Multi-step Synthesis of Methyl Meta-Nitrobenzoate from Bromobenzene

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Abstract

We had to utilize our knowledge of synthetic steps and the mechanisms involved to determine how to create methyl 3-nitrobenzoate from bromobenzene as our starting compound. Using our experience from previous labs and lectures, we determined that we could create our desired product through the process of 4 synthetic steps: creating a Grignard reagent, utilizing the Grignard reagent to produce benzoic acid, performing esterification to produce methyl benzoate, and finally nitration resulting in our desired end product, methyl 3-nitrobenzoate. While we were able to produce the desired products after each synthetic step in our experiment, the amount of product yielded during some steps was not enough to perform sequential synthetic steps and collect the data to verify product quality.

Introduction

Most organic chemistry courses focus on theoretical synthesis, with labs reserved for upper-division courseware. This project provided early exposure to synthetic organic chemistry, letting us apply our classroom knowledge to a real-world synthesis, and deepen our understanding.

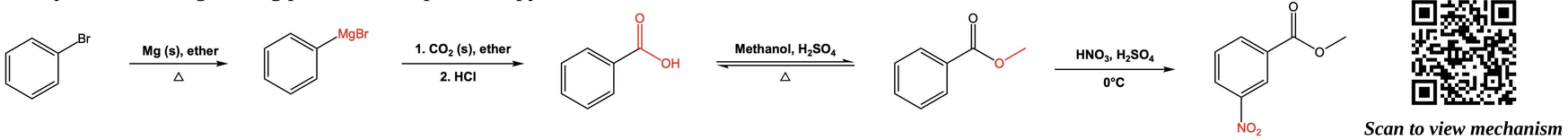
Methods

Materials & Instrumentation:

Starting reagent: bromobenzene. Additional reagents: magnesium turnings, diethyl ether, solid carbon dioxide (dry ice), hydrochloric acid, concentrated nitric acid, concentrated sulfuric acid, methanol. Specialty equipment used: stirring hotplates, spinvane, Erlenmeyer flasks (10, 25 mL), conical vials (5 mL), round bottom flask (10 mL), Buchner funnel, Hirsch funnel, Craig tube, air condenser, water jacketed condenser, capillary tubes, Thermo Fisher Scientific IR Spectrometer, Mel-temp Capillary Melting Point Apparatus.

Procedure:

Carboxylation of benzene to form benzoic acid was conducted following experiments 35 and 35a from *A Microscale Approach to Organic Laboratory Techniques* (6th ed.). Fischer esterification was then carried out using the procedure for experiment 49, substituting methanol for ethanol to produce methyl benzoate. Finally, nitration was performed according to experiment 45 to produce the target molecule, methyl 3-nitrobenzoate. All procedures were scaled up by a factor of two to ensure sufficient product for subsequent synthetic steps and analysis via melting/boiling point and IR spectroscopy.



Scan to view mechanism

Data & Results

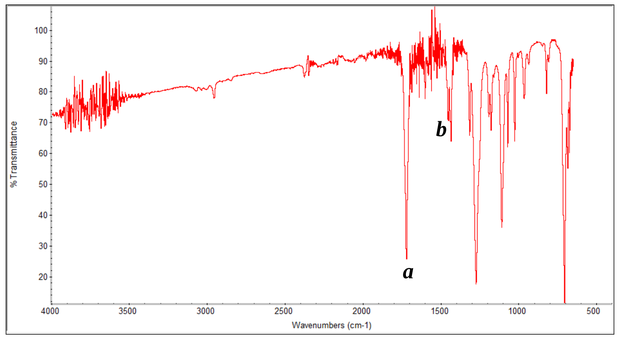
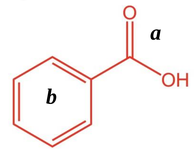


Figure 1. Benzoic Acid IR
Pertinent Absorbencies:

- Carboxylic Acid @ 1710 cm^{-1}
- Aromatic Ring @ 1450-1550 cm^{-1}



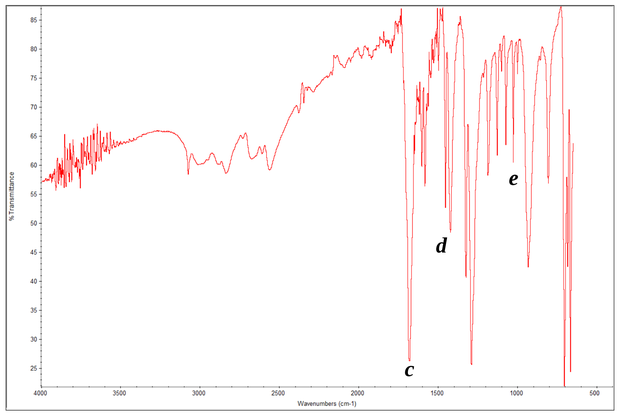
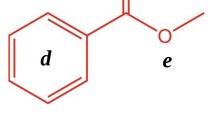


Figure 2. Methyl Benzoate IR
Pertinent Absorbencies:

- Ester C=O @ 1700 cm^{-1}
- Aromatic Ring @ 1450-1550 cm^{-1}
- Ester C-O @ 1050 cm^{-1}



Synthesized Compound	Observed Melting Range (°C)	Literature Melting Range (°C)	Percent Recovery
Benzoic Acid	*Trial 1:* 122.3-124.4	122	26.91 %
Methyl Benzoate (liquid)	*Trial 1:* N/A	199.6 (boiling point)	29.12 %
	Trial 2: 196.0-200.0		36.95%
Methyl 3-Nitrobenzoate	*Trial 1:* 79.0-79.9	78	43.29%
	Trial 2: 77.6-78.3		43.53%

Table 1. Summary of the chemical properties and percent recovery for each synthesized compound at various synthetic stages, including a comparison between observed and literature melting ranges.

Discussion

Using the knowledge from our organic chemistry lectures and labs, we synthesized methyl 3-nitrobenzoate from bromobenzene as our starting reagent. Using our lab textbook as a guide, we devised a 4-step synthesis (pictured below). Throughout each step, we recovered 26.91% benzoic acid, 36.95% methyl benzoate (trial 2), and 43.53% of our final product, methyl 3-nitrobenzoate (trial 2).

Starting with bromobenzene, we added magnesium turnings to produce a Grignard reagent. This reacted with solid carbon dioxide to yield benzoic acid. We then esterified benzoic acid with methanol and sulfuric acid to create methyl benzoate. Lastly, we nitrated methyl benzoate under cold conditions to produce methyl 3-nitrobenzoate.

We felt confident in creating phenylmagnesium bromide, our Grignard reagent since we had formed it successfully in the previous quarter. In our first trial, however, when extracting benzoic acid after the addition of dry ice, no precipitate formed. In our second attempt, we were more successful, yielding 26.91%. Due to our low percentage recovery, we used pure benzoic acid for the esterification and nitration steps to account for potential losses.

Although our percent recoveries for benzoic acid and methyl benzoate were lower than we hoped, we verified the purity of these products via melting/boiling points and IR spectroscopy. Our final product, methyl 3-nitrobenzoate, had a 43% recovery but couldn't be confirmed by IR due to equipment issues. For future experiments, we recommend starting with more material to improve the percent recovery and suggest other spectroscopy techniques, like Nuclear Magnetic Resonance to verify the structures of our compounds.

Acknowledgments

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Works Cited

Pavia, D. L., Lampman, G. M., Kriz, G. S., & Engel, R. G. (2018). Experiment 35: Benzoic Acid, Experiment 49: Benzocaine, Experiment 45: Nitration of Methyl Benzoate. In *A Microscale Approach to Organic Laboratory Techniques* (6th ed.). Cengage Learning.