Experiment #6: Regioselective Nitration of Acetanilide

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CHM 1321 Section Z07

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Introduction

Fig. 1 *Activation of nitrogen dioxide*

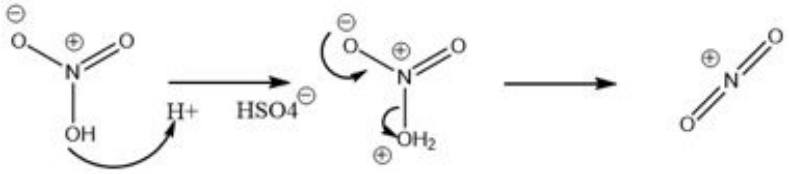


Fig. 2 *Formation of the Meta product*

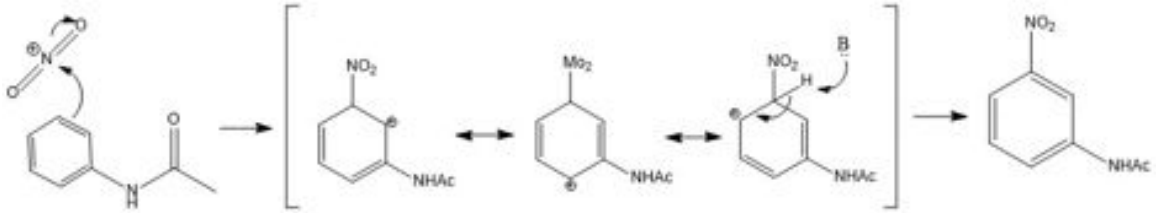


Fig. 3 *Formation of the Ortho product*

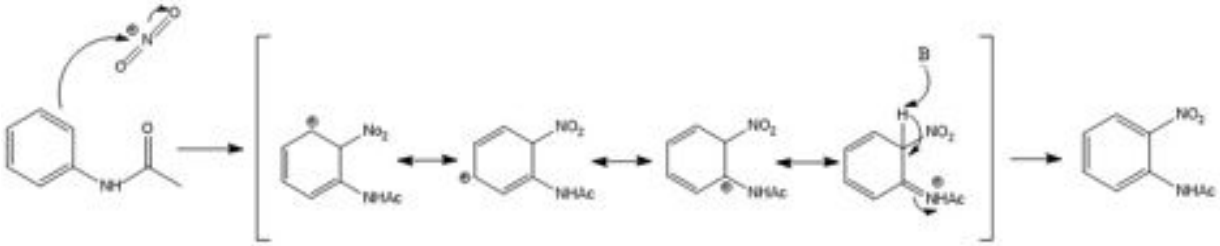
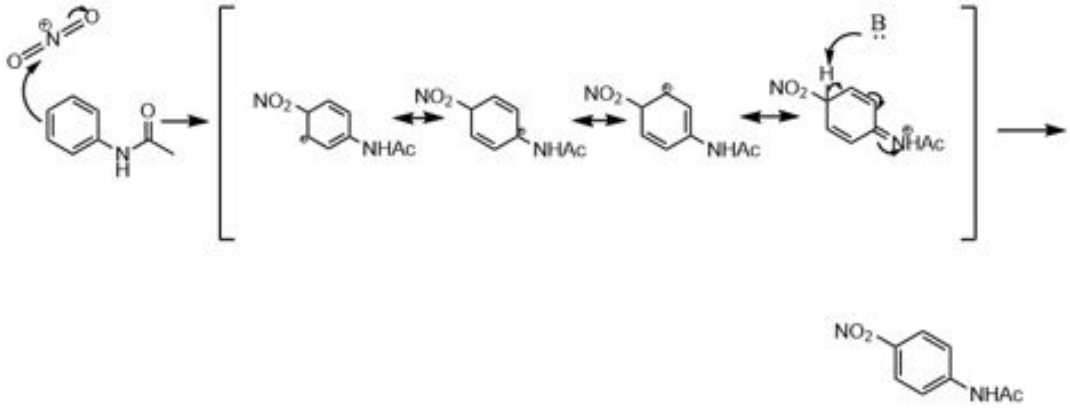


Fig. 4 *Formation of the Para product*



Procedure

Refer to Organic Chemistry Laboratory Manual 2019 by Dr. Tony Durst, Dr. Tito Scaiano, Dr. William Ogilvie, Dr. Alison Flynn and Dr. Kathy Focsaneanu. Revised by Dr. Bianca van Lierop, Mr. Alex Bush, Dr. Rashmi Venkateswaran and Dr. Wendy Pell.

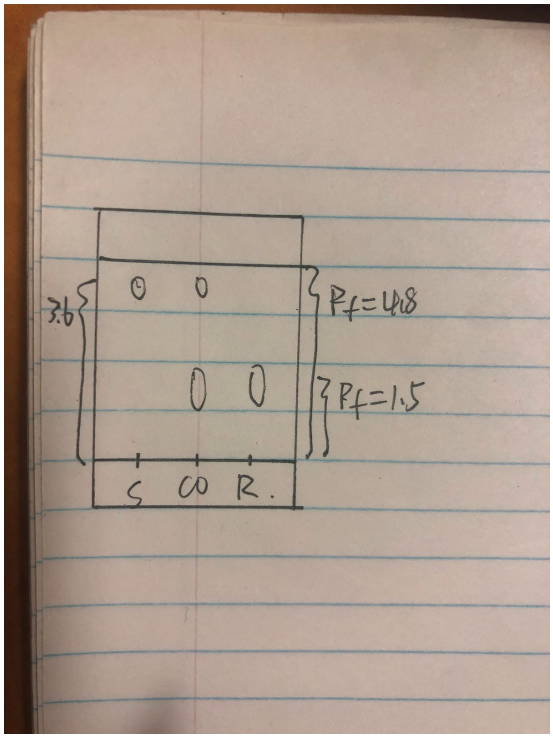
Table of Reagents

Reagent	Amount (g or mL)	Molecular Weight (g/mol)	Density (g/mL)	No. of moles
Acetanilide	1.0 g	135.17	1.22	0.00739809
H_2SO_4	5 mL	98.079	1.84	0.050979
H_2SO_4 (concentrated)	0.8 mL	98.079	1.84	0.01500830962
HNO_3	0.6	63.01	1.51	0.01437867005
Water (liquid and ice)	20 mL 4 ice cubes	18.02	1	-

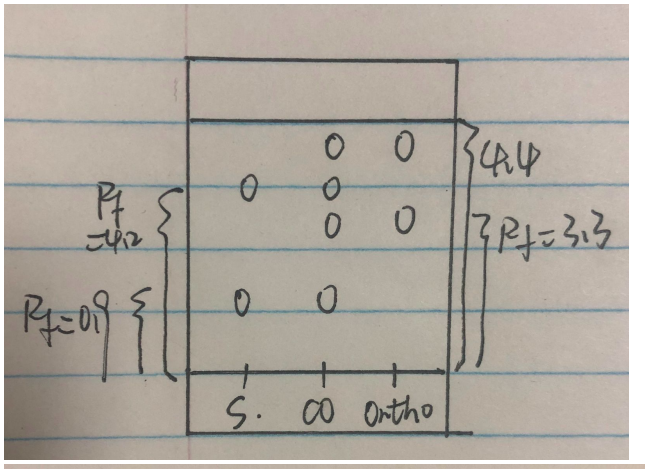
Observations

- Acetanilide is light brown in colour and had a flaky texture in solid form
- H_2SO_4 was a clear, colourless and odourless liquid
- When the acetanilide was dissolved in the H_2SO_4, the resulting solution was dark brown in colour
- HNO_3 was a clear, colourless and odourless liquid
- When H_2SO_4 and HNO_3 were combined, the result was a solution that was clear, colourless and odourless
- The solid that was collected was yellow in colour and had a smooth consistency

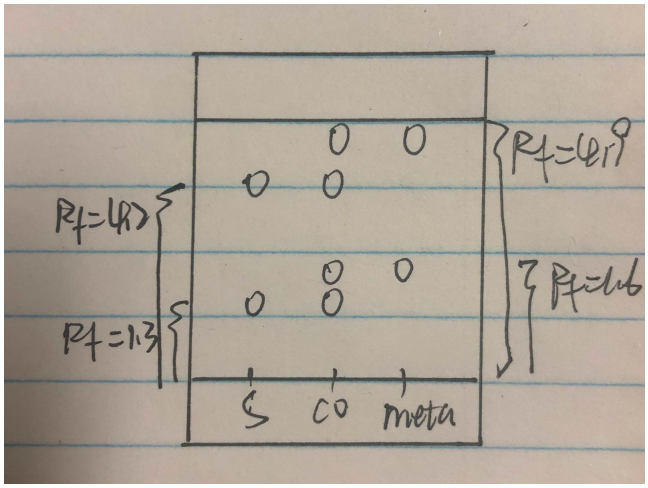
TLCs



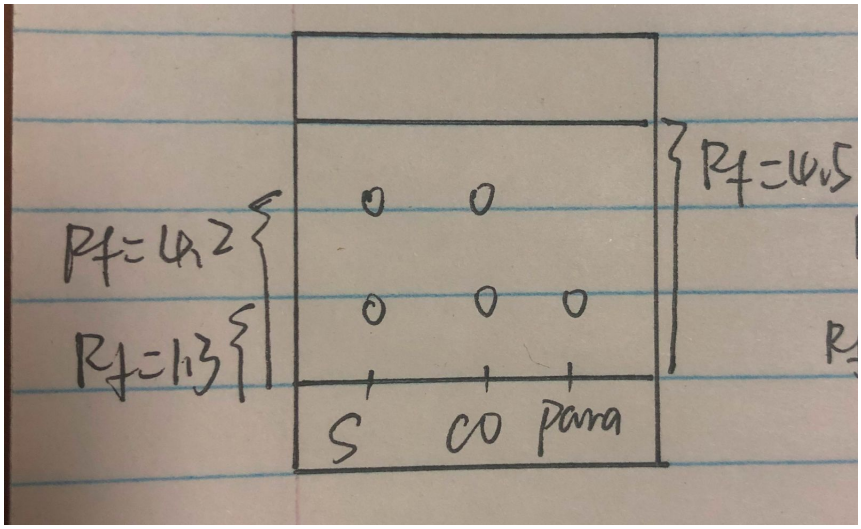
1.solvent:EtOAc:hexanes 5:5
Reference: solide dilute in DCM
Rf1=4.8
Rf2=3.6
Rf3=1.5
Rf= Rf2/Rf1=3.6/4.8=0.75



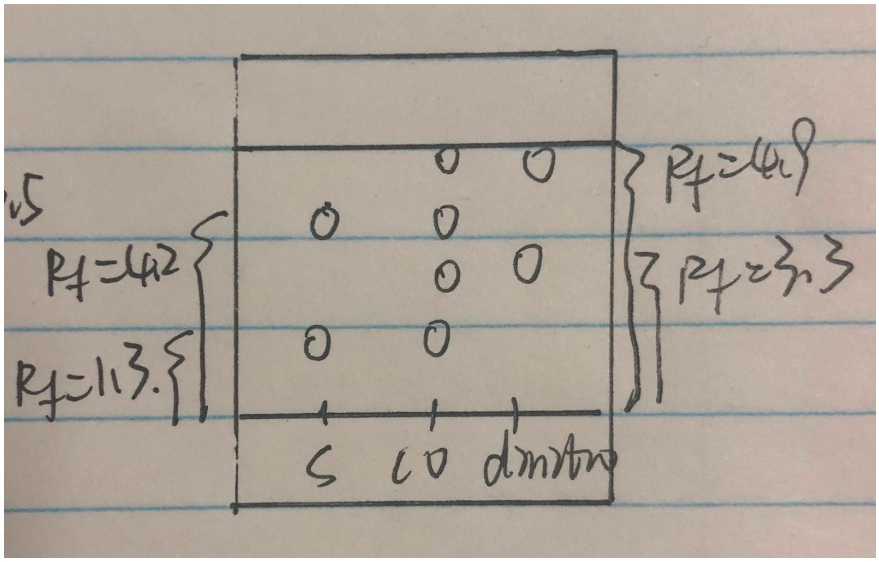
2. Solvent: EtOAc:hexanes 5:5
Refernce: ortho
Rf1=4.4
Rf2=4.2
Rf3=3.3
Rf4=0.9
Rf=Rf2/Rf1=4.2/4.4=0.95
Rf=Rf4/Rf1=0.9/4.4=0.2



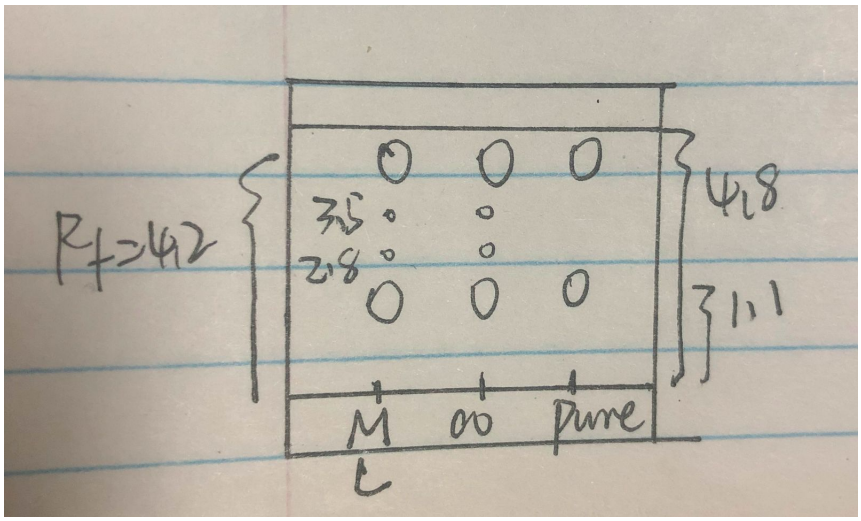
3. Reference: meta
Rf1=4.9
Rf2=4.2
Rf3=1.6
Rf4=1.3
Rf=4.2/4.9=0.86
Rf=1.3/ 4.9=0.27



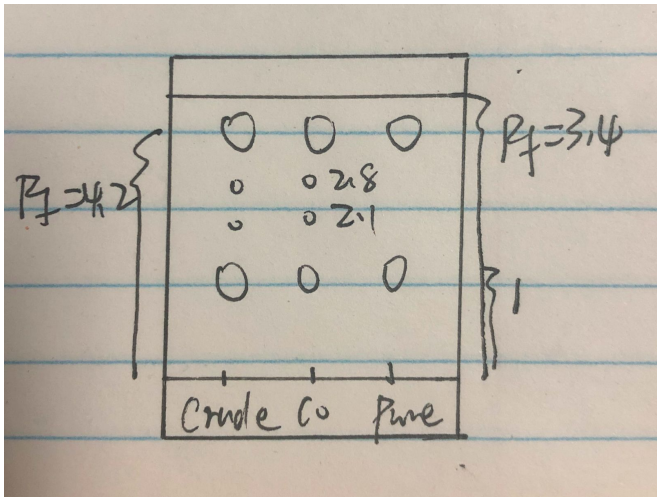
4.
Reference: para
Rf1=4.5
Rf2=4.2
Rf3=1.3
Rf=4.2/4.5=0.93
Rf=1.¾.5=0.29



5.
refernce: 2,4-dinitro
Rf1=4.9
Rf2=4.2
Rf3=3.3
Rf4=1.3
Rf=4.2/4.9=0.86
Rf=1.¾.9=027



6.
Compare mother liquor with pure product in EtOAc:hexanes 5:5
Rf1=4.8
Rf2=4.2
Rf3=3.5
Rf4=2.8
Rf5=1.1
Rf=4.2/4.8=0.875
Rf=3.5/4.8=0.73
Rf=2.8/4.8=0.58
Rf=1.¼.8=0.23



7.compare the crude product with pure product
Rf1= 4.2
Rf2=3.4
Rf3=2.8
Rf4=2.1
Rf5=1
Rf=3.4/4.2=0.8
Rf=2.8/4.2=0.67
Rf=2.¼.2=0.5
Rf=¼.2=0.24

Table of Results

Product	Amount (g)	Molecular Weight (g/mol)	No. of moles	% Yield
Nitroacetanilide	1.16	180.16	0.00643872	87

Calculations

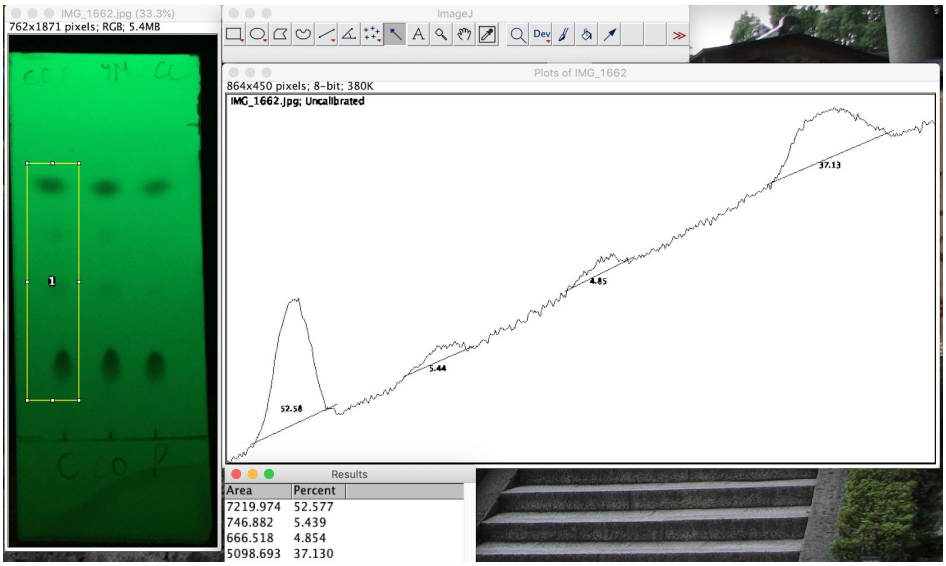
% yield

# of moles of nitroacetanilide = (mass (g))/ (molar mass (g/mol))
# of moles = (1.16 g)/ (180.16 g/mol)
# of moles = 0.00643872

# of moles of acetanilide = (mass (g))/ (molar mass (g/mol))
# of moles = (1.0 g)/ (135.17 g/mol)
# of moles = 0.00739809

Percentage yield = (# of mole of nitroacetanilide)/ (# of mole of acetanilide) x 100 %
Percent yield = (0.00643872 mol) / (0.00739809 mol) x 100%
Percent yield = 87%

Image J Calculations Part 1 : Ratios of Compounds in Crude Product



Percentage of absorbance:

- Absorbance of para compound = 52.6%
- Absorbance of 2,4 dinitro compound = 37.1%
- Absorbance of ortho compound = 5.4%
- Absorbance of meta compound = 4.9%

Calculation of mole percentage:

Ortho: 5.4/(52.6+5.4) = 9.3%
Para: 52.6/(52.6/5.4) = 90.7%

Using the ortho:para calibration curve:

x = % Absorbance (ortho) = 9.3 %
$y = 0.0079391\ (9.2^2) - 0.15962\ (9.3) + 3.3788$
y = 0.672 - 1.484 + 3.3788
y = 2.57

Hence ortho = 2.57% and para = 97.43%

Para = 52.6/(52.6+37.1) = 58.6%
Dinitro = 37.1/(52.6/37.1) = 41.4%

Using the dinitro:para calibration curve:

y = % Absorbance (2,4-dinitro) = 41.4 %
$y = 0.0223 (x^2) – 1.681(x) + 37.4$
$41.4 = 0.0223 (x^2) – 1.681(x) + 37.4$
$0 = 0.0223 (x^2) – 1.681(x) - 4$

Using the quadratic formula, solve for x when a = 0.0223, b = -1.681 and c = -4,
X = 77.6%

Hence dinitro = 77.6% and para = 22.4%

Ortho = 5.4/(5.4+4.9) = 52.4%
Meta = 4.9/(5.4+4.9) = 47.6%

Using the meta:ortho calibration curve:

x = % Absorbance (meta) = 47.6 %
$y = 0.0077570 (47.6^2) + 0.067612 (47.6) + 1.6469$
y = 17.6 + 3.2 + 1.6469
y = 22.5

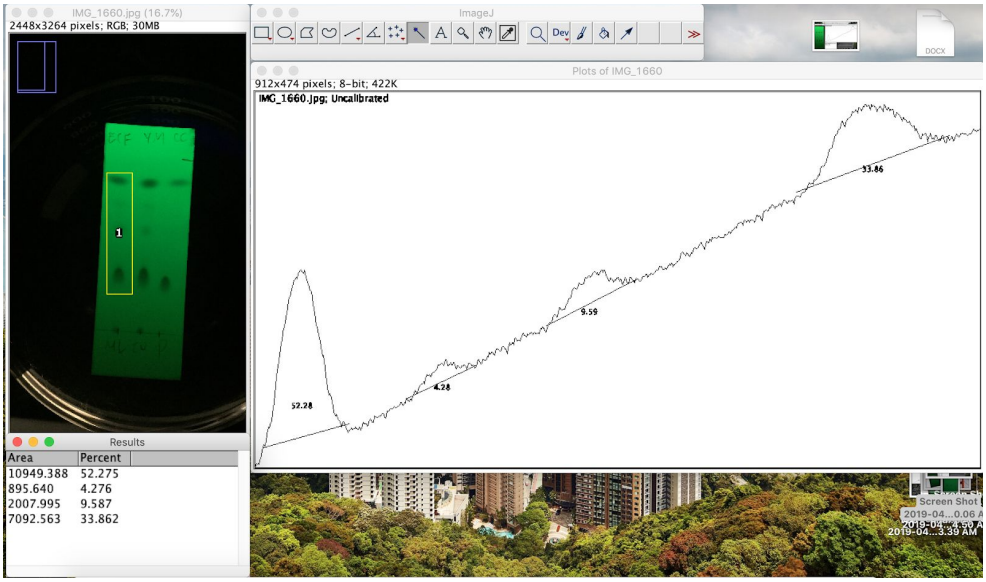
Hence, meta = 22.5% and ortho = 77.5%

To simplify the ratios, the calculated percentages will be rounded.

ortho : para → 2 : 98 = 1 : 49
para : dinitro → 22 : 76 = 11 : 38
ortho : meta → 22 : 76 = 11 : 38

Ratio of of compounds in crude product:
meta : ortho : para : dinitro → 3.5 : 1 : 49 : 171

Image J Calculations Part 2 : Ratios of Compounds in Mother Liquor Product



Percentage of absorbance:

- Absorbance of para compound = 52.3%
- Absorbance of 2,4 dinitro compound = 33.9%
- Absorbance of ortho compound = 9.6%
- Absorbance of meta compound = 4.2%

Calculation of mole percentage:

Ortho: 9.6/(52.3+9.6) = 15.5%
Para: 52.3/(52.3/9.6) = 84.5%

Using the ortho:para calibration curve:

x = % Absorbance (ortho) = 15.5 %
$y = 0.0079391\ (15.5^2) - 0.15962\ (15.5) + 3.3788$
y = 2.81

Hence ortho = 2.57% and para = 97.19%

Para = 52.3/(52.3+33.9) = 60.7%
Dinitro = 33.9/(52.3/33.9) = 39.3%

Using the dinitro:para calibration curve:

y = % Absorbance (2,4-dinitro) = 39.3 %
$y = 0.0223 (x^2) – 1.681(x) + 37.4$
$39.3 = 0.0223 (x^2) – 1.681(x) + 37.4$
$0 = 0.0223 (x^2) – 1.681(x) - 1.9$

Using the quadratic formula, solve for x when a = 0.0223, b = -1.681 and c = -1.9,
X = 76.5%

Hence dinitro = 76.5% and para = 23.5%

Ortho = 9.6/(9.6+4.2) = 69.6%
Meta = 4.2/(9.6+4.2) = 30.4%

Using the meta:ortho calibration curve:

x = % Absorbance (meta) = 30.4 %
$y = 0.0077570 (30.4^2) + 0.067612 (30.4) + 1.6469$
y = 10.9

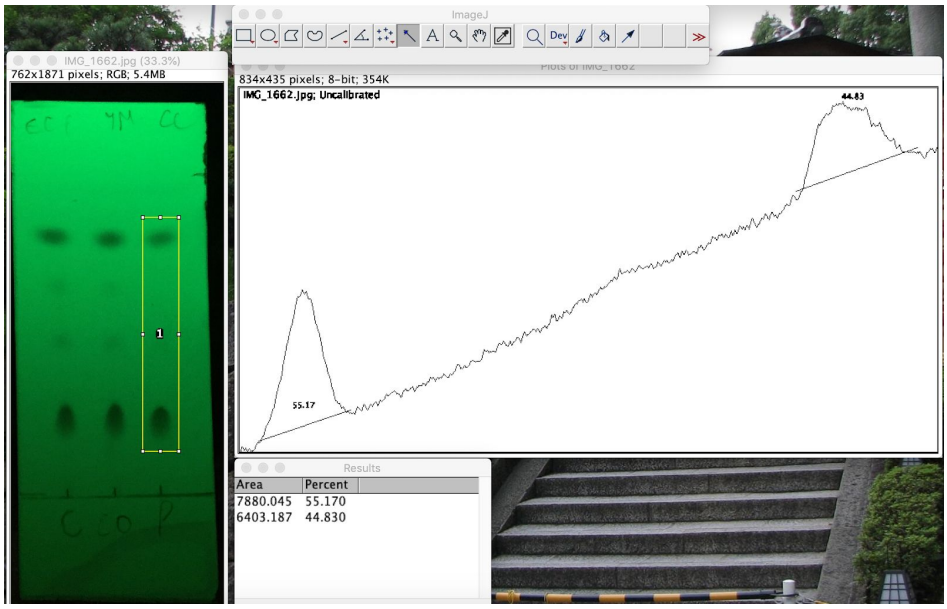
Hence, meta = 10.9% and ortho = 89.1%

To simplify the ratios, the calculated percentages will be rounded.

ortho : para → 2 : 98 = 1 : 49
para : dinitro → 25 : 75 = 1 : 3
ortho : meta → 10 : 90 = 1 : 9

Ratio of of compounds in mother liquor:
ortho : para : dinitro : meta → 1 : 49 : 147 : 9

Image J Calculations Part 3: Ratios of Compounds in Pure Product



Para = 52.6/(52.6+37.1) = 55.2%
Dinitro = 37.1/(52.6/37.1) = 44.8%

Using the dinitro:para calibration curve:

y = % Absorbance (2,4-dinitro) = 44.8 %
$y = 0.0223 (x^2) – 1.681(x) + 37.4$
$44.8 = 0.0223 (x^2) – 1.681(x) + 37.4$
$0 = 0.0223 (x^2) – 1.681(x) - 7.4$

Using the quadratic formula, solve for x when a = 0.0223, b = -1.681 and c = -7.4,
X = 79.5%

Hence dinitro = 79.5% and para =20.5%

Discussion

Justification of procedure

- After dissolving the acetanilide in sulfuric acid, it is important to cool the reaction down. This is because performing the reaction at high temperatures increases the amount of energy in the system, which favours the production of the meta product (which is undesired)
- The para product is formed in the lower energy pathway because it requires less activation energy, hence cooling the reaction favours the production of the desired product
- Sulfuric and nitric acid need to be added slowly to the reaction because this addition is exothermic. Hence this slow addition serves the same purpose as described above, which is to keep the temperature of the reaction from increasing such that the undesired product is formed.
- Ice and water and needed to neutralize and precipitate the desired product

TLCs and Analysis

- TLC 1 showed that no spots on the sample lane corresponded with the reference lane, hence indicating that the reaction was complete and that it was acceptable to move on to the next step
- The TLCs comparing the sample of the crude product to the ortho, para, meta and dinitro references showed the following results
    - TLC with para reference: clear spot in the sample lane corresponding with spot in reference lane
    - TLC with ortho reference: no clear spot in the sample lane corresponding with spot in reference lane
    - TLC with meta reference: no clear spot in the sample lane corresponding with spot in reference lane
    - TLC with dinitro reference: no clear spot in the sample lane corresponding with spot in reference lane
- The TLC comparing the crude product and the pure product was used to calculate the mole ratios (using Image J software) because the spots in the sample lane were clearer than the spots in the previous TLCs
- R_f values were used to determine that dinitro is the most polar compound, and hence must be the spot that travelled furthest in the TLC
- Likewise, the meta compound has a lower R_f value than the ortho compound, and hence must be the spot that travelled second furthest
- The results from the Image J calculations show a large proportion of the compound in the crude product and the mother liquor are firstly the dinitro compound and secondly the

para compound. This indicates that there was a large amount of secondary reaction, which formed the dinitro compound

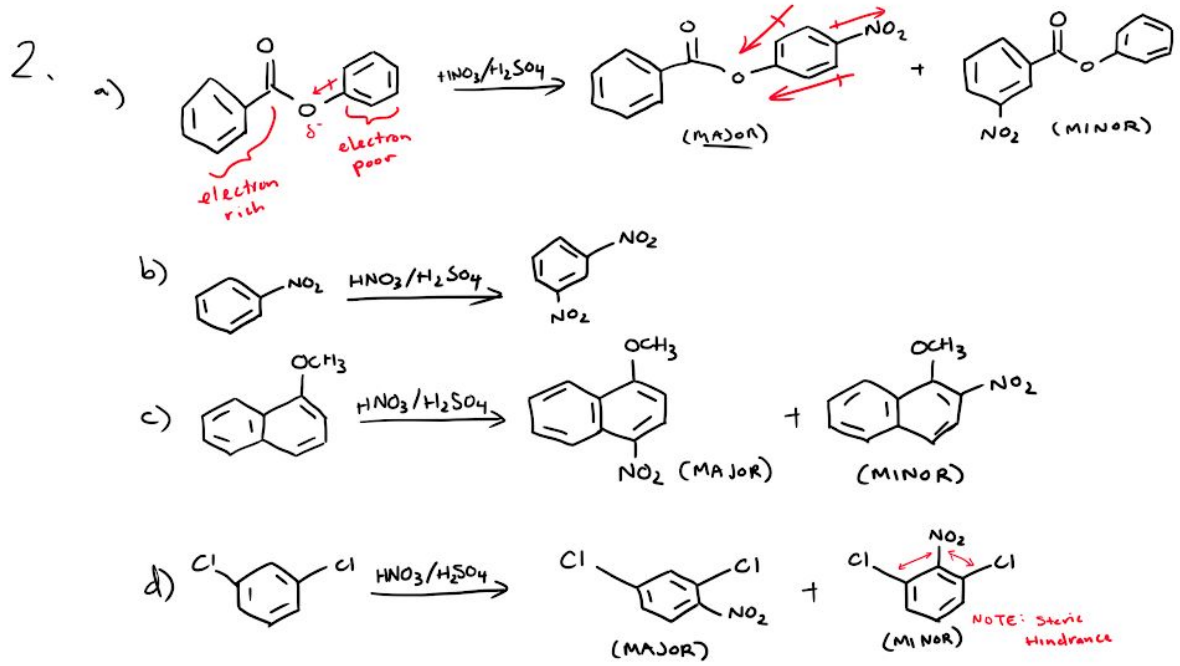
- The TLCs comparing the crude product and the mother liquor to the pure product show very little difference in terms of spots in the sample lane, but also show a lack of ortho or meta compound in the pure product lane
- The percent yield was 87%. This yield is fairly decent, but may be explained due to some sources of error

Sources of Error

- During suction filtration, some of the crude product made its way into the mother liquor, with explains why the composition of the crude product and the mother liquor are not to different according to the TLCs
    - This may also be a source of error for the yield, as some of the precipitate may have been lost during the suction and the gravity filtration
- When clamped with the ice bath over the magnetic plate, it was hard to judge whether or not the reaction vessel was close enough to the plate in order for the magnetic stir bar to function properly. This may have affected the progression of the reaction

Questions

1. Nitro groups have the property of being able to strongly lower the reactivity of aromatics that they are attached to, which makes it difficult for multiple nitro groups to attach to the same aromatic molecule. This is because the nitro groups are very electronegative, lowering the electron density of the aromatic ring, making it harder for subsequent nitro groups to react with the aromatic molecule. This lowered reactivity makes it take longer for each subsequent nitro group to react with the aromatic molecule.
2.



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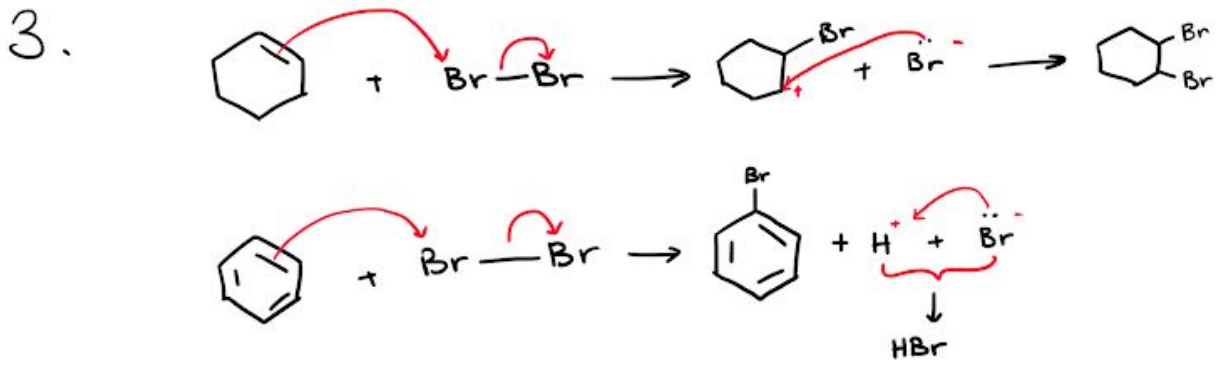
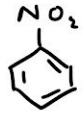


4.

+ HNO_3 + H_2SO_4 →  + Unknown

Benzene

$m = 10\,g$

$g/mol = 78.11\,g/mol$

$mol = \frac{10\,g}{78.11\,g/mol} = 0.128\,mol$

Nitric Acid

$9\,mL$

$\rho = 1.51\,g/mL$

$m = 9\,mL \cdot 1.51\,g/mL = 13.59\,g$

$mol = \frac{13.59\,g}{63.01\,g/mol} = 0.216\,mol$

Sulfuric Acid

$9\,mL$

$\rho = 1.84\,g/mL$

$m = 9\,mL \cdot 1.84\,g/mL = 16.56\,g$

$mol = \frac{16.56\,g}{98.079\,g/mol} = 0.169\,mol$

Nitrobenzene

NOTE: 1:1 stoichiometry

∴ The limiting reagent is benzene, due to it being the reagent in least abundance.

$$\%\ yield = \frac{observed\ yield}{theoretical\ yield} \times 100\% = \frac{0.066\,mol}{0.128\,mol} \times 100\% = 51.56\%$$

observed yield of nitrobenzene:

$m = 8.1\,g$ of nitrobenzene

$g/mol = 123.06\,g/mol$

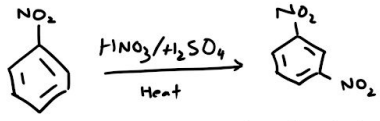
$mol = \frac{8.1\,g}{123.06\,g/mol} = 0.066\,mol$

Theoretical yield:

mols of limiting reagent (benzene): $0.128\,mol$

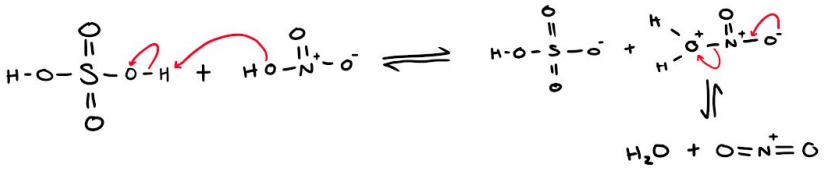
NOTE: 1:1 stoichiometry

4. c)



Nitrobenzene — meta-dinitrobenzene (1,3-dinitrobenzene)

d) H_2SO_4 acts as acid, HNO_3 as base



$H_2O + O{=}N^+{=}O$

e) % yield = $\frac{\text{observed yield}}{\text{theoretical yield}} \times 100\% = \frac{0.007\,mol}{0.128\,mol} = 5.47\%$ yield

observed yield

m = 1.2g of $C_6H_4N_2O_4$

g/mol = $((6 \cdot 12.01) + (4 \cdot 1.01) + (2 \cdot 14.01) + (4 \cdot 16.00))$ g/mol

= 168.02 g/mol

mol = $\frac{1.2\,g}{168.02\,g/mol}$ = 0.007 mol observed

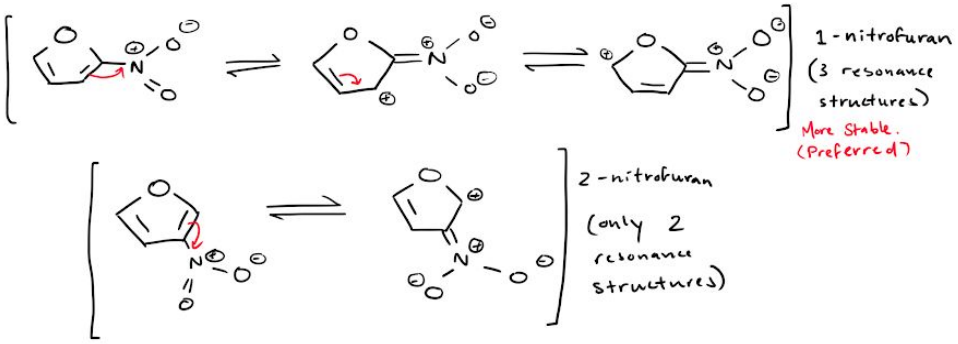
theoretical yield NOTE: 1:1 stoichiometry as $C_6H_4N_2O_4$ is a side product

Assuming 100% conversion of reagents to $C_6H_4N_2O_4$ for theoretical yield.

Using 0.128 mol of limiting reagent

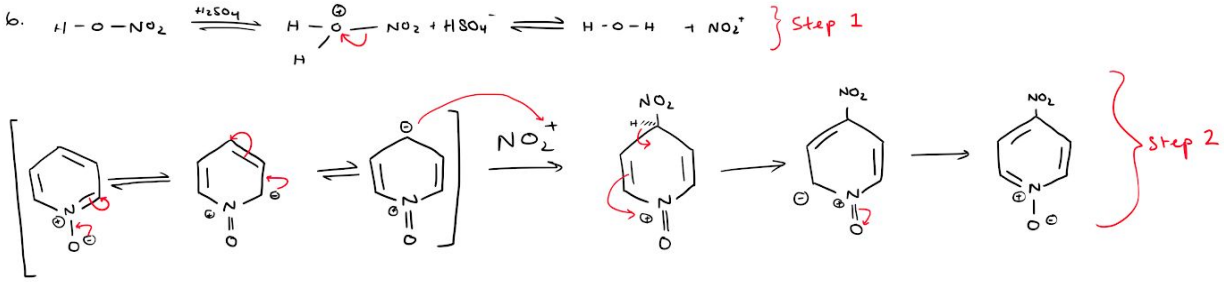
5.

5.



6.

6.



Peer Evaluation Form

Raw Data

Experiment 6

Calvin Chan
30008109 7

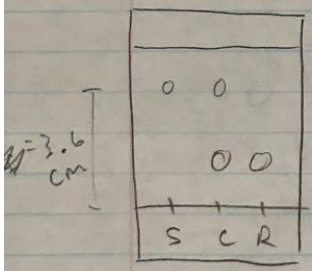
1.009 ↘
- kg of acetanilide

- Both nitric and sulfuric acids clear liquids
S:S EtOAc:Hexanes is clear liquid

Step 3: H_2SO_4 + Acetanilide solution bubbled a bit and turned a translucent golden brown

For first TLC: ↗ Reference is acetanilide in solution
DCM as solvent ↘ Co spot is both
↘ Sample is diluted sample solution

Step 4: After nitration & acids is added to solution, the solution turns a shade of bright yellow, still translucent. It becomes dark brown afterwards with more stirring.



3.6 cm

4.8cm

1.5cm

First TLC

Step 8: Pasty yellow liquid forms, with very small chunky precipitate

Step 9: After filtration: Yellow transparent liquid is in flask (removed). Product is a yellow paste.

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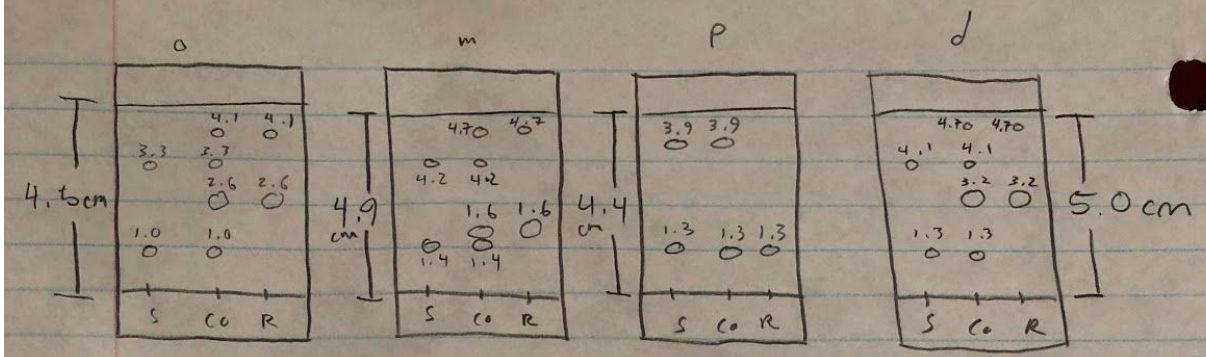
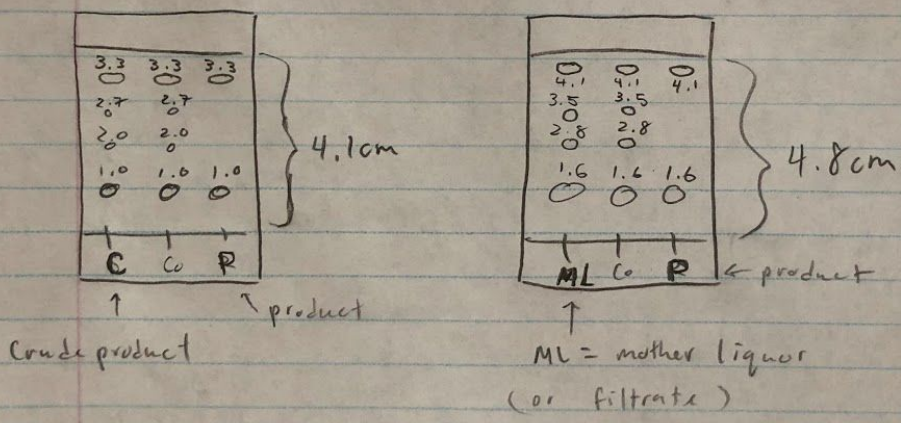


Step 16: Orange-yellow solution with visible yellow crystals.

Final Yield: 1.16g



28-3-2019