25. Aldol Condensation Reactions

In this reaction two molar equivalents of an aldehyde will react with one molar equivalent of a ketone to form a disubstituted dienone product. Two dehydrations occur which form the two double bonds. The crude product is isolated by vacuum filtration and weighed. The crude product is recrystallized. The purity of the crude and recrystallized product are assessed and compared by melting point and percent yield. The recrystallized product melting point is used to determine the probable composition of the product. During the next class, the 1H NMR of the product will be obtained. The 1H NMR and the melting point data will allow the product structure to be proposed. From the product structure, the starting aldehyde and ketone will be determined.

PRE-EXPERIMENT ASSIGNMENT

Study this chapter in the manual, the procedure and notes relating to recrystallization on the web site and the lecture notes on Aldols on the Chemistry Department web site. You will also find it helpful to review sections 22.1 and 22.3 of Klein. Do the first seven parts of your notebook writeup.

A student who has prepared for the Aldol Condensation experiment should be able to:
1. Define enolate, aldol reaction, aldol condensation, and condensation reactions.
2. Give a drawing of, and identify the components from a drawing of, the apparatus used in the various steps of the reaction and its components.
3. Calculate the theoretical yield and the percent yield for this and similar experiments given the necessary data, and perform any of the intermediate calculations required by this process. For this reaction, "necessary data" may include the volume of a given starting material and its density rather than simply the mass.
4. Draw the structure given the name, or give the name from the structure, of the compounds used in the day's experiment, and give the role of each.
5. Understand the mechanism of the condensation of an aldehyde and a ketone.
6. Identify and explain safety considerations for this experiment.
7. Perform the day's experiments safely and successfully.

Quizzes given after the experiment has been performed may also include:

8. Predict the products of aldol reactions and aldol condensations if given starting materials.
9. Explain the mechanism of aldol reactions and aldol condensations if given the balanced equation. Important topics include enolate anions, electrophiles,
and nucleophiles. For more details see your CHEM 2220 lecture materials and Klein.

**Safety Considerations**

All of the starting organic liquids are flammable. Do not have any open flames or sparking devices in the vicinity of the reaction. Swirl Erlenmeyer flasks in hood to keep vapors to a minimum.

Sodium hydroxide is a strong base and very corrosive. Keep away from skin and eyes. If contact is made, flush with copious amounts of water.

**EXPERIMENT**

Place a 400 mL beaker with approximately 3 inches of water, a thermometer, and a boiling stone on a hot plate. Set to about 4. Desired temperature is 70-80°C.

Obtain approximately 4 mL of 5 M aqueous sodium hydroxide solution and approximately 4 mL of 95% ethanol. (These are solvent and catalyst so obtaining the exact target volume is not critical.) Add this to a 50 mL Erlenmeyer flask and swirl to mix. Into a separate 50 mL Erlenmeyer, add approximately 2.0 mL of Unknown Aldehyde (I, II or III). This is one of two starting reagents. Read and record volume precisely. Using your small syringe, measure 0.50 mL of unknown Ketone (A, B, C) and add to the aldehyde. Read and record volume precisely. Swirl to mix. In 2-3 portions, add the Ethanol/Sodium Hydroxide solution to the Aldehyde/Ketone flask. Swirl to mix.

Record all color, temperature and consistency changes. If you do not see any precipitation or solids forming within 5 minutes, place Erlenmeyer in hot water bath for ~15 minutes. Allow the reaction to proceed for about fifteen minutes, swirling occasionally.

**The Workup**

Recover the solid by suction-filtering the mixture using your large Büchner funnel and filter flask. Disconnect the vacuum, wash the product with a few milliliters of cold ethanol, and reconnect the vacuum. Allow the suction to run for about five minutes longer to help dry the crude product. Note the texture and color of the product. Weigh the crude product and put some in a capillary so you can determine its melting point later.

**Recrystallization Solvent Choice**

The different mixes of Aldehydes and Ketones need different recrystallization solvents. Validate with your instructor that the recrystallization solvent choices in the on-line notes are still current.
Fill a clean test tube about half to 2/3 full of recrystallization solvent. Add a boiling stone. Check the boiling point of your solvent. The hot water should be approximately 10°C, below the boiling point of your solvent. If the water is too hot, add some tap water (or ice) to cool it down and adjust the hot plate setting. Place the test tube of solvent in the hot water beaker to heat. Place about 0.2-0.4 grams of the crude solid in a clean test tube add a clean stir rod. Hold test tube with solid in the hot water. Pipette hot solvent into the test tube containing the solid. Stir to mix. Add just enough solvent to dissolve all the solid. Any additional solvent will only decrease yield. As soon as all of the solid has dissolved, remove Erlenmeyer from water bath and place on benchtop to cool. Do not disturb. Observe. After about 5-10 minutes small crystals should begin to form. When test tube has cooled to room temperature, place in 250 mL beaker with ice and water. Leave in ice bath a minimum of 10 minutes.

Collect the crystals by suction filtration using 1.5 cm filter paper, Hirsch funnel, and small suction flask. Scrape out as many crystals as possible using spatula. To help the crystals dry faster, allow the vacuum to run for about five minutes after the last of the liquid has been pulled through the funnel. Note the texture and color of the product. Determine the mass of these crystals. (Place both in the Mel-Temp together to save time.)

Take the melting point of both these crystals and the crude product. Place recrystallized product in a small shell vial with your name. Turn into your instructor. Next week you will prepare a 1H NMR sample and take a proton NMR.

**Product Identification**

Compare the melting point of the recrystallized purified product with the literature value of possible products. Identify which is most likely your product. Next week you will confirm or refute this by using NMR. From this product structure, deduce the identity of the aldehyde and ketone which were used.

**CLEANUP**

Used Pasteur pipettes and melting point capillaries are placed in the broken glass box. Leftover non-halogenated organic solvents are placed in the non-halogenated organic liquid waste bottle in the hood. Product goes in the non-halogenated solid organic waste bottle if your instructor does not collect it. Leftover NaOH solution is washed down the drain with plenty of water.

**POST-EXPERIMENT ASSIGNMENT**

Write the lab report and have it ready to turn in by the beginning of the next lab. Your writeup of this experiment (as for every synthesis experiment) should include a calculation of the percentage yield for both the crude product and the recrystallized product. Your conclusions section should include a comparison of the melting point of your crude and recrystallized product with the literature value. Provide a reasonable explanation for any differences. Explain the success or failure of the condensation reaction. Explain the
success of failure of the recrystallization. If your percent yield was not 100%, you should explain where the missing material might have gone (or where extra material might have come from). Prepare for the Aldol Condensation portion of the next quiz.

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