

CHEM 2229 EXP 1: The Borohydride Reduction of 9-Fluorenone to 9-Fluorenol

Background:

In this week's experiment, a metal hydride will be used as a reducing agent. Metal hydrides can be quite reactive, and therefore, difficult or even dangerous to handle. Sodium borohydride, NaBH_4 , was discovered in the 1940s by H. I. Schlesinger, who led a team that developed metal borohydrides for wartime applications. It was later determined by H. C. Brown (Nobel Prize, 1979) and co-workers at Purdue, who were investigating many reducing agents, that sodium borohydride was a mild and selective reducing agent. Thus, it is safe to use in the undergraduate organic laboratory.

For this experiment, the sodium borohydride has been dissolved in ethanol to form an alkaline solution, where 100 μL of solution provides approximately 4.0 mg of NaBH_4 . The ketone being reduced is 9-fluorenone and the resultant secondary alcohol is 9-fluorenol. The progress of the reduction will be monitored by Thin Layer Chromatography, TLC, using fluorescent silica gel sheets $\sim 2.5 \text{ cm} \times 10 \text{ cm}$ developed with the provided 30% acetone in hexane solution and visualized under UV light. Identification of the product will also be verified by measuring the melting point using a Fisher-Johns melting point apparatus.

Procedure:

I. Reduction of the Ketone

In a tared 5-mL conical vial, weigh about 50 mg of 9-fluorenone. Record mass to nearest 0.001 g. To the 5-mL conical vial add a magnetic spin vane and attach an air condenser. Place the conical vial in an aluminum block atop the stirring hot plate and clamp in place. Introduce about 1 mL of ethanol as solvent and stir to bring about dissolution. Once the solid is completely dissolved, add the NaBH_4 solution dropwise ($\sim 0.3 \text{ ml}$ or 8 drops). Wait 10 minutes. While waiting, **prepare TLC chamber*** with 30% acetone in hexane and TLC strip. Label TLC strip for 9-fluorenone, 9-fluorenol and reaction solution. Then using a separate capillary tube for each, spot with pure ketone and pure alcohol. Once 10 minutes have lapsed, pause the stirring and spot TLC strip with solution. While the TLC strip is developing, resume stirring the solution. The color of the solution will disappear when all of the ketone is reduced. (*If the TLC analysis reveals the presence of unreacted ketone, check with the TA to determine if more hydride reagent is needed.*) Once the ketone is reduced, stop stirring. Attach labeled TLC strips to yellow pages in lab notebook with 2" clear packing tape.

***Check first semester notes and MTOL for the proper procedure for TLC analysis and TLC notes at end of experiment.**

II. Isolation of Alcohol Product

Add $\sim 1.5 \text{ ml}$ of chilled 1M HCl dropwise to the conical vial to neutralize the alkaline reduction medium and isolate the product 9-fluorenol. (The acid should be added dropwise because H_2 gas will be produced during the decomposition of any excess NaBH_4 .) Check the pH of the solution by placing a drop of the solution on pH paper to verify that the base had been removed and excess acid is present ($\text{pH} \leq 5$). The alcohol should be noticeable as a white fluffy precipitate. Remove the air condenser.

III. Extraction of the Product

Note: If your combined mixture volume will exceed 5 ml, use a centrifuge tube to perform the extraction.

Add ~ 1.0 ml of methylene chloride, CH_2Cl_2 , to the solution in the conical vial. Shake the reaction mixture. Allow the mixture to settle into two layers. (Methylene chloride is immiscible with and more dense than water. If only a single layer is present, add ~1 ml of saturated sodium chloride solution to help separate the layers.) Check the pH of the top layer again to ensure it is still acidic. (*If not, check with TA.*) Using a Pasteur pipet, remove the lower CH_2Cl_2 layer containing the extracted 9-fluorenone and add it to a clean dry beaker. Repeat extraction twice by adding 0.5 ml portions of CH_2Cl_2 to the water in the conical vial, shaking the mixture, allowing the solution to settle into two layers, removing the lower layer and adding it to the previously extracted 9-fluorenone in the clean dry beaker.

IV. Drying the Product

Add a heaping spatula of anhydrous sodium sulfate, Na_2SO_4 , to the methylene chloride solution in order to dry it. Swirl the beaker to increase contact of sodium sulfate with the solution. The sodium sulfate will clump as it removes any remaining water in the solution. If only relatively large clumps form, add more sodium sulfate until it is “free-flowing.” Swirl occasionally for 5 minutes. Weigh a 50 ml clean dry beaker. Record the mass to the nearest 0.001 g. Decant methylene chloride solution into the 50 ml beaker. Rinse the sodium sulfate twice with 0.5 ml portions of methylene chloride. Add rinsings to the 50 ml beaker. The combined dried eluate should be about 2 ml.

V. Recovery & Verification of Product

Remove the methylene chloride by gentle evaporation using a hair dryer. (*Do not directly inhale the CH_2Cl_2 vapors as they are somewhat toxic.*) In order to verify the removal of all of the solvent, weigh the beaker periodically until it reaches a constant weight. Record the mass of the beaker and product to the nearest 0.001 g. Determine the mass of the product to the nearest 0.001 g and record it.

Using a Fisher-Johns melting point apparatus, determine the melting point range of the product. Record the model and number of the MP apparatus. Record the melting point range.

Calculations:

Note: Label and show all calculations along with answers in lab report.

1. Determine the theoretical yield of the alcohol based on the starting mass of the ketone.
2. Determine the percent yield of the alcohol.
3. Determine the percent error for the MP.
4. Determine the R_f values for the pure 9-fluorenone, pure 9-fluorenone and reaction mixture.

TLC Notes

1. Prepare TLC chamber:
 - a. Add $\sim \frac{1}{4}$ inch of 30% acetone in hexane to plastic beaker.
 - b. Place filter paper along wall of beaker and watch glass on top of beaker to create a space for vapor to saturate.
2. Prepare TLC strip:
 - a. Avoid touching TLC strip – handle only by the edges.
 - b. Using a pencil, draw a horizontal line $\sim \frac{1}{2}$ inch from and parallel to the bottom of the strip. This is the origin line.
 - c. Using a capillary, spot strip with reference ketone, alcohol and reaction mix.
3. Develop TLC strip:
 - a. Place TLC strip in chamber being careful to make sure strip does not touch filter paper and solvent front is parallel to drawn starting line.
 - b. Once solvent front has move to $\sim \frac{1}{2}$ inch from top of strip, remove strip and with a pencil mark the solvent front.
4. Visualizing TLC strip:
 - a. Allow TLC strip to dry. A hair dryer may be used to help evaporate solvent.
 - b. View strip under UV lamp and mark exterior of sample spots.
 - c. Once reaction mixture does not have a spot corresponding to the ketone, the reaction is complete.
5. Determine the Retention Factor, R_f , values for each spot.
 - a. Mark center of each spot. Measure distance from origin to center of spot.
 - b. Measure distance from origin to solvent front.
 - c. $R_f = \text{distance spot travelled} / \text{distance solvent front travelled}$

Concepts To Consider Before Answering Prelab Questions on Canvas

(See Solomon's Organic Text for more information on reduction reactions.)

1. At room temperature, what functional groups can be reduced by a.) lithium aluminum hydride, LiAlH_4 ?
b.) sodium borohydride, NaBH_4 ?
2. How compatible are lithium aluminum hydride, LiAlH_4 , and sodium borohydride, NaBH_4 , with protic solvents (water, alcohols, etc.)?
3. Balance the following sodium borohydride reduction equations showing the structures for the following organic compounds: a.) benzil to benzoin; and b.) benzil to hydrobenzoin.
4. Calculate the theoretical amount of NaBH_4 needed to convert 100 mg of a.) benzil to benzoin; and b.) benzil to hydrobenzoin.
5. Draw the structural formulas and balance the equation for this week's experiment.
6. For this week's experiment, is the reactant more polar or the product? Explain.
7. Will the reactant or the product move the farthest on the TLC strip? Explain.