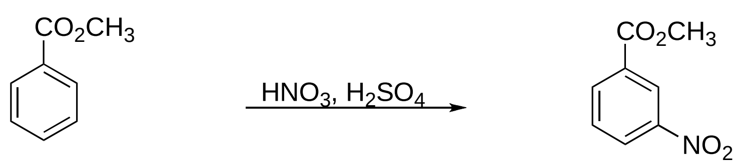
7. Nitration of Methyl Benzoate

M. Jones: Electrophilic Aromatic Substitution, Nitration, 14.4e, pp 686-687.
Disubstituted Benzenes: *ortho, meta,* and *para* Substitution, 14.9, pp 704-717.

This procedure has been adapted from the microscale procedure described in the third edition of *Macroscale and Microscale Organic Experiments* by Kenneth L. Williamson (Houghton Mifflin, Boston, 1999).

Background

In this laboratory, you will be nitrating methyl benzoate with nitric acid using sulfuric acid as your catalyst. Methyl benzoate is a methyl ester. As in our previous naming conventions, the "-e" suffix of the alkane is replaced by "-oate". Therefore, benzene becomes benzoate. Then, the other part of the ester (may be considered the ether portion) is put in front of the benzoate. Since the product is a methyl ester, the methyl comes before the benzoate.



Methyl benzoate
bp 198-199 ^oC
M.W. 136.15
d 1.09

Methyl 3-nitrobenzoate
mp 78 ^oC
M.W. 181.15

Figure 1. The overall reaction for the nitration of methyl benzoate.

The overall reaction is depicted in Figure 1. The nitration of a benzene ring is an electrophilic aromatic substitution reaction, and its general mechanism is summarized in Figure 2.

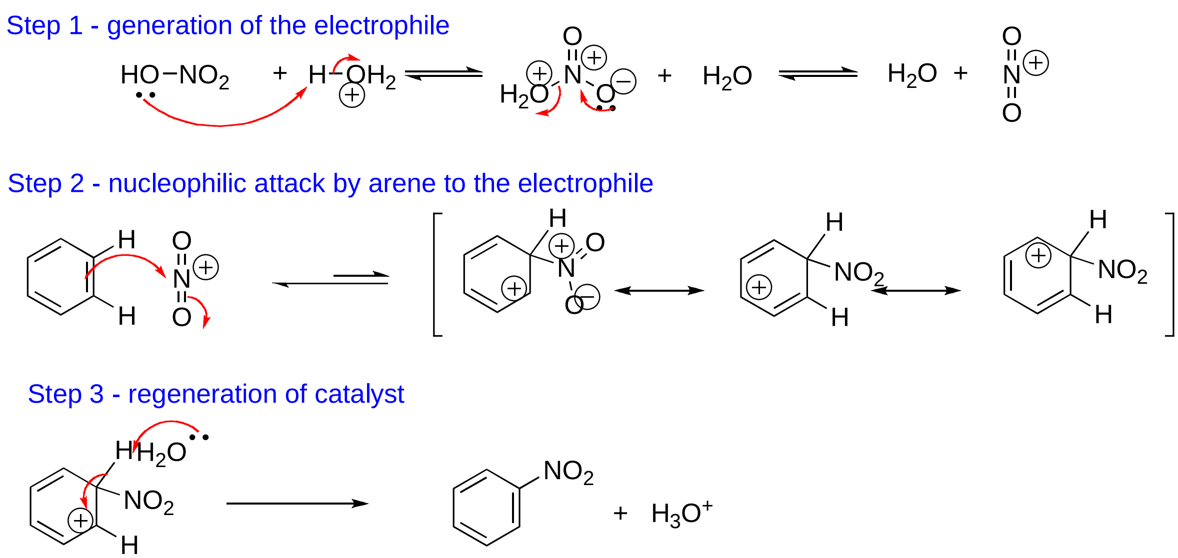


Figure 2. The generic nitration mechanism.

The carbonyl group is an electron withdrawing group (EWG) which deactivates the benzene ring. Protonation of the ester carbonyl group by the solvent (H_2SO_4) increases even further its EW effect (see Fig. 3). However, the reaction is feasible even at the fairly low temperatures (needed to cool the highly exothermic process), and the substitution occurs in *meta* position.

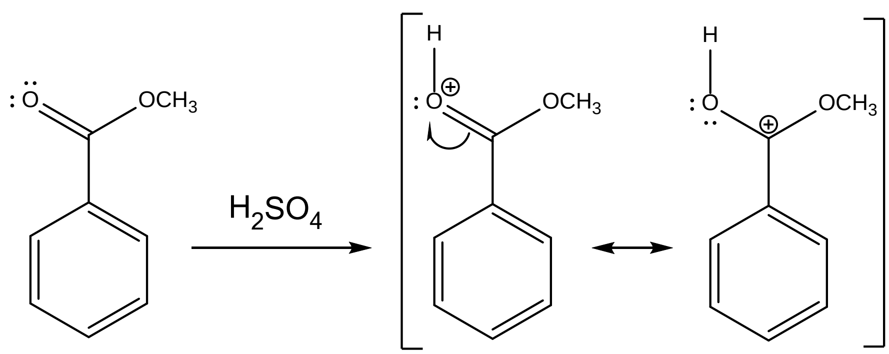


Figure 3. Protonation of the ester group.

Cautions:

- *Make sure to wear old, unimportant clothes (and proper shoes), and make sure to pull hair back.*
- *Take extra care when handling concentrated nitric and sulfuric acid.*
- *Make sure to use a clean spatula, filter flask, and reaction tube. The reaction tubes should be cleaned with soap, water and a brush first, rinsed thoroughly, and dried (if needed rinse with acetone).*
- *Make sure to return the top to the bottles.*
- *Do not return unused chemicals and reagents to the original bottles.*

Experiment

Add 1.0 mL (full pipette) of concentrated sulfuric acid to a large reaction tube and place the tube in an ice water bath. Using a syringe, add 0.4 mL of methyl benzoate to the sulfuric acid. In another small vial (cooled in ice), carefully add 0.5 mL (1/2 pipette) of concentrated sulfuric acid and 0.5 mL (1/2 pipette) of concentrated nitric acid. Add this acidic mixture dropwise to the large reaction tube. Stir after each drop. After the addition is complete, remove the tube from the ice water bath and let it warm to room temperature. While warming, use a glass stirring rod to gently mix your sample, which should be a yellow, homogeneous mixture. If two layers form or the mixture is oily, add a small amount of sulfuric acid. When the mixture has reached room temperature, let it stand for an additional 15 minutes. After this time period, pour the mixture into a 50 mL beaker that contains ice to the 10 mL mark. As the ice melts, a white precipitate will form. Vacuum filter to collect the solid. Wash the solid well with water. The solid is then recrystallized from methanol or methanol/water (if necessary).

For this lab, report your percent yield and melting point. Also, record your observations of your starting materials and product. Take an IR spectrum of your product using methylene chloride as the solvent. Assign the characteristic frequencies. .