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The Aldol Condensation: Synthesis of Dibenzalacetone

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PURPOSE OF THE EXPERIMENT

Use a base-catalyzed reaction to condense acetone with benzaldehyde, forming a colored, crystalline product. Recrystallize and characterize the product by its melting point.

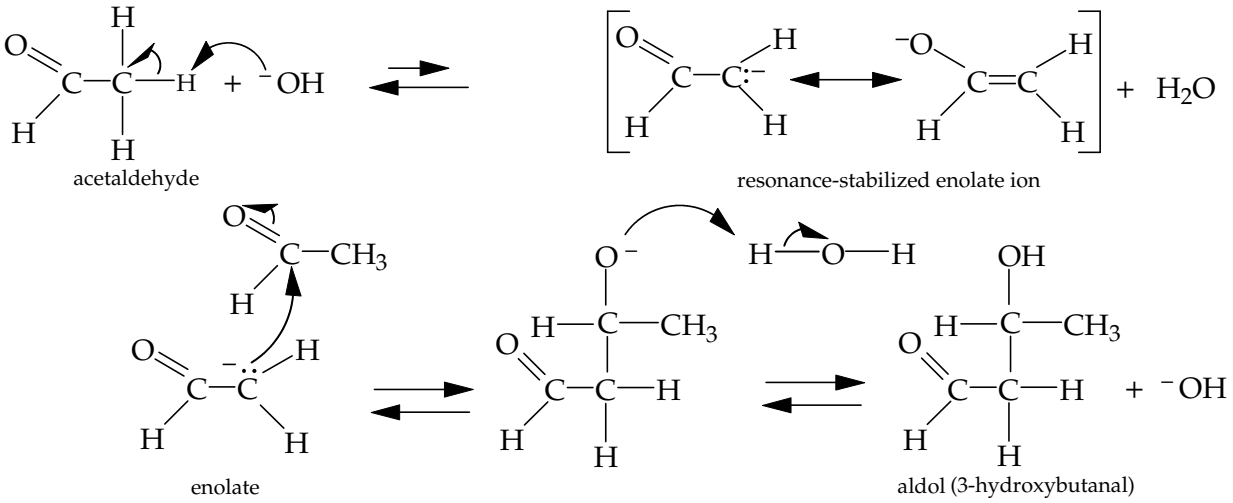
EXPERIMENTAL OPTIONS

BACKGROUND REQUIRED

You should be familiar with vacuum filtration, melting point measurement, and recrystallization.

BACKGROUND INFORMATION

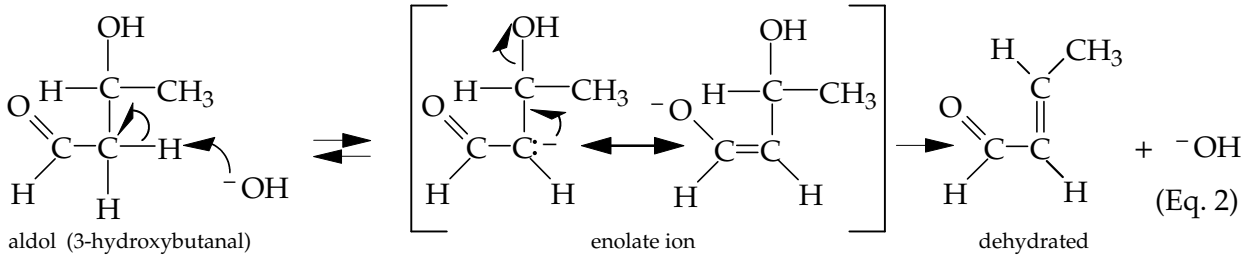
Condensations are reactions that add together two or more molecules, often with the loss of a small molecule such as water or an alcohol. In its simplest form, the **aldol condensation** combines two carbonyl compounds to give a β-hydroxy aldehyde or ketone. The product is also called an **aldol** because it contains both an aldehyde group and an alcohol. The base-catalyzed condensation of two molecules of acetaldehyde to give 3-hydroxybutanal is shown in Equation 1.



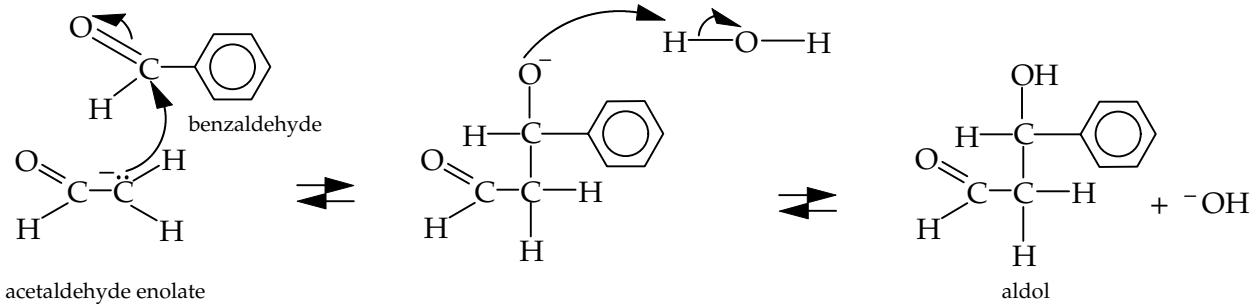
(Eq. 1)

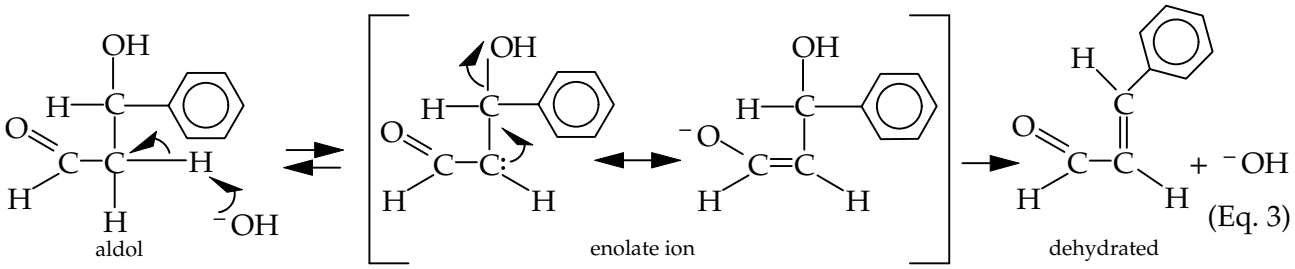
Hydrogens adjacent to a carbonyl group are weakly acidic. Loss of a proton leads to a resonance-stabilized enolate ion. The enolate ion is a strong nucleophile that adds to another carbonyl group.

Aldol products can dehydrate under either acidic or basic conditions to give , α, β-unsaturated aldehydes and ketones. Although aldol condensations are often evenly balanced equilibria, the dehydration is usually exothermic, driving the condensation to completion. The base-catalyzed dehydration of 3-hydroxybutanal is shown in Equation 2.

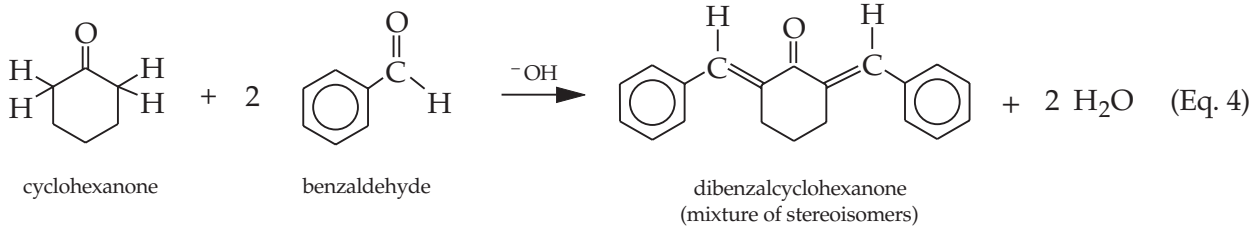


A **crossed aldol condensation** is an aldol condensation in which one aldehyde or ketone adds to the carbonyl group of a different compound. The compounds used in a crossed aldol condensation must be carefully selected to avoid unwanted product mixtures. Crossed aldol condensations are most effective if only one of the reactants can form an enolate ion and the other reactant is particularly electrophilic toward enolates. Benzaldehyde is an excellent reagent for crossed aldols because it has no α-hydrogens, so it cannot form an enolate. The base-catalyzed condensation of acetaldehyde with benzaldehyde is shown in Equation 3.

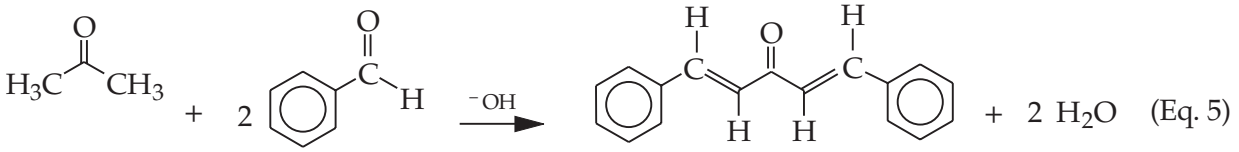




Historically, the benzylidene group (=CHPh) has been called the benzal group because it is easily added to a carbonyl compound by aldol condensation with benzaldehyde. For example, the formation of dibenzalcyclohexanone is shown in Equation 4.



In this experiment, acetone is used as the enolate-forming compound, adding to benzaldehyde followed by dehydration to form a benzal group. Like cyclohexanone, acetone has enolizable α-hydrogens on both sides of the carbonyl group, so acetone can add to two molecules of benzaldehyde. The condensation of acetone with two molecules of benzaldehyde to give dibenzalacetone is shown in Equation 5. The systematic name for dibenzalacetone is 1,5-diphenyl-1,4-pentadien-3-one.



acetone benzaldehyde dibenzalacetone (mostly *trans, trans)*

Semi-Microscale Aldol Condensation

Equipment

2 beakers, 100-mL	labels
250-mL beaker	magnetic stir bar
400-mL beaker	magnetic stirrer
Büchner funnel, with adapter	micropipet, 100–1000 µL
capillary tubes, melting point	Pasteur pipet, with latex bulb
125-mL Erlenmeyer flask	product vial
filter flask, 125-mL, with tubing	red litmus paper
filter paper	13 × 100-mm test tube
glass stirring rod	18 × 150-mm test tube
25-mL graduated cylinder	thermometer, –10 to 260 °C
100-mL graduated cylinder	2 watch glasses
hot plate	

Reagents and Properties

substance	*quantity*	*molar mass (g/mol)*	*mp (°C)*	*bp (°C)*	*d (g/mL)*
acetone	0.6 g	58.08		56	0.791
benzaldehyde	2.1 g	106.12		178	1.044
dibenzalacetone*		224	110		
ethanol	55 mL	46.07		78	
sodium hydroxide, 10% aqueous	20 mL	40.00			

*product

Preview

- Prepare an ice-water bath
- Place ethanol and NaOH solution into a beaker
- Cool the ethanol–NaOH solution to 20 °C

- Prepare a mixture of benzaldehyde and acetone
- Add the benzaldehyde–acetone mixture to the ethanol–NaOH solution
- Stir the mixture for 30 min
- Cool the mixture in an ice-water bath
- Collect the crystals by vacuum filtration
- Wash the crystals with water and again collect the crystals by vacuum filtration
- Test the filtrate with red litmus paper
- Recrystallize the crystals from ethanol
- Collect and dry the crystals
- Weigh the product
- Measure the melting point of both the crude and recrystallized products

PROCEDURE

Chemical Alert

acetone—*flammable and irritant*

benzaldehyde—*toxic and suspected carcinogen*

ethanol—*flammable and irritant*

10% aqueous sodium hydroxide—*corrosive and toxic*

Caution: Wear departmentally approved safety goggles at all times while in the chemistry laboratory.

NOTE 1: While benzaldehyde is a suspected carcinogen, it is a certified food flavoring: almond extract. Food substances undergo a much higher scrutiny than do most other chemicals. Use normal precautions when working with benzaldehyde.

1. Condensing Acetone with Benzaldehyde

Caution: Acetone and ethanol are flammable and irritating. Keep away from flames or other heat sources. Benzaldehyde is toxic and a suspected carcinogen. [NOTE 1] Aqueous sodium hydroxide (NaOH) is corrosive and toxic. Wear gloves when handling these compounds. Prevent eye, skin, and clothing contact. Do not inhale and ingest these compounds. Use a ***fume hood***.

Prepare an ice-water bath in a 250-mL beaker. Place 15 mL of USP ethanol and 20 mL of aqueous 10% NaOH into a 100-mL beaker. [NOTE 2] Add a stir bar.

NOTE 2: The ethanol used must be free of ketone contaminants, such as methyl isobutyl ketone, found in most denatured alcohol. Use USP ethanol (95% or 100%).

Place the 100-mL beaker into the ice-water bath. Set the entire assembly onto a magnetic stirrer. While stirring, cool the solution to 20° C. After the solution reaches 20 °C, remove the ice bath. Continue to stir the solution.

Prepare a mixture of 2.1 g (2.0 mL) of *fresh* benzaldehyde and 0.6 g (758 µL) of reagent-grade acetone in a test tube. Over a period of 5–10 min, add the benzaldehyde–acetone mixture to the ethanol–NaOH solution in small portions. Then stir the reaction for another 30 min.

Cool the mixture using the ice-water bath. Collect the crystals by vacuum filtration. Wash the crystals by suspending them in 50 mL of distilled or deionized water. Again collect the crystals by vacuum filtration.

Check the filtrate by testing the last few drops of water using red litmus paper. [NOTE 3] If the litmus turns blue, wash the crystals again until red litmus does not change color. Set a small sample aside to dry for a crude melting point measurement.

NOTE 3: Incomplete removal of NaOH results in an oily product during recrystallization.

2. Purifying the Product Prepare a hot-water bath using 200 mL of water in a 400-mL beaker. Place the beaker on a hot plate and heat the water to boiling.

Place the product into a 125-mL Erlenmeyer flask. To recrystallize the product from ethanol, add ethanol and swirl the flask in the hot-water bath. While keeping the solution at or near its boiling point, add more ethanol in small amounts until all the solid is dissolved or no more solid appears to dissolve. Do not add more than 40 mL of ethanol.

If any insoluble material remains, decant the solution into a 100-mL beaker to obtain a clear yellow solution. Cover the hot solution with a watch glass and let the solution cool slowly to room temperature.

If the product does not crystallize, scratch the bottom of the flask with a glass stirring rod to induce crystallization. Cool the flask in ice water for 5–10 min. Collect the crystals by vacuum filtration. Dry the crystals, spreading them thinly over a clean watch glass, and allow them to stand for 30 min. Stir the crystals occasionally to allow any remaining ethanol to evaporate.

Alternatively, dry the product overnight by placing a thin layer of crystals in the bottom of a beaker. Cover the beaker with a paper towel held in place with a rubber band.

Weigh the product. Measure the melting points for both the crude product and the recrystallized product. Place the product in a properly labeled product vial.

3. Cleaning Up Place your recovered materials in the appropriate labeled collection containers as directed by your laboratory instructor. Clean your glassware with soap or detergent.

Caution: Wash your hands thoroughly with soap or detergent before leaving the laboratory.

Microscale Aldol Condensation

Equipment

2 beakers, 100-mL	melting point capillary tubes
2 conical vials, 5-mL	10–100 μL micropipet
10-mL Erlenmeyer flask*	3 Pasteur pipets, with latex bulb
25-mL filter flask, with tubing	2 pipets, 1.0-mL
filter paper	product vial
glass stirring rod	red litmus paper
Hirsch funnel, with adapter	support stand
hot plate	2 test tubes, 13 × 100-mm
labels	thermometer, –10 to 260 °C
magnetic stir bar	utility clamp
magnetic stirrer	2 watch glasses
marking pen	

*or 10-mL reaction vial

Reagents and Properties

substance	*quantity*	*molar mass (g/mol)*	*mp (°C)*	*bp (°C)*	*d (g/mL)*
acetone	30 mg	58.08		56	0.791
benzaldehyde	105 mg	106.12		178	1.044
dibenzalacetone*		224	110		
ethanol	2.8 mL	46.07		78	
sodium hydroxide	1.0 mL	40.00			

*product

Preview

- Prepare an ice-water bath
- Place ethanol and NaOH solution into a beaker
- Cool the ethanol–NaOH solution to 20 °C
- Prepare a mixture of benzaldehyde and acetone
- Add the benzaldehyde–acetone mixture to the ethanol–NaOH solution
- Stir the mixture for 30 min
- Cool the mixture in an ice-water bath
- Rinse the crystals with water
- Test the filtrate with red litmus paper
- Recrystallize the crystals from ethanol
- Collect the crystals by vacuum filtration
- Dry the crystals
- Weigh the product
- Measure the melting point of the product

PROCEDURE

Chemical Alert

acetone—*flammable and irritant*

benzaldehyde—*toxic and suspected carcinogen*

ethanol—*flammable and irritant*

10% aqueous sodium hydroxide—*corrosive and toxic*

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NOTE 1: While benzaldehyde is a suspected carcinogen, it is a certified food flavoring, almond extract. Food substances undergo a much higher scrutiny than do most other chemicals. Use normal precautions when working with benzaldehyde.

Prepare an ice-water bath in a 100-mL beaker. Place 0.8 mL of USP ethanol and 1.0 mL of aqueous 10% NaOH into a 10-mL Erlenmeyer flask or 10-mL reaction vial. [NOTE 2] Add a stir bar.

NOTE 2: The ethanol used must be free of ketone contaminants, such as methyl isobutyl ketone, found in most denatured alcohol. Use USP ethanol (95% or 100%).

Place the flask into the ice-water bath. Set the entire assembly onto a magnetic stirrer. While stirring, cool the solution to 20 °C. After the solution reaches 20 °C, remove the ice bath. Continue to stir the solution.

Prepare a mixture of 105 mg (100 μL) of *fresh* benzaldehyde and 30 mg (38 μL) of reagent-grade acetone in a test tube. Add the benzaldehyde–acetone mixture to the ethanol–NaOH solution in two portions, 5 min apart. Then stir the reaction for another 30 min.

Cool the mixture in an ice-water bath. Use a Pasteur pipet to remove the solvent, taking care to leave the crystals in the flask. Place the solvent into the container labeled "Recovered Ethanol–NaOH", supplied by your laboratory instructor.

Rinse the crystals with 2 mL of distilled or deionized water. Remove the water. Rinse again with 1 mL of water. Remove the water to a watch glass.

NOTE 3: Incomplete removal of NaOH results in an oily product during recrystallization.

Check the filtrate on the watch glass using red litmus paper. [NOTE 3] If the litmus turns blue, rinse the crystals again until the red litmus does not turn blue.

2. Purifying the Product

Prepare a hot-water bath by placing 50 mL of water into a 100-mL beaker. Place the beaker on a hot plate and heat the water to boiling.

Place the product into a 5-mL conical vial. To recrystallize the product from ethanol, add ethanol and swirl the vial in the hot-water bath. While keeping the solution at or near its boiling point, add more ethanol in small amounts until all the solid is dissolved or no more solid appears to dissolve. Do not add more than 2.0 mL of ethanol.

If any insoluble material remains, use a Pasteur pipet to transfer the solution to another 5-mL conical vial. Allow the solution to cool slowly to room temperature.

If the product does not crystallize, scratch the bottom of the vial with a glass stirring rod to induce crystallization.

Clamp the vial to a support stand. Then cool the flask in ice water for 5–10 min. Collect the crystals by vacuum filtration.

Dry the product crystals, spreading them thinly over a clean watch glass and allowing them to stand for 30 min. Stir the crystals occasionally to allow any remaining ethanol to evaporate.

Alternatively, dry the product overnight by placing a thin layer of crystals in the bottom of a beaker. Cover the beaker with a paper towel held in place with a rubber band.

Weigh the product. Measure its melting point. Place the product in a properly labeled product vial.

3. Cleaning Up Place your recovered materials in the appropriate labeled collection containers as directed by your laboratory instructor. Clean your glassware with soap or detergent.

Caution: Wash your hands thoroughly with soap or detergent before leaving the laboratory.

Post-Laboratory Questions

1. Calculate the percent yield for your product.
2. Propose a mechanism for the base-catalyzed condensation of cyclohexanone with two molecules of benzaldehyde to give dibenzalcyclohexanone.
3. A student habitually adds excess reagents to try to maximize yields. In this procedure, he adds a two-fold excess of acetone. What product is he likely to isolate?
4. Dibenzalacetone is commonly used in sunscreens. Suggest what properties are valuable in a compound for use as a sunscreen. You may need to consult reference sources.

NAME SECTION DATE

SYNT 720/The Aldol Condensation: Synthesis of Dibenzalacetone

Pre-Laboratory Assignment

1. Briefly describe the hazards you should know about when you use acetone, benzaldehyde, ethanol, and 10% aqueous NaOH.

2. Calculate the theoretical yield for your product. Record your calculation here and in your laboratory notebook.

3. Propose a mechanism for the base-catalyzed condensation of one molecule of acetone with two molecules of benzaldehyde to give dibenzalacetone.

4. Predict what compound(s) might result from the base-catalyzed condensation of acetone with acetaldehyde.

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