

Stereochemical Analysis of the Reduction of Benzil

Experiment 4

TA: Daliane Regis

CHM1321 Z05

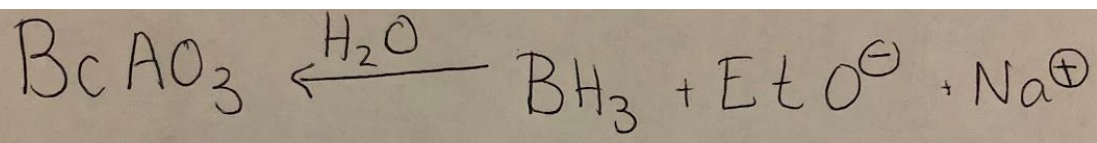
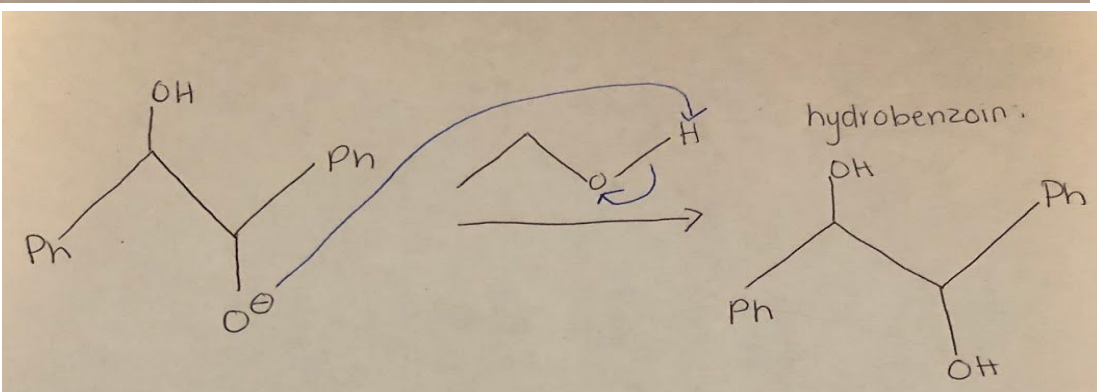
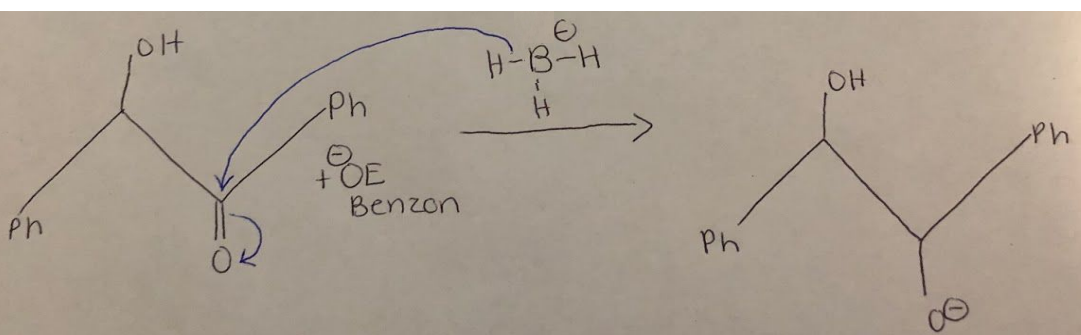
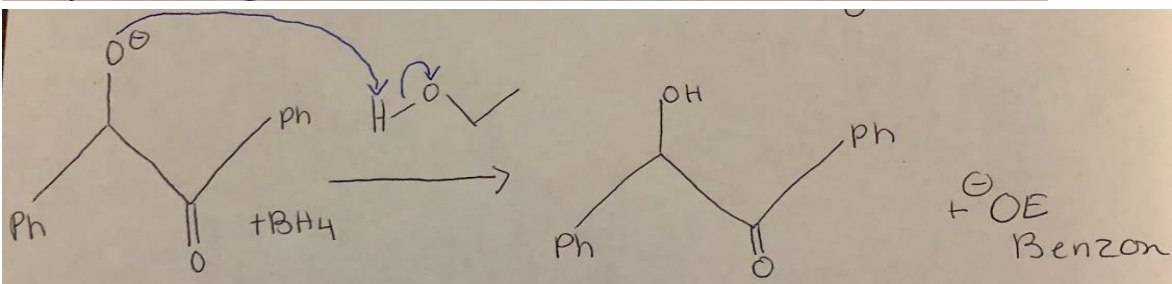
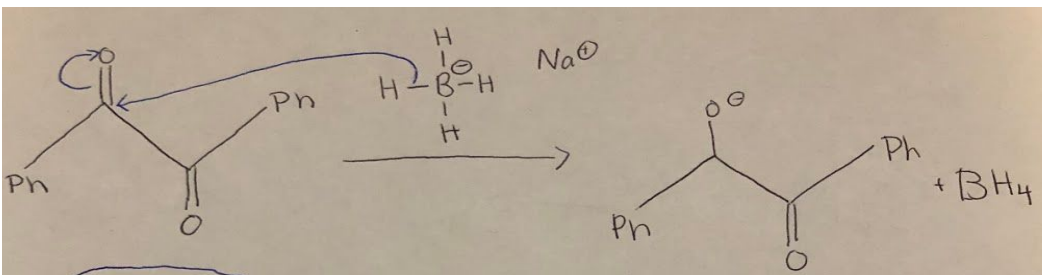
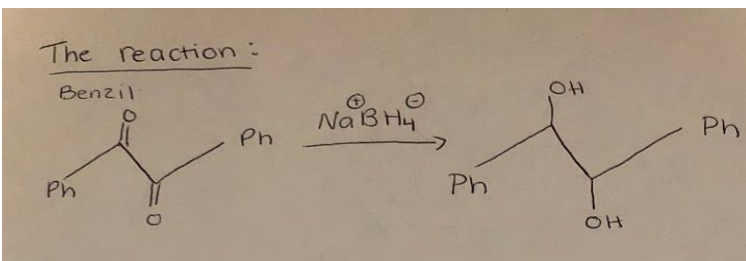
Written by

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Date: Friday, March 1, 2019

Introduction



Procedure

As described in the lab manual. (Durst et al., *Organic Chemistry Laboratory Manual*, exp. 4, 2019)

Observations

- When benzil, dichloromethane and ethanol were added together it created a yellow, transparent solution
- As sodium borohydride was added, the solution gradually became clearer and lost its colour and precipitated a small amount on the bottom
- The final solution was pale yellow with a bit of precipitate on the bottom
- After being stirred for 10 minutes, the solution became a murky yellow, and had a white precipitate in it
- After being taken off the stir plate, the solution began to foam
- Heating up the solution caused the solution to foam up, then after a while still on the heat it went down

Data

Table of Reagents

Reagent	MM(g/mol)	Quantity	Density	Mmol
Benzil	210.23	1.0g	-	4.76
Sodium borohydride	37.83	0.3g	-	7.93
Dichloromethane	-	5mL	-	-
Ethanol	-	5mL	-	-

Table of Results: Hydrobenzoin

Isolated mass	1.14 g
MM (g/mol)	214.26
Mmol	5.32
% yield	112%
Appearance	Crystals were a somewhat chunky, possibly still wet

Part A

Mass of benzil= 1.00g

Volume of dichloromethane =0.5 mL

Volume of ethanol= 5.0 mL

Mass of borohydride= 0.1g + 0.1g + 0.1g = 0.3g

Paper= 0.42 g

Paper + salt =1.56 g

Salt = (Paper + salt) - paper

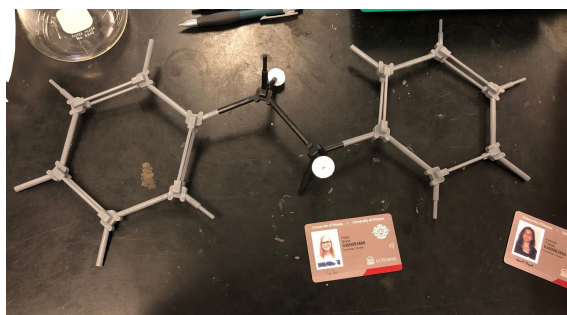
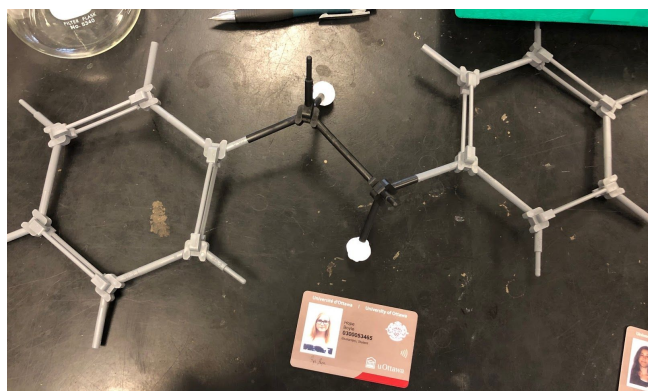
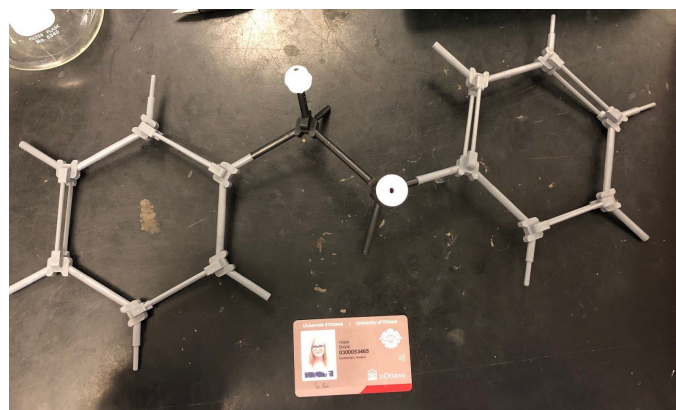
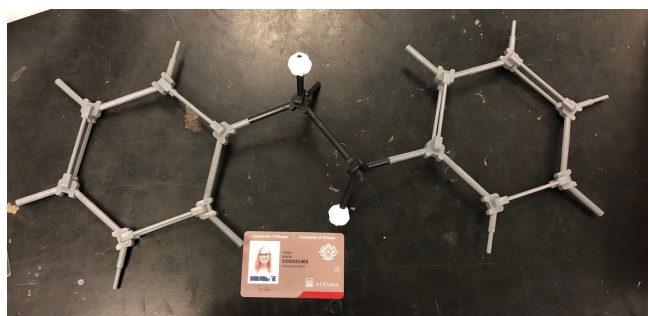
= 1.56 g - 0.42 g

= 1.14 g

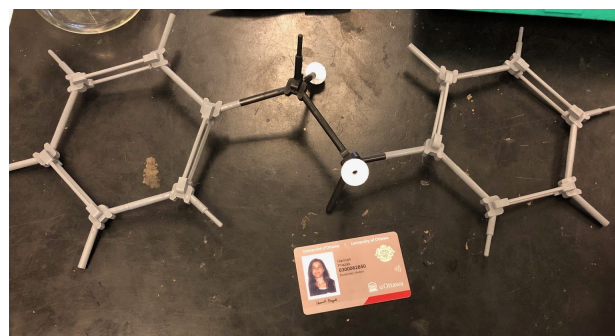
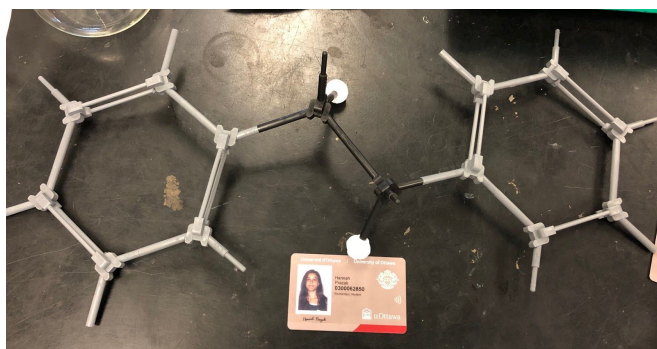
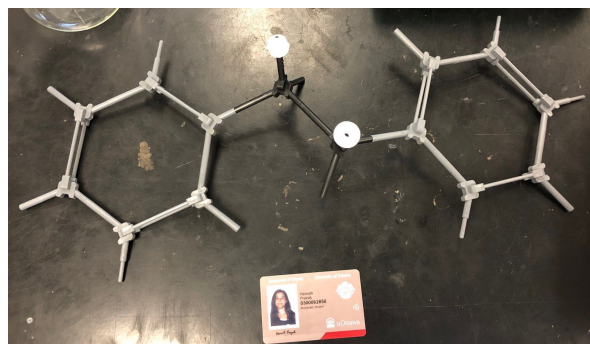
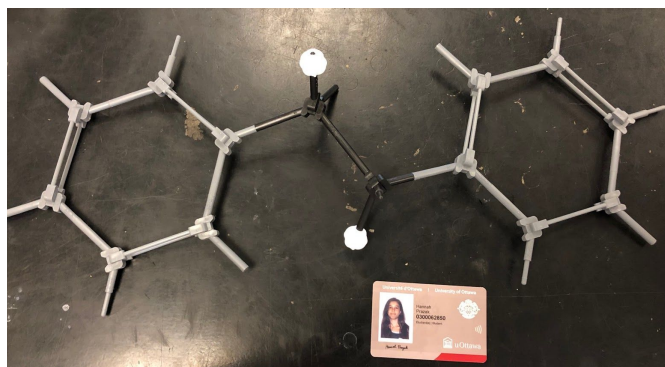
Part B

- White balls represent the OH bonds

Hope



Hannah



TLC

TLC #1

$$D_s = 4.3 \text{ cm}$$

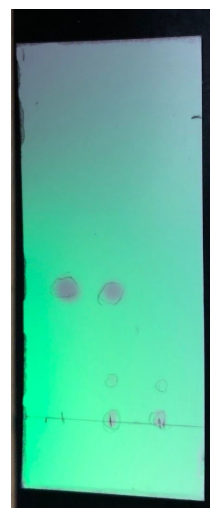
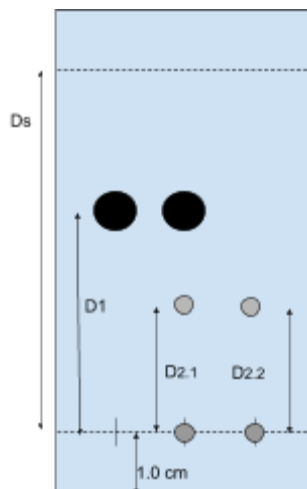
$$D_1 = 1.9 \text{ cm}$$

$$D_{2.1} = 0.6 \text{ cm}$$

$$D_{2.2} = 0.5 \text{ cm}$$

The bottom two have a length of 0 cm

$$D_{1 \text{ avg}} = (0.5 + 0.6)/2 \\ = 0.55 \text{ cm}$$

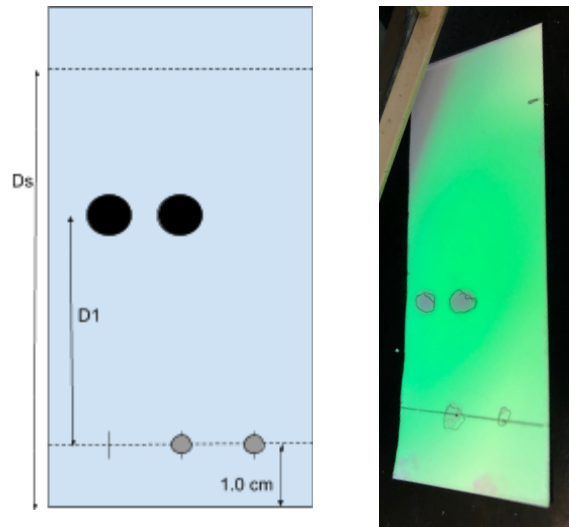


TLC #2

$$D_s = 4.5 \text{ cm}$$

$$D_1 = 1.6 \text{ cm}$$

The bottom two have a length of 0 cm

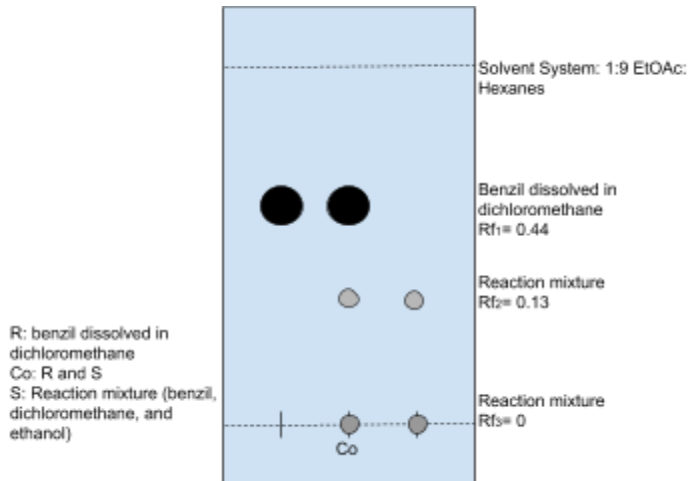


Rf Calculations:

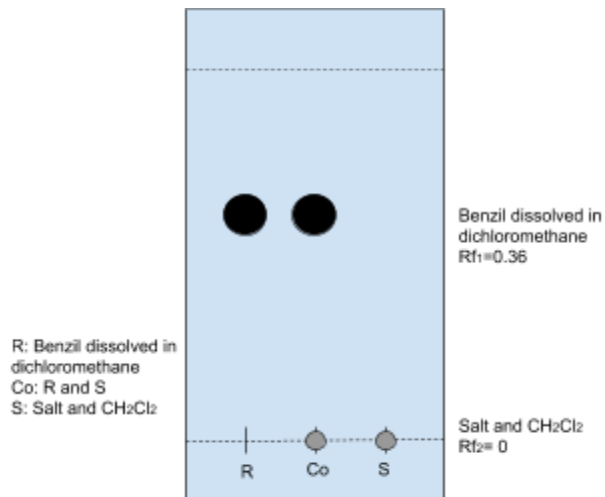
	<u>TLC #1</u>	<u>TLC #2</u>
D_s	4.3 cm	4.5 cm
D_1	1.9 cm	1.6 cm
D_2	0.55 cm	-----
Rf1	0.44*	0.36
Rf2	0.13	-----

$$* Rf_1 = \frac{D_1}{D_s} = \frac{1.9}{4.3} = 0.44186047 \text{ (TLC #1)}$$

TLC #1



TLC #2



Calculations

% yield

$$\frac{\text{mmol crystals (hydrobenzoin)}}{\text{mmol limiting reagent (benzil)}} \times 100\%$$

$$= \frac{5.32 \text{ mmol}}{4.76 \text{ mmol}} \times 100\%$$

$$= 112\%$$

Questions

1. "A compound can *oil out* if the boiling point of the recrystallization solvent is higher than the melting point of the compound." is this statement true or false?

The statement is true. When the boiling solvent is added to a compound that has a lower melting point than the solvent does boiling point, the compound will melt into an oil. The oil will separate from the solvent. There will be nothing left in the solvent to recrystallize because the compound is completely oil and separate from the solvent.

2. The solubility of a compound is 35.6g/100 mL at 25°C and 39.1 g/100 mL at 108°C. If a saturated solution of the compound at 108°C is allowed to slowly cool to 25°C, what is the maximum yield of solid crystals that can be obtained?

Using a volume of 100 mL of saturated solvent, the following calculations can be completed:

$$100 \text{ mL} \times \frac{39.1 \text{ g}}{100 \text{ mL}} = 39.1 \text{ g/mL}$$

$$100 \text{ mL} \times \frac{35.6 \text{ g}}{100 \text{ mL}} = 35.6 \text{ g/mL}$$

$$39.1 \text{ g/mL} - 35.6 \text{ g/mL} = 3.5 \text{ g}$$

The maximum amount of crystals that can be obtained is 3.5 g.

3. **A student dissolves 80 mg of a crude product in 4.5 mL of methanol at 25°C. She cools the solution in an ice bath and obtains crystals. The crystals are recovered by filtration and rinsed with 0.5 ml of ice-cold methanol. After drying, the weight of the crystals is 5 mg. Why was the recovery so poor? What could she do to improve the process?**

The recovery was so poor because the change in temperature was very small, and hardly change the solubility difference. To improve the process she could have a greater overall change in temperature. For example if she heated the methanol to its boiling point of 64.7°C, and then cooled it to 0°C, there would be a greater overall change in temperature, therefore increasing the solubility difference, and there will be more crystals formed. She could also change the solvent so that the product is less soluble in the solvent at 25°C.

4. **When butanoic acid reacts with sodium borohydride, 1-butanol is not obtained. However, bubbling is still observed and heat is produced.**

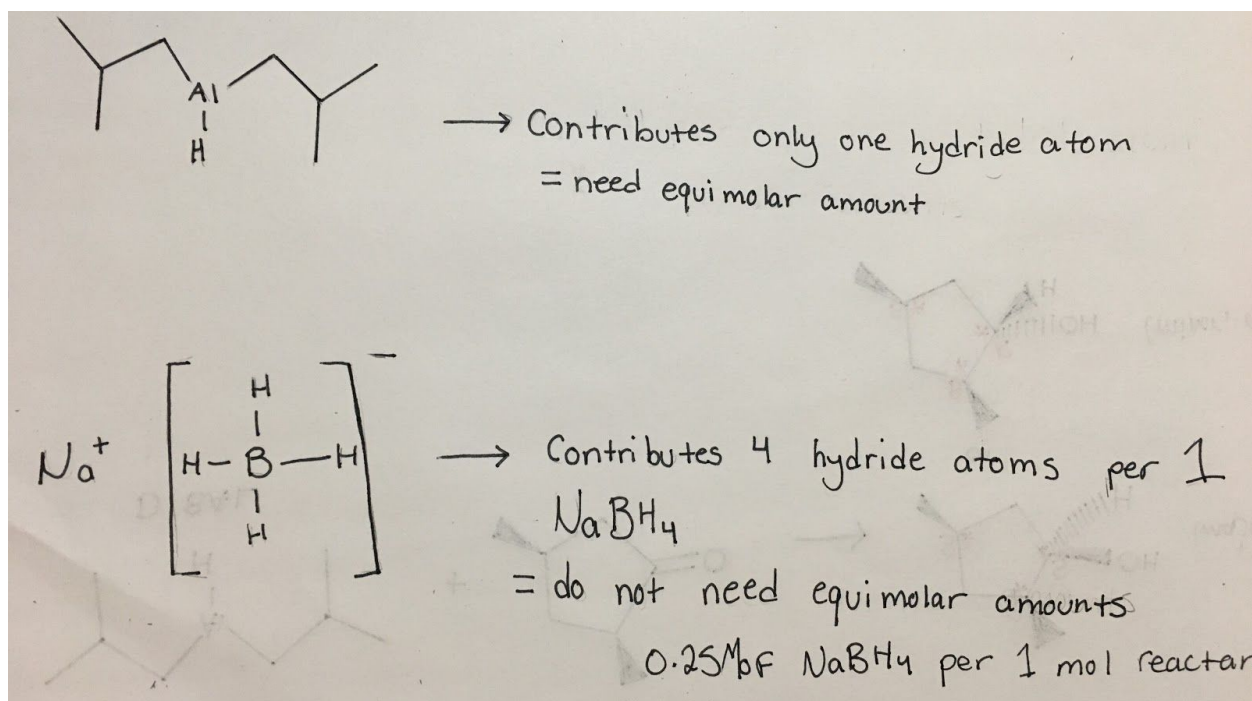
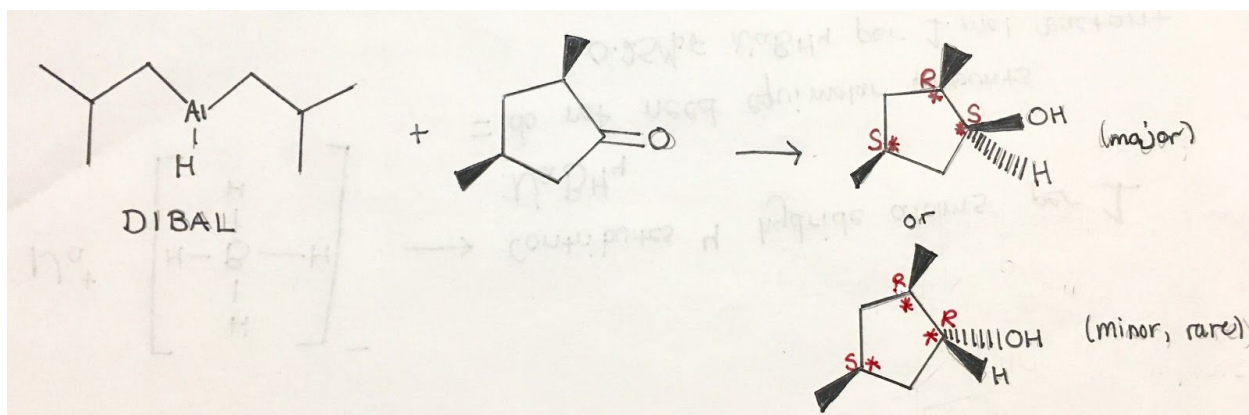
- a. **Why is 1-butanol not obtained?**

1-butanol is not obtained because it is not a reduction reaction that is happening. In a reduction reaction the sodium borohydride would react with the butanoic acid to reduce the bonds to oxygen and add a hydrogen. However, what is actually happening is an acid-base reaction. Sodium borohydride is really active and only reduces really reactive reagents. However the reagent is a carboxylic acid, which isn't very reactive, which is why instead, the acid base reaction is happening. If instead of sodium borohydride, something such as lithium aluminum hydride was used, which reduces less reactive reagents such as carboxylic acid, the reduction reaction would take place and 1-butanol would be a product.

- b. **What is the product of this reaction?**

The products of the reaction are hydrogen gas, which is the bubbling that is observed, and BH_3 which produces the heat.

5. **The reagent used is DIBAL. Like sodium borohydride, it is a source of nucleophilic hydride. Predict the configurations of each stereocentre in the product of the following reaction and provide a justification for your choice. Unlike NaBH_4 , reductions with DIBAL require equimolar amounts of DIBAL and substrate. Can you explain this difference?**



Discussion

This lab requires cautiousness as if a step is missed or skipped there could be an explosion, as most steps are essential. Sodium borohydride is used because it is a useful reducing agent, used to reduce ketones to alcohols. One essential step is stirring the contents of the flask while the flask is ice bathed. The use of the ice bath prevents excessive heat and reduces bubbling and slows the reaction itself. The sodium borohydride is the reagent that produces the heat, and if there is excessive heat and bubbling, there could be an explosion.

The next essential step is the addition of hot water to the reaction mixture. The hot water is added because of the excess amount of sodium borohydride in the reaction mixture. The water quenches the remaining reagent, making it more safe for isolation. Since BH_3 is moderately soluble in water, when the water is mixed with the reaction mixture and then brought to a gentle boil, followed by cooling to room temperature, this is where the crystallization occurs.

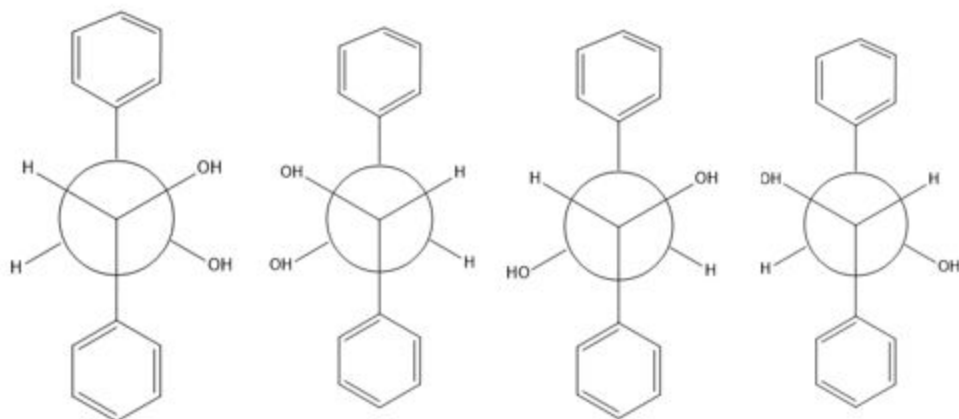
When the reaction mixture is cooled and the crystals form, the crystals must be separated from the solution first via gravity filtration, then using suction filtration. The diol, which is the desired product, is moderately soluble in water while the other reagents are very soluble in water. So, by rinsing the crystals with cold water, any impurities and leftover reagents will be rinsed away. However, if cold water is not used, the crystals could dissolve into it and some of the crystals will be lost, therefore affecting the percent yield.

In the experiment, a few problems occurred. One issue was that, as seen on the first TLC, the reaction was not complete. The TLC displayed, 1 spot in the reference lane, 3 in the co-spot lane, and two in the sample lane. This indicates that the reaction was not complete, however, it was around halfway complete. The TLC shows that there wasn't any starting material left in the reaction mixture, there was, however, some intermediates present along with the product. This means that the reaction should have been left to mix for a little longer. This will affect the purity of the product, but since it is at least halfway complete and does have some products present, it will not affect the purity by much.

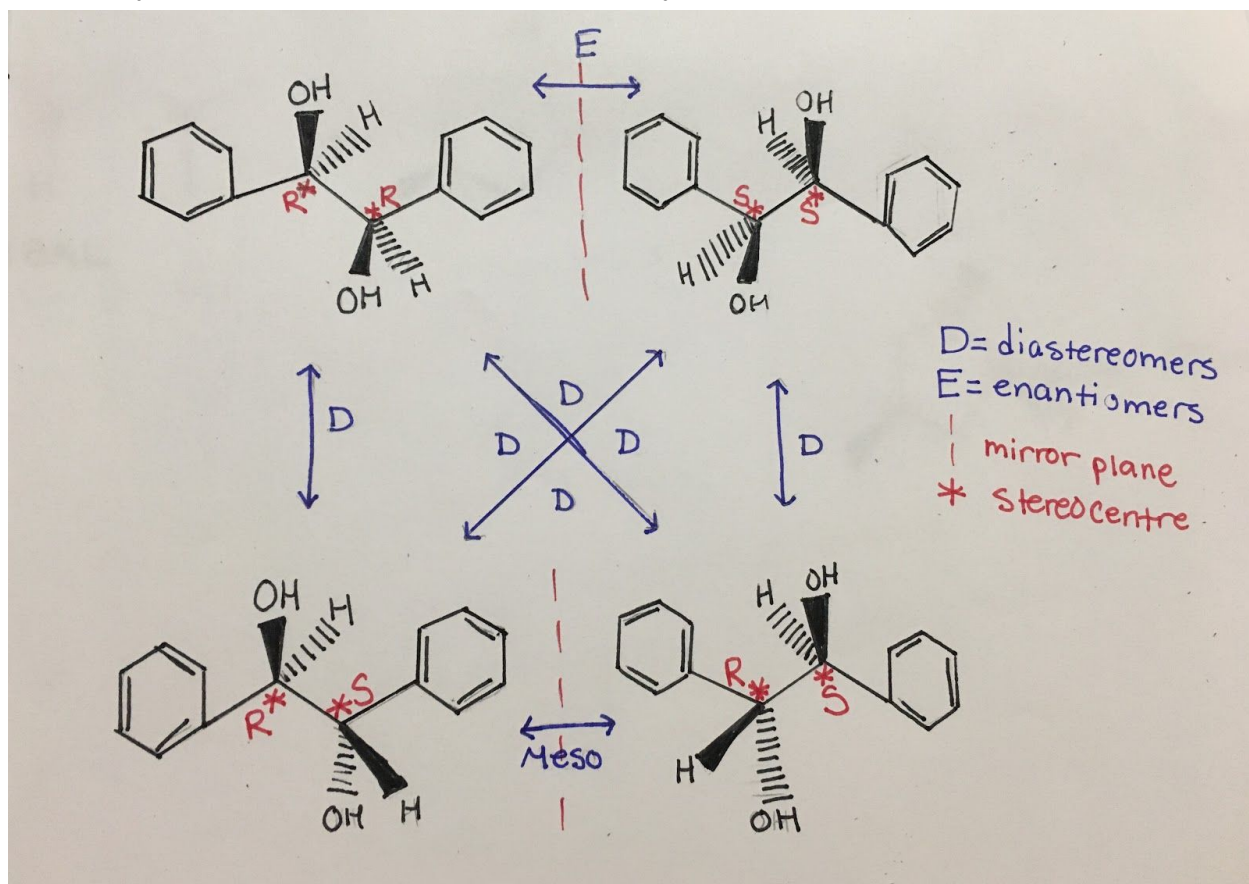
The other error that occurred was the percent yield. The calculated percent yield of crystals obtained was 112%. It is suspected that this occurred because the crystals were not completely dry, and that when they were rinsed with water, the crystals clung to it because they are so polar, making the mass much heavier than it should have been, therefore increasing the percent yield. This can be avoided by allowing the suction filtration of the crystals to run for several hours to ensure they are completely dry. However, due to time constraints in the lab, there was not enough time to completely dry them, resulting in an obtained mass of 1.16 g.

By analysing the TLC for the end of the experiment, it is clear that the reaction was complete by this time. As there is only one spot in the sample (Reaction mixture) lane. However, as the reaction mixture dot and corresponding dot in the co-spot lane are both on the starting line of the TLC, it is clear that the mobile phase (1:9 EtOAc) is not polar enough and the applied spots are hardly eluted, and are doing more hydrogen bonding with the silica than they are with the mobile phase. To solve this problem, a more polar eluent could be used.

Part B of the experiment was to build models of each of the benzoin products. Of these products, the major and minor products can be predicted. In each of the molecules the hydroxyl group is moved between positions on the corresponding carbon. This gives 4 possible products. To determine the major and minor products, any strain between molecules must be considered. Steric strain is the energy produced when two large molecules are forced to take up the same space. In the benzoin molecule, there is no steric strain from the phenyl groups affecting hydroxyl groups. The steric strain lies only between the hydroxyl groups bonded to adjacent carbon atoms, as shown below using newman projections.



The newman projects are looking down the C2-C3 bond. The first two newman projects display steric strain between the two hydroxyl groups on the left and right side of carbon-carbon bonds. It is because of this steric strain that these two products are less likely to be formed because the condition is undesirable as it is less stable. The last two projections show the two products that are more likely. They are more likely because the hydroxyl groups are not interfering with each other and do not have to compete for the same space, thus, reducing the energy and increasing the stability of the molecule. A stereochemical analysis for all products is seen below.



The bottom two compounds, the (2R,3S) and (2S,3R) are the two more stable products that will be formed, shown with complete stereochemistry. These two molecules are also meso compounds, as they are superimposable on their mirror image (each other) even though they have two chiral centres.

Conclusion

The major products of benzoin are the (2R,3S) and (2S,3R) isomers of benzoin, and the percent yield of the recrystallization was 112% meaning that the crystals were still holding some water, and the yield was artificially high.

Raw Data

Hope's Data:

Exp. 4

Feb 27

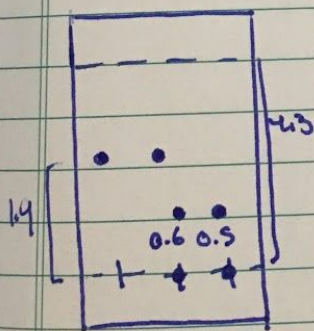
Benzil: 1.00g
Dichloromethane: 5ml
Ethanol: 5ml

Benzil + dichloro + ethanol = yellow transparent
Stirred for:

Borohydride

- 1: 0.1g → less yellow, some precipitate
- 2: 0.1g → almost clear w yellow tint
- 3: 0.1g → same

After stirring for 10 minutes the solution turned remained almost clear
• Some bubbling



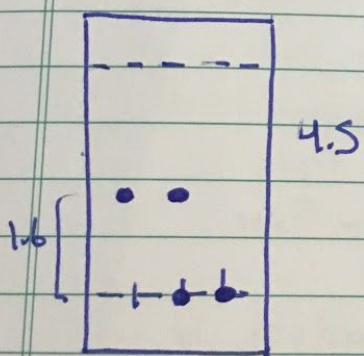
reference: benzil in dichloro
sample: reaction mixture

QRS

When added 10ml 80° water there was
intense bubbling
almost clear

after 20ml water

- layer of white precipitate formed
white gently boiling



DRS

paper weight - ~~0.42g~~ 0.42g
paper + crystal - 1.56
crystal:

Feb. 27

Exp. 4

Mass benzil = 1.00g

Was yellow (benzil, dichloro ethane) and see through borohydrate

~~0.10, 0.10, 0.10~~

As sodium was added,

Dichloro = 5.0 mL

Solution lost it's colour

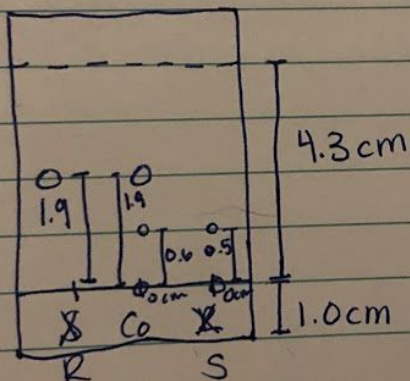
Ethanol = 5.0 mL

gradually and precipitated

Borohydrate : 0.1g, 0.1g, 0.1g

Stirred for 10 min after: murky yellow, white precipitate foaming after was taken off stir plate

TLC #1



*White balls → OH bands

S: Reaction mixture

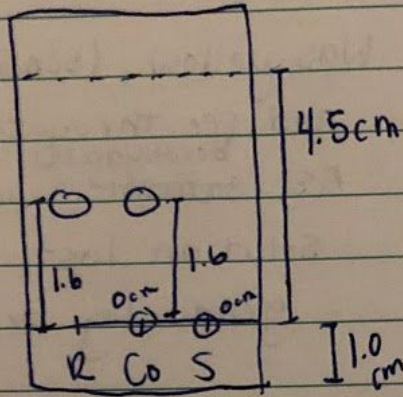
C₀: R + S

R: benzyl + dichloro

Heating up: solution foamed up, then foam went down

Q R S

Feb 27



R: benzil dissolved in dichloro

Co: R + S

S: Salt and CH_2Cl_2

Paper = 0.42 g

Paper + salt = 1.56 g

R R S S

COURSE: CHM 1321 TA Name: Daliane Regis
YOUR NAME (PRINT): Hope Boyle SIGNATURE: Hope Boyle

CONFIDENTIAL PEER EVALUATION FORM FOR EXPERIMENT 4

Each team member must submit one assessment form evaluating each **other** member of the team.
Teams will consist of 2 (max 3) members for reports.

You may edit this form.

Do not share or discuss the contents or possible contents of this assessment with others.

In assessing the work of your fellow team members, consider the following aspects:

- Quality of work
- Contribution to the work as a whole
- Ability to get along with others
- Improvements when asked to correct

Team member name	Comments	Grade (/5)
Hannah Prozok	Great partner	5

A - Excellent (5) B: Great (4) C: Good (3) D: Fair(2) F: Poor (1)

Note: Do not evaluate yourself on this form