Purpose

To synthesize methyl nitrobenzoate via electrophilic aromatic substitution and determine the regio-specificity of the product.

Calculations

$$m_{methyl\ benzoate} = 3.05g\ methyl\ benzoate$$

$$m_{theoretical\ yield} = m_{methyl\ benzoate}\left(\frac{1mol_{methyl\ benzoate}}{MW_{methyl\ benzoate}}\right)\left(\frac{MW_{methyl\ nitrobenzoate}}{1mol_{methyl\ nitrobenzoate}}\right)$$
$$= 3.05g\left(\frac{1mol}{131.16g}\right)\left(\frac{181.15g}{1mol}\right) \approx 4.21g\ product$$

$$m_{crude\ product} = m_{watch\ glass\ and\ crude\ product} - m_{watch\ glass} = 57.35g - 53.60g$$
$$= 3.75g\ crude\ product$$

$$\%\ yield_{crude} = \left|\frac{m_{crude}}{m_{theoretical\ yield}}\right| \times 100 = \left|\frac{3.75g}{4.21g}\right| \times 100 \approx 89.1\%\ crude\ yield$$

$$m_{crude} = m_{crude\ and\ watch\ glass} - m_{watch\ glass} = 57.18g - 53.60g = 3.58g$$

Note: m_{crude} differs from $m_{crude\ product}$ in that the former refers to only the portion which was used for recrystallization (some of $m_{crude\ product}$ was set aside for melting point evaluation). Since not all ofthe crude was used for recrystallization, percent yield for the recrystallized product was only calculated with respect to the crude used.

$$m_{recrystallized} = m_{recrystallized\ and\ watch\ glass} - m_{watch\ glass} = 56.40g - 53.60g$$
$$= 2.80g\ recrystallized$$

$$\%\ yield_{recrystallized} = \left|\frac{m_{recrystallized}}{m_{crude}}\right| \times 100 = \left|\frac{2.80g}{3.58g}\right| \times 100 \approx 78.2\%\ yield\ recrystallized$$

Results

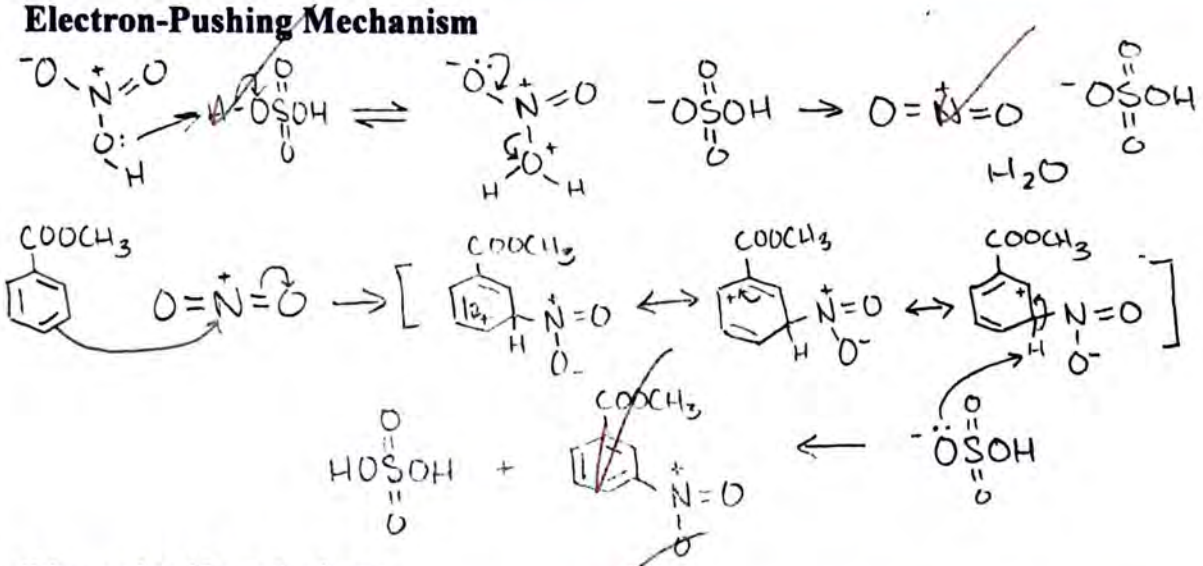
Table 1 Mass and yield of products

Category	Experimental Yield (g)	Theoretical Yield (g)	Percent Yield (%)
Crude Product	3.75	4.21	89.1
Recrystallization	2.80	3.58	78.2

Table 2 Melting points of relevant compounds

Compound	Melting Point (° C) Experimental	Literature
Crude Product	67.9-71.7	—
Recrystallized Product	74.3-76.2	—
Methyl Benzoate	—	-12
Methyl 2-nitrobenzoate	—	-8
Methyl 3-nitrobenzoate	—	78
Methyl 4-nitrobenzoate	—	96

Electron-Pushing Mechanism



Discussion/Conclusions

Nitration of 3.05g methyl benzoate yielded 3.75g methyl nitrobenzoate. Compared to the theoretical yield of 4.21g, this 89.1% yield is consistent with many electrophilic benzene substitution reactions which fail to reach 100% yield. Of the crude purified, 78.2% was recovered as recrystallized product. Melting point analysis revealed slightly different melting point ranges among the products—67.9-71.7° C for the crude and 74.3-76.2° C for the recrystallized product. While both of these values most closely resemble methyl 3-nitrobenzoate, it is clear that the recrystallized product is much purer as the range is significantly closer to the 78° C literature value. This identification of the nitration reaction's major product as the result of a meta-substitution is consistent with what was expected. Since the methyl benzoate is a benzene ring with only an electron-withdrawing substituent, any electrophilic substitution reaction is expected to add at the meta-position due to a more stable intermediate that forms as a part of a meta-substitution. While substitution to any part of the ring would lead to three resonance structures, substitution at the meta position avoids an especially unstable resonance structure in which two adjacent atoms have positive character (a positive charge and a partial positive).

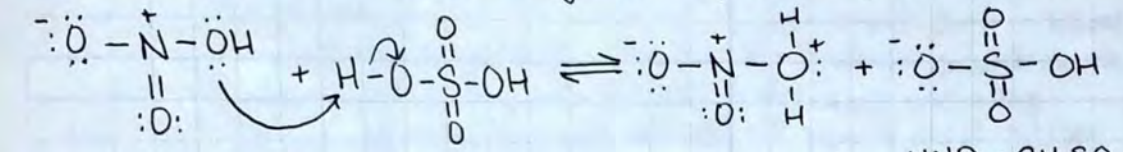
References

Experiment 1 Electrophilic Aromatic Substitution: Nitration of Methyl Benzoate, Chemistry 52 Laboratory. Department of Chemistry, Dartmouth College, 2019.

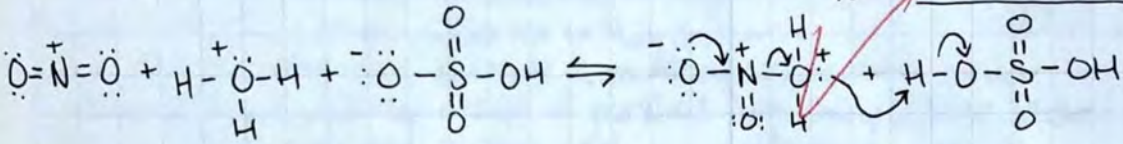
Sigmaaldrich.com. (2019). Sigma Aldrich, 2019.

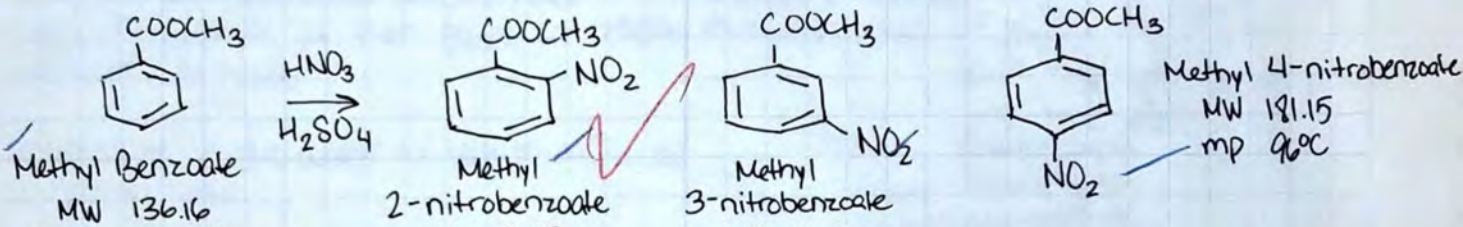
Exp. No. 1	Experiment/Subject Nitration of Methyl Benzoate	Date 6/27/19	
Name Matthew Fam	Lab Partner	Locker/ Desk No.	Course & Section No. CHEM 52

Objective: To synthesize methyl nitrobenzoate via electrophilic aromatic substitution and determine the regiochemistry of the product.



1L $HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$





Methyl Benzoate
MW 136.16
bp 199.6°C
density 1.09

Methyl 2-nitrobenzoate
MW 181.15
~~bp~~ mp -8°C
~~density~~

Methyl 3-nitrobenzoate
MW 181.15
mp 78°C

Methyl 4-nitrobenzoate
MW 181.15
mp 96°C

- Lab Procedure

Sulfuric acid - corrosive, causes skin burns/eye damage; move to fresh air, change clothes, wash w/ soap and water, rinse
Methyl benzoate (mp: -12°C) - combustible liquid, harmful if swallowed; fresh air, wash w/soap and water, flush
Nitric acid - oxidizing liquids, corrosive, acute toxicity, skin corrosion, eye damage; fresh air, wash off w/ soap and water, rinse
Methanol - flammable, acute toxicity (oral, inhalation, dermal), eye damage; fresh air, wash, flush
Sodium carbonate - eye irritant; fresh air, wash, rinse

- Sigma Aldrich

Procedure: Cool 6mL conc. sulfuric acid in 50 mL Erlenmeyer flask w/ stir bar in ice bath (to 0-10°C) then add 2.8 mL (3.05 g) methyl benzoate.
Cool mixture again to 0-10°C.
Stir and add dropwise w/ Pasteur pipet, a cooled mixture of 2 mL of conc. sulfuric acid and 2 mL conc. nitric acid. Maintain temp of rxn mixture in range of 5-15 °C.
Allow mixture to warm to room temp, then wait 15 min before pouring onto 25 mL cracked ice in 250 mL beaker.
Use spatula to crush large chunks of solid

Observations:
- 6mL sulfuric acid cooled in ice bath to ~8°C
- Methyl benzoate (2.8 mL) added
→ Temp went up to ~12°C from ~8°C
- Mixture 2mL sulfuric and 2 mL nitric added dropwise
→ got warm so cooled (mixture)
- ~~Allowed~~ mixture allowed to warm to room temp before waiting 15 min and pouring onto 25 mL ice
- Large chunk of solid crushed

Signature	Date	Witness/TA	Date

Exp. No. 1	Experiment/Subject Nitration of Methyl Benzoate	Date 6/27/19	
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Procedure (cont.): into precipitate of small particle size to ensure all acid dissolves into aqueous phase.
Isolate solid product by suction filtration w/ small Buchner funnel and wash w/ cold water, then 2 5mL portions ice-cold methanol
Reserve enough of crude to determine mp range.
Record yield of crude. (need not be fully dry).
Recrystallize remainder of crude from methanol
Determine mass and mp range of purified material and determine percent yield.
Show product to TA, then place in collection bottle in side hood.

Neutralize acidic waste w/ sodium carbonate or baking soda.

Observations (cont.):
- Solid products isolated by suction filtration and washed
  → White powdery substance
- Product weighed
  → Watch glass 53.60g
  57.35 g *crude
  57.18 g *crude after saving some for mp analysis
- Remaining crude recrystallized
  → Shiny, white, flakey substance
- Product weighed
  → Watch glass 53.60g
  56.41g *recrystallized product

→ re crude
~~Crude~~ re
~~Start~~ ~~67.9~~
~~Stop~~ ~~71.7~~

- Mp analysis of crude and recrystallized products ~~observed~~ conducted

→

	recrystallized	crude
Start melting	74.3°C	67.9°C
Stop melting	76.2°C	71.7°C

More qualitative Data

Signature	Date	Witness/TA	Date