Experiment: Synthesis of 1-Bromo-4-nitrobenzene

Background

For being so highly unsaturated (degree of unsaturation = 4), aromatic hydrocarbons are remarkably unreactive. Unlike other unsaturated compounds such as alkenes, dienes, and alkynes, aromatic hydrocarbons do not undergo addition reactions. The most common reactions that these compounds undergo are called electrophilic aromatic substitution reactions, reactions that are much slower than the electrophilic addition reactions of other unsaturated hydrocarbons. There are five basic electrophilic aromatic substitution reactions: halogenation, nitration, sulfonation, alkylation, and acylation.

In this experiment, we will carry out the nitration of bromobenzene. Bromine, substituted on an aromatic ring, is an ortho-para directing group. It will direct an incoming electrophile to the ortho and para positions. It is also deactivating, meaning that its reactions will be slower than the identical reactions of benzene. For nitration, the electrophile is the nitronium ion. It is produced from the reaction of nitric acid with sulfuric acid.

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\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^{+1} + \text{HSO}_4^{-1} + \text{H}_2\text{O}
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The nitronium ion will react with bromobenzene primarily at the ortho and para positions to form two products, 1-bromo-2-nitrobenzene and 1-bromo-4-nitrobenzene.

The para product, 1-bromo-4-nitrobenzene, has a melting point of 127°C. The ortho product has a melting point of 43°C. In this experiment, both products will form and crystallize together during the purification process. Recrystallization of this mixture from ethanol will result in the formation of crystals of the less soluble para product. The more soluble ortho product remains in the ethanol. Evaporation of the solvent from the recrystallization filtrate will produce an oil, the impure low melting ortho product. In this experiment, we will isolate only the para product, the 1-bromo-4-nitrobenzene.
**Pre-lab Preparation**

Before coming to lab, you should have done the following things:

1. Read the background and procedure sections of this experiment thoroughly.

2. Review thoroughly the theory and practice of recrystallization, from this lab text, your techniques manual, and your lab lecture notes.

3. In your notebook, write in tabular form only the relevant physical constants of bromobenzene, 1-bromo-4-nitrobenzene, 1-bromo-2-nitrobenzene, and ethanol.

4. Answer the following questions about the procedure in this experiment:
   a. What is the purpose of keeping the reaction temperature low during the reaction?
   b. Consider the solubility properties listed in your table. What are the crystals that form when the reaction mixture is poured into water? Why do they form at this point?
   c. Why is it so important to wash these crystals so thoroughly with water after the first filtration?

**Experimental Procedure**

**Safety Considerations**

- Concentrated sulfuric acid and concentrated nitric acid are both strong acids and will cause serious burns if you spill them on the skin. If either of these acids comes in contact with your skin or clothing, wash the area affected area thoroughly with water. Then report to your instructor. When dispensing either of these acids, if some of it spills, clean the spill thoroughly with water. If acid spills down the side of the bottle, wash it thoroughly so that the next person who touches the bottle won’t be burned on the fingers.

- Nitric acid reacts violently with acetone when mixed in high concentrations. During this lab, no acetone should be used.

- Bromobenzene is a skin irritant. Wearing gloves is recommended. If you get any of this material on the skin, wash it thoroughly with soap and water. Avoid touching sensitive skin on your face while working with these compounds.
The products of this reaction are toxic if ingested. Wash your hands at the conclusion of the lab to prevent accidental ingestion.

1. In the hood, prepare a warm water bath (50° – 60°C) using a large beaker on a hot plate. This will be needed in step 4.

2. Use gloves! Into a 50-mL Erlenmeyer flask, place 4.0 mL of concentrated nitric acid (15.8M, d = 1.42 g/mL) and 4.0 mL of concentrated sulfuric acid (17.8M, d = 1.84 g/mL). Swirl the mixture to mix the acids and cool it to room temperature with an ice water bath in a beaker in the hood.

3. At this point you will begin very slowly adding bromobenzene to the nitrating acid mixture. Because the reaction is exothermic, it is important to keep the temperature under control to minimize formation of dinitro product. Measure 3.0 mL of bromobenzene into a graduated cylinder and, over a 5 minute period, add 0.5 mL portions of bromobenzene to the reaction flask. This addition is done slowly in order to keep the temperature from rising too high as excess heat will cause dinitration. If the flask begins to feel very warm through your gloves, cool it using the ice bath. During the addition of bromobenzene, swirl the flask regularly to mix the reagents. You should begin to see solid product forming.

4. After you have added all of the bromobenzene, swirl the flask for another 15 minutes in your warm water bath. If your water bath has become too warm, add cool water to adjust the temperature. Continue to monitor your reaction visually for overheating. If you see any dark yellow-brown gas forming, remove the flask immediately from the heat. You may resume heating once the reaction has cooled and the gas has dissipated. (If you significantly overheat your flask, you will continue to see excessive yellow-brown color in the contents of the flask. This also may result in failure to form significant solid product. If this happens, check with your instructor for further guidance.)

5. After the reaction period is complete, cool on ice. You should see significant amounts of solid product. Carefully pour the acidic mixture into a beaker containing 50 mL of water. (This step is done to dilute the acid before suction filtration.) Use a spatula to scrape any crystals that have stuck to the reaction flask to transfer them to the beaker. You may also use water to help transfer the solid.

6. Filter the crystals with suction and wash them thoroughly with cold water. The crystals are insoluble in water, so don’t be afraid to use too much water. Keep suction on the funnel and the crystals to dry them as much as possible. Press them with a spatula tip to force out as much water as possible. Dispose of the filtrate in the waste container in the hood.

7. Place the solid product into an Erlenmeyer flask and recrystallize with 95% ethanol. First bring some ethanol to a boil in a separate flask and then transfer about 5 mL of ethanol to the flask containing the solid product. Bring the mixture back to a boil with swirling.
Don’t forget to use a boiling stick. Keep adding hot ethanol until all of the crystals have just dissolved at the solvent’s boiling point.

8. Allow the solution to cool. Once all of the crystals appear to have formed, filter them with suction and wash them with a small amount of ice cold ethanol. Dispose of the recrystallization filtrate in the waste container in the hood.

9. Remove the crystals from the funnel and place them between two pieces of filter paper to dry. After at least 24 hours, weigh your crystals and take their melting point. Turn them into your instructor in a test tube labeled with your name, your instructor’s name, and the name of the product.

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### Post-Lab and Report Requirements

1. Write an equation for the reaction of bromobenzene with nitric acid in the presence of sulfuric acid acting as a catalyst.

2. Write a detailed mechanism for the formation of 1-bromo-4-nitrobenzene from bromobenzene. Your mechanism must show all relevant resonance, including all resonance contributing structures.

3. Calculate the moles of bromobenzene and the moles of nitric acid you used in this synthesis. From this data, calculate the theoretical yield of bromonitrobenzene product. Note: In this reaction two organic products are formed. One mole of bromobenzene will react with one mole of nitric acid to produce one mole of mononitration product. That one mole will be made up of both the ortho and para products. You cannot predict accurately how much ortho or how much para product is formed. You can only calculate the theoretical yield of the combined products.

4. Using the theoretical yield of the combined products calculated in question 3, calculate the percentage yield of 1-bromo-4-nitrobenzene you obtained based on your starting quantity of bromobenzene.

5. Give a detailed description of sources of yield loss. Give both chemical reasons (side reactions of the limiting reagent or further reactions of the product) and physical reasons (procedural loss of limiting reagent or product) why you got a lower than 100% yield.