Experiment 6: Regioselective Nitration of Acetanilide

By: Yodit .A

CHM1321

Week 1

Section:A

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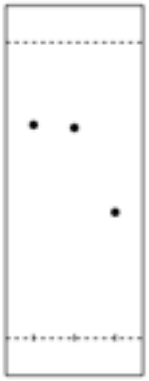
Procedure

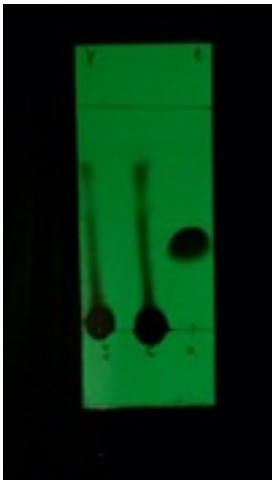
1. Measure 1 g of acetanilide into a clean 25mL round bottom flask and add a stir bar and clap it over a magnetic stir plate, then dissolve 5mL of H_2SO_4 into the acetanilide and cool the solution in an ice bath.
2. Add 0.9 mL of nitric acid and 1.2 mL of sulphuric acid into a 50mL Erlenmeyer flask and after 10 minutes, make a TLC using 5:5 EtOAc: hexanes to test if the reaction has gone to completion. If it has not gone to completion, continue to stir.
3. Get 3 ice cubes into the a 125mL erlenmeyer flask and 20 mL of water and stir it and pour the reaction flask into this flask and stir until the ice cubes are gone
4. Then collect the solid product by a suction filtration, then make a TLC of of the and add 2mL of CH_2Cl_2 to dissolve it and compare the product using ortho, meta, para, and 2,4 dinitro product isomers using the 5:5 EtOAc: hexanes and the solvent
5. Do not circle the TLC plates as they have to be observed in the UV chamber.
6. The remaining crude product will be dissolved in a 50 mL erlenmeyer flask with boiling ethanol with a stir bar and then allow the flask to cool down until the crystals to form
7. Then get the crystals and isolate them by a suction filtration, weigh the product and then make a final TLC by comparing your mother liquor and the purified product and another by comparing the purified product to the crude.

Reagent Table

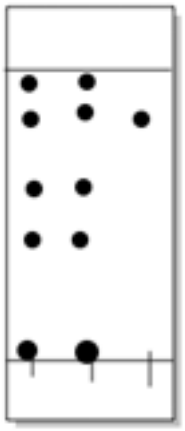
Compound	Density (g/mol)	mmol	Amount	Mol
Nitric Acid	N/A	N/A	0.9 g	N/A
Sulfuric Acid	N/A	N/A	1.2 g	N/A
Ethanol	N/A	N/A	50 mL	N/A
Acetanilide	N/A	N/A	1 g	N/A
water	N/A	N/A	20 mL	N/A

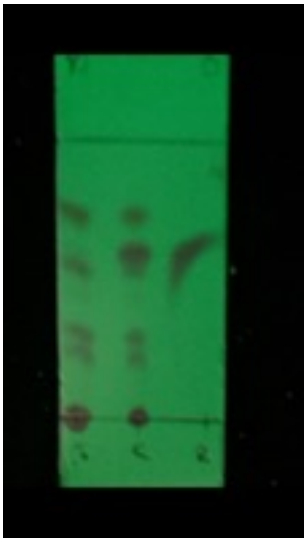
TLC Plates



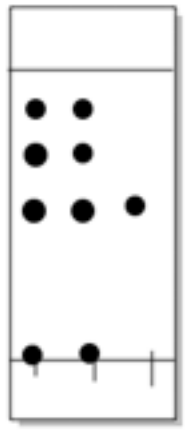


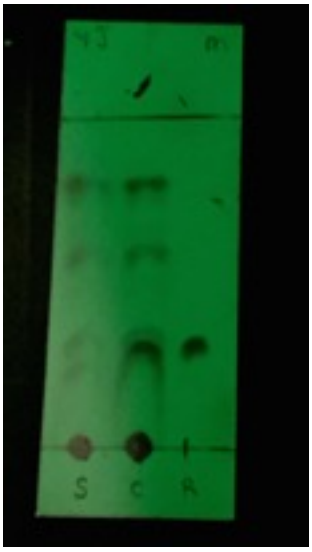
#1) Rf1: 0.79
Rf2: 0.79
Rf3: 0.34



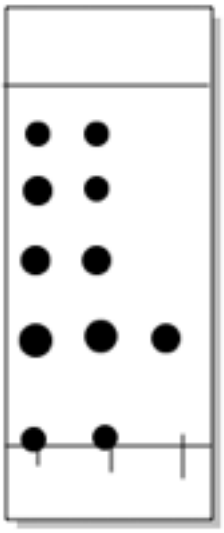


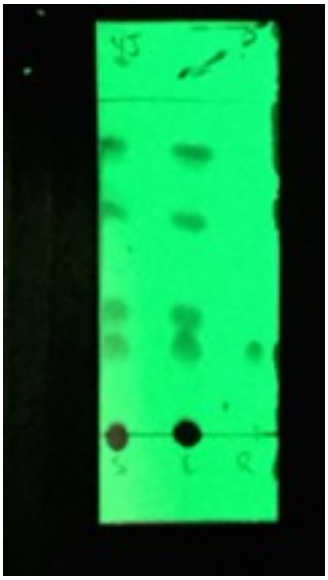
#2) Ortho TLC
Rf1: 0.73 Rf9: 0.22
Rf2: 0.73 Rf10: 0
Rf3: 0.53 Rf11: 0
Rf4: 0.53
Rf5: 0.53
Rf6: 0.31
Rf7: 0.31
Rf8: 0.22



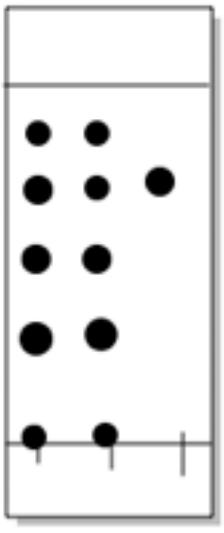


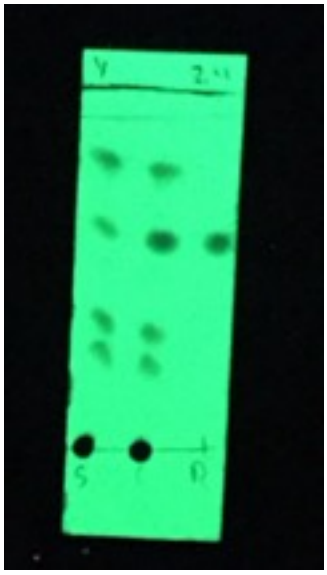
#3) meta TLC
Rf1: 0.76
Rf2: 0.76
Rf3: 0.45
Rf4: 0.45
Rf5: 0.24
Rf6: 0.24
Rf7: 0.24
Rf8: 0
Rf9: 0



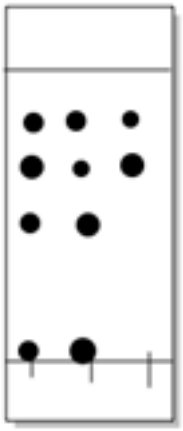


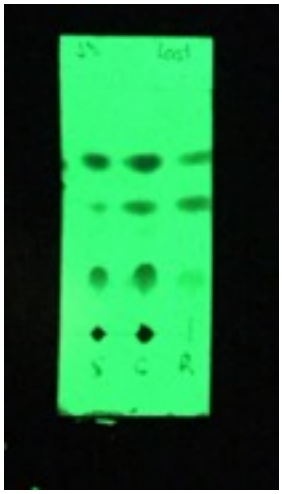
#4) Para TLC
Rf1: 0.88 Rf10: 0
Rf2: 0.88 Rf11: 0
Rf3: 0.66
Rf4: 0.66
Rf5: 0.33
Rf6: 0.33
Rf7: 0.24
Rf8: 0.24
Rf9: 0.24



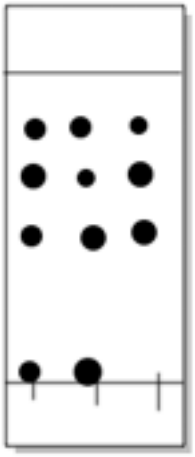


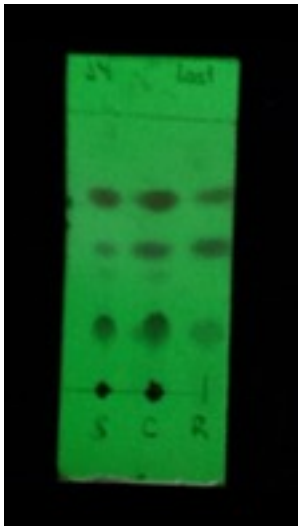
#5) 2,4 dinitro
Rf1: 0.73 Rf9: 0.22
Rf2: 0.73 Rf10: 0
Rf3: 0.55 Rf11: 0
Rf4: 0.55
Rf5: 0.55
Rf6: 0.28
Rf6: 0.28
Rf7: 0.22





#6) Comparison of crude
Rf1: 0.66 Rf9: 0
Rf2: 0.66 Rf10: 0
Rf3: 0.66
Rf4: 0.50
Rf5: 0.50
Rf6: 0.50
Rf7: 0.19
Rf8: 0.19





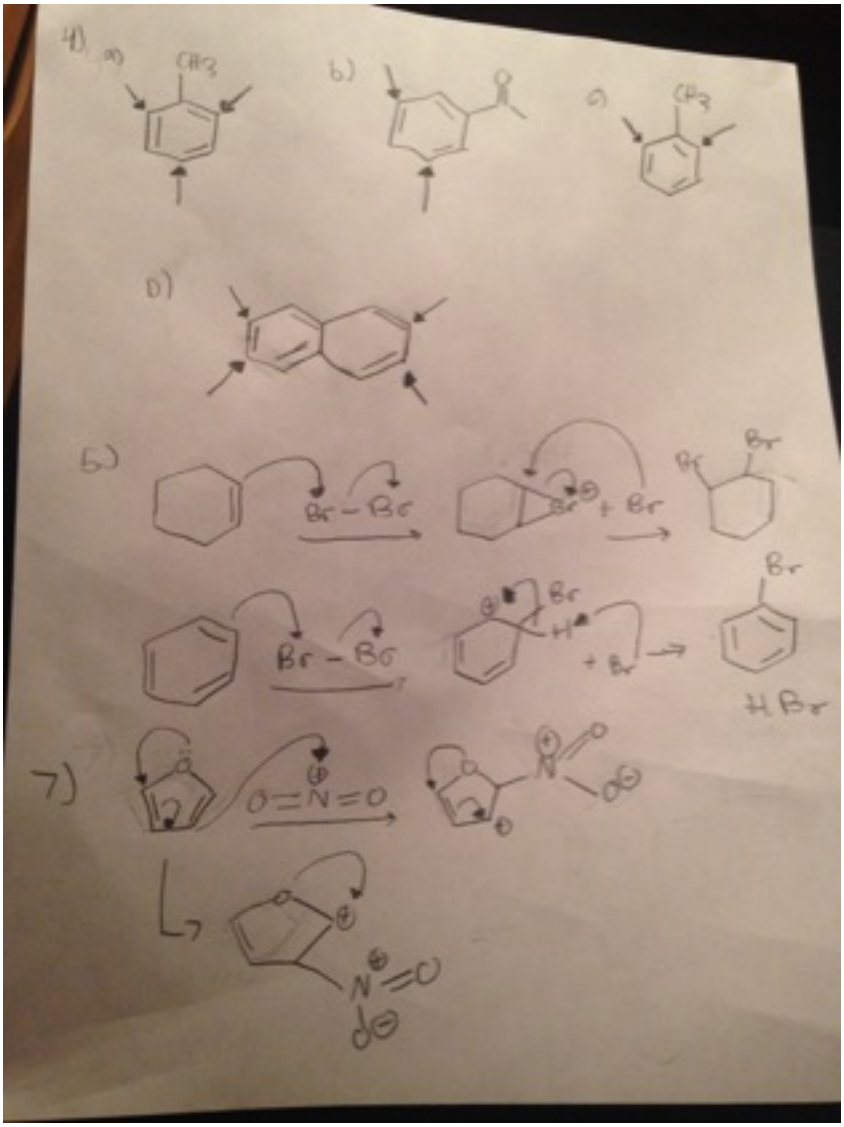
#7) Comparison of Mother Liquor
Rf1: 0.70 Rf10: 0
Rf2: 0.70 Rf11: 0
Rf3: 0.70
Rf4: 0.52
Rf5: 0.52
Rf6: 0.52
Rf7: 0.20
Rf8: 0.20
Rf9: 0.20

Observations

The acids mixed together were clear and then it turned into a dark orange colour and the mixture was no longer transparent. once the ethanol was added to the mixture, it felt hot and it was put into an ice bath, then as it cooled the crystals formed.

Questions

1) The difference in polarity in the ortho and para isomers is the …. has a larger dipole and interacts with silica gel more and moves up the plate more
2) The reason why the second nitro group is slower because the rate of the reaction is slower and has a weaker nucleophile and has a higher activation energy.
3) The reason why the para isomer is favoured over the ortho is because there is too much steric interference in the ortho isomer.



4)

5)

7)

6a) n of benzene = (780g)/(78g/mol)
= 10 mol
n of nitrobenzene = (1000g)/(123g/mol)
= 8.14 mol
Therefore, nitrobenzene is the limiting reagent

6b)% yield = grams of starting martial / grams of product x 100%
grams of starting martial= 1000g
grams of product = 250g

% yield = 250g/ 1000g x 100%
= 25%
6c) ortho

6d) H_2SO_4, sulfric acid is used in the nitration reaction to help form the nitronium ion in the reaction.

6e)% yield = grams of starting martial / grams of product x 100%

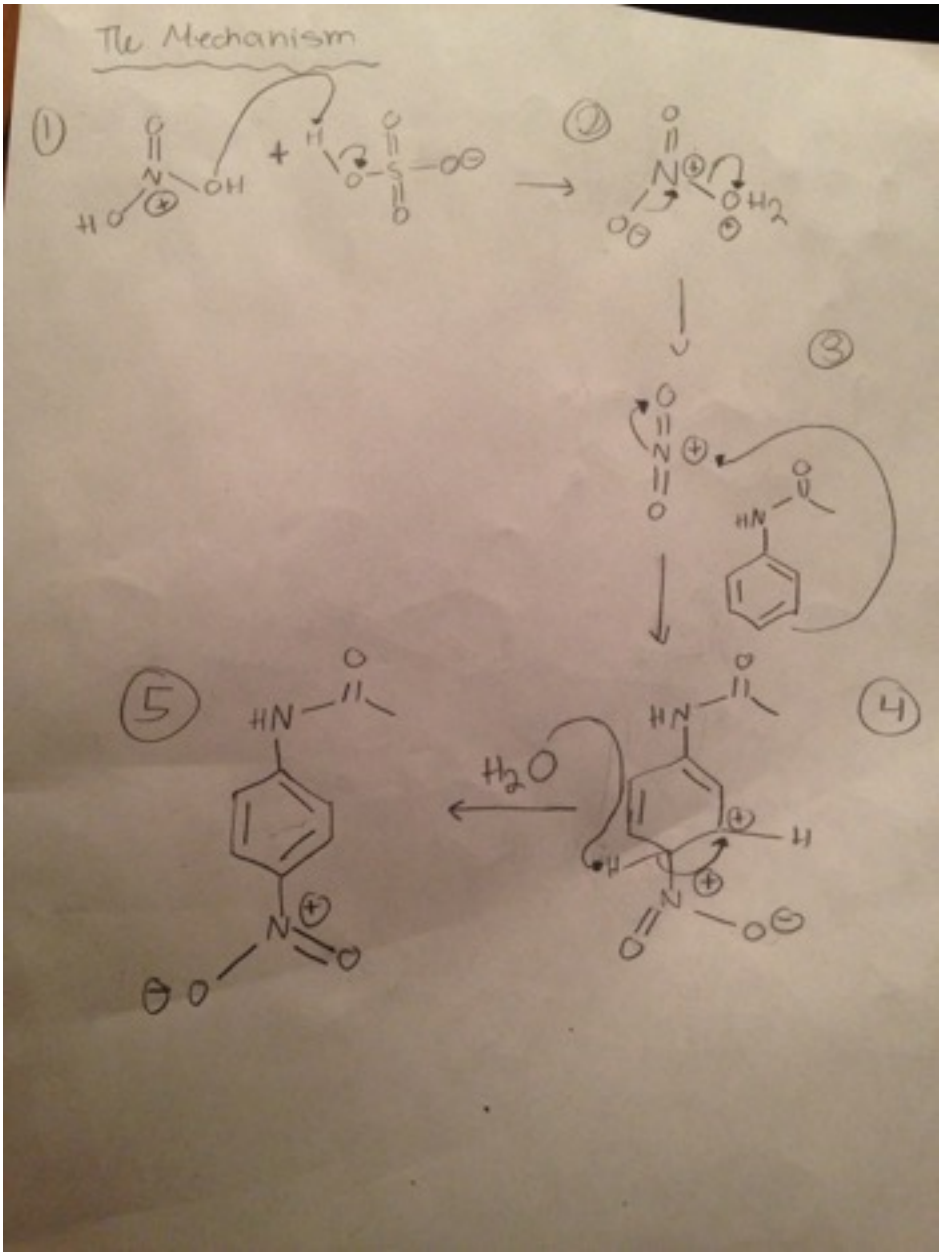
$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + C_6H_4N_2O_6$

n of benzene = (780g)/(78g/mol)
= 10 mol
n of nitrobenzene = (1000g)/(123g/mol)
= 8.14 mol
n of sulfuric acid = (0.780L) x (18M)
= 14 mol
the limiting reagent is benzene and through stoichiometric ratios the theoretical mass of the crystalline compound is 1230 g

mm of $C_6H_4N_2O_4$ = 168.11 g/mol
m of $C_6H_4N_2O_4$ = 250 g
n of $C_6H_4N_2O_4$ = 1.48 mol

% yield = 250g/1230 g x 100%
= 20%

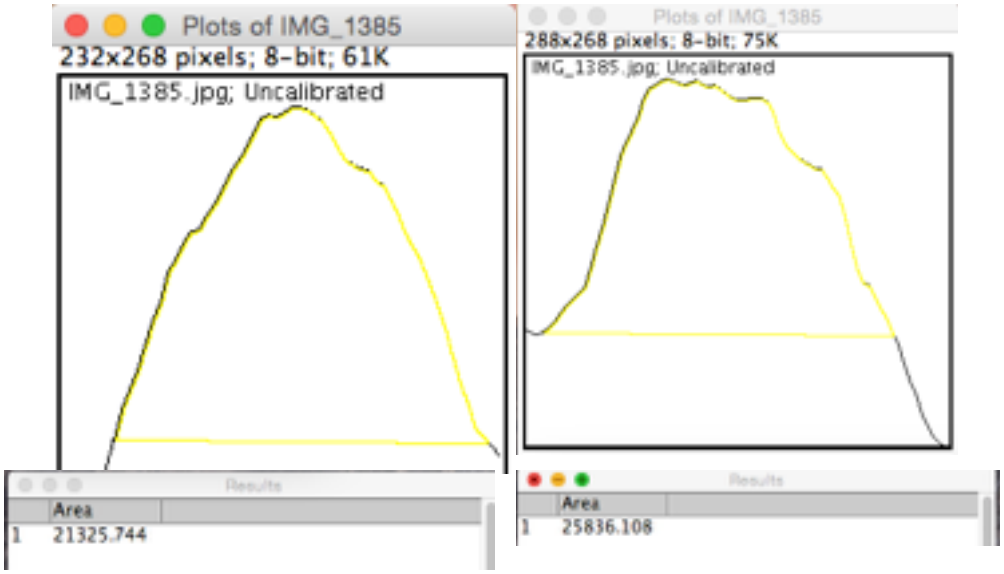
The Mechanism



TLC Plates (Image J)

Para TLC

lane1 lane 2



% Peak 1 = Area of peak 1 / (Area of peak 1) + (Area of peak 2) X100%

= 21325.744/ 47161.852

=0.452x 100%

= 45.2%

% Peak 2 = Area of peak 2 / (Area of peak 1) + (Area of peak 2) X100%

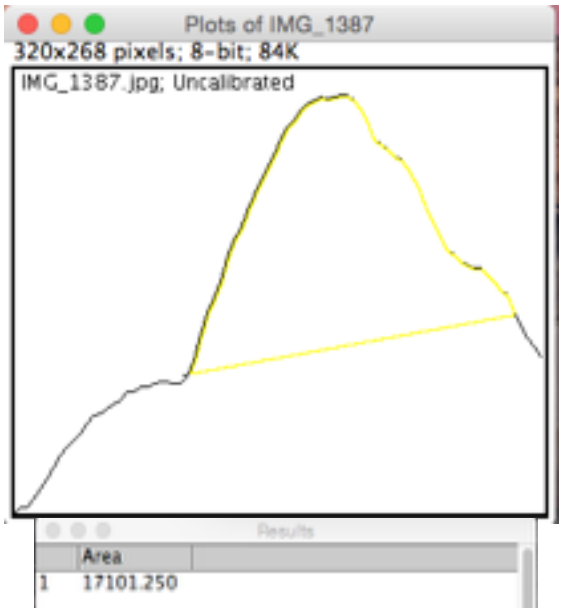
= 25836.108 / 47161.852

= 0.547x 100%

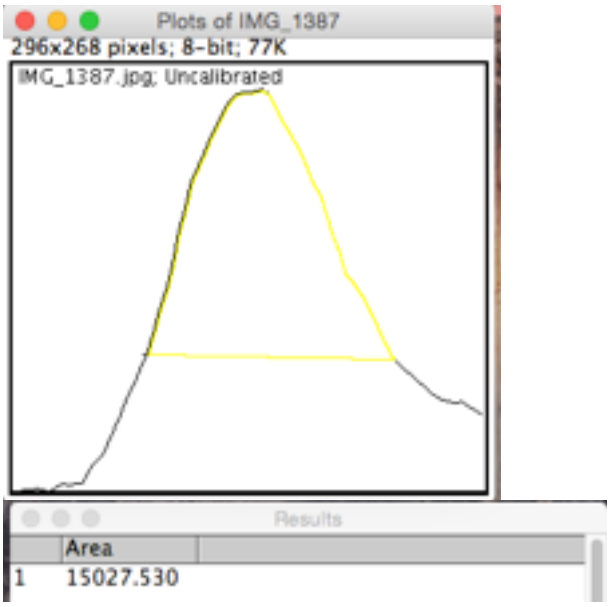
= 54.7%

Meta TLC

lane1



lane 2



% Peak 1 = Area of peak 1 / (Area of peak 1) + (Area of peak 2) X100%

= 17101.250/ 32128.780

=0.532x 100%

= 53.2%

% Peak 2 = Area of peak 2 / (Area of peak 1) + (Area of peak 2) X100%

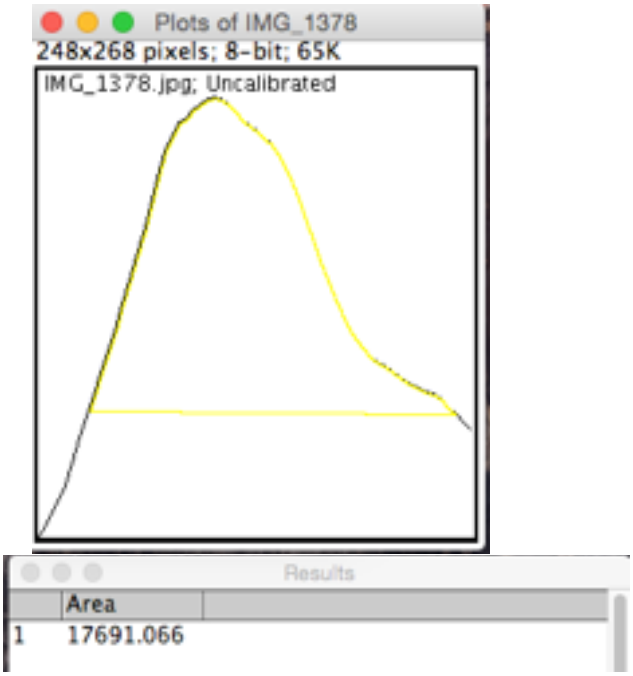
= 15027.530 / 32128.780

= 0.467x 100%

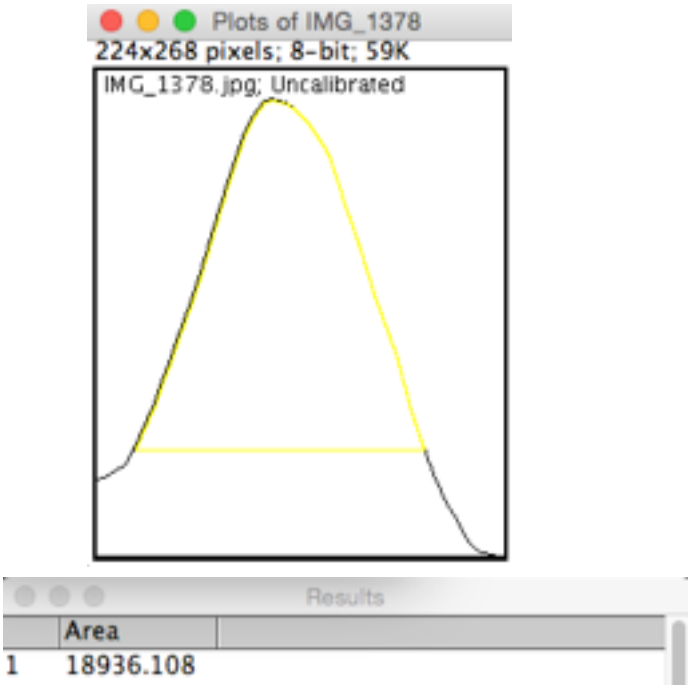
= 46.7%

Ortho TLC

lane1



lane 2



% Peak 1 = Area of peak 1 / (Area of peak 1) + (Area of peak 2) X100%

= 17691.066/ 36627.174

=0.483x 100%

= 48.3%

% Peak 2 = Area of peak 2 / (Area of peak 1) + (Area of peak 2) X100%

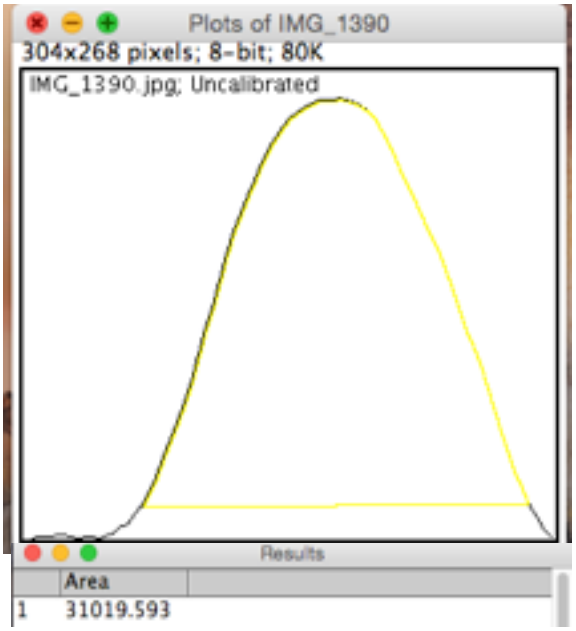
= 18936.108/ 36627.174

= 0.516x 100%

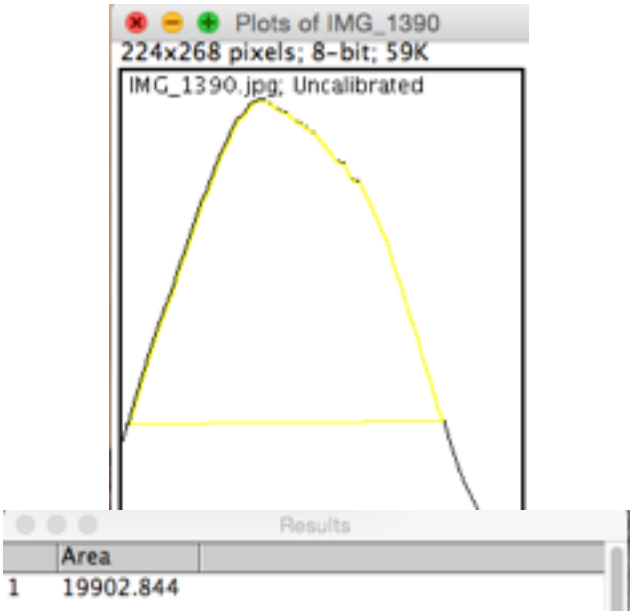
= 51.6%

2,4 Dinitro

lane1



lane 2



% Peak 1 = Area of peak 1 / (Area of peak 1) + (Area of peak 2) X100%

= 31019.593/ 50922.437

=0.609x 100%

= 60.9%

% Peak 2 = Area of peak 2 / (Area of peak 1) + (Area of peak 2) X100%

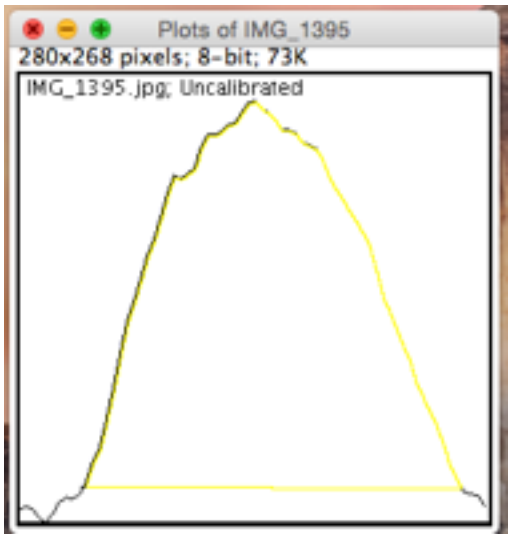
= 19902.844/ 50922.437

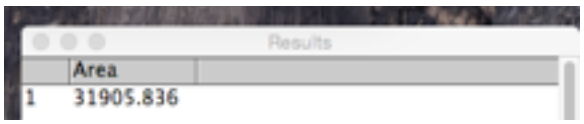
= 0.391 x 100%

= 39.1%

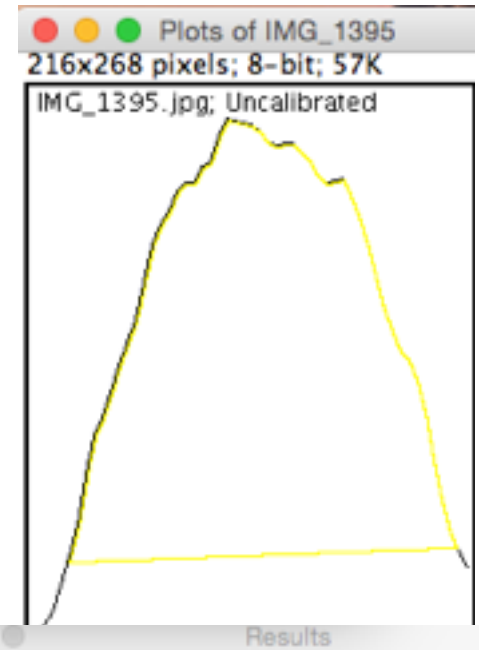
Comparison of the crude

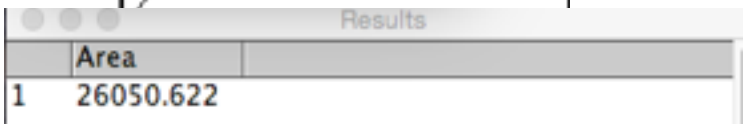
lane1





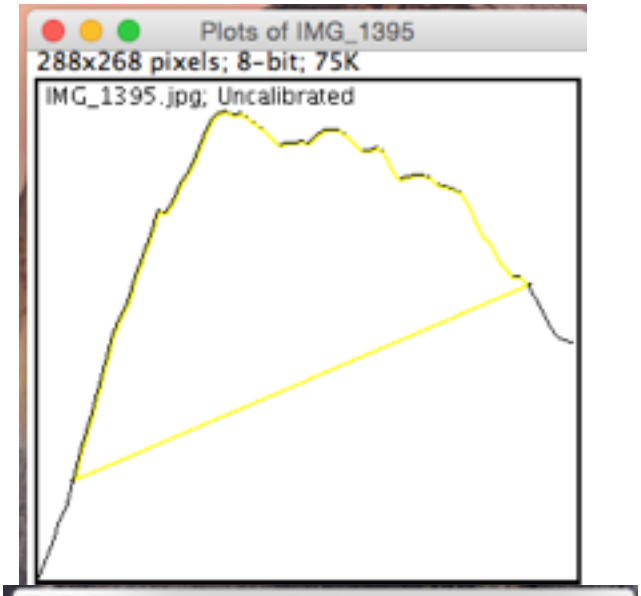
lane 2

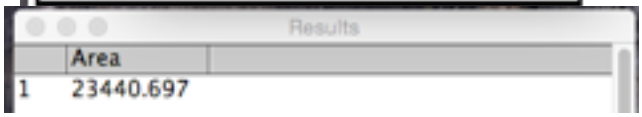




Comparison of the mother liquor

lane1





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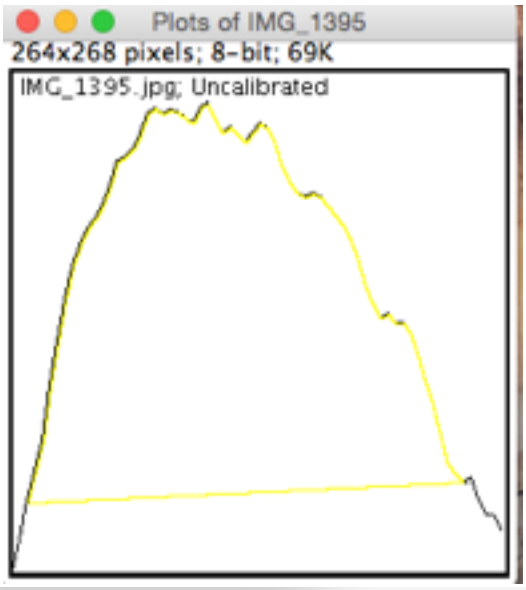

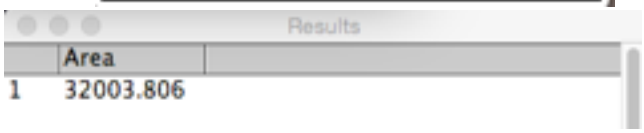

Yield of product

what was made is nitrobenzene

%yield= moles of starting martial / mole of product x 100%

molar mass of nitrobenzene = 123.06 g/mol
mass= 0.58g
mol = 0.0047mol

molar mass of acetanilide = 135.17 g/mol
mass= 1g
mol = 0.0073mol

%yield = 0.0047mol / 0.0073 mol x 100%
= 64.4%

Discussion

This experiment had some errors. There was unclean glassware, as some of the beakers had this red substance before they were washed again. In addition, the chemicals may have been added in uneven proportions to the mixture. The contamination is what that affected the TLC plates, which caused all of the errors on the TLC plates and the impurities in the chemicals. The first TLC shows that the reaction did go to completion. The other TLC plates shows that meta is, present in the mixture, along with orther, 2,4 dinitro, and para and this is incorrect and this shows that there is major errors that happened in the reaction. Also the TLC plates comparing the product to the crude and the other TLC comparing the product to the mother liquor shows that the product was impure, as the spots on the TLC matched up to the rows, showing the impurity on both TLC plates. After the calculations were done it was found that there is 51.6% ortho, 53.2% meta, 45.2% para, which does not make sense as the percentage of the mixture goes over 100 percent, which shows that there was a larger error. There may have been a side reaction that could have taken place instead of what was suppose to happen. the percent yield from the overall was 64%, which is a decent yield, showing that some parts of the reaction were done correctly.

Conclusion

In conclusion, there were many errors that happened during the experiment and there is 51.6% ortho, 53.2% meta, 45.2% para in the mixture.

References

molar mass of nitrobenzene was used from https://pubchem.ncbi.nlm.nih.gov/compound/nitrobenzene

molar mass of acetanilide was used from https://pubchem.ncbi.nlm.nih.gov/compound/acetanilide

molar mass of C6H4N2O4 was used from http://www.webqc.org/molecular-weight-of-C6H4N2O4.html