

CHEM 2229 Exp 4: The Aldol Condensation Preparation of Tetraphenylcyclopentadienone (Cyclone)

Background:

Aldol condensations are reactions leading to C-C bond formation via carbanions generated from aldehydes or ketones possessing α hydrogens. In this week's experiment, a crossed aldol condensation will be conducted between benzil and 1,3-diphenylacetone to produce tetraphenylcyclopentadienone. The tetraphenylcyclopentadienone is a dark purple color due to extended conjugation; and, it is used for the synthesis of other highly conjugated compounds used in electroluminescent devices.

Procedure:

1. To a tared 5 ml conical vial, add 0.100g of 1,3-diphenylacetone, 0.100 g of benzil, and 2.5 ml of 100% ethanol. Place conical vial in an aluminum block on top of a magnetic stirring hotplate. Add a magnetic stir bar to the vial. Warm and stir the reactants to dissolve them. ($BP_{EtOH} = \sim 78\text{ }^{\circ}\text{C}$)
2. Using a pipet, slowly add 1.5 ml of KOH in ethanol solution to the mixture in the vial. Attach a water condenser to the 5 ml conical vial. (*Verify that water is coming into the condenser from the lower tubing and out to the sink from the upper tubing.*) Heat the mixture to reflux. Once condensation is observed, continue to reflux for 15 minutes.
3. When the reflux is complete, remove vial from heat source. Remove jacketed condenser and place vial in a beaker to prevent it from tipping over. Cool the reaction mixture to room temperature. (*A water bath may be used to aid cooling. Cap the 5 ml conical vial and place vial upright in a room temperature water bath.*)
4. Once the vial is room temperature, cool the mixture further in an ice-water bath. Add a cap to the vial and pack ice around it. Obtain ~ 30 ml of distilled water in a small beaker and ~ 1 ml of ethanol in a graduated cylinder. Pack the beaker and the graduated cylinder in the ice bath alongside the vial. Wait 5 minutes. Check the conical vial, dark purple/black crystals should have formed. (*If not, place the vial back in the ice bath and wait until crystals form. Salt may be added to the ice bath to lower the freezing point of the ice.*)
5. Isolate the dark purple crystalline product by vacuum filtration using the large (3 cm) Hirsch funnel. Wash the product with the ice cold distilled water until the filtrate is practically neutral ($\text{pH} \leq 8$). To test the pH, remove the vacuum hose from the side arm of the filter flask. Carefully remove the Hirsch funnel making sure not to spill any crystals and not to drip any filtrate on the lab bench. With the pH paper, test the tip of the Hirsch funnel, not the bulk filtrate. Reassemble the vacuum filtration system. If the pH is in the correct range, rinse the crystals with 1 ml of ice cold ethanol. If the pH is still too high, continue to rinse with the ice cold distilled water until the pH is within range. Allow crystals to dry under vacuum.
6. Determine the mass of the product to the nearest 0.001 g and record it. Dissolve a speck of product in CH_2Cl_2 . Check the product for the presence of byproducts using TLC with fluorescent Silica gel plates and a 2:1 mixture of CH_2Cl_2 : hexane for development. Starting material TLC stds should also be spotted. The product should have an R_f of about 0.85. Other byproducts will have smaller R_f values with this solvent. Attach labeled TLC strip to yellow pages in lab notebook with 2" clear packing tape.

7. Using a Fisher-Johns melting point apparatus, determine the melting point range of the product. (*If the range is high and time permits, the product may be recrystallized from 95% ethanol.*) Record the model and number of the MP apparatus. Record the melting point range.
8. Transfer any remaining product to the container labeled "228 (2229) Aldol product."

Calculations:

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

1. Determine the theoretical yield of the tetraphenylcyclopentadienone based on the starting mass of the limiting reagent.
2. Determine the percent yield of the tetraphenylcyclopentadienone.
3. Determine the percent error for the MP.
4. Determine the R_f values for the product and any byproducts.
5. Determine the percent error for the R_f value for the tetraphenylcyclopentadienone.

Concepts To Consider Before Answering Prelab Questions on Canvas

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

1. Define an Aldol condensation.
2. Define self-condensation.
3. Write a reaction mechanism for the base catalyzed Aldol self-condensation of acetaldehyde including the dehydrated product.
4. Draw the structure for benzil. Explain why the benzil used in this experiment does not undergo self-condensation.
5. Write a mechanism for the crossed Aldol condensation reaction in this week's experiment that leads to the formation of tetraphenylcyclopentadienone.