DAVIDS EXPERIMENTAL LAB NOTEBOOK

CREATED: 09/07/2022

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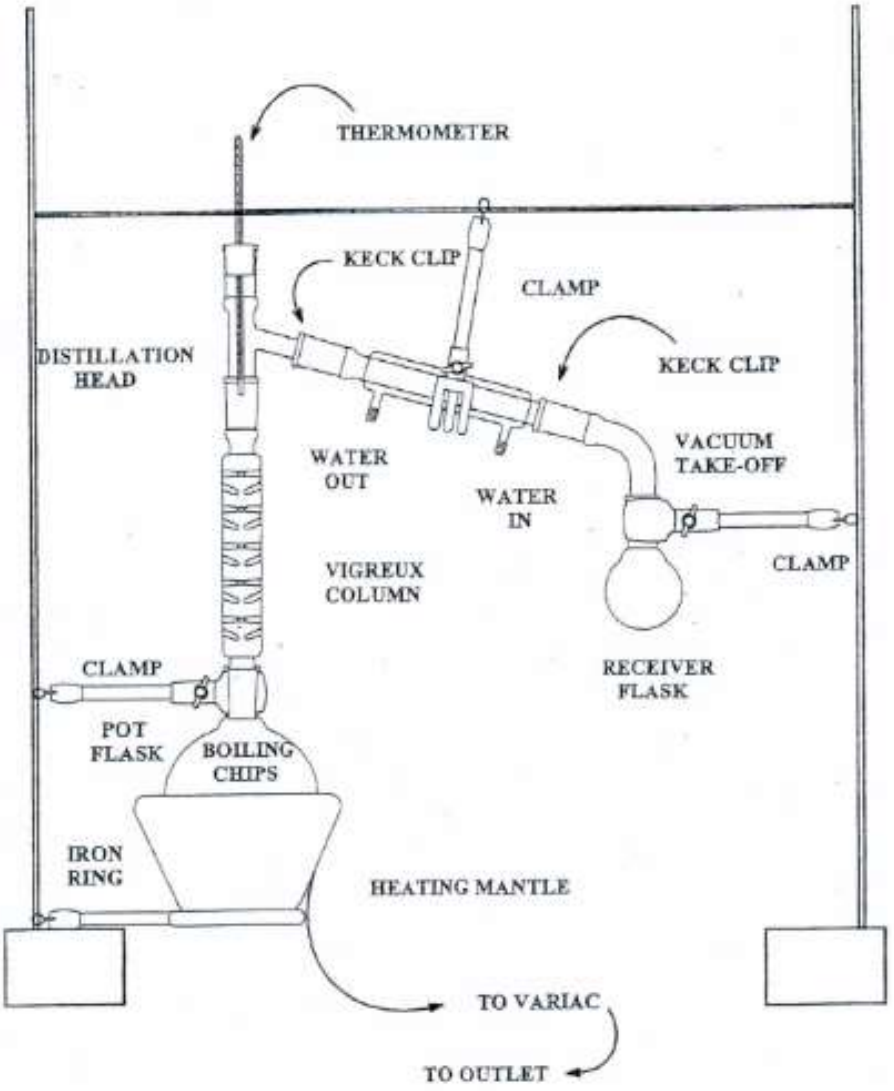
DISTILLATION OF AN UNKNOWN BINARY MIXTURE



Experiment #1 9/7/2022

Pre Lab: Distillation 2-ways

- Title: Distillation Methods
- Objective: To use 2 techniques of distillation to purify, then identify an unknown liquid. The identification will be carried out using multiple diagnostic methods that will be cross-referenced with the properties of the possible chemicals.

- References: 1. ChemSurvival, Youtube. A Brief Introduction to Fractional Distillation. (2012, Jul).
2. Experiment 1, Distillation. Labflow.com. (N.D)
3. Video - Simple Distillation. Labflow.com. (N.D.)
4. Video - Fractional Distillation. Labflow.com. (N.D.)

- Theory:

-Through distillation, one can effectively separate the azeotrope* into it's respective components. This is done by taking advantage of each miscible substances point of vaporization. and recondensing the pure vapor into a separate vessel... The purity can be enhanced using fractional distillation as the compound with the higher boiling point can get mixed in with the vapor of the desired compound. It is enhanced because fractional distillation essentially performs a simple distillation many times over through condensation and re-vaporization up the fractionating column.

-The boiling point of the distillate will be recorded over time and a graph will be created... by using refractometry along with the boiling point, we can deduce the identity of the compound by cross referencing it with the given table of possible compounds.

~~Post~~ PEM Pre-Lab: Distillation Methods

Theory cont.:

Chemical equations for rxns...

1. (unknown + Mixture)$_{(aq)}$ $\xrightarrow{\text{vaporization}}$ unknown$_{(g)}$ + Mixture$_{(g)}$
2. unknown$_{(g)}$ + Mixture$_{(g)}$ $\xrightarrow[\text{separation (crude)}]{\text{distillation}}$ unknown$_{(g)}$ + Mixture$_{(aq)}$
3. unknown$_{(g)}$ $\xrightarrow{\text{condensation}}$ unknown$_{(l)}$

Simple Distillation

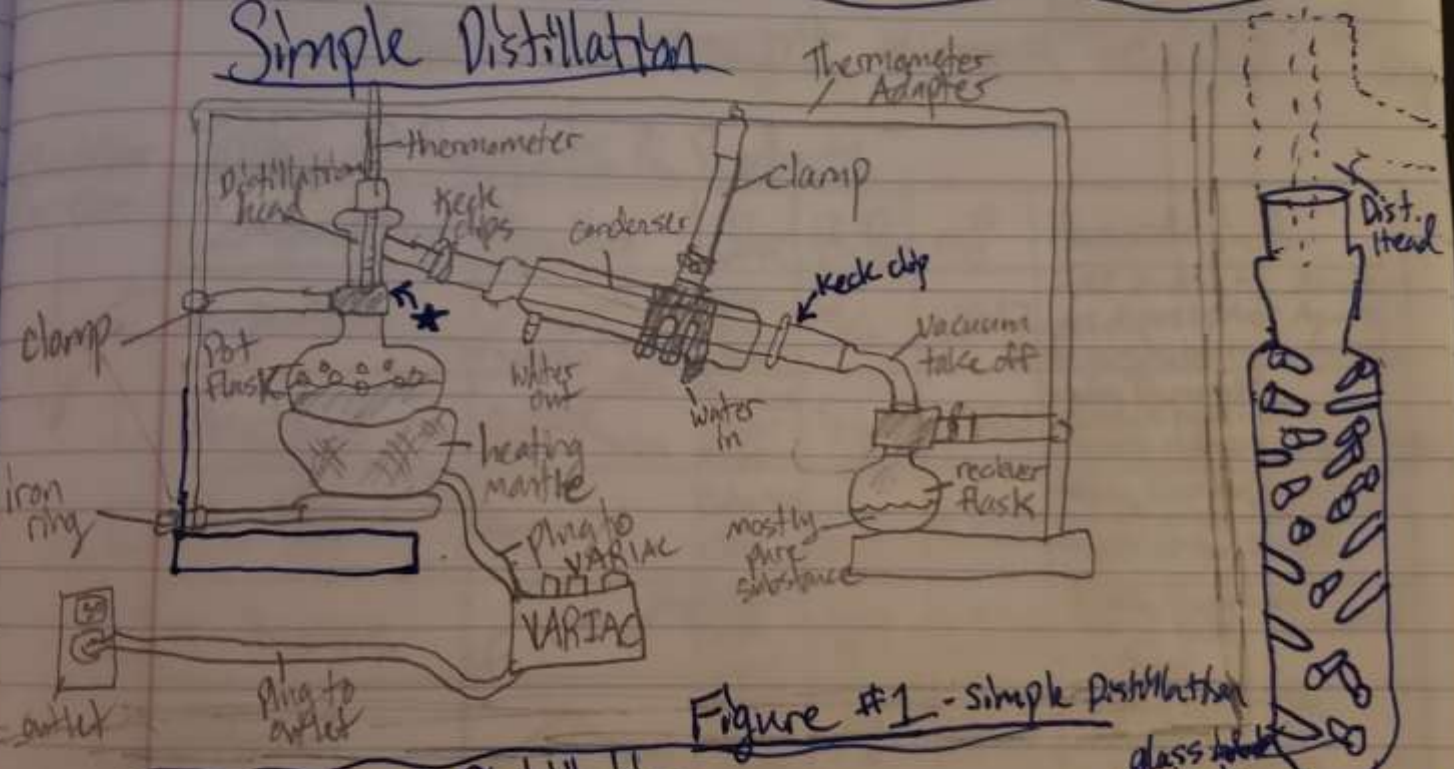


Figure #1 - simple distillation

Fractional Distillation

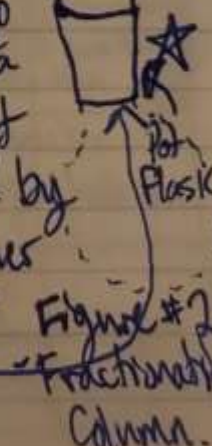


Figure #2 - Fractionating Column.

- This method uses the same set up as above, but adds a Fractionating column to the joint marked by a ☆... This piece of equipment condenses the higher BP substance continuously and therefore further purifies the target distillate...

Pre Lab: Distillation Methods

Theory cont:

Calculations for Theoretical Yield:

- The theoretical yield can not be calculated beforehand due to the proportion of substance A & B being unknown... However, once they are known, ~~I can~~ DEM The following formula will be used

$$\text{Actual mL(A) given} \times \frac{\text{g(A)}}{\text{mL(A)}} \times \frac{\text{mol(A)}}{\text{g(A)}} = \text{Theo yield(A)}$$

~~% yield = Theo yield~~

~~Measured Yield Theo yield~~

DEM

$$\%\text{Error} = \left(\frac{\text{Theo yield} - \text{actual yield}}{\text{Theo yield}}\right) \times 100\%$$

Tables of Reagents & Products

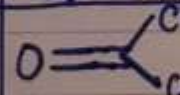
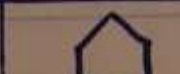
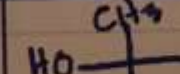
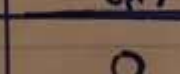
Checkbox for eltrn.	Compound Name	Structure	Color	B.P(C)	n_D^{25}	Hazards info
☒	n-pentane		Color-less, clear	36	1.3547	mild irritant... Acute CNS depressant Acute sensory/motor nerve damage
☑	Acetone		Colorless clear odorous	56	1.3561 1.353	highly flammable • serious eye irritation • chronic exposure organ damage
☒	Methanol		Colorless clear	65	1.3288	• highly flammable (liq) • causes organ damage • toxic if swallowed
☒	n-Hexane		Color-less, clear	69	1.3723	• highly flammable • May be fatal if swallowed • irritant
☒	Ethanol		Clear color-less	78	1.3610	• Highly flammable • causes serious eye irritation
☒	Cyclohexane		Color-less, clear	81	1.4246	• Highly flammable • May be fatal if swallowed • causes irritation
☒	2-Methyl-2-Propanol		Color-less, ~~pale~~ clear	82	1.3878	highly flammable harmful by inhalation irritant
☒	Water		Colorless, clear	100	1.3330	Non-Toxic You could drown if you inhale enough.

Table continued on next page →

Pre-Lab: Distillation Methods

Checkboxes for elimination

Table cont.

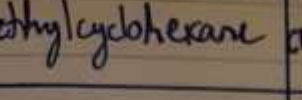
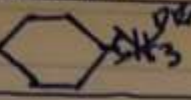
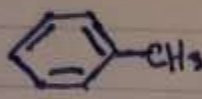
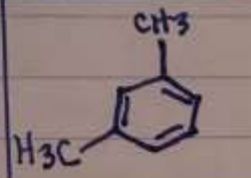
Compound Name	Structure	Color	B.P. (°C)	n_D^{25}	Hazards Info
☒ Methylcyclohexane		color-less clear	101	1.4231	flammable, skin irrit. toxic to aquatic org.
☑ 2-Methyl-1-propanol		colorless clear aromatic	108	1.3937 1.3935	• causes serious eye damage • flammable • skin irritant • may cause dizziness
☒ Toluene		colorless clear A	110	1.4941	• Highly flammable • may be fatal if swallowed • can damage fetus • may cause dizziness
☒ 1-Butanol		colorless clear Alc-like	117	1.3993	• Flammable • Skin irritant • may cause dizziness • Harmful if swallowed
☒ m-Xylene		colorless clear	139	1.4941	• Highly flammable • serious eye irrit. • may cause dizziness • Chronic organ dmg.

Table #1 - Chemical Data table (possible chem)

References:

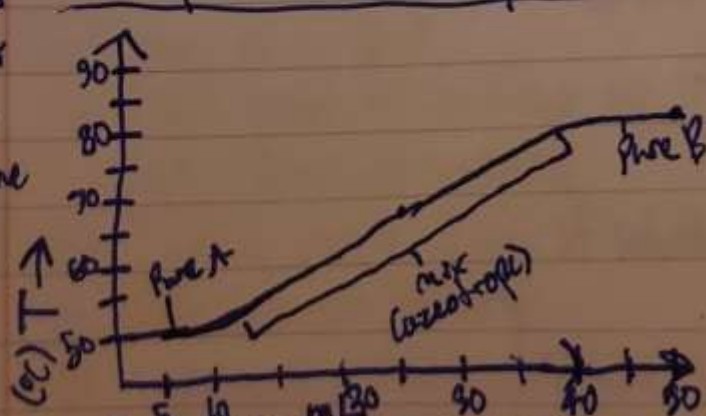
1. "Experiment 1". (2022). Labflow.com. Storage-cbn.labflow.com/data/filedir/0f/c0/0fc0c29d3f3#4409a860f928d
2. National Institute of Standards and Technology (NIST). N/D. webbook.nist.gov
3. Fisherscientific. N/D. Fishersci.com.

Graph Ex. of Simple Dist. Vs. Fractional Dist

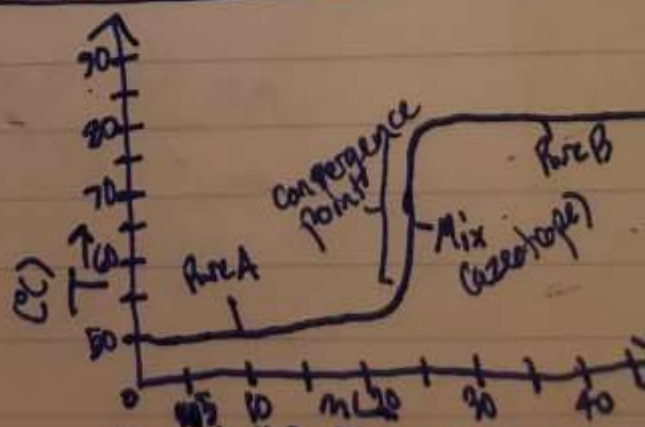
50mL total of a 50/50 mix of Acetone & Cyclohexane

Acetone = 56°C

Chex = 81°C



Graph #1 - Simple Dist. example



Graph #2 Frac. Dist. exam

PART I Pre-Lab: Distillation Methods

Notes box

Procedure — Simple Distillation

- ☒ Obtain a 50 mL sample from Dr. G... It will be 2 of the chems in table in any proportion
  (Binary Mixture!)

- ☒ Set up a simple distillation
  - refer to p. 5 of ~~pre-lab~~ PEM book
  - ☒ - use a 100mL round bot. flask as a pot flask & a 10mL graduated cylinder as a receiver.
  - ☒ - use wood blocks to elevate receiver to a proper height.
  - ☒ - be sure to grease joints!
  (Water in is the low side of condenser) (Ice bath?)

- ☒ Transfer unknown liquid (50mL) to the pot flask...
  - ☒ - use a long-stemmed funnel
  - ☒ - don't forget boiling chips
  - ☒ Have Dr. G give the O.K.

- ☒ Use a heating mantle w/ the VARIAC to slowly bring the solution to a boil.
  - ☒ - set VARIAC to about 40 and adjust as needed.
  (Be ~ Don't Forget to record ~ every 1mL of distillate.)

- ☒ Boil until about 2mL of solution is left... Do not boil dry!
  - ☒ - be sure to keep distillate rate @ 1-2mL/min
  (I repeat, do Not dist. to dryness... Sorry SDS's)

Data — Simple Distillation

(Use for Report)

- Obtained 51.5 mL of unknown #6...
  - has an alcoholic odor, slightly fruity...

- Set up apperatus...
  - ☒ approved by Dr. G

2:15 - VARIAC was powered on 50 to begin boiling azeotrope... 130V was set.

2:35 - T shot up to 60°C

- recorded 28 drops/min

3:00 - cranked up to 60 .5mL/min

3:12 - cranked up to 65

3:25 - ~60 drops/min

- Distillation complete 46.75 mL of azeotrope left.

~ don't Forget to change vials PEM as B.P. raises to get A azeotrope and B for the fractional dist later... LATER

Simple Dist

T°	mL
60°	0
61.5	1
62.5	2
63.5	3
64.5	4
64.5	5
65.0	6
65.0	7
66.0	8
66.5	10
66.5	11
67.0	12
67.5	13
68.5	14
69.5	15
71.0	16
72.5	17
74.5	18
76.5	19
78.5	20
80.0	21
82.5	22
85.0	23
88.5	24
92.5	25
95.0	26
98.5	27
100.0	28
101.5	29
103.0	30
103.6	31
104.0	32
105.0	33
105.0	34
105.0	35
105.0	36

Table 1

Create a data table

Pre-Lab DEM: Distillation Methods

Notes/Book

Procedure simple cont. Distillation

- ☒ • After finishing, take off the mantle and unplug everything...
- ☒ • Transfer the distillate back to the 100mL boiling (RB) flask.
  - ☒ - cork it and store safely
  - ☒ - graph data!

Clean all glassware!

Data simple cont. Distillation

- Side note: I almost distilled to dryness! there was only about .5mL left...
- Stop after ~5 constant temps next time and be sure to check under Al foil...

T°C	mL
105.0	37
105.5	38
105.5	39
105.5	40
105.5	41
105.5	42
105.5	43
105.5	44
105.5	45
105.5	46
	47
STOP	48
DIST.	49
DON'T	50
STIR	

PART II Fractional Distillation of a binary mixture

- ☒ • Set up a fractional dist. appesatus (p. 5 of lab book).
  - ☒ - exactly the same as simple w/ a Vigreux colmn.
  - ☒ - Obtain 2 dry 25mL E. Flasks for pure samples... ~~maybe a third for the mix~~
  - ☒ - Wrap column in glass wool ~~or~~ and Al foil to help heat.
- ☒ • Repeat the procedure for simp. dist. with collections of A, AB, & B in separate flasks.
- ☒ • Determine Refractive index for A & B... using B.P. & RI, determine identity...
- ☒ • Graph T vs. mL DEM

(Label and turn in samples w/ the reports.)

- T°C @ 0mL = 56
- Starting amount is about 46.5mL of azeotrope...
- Some solution may be lost during transfr.
- rate is about 1.25mL/min for A
- At 20.5mL, my H2O flow shut off
- Heat set to 65 for B
- 7.5mL was wasted at the end of B
- 6.0mL wasted at AB

T°C	mL	T°C	mL
57.0	1	105.0	26
57.5	2	105.0	27
58.5	3	105.0	28
59.0	4	105.0	29
60.0	5	105.0	30
60.5	6	105.0	31
60.5	7	105.0	32
61.0	8	105.0	33
61.0	9	105.0	34
61.0	10	105.0	35
61.0	11		36
61.5	12		37
61.5	13		38
61.5	14		39
62.0	15		40
62.0	16		41
60.5	17		42
61.0	18		43
61.0	19		44
62.0	20		45
108.5	21		46
104.0	22		47
104.5	23		48
104.5	24		49
104.5	25		50

F-Dist table for data

Tab/Graph Checklist

Tab.: ☒ S-Dist ☒ F-Dist ☒ R-Index

Graph: ☒ S-Dist ☒ F-Dist

°C vs. mL

Report: Distillation Methods

→ ## Summary Table

Distillates →	A (Acetone)	B (2-Methyl-1-propanol)
Observed B.P. (°C)	~61.0°C	105.0°C
R.I. (corrected) n_D^{25}	1.35855	1.39390
Molar Mass (g/mol)	58.08 g/mol	74.12 g/mol

→ ## Critique of Experiment (ERROR)

Simple Distillation (Part I)

- As the data in the graph shows (and the table), the separation of A and B is not very clean and leaves a lot of room for A to contaminate B and vice versa... This is due to the vapors of the two compounds being able to "hitch a ride on eachother".
- During experimentation, 50 51.5 DEM mL of azeotrope was obtained and due to the small amount of vapor loss and pouring, there was only about 46.5mL of solution at conclusion...
- The azeotrope was almost distilled to dryness and got a light brown coloration... This could have an effect on R.I. due to it being added to the main batch...

Fractional Dist. Error ——————→

Report: Distillation Methods cont.

Fractional Distillation (Part II) ERROR

- loss of product due to residue in glassware and pouring
- Product was also lost (sacrificed) due to a pause in collection during the phase change period. (6.0mL)
- Too much of the azeotrope was disposed of at the end (7.5mL)... At a glance, the O.K. to remove from heat was given by instructor, but it was the fault of the experimenter to not use their judgment after observing the large quantity of solution remaining...
- The water for the condensor turned itself off and the lack of flow was not noticed for roughly 5-10min.

X. [signature] Miller.

DATE ★ 09/20/2022.

★ Data explained in the excel data sheet.

Conclusions

By implementing Knowledge of phase changes of chemicals into the process of distillation, Compound A & B were able to be successfully separated using fractional distillation. To further increase the accuracy of identification, the boiling points were compared to the textbook values as well as refractive index. By using these values, A is Acetone and B is 2 methyl-1-propanol as shown on the table of reagents and the excel data sheet★. This conclusion can be proven to have even more accuracy when referencing the values of purity through analysis of the liquids.

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RECRYSTALIZATION METHODS AND MELTING POINTS

Pre-Lab: Recrystalization Methods

★ Objective:

PI: To screen reaction solvents by testing the solubility of a number of known compounds.

PII: To carry out the crystalizatted of a known compound using the screening method from PI as a prerequisite to the experiment. A yellow impurity will also be purged from solution using Norit to yield a pure product.

PIII: To carry out the recrystalization of an unknown compound by using a "good" solvent followed by a "bad" solvent to optimize purity. Melting point analysis and infrared spectroscopy will be used to meet the objective of identifying the unknown.

★ References:

1. "Experiment 2". (2022). Labflow.com
   - Storage-cdn.labflow.com/data/filedtr/6c/17/4c174c69ac0693022
2. Fisherscientific, N/D. Fishersci.com
3. d2l.wcnpa.edu/d2l/home/3444418
   - Solubility table

Theory →

Pre-Lab: Recrystalization Methods

★ Theory

• Techniques:

PI — Recrystalization is a technique used to remove impurities from a crystal sample to obtain the desired pure product. This is done by taking advantage of the crystal's solubility by testing it with different solvents (polar → NP). A proper solvent is chosen by performing a screening of the solvents. This is performed by figuring out what solvent the crystal is insoluble with at room temperature and completely soluble with at hot/boiling temperature. After the solvent is chosen, the solution is heated up and the

PII — impurities are removed using hot gravity filtration through a fluted filter paper (heat is used to prevent crystalization of desired product). Activated charcoal (Norit) can also be used as a purifier (with an expense to final yield)...

PIII — Recrystalization can also be done using a method of a "good" and "poor" solvent with regards to the crystal. The "good" solvent (S @ R.T. & Hot) dissolves the crystal and is heated to boil. The "bad" solvent (I @ R.T. & Hot) is then added to the filtrate until cloudiness forms... (This forces the crystal out of solution). For all procedures, after the crystals form, they are extracted using a Büchner funnel in a vacuum filtration apperatus. This is done to separate out the crystals for the final yield.

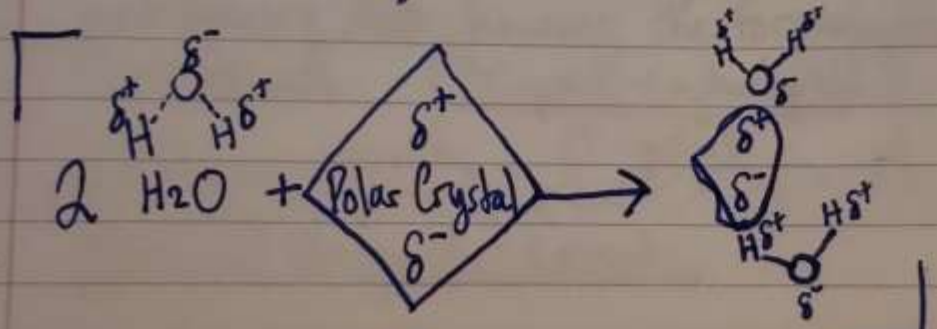
— After the unknown has been recrystalized, one can determine its purity by using melting point determination analysis. This is done by using a Mel-Temp to slowly raise T[°C] until a melting point has been reached. The narrower the melting range, the purer the product. Cont. →

Pre-Lab: Recrystalization Methods

Theory cont... Techniques cont.

- Another method of analysis is infrared spectroscopy. This is a technique of fitting infrared rays at a substance using different energy levels and analyzing the emmision specra of the resonating atomic characteristics. This method gives the experimenter information that can be used alongside the melting point to determine which of the possible crystals the unknown could be.

- Chemical Eqns. For rxns./side rxns.



Equation 1: Dissolving of a polar Crystal solute

- Diagrams for Apperatus

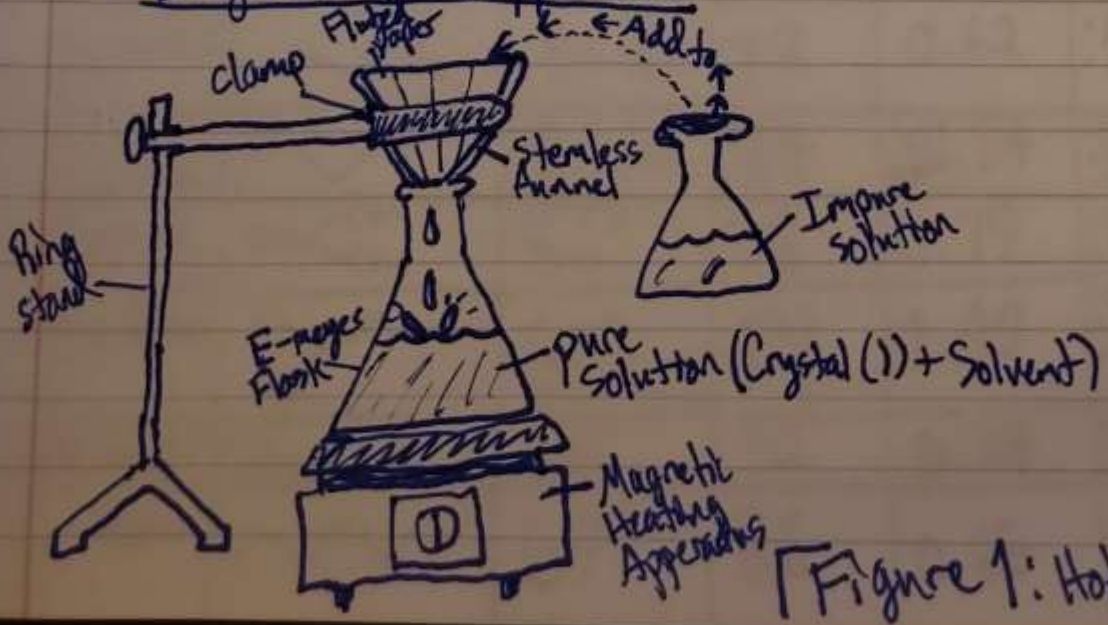


Figure 1: Hot Gravity Filtration

Pre-Lab Cont. (DEM): Recrystalization Methods

Theory cont... Diagrams for apperatus cont.

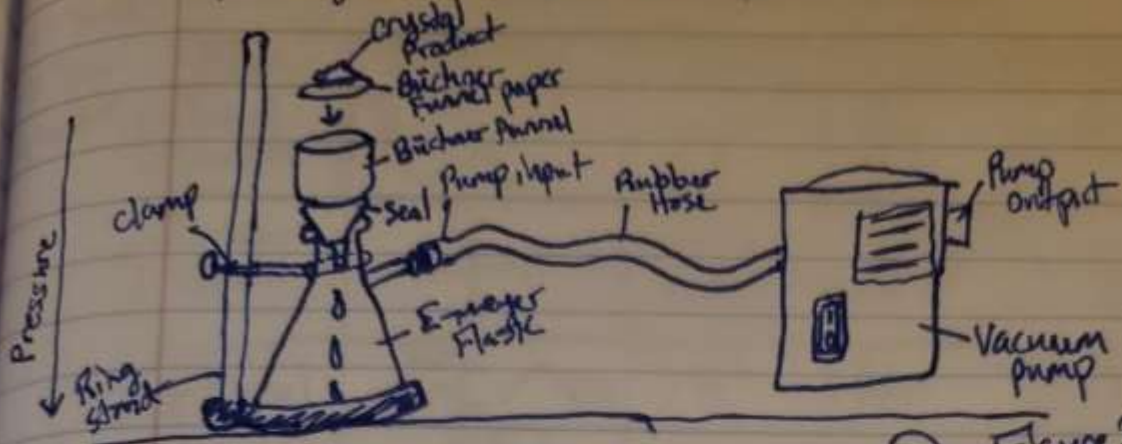
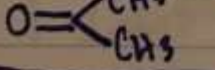
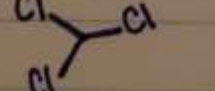
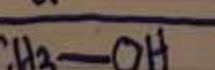


Figure 2: Vacuum Filtration

- Calculations for Theoretical yield
  - T-Yield can't be accurately calculated due to not having data, however, the formula for % yield is as follows. $\left[\frac{(\text{T-yield}) - (\text{actual yield})}{(\text{T-yield})}\right] \times 100\% = \%\text{ yield}$

Table of Reagents: Solvents

Name	Structure	B.P. (°C)	MW (g/mol)	Density (g/mL)	Hazard info
~~Diethyl~~ Ether / Diethyl ether		35°C	74 g/mol	0.71	~~• May Damage Fertility~~ • Harmful if inhaled • Highly Flammable • May cause organ damage
n-pentane		36°C	72	0.62	• Acute CNS depressant • mild irritant
Dichloro-methane		41°C	84	1.34	• Carcinogenic • May cause dizziness • May cause organ damage
Acetone		56°	58	0.79	• Flammable • May cause organ damage
Chloroform		61°	118	1.49	• Carcinogen • Damages unborn child • Toxic if inhaled
Methanol		65°	32	0.79	• Flammable • toxic if swallowed
n-Hexane		69°	86	0.65	• Flammable • Harmful if swallowed

Pre-Lab: Recrystalization Methods

Table of Reagents: Solvents cont.

PIII solvents
+ = "Good"
- = "poor"
+/- = neither

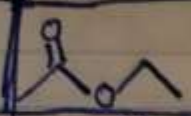
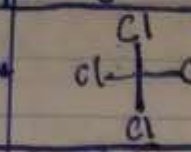
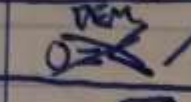
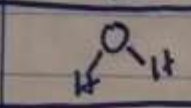
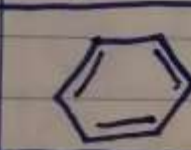
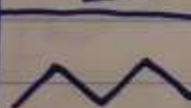
	Name	Structure	B.P. (°C)	MW (g/mol)	Density (g/mL)	Hazard Info
+ -	Ethyl Acetate		77°	88	0.90	• Flammable • organ tox. • Harmful if swall.
* -	Carbon Tetrachloride		77°	153	1.58	• carcinogenic • tox. if inhaled • tox. to organs
+ -	Ethanol		78°	46	0.79	• Flammable • Serious eye irr.
+ -	Benzene		80°	78	0.88	• Flammable • tox. if swallowed
* -	Water		100°	18	1.00	N/A
+ -	Toluene		111°	92	0.86	• Flammable • tox. to child • tox. if swall • organ dmg.
* -	Heptanes (Ligroin)		98°	87	0.68	• Flammable • CNS damage • Fatal if swall. • Organ dmg.
* -	~~ATEXed~~	END OF SOLVENT TABLE				

Table 1.: Table of reagents: Solvents

Table of Reagents: Unknowns chart of Crystals

Name	~~Color~~ Structure	MP (°C)

Pre-Lab: Recrystalization Methods

Table of Reagents: Unknowns chart of Crystals ~~cont.~~

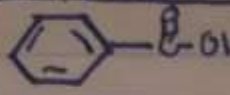
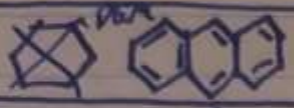
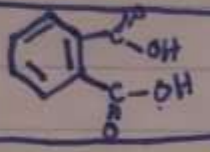
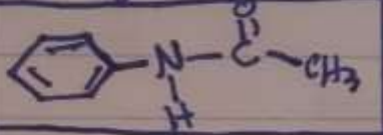
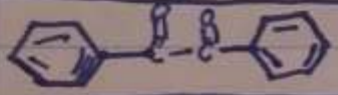
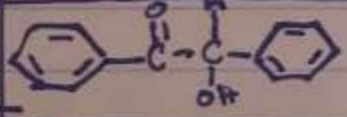
Name	Structure	MP(°C)	Color	Hazards
Benzoic Acid		122°	colorless	• Eye irritant
Anthracene		216°	Colorless to pale yellow	• ~~flam~~ combustable powder • eye irrit.
Stearic Acid	$CH_3(CH_2)_{16}$-C(=O)-OH	70°	colorless	• May form combustable dust
Phthalic Acid		206-208°	Colorless	• Causes serios eye damage
Acetanilide		113°-114°	Colorless	• tox. if swallowed
Benzil		~~LSM~~ 95°	~~off white~~ yellow	• skin irrit • resp irrit • eye irrit
Benzoin (dl)		137°	off-white	N/A
Diphenyl-acetic Acid	$(C_6H_5)_2CHC(=O)OH$	146°	colorless	• Causes skin irrit • Causes eye irrit
Triphenyl-methanol	$(C_6H_5)_3C$-OH	164°-165	colorless	• Slightly flammable • eye irritant

Table 2: Table of Reagents - Unknowns chart of Crystals

Procedure on next pg →

Pre-Lab: Recrystalization Methods

Procedure

Part I:

- ☑ Obtain 5 pipettes and 1 bulb
- ☑ label paper to keep track of pipettes.
- ☑ Transfer 1 head of a small spatula (50mg) of powder to the test tubes and test against all solvents...
- ☑ follow elimination method learned in lab vids... Fill in table.
- ☑ heat all applicable solutions (test tubes) over a hot plate in a beaker with H_2O.
- ☑ Recrystallize all suitable solutions in an ice bathed beaker. (w/ethanol)
- ☑ Clean tt and dump mixture in waste containers.
  - ○ scrub out w/ soap & H_2O

Data

I = insoluble SS = slightly soluble S = soluble

Name ☺ ♥

	Anthracene	Diphenylacetic Acid	Benzil	Triphenylmethanol
Water	SS RT, S Hot	SS RT, I Hot	I RT, I Hot	SS RT, I Hot
Methanol	S RT, S Hot	S RT, S Hot	S RT, S Hot	S RT, S Hot
Ethanol	SS RT, S Hot	S RT, S Hot	S RT, S Hot	S RT, S Hot
Hexane	SS RT, S Hot	SS RT, S Hot	S RT, S Hot	S RT, S Hot
Dichloromethane	I RT, I Hot	SS RT, I Hot	SS RT, S Hot	SS RT, S Hot
	216°C	146°C	95°C	165°C
	white/crystalline	Powder-like colorless	Benzil floats in H_2O Seems to be non-P yellow colored	Colorless powdery

Table 3: solubility Table

Data (Expanded)

Benzoin	Acetanilide	H_2O
H	SS	S
S	S	SS
S	SS	S
S	S	SS
—	S	H
S	H	H

Pre-Lab: Recrystalization Methods

Procedure

Part II

- Obtain impure phthalic acid (0.2% colored impurity)
- Weigh Vial w/cap
  - transfer phthalic acid
  - weigh V+cap again
- use powder funnel to transfr. P-acid to E-Flask (125mL)
  - return vial to Dr. G
- Weigh roughly 300mg (10-15%) Norit using weighing pages.
- add 25mL DI water & boiling stick to E-Flask... Boil it
  - add H_2O 1 drop at a time until sample dissolves.
  - record total solvent needed
- add 100% excess H_2O
- remove from heat and add Norit, swirl to mix
- Boil for 5 min
- Fold a fluted filter paper and perform a hot gravity filtration.

Matls: · Stemless funnel · E-flask · boiling stick · Fluted pages · Ring stand · a bit of solvent (~1/3 full)

Data

Color: slightly yellow Texture: grainy sand-like

Weights

V+C+PA (g): 19.68g

V+C (g): 17.64g

gPhthalicAcid = 2.04g

start solvent = 25.7mL ÷ 100% = 51.8mL

Tot. solv. (H_2O) needed = 25.7mL

↓ 2x

about = 51.8mL

(before boiling)

Hot gravity solvent start = ~30mL

150–155°C

- Bubbles on outsides have formed w/ heat and solute has dissolved...

1:58 - Added norit @ 1:58

300mg

- Solution re-simmered 2:02p

2:07 - Remove soln. from heat

Pre-Lab: Recrystalization Methods

Part II cont.

Procedure

- Observe filtrate color
  - More Norit needed?
  - Color OK? (clear)
- When colorless, cover flask w/ inverted beaker and cool to R.T. slowly
- Cool in ice bath after crystal formation for highest crop.
- Collect crystals using vacuum filtration.
  - Do not filter over 2/3 full
  - wet paper a bit w/ solvent before adding powder for maximum stick.
  - use ice cold solvent (H_2O) to rinse the last of the crystals out of E-flask
- For a higher yield, evaporate filtrate to 2/3 volume by boiling and repeat process.
- Transfer crystals to watch glass
- Test MP, if ranges are identical, combine crops.

Data

- Performed Hot vac filtration.

Color of filtrate 1 = Clear

2:12 placed filtrate in ice bath

Have crystals accured?

- Solvent volume post filtration = ~75mL

DEM

- ~~No crystals formed so I put back on heat to attempt to reduce down to 30mL~~

2:20 They formed!

- Crystals are white
- performed vacuum filtration.
  - The vacuum busted a hole in my paper and I lost yield :(
  - Some paper shreds maybe in yield.
- ~~repeated recrystallization process using filtrate 2.~~ DEM

watch glass = ~~47.28g~~

Dry weight crop 1 = 47.28 - 46.24 =

crop 2 = N/A

M.P. crop 1 = 203.1°C

crop 2 = N/A

% recovery crop 1 = 51.09%

crop 2 = N/A

crop 1 + 2 = 51.09%

Pre-Lab: Recrystalization Methods

Procedure

Part III

- Obtain unknown & note color/texture ~~weigh unknown~~
- repeat solubility test from PI and determine "good" and "bad" solvents. ~~weigh unknown~~ → (after tests)
- add powder to 125mL E-Flask
- add small amount of "good" & bring to boil and cont. to add hot solvent until solute dissolves.
- add extra solvent to prevent crystals during hot grav. filtration
  - +50% for organic
  - +100% for H_2O
  - +25% for mixed solv.
- add Norit if it is colored (crystallization)
- Repeat Hot gravity filt. from PII
  - don't forget the beaker
- For MIXED: add "poor" solvent drop by drop to hot filtrate. Keep all solvents hot. Do this until cloudy
- After crystalization occurs, use vacuum filtration

Data

Unknown #33

Color: Sand colored (tan) Texture: Sugar-sized crystals (cane)

Vial+cap+X (g) = 18.48g - scales were being wonky

Vial+cap (g) = 17.54g

(g) X = 0.21g

H_2O > MeOH > EtOH > Toluene > Ligroin

RT	RT	RT	RT	RT
SS / S_B	S / S_B	S / Se	SS / S_B	I / SS_B

~~Tot. solv. added~~:

- performed a solubility test
- Ligroin was insoluble, ~~leaving~~ sandy bits behind
- MeOH and EtOH are viable for A
- MeOH > EtOH - H_2O is miscible

Total solvent added: (MeOH)

20mL + 50% = 30mL

Total norit added = .28g

- Heated solvent + solute Boil @ 2:30
- performed hot grav Filtration @ 2:34
- recrystalized using 2-solvent method 10+10+10+10

(g) Dry weight c1 = 0.47g (60mL added)

~~c2 =~~

M.P. (°C) c1 = ~175 (+1, +2)

~~c2 =~~

% recovery c1 = .47 / .91 = 51.6%

~~c2 =~~

(g) c1 + c2 =

Pre-Lab: Recrystalization Methods 22

Part III cont.

Procedure

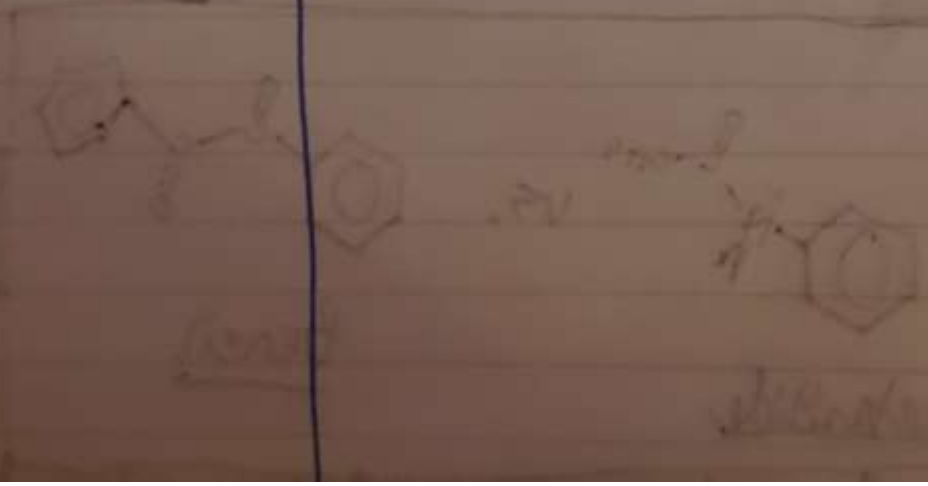
- ✓ Carry out M.P. Analysis
- ✓ carry out infrared spectroscopy
- ✓ Determine unknown accross ref from given M.P. & structure.

Data

Approx M.P. #1 = 115°C #2 = ~~112.6°C~~ DEM DEM
Actual M.P. #1 = 112.6°C #2 =
Literature M.P. = 113-114°C

Notes

- 60mL H_2O added with no results of cloudiness...
- I dunked it in an ice bath to try and get crystals
- I attempted to blow out the crystals by boiling off MeOH
- Unknown = DEM - Reduced by half ~125mL - ~60mL
- weight of ~~final~~ vial + cap = 17.98g
- weight of final V + cap + UK = 18.45
- Dunked reduced solution in ice bath after cloudiness formed
- crystals formed @ 3:55
- performed vacuum filtration on the crystals...
- Vacuum filtration ended @ 4:20



Report: Recrystalization Methods

Table 1: Summary of Results

Identity	Acetanilide →	
M.P. °C	Observed: 112.6	Literature: 113
Color Before	A tan, sand colored granule	
Color After	A colorless, fragmented crystal	

Structure

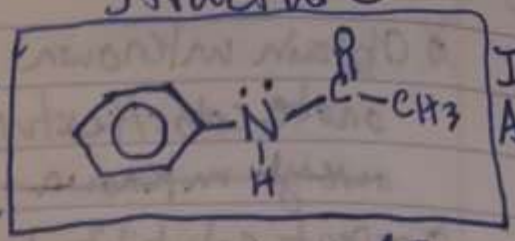


Image 1: Acetanilide

% yield = $\frac{.47}{.91}$ = 51.6%

Possible Error during Experimentation/conclusions

Part I: During the solubility testing, an error that could have been made was the misinterpretation of insoluble at R.T. and SS at R.T. since it was purely a qualitative observation. Many of the samples were small so this mistake could have been made.

Part II: A large source of error during this experiment was the fact that the filter in the büchner funnel busted a hole during filtration and I lost yield. During this experiment I seemed to struggle a bit due to the amount of estimation and lack of precision during a recrystalization... since I had never done one before, it was challenging.

Part III: During this experiment, I added too much "poor" solvent and ended up boiling off a lot to reach a ~~dense~~ cloud point in solution. I believe the amount of "boiling off" that was done affected my yield.

Conclusion of M.P. Analysis/spectroscopy →

Report: Recrystalization Methods

Part III conclusions cont.

M.P. Analysis: After obtaining the M.P. of 112.6°C, Acetanilide was the most likely contender as my open the unknown, but benzoic acid could have also been possible if my purity was off due to increased impurities lowering the M.P. of a substance... to be 100% sure of what the unknown was, spectroscopy was performed.

Infrared Spectroscopy: Upon investigation of the graph, there were three main features.
- A spike at 1700 cm^{-1} which indicates a carbonyl group
- High activity at 700-1000 cm^{-1} which indicates a benzene ring
- A broad spike at 3400 cm^{-1} which indicates an amine

After taking this information into consideration, the unknown was deduced as Acetanilide due to the amino group being present as well as both common groups shown above.

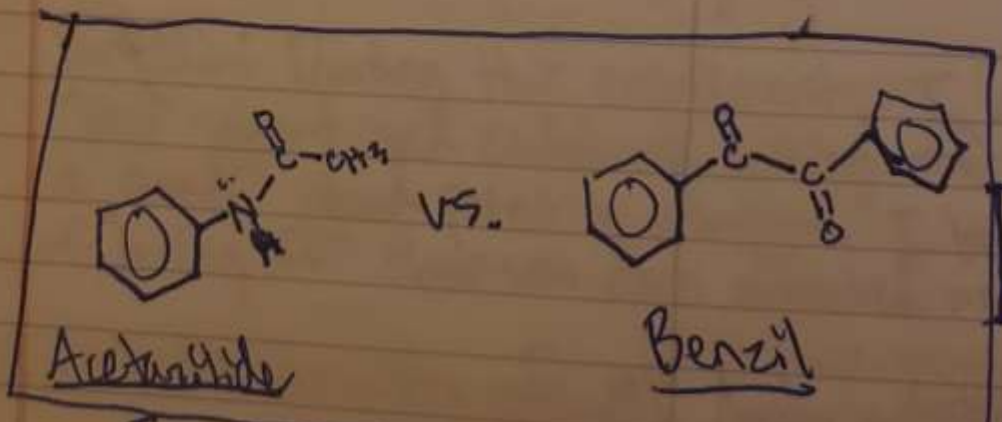


Image 2: Comparison of Acetanilide and Benzil

x David Miller 10/19/22

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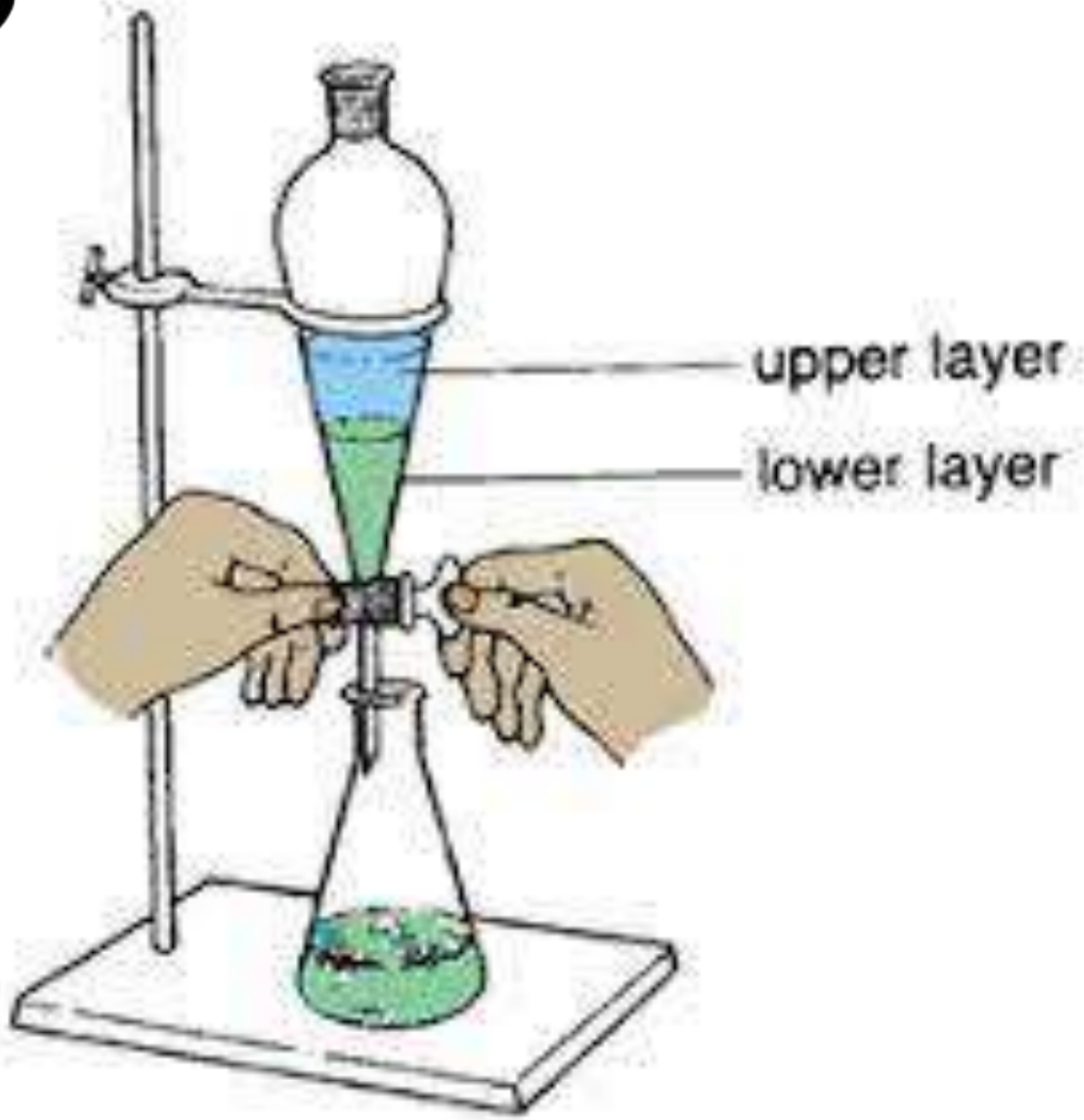
EXTRACTION METHODS USING ACIDS AND BASES



Pre-Lab: Extraction Methods

- Objective

-To separate a solution of Benzil and 4-methylbenzoic acid using extraction methods and to recrystalized the respective compounds.

- Theory

- Extraction is an important technique that is used by chemists to separate out two different organic solutes in the same solution. This is done by using an acid or base to "attack" the protonation site of the molecule, thereby making it slightly polar ± through dipole moments and therefore miscible in a polar solvent such as H_2O. This is important because it allows the chemist to separate the two solutes and perform various techniques on either one. (recrystalization/ ~~repo~~ distillation re/deprotonation)

- The most efficient way (for yield) is to perform multiple extractions... This can be demonstrated by the partition coefficient which, when calculated using multiple yields will read as follows...

$$K_p = \frac{\text{Amount A in Organic solvent / V(mL) of organic solvent}}{\text{Amount A in Aqueous solvent / V(mL) aqueous solvent}} = 20$$

cont. →

Pre-Lab: Extraction Methods

- If you enter in A = 2.0g and compare it with a single & double extraction you get as follows...

Single

$$K_p = \frac{x/100(mL)}{(2.0_g - x)/100(mL)} = 20$$

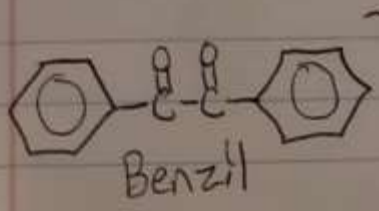
$$x = 1.90$$

Double

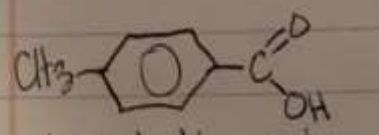
$$K_p = \frac{x/50(mL)}{(2.0-x)/100(mL)} = 20$$

$$X_1 = 1.82_g \quad X_2 = 0.16_g$$

$$X_{tot} = 1.98_g$$

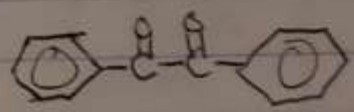


Benzil



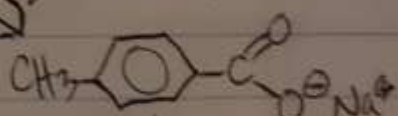
4-Methylbenzoic acid/p-Toluic acid

Ethyl Acetate (Solvent) → Extract w/ $NaHCO_3$ (weak base)



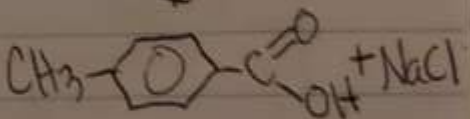
ether Layer (top)

aqueous Layer (bottom)



Mechanism 1: Extraction

dilute HCl



- After this phase is complete and both compounds are back in their organic layers, a <u>wash</u> is performed to eliminate any traces of H_2O in the organic layer... <u>Drying agents</u> can also be used to eliminate unwanted aqueous layer.

Pre-Lab: Extraction Methods

Diagrams

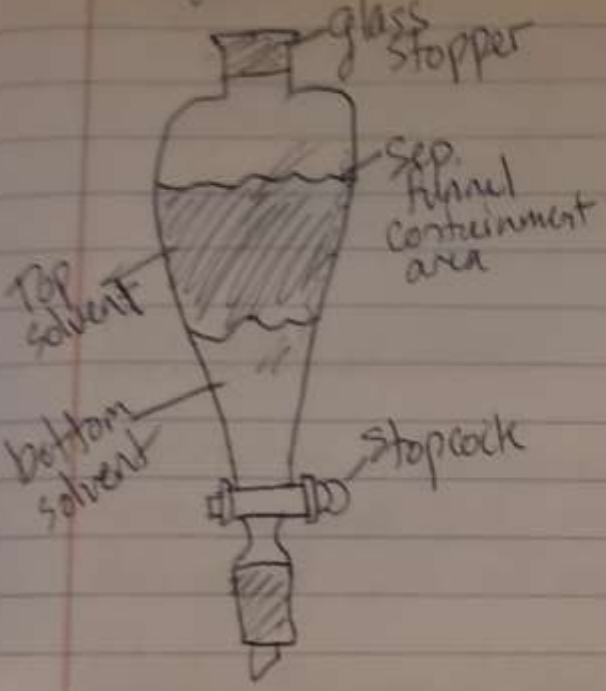


Diagram 1: Seperatory Funnel

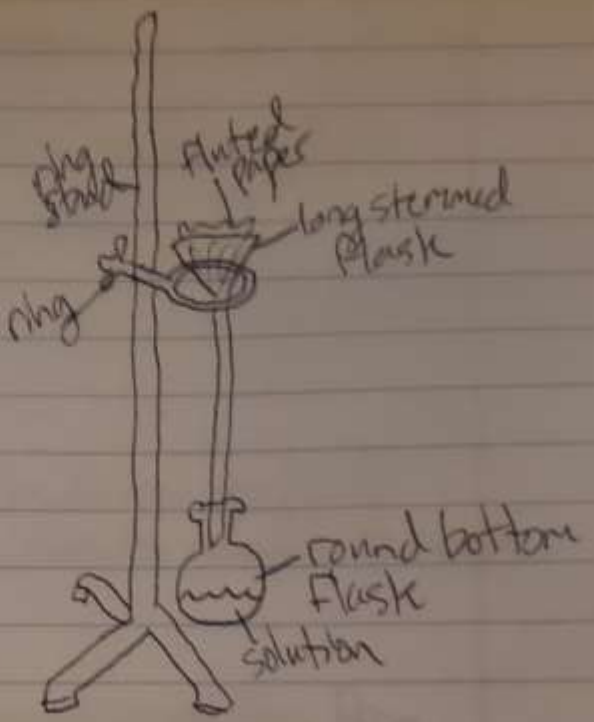
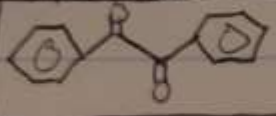
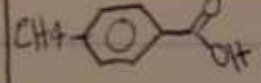
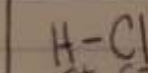
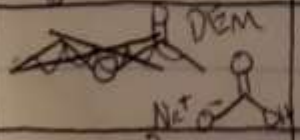
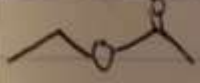


Diagram 2: Gravity filtration

Tables of Reagents & Products

Name	Structure	M.P.	Color	Hazards
Benzil		94-97°C	yellow (solid)	• Causes serious eye irritation • May cause resp. irrit.
p-Toluic acid		215-217°C	White (solid)	• serious eye/resp irrit. • skin irrit. • Harmful if swallowed
HCl Hydrochloric acid		-35°C	Colorless (liquid)	• Causes severe burns • Strong acid
Sodium bicarbonate		270°C	White (solid pow)	• it's baking soda, you're good
Ethyl Acetate		-83.5°C	Colorless (liquid)	• flammable • may cause dizziness • eye irrit.
Water (l) H_2O		100°C	colorless (liquid)	• may choke if you suck at drinking

Pre-Lab: Extraction Methods

References

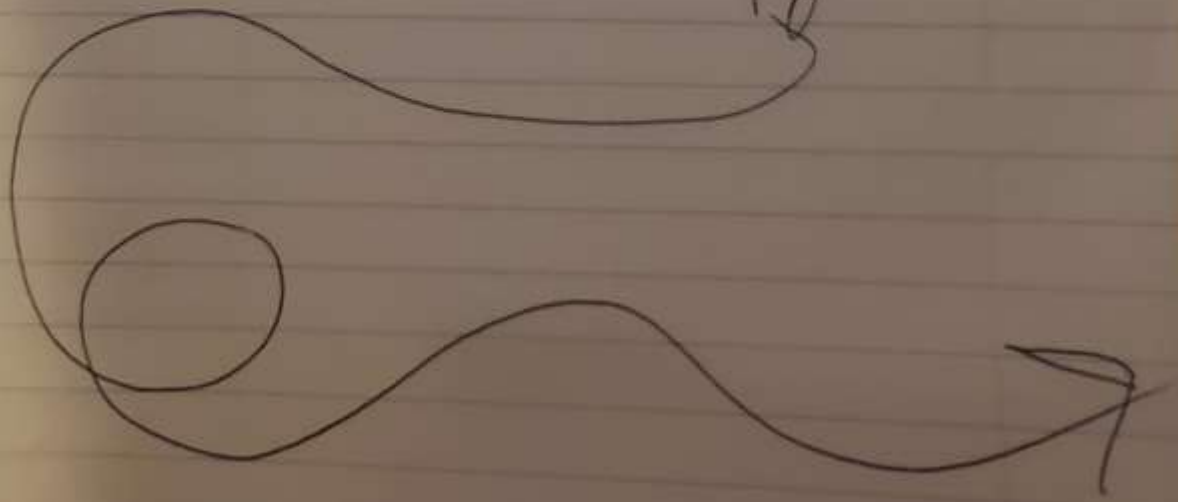
1. Fisher Scientific (N/D). Fishersci.com
MSDS (Table of reagents)
2. LabFlow.com (2022). Experiment 3, Extraction Methods
storage-cdn.labflow.com

Definitions of Terms

Extraction: The moving of the desired compound from one layer to the other in immiscible solvents through the use of acids and bases.

Wash: The use of salts to remove impurities from the organic layer and transport them to the aqueous layer.

Procedure on next pg



Pre-Lab: Recrystallization Extraction Methods

Table of Drying agents

Agent	Advantage	Disadvantage
Anhy $MgSO_4$	Rapid, high cap	Reacts w/ alcohols & amines
Anhy $CaSO_4$	Very powerful	" " + low H_2O cap
Anhy Na_2SO_4	Chemically inert	Slow; best for initial drying
Anhy K_2CO_3	Rapid	Reacts w/ acids
Anhy $CaCl_2$	Rapid	Reacts w/ alcohols

Procedure

- Obtain 1.0g mixture of approx 0.5g each of 4-meth... & Benzil weighed
- Dissolve mixture in about 25mL of ethyl acetate
  - 100mL beaker
  - 125mL sep funnel
  - powder funnel
- after dissolved, pour beaker contents into the 125mL sep funnel
  - rinse beaker w/ 5mL more acetate
  - use the powder funnel to add to sep ~~funnel~~ funnel
- Extract using 10mL (2×5mL) $NaHCO_3$ (saturated) and drain into a 250mL beaker
  - repeat 2 times ☒☒☐
- Chill the 250mL beaker.

Data

$$K_p = \frac{x/30mL}{(.97g - x)/10mL} = 20$$

Vial + cap + powder (g) = 18.78g
" " - powder = 17.81
powder = .97g

- added 25mL Ethyl acetate + 5mL
  - 30mL total
- Added $NaHCO_3$ to organic layer
  - performed extraction and ~~to~~ separated into a Flask 2x
- Added HCl (10-15mL) to the soln. (aq)
- Added NaCl to the organic soln to wash the water out

Pre-Lab: Extraction Methods

Procedure

- Neutrilize the chilled solution using 1M HCl. Stir vigorously.
  - Do I see a precipitate?
  - Is it slightly acidic to the pH paper? ICE IT
- While ↑ is cooling, add about 10mL of saturated NaCl(aq) to the organic solution to remove H_2O...
  - Drain excess into a new beaker
  - Label beaker "NaCl soln"
- Transfer clean organic ~~phase~~ solution to a 125mL E. Flask and dry w/ $MgSO_4$...
  - cork the flask
  - swirl flask
  - inspect $MgSO_4$
- use vacuum filtration through a büchner funnel to obtain precipitate from chilled soln
  - rinse w/ DI water (cold)
  - make sure DI water is ICY
- Decant organic layer through gravity filtration (Diagram 2) and store in a 250mL RB ~~Flask~~.
  - Discard drying agent!

Data

- Transferred Benzil soln. to the 125mL E-flask
- Added drying agent after pulling H_2O out of the bottom of the flask
- After adding adequate HCl to aqueous soln. a lot of precipitate formed
- I removed precipitate using vacuum filtration and rinsed with Icy DI water.
- I performed a gravity filtration on the organic solution.
- Cleaned up station
- Evaporated off the ethyl acetate in the rotovac device.

Pre-Lab: Extraction Methods

WEEK #2

Procedure

✓ Benzil
- obtain a gross weight of RBFlask and it's contents.
- add 10mL methanol and heat on a hot plate until residue dissolves.
- Transfer solution to a 50mL E-Flask.
  - rinse w/ 5mL MeOH to get all the benzil
- Add a boiling stick and bring to a simmer on a hot plate.
- perform a hot grav. filt. using a Kim wipe capped pipette (Monstrer)
- concentrate to about 9-10 mL and add H_2O until a cloud point is reached
- MeOH until soln. has cleared and allow to cool to R.T.
- If Benzil "oils out" of soln. add a bit more MeOH and repeat boiling process
- Chill in an ice bath and Vacuum filter crystals
  - obtain M.P.
  - obtain mass

Data

Benzil

Weight RBF = 135.70 g
RBF = 135.05 g

- Gathered supplies
- Started heating process 1:55p
- began hot grav. filtration 2:00

- Reduced filtrate until about 10mL remain
- Added H_2O until cloud point was reached
- dispersed clouds w/ MeOH
- placed benzil solution in ice bath until crystals formed

- Used vacuum filtration to remove crystals and stored on watch glass. - I lost a bit from the solvent used to "stick" the filter

4-Me Benzoic acid

- repeated process of recrystalization used previously

Notes that differ from previous
- The cloud point method didn't go as smoothly as benzil.

Pre-Lab: Extraction Methods

Procedure	Data
✓ 4-Methyl benzoic acid recrystalize using an H2O/MeOH two solvent system. o obtain M.P. & mass opresent both vials to instructor.	-Performed MP analysis 4-Me = 180-181°C Benzil = 94-97°C M.P. Benzil = 95.8°C Mass Benzil = .46g % yield Benzil = 92% M.P. 4-Me B-Acid = 181.1°C Mass " " = 47.95-47.81 = 0.14g % yield " " = 28%

Report: Extraction Methods

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Summary Table

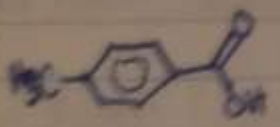
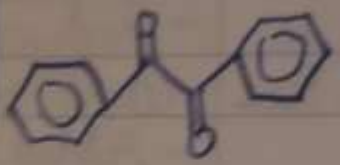
Name	4-Methylbenzoic acid	Benzil
Observed M.P	181.1°C	95.8°C
Observed color	colorless	~~184.4°C~~ pale yellow
% yield	28%	92%
Structure		

Table 1: Summary Table for extraction Methods

Critiques

Benzil ~ The recrystalization of benzil went very well with a 92% yield... My only critique with this is the fact that the büchner funnel was not dampened and I lost yield into the waste solution.

4-Mebenzoic acid ~ Upon extraction of the 4-Me benzoic acid, yield must have been lost. I believe the most yield was lost when adding the HCl to obtain the precipitate... I either added too much or too little. I suspect something went wrong at this step because the recrystalization process went fairly smooth. Overall, these mistakes majorly hurt the yield making it 28%

x David Miller 11/1/22

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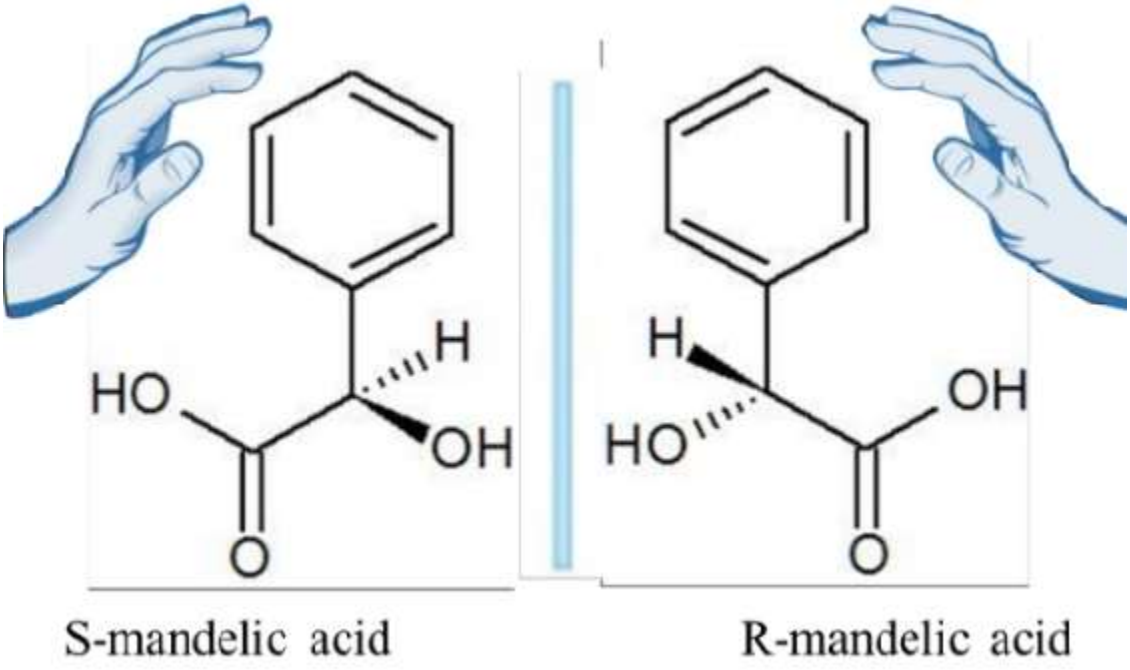
OPTICAL RESOLUTION OF (+-)MANDELIC ACID



S-mandelic acid R-mandelic acid

Pre-Lab:
Optical Resolution of (±) Mandelic Acid

Objective: To separate a racemic mixture of ± Mandelic acid into it's respective enantiomers using extraction, recrystalization, and rotary vacuum evaporation. The purpose of this is to obtain the optical resolution of the (R) and (S) enantiomers.

Theory: To meet the objective of separation of enantiomers, one must manipulate the chemicals in a way that lets them exploit a difference... This is done by using (+)-cinconine to act as a base and deprotonate (R) and (S) Mandelic acid. by doing this, the enantiomers that once had the same properties become diastereomers with differing properties regarding solubility. This allows us to separate the diastereomers using recrystallization. After this, the diastereomers must be reprotonated to become (R) and (S) enantiomers again, so HCl is added to the mixture of the deprotonated mandelic acid still in solution with the cinconine. After this, they are separated through extraction due to differing solubilities. After the (R) and (S) enriched solutions of Mandelic acid have been synthesized, an optical resolution is performed to calculate the specific rotation and % enantiomeric excess of the enantiomers. The reason optical resolution is so crucial is because of how enantiomers will bend light opposite of each other in either a dextrorotary or levorotary direction. Using this information, we can calculate how pure the enantiomer in a solution is.

Eqns, diagrams, mechanisms →

Pre-Lab!

Optical Resolution of (±) Mandelic Acid

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Theory cont.

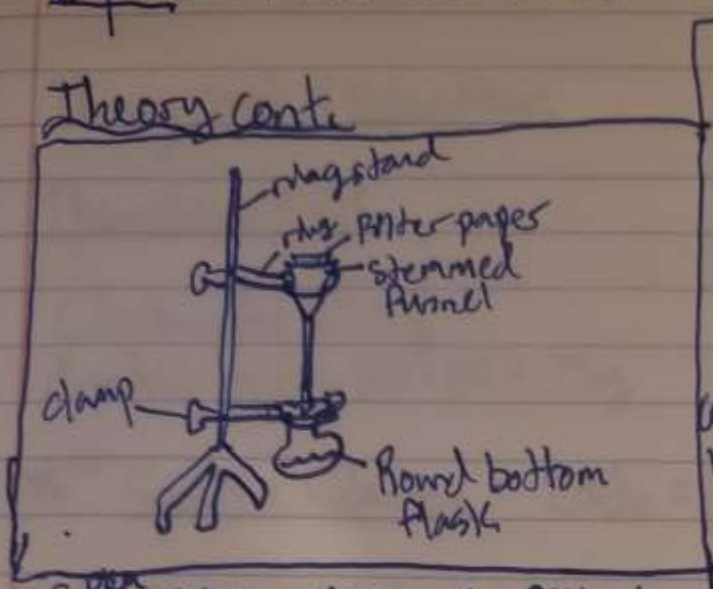
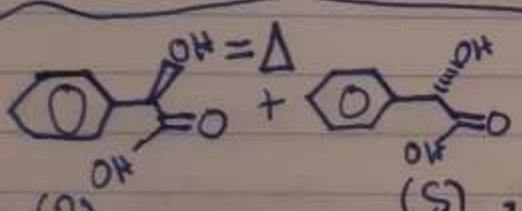
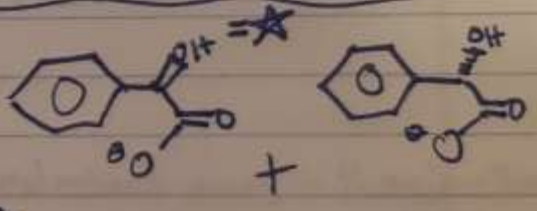


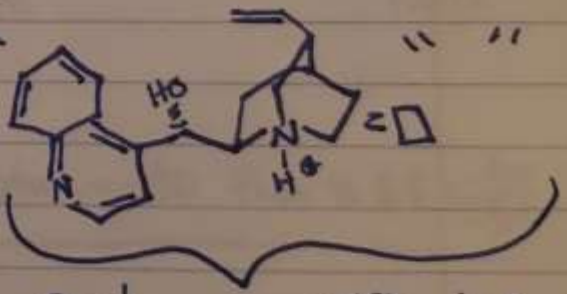
IMAGE 1: Gravity Filtration | IMAGE 2: Seperatory Funnel

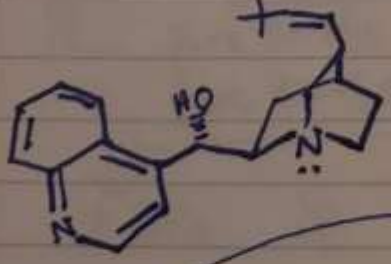


Enantiomers: Same physical props.

Deprotonation / Protonation







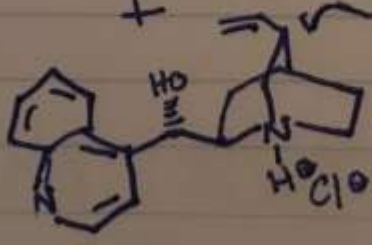
Diastereomers: Different phys properties... seperate using recryst.

less soluble diastereomer

HCl / Et Acetate → reprotonation

organic phase

(aq) phase



Pre-Lab!

Optical Resolution of (±) Mandelic Acid

Theory cont. : Equations

Theoretical Yield

Cinchonine = 1.5 g
Mandelic Acid = (R) + (S) = .75 g

Specific Rotation $[\alpha]_D = \frac{\alpha}{c\ell}$

α = Degrees rotated c = g substance / mL solvent $\ell = 1\ dm = 20\ cm$
(Mand Acid) (Etacetate)

% Enantiomeric Excess

$$\%EE = \frac{[\alpha]_D \text{ sample}}{[\alpha]_D \text{ from major Enant}} = \frac{\text{mol major E} - \text{mol minor E}}{\text{Total mol both}} \times 100\% = \frac{\%\text{ major} - \%\text{ minor}}{100\%}$$

↓ ex.

Calculating % R and % S

if... pure S = +50 and rotation mixture = -40 then $\%EE = \frac{-40}{-50}$

↓

= 80% if R + S = 100% and R − S = 80% then R = 100% − S

↓

and therefore $100\% - S - S = 80\%$ (−100% from each side) $= -2S = -20\% = \frac{-2S}{-2}$

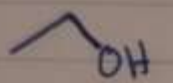
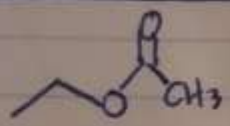
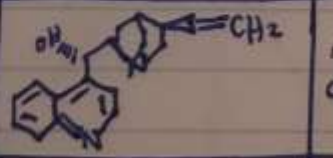
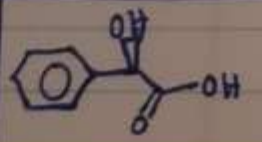
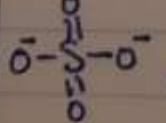
S = 10%
R = 90%

TABLE OF REAGENTS NEXT →

Pre-Lab:

Optical Resolution of (±) Mandelic Acid

Table of Reagents

Name	Structure	MM g/mol	Hazards info
Water		18.02g	May cause a sudden urge to urinate
EtOH (absolute)		46.08	• Highly flammable • Causes serious eye irritation
Ethyl Acetate		88.11	• Highly flammable • Causes serious eye irritation • May cause drowsiness or dizziness
HCl	H-Cl	36.46	• May be corrosive to metal • Highly acidic • Causes severe burns
Cinchonine		294.4	• Harmful if swallowed • may cause an allergic skin reaction.
Mandelic Acid (±)		152.15	• corrosive • causes serious eye damage
Magnesium Sulfate		120.36	• Non Hazardous

References

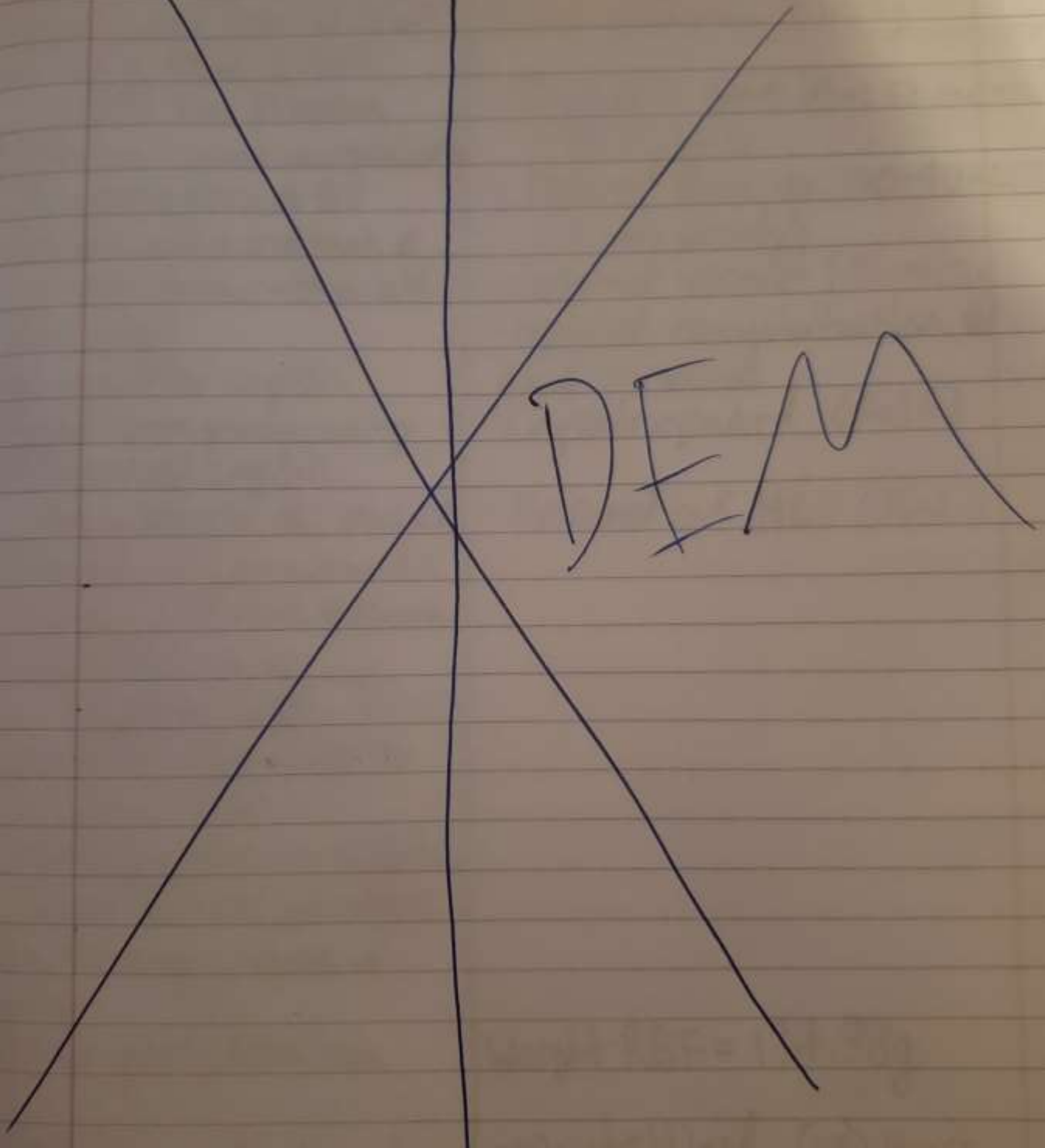
- Labflow - Optical Resolution of Mandelic acid; Enantiomeric excess (2022). https://www.Labflow.com/app/course/2063
- Experiment 4 - Optical Resolution. Labflow.com (2022). https://www.Labflow.com/app/course/2063
- Fisher Scientific MSDS - H_2O; EtOH; HCl; $MgSO_4$; Cinconine; Mandelic acid; Ethyl Acetate. (2020). Fishersci.com

Pre-Lab

Optical Resolution of (±) Mandelic Acid

Procedure

Data



Pre-Lab

Optical Resolution of Mandelic Acid

Procedure

- Obtain 0.75g racemic and 1.5g cinchonine from Dr. G and put into a 125mL E flask.
  - Add 30mL Et Acetate
- Perform a 1 solvent recrystalization
  - completely dissolve at B.P
  - Reduce until a small amt. of crystals form, ~40mL left
  - ice bath!
- Vacuum filter crystals
- Repeat above process using the dried crystals.
  - Recrystalize in the 125mL E fl.
- Separate using extraction 2x
  - organic = 2x 25mL Et Acetate
  - (aq) = 25mL 3M HCl
  - add HCl first! 25mL
  - transfer organic layer to a 200mL E flask
  - Drain (aq) phase into a 250mL beaker for both extractions
- Dry the organic phase w/ $MgSO_4$
- Perform gravity filtration
- Neutrilize cinchonine w/ 3x25mL NaOH and vacuum filtrate the precipitate

Data

Actual weight MA = 0.74g
Actual cinchonine = 1.52g

- Dissolved in about 55mL Et acetate
  - 30 + 25mL = 55mL
- Reduced down to 30-40mL (it was cloudy)... Recrystalized
- Performed vacuum filtration
- repeated recrystalization @ about 35-60mL
- Crystals dried (salt) cinch + mand
  - enriched in (R)
- Measured out HCl (25mL)
- added HCl to mand acid

- After extraction I reprotonated the cinchonine with NaOH and set the (R) mand acid aside as the organic phase.
- I vacuum filtrated cinchonine to get my yield after it was pH 7

Weight RBF = 134.98g

- Neutrilized (aq) phase with NaOH... it was slightly basic but I proceeded anyways. ~28.5mL
- Obtained precipitate w/ vacuum filt

Pre-Lab:

Optical Resolution of Mandelic Acid (±)

Procedure

- Recrystalize the precipitate using a MeOH/H_2O scheme
- Vacuum filter crystals and weigh/turn it in with the report sheet.

Mandelic acid

- Use the Rotovac to evaporate the solvent to leave only the Mandelic acid..
- Add 10mL Absolute EtOH to the flask to dissolve all contents. and PEM
  - Transfer to a clean sample vial via a clean pipette..
    - if soln. is cloudy, filter through filt. paper.
- obtain a polarimeter cell...
  - rinse w/ a pipet of solution
  - Discard rinsate
  - Fill to the bottom like videos
- Obtain info for specific rotation
- Discard contents of cell
  - Organic waste
- rinse cell w/ EtOH
- Calculate the following

Data

- performed recrystalization of cinchonine using MeOH/H_2O
  - Added 35mL MeOH to start

Mass cinchonine = 0.4g

- Added 15mL MeOH
- Added 30mL more
- Reduced to about 40mL

Mass Crude Mand Acid = 0.4g

Concentration of Solution = ~~0.4~~ g mandelic acid/mL EtOH

- Added H_2O to recrystalize cinchonine
- performed vacuum filt (10mL)
- Added EtOH to MA (R enriched)
- Obtained observed rotation

- Disposed of MA and placed cinchonine in a vial
- Performed a M.P. Analysis on cinchonine (+)

MP = 248.8

- it burned, but didn't melt haha

Amount polarized = −1.45°

Temp of room(°C) = 21.4°C

Pure (S) = ±160° in EtOH Pure (R) = −160°

Specific Rotation = −36.25°

%EE = 22.66%

% (S) = 38.7%

% (R) = 61.3%

Report: Optical Resolution of Mandelic Acid (±) 36b

Critique of Experiment

-The experiment seemed to go smoothly for the most part. A perfect yield was not obtained so I will begin by coming up with possible explanations. There is a good chance I lost yield during recrystallization of mandelic acid since the solubilities of (R) and (S) are very similar when (R) is bound to (+) cinchonine.

-My yield for cinchonine was around 90% which was not great. I believe there was error during both recrystalization and reprotonation to form the precipitate.

November 16th '22

X David Miller

Summary Table for (R) Mandelic Acid

Theoretical yield	.75g (R+S racemic) / 2 = .375g
Observed Rotation	-1.45°
Specific Rotation $[\alpha]_D^{21.7°}$	-36.25°
Enantiomeric Excess	% EE = 22.66%
%(R) & %(S)	61.3% (R) 38.7% (S)

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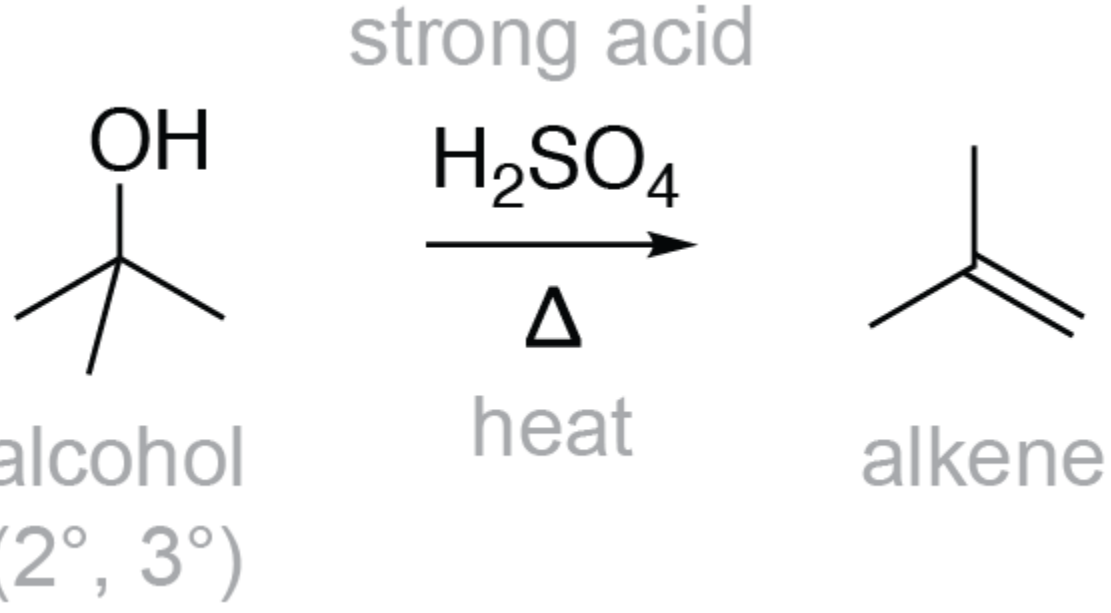
DEHYDRATION OF TETRAHYDROLINALOOL.

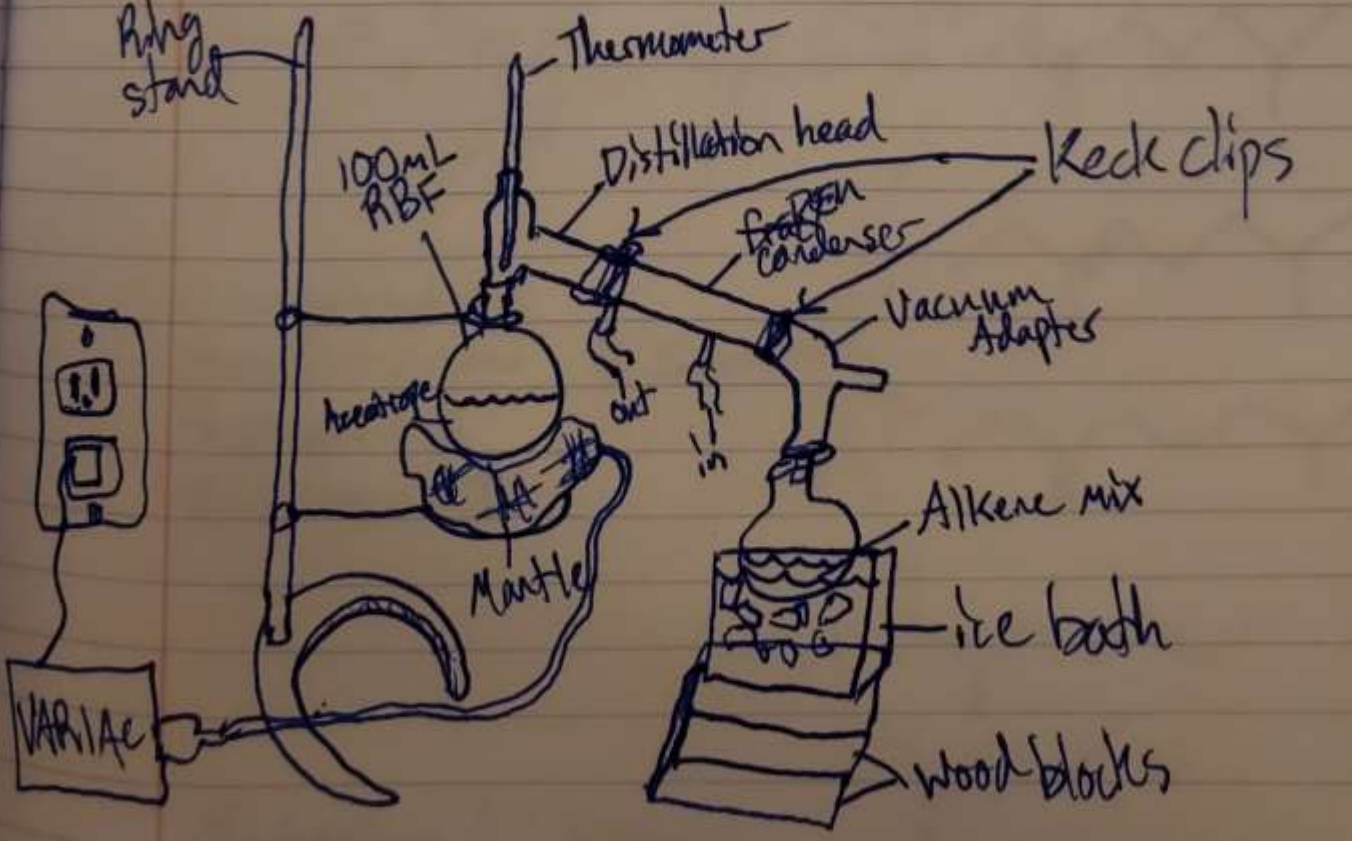
(ALKANE → ALKENE)



Pre-Lab: Dehydration

Objective: To use an acid to dehydrate a tertiary alkane alcohol to create and isolate a desired alkene.

Theory: In a dehydration ~~one uses~~ DEH, an E1 mechanism occurs which is a multi-step process that "cleaves" the leaving group and forces the carbocation that is left to form a double bond through "kicking out" the β hydrogen. After these alkenes are formed, they are then separated using distillation since their boiling points have changed. Since tetrahydrolinalool has 5 possible isomers (constitutional), we must determine the percentages of trisubstituted vs. Di"".



Apparatus 1: Distillation

Pre-Lab: Dehydration

Theory cont.

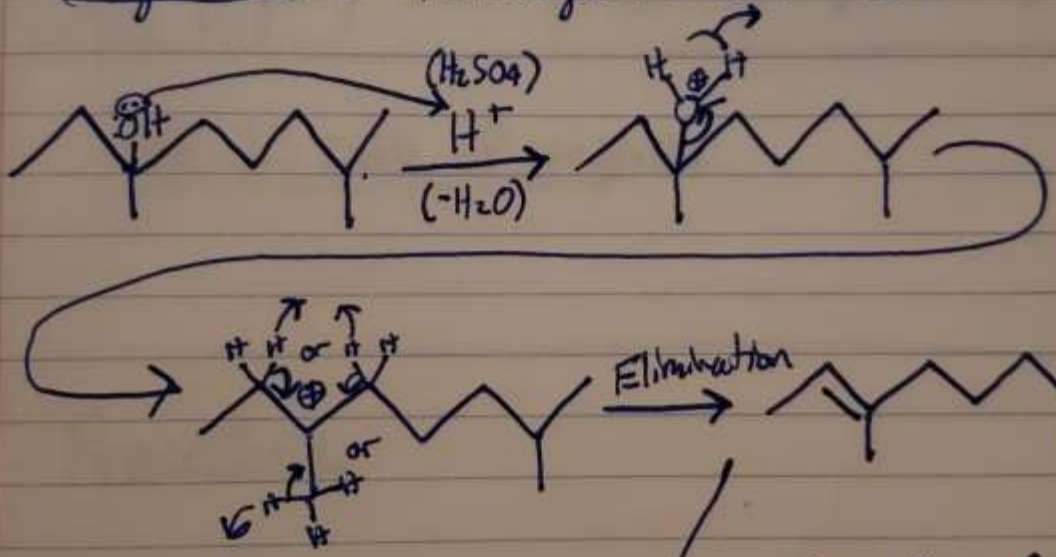
Theoretical yield

MW tetrahydrolinalool = 158.285 g/mol

mol "" = g sample $\times \frac{1\ mol}{158.285\ g}$ = mol sample = Theoretical yield

$\frac{mol\ product}{mol\ sample} \times 100\% =$ % yield.

Dehydration of tetrahydrolinalool ~ E1



ΔE

ΔE

5 Isomers

~

ΔZ

ΔZ

Trisubstituted = Δ
Disubstituted = ~
Entgegen = E
Zusammen = Z

Mechanism 1: Isomers

Pre-Lab: Dehydration

Table of Reagents

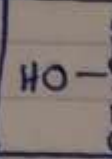
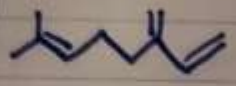
Name	Structure	B.P. (°C)	Hazards
Sulfuric Acid		290	• Strong acid! • Causes severe burns • Respiratory irritation.
Myrcene (similar to product)		165°C	• flammable • skin irritant • may cause cancer • eye irrit
Magnesium Mg^{2+} Sulfate SO_4^{2-}	Mg^{2+} SO_4^{2-}	N/A	• Harmful if swallowed • may cause eye irritation

Table 1: Table of reagents

Procedure

Mise en place:

- 100 mL RBF
- 50 mL RBF
- Distillation setup
- Wood blocks
- Ice bath
- Boiling chips!
- 10 mL grad cyl
- Monstoner pipette + Kim Rilter
- pipettes
- Vial
- Erlenmeyer (for drying)
-

Pre-Lab: Dehydration

Procedure

- clamp a 100mL RBF in Hood station
- Tare a 10mL G-cyl and weigh out exactly 5.0mL in grams
- Transfer to RBF
- Clean all equipment used very well
- Measure out 10mL 6M H_2SO_4... reuse funnel to pour into the RBF
- add boiling chips
- Set up the RBF just like "Apparatus #1" for distillation.
- Crank VARIAC to 90-100% at 120V and dial back to a simmer after boiling occurs.
  - RECORD temp at first drop distilled
- Distill until most of the liquid is gone.
- Remove aqueous layer in the 50mL collection RBF using a pipet and transfer to an E-flask...
  - Dry w/ $MgSO_4$

Data

G-cyl mass = ~~44.24g~~
Vial Mass = 17.72g ~~20.78g~~
G-cyl + tetra = 49.11g
tetra = ~~30.86~~ 4.13g
Product = ~~20.28g~~ 2.56g

- Set up RBF and distillation setup
- Measured out 5.0mL of tethyl

DONT FORGET TO NEUT. THE ACID!

- Measured out 10mL H_2SO_4
  - added to RBF
- Started distillation.

Temp ~~at~~ First drop = 84.5°C

Temp at stop of dist = N/A

- After removing H_2O, it is a bit soapy and forms bubbles.
- I dried the organic phase ~~and~~
- filtered through a monster pipette

Pre-Lab: Dehydration

Procedure

- obtain a tare weight of the sample vial and setup a monstomer gravity filtration.
- obtain weight of product obtained and compare to T-yield to get % yield.
- Rinse pipet with acetone before disposal.
- Get an IR spectrum of the product
- Get a reading from the NMR spectrometer
- Turn in product.

Data

- Obtained IR
- evaluated spectra
- There seems to be little to no -OH bonds in product... this is indicative of alkenes

- Obtained NMR
- evaluated shielded and unshielded protons and data collected.

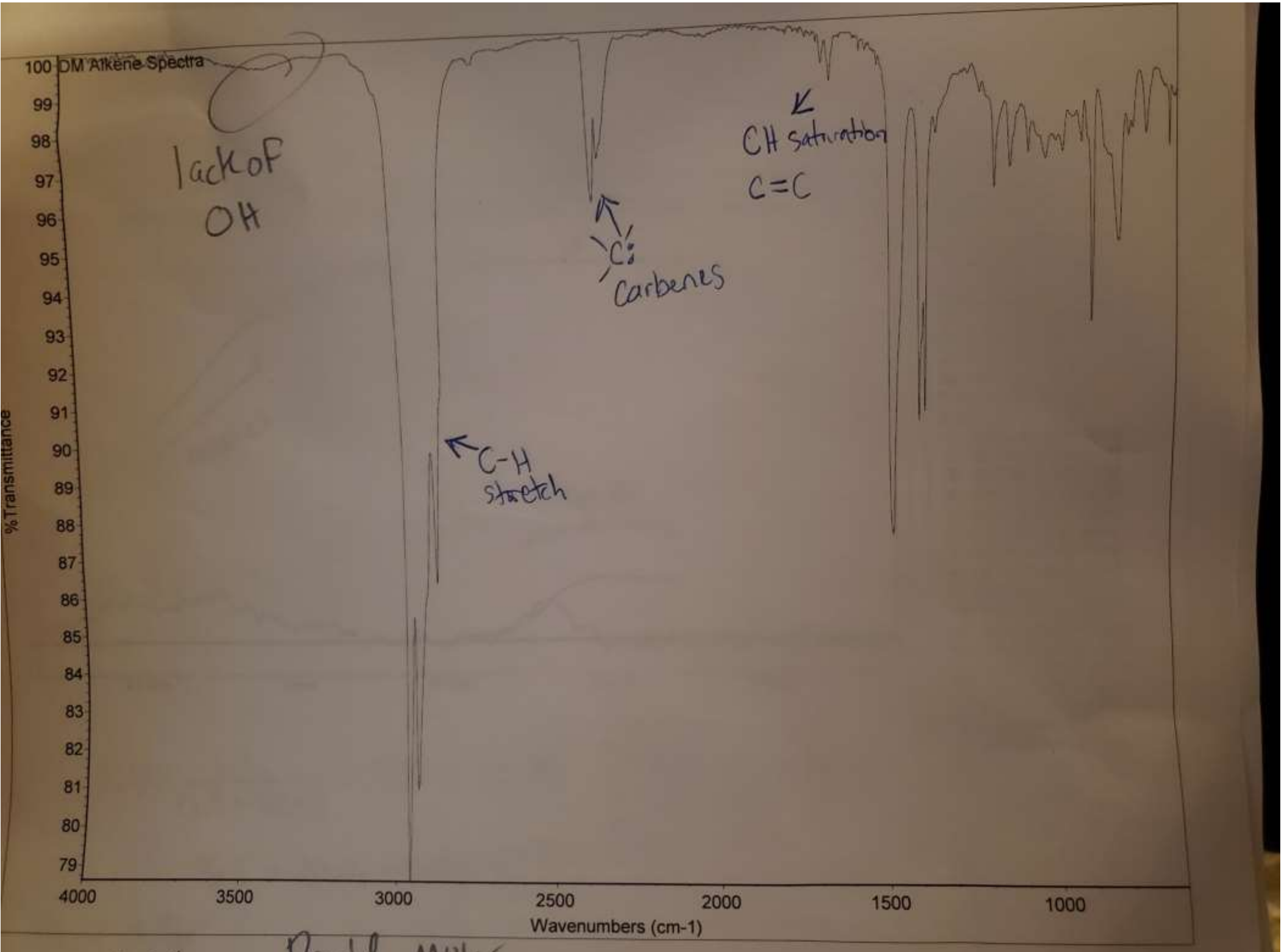
$\%D = 42.9\%$

$\%T = 57.1\%$

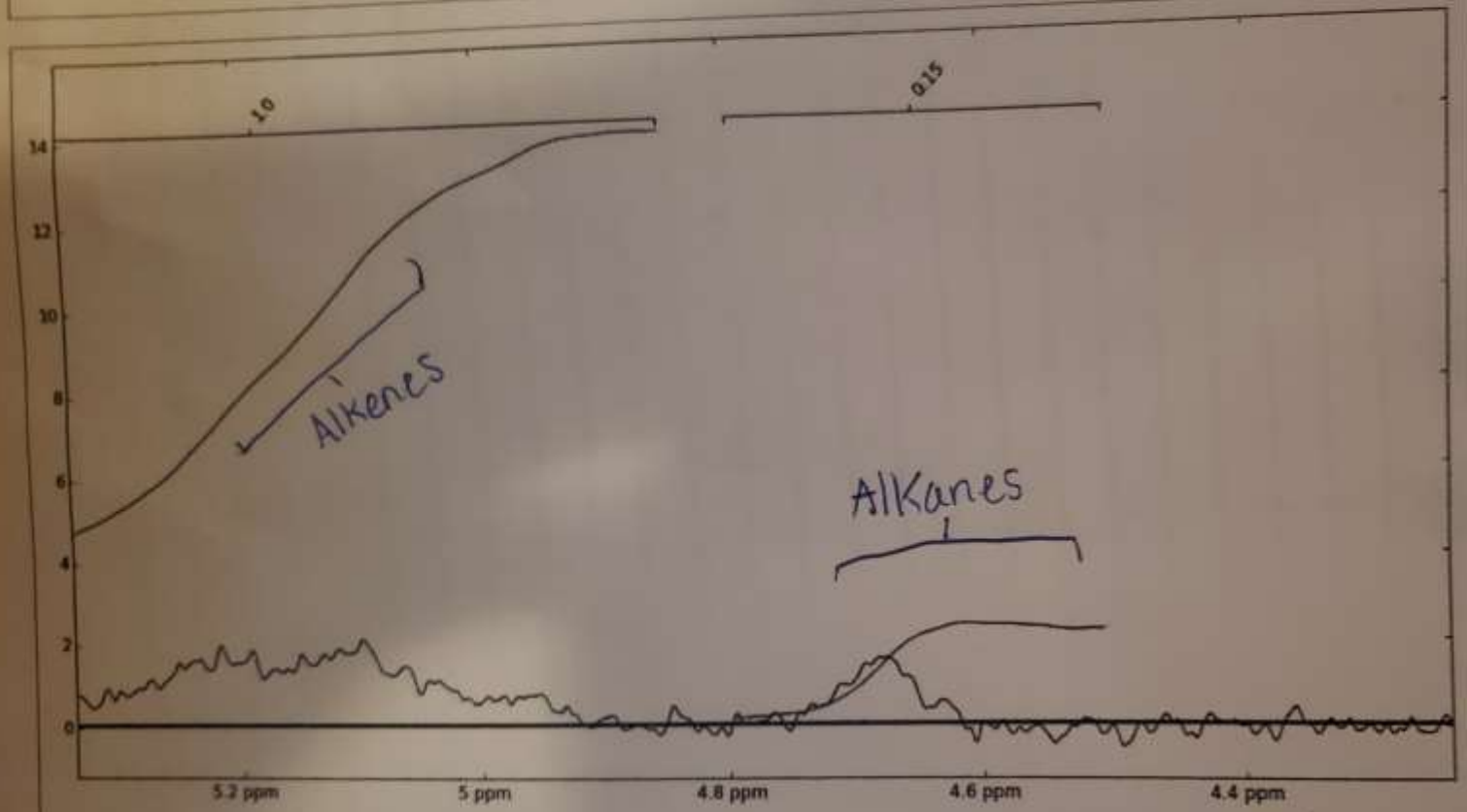
$$\%D = \left(\frac{I_{4.7}}{I_{4.7} + 2I_{5.1}}\right) \times 100$$

$$\%T = \left(\frac{I_{5.1}}{I_{5.1} + .5I_{4.7}}\right) \times 100$$

$\%\text{yield} = 62.00\% = \frac{2.56\text{g product}}{4.13\text{g reagent}}$


DM Alkene Spectra
lack of OH
C-H stretch
C: carbenes
CH saturation
C=C
%Transmittance
100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
85
84
83
82
81
80
79
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

2022-11-17



$$\%D = \frac{1.5}{(1.5 + 2(1.0))} = .429 = 42.9\%$$

$$\%T = 100\% - \%D = 57.1\%$$

-OH being low in IR parallels the evidence of lower levels of alkanes.

David Miller

Processing Parameters

Acquisition Time:
2022/11/17 13:33:18
Nucleus: 1H
Solvent: Chloroform-d
TX Frequency: 60.53 MHz
Scans: 16
Time Per Scan: 4.70 s
Spectral Width: 12 ppm
Dwell Time: 0.29 uS
Digital Resolution: 0.04 Hz
NPoints (Complex): 2048
Zero Filling: 7.00
Apodization: 0.10
Receiver Gain: 40.89
Pulse Width: 14.4 us
Peaks:
1: -63.5 Hz (-1.05 ppm)
2: -62.4 Hz (-1.03 ppm)
3: -60.9 Hz (-1.01 ppm)
4: -59.5 Hz (-0.98 ppm)
5: -57.2 Hz (-0.95 ppm)
6: -55.7 Hz (-0.92 ppm)
7: -51.6 Hz (-0.85 ppm)
8: -48.7 Hz (-0.80 ppm)
9: -45.6 Hz (-0.75 ppm)
10: -43.1 Hz (-0.71 ppm)
11: -42.0 Hz (-0.69 ppm)
12: -35.4 Hz (-0.59 ppm)
13: -1.0 Hz (-0.02 ppm)
14: 1.4 Hz (0.02 ppm)
15: 3.3 Hz (0.05 ppm)
16: 49.0 Hz (0.81 ppm)
17: 54.8 Hz (0.90 ppm)
18: 66.3 Hz (1.10 ppm)
19: 68.2 Hz (1.13 ppm)
20: 72.6 Hz (1.20 ppm)
21: 75.2 Hz (1.24 ppm)
22: 78.9 Hz (1.30 ppm)
23: 80.8 Hz (1.34 ppm)
24: 91.0 Hz (1.50 ppm)
25: 95.3 Hz (1.57 ppm)
26: 104.5 Hz (1.73 ppm)
27: 107.5 Hz (1.78 ppm)
28: 109.0 Hz (1.80 ppm)

Report: Dehydration of Alkanes 41b

Summary

Procedure: My yield was not perfect, but it was decent. The only thing that I believe could have hurt my yield was the drying process as I added quite a bit of $MgSO_4$.

IR spectroscopy: Upon observation of the IR, the experiment seems to be successful. There was a lack of an "-OH bulge" at 3200-3500 cm^{-1} which indicates dehydration was successful. There was also significant evidence of C=C due to a reading at around 1650 cm^{-1}.

NMR: The NMR confirms the success due to the deshielding downfield on the graph which indicates the presence of alkenes with low levels of alkanes.

Summary Table

A-yield	2.56 g
T-yield	4.13 g
% yield	62%
%D	42.9%
%T	57.1%
Observed BP	84.5°C

X. David Miller 11/30/2022

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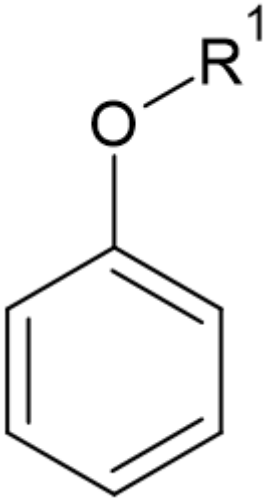
WILLIAMSON ETHER SYNTHESIS

THE ETHER BUNNY



Pre-Lab: Will Ether Synthesis

Objective: To utilize a stoichiometric mixture of eugenol, NaOH, and ethylene glycol ditosylate to create an ether product through refluxing the reaction.

Theory:
The following reaction takes place in a reflux of reactions which is when a constant flow of energy is provided to the reaction via boiling, but none of the vapors are boiled off; instead they are condensed back down into the flask. Todays experiment will be carried out in a safer manner than NaCl being added by using NaOH to form a salt out of the eugenol. This salt is then used to "cleave" the two halves of the ditosylate to create the Ethelene glycol Ether. This happens due to the two halves being held together are "tosyl" groups which are good leaving groups for an SN2 reaction to occur.

To analyze the samples, a nuclear magnetic resonance will be taken which is a spectroscopic procedure in which the frequencies of the molecules resonating is measured and graphically presented.

Pre-Lab: Williamson Synthesis of Ethers

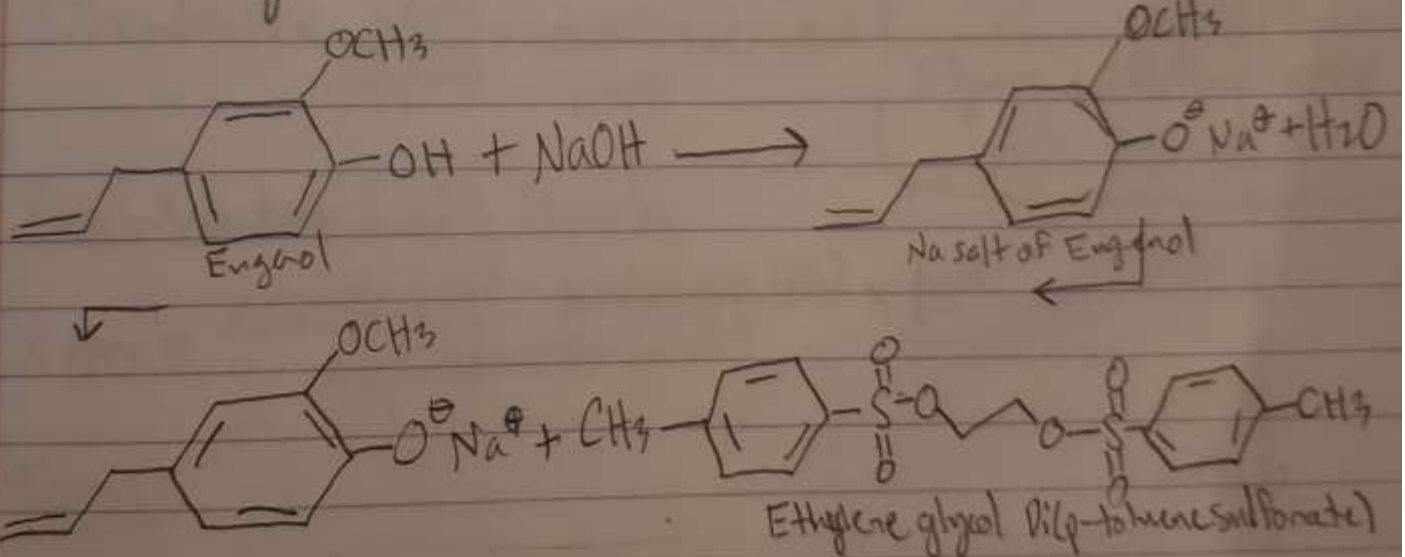
Equations/Mechanisms

$$R\text{-}OH + Na \longrightarrow R\text{-}O^{\ominus}Na^{\oplus} + \tfrac{1}{2}H_2$$

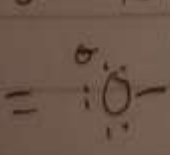
$$R\text{-}O^{\ominus}Na^{\oplus} + R'CH_2X \xrightarrow{S_N2} R\text{-}O\text{-}CH_2\text{-}R' + NaX_{(s)}$$

Equation 1: Basic Williamson Ether synthesis using Na metal.

A way to get around using Na(s) is to do the following reaction (much safer)



OT = Tolsyl group



Good leaving group

Pre-Lab: Williamson Ether Synthesis

Equations needed (Theory)

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{Theoretical yield}} \times 100\%$$

Calculations for stoichiometry

$$\text{g ditosylate} \times \frac{\text{mol ditos}}{\text{g ditos}} = X \text{ mol}$$

$$3 \times \text{mol} \times \frac{\text{g Eugenol}}{\text{mol Eugenol}} \times \frac{\text{mL Eug}}{\text{g Eug}} = \text{mL needed}$$

$$3.3 \times \text{mol NaOH} \times \frac{\text{g NaOH}}{\text{mol NaOH}} \times \frac{1 \text{ mL NaOH}}{1 \text{ g NaOH}} = \text{mL needed}$$

Diagram for reflux

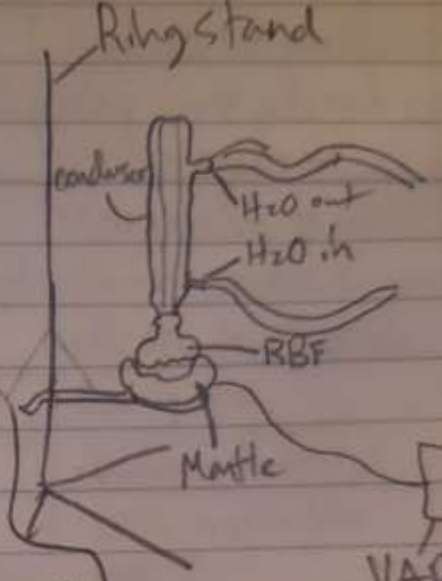


Figure 1: Reflux setup

Freq. independent δ scale Formula

$$\delta \text{ ppm} = \frac{\nu \text{ sample (Hz)} - \nu \text{ reference (Hz)}}{\nu \text{ spectrometer (MHz)}} \times 10^6$$

Terms:

Upfield: Right part of spectrum... contains "shielded" protons.

Downfield: Left part of the spectrum.... contains "deshielded" protons.

Pre-Lab: William Ether Synthesis

Table of Reagents/Products

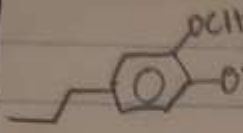
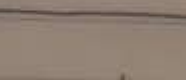
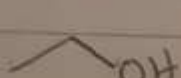
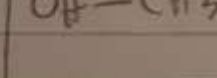
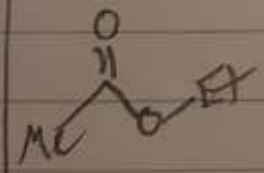
Name	Structure	M.P/B.P		M.W.	Hazards
Eugenol		-11°c	254°c	164.2g/mol	• Harmful if swallowed • May cause allergic rxn • Causes eye irr.
Sodium Hydroxide		450°c	2000°c	40g/mol	• Corrosive to metals • Causes severe burns • Resp. irritation
Ethanol		~~-20°c~~	78.1°c	46g/mol	• flammable • suspected of causing cancer • Damages fertility
Ethelene glycol bis-p-toluenesulfonate.		122°c	N/A	370.45g/mol	• Skin irritation • eye " " • respiratory " "
Methanol		-98°c	64.7°c	32.04g/mol	• Dmg to organs • Resp irr. • Flammable • Toxic, if swallowed
Ethyl Acetate		-85°c	76°c	88.11g/mol	• Flammable • May cause dizziness • eye irrit
~~X~~	~~X~~	~~X~~	~~X~~	~~X~~	~~X~~

Table 1: Table of reagents

Pre-Lab: Williamson Ether Synthesis

Procedure

- Measure out 1.25mL (1.378g) of eugenol into a 10mL G-cyl
  - use a pipet
- put eugenol in RBF w/ stir bar
- Add .356 g (.008908mol) NaOH to the RBF
- Rinse into the flask with 4mL EtOH
- turn on magnetic stirrer
  - stir for 10 min @ RT
  - observe yellow color
- obtain approx 1g ditosylate
- Add to RBF
- Add 4mL EtOH to rxn
- Reflux for 30 min
  - note exact time reflux begins (boiling start)

- Pour mixture while still hot into a sep funnel w/ 25mL H_2O
  - remove stir bar
- Rinse RBF using H_2O & ethyl acetate into the sep funnel
- extract w/ 25mL Et acetate

Next

Data

- Measured out .29g NaOH
- Measured about 1.3mL Eugenol

- I began stirring at 1:32p and noticed the orange-y eugenol change to a dark green.
- eugenol smells like cloves! yum!

- added EtOH and ditosylate
- started VARIAC on 40

Mass Vial+cap+ditos = 18.58
Mass Vial+cap = 17.60
Mass ditosylate = .98g

Reflux start: 2:11p
Reflux end: 2:45p

- Reflux mixture got sludgy... I added 5mL more EtOH.

- ended reflux

Pre-Lab: Williamson Ether Synthesis

Procedure

- Drain the (aq) phase
- Rinse organic phase with 15mL Saturated (aq) NaCl
- Discard both (aq) phases
- Dry organic phase using $MgSO_4$
- Gravity filter out $MgSO_4$
- Evaporate Filtrate using rotovap
- Recrystalize from methanol using a norit/hot grav filtration (if needed)
- Perform vacuum filtration
- Obtain NMR spectrum
- Obtain M.P. of crystals.

Data

- While waiting for the reflux to finish, I measured out the H_2O, NaCl, and EtOAc...
- I also measured out $MgSO_4$
- Folded a Fluted Filter paper
- Reflux started to get gooky and a very dark green.
- Reflux has a film on top
- Performed H_2O, EtOH, EtOAc extraction
- dried organic phase
- disposed of (aq) phase
- Filtered organic phase
- roto vapped organic phase
- performed recrystalization in MeOH
- added .04g norit
- treated again w/ norit using .92g this time.
- After the hot grav filtration, I recrystalized the product.
- I vacuum filtrated product for 15 min
- Crystals oxidized upon start of next lab

Mass Crystals: 0.33g

Di Ether M.P. = 82.5°C

Report: Will Ether Synthesis

Critique: During the experiment, a few things occurred that I believe significantly affected my yield.

1. When doing the norit treatment, I believe too much was added and it removed some of my product.
2. During reflux, a reflux ring was not able to be observed which possibly means some of the product was boiled off and lost.

3. One last point is that the MP measurement might not be as accurate as it could be due to the thickness and static electricity of the crystals preventing them from properly falling into the MP analysis rod.

Summary Table

Mass Di Ether	0.33g
% yield	23%
M.P. Di Ether	82.5°C
Color	Pink and white crystals.

X. David Nin

END OF ORGANIC CHEMISTRY LAB 2022