Student Name: *Stefanie Mayer*

Student Number: *8202777*

Partner's Name and Student #: *Emily Valko - 7813342*

Demonstrator's Name: *Andrew Hollingshead*

PLEASE NOTE: If ANY of the above information is UNCLEAR or not provided, your grade will NOT be recorded!!

- *Lab Day: Tuesday*
- *Lab Week: One*

Laboratory Report Form

Experiment 6: 28/03/2016

Regioselective Nitration of Acetanilide

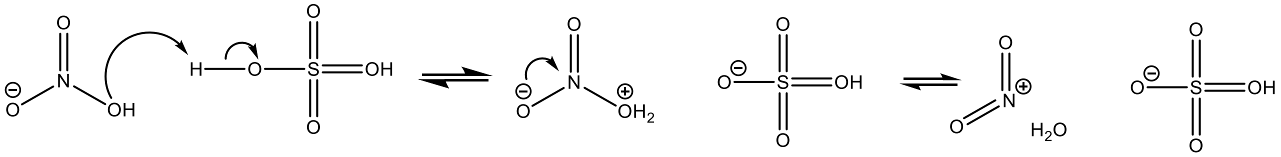
Checklist:

- ○ **Raw Data Sheet written in pen, signed by TA and attached**
- ○ **Completed Report Form attached**

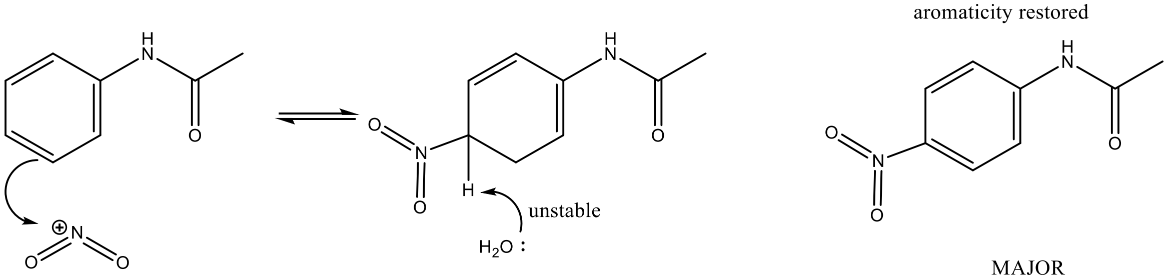
Student's Initials: ***S.M.***

Introduction:

1) Formation of Nitronium

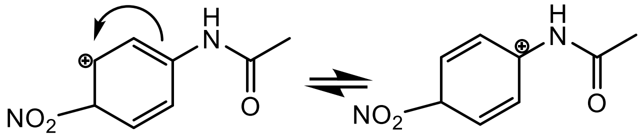


2) Addition of Nitronium to Aromatic Ring

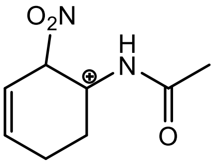


3) Various isomers of the Final Product. Why para form is favored

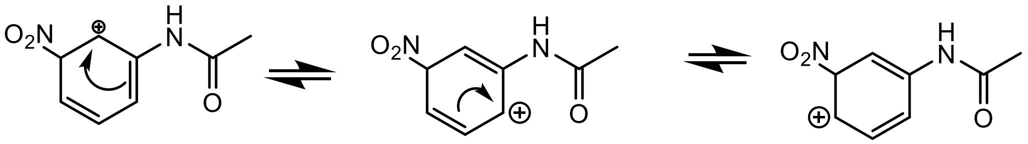
Para



Ortho



Meta



The electron donating group is the Nitronium ion, it is a (o/p) director. The final product should have more para due to steric interactions.
The purpose of the lab is to see and understand regioselectivity of reactions involving aromatic compounds.

Procedure:

See *Experiment 4: Regioselective Nitration of Acetanilide* in the *CHM 1321 – Organic Chemistry Lab Manual*

Table of reagents:

Compound	Molecular Weight ($g.mol^{-1}$)	Quantity [a]	Moles (mol) [b]	Density (gmL-1)
Acetanilide	135.17	1.01g	0.0075	1.129
Sulphuric Acid	98.08	1.2mL	0.026	1.84
Nitric Acid	63.01	0.9mL	0.022	1.5129

a. Quantity used in experiment given by procedure

b. See Calculations

Calculations:

mmol of compound:

$M = \frac{m}{n} \rightarrow n = \frac{m}{M}$ with n in moles, m in grams and M the molecular weight

Ex: $n(\text{H2SO4}) = \frac{1.84*1.2}{98.08}$ = 0.026 mol

Theoretical yield of Final Product= 0.0075*180.16 = 1.35

Experimental yield = 3.9g

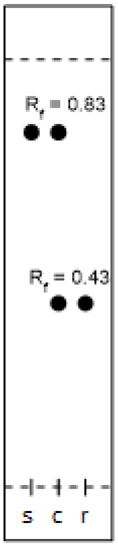
Yield % $= \frac{experimental\ yield}{theoretical\ yield} * 100 = \frac{3.9}{1.35} * 100 = 289\%$

Observations:

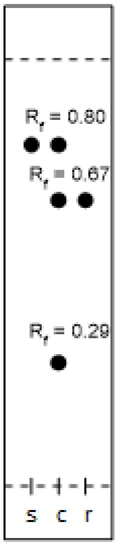
- There was no change following the addition of the acetanilide to the sulfuric acid.
- When adding HNO_3 and the concentrated H_2SO_4 together the Erlenmeyer flask felt warmer, due to the reaction being exothermic.
- When the mixture of the two acids were added to the acetanilide, the solution turned brown/black in colour. Also, some foam was observed on the surface of the mixture.
- After 10 minutes of mixing the following TLC confirmed that the reaction reached completion. This is because there was only one product visible in the sample lane which was different from the starting product, suggesting that all the original product has been completely reacted.
- Isolating the crude product first involved adding ice cubes as well as water. Following the addition of water, crystals formed. They were bright yellow in colour. Similar to the colour of mustard. In addition to having a mustard-like colour, the contents released a strong pungent smell. When isolating the crystals via suction filtration, the crystals was like a bright yellow paste.

Thin Layer Chromatography

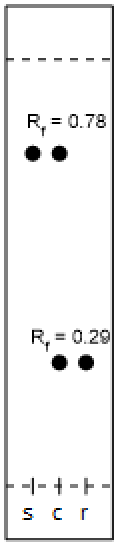
Eluents used: **Hexanes:EtAOc 5:5**



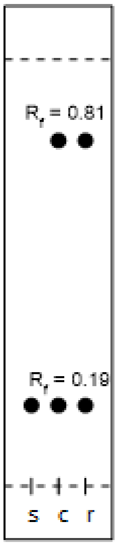
TLC Plate #1:
S: Acetanilide + Acetone
C: S+R
R: Reaction



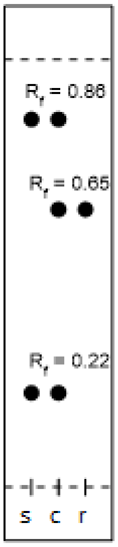
TLC Plate #2:
S: crude product
C: S+R
R: ortho-nitroacetanilide



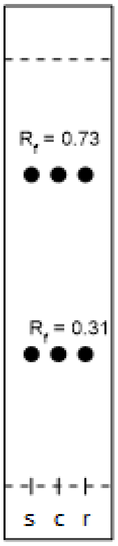
TLC Plate #3:
S: crude product
C: S+R
R: meta-nitroacetanilide



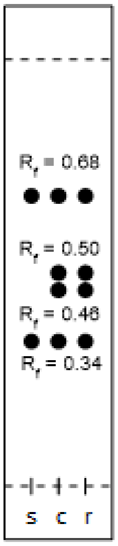
TLC Plate #4:
S: crude product
C: S+R
R: para-nitroacetanilide



TLC Plate #5:
S: crude product
C: S+R
R: dinitro-acetanilide



TLC Plate #6:
S: pure product
C: S+R
R: crude product



TLC Plate #7:
S: crude product
C: S+R
R: mother product

By the looks of the TLC plate 6, the crude product and the pure product are composed of the same things as intended. However, by observing the 7th TLC plate, we see some similarities between the mother product and the crude product but many impurities.

IMAGE J:

Area: (Area of Peak 1/ (Area of Peak 1 + Area of Peak 2))*100

Meta

Area: (2586.317/ (2586.317+1658.033))*100 = 60.9%

$Y=7.7570 *10^{-3}*60.9^{2} + 6.7612*10^{-2}*60.9 +1.6469 = 34.6\%$ meta

Ortho:

7.7% → percent taken from Image J

Y= ((7.9391 *10^-3)*7.7^2) + ((6.7612*10^-1)*7.7) + 3.3788 = 9.1%

Para:

25.8% → percent taken from Image J

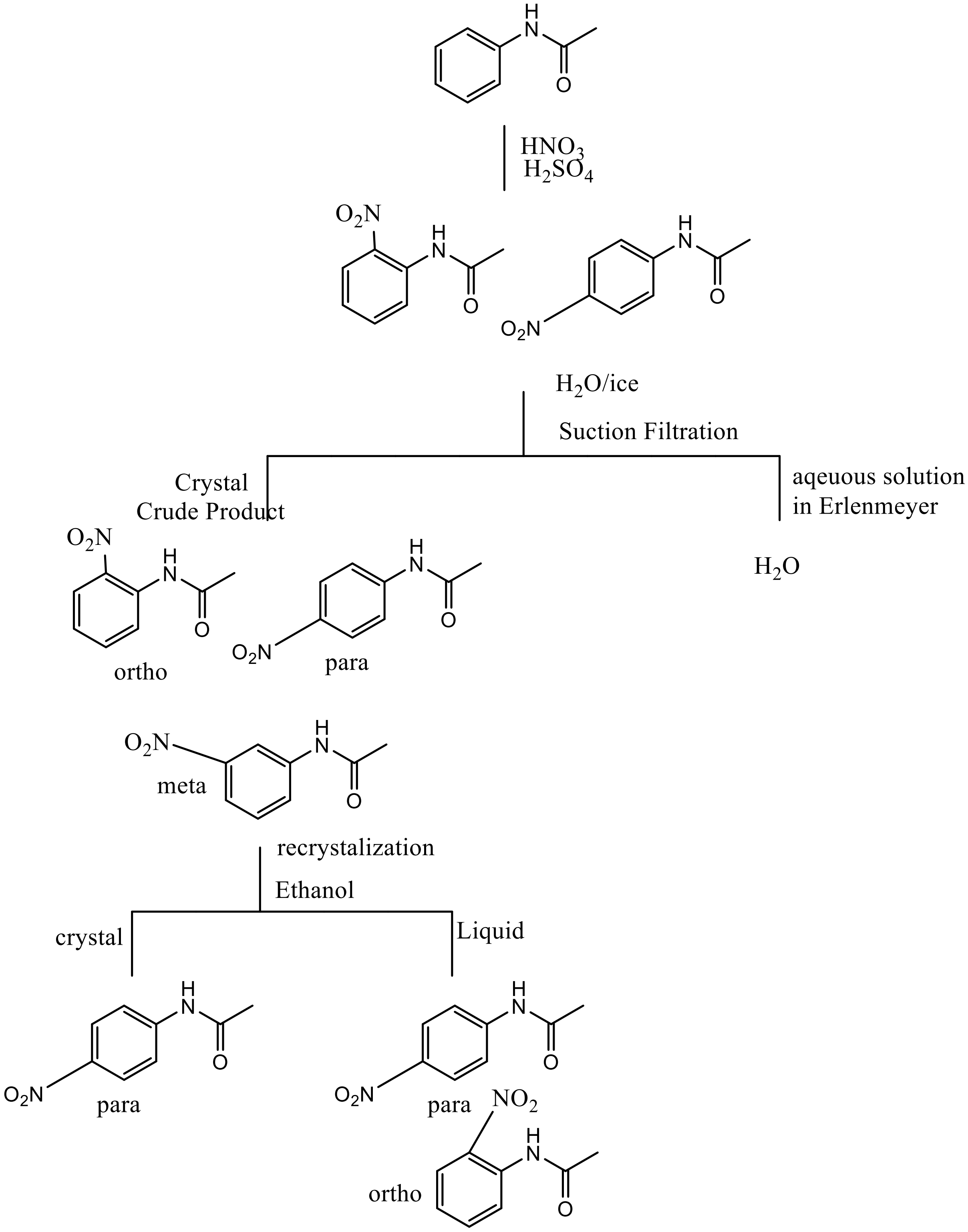
$Y= ((2.2273 *10^{-2})*25.82^{2}) + (1.6809*25.8) + (3.7421*10\hat{}1) = 95.6\%$

Dinitro

Area: (2111.74/ (2111.74+2606.719))*100 = 44.8%

$((2.2273 *10^{-2})*25.82^{2}) + (1.6809*25.8) + (3.7421*10\hat{}1)$

Flow Chart :


HNO_3
H_2SO_4
O_2N
H_2O/ice
Suction Filtration
Crystal
Crude Product
aqeuous solution
in Erlenmeyer
H_2O
ortho
para
meta
recrystalization
Ethanol
crystal
Liquid
para
para
NO_2
ortho

Discussion:

The focus of the lab was to observe regiochemistry and predicting whether ortho, meta, or para products would be formed. The substituent on the aromatic ring in this lab is an electron donating group. Thus, it will lower the Energy of areniums, theoretically leading to more ortho/para products produced. In fact, this is due to the substituent that stabilizes the adjacent positive charges created and accelerates the rate of formation of o/p products by reducing the amount of energy needed to reach transition state.

Generally, the experimental results show that para was the most favored product. This is because it consistently had the highest % composition in all the reaction samples. These results were shown through analysis using Image J.

With a final yield % of 289% sources of errors are recognisable. In this experiment, the sources of error include inadequate drying of the crystals, poor TLC as well as temperature control during the reactions. The reason why the actual yield was so high could be due to water present in the crystal mixture. This is proved by the wet sand appearance of the crystals following suction filtration. That would add significant amounts of mass to product. To fix this, the crystals could be dried out for a much longer time to ensure all liquid is sucked out.

Theoretically, there should be a larger discrepancy between the amount of each product isomer. This did not occur because the TLCs were not spotted enough. The peaks were not as tall as the one shown in the example, making it difficult for Image J to correctly analyze the results. This means that the percent composition could be slightly inaccurate. To fix this, the TLC should be spotted with more of both the sample and reference solution to get better TLC resolution.

The last source of error which could affect results is heat. Generally, more o/p products should be made with relatively less meta products under cold conditions. This is because the o/p products have a lower activation energy in this experiment and thus would form faster, leaving less reactants to achieve the meta form. However, if the ice cubes did not adequately cool the water enough. This leads to more meta products being produced and thus, increasing the composition of meta products. This leads to decrease in yield of the final ortho/para product. To fix this, a thermometer could be used to make sure that the water is adequately cooled and the maximum amount of ortho/para product is formed.

Conclusion:

3.5g of NO_2-*Ph – NHAc* (aq) was synthesized from *acetanilide* in this experiment resulting in a percent yield of 174%.

Questions:

1. **Explain the difference in polarity of the ortho and para isomers of nitroacetanilide with respect to the TLC, commenting on why one compound has moved further than the other.**

Through observations of the TLC plates we determine differences of polarity between the ortho and para isomers of nitroacetanilide. We deduct that the *ortho* isomer is more polar. In fact, the charges on the *para* isomer are on opposite sides of the molecule and ergo cancel themselves out. This decreases the polarity. This is illustrated by the position of the spots that are higher on the TLC plate because of the attraction to the charged silica gel.

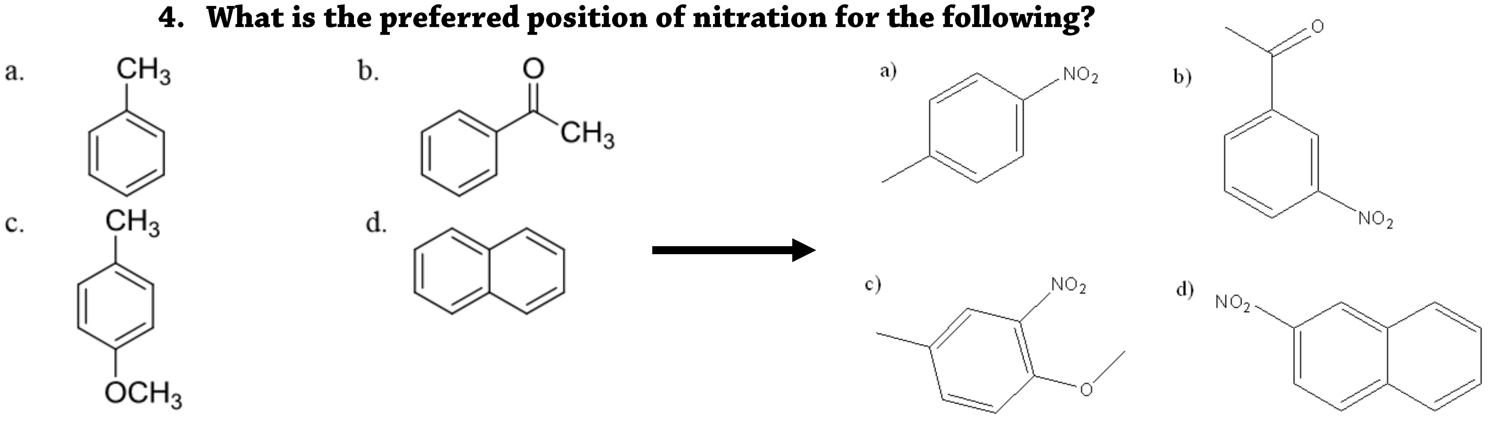
2. **Why is the addition of a second nitro group in this reaction much slower than the first nitration of acetanilide?**

The nitro groups are strong meta deactivators and create inductive electron withdrawal. This makes the π system more nucleophilic. The first addition of a nitro group moves the molecules to a lower energetic level. The second nitration has a higher energy barrier compared to the first. Therefore, the second addition is an attack on a less reactive molecule and it occurs much slower.

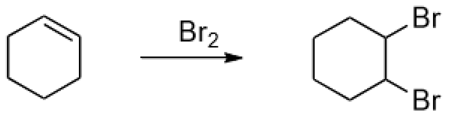
3. **Why are para isomers favored over ortho isomers in electrophilic aromatic substitution?**

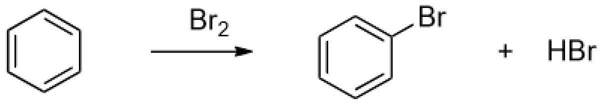
The charge distribution in the benzene ring is greatest at para sites to the substituents, thus the para isomer is favored.

4. **What is the preferred position of nitration for the following?**

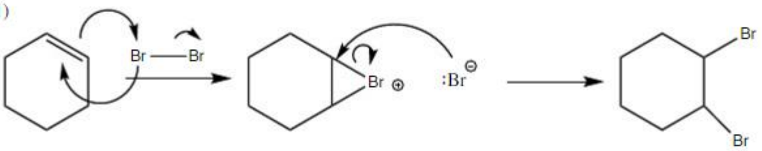


5. **Explain the following observation**

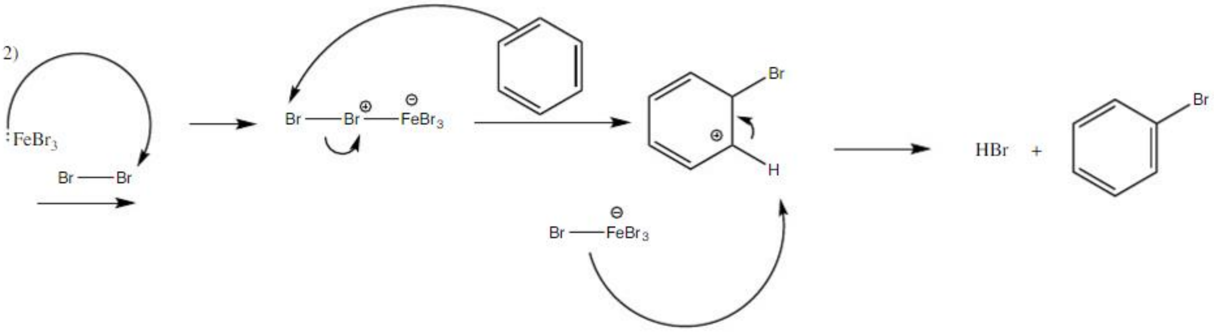




1)



2)



6. **When 780 g of benzene (Molar mass = 78 g/mol) reacts with 750 mL of concentrated HNO3 (16 M) and 750 mL of H2SO4 (18 M), 1000 g of nitrobenzene (molar mass = 123 g/mol) and 250 g of an unknown compound with a high boiling point are obtained.**

a. **Identify the limiting reagent:**

- Benzene: 780/78 = 10 mols
- HNO_3: 0.750*16 = 12 mols
- H_2SO_4: 0.750*18 = 13.5 mols

Benzene is the limiting reagent.

b. **Calculate the percent yield of nitrobenzene.**

%YIELD = (actual/theoretical) *100 = (1000/1230)*100 = 81.3%

c. **Give the name of the most probable side product with the high melting point.**

The most probable side product is dinitrobenzene.

d. **Explain, with the aid of a mechanism, the role of H2SO4 in the reaction.**

The role of H_2SO_4 in this reaction is to activate the electrophile, nitric acid. It is used as a catalyst.

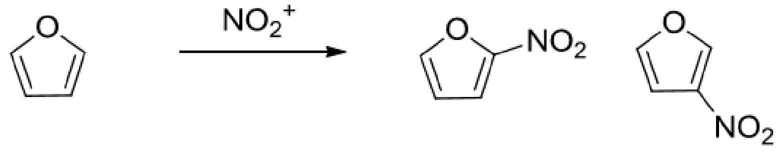
e. **Supposing the crystalline compound (250 g) has the formula C6H4N2O4, calculate the yield of this side product.**

Molecular weight of $C_6H_4N_2O_4$ = 168.10704

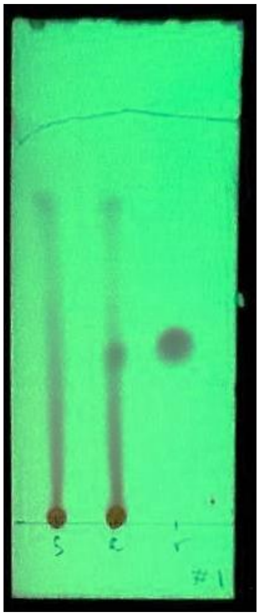
n = M/m = 250/168.10704 = 1.487 mol

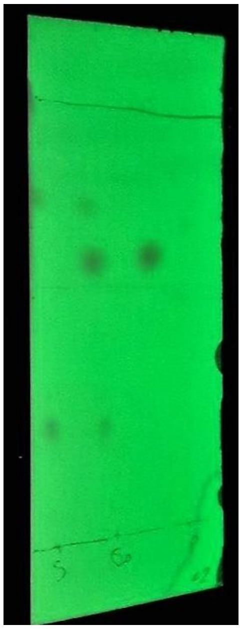
%YIELD OF SIDE PRODUCT: (actual/theoretical) *100 = (1.487/(10-8.13))*100 = 79.52%

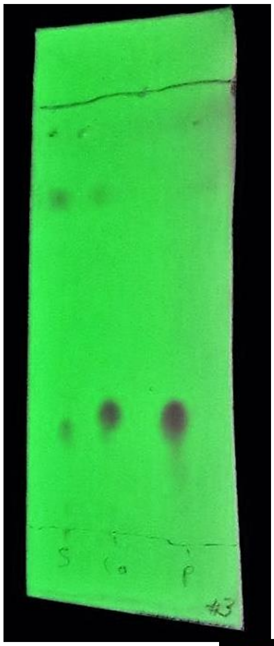
7. **The nitration of furan leads preferentially to 1nitrofuran rather than the 2-nitrofuran isomer. Explain by considering carefully the stability of the σ-complex leading to each isomer.**

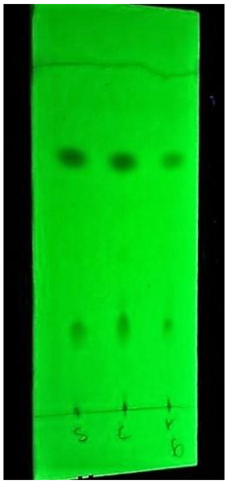


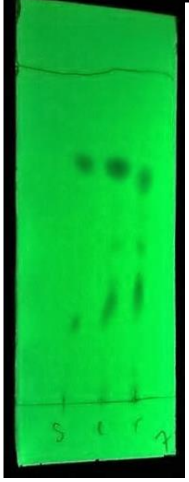
The regioselectivity of furan is explained in reference to resonance. When 1-nitrofuran is formed, the positive charge is delocalized by C-3, C-5 and O. The charge is not delocalized as nicely when 2-nitrofuran is formed. Thus, 1-nitrofuran is more stable than 2-nitrofuran.









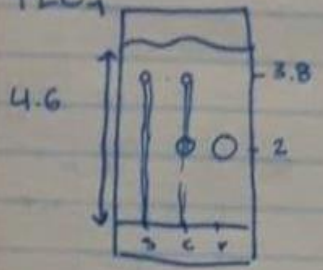


$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$

Lab 6 -

- 1.01 g of acetanilide (starting material)
- 5mL H_2SO_4
- 0.9mL nitric acid
- 1.2mL sulfuric acid

TLC1



s: starting material
~~1g~~ acetanilide in acetone

c: co-spot
S: product

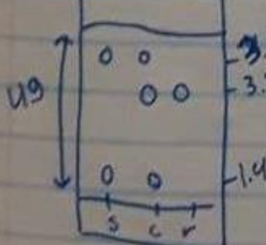
weight of the funnel ~~[illegible]~~ 14.70g

original solution clear, transparent, ~~ø~~ strong odor
↳ gold/brown crystal flakes of acetanilide (limitant)
after adding acids → black, clear,
while adding acids → vapor → exothermic reaction

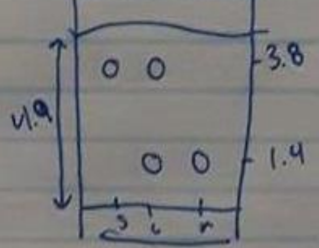
When solution is poured into icewater:
instantaneously turns yellow, thick like paint/mustard ↗ legit looks like mustard paint
↳ precipitate + foamy

18.20 - 14.70 = 3.5g

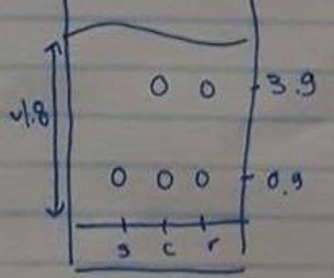
TLC2: ortho



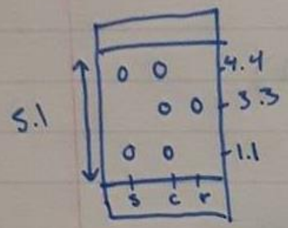
TLC3: meta



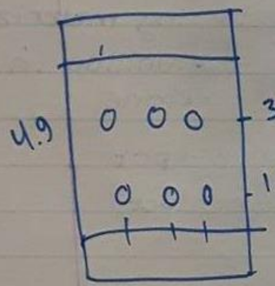
TLC4 para



TLC$_5$ 2,4 dinitro-product

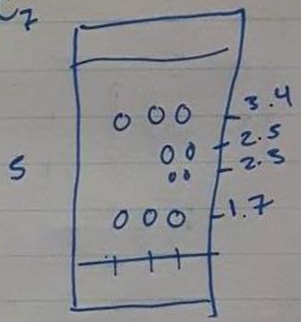


TLC$_6$



S: pure	crude
co:	both
p: crude	mother

TLC$_7$



15.[illegible]4 - 14.70