of appropriate size and add enough ethanol to make a thick slurry of the crystals. Place a boiling chip in the flask (to prevent "bumping") and warm the mixture on a steam bath or hot plate.

While it is boiling gently, slowly add ethanol until the crystals just dissolve. Filter the hot solution.

Allow the solution to cool until crystals have formed and it is no longer hot. You may cool the mixture in ice at this point.

After crystals have stopped forming, collect the recrystallized dibenzalacetone in a Buchner funnel and wash the crystals with a little cold ethanol. Determine the melting point and weight of the crystals.

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Aldol Condensation:

Compound	MW	Mp	Bp	Density
Benzaldehyde	106.13		178°C	1.04
Acetone (reagent)	58.08		56°C	0.79
Dibenzalacetone	234.30	113°C		