Experiment 5 - Nitration of Methyl Benzoate

OBJECTIVE

to demonstrate "Electrophilic Aromatic Substitution"

to provide experience with small-scale synthetic methods

INTRODUCTION

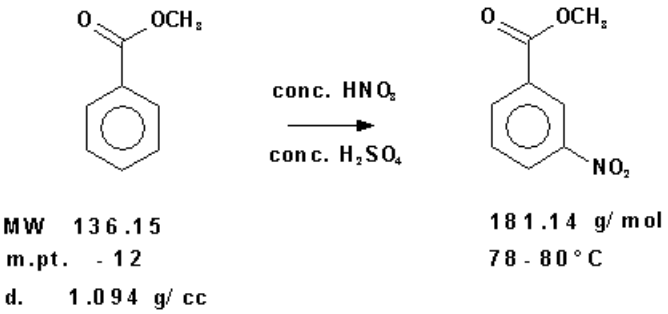

Figure 1

This reaction is a typical example of "Electrophilic Aromatic Substitution". The use of a mixture of Sulfuric Acid and Nitric Acid is the "classic" way to make the Nitronium Ion ($NO_2{}^+$).

$$2\ H_2SO_4 + HNO_3 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (1)$$

This "Electrophile", the Nitronium Ion, is the active species that attacks the electron-rich aromatic ring in the first step of the mechanism of this reaction. If the aromatic ring contains electron donating groups like hydroxyl (–OH) , or alkoxy (–OR) groups, the reaction is very rapid, and often more than one nitro group will become attached to the aromatic ring.

In the example we will use in this laboratory exercise, the ring substituent, the ester group (–CO_2R), is electron withdrawing. This substituent slows the attack of the electrophile and allows isolation of a monosubstituted product.

CAUTION: Concentrated Nitric (HNO_3) and Sulfuric Acids (H_2SO_4) are highly corrosive! *Any* spills should be promptly flushed with cold water. Discoloration of the skin will result from even a drop of nitric acid.

PRE-LAB

Complete the pre-lab assignment in WebAssign.

PROCEDURE

1 Place 1.0 mL of concentrated sulfuric acid into a clean, dry, 6" test tube.

2 Cool sulfuric acid for 10 minutes by swirling in an ice bath (make sure the test tube stays submerged in the ice bath).

3 Add 0.7 mL of methyl benzoate carefully.

4 Shake the mixture to produce *one layer*. (Do not shake vigorously, just side to side enough to form one layer.)

5 Cool the solution in an ice bath for 5 minutes.

6 In a separate 6" test tube, prepare a mixture of 0.4 mL of concentrated nitric acid and 0.4 mL of concentrated sulfuric acid.

7 Cool this mixture in an ice bath for 10 minutes.

8 Using a Pasteur pipet, add the cold mixture of acids drop by drop to the cold solution of the ester in sulfuric acid. Continuously swirl the ester solution in the ice bath as you add the mixture of acids. *Keep the temperature of the reaction at around 0° C throughout the reaction.* This should take 5-10 minutes.

Note: Make sure that you keep the reaction cold. If the reaction isn't cold, you will get another product that you cannot filter and purify.

9 After the mixed acids have been added, swirl the test tube in the ice bath for another 5-10 minutes.

10 Finally, allow the reaction mixture to stand at room temperature, with occasional swirling, for another 10 minutes.

11 Fill another 6" test tube about 1" deep with crushed ice (do not allow water in your test tube). Slowly add the reaction mixture dropwise (via Pasteur pipet) onto the ice with swirling.

12 Allow the ice to melt and then collect the solid material by vacuum filtration on a Buchner funnel. Here is a video that shows how to do vacuum filtration[1].

13 Carefully rinse the solid on the filter with 0.5-1.0 mL of cool water to remove traces of acid.

14 Carefully rinse the solid with about 0.5 mL of ice-cold 95% ethanol.

15 Allow the crystals to dry by placing them on a watch glass in the oven for 15 minutes.

16 When dry, determine the weight and melting point range of the solid. Here is a video that shows how to determine the melting point[2].

[1] https://www.youtube.com/watch?v=zHfnwOHCDWM
[2] https://www.youtube.com/watch?v=oKPqXAT0bG8

Waste Disposal

Place the filtrate (the liquid left over from the filtering process) in the 1 L beaker labeled Filtrate Waste.

IN-LAB QUESTIONS

Download and print the worksheet. You will use this worksheet to record your answers to the In-Lab questions.

Questions

Record the following data.

Question 1: Amount of methyl benzoate _____ mL, _____ g, _____ mol

Question 2: Amount of concentrated nitric acid (16 M) _____ mL, _____ mol

Question 3: Amount of concentrated sulfuric acid (18 M) _____ mL, _____ mol

Question 4: Show your calculations.

Question 5: Theoretical Yield of methyl 3-nitrobenzoate _____ mol, _____ g

Question 6: Actual Yield of product _____ g

Question 7: Percentage Yield _____

Question 8: Melting Point of product (observed) _____

Question 9: Reported Melting Point of methyl 3-nitrobenzoate _____

