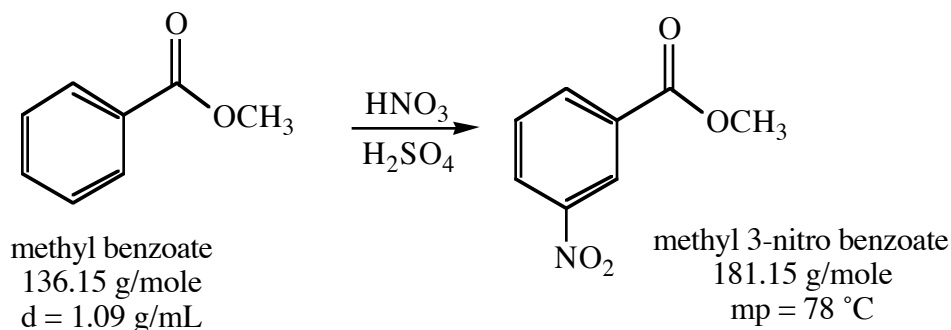
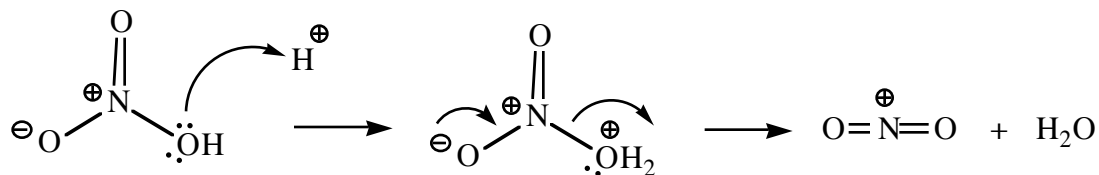


Nitration of Methyl Benzoate



The nitration of methyl benzoate is a classic example of an Electrophilic Aromatic Substitution (EAS) reaction. The aromatic ring is very stable, so it will only be able to react with a very reactive electrophile (E^+). In addition, our starting material is a deactivated benzene ring, due to the electron withdrawing ability of the carbonyl group attached to the ring. Therefore, we must use the very reactive mixture of nitric acid and sulfuric acid to generate the nitronium ion ($^+NO_2$). This mechanism is shown below; the sulfuric acid is providing the H^+ . It is the removal of water that drives this mechanism to completion. More reactive aromatic rings (such as phenols) do not require the addition of the dehydrating agent sulfuric acid.

Generation of the electrophile: NO_2^+



The ensuing EAS reaction with methyl benzoate forms the *meta* product almost exclusively; your discussion should clearly indicate why this is so. Use resonance structures and energy diagrams to explain this selectivity! Pictures are worth a thousand words!!!

Experimental Procedure

Place 1.2 mL of concentrated sulfuric acid and a magnetic stir bar in a small round bottomed flask (5 or 10 mL flask) and cool this flask in an ice bath on a magnetic stirrer. Add 0.6 g of methyl benzoate by syringe (use the density to determine the volume needed) and keep the reaction flask in the ice bath. While stirring this mixture, use a pasteur pipet to slowly add (dropwise) a mixture of 0.4 mL of concentrated nitric acid and 0.4 mL of concentrated sulfuric acid. The storeroom may provide us with this nitric/sulfuric acid mixture already. If so, use 0.8 mL of this pre-made mixture.

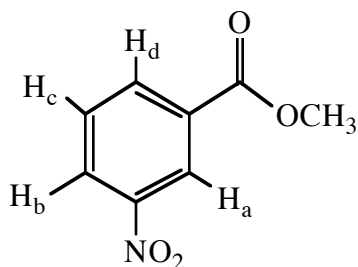
After this addition, remove the ice bath and allow the reaction mixture to warm to room temperature while stirring. Then stir this reaction at room temperature for 30 minutes. Place approximately 5 g of ice in a small beaker and pour the reaction mixture onto the ice (the reaction of sulfuric acid with water is very exothermic). Cool this resulting mixture in an ice bath for a few minutes and isolate the solid product by suction filtration with your Hirsch funnel. Wash the product with ice cold water very thoroughly.

Recrystallize the product from hot methanol in your small Erlenmeyer flask. It will not require very much methanol. If you do not obtain any crystals when cooling this solution, allow the solution to

warm to room temperature, add a few drops of water, and then cool again in the ice bath. This will make the solvent less organic and thus the organic product should be less soluble. Allow your product to dry, weigh it to determine your percent yield, and obtain its mp, IR, and ^1H NMR.

QUESTIONS

1. Explain - using mechanisms, resonance structures, and energy diagrams – why the meta product is obtained, rather than the ortho or para product.
2. Is the product more or less reactive than the starting material?
3. If a second nitronium ion reacted, what would be the product of this second addition?
4. Why don't we see very much (if any) of the product of a second addition?
5. The structure of the product is shown below. Due to the electron withdrawing nature of the ester and nitro substituents, the ^1H NMR shows unusually high ppm shifts for the aromatic hydrogens.



There are 4 unique aromatic hydrogens labeled a-d. In the ^1H NMR, two of these hydrogens have similar ppm shifts and their peaks overlap. The other two aromatic hydrogens have unique ppm shifts and distinct peaks in the NMR.

Explain both the ppm shifts and splittings shown by these two unique hydrogens. Remember that more electron density lowers ppm shifts and less electron density raises ppm shifts (hint: resonance structures). To explain the splittings, a “splitting tree” (like I have drawn in lecture) can help. Aromatic coupling: *ortho* is $\sim 7\text{-}9$ Hz, *meta* is $\sim 1\text{-}3$ Hz, *para* is very small and rarely seen.