

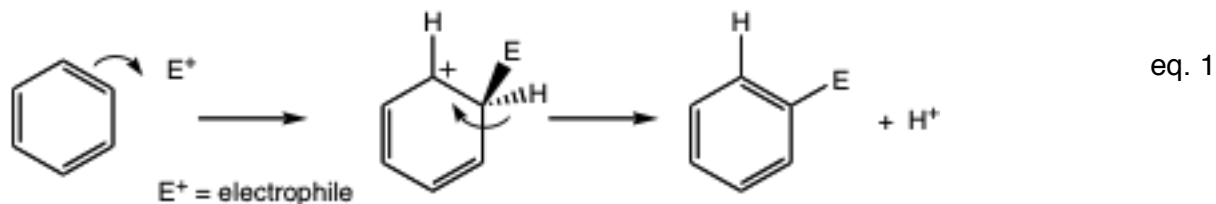
An Electrophilic Aromatic Substitution: The nitration of methyl benzoate

Objective

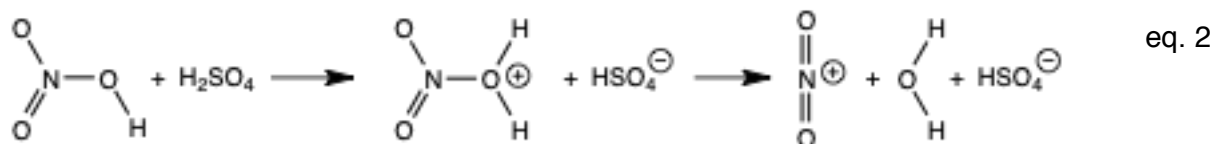
To investigate the reactivity of substituted benzenes and to examine the relationship between electron withdrawing/donating groups and reactivity.

Background

Because aromaticity is a stabilizing influence, benzene rings do not undergo electrophilic additions as typical alkenes or non-aromatic conjugated π systems do. Instead, benzene rings undergo substitution reactions referred to as electrophilic aromatic substitution (eq. 1). Additionally, the low reactivity of benzene rings requires that the electrophile be extremely reactive. For example, Cl_2 will not react with benzene, whereas $\text{FeCl}_3 \cdot \text{Cl}_2$ will. Due to the Lewis acidity of FeCl_3 , the Cl_2 bond is strongly polarized producing the super electrophile $[\text{FeCl}_4^-][\text{Cl}^+]$. This incipient Cl^+ is reactive enough to initiate the reaction. This is a fairly general scheme, start with an electrophile and make it more electrophilic using a strong acid.

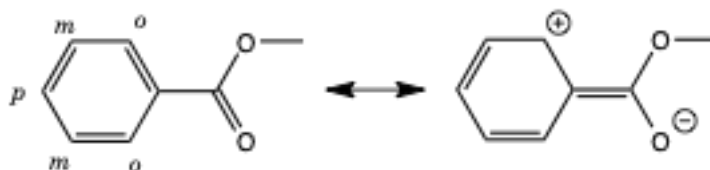


For this activity, the nitric acid will be converted to an excellent electrophile by adding H_2SO_4 . Sulfuric acid reacts with nitric acid by protonating it. Once the nitric acid is protonated, a water molecule and a nitronium ion form (eq. 2.)



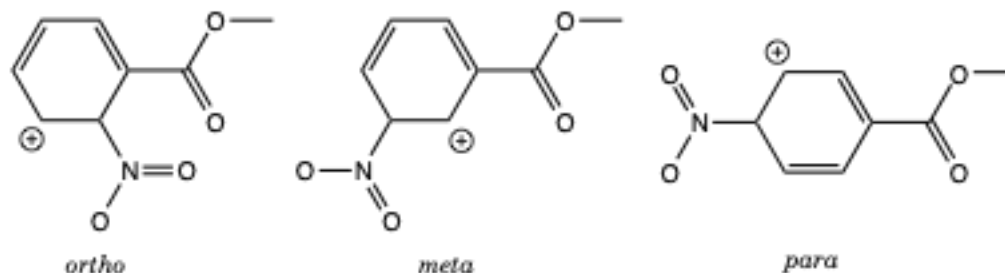
Benzene rings can donate electron density from their extended π systems to an electron deficient atom at a benzylic position. Similarly, benzene rings can accept electron density into their π system from electron rich benzylic atoms. Thus, substituents can increase or decrease the electron density on a benzene ring (see Figure 1). Additionally, these changes are not equally distributed across all of the C atoms of the benzene ring. In fact, the changes to the electron density at the ortho (*o*), meta (*m*), and para (*p*) positions can be quite different, this can lead to substantial reactivity differences in substituted benzenes.

Figure 1



When an electrophile attacks a substituted benzene ring, the attack could conceivably occur at three different locations, the *ortho*, the *meta*, or the *para* positions (fig 2.). In this reaction, the *meta* position is preferred.

Figure 2



Procedureⁱ

Nitration of Methyl Benzoate

Tare a 5-mL conical vial and add 0.21 mL of methyl benzoate to the vial. After determining the mass of the methyl benzoate place a magnetic spin vane in the vial and carefully add 0.45 mL of sulfuric acid to the vial containing the methyl benzoate. Cap the conical vial with an air condenser, secure the apparatus with a clamp, and place the conical vial in an ice-water bath.

Charge a 3-mL vial with 0.30 mL of a 1:1 nitric acid:sulfuric acid solution. Secure the vial with a clamp, and cool the solution in an ice-water bath.

With stirring (using the magnetic spin vane) over 15 minutes slowly and carefully transfer the cooled nitric/sulfuric acid solution to the methyl benzoate mixture using a nine inch pipette. After adding the nitric/sulfuric acid solution, warm the reaction to room temperature using a room temperature water bath, discontinue stirring, and allow the reaction to stand for 15 minutes.

Be careful when transferring the nitric/sulfuric acid solution. The solution is extremely corrosive and adding the acid solution too quickly to the reaction will cause the formation of an unwanted byproduct. Thus, when transferring the acid, only draw a small amount of acid into the pipette.

Isolation and Purification of the Product

Transfer the reaction mixture to a small beaker that contains 2 grams of ice. After the ice has melted, isolate the product by vacuum filtration on a Hirsch funnel. Wash the crude product twice with 1 mL of cold water and twice with 0.3 mL of ice-cold methanol. Recrystallize the crude product from hot methanol.

Identification of the Product

Determine the melting point of the product and collect IR data by depositing a thin film of the product on the ATR crystal (it is generally considered a bad idea to compress nitrated organic materials into a KBr pellet or to compress them against an ATR crystal using an anvil). Dissolve 20 mg of the product in 0.25 mL of methylene chloride. Coat the crystal

with the methylene chloride solution, wait for the methylene chloride to evaporate, and collect a spectrum of the solid that remains on the crystal. Remember to collect a background before placing the solution on the crystal, and remember to wait for the methylene chloride to evaporate before collecting the spectrum.

Experimental Report

In addition to answering the questions that follow, identify your product (draw its structure), report the amounts of the methyl benzoate (mass and moles) used, the actual yield in g and mol, and the percent yield (if your yield was too low to be determined reliably, report the theoretical yield). Report your observed melting point and include a printout of the IR spectrum with the report. To determine the identity of your product you will need to look up the melting points of the three possible methyl nitrobenzoates (methyl 2-nitrobenzoate, methyl 3-nitrobenzoate, and methyl 4-nitrobenzoate).

Examine the resonance structures in figure 1. Draw two more resonance structures. Which benzene carbon atoms are the most electron rich, carbon atoms at the *ortho*, *meta*, or *para* positions? Explain your response.

Examine the intermediates in figure 2. For both of the structures where the nitronium has added to the *meta* and *para* positions draw two resonance structures that involve the benzene and carboxyl (the substituent) π systems. Which of the intermediates would be lower in energy? Explain your response.

ⁱAdapted from Pavia, Lampman, Kriz, and Engel, "Relative Reactivities of Several Aromatic Compounds", *Introduction to Organic Laboratory Techniques: A Microscale Approach*. Saunders College Publishing, 1999.