

Experiment 15 —

Nitration of Methyl Benzoate

Pre-lab preparation. (1) Write the balanced equation for the reaction that you will be carrying out, including structures of the reactant and product. Do you expect *ortho*-, *meta*-, or *para*-nitration? (2) Just because you expect a particular result doesn't mean that's what will happen. So in addition to looking up relevant physical properties of the methyl benzoate starting material, look up properties of all three possible mono-nitrated products. (You may have to search beyond the usual sources, but the data should not be difficult to locate.) Focus on the physical property that will be most useful to you in determining which one(s) were formed. (3) List quantities of reactant, reagents, and amount of product expected as you did in the last experiment, but this time you're given with the quantity of the starting material. Directly below the aromatic reactant and product — and let's include the nitric acid as well (commercial conc. nitric acid is 70% aqueous HNO₃, density 1.5 g/ml) — list (a) the molecular weight, (b) the mass (and volume, if relevant), (c) the number of moles, (d) mol ratio of reactants, and (e) any relevant physical data. (4) Write the mechanism for formation of the product(s) you expect. (5) What characteristic IR absorptions would you expect for a nitro group? What vibrations do these correspond to?

Carrying out a nitration with a mixture of concentrated nitric and sulfuric acids is an important rite of passage within the introductory organic chemistry course. If you can do it successfully you will be well on your way to earning the title Organic Chemist.

The nitration itself is not especially hazardous, but you must *be very careful with the concentrated nitric and sulfuric acids*. Be especially careful of acid residue on glassware, on the benchtop, etc. Any drips, drops, or dribbles need to be cleaned up immediately. Each acid alone will eat your flesh (and nitric will turn your skin yellow); together they are even more menacing. Wear goggles and gloves, be careful, think about what you're doing, and everything will be fine.

In this experiment you will nitrate methyl benzoate. The product will be recrystallized from methanol. Melting point and IR analysis may be helpful in determining the structure of the product. You will also get copies of NMR spectra of crude and recrystallized material at the end of the lab.

Procedure. *As you go, record in your notebook what you actually did and what you observed in enough detail that you or someone else can understand and repeat your procedure.*

Start with 10 mmol of methyl benzoate. Your pre-lab prep should include determination of the quantity of methyl benzoate needed (mass or volume depending on its physical state). Just to be safe, have your TA check that you determined the correct quantity before you begin. (Hint: if you plan to start with something on the order of a kilogram of ester and a gallon of sulfuric acid, please go back and redo the calculation using 10 *milimoles* rather than 10 moles.)

Do the reaction in a fume hood. Caution: sulfuric and nitric acids are extremely strong and corrosive acids. Be very careful with them. Begin by placing 4 ml of H_2SO_4 in a small Erlenmeyer flask. Cool this in ice, then add the aromatic ester. It should dissolve completely to form a homogeneous solution. Slowly, drop-by-drop, add 1.0 ml of conc. HNO_3 to your PhCO_2CH_3 /sulfuric acid solution. Swirl the flask gently during the addition. The temperature should remain below $15\text{ }^\circ\text{C}$ — just feel the flask with your fingers to make sure it doesn't get warm. Rumor has it that if the temperature gets too high the yield decreases due to formation of byproducts.

After the addition is complete, allow the reaction mixture to warm to room temperature with occasional swirling. After about 15 min at room temperature, add the conc acid solution to 25 – 30 ml of crushed ice in a small beaker (since we don't have deionized water ice, the regular tap water ice will have to do), and rinse the reaction flask with a little water. The expected product is insoluble in water. If you have solid precipitate at this point, give yourself (and your partner) a pat on the back. If you're lucky this will be something you want. Isolate it in the usual manner and rinse it with little water and a tiny bit of ice-cold methanol. This acid solution is dilute enough that you should be able to get away with regular filter paper. *Discard the filtrate in the specially marked waste container.*

Recrystallize the solid from methanol. Published procedures suggest using about 1 - 3 ml per g of product. Don't waste time weighing it — you know about how much you should have, so just guesstimate. You now have a choice — either (a) start with a little solvent and add more if all the solid doesn't dissolve upon heating, or (b) start with a lot of solvent, then get no crystals when you cool the solution, heat it up again to boil off solvent, try cooling it again, etc. Hmm... tough decision. Also, look carefully at your hot solution — if there's undissolved junk, you'll need to separate that from the solution. With a larger volume you'd do a hot filtration, but since you're working on such a small scale, it may be easier to cool the solution a bit, then pipet it away from the junk, into a clean vessel.

Keep in mind that in a recrystallization one wants to encourage crystals of product to grow *slowly* from a supersaturated solution, leaving impurities in the solution. You will not accomplish a purification by forcing the solid to crash out of solution as a powdery mass, nor if you boil off all the solvent and then cool the molten product.

After you've completed the recrystallization, press your beautiful crystals between two pieces of filter paper to sop up the excess solvent, then give them some time to air-dry (see below). Spend some time admiring them, then measure the IR spectrum, yield, and mp. Remember that the melting "point" will almost certainly be a *range*, not a single temperature! You will be given NMR spectra of crude and recrystallized material prepared by your instructor. Interestingly, material that was allowed to air-dry for about an hour still shows small methanol signals in the ^1H NMR (can you find them? Look carefully.) This is why the management recommends waiting as long as possible to measure your mp. Get everything else done first to give your solid as long as possible to dry.

Waste disposal. *It's important to discard all nitric acid-containing solutions in the specially marked waste container.* HNO_3 is an oxidizer and will react with many organic compounds. Some of the reaction products are volatile and have been known to cause explosions, start fires, and even rob nearby convenience stores. Although this is unlikely with the scale we're using, it's much easier to play it safe than to deal with the aftermath.

Report. Are the spectral data consistent with the structure of the expected product? Do the data tell you if the product is mono-nitrated vs dinitrated vs trinitrated? How can you tell which isomer(s) were formed? Which IR stretches support your proposed structure? Assign the ^1H NMR signals to the various Hs in your proposed product. How do you account for the chemical shifts and splittings of the aromatic Hs in terms of the structure? The NMR spectra of crude and purified product look a bit different, eh? What compounds do you think were removed in the recrystallization step? Make an educated guess. You may get a ^{13}C spectrum too. How does this support your proposed structure?

Turn in the duplicate copies of your notebook pages, attach your NMR spectra, and attach your IR spectrum (or make reference to your partner's report if that's where the IR is attached).

Unfortunately, there is no lab for the next two weeks. But the next one (the week after spring break) will be a real "humdinger", as then say.

Adapted from *Macroscale and Microscale Organic Experiments*, K.L. Williamson; 3rd ed, 1999; pp. 355–9.