

# Nitration of Substituted Aromatic Rings and Rate Analysis

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September 13, 2010

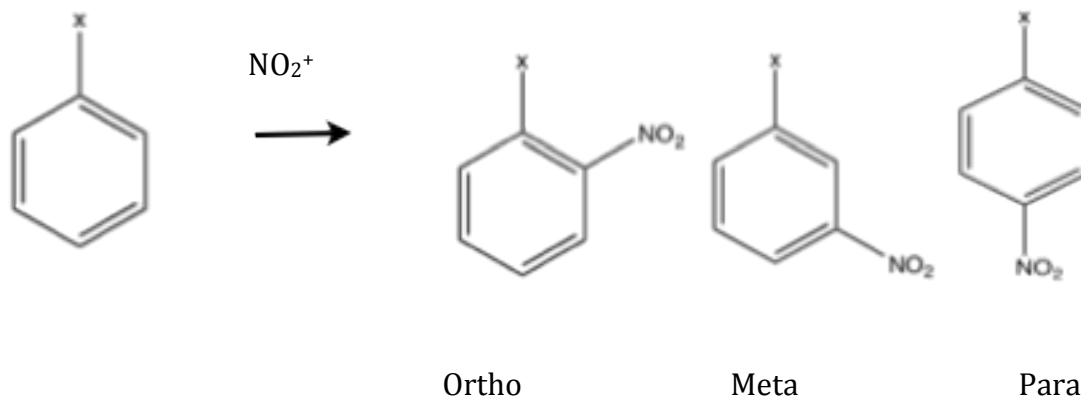
## **Abstract**

This project studied the electrophilic aromatic nitration of many monosubstituted aromatic rings under a standard set of conditions. A wide range of starting materials were tested until a set of 10 starting materials that could easily be nitrated using concentrated sulfuric acid and concentrated nitric acid were found. In order to determine relative rates of the starting materials competitive nitration reactions were run. This information was collected in order to design a new laboratory experiment to be used in an undergraduate organic chemistry laboratory. The goal of designing the laboratory experiment was to find reactions that give meaningful results that will allow students to establish trends between substituents and rate and directing effects.

## **Introduction**

Electrophilic aromatic substitution is the addition of a nitro ( $\text{NO}_2^+$ ) group to an aromatic ring. When the aromatic ring is monosubstituted, meaning it already has one substituent on it, the nitro group can be added to either the ortho, meta or para position as seen in figure 1.

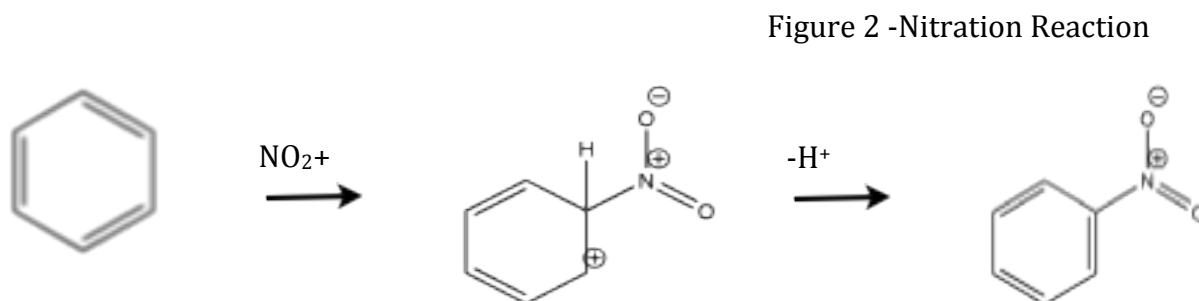
Figure 1 – Ortho, Meta, Para positions



The position that the nitro group adds to on a monosubstituted ring is determined by the type of substituent on the ring. A substituent can either be an electron releasing group or an electron withdrawing group. Electron releasing groups are substituents that donate electron density to the aromatic ring and activate it towards the nitration reaction, speeding up the reaction. Electron releasing substituents cause the nitro group to add in the ortho or para position. Electron withdrawing groups are substituents that remove electron density from the aromatic ring and deactivate it towards the nitration reaction, slowing the reaction down. In general deactivating groups cause the nitro group to add to the meta position except for the halogens which add to the ortho or para position.

Using a standard set of conditions many different monosubstituted rings were nitrated in order to find a large range of both activating and deactivating substituents that would work under the given conditions. [The general procedure for the reaction was adopted from *Organic Laboratory Techniques, A Small Scale Approach*<sup>1</sup>.] The general procedure involves mixing concentrated sulfuric and concentrated nitric acid, which produces the electron deficient nitronium ion. The

nitronium ion is attacked by the conjugated pi system of the benzene ring to form an unstable carbocation. The carbocation will then lose a hydrogen ion to form the final product; this reaction can be seen in figure 2.



Once the starting materials that worked best under the nitration reaction conditions were identified their rates were studied by running competitive nitration reactions. A competitive nitration reaction reacts 2 starting materials with concentrated nitric and sulfuric acid, using the nitric acid as the limiting reagent. This means there is only enough nitric acid to nitrate one starting material. The starting material that gets nitrated in the majority has a faster rate. This type of reaction allows the rates of the starting to be compared relative to each other. The competitive nitration reactions are run in a glacial acetic acid in order to dissolve the starting materials. The general procedure for the competitive nitration reaction was adopted from the *Laboratory Manual for Organic Chemistry*<sup>2</sup>

The information from these reactions was gathered with the intention of designing a laboratory experiment that can be used in an undergraduate organic chemistry laboratory. Many different starting materials were studied in order to find the ones that gave the most meaningful results. The relative rates were measured so that students will be able to see how the type of substituent affects the

rate and then deduce a set of rules about how the different types of substituents effect the reaction.

## Results

Of the twenty-one starting materials that were nitrated under the given conditions, there were many that easily yielded the desired products and other reactions that didn't yield the intended product or were very difficult to run. Table 1 shows all of the starting materials that worked well and achieved the desired nitrated product under the reaction conditions.

Table 1- Successful Nitration Reactions

Starting Material	Type of Substituent	Major Product	Percent Yield
Acetanilide	Strongly Activating	4-nitroacetanilide	51.0%
Toluene	Activating	4-nitrotoluene	43.2%
Ethylbenzene	Activating	Mixture of two liquids; 2-nitro ethyl benzene and 4-nitroethylbenzene	crude 71.2%
Tert-butylbenzene	Activating	Mixture of two liquids; 1-tert-butyl-4-nitrobenzene and 1-tert-butyl-2-nitrobenzene	crude 88.8%
Chlorobenzene	Deactivating	2-nitrochlorobenzene and 4-nitrochlorobenzene	14.3%
Bromobenzene	Deactivating	4-nitrobromobenzene	30.8%
Benzonitrile	Strongly Deactivating	3-nitrobenzonitrile	45.1%
Methyl Benzoate	Strongly Deactivating	Methyl 3-nitrobenzoate	73.3%
Benzoic Acid	Strongly Deactivating	3-nitrobenzoic acid	73.5%
Nitrobenzene	Very Strongly Deactivating	1,3-dinitrobenzene	69.0%

More detailed information about each of the reactions can be found in the experimental section.

There were also many starting materials that didn't yield the desired product or were very difficult to run under the given conditions. Problems that were seen in some of the starting materials included side reactions and multiple nitrations; these starting materials can be seen in table 2.

Table 2 – Unsuccessful reactions

Starting Material	Type of Substituent	Problem
Phenetole	Strongly Activating	Made a crystal that has some characteristics of 4-nitrophenetole but not all, may have been dinitrated product
Phenol	Very Strongly Activating	Made a tar of multiple nitration products
Anisole	Strongly Activating	Multiple nitrations
Phenyl Acetate	Strongly Activating	Multiple nitrations
Isopropyl Benzene	Activating	Made some product but also some tar from multiple nitrations
Biphenyl	Activating	Made a very sticky product that was hard to work with and didn't resemble the desired product
Styrene	Activating	Was sulfonated by the sulfuric acid <sup>3</sup>
Benzaldehyde	Strongly Deactivating	Only very trace amounts of intended product were produced, a chunky yellow unidentified solid was produced that made the reaction difficult
Acetophenone	Strongly Deactivating	Made a tar
Alpha, alpha, alpha-trifluorotoluene	Very Strongly Deactivating	Produced only trace amounts of the product

More information about each of the reactions and product identification can be found in the experimental section.

Several sets of competitive nitrations were run in order to determine the relative rates of the starting materials seen in table 1. The different reactions that were run along with the major product can be seen in table 3.

Table 3- Competitive Nitration Reactions

Starting Material #1	Starting Material #2	Major Product
Acetanilide (Strongly Activating)	Methyl Benzoate (Strongly Deactivating)	4-nitroacetanilide
Bromobenzene (Deactivating)	Nitrobenzene (Very Strongly Deactivating)	4-nitrobromobenzene
Toluene (Activating)	Nitrobenzene (Very Strongly Deactivating)	Crude: 4-nitrotoluene
Acetanilide (Strongly Activating)	Bromobenzene (Deactivating)	4-nitroacetanilide
Bromobenzene (Deactivating)	Chlorobenzene (Deactivating)	Mixture of bromo and chloro products
Acetanilide (Strongly Activating)	Toluene (Activating)	4-nitroacetanilide
Acetanilide (Strongly Activating)	Nitrobenzene (Very Strongly Deactivating)	4-nitroacetanilide

More information about the competitive nitration reactions can be found in the experimental section. TLC (thin layer chromatography), which is a method used to separate the components of mixture, and melting point were the main tools that were used to identify the major products of the competitive nitration reactions. The crude and final products for each of the reactions were analyzed and the major product demonstrated which starting material had a faster relative rate but all products showed up in at least trace amounts in the crude product. For many of the solid products once they were recrystallized only the one major product(s) was isolated for identification.

## Discussion

For the monosubstituted reactions it can be seen in table 1 and 2 that there were many reactions that worked and also many that didn't work. It can be seen from looking at table 1 that there were many more successful deactivating groups than activating groups. The explanation for this trend is that when there is an activating substituent on the ring, the ring may be so activated that multiple nitrations occur. For many of the reactions it was not that the ring would not nitrate under the given conditions but instead would nitrate multiple times resulting in the tars that were often observed in the activating groups.

The other trend that can be observed from table 1 is that in general the deactivating groups had a higher yield than the activating groups with the exception of chlorobenzene and bromobenzene, which had very low yields. The explanation for this is that the activating groups and the halogens are ortho para directors, meaning that there are two possible locations for the nitro group to add. For most of the crude samples two different products could be detected but after purification only one major product remained. Because one of the products was washed away a lower yield was observed compared to the strongly deactivating groups where the meta product was the only expected product. In general the deactivating groups were easier reactions to run because the ring was already deactivated towards the reaction and once the very strongly electron withdrawing nitro group was added to the ring multiple nitrations were not an issue.

Very strongly activating groups could not be done by this method as demonstrated by phenol. For this reaction it was observed that even with the addition of a few drops of the nitrating mixture into the starting material, a black tar began to form. The reason for this is because the phenol activates the ring so much that even the very strongly deactivating nitro group does not stop the phenol from dinitrating and even trinitrating, which resulted in tar. The very strongly activating group was the only group that could not be used at all using the standard set of conditions.

Competitive nitrations were a way to compare the rate of the reactions of the different starting materials seen in table 1. The major product shows which one of the starting materials has the faster rate of reaction. Trends can then be established over a wide range of molecules to compare the rates. For example the reaction of bromobenzene and nitrobenzene yielded 4-nitrobromobenzene as the major product meaning bromobenzene has a faster rate of reaction than nitrobenzene. The reaction of bromobenzene and chlorobenzene yielded a mixture of both nitrated products meaning the starting materials reacted at about the same rate. When bromobenzene was reacted against acetanilide the acetanilide nitrated product was the major product meaning that acetanilide has a faster rate of reaction than bromobenzene. These three different reactions can be put together to give the general scheme of rates:

Acetanilide > Bromobenzene = Chlorobenzene > Nitro benzene.

This trend is then backed up by the competitive nitration reaction between acetanilide and nitrobenzene, which yielded acetanilide as the major product. Once



more competitive nitration reactions are run the comparisons can be made on all of the starting materials seen in table 1. These reactions will be useful in making a new organic chemistry laboratory experiment because the students can identify the general trends they see and then establish trends on what kind of substituents cause reactions to go slower or faster.

The UV-Vis spectrometer (Ultraviolet-Visible) was used to try and measure the rates of the nitration reactions. The consumption of the starting material was measured rather than the formation of products because many of the reactions have multiple products. The first method of using the UV-Vis involved scaling down the reaction and running it in the cuvette, taking absorption readings every 30 seconds. This method presented a problem because all the starting materials absorbed at wavelengths in the 200-350 nanometer region, which is where nitric acid absorbs very strongly. In order to try and avoid this problem the reaction was run in a round bottom flask and aliquots of the reaction were taken out and worked up to remove the nitric acid before the UV-Vis reading were taken. This method still did not work because with most reactions the starting materials and products absorb at wavelengths very close to each other, sometimes only 5-10 nanometers apart making it hard to get accurate absorption readings. Due to all the problems the UV-Vis spectrometer rate measurements were not pursued and instead attention was focused on the competitive nitration reactions.

Future research will include running more sets of competitive nitration reactions so that more overall trends can be established covering all of the starting materials that are seen in table 1. HPLC can also be used on the competitive

nitration reactions to determine how much of the different products were made. In each of the reactions there were traces of the minor products, but HPLC can give insight into the quantity of minor product was made and how it varies from reaction to reaction. Disubstituted compounds can also be examined for testing under the general reaction conditions and also for studying using competitive nitration reactions. The disubstituted compounds would add a new level to the lab because they would force students to figure out what happens when there is more than one substituent on the ring and which substituent's directing effects are more prominent.

## **Conclusion**

A set of 10 monosubstituted aromatic starting materials that could be nitrated using concentrated sulfuric and nitric acid easily was found. The reactions ran easily and produced plenty of product so they can be used in an undergraduate organic chemistry laboratory. In order to do a rate analysis of the different starting materials, competitive nitration reactions were run. Competitive nitration reactions gave insight to the relative rates of the reactions, which would allow students to establish trends of how different substituents activate or deactivate the molecule towards electrophilic aromatic substitution.

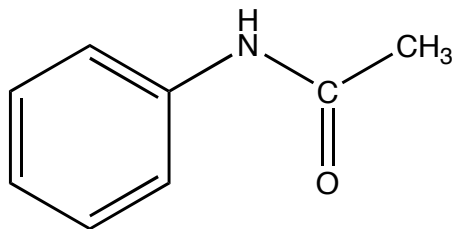
## **References**

1. Pavia, Donald L. *Introduction to Organic Laboratory Techniques: a Microscale Approach*. Fort Worth: Saunders College Pub. 1999.

2. Moore, William R., and Anthony Winston. *Laboratory Manual for Organic Chemistry: a Microscale Approach*. New York: McGraw-Hill, 1996. Print.
3. Carey, Francis A. *Organic Chemistry*. 6th ed. New York, NY: McGraw-Hill, 2006.

## Experimental Procedure

### Acetanilide



4.0652 grams (30.07 mmols) of acetanilide were mixed with 6.00 ml (0.106 mols) of 95% concentrated sulfuric acid. A mixture of 2.00 ml (35.45 mmols) of concentrated nitric acid and 2.00 ml (31.55 mmols) of concentrated sulfuric acid was slowly added over 16 minutes while the reaction was on ice and stirred occasionally. The reaction turned a yellow/brown color and remained at room temperature for 20 minutes with occasional stirring. The reaction was poured over 25 grams of ice and yellow crystals were formed. TLC of the crude product showed that the starting material was consumed and that two products were formed, most likely the ortho and para products. The crude crystals were recrystallized in methanol yielding 2.7556 grams of 4-nitroacetanilide as yellow crystals. The other product seen by TLC was most likely 2-nitroacetanilide and was washed away during the recrystallization.

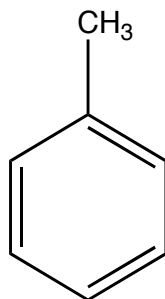
Percent Yield: 51.0%

Melting Point: 198-201 degrees Celsius

NMR (60 MHz, CDCl<sub>3</sub>):  $\delta$  2.1 (3H, s), 4.0 (1H, s), 8.0 (4H, m)

IR (wavenumbers cm<sup>-1</sup>): 3277.04, 1681.21, 1619.08, 1597.94, 1567.15, 1503.33, 1347.29, 1302.95, 1269.60, 1113.56, 849.14, 750.04

## Toluene



2.7753 grams (30.04 mmols) of toluene were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over 11 minutes a mixture of 2.00ml (31.55 mmols) of concentrated nitric acid and 2.00 ml (35.44 mmols) of concentrated sulfuric acid was added while the reaction was stirred on ice. The reaction turned a yellow/orange color and was quenched over 35 grams of ice after stirring at room temperature for 87 minutes. A yellow solid was suction filtered and trace amounts of a liquid product were isolated from the organic phase. The crystals were recrystallized in water to yield 0.9554 grams of a yellow shiny crystal. TLC showed the final product to have 1 major component identified as 4-nitrotoluene and 1 minor product, identified as 2-nitrotoluene.

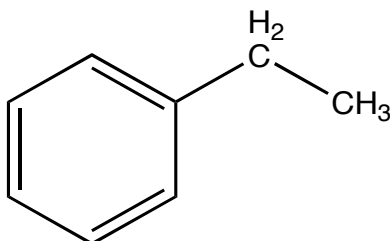
Percent Yield: 43.2%

Melting Point: 65-57 degrees Celsius

NMR (60 MHz, CDCl<sub>3</sub>):  $\delta$  2.8 (3H, s), 7.0-9.0 (4H, m)

IR (wavenumbers cm<sup>-1</sup>): 3103.72, 1608.21, 1347.56, 912.92, 835.83, 733.08

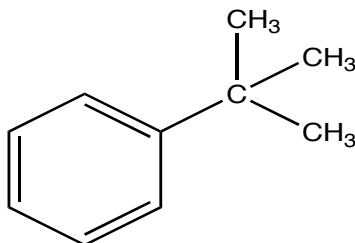
## Ethylbenzene



2.7598 grams (25.99 mmols) of ethylbenzene were measured out into 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over 12 minutes a mixture of 2.00 ml (31.55 mmols) of concentrated nitric acid and 2.00 ml (35.45 mmols) of concentrated sulfuric acid was added to the reaction while it was stirred on ice. The reaction turned a yellow/ orange color and remained at room temperature stirring for 21 minutes. The reaction was quenched with 25 grams of ice and it turned a milky white and a yellow liquid was formed. The organic phase was extracted with ether, which yielded a yellow liquid crude product. TLC shows the crude product being a mixture of two components, which are most likely, the ortho and para products. The mixture of liquids needs to be separated for further testing.

Crude Percent Yield: 71.2%

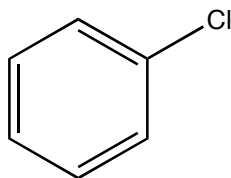
## Tert-Butyl Benzene



3.2256 grams (24.03 mmols) of tert-butyl benzene were measured out into 6.00 ml (0.106 mols) of concentrated sulfuric acid, which turned purple. Over 12 minutes a mixture of 2.00 ml (31.55 mmols) of concentrated nitric acid and 2.00 ml (35.45 mmols) of concentrated sulfuric acid was added to the reaction while it was stirred on ice. The reaction turned to a yellow color and was stirred at room temperature for 26 minutes. The reaction was quenched by being poured over 25 grams of ice. The organic phase was extracted with diethyl ether, which evaporated off leaving a yellow/orange liquid. TLC showed that the crude liquid product had two obvious products, which are most likely the ortho and para products, and a small amount of starting material and a very minor product which could be dinitrated product or the meta product.

Crude percent Yield: 88.8%

## Chlorobenzene



2.5927 grams (23.03 mmols) of chlorobenzene were measured out into 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over a period of 11 minutes a mixture of 2.00 ml (35.45 mmols) of concentrated sulfuric acid and 2.00 ml (31.55 mmols) of concentrated nitric acid was added to the reaction while it was stirred on ice. The reaction turned yellow and was allowed to mix at room temperature for 53 minutes. The reaction was quenched by being poured over 25 grams of ice and turned cloudy white and formed a yellow solid. TLC of the crude product showed it to have three components, two of them most likely being the ortho and para products. The crude solid was recrystallized in ethanol yielding 0.4332 grams of yellow flaky crystals. TLC of the product revealed it to have two components, which is a mixture between the ortho, and para products.

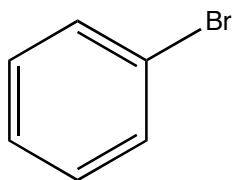
Percent Yield: 14.3%

Melting Point: 87-89 degrees Celsius

IR (wavenumbers  $\text{cm}^{-1}$ ): 1603.84, 1537.97, 1519.74, 1344.09, 1093.46, 845.80, 740.34



## Bromobenzene



3.4533 grams (21.99 mmols) of bromobenzene were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over a period of 12 minutes 2.00 ml (35.45 mmols) of concentrated sulfuric acid and 2.00 ml (31.55 mmols) of concentrated nitric acid were added to the starting material while it was stirred on ice. The reaction was allowed to stir at room temperature for 56 minutes and turned a soft yellow with a white solid. The reaction was quenched by being poured over approximately 25 grams of ice yielding a yellow solid. TLC of the crude product revealed it to have 3 components, two of which are most likely the ortho and para products. The crude crystals were recrystallized in methanol to yield 0.9233 grams of a mixture between 1-bromo-2-nitrobenzene and 1-bromo-4-nitrobenzene as a yellow flaky solid.

Percent Yield: 30.8%

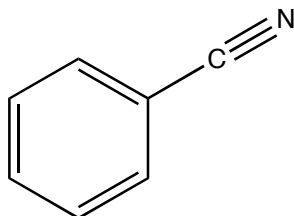
Melting Point: 117-119 degrees Celsius

NMR (60 MHz, CDCl<sub>3</sub>):  $\delta$  7.5-9.1 (4H, m)

IR (wavenumber cm<sup>-1</sup>): 1600.13, 1517.29, 1354.81, 1105.89, 1066.45, 839.66,

738.36

## Benzonitrile



2.3112 grams (22.42 mmols) of benzonitrile were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over 13 minutes a mixture of 2.00 ml (35.45 mmols) of concentrated sulfuric acid and 2.00 ml (31.55 mmols) of concentrated nitric acid was slowly added while the reaction was stirred on ice. The reaction was stirred at room temperature for 45 minutes and turned a yellow/orange color. The reaction was quenched by being poured over 25 grams of ice forming a yellow/orange solid. TLC of the crude product revealed it to have one major product, most likely the meta product and two minor products. The crude product was recrystallized in water to yield 1.4980 grams of 3-nitrobenzonitrile as yellow crystals.

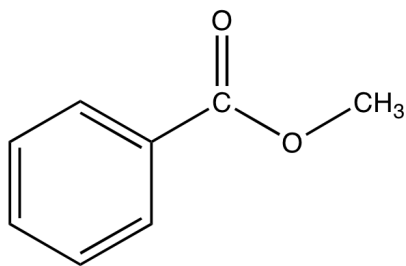
Percent Yield: 45.1%

Melting Point: 116-119 degrees Celsius

IR (wavenumbers  $\text{cm}^{-1}$ ): 2237.23, 1539.70, 1534.13, 1356.12, 817.35, 789.66,

784.45, 668.56

## Methyl Benzoate



3.0540 grams (22.34 mmols) of methyl benzoate were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid. A mixture of 2.00 ml (31.55 mmols) nitric acid and 2.00 ml (35.45 mmols) of concentrated sulfuric acid was slowly added to the starting material over a 15 minutes time period while the reaction was stirred on ice. The reaction had turned yellow and was removed to room temperature for 22 minutes while being stirred occasionally. The reaction was quenched by being poured over 25 grams of ice. TLC of the crude product revealed that all of the starting material was consumed and that one product was formed, most likely the meta product. The crude crystals were recrystallized in methanol to yield 2.9778 grams of methyl 3-nitrobenzoate as a fluffy white solid.

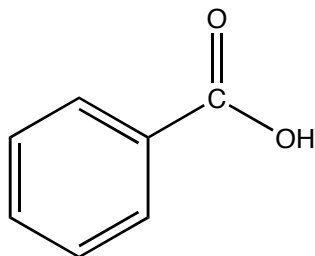
Percent Yield: 73.3%

Melting Point: 75-77 degrees Celsius

NMR (60 MHz, CDCl<sub>3</sub>):  $\delta$  4.0 (3H, s), 7.5-9.0 (4H, m)

IR (wavenumbers cm<sup>-1</sup>): 1718.27, 1527.23, 1351.63, 1291.65, 1269.57, 1135.86, 977.07, 727.75

## Benzoic Acid



2.17411 grams (22.45) mmols of benzoic acid were mixed with 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over 12 minutes a mixture of 2.00 ml (35.44 mmols) of concentrated sulfuric acid and 2.00 ml (31.55 mmols) of concentrated nitric acid was added while the reaction was stirred on ice. The reaction turned cloudy and was stirred at room temperature for 75 minutes. The reaction was quenched by being poured over approximately 25 grams of ice, a white/yellow solid immediately formed. TLC of the crude product revealed that one product had been formed, most likely the meta product. The crude solid was recrystallized in water yielding 2.7558 grams of 3-nitrobenzoic acid as a white powdery solid.

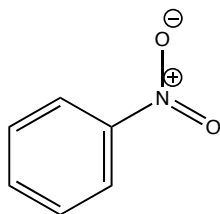
Percent Yield: 73.5%

Melting Point: 139-142 degrees Celsius

NMR (60 MHz, CDCl<sub>3</sub>):  $\delta$  7.3-9.1 (4H, m)

IR (wavenumbers cm<sup>-1</sup>): 3093.29, 1705.66, 1618.48, 1529.63, 1482.79, 1352.84, 1302.43, 720.05

## Nitrobenzene



2.7701 grams (22.50 mmols) of nitrobenzene were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over 18 minutes a mixture of 2.00 ml (31.55 mmols) concentrated nitric acid and 2.00 ml (35.45 mmols) concentrated sulfuric acid was slowly added while the reaction was stirred. 5 minutes after all the acid was added the reaction became a white yellow solid. TLC of the reaction showed that there was some starting material left but also a new product was forming. After 170 minutes the reaction was quenched by being poured over 25 grams of ice and bright neon green crystals immediately formed. TLC of the crude product showed that 1 major product, most likely the meta product and 1 very minor product had been formed. The crude crystals were recrystallized in ethanol to yield 2.5938 grams 1,3-dinitrobenzene as of a green solid.

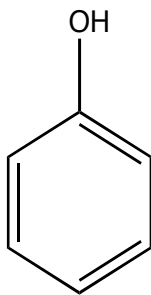
Percent Yield: 69.0%

Melting Point: 87-88 degrees Celsius

NMR (60 MHz, CDCl<sub>3</sub>):  $\delta$  7.5-8.3 (4H, m), 8.5-9.5 (4H, m)

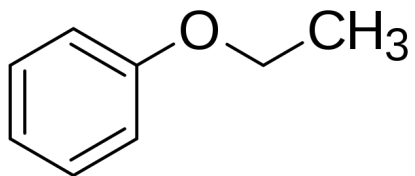
IR (wavenumbers cm<sup>-1</sup>): 1616.16, 1540.16, 1528.05, 1347.03, 1068.11, 913.26, 817.06, 711.70

## Phenol



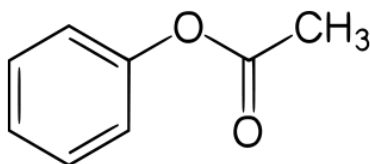
2.1138 grams (22.46 mmols) of phenol were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid. A nitrating mixture of 2.00 ml (31.55 mmols) concentrated nitric acid and 2.00 ml (35.45 mmols) concentrated sulfuric acid was added to the starting material. At the addition of the first few drops of the nitrating mixture the reaction immediately started to turn black and form a sticky tar solid. TLC of the reaction showed one long streak on the plate revealing that many different products were being formed. Phenol was so activating that multiple nitrations made a whole wide range of products instead of just the two intended products. The reaction was also tried again when phenol was the limiting reagent rather than nitric acid but similar results were observed.

## Phenetole



3.7376 grams (30.60 mmols) of phenetole were measured out into 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over 11 minutes a mixture of 2.00 ml (35.45 mmols) of concentrated sulfuric acid and 2.00 ml (31.55 mmols) of concentrated nitric acid was added to the reaction while it was stirred on ice. The reaction turned a dark brown / purple color stirred at room temperature for 17 minutes before it was quenched by being poured over 25 grams of ice. A brown metallic crude crystal was isolated and was shown by TLC to have at least two components. The crystals were recrystallized in ethanol and yielded 1.3919 grams of a brown solid that looked like pencil shavings. The solid had a melting point of 79- 81 degrees Celsius, which was not characteristic of any of the expected products.

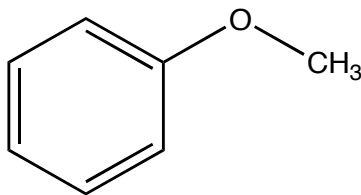
## Phenyl Acetate



4.0711 grams (29.90 mmols) of phenyl Acetate were measured out into 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over 12 minutes a mixture of 2.00 ml (35.45 mmols) of concentrated sulfuric acid and 2.00 ml ( 31.55 mmols) concentrated nitric acid were added while the reaction was stirred on ice. The reaction turned a dark brown and was allowed to stir at room temperature for 15 minutes. When the reaction was quenched by being poured over 25 grams, very trace amounts of a red solid were isolated but nowhere near the expected 5.4 grams. The dark brown filtrate was examined but the intended product could not be isolated.

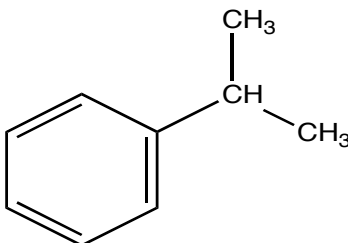


## Anisole



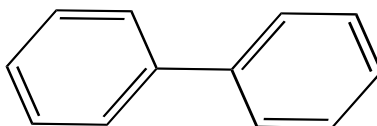
3.2483 grams (30.05 mmols) of anisole were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over 11 minutes a mixture of 2.00 ml (31.55 mmols) of concentrated nitric acid and 2.00 ml (35.45 mmols) of concentrated sulfuric acid was added while the reaction was stirred on ice. The reaction turned a dark black color and TLC of the reaction indicated that multiple products were being formed. After 15 minutes of stirring at room temperature the reaction was quenched by being poured over 25 grams of ice and a black tar like solid could be seen. From the organic phase of the reaction a brown solid was isolated and recrystallized using water leaving light brown crystals that resembled pencil shavings. IR and NMR showed the crystals to have characteristics of the intended product but most likely contained a mixture of multiple nitration products. Melting point of 78-81 degrees Celsius did not match the intended products.

## Isopropyl Benzene



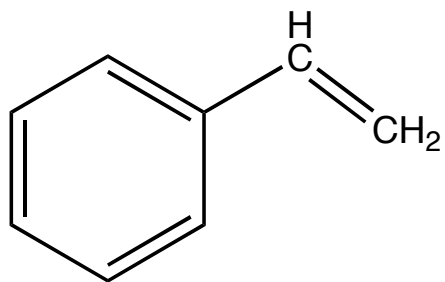
2.8886 grams (24.03 mmols) of isopropyl benzene were added to 6.00 ml ( 0.106 mols) of concentrated sulfuric acid which turned a orange/brown color. Over 11 minutes a mixture of 2.00 ml (35.45 mmols) of concentrated sulfuric acid and 2.00 ml (31.55 mmols) of concentrated nitric acid was added while the reaction was being stirred on ice. The reaction turned a dark red/brown color and was stirred for 18 minutes at room temperature. The reaction was quenched by being poured over 25 grams of ice and a black tar like solid immediately formed. The tar was most likely a product of multiple nitrations instead of the intended products.

## Biphenyl



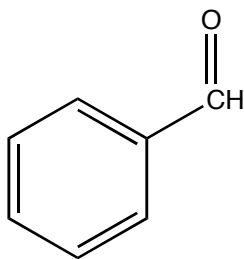
2.0885 grams (13.54 mmols) of biphenyl were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over 14 minutes a mixture of 2.00 ml (35.45 mmols) of concentrated sulfuric acid and 1.00 ml (15.78 mmols) of concentrated nitric acid was added while the reaction was stirred on ice. The reaction was allowed to stir at room temperature for 40 minutes and was quenched by being poured over 25 grams of ice. A rubbery tan product was collected that was very hard to work with. The solid was recrystallized in methanol and a yellow solid was collected. TLC revealed that the final product was a mixture of starting material and at least 3 different products, which were most likely a result of multiple nitrations due to the two benzene rings. A melting point of 160-162 degrees Celsius did not match any of the intended products.

## Styrene



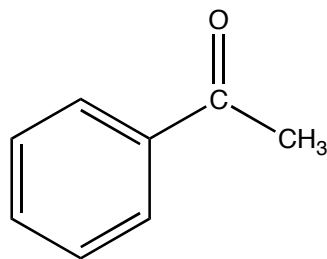
2.7183 grams (26.01 mmols) of styrene were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid. As soon as the styrene was added the reaction immediately turned an orange/brown and went completely solid. The double bond was sulfonated<sup>3</sup> so styrene is not a starting material that can be nitrated using this procedure.

## Benzaldehyde



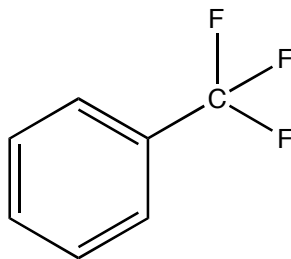
2.3383 grams (22.03 mmols) of benzaldehyde were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over 14 minutes a mixture of 2.00 ml (31.55 mmols) of concentrated nitric acid and 2.00 ml (35.45 mmols) of concentrated sulfuric acid were added while the reaction was stirred on ice. The reaction turned bright red and stirred at room temperature for 35 minutes. The reaction was quenched by being poured over 25 grams of ice. Two distinct solids could be seen, a yellow chunky rubbery solid and a flaky yellow solid. The chunky solid was separated out and by TLC appeared to be a mixture of at least three different compounds. The flakier crystals were recrystallized in water and 0.2564 grams were isolated. A melting point of 55-57 degrees Celsius indicated that 3-nitrobenzaldehyde had been formed but only in trace amount with much difficulty, so it was decided not to pursue this reaction.

## Acetophenone



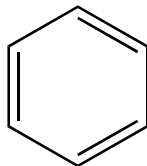
2.8878 grams (24.03 mmols) of acetophenone were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid. Over a period of 12 minutes a mixture of 2.00 ml (35.45 mmols) of concentrated sulfuric acid and 2.00 ml (31.55 mmols) of concentrated nitric acid was added to the reaction while it was being stirred on ice. The reaction turned blacked and fumed orange as the acids were added. When the reaction was quenched by being poured 25 grams of ice it turned into a tar that had no characteristics of the intended product.

## Alpha, alpha, alpha - trifluorotoluene



Alpha, Alpha, alpha-trifluorotoluene is a deactivated molecule so the reaction is expected to run slower and yield the meta product which is a liquid. 22.47 mmols of alpha, alpha, alpha-trifluorotoluene was added to 6.00 ml of concentrated sulfuric acid. Over 11 minutes a mixture of 2.00 ml of concentrated nitric acid and 2.00 ml of concentrated nitric acid while the reaction was mixed. The reaction turned a very bright yellow and was quenched over 25 grams of ice after stirring at room temperature for 84 minutes. A yellow liquid was extracted out from the reaction using diethyl ether though only trace amounts of the liquid could be isolated. The product was very hard to separate out so it was decided not to pursue this reaction.

## Benzene

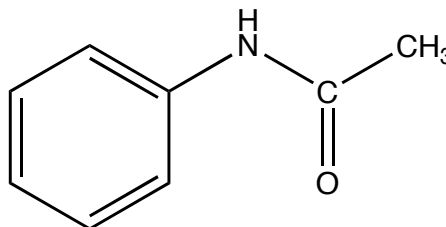
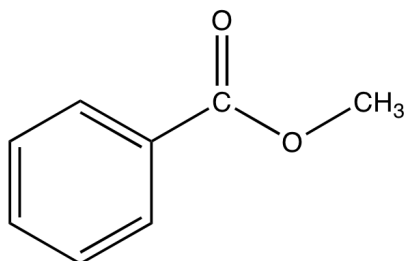


2.0383 grams (26.09 mmols) of benzene were added to 6.00 ml (0.106 mols) of concentrated sulfuric acid and over a 13 minutes period a mixture of 2.00 ml (35.45 mmols) of concentrated sulfuric acid and 2.00 ml (31.45 mmols) of concentrated nitric acid was added while the reaction was stirred on ice. After stirring at room temperature for 23 minutes the reaction was quenched by being poured over 25 grams of ice. The major product isolated was a shiny yellow crystal and trace amounts of a yellow liquid were isolated. The yellow crystals were recrystallized in ethanol to yield 0.7034 grams of yellow/green crystals. By TLC these crystals were identified to have two components one being the dinitrated product, 1,3-dinitrobenzene. The trace amounts of liquid isolated was most likely benzene but not enough was isolated to run tests on. The reaction conditions could be improved by making benzene the limiting reagent so that dinitration would not be as much of an issue.



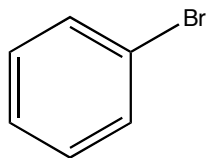
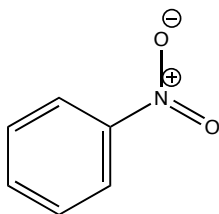
## Competitive Nitration Reactions:

### Methyl Benzoate and Acetanilide



1.6387 grams of 70% nitric acid (18.2 mmols) were weighed out and set aside. 2.4745 grams (18.31 mmols) of acetanilide and 2.4929 grams (18.31 mmols) of methyl benzoate were combined with 3.60 ml (62.89 mmols) of glacial acetic acid and 7.20 ml (0.127 mols) of concentrated sulfuric acid. Over a period of 14 minutes a mixture of 7.20 ml (0.127 mols) of concentrated sulfuric acid, 3.60 ml (62.89 mmols) of glacial acetic acid and the nitric acid was added to the reaction while it was stirred at 10 degrees Celsius. The reaction was stirred at room temperature for 7 minutes followed by quenching with 35 grams of ice. A sticky white/yellow solid immediately appeared and was recrystallized in ethanol to yield a pale yellow hard solid. TLC analysis showed that the crude product contained 5 components, both acetanilide and methyl benzoate starting materials, trace amounts of the methyl benzoate product, and both of the acetanilide product. The recrystallized product had just one component that matched the final product of the acetanilide reaction, which was identified to be 4-nitroacetanilide. This major product was confirmed by a melting point of 187-190 degrees Celsius.

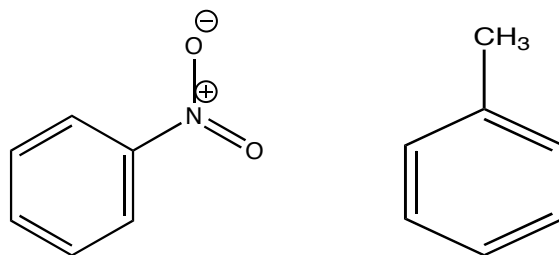
## Nitrobenzene and Bromobenzene



1.1432 grams of 70% nitric acid (18.14 mmols) were weighed out and set aside.

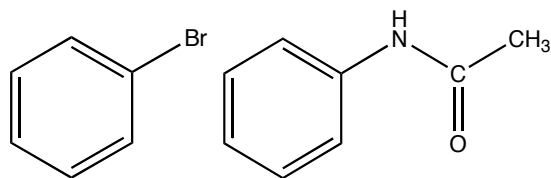
2.8597 grams (18.21 mmols) of bromobenzene and 2.2494 grams (18.27 mmols) of nitrobenzene and 3.60 ml were combined with 3.60 ml (62.89 mmols) of glacial acetic acid and 7.20 ml (0.127 mols) of concentrated sulfuric acid. Over a period of 14 minutes a mixture of 7.20 ml (0.127 mols) of concentrated sulfuric acid, 3.60 ml (62.89 mmols) of glacial acetic acid and the nitric acid was added to the reaction while it was stirred at 10 degrees Celsius. The reaction was stirred at room temperature for 22 minutes, it turned a soft yellow and a slushy solid could be seen. The reaction was quenched by being poured into approximately 35 grams of ice and white/yellow crystals immediately formed. The crystals were recrystallized in ethanol and yielded a white snowy crystal. TLC analysis showed that the crude product contained nitrobenzene starting material (bromobenzene is not able to be detected by TLC), nitrobenzene product and both bromobenzene products. The recrystallized product was shown to have only one component which matched one of the bromobenzene products and was identified to be 4-bromo-1-nitrobenzene which was confirmed by a melting point of 125-126.5 degrees Celsius.

## Toluene and Nitrobenzene



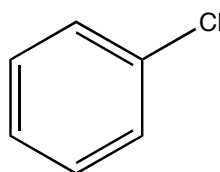
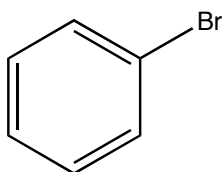
1.6212 grams of 70% nitric acid (18.01 mmols) were measured out and set aside. 1.6762 grams (18.14 mmols) of toluene and 2.2270 grams (18.08 mmols) of nitrobenzene were combined with 3.60 ml (62.89 mmols) of glacial acetic acid and 7.20 ml (0.127 mols) of concentrated sulfuric acid. Over a period of 14 minutes a mixture of 7.20 ml (0.127 mols) of concentrated sulfuric acid, 3.60 ml (62.89 mmols) of glacial acetic acid and the nitric acid was added to the reaction while it was stirred at 10 degrees Celsius. The reaction turned a red/orange color and was stirred at room temperature for 17 minutes. The reaction was quenched by being poured over approximately 35 grams of ice. A yellow liquid product was extracted out using diethyl ether. The TLC of the crude product showed the toluene product (4-nitrotoluene) as the main product and also showed nitrobenzene starting material and very trace amounts of the nitrobenzene product.

## Bromobenzene and Acetanilide



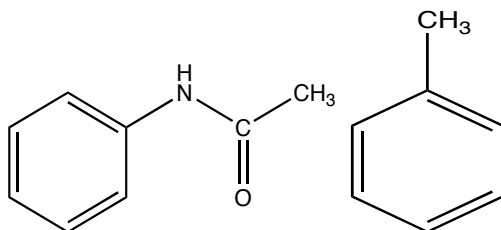
1.6195 grams of 70% nitric acid (17.99 mmols) were measured out and set aside. 2.4421 grams (18.06 mmols) of acetanilide and 2.8345 grams (18.05 mmols) of bromobenzene were combined with 3.60 ml (62.89 mmols) of glacial acetic acid and 7.20 ml (0.127 mols) of concentrated sulfuric acid. Over a period of 13 minutes a mixture of 7.20 ml (0.127 mols) of concentrated sulfuric acid, 3.60 ml (62.89 mmols) of glacial acetic acid and the nitric acid was added to the reaction while it was stirred at 10 degrees Celsius. The reaction turned a light yellow color and was stirred temperature for 9 minutes. The reaction was quenched with approximately 35 grams of ice and turned a yellow/green color and a yellow/white crude solid was isolated. The solid was recrystallized in methanol to yield light yellow crystals. TLC showed the final product had only one component and a melting point of 210-212 degrees Celsius identified the product as 4-nitroacetanilide.

## Bromobenzene and Chlorobenzene



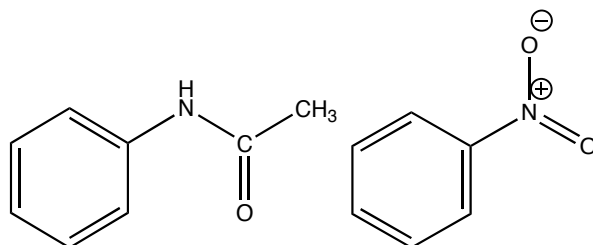
1.6361 grams of 70% nitric acid (18.17 mmols) were measured out and set aside. 2.8702 grams (18.28 mmols) of bromobenzene and 2.0555 grams (18.26 mmols) of chlorobenzene were combined with 3.60 ml (62.89 mmols) of glacial acetic acid and 7.20 ml (0.127 mols) of concentrated sulfuric acid. Over a period of 14 minutes a mixture of 7.20 ml (0.127 mols) of concentrated sulfuric acid, 3.60 ml (62.89 mmols) of glacial acetic acid and the nitric acid was added to the reaction while it was stirred at 10 degrees Celsius. After 22 minutes of stirring at room temperature the reaction was quenched by being poured over approximately 35 grams of ice and a white/ light green solid was formed. Half of the solid was recrystallized in methanol and half in ethanol. TLC analysis revealed that the crude crystal as well as the final product contained large amounts of chlorobenzene and one bromobenzene product. The melting point of 116-119 degrees Celsius supports that the final product is a mixture of nitrated bromobenzene and nitrated chlorobenzene.

## Acetanilide and Toluene



1.6234 grams of 70 % nitric acid (18.03) mmols were measured out and set aside. 1.6743 grams (18.12 mmols) of toluene and 2.449 grams (18.12 mmols) of acetanilide were combined with 3.60 ml (62.89 mmols) of glacial acetic acid and 7.20 ml (0.127 mols) of concentrated sulfuric acid. Over a period of 14 minutes a mixture of 7.20 ml (0.127 mols) of concentrated sulfuric acid, 3.60 ml (62.89 mmols) of glacial acetic acid and the nitric acid was added to the reaction while it was stirred at 10 degrees Celsius. The reaction was stirred at room temperature for 6 minutes and turned a dark yellow/ orange color. The reaction was quenched by being poured over approximately 35 grams of ice and yielded a white/yellow solid. The solid was recrystallized in methanol and yielded a white/yellow powdery solid. TLC showed the final product to have one component that matched the product of the acetanilide reaction and was confirmed to be 4-nitroacetanilide by a melting point of 214-216 degrees Celsius.

## Acetanilide and Nitrobenzene



1.6203 grams of 70% nitric acid (18.00 mmols) were measured out and set aside. 2.4446 grams (18.09 mmols) of acetanilide and 2.2264 grams (18.08 mmols) of nitrobenzene were combined with 3.60 ml (62.89 mmols) of glacial acetic acid and 7.20 ml (0.127 mols) of concentrated sulfuric acid. Over a period of 16 minutes a mixture of 7.20 ml (0.127 mols) of concentrated sulfuric acid, 3.60 ml (62.89 mmols) of glacial acetic acid and the nitric acid was added to the reaction while it was stirred at 10 degrees Celsius. The reaction turned a light orange/pink color and stirred at room temperature for 6 minutes. The reaction was quenched by being poured over approximately 35 grams of ice and yielded a white/yellow solid. The solid was recrystallized with methanol to yield a light yellow/white powder. TLC of the final product revealed it to have one component that matched the product of the acetanilide reaction and was confirmed to be 4-nitroacetanilide by a melting point of 210-211 degrees Celsius.

