Experiment 9 • The Claisen-Schmidt reaction: 
A base-catalyzed aldol condensation

Pre-lab questions
Answer these questions and hand them to the TF before beginning work.

1 What is the purpose of this experiment?

2 Heat is usually required to promote the dehydration of the intermediate β-hydroxycarbonyl. Why does the dehydration in the present experiment take place even though the reaction is carried out at room temperature?

3 Which compound is expected to have the lower frequency carbonyl stretch, acetone or dibenzylideneacetone? Justify your answer.
Experiment 9 • The Claisen-Schmidt reaction: A base-catalyzed aldol condensation
Pre-lab questions
Continued

4 Using the Claisen-Schmidt reaction, how would you synthesize benzalacetone (PhCH=CHCOCH₃)? Benzalacetophenone (PhCH=CHCOPh)?

5 The procedure directs that benzaldehyde should be mixed with the theoretical amount of anhydrous acetone; show the calculation of this quantity in grams and in milliliters.
Experiment 9 • The Claisen-Schmidt reaction:  
A base-catalyzed aldol condensation  
Pre-lab questions  
Continued

6 How will you recrystallize the dibenzylideneacetone from ethanol? Provide an outline of the procedure.

7 In general, nucleophiles attack the carbonyl carbon of an aldehyde more readily than the carbonyl carbon of a ketone. Explain why is this so.
The name dibenzylideneacetone (systematic name: 1,5-diphenyl-1,4-pentadien-3-one) does not completely characterize the product of this experiment. In fact, there are three isomeric dibenzylideneacetones: two are solids and one is a liquid. (a) Draw the structures of the three isomeric dibenzylideneacetones. (b) The \(^1\)\(\text{H}\)-NMR spectrum of the dibenzylideneacetone isomer that is the product of this experiment is shown on the next page. Which of the three isomers is the product of this experiment? Explain what features of the NMR spectrum lead to your conclusion.
Experiment 9 • The Claisen–Schmidt reaction:
A base-catalyzed aldol condensation
Pre-lab questions
The Claisen–Schmidt reaction: A base-catalyzed aldol condensation

**Summary**
Dibenzylideneacetone is prepared by the base-catalyzed crossed-aldol condensation of benzaldehyde and acetone. The product is characterized by IR spectroscopy and by its melting point range.

**Zubrick**
Read about IR spectroscopy, recrystallization techniques and determination of a melting point range.

**Lab manual**
Read Appendix E and review techniques in Experiments 1 and 6.

**Lecture text**
Read about the aldol condensation.

Under basic conditions, two equivalents of benzaldehyde [1] combine with one equivalent of acetone [2] to afford dibenzylideneacetone [3]:

![Chemical structure](https://example.com/structure.png)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>[2]</td>
</tr>
<tr>
<td>bp 178-179 °C</td>
<td>bp 56 °C</td>
</tr>
<tr>
<td>density 1.044 g/mL</td>
<td>density 0.791 g/mL</td>
</tr>
</tbody>
</table>

The reaction is an example of a base-catalyzed crossed-aldol condensation, also called a Claisen-Schmidt reaction in honor of its discoverers.

Carbonyl compounds that have α-protons on an sp³-hybridized carbon undergo deprotonation in the presence of base to afford resonance-stabilized, nucleophilic enolate anions. Acetone undergoes this acid-base reaction (called enolization), whereas benzaldehyde cannot because it has no α-protons:
The equilibrium constant of this particular enolization is only about $10^{-4}$. Nevertheless, the enolate anion, once created, goes hunting for an electrophile. In the Claisen–Schmidt reaction under discussion, the enolate anion can react either with unionized acetone (called a “self-condensation”) or with benzaldehyde (called a “crossed condensation”). Because aldehydes are generally more reactive than ketones toward addition of a nucleophile, the enolate preferentially attacks benzaldehyde:

A key intermediate in any aldol condensation is a β-hydroxycarbonyl compound (in the present case [4]), also called an aldol. Although β-hydroxycarbonyls can be isolated, they frequently undergo dehydration to afford α,β-unsaturated carbonyl compounds [5]:

Note that the α,β-unsaturated carbonyl [5], like acetone, has α-protons on an sp$^3$-hybridized carbon: enolization, attack on a sec-
In your study of organic chemistry you have encountered reactions that chemists use in the laboratory to create new carbon-carbon bonds: the Grignard reaction, $S_N2$ displacement by alkynyl anions, Friedel-Crafts acylation and alkylation, chloromethylation of aromatic compounds, alkylation of an enamine, etc. The importance of the aldol condensation rests on the fact that nature uses the aldol condensation to create most of the carbon-carbon bonds in living organisms. For example, the biosynthesis of fructose [8] is essentially a crossed-aldol condensation between the enolate of dihydroxyacetone [6] and glyceraldehyde [7]; the reaction takes place in the active site of the enzyme transaldolase:

![Chemical structures](image)

**PROCEDURE**

In a screw-top vial, mix 0.050 mol of benzaldehyde with the theoretical amount of anhydrous acetone; cap the vial. In a 250-mL Erlenmeyer flask, dissolve 5.0 g of NaOH in 50 mL of water and 40 mL of ethanol. After the basic solution has cooled to room temperature, add one-half of the benzaldehyde–acetone mixture to the Erlenmeyer and swirl. After 15 min add the rest of the benzaldehyde–acetone mixture and rinse the vial with a few milliliters of ethanol to complete the transfer. Swirl the mixture frequently over a 30-min period. Collect the solid product on a filter paper in a Büchner funnel. To wash the product free of NaOH and unreacted starting material, interrupt suction, add 100 mL of water and reapply suction; repeat three times. Dry the product under aspirator vacuum and then press it between sheets of filter paper.

The Claisen-Schmidt reaction: A base-catalyzed aldol condensation • 9-8
paper to remove as much water as possible. Weigh the crude product and record its melting point range. Recrystallize one-third to one-half of the crude product from ethanol, being careful not to use too much hot ethanol.

Record the IR spectrum of the pure dibenzylideneacetone by dissolving about 25 mg of the solid in about 1 mL of ether and applying this solution to a KBr pellet. Determine the melting point range of both the crude and pure product.

In your report include the yield, percent yield and a copy of the IR spectrum. Carefully and completely interpret the IR data, paying particular attention to the carbonyl stretching frequency. For purposes of comparison, consult the IR spectra of acetone (see Figure 9-1) and of benzaldehyde (see Figure 9-2).
Figure 9-1 IR spectrum of acetone (liquid film)

Figure 9-2 IR spectrum of benzaldehyde (liquid film)
Experiment 9 • The Claisen-Schmidt reaction: A base-catalyzed aldol condensation
Lab report form

1 Write the overall balanced reaction of the experiment.

2 Report the amount of benzaldehyde and acetone used in grams, moles, and milliliters; report the amount of NaOH used in grams and moles. Show calculations.

3 Show the calculation of the theoretical yield of product in grams and moles.
Experiment 9 • The Claisen-Schmidt reaction: 
A base-catalyzed aldol condensation 
Lab report form
Continued

4 Report the appearance, melting point range and amount of crude product obtained in grams and moles.

5 Report the appearance and melting point range of purified product.

6 Report the percent yield of crude product; show calculations.
Experiment 9 • The Claisen-Schmidt reaction:
A base-catalyzed aldol condensation
Lab report form
Continued

7 Comment on the percent yield of product you obtained; speculate on the reasons why you did not obtain a 100% yield.

8 Attach a copy of your IR spectrum. Try to assign as many absorption bands above 1500 cm\(^{-1}\) as you can. Comment on the purity of the sample as diagnosed by IR.