EXPERIMENT 9

Aldol Condensation
Synthesis of dibenzalacetone

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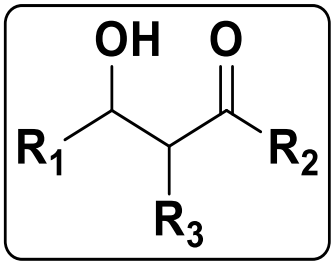

Generalized structure of the aldol moiety

- **Aldol: Aldehyde and alcohol**
- A class of compounds containing both an alcohol and an aldehyde functional group, formed by a condensation reaction between aldehyde or ketone molecules.

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

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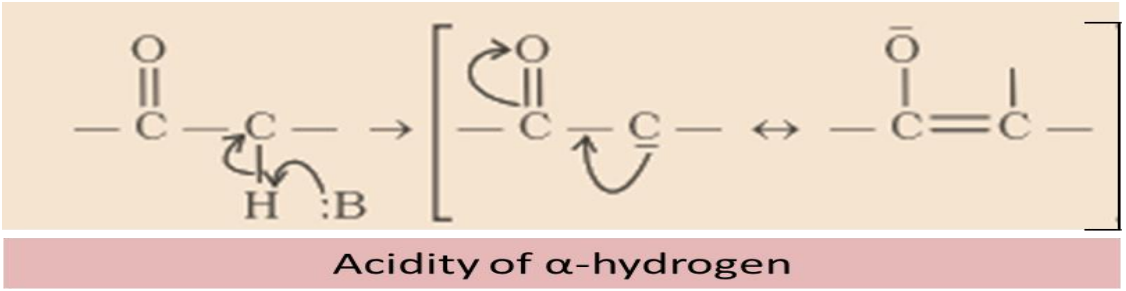
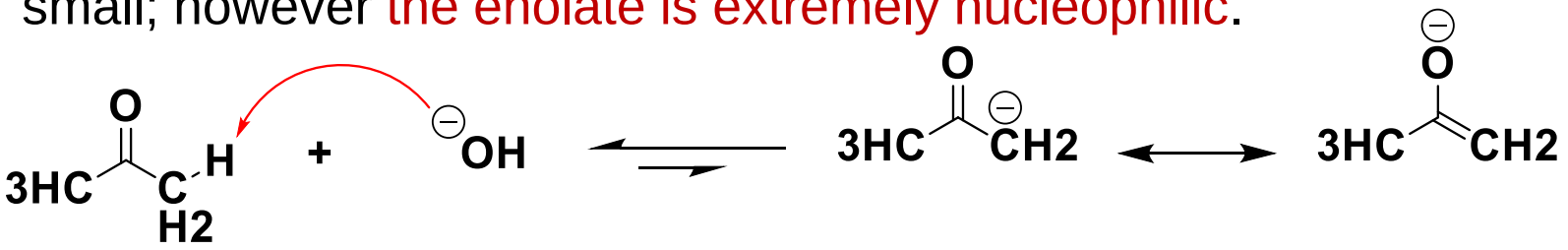
- The synthesis begins by using strong base to generate the acetone enolate ion. Water (not shown) is formed as a byproduct.



Acidity of α-hydrogen

- 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.



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

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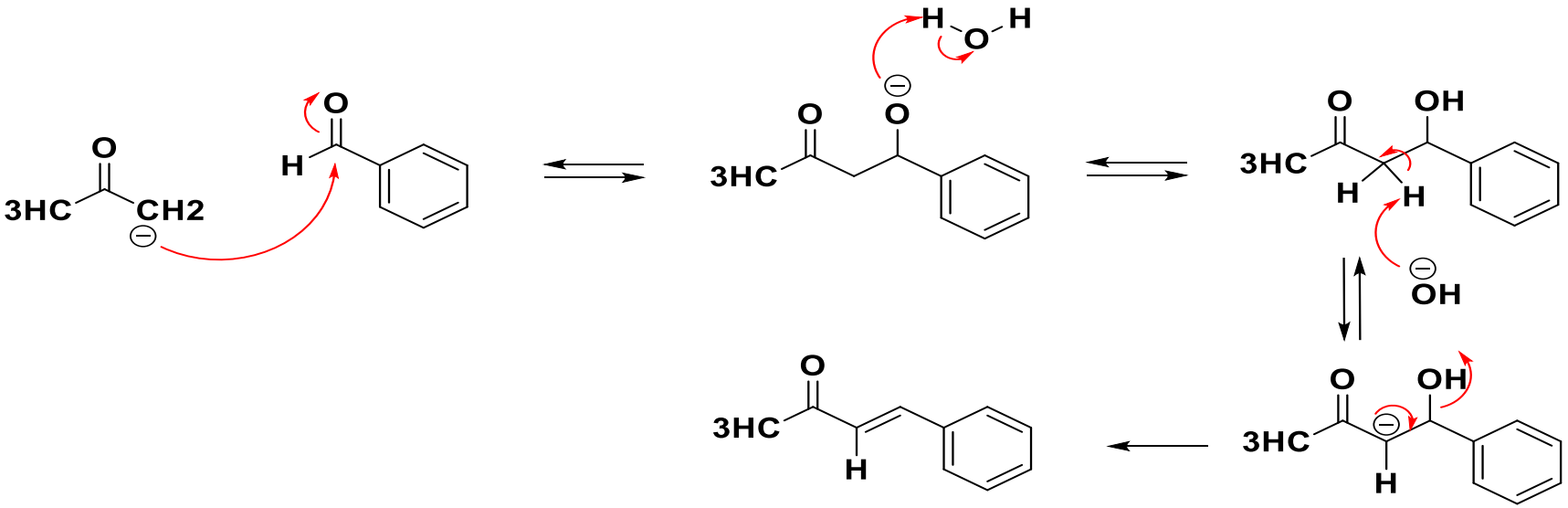
- This alkoxide ion abstracts a proton from water to form a **beta hydroxy ketone.**
- Sodium hydroxide abstracts another acidic alpha H to form a stabilized carbanion. The electron pair on carbon is used to eliminate the hydroxide ion, forming a alpha-beta unsaturated ketone in an irreversible step.



- This is an example of an **E1c** (**E**limination **U**nimolecular **c**onjugate **B**ase) mechanism.

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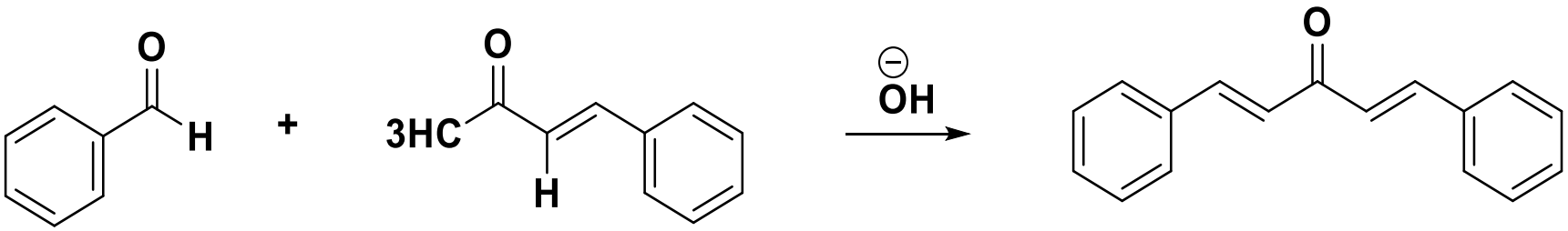
- **Note:** In this reaction, the intermediate alcohol is dehydrated under basic conditions, unlike most alcohol dehydrations, which are generally E1 mechanisms under acid conditions. The E1cb mechanism is made possible by the presence of the carbonyl, which stabilizes the intermediate carbanion.
- Since this newly formed ketone still possess 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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- **Experimental 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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6. Add to the solid on the filter paper an ice-cold solution of ethanol and acetic acid (**1.0 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:

a) Place it in an Erlenmeyer flask of appropriate size and add enough ethanol to make a thick slurry of the crystals.

b) Place a boiling chip in the flask (to prevent "bumping") and warm the mixture on a hot plate.

c) While it is boiling gently, slowly add ethanol until the crystals just dissolve.

d) 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.)

e) After crystals have stopped forming, collect the recrystallized dibenzalacetone in a Buchner funnel

f) Wash the crystals with a little cold ethanol.

g) Determine the melting point ,the weight of the crystals and the percentage yield.

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Physical properties of reactants and products

Compound	Molar mass	M.p.	B.p.	Density
Benzaldehyde	106.13		178°C	1.04
Acetone	58.08		56°C	0.79
Dibenzalacetone	234.30	113°C		