

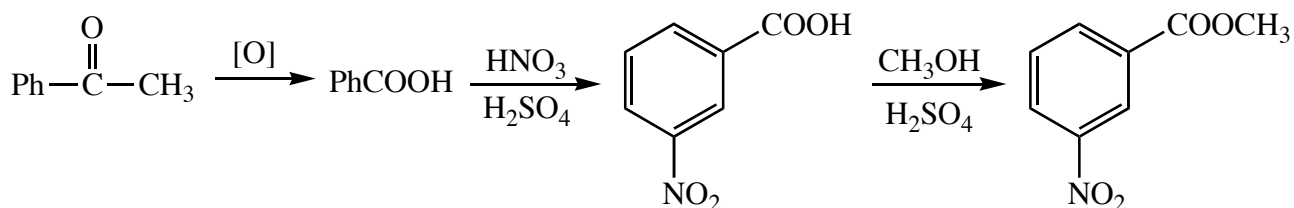
Multi-Step Synthesis of Methyl *m*-Nitrobenzoate

AEM – Last update July 2013

You should have previously prepared benzoic acid by the bleach oxidation of acetophenone. In addition, you should have measured its mass and characterized your benzoic acid product by mp, IR, and/or NMR before you go on to the next reaction step, which is today's experiment.

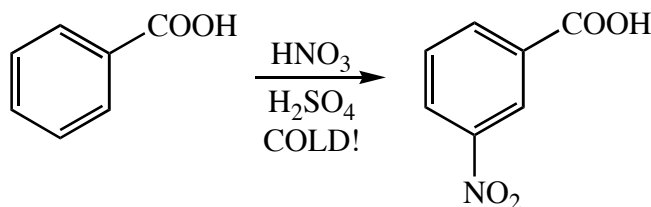
In this lab, you will nitrate your benzoic acid to *m*-nitrobenzoic acid via electrophilic aromatic substitution. Again, characterization of this product must occur before you move on to the final step, which is a Fischer Esterification to produce methyl *m*-nitrobenzoate. Abbreviated versions of the three reaction steps are given here, with more complete versions of the overall reactions given with each lab prompt.

All Three Steps of the Multi-Step Reaction Sequence:



Step 2: Electrophilic Aromatic Substitution of Benzoic Acid to Produce *m*-Nitrobenzoic Acid

Overall Reaction:



CAUTION! You are using very strong concentrated acids in this experiment. Be careful with and respectful of these materials, and clean up all spills promptly!

You should recall from your lecture class that a carboxylic acid would be a *meta*-director in an electrophilic aromatic substitution reaction. In practice, this nitration reaction can result in the production of quite a bit of the *ortho* product as well, unless the temperature is kept very cold throughout the reaction. All of the materials that you will use in the experiment are in proportion to the amount of

benzoic acid that you are reacting. You should use between 1.5 and 2 g of PhCOOH, and record its mass carefully.

First, prepare a nitrating mixture (NM) by slowly adding concentrated H₂SO₄ to concentrated HNO₃ while you are cooling it in a small Erlenmeyer flask in an ice/water/salt bath to 0°C or less. You will make this NM in proportion to the amount of benzoic acid that you will be reacting, although the benzoic acid will not be in this mixture. For each g of benzoic acid, use 1 mL of concentrated H₂SO₄ and 0.67 mL of concentrated HNO₃ to prepare this NM. Keep it cold! You may want to clamp it to keep it from falling over in your ice bath.

Second, prepare your reaction mixture (RM) in a large Erlenmeyer flask; this container will maximize cooling during the reaction. Add concentrated H₂SO₄ to the Erlenmeyer and cool it to 0°C or less. Here you need 2.5 mL of H₂SO₄ for each g of benzoic acid. Add the benzoic acid slowly to the H₂SO₄, keeping the temperature below 0°C. During the course of this mixing and the reaction to follow, your RM should stay below 0°C and never exceed 5°C! When all of the benzoic acid has been added to the H₂SO₄, it will be rather paste-like.

Now, double-check that your RM is colder than 0°C and slowly add the COLD NM to the COLD RM, mixing carefully and keeping it cold. Use a short disposable pipet to transfer it and be sure that the rate of addition allows for efficient cooling; remember that your RM should stay below 0°C and never exceed 5°C! You will have to add the NM very slowly at first, but the rate can be sped up as the reaction proceeds. Use the temperature as a guide. After all of the NM has been added, keep the mixture cold for another 10-15 minutes with occasional stirring.

Finally, pour the mixture over an ice/water slurry of about 100 g of ice and 100 mL of water. Stir vigorously and your product should precipitate. Filter the product from the mixture, wash well with cold water, and allow it to dry. When the product is completely dry (next lab period or later), obtain its mass and calculate the theoretical and percent yield for your reaction. Check its purity by mp, IR, and/or NMR, as directed by your professor. The product is usually of sufficient purity to use for the next step, but if that is not the case, you can recrystallize it from water.

Clean-up. Check the pH of all the solutions, neutralize as needed, and flush down the drain with lots of water.