Formal Lab – Experiment 4 CHM 1321 z10

Experiment Title: Experiment 4: Stereochemical Analysis of the Reduction of Benzil

Author's Name: [redacted]

[redacted]

Submitting Author's Partner: [redacted]

TA (Demonstrator)'s Name: [redacted]

Date Experiment Performed: 05/03/20

Date Experiment Submitted: 12/03/20

Introduction:

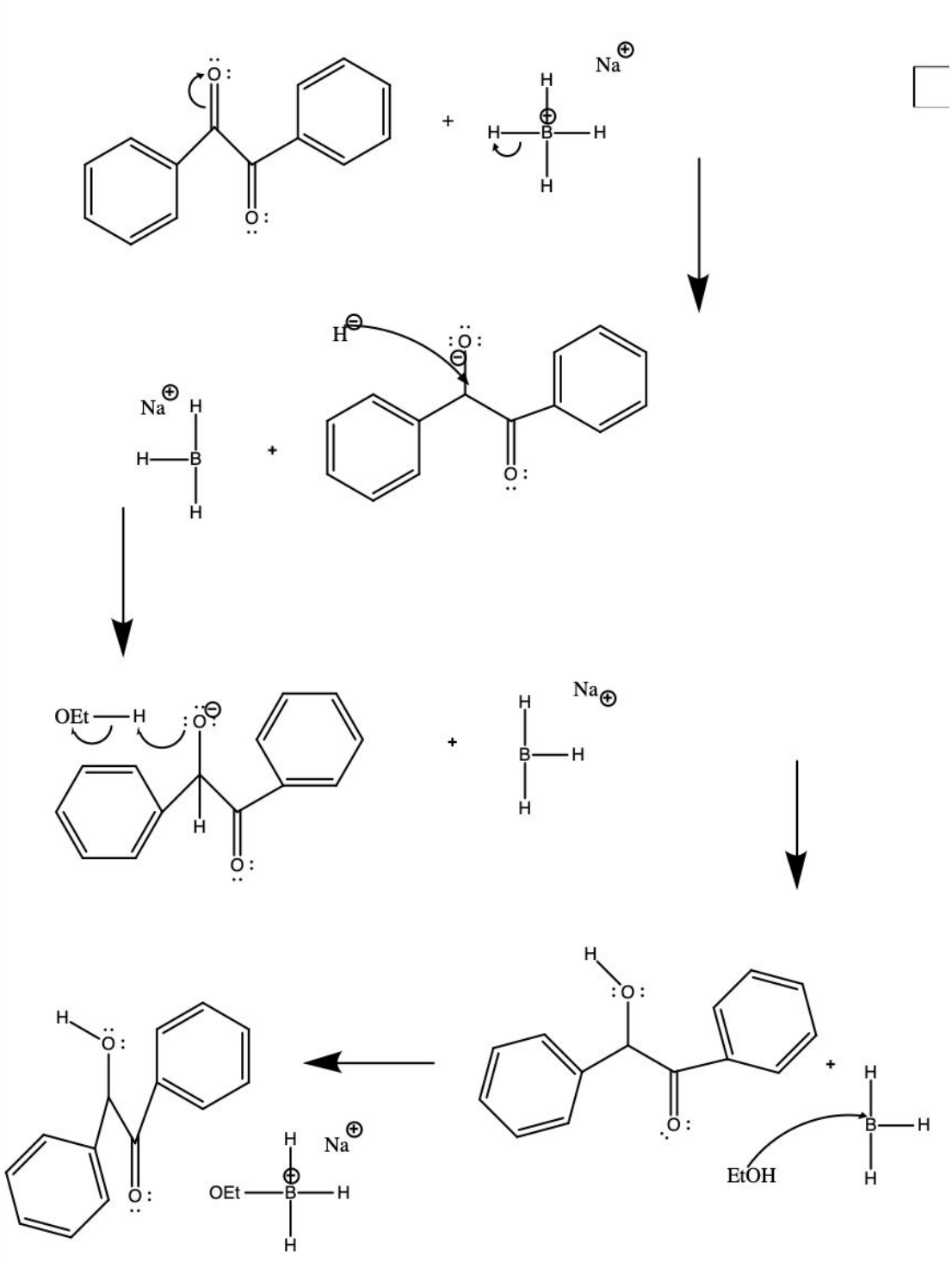
In order to understand the reduction of benzil performed in this experiment the concept of oxidation and reduction must be understood. When a substance loses electrons it is referred to as oxidized and a substance that gains electrons is considered to be reduced. In organic chemistry hydrogen atoms are used to explain these terms. In an oxidation the number of hydrogen atoms on a molecule decreases and for a reduction the number of hydrogen atoms increases. Many reductions involve interactions between nucleophiles (molecules with a tendency to donate electrons to an electron poor site) and electrophiles (molecules with a tendency to accept lone pairs of electrons from an electron rich site) or electrophilic pi bonds.

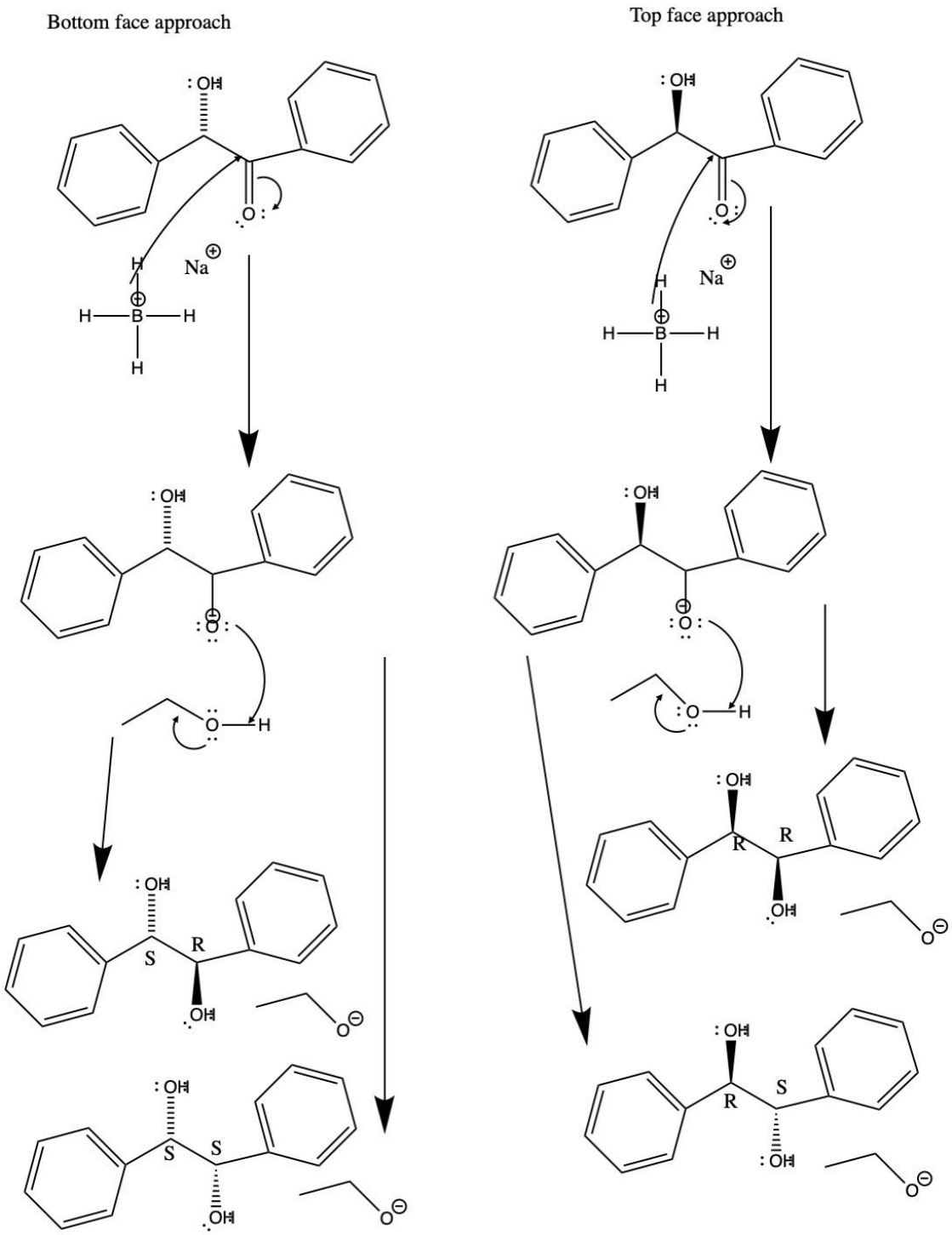
Stereochemistry is also important to understand, when reducing a carbonyl group to an alcohol an sp2 hybridized carbon is converted to an sp3 hybridized carbon and if two groups on the carbonyl differ then they are stereogenic (and contain different stereogenic centers). In this experiment the starting material benzil (which has no stereoisomers) was converted into benzoin which has two stereogenic carbons (four stereoisomers). Out of these stereoisomers two will be enantiomers, meaning they are non superimposable mirror images of each other (source 1). The other two benzoin products have anti-stereochemistry, these compounds are the same simply rotated and are called meso compounds.

Recrystallization is also an important concept in this experiment. It is a method of purifying an organic compound. Recrystallization works by using the different solubilities of the compound being purified in solvents of varying temperatures (typically hot and cold) followed by filtering the solution to remove impurities (in this experiment using gravity and vacuum filtration) and then by allowing the compound to crystallize by cooling and drying and removing the crystals. However, this method is not effective if the material is very impure. The solvent is the most important factor in recrystallization. The solubility has the largest impact, the best solvent will have a high solubility in the solvent at a high temperature and low solubility at a low temperature. A good solvent will not readily dissolve in high quantities; it must be added in small portions and maintain boiling for it to dissolve. The solvent should also easily remove form the crystal. It is not desired that small amounts of solvent stick to the crystal after filtering, this is removed by drying the crystals. When performing the cooling stage it is also important that the cooling be done slowly as quickly cooling may lead to a larger production of impurities (crystals grow around impurity pockets). Another separation that may occur is the separation from the solution as liquids this is called oiling out. This is caused by the compound having a low melting point or when the molecules molecular structure can make crystal formation difficult. If a single solvent does not give an effective recrystallization then use a mixed solvent or solvent pair (to miscible liquids). Recrystallization does not remove all of the compound from the solution.

The reaction mechanism also plays a crucial role in understanding the experiment taking place. Below is the reaction mechanism for the experiment performed.

Mechanism for the reduction of benzyl when sodium borohydride is added to an ethanol solvent:





Due to a nucleophilic attack of the hydride which is from the sodium borohydride there is a reduction of the carbonyl carbon attached to the benzene ring(s). The carbon oxygen pi bond will then break and form a negative charge on the oxygen which will attract the hydrogen atoms

residing on the ethanol solvent molecule. As one of the carbonyls on benzoin has been protonated it has become benzoin as a result. The second carbonyl group on the benzoin can be reduced using the same set of steps which will result in the creation of the final product, hydrobenzoin. Some of the bi-producs or reaction intermediates include the sodium ion and a borate ester hydride.

Procedure:

Refer to source 2: *Experiment 4: Stereochemical Analysis of the Reduction of Benzil*, Department of Chemistry, University of Ottawa (2019)

Observations and Results:

OBSERVATIONS:

Before the reaction:

- Ethanol was a clear and colourless liquid
- Dichloromethane was a clear and colorless liquid
- Benzil was a yellow powder

During the reaction

- Benzil dichloromethane and ethanol were mixed and a yellow solution was formed. After the addition of the sodium borohydride the solution cleared up.
- When the hot water was added the solution did not return to a yellow colour, it did clear but remained colourless (unlike what was depicted in the lab manual).

After the reaction

- Sodium borohydride was a white crystalline solid

RESULTS:

Table 1: Table of Reagents for the Reaction Mixture Performed:

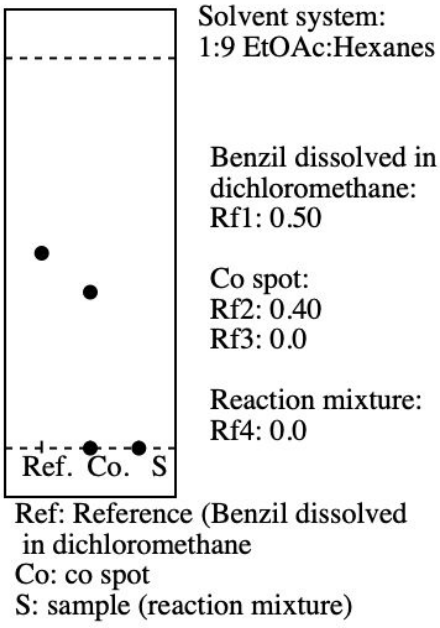
Compound	Molar mass (g/mol)	Density (g/mL)	Mass (g)	Moles (mol)
Benzil	210.23	1.23	1.00	0.0047
Sodium borohydride	37.82	1.07	0.30	0.0079
Ethanol	46.072	0.789	5.00	0.1085
Dichlorometh	84.93	1.33	5.00	0.0581

ane				

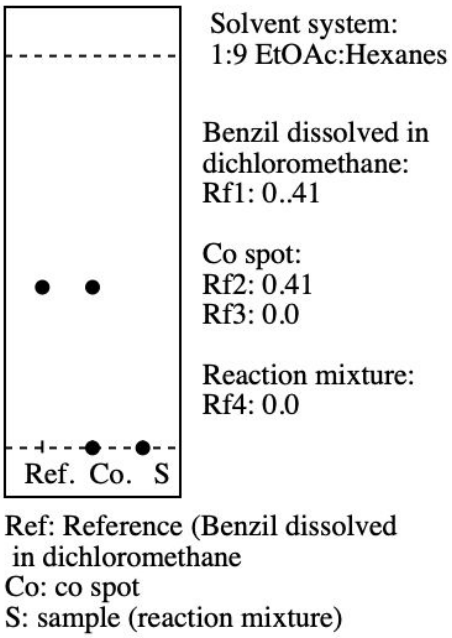
Table 1: Table of Reagents of final product:

Compound	**Molar mass (g/mol)**	**Density (g/mL)**	**Mass (g)**	**Moles (mol)**
Benzoin	212.24	1.31	NA	NA
Hydrobenzoin	214.26	1.19	2.84	0.013

TLC PLATES:



TLC plate 1



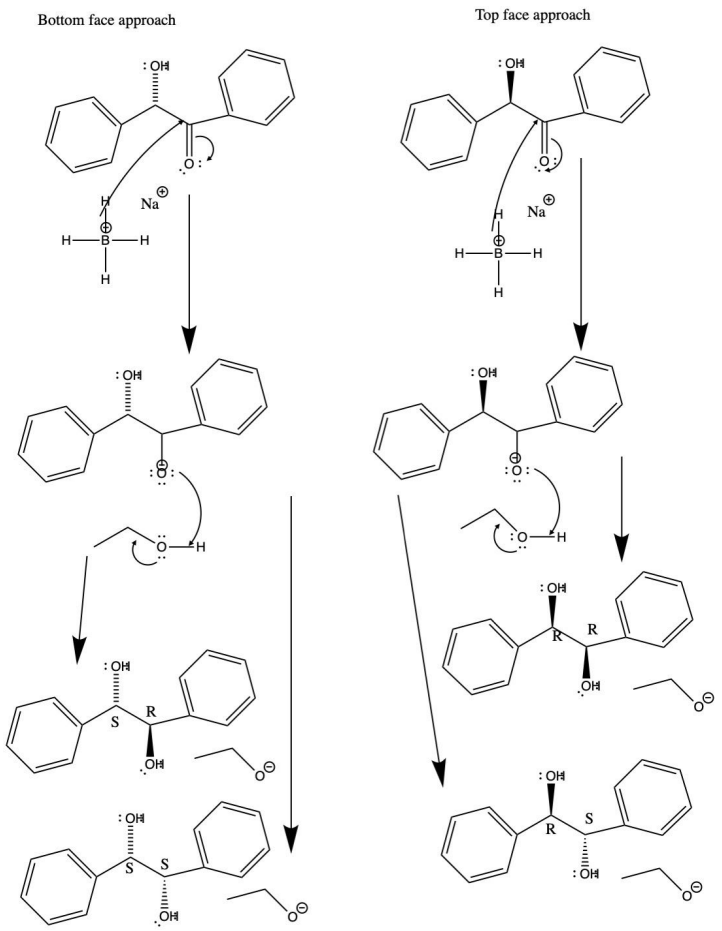
TLC plate 2

Discussion:

This experiment had a goal of observing the reduction and recrystallization of benzil. Due to a carbonyl group being reduced to an alcohol an sp2 hybridized carbon is converted into an sp3 hybridized carbon. There are also two different groups located on the carbonyl carbon. In order to cause the reduction (and purification) reaction sodium borohydride was added in three small (0.1 g) amounts (two minutes apart) to a solution containing benzil, dichloromethane and ethanol while mixing constantly. This caused the formation of hydrobenzoin. The sodium

borohydride was added in these small installments to control the heat (energy) that would be produced by the reaction and the reaction rate. This is due to the fact that it is a very strong reducing agent and is a highly exothermic substance. During this process an ice water bath was used in order to help control the temperature (heat) of the reaction as well. After allowing the flask of materials to cool to about room temperature a TLC plate was created (TLC plate #1). The TLC plate demonstrated that there was no benzil present (the initial substance), this is demonstrated by the reaction lane (Rxn).

A recrystallization and an isolation were also performed. Hot water was added to the reaction mixture in parts, this caused the acid work-up to quench the reaction which would deactivate any of the reactants that may have been left over, in other words to remove the excess hydrogen atoms from the $NaBH_4$ which had not reacted. . When the hot water was added there was intense bubbline that occured. This was caused by hydrogen gas being produced. As the solution cools the solubility of the substance began to decrease and as a consequence crystals of pure product were produced (precipitate). The crystals were then filtered with gravity and then using a vacuum filtration to remove any other solution or impurities. The crystals were then left to dry before they were massed. Finally, a sample of the crystals was dissolved in dichloromethane and spotted on a second tlc plate (TLC plate #2) to determine the purity of the product. However, the two hydrobenzoin enantiomers have very similar Rf values which makes identifying them difficult through analyzing the TLC plate. The TLC plate showed that there was no sign of benzil in the final product which would meant that there was none or very little benzil contaminating the product. There was a percent yield of 284% for the [rocut, this is unusually high and would have been impacted negatively by the crystals not being completely dried when massed, this would give the crystals a larger weight than the actual weight they would have when dried.



Part two of the lab was constructing and identifying the possible products (with different stereochemistry). The diagram above shows the formation of each. The SR stereogenic compound from the bottom faced approach and the RS stereogenic compound from the top faced approach are meso compounds. This means they are the same compound and if you rotate one of them you get the other. The SS stereogenic compound from the bottom faced approach and the RR compound from the top faced approach are enantiomers of each other as both stereogenic centers have flipped. The SR and SS, RR and RS, RR and SR and the SS and RS stereogenic compounds are all diastereomers of each other as they all have one switched stereogenic center. These compounds were constructed in the lab as seen below:

RR stereochemistry RS stereochemistry SS stereochemistry

SR stereochemistry

There are many sources of error that may have occurred during the experiment. One of these sources of error could have been that there was still some solid sodium borohydride left on the weighing paper after adding it to the solution. This would result in not exactly 0.3 g of the substance being added and therefore impacting the amount of crystals formed at the end of the experiment. Another possible source of error is that the crystals were still slightly damp when

weighing, this would have resulted in an inaccurate mass as there would be some mass of fluid included.

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? Explain your answer.*

The statement above is correct. This is because if the boiling point of the recrystallization solvent was lower than the melting point of said compound the solvent would end up vaporizing during the recrystallization process. Once the solvent becomes completely vapourized there would be no solvent remaining. If the boiling point were higher on the other hand, the crystals that are formed can melt and will form an "oil" instead of forming crystals. This means that for an effective recrystallization the solvent should have a lower boiling point inorder for the solvent to evaporate out of the solution as it dries.

2. *The solubility of a compound is 35.6 g/100 mL at 25°C and 39.1 g/100 mL at 108°C. If a saturated solution of the compound at 1080C is allowed to slowly cool to 250C, what is the maximum yield of solid crystals that can be obtained?*

Quantity dissolved in 100 mL at 108°C: 35.6 g
Quantity dissolved in 100 mL at 25°C: 39.1 g

Maximum yield cooling from 108°C to 25°C

$$39.1\ g\ -\ 35.6\ g\ =\ 4.5\ g$$

3. *A student dissolves 80 mg of a crude product in 4.5 mL (the minimum required) 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?*

There are a few reasons for which the recovery could have been low. To start by dissolving the product at room temperature (25 °C) and then cooling it would not be an effective method to recrystalize. To improve this the student shou;d have heated the solution (if it was safe to do so) to reflux as this would result in being able to dissolve the greatest amount product with the least amount of solvent. After this step is complete the student should have cooled the mixture to about 0°C. This change in temperature would result in a larger amount of product being recovered. An anti-solvent could have also been used to increase the yield. A miscible solvent that could not dissolve a product would force multiple products out of the solution which would

therefore increase the yield. Finally, the wash volume of theresult (of crystals) was quite big compared to the amount present.

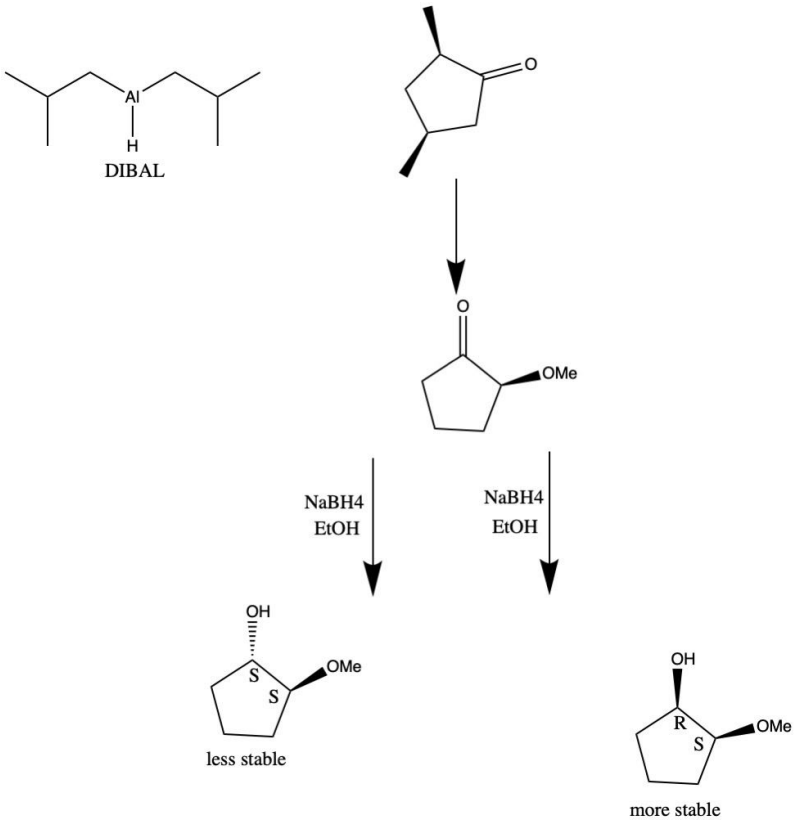
4. *When butanoic acid reacts with sodium borohydride, 1-butanol is not obtained. However, bubbling is still observed and heat is produced.*
    - *Why is 1-butanol not obtained?*
    - *What is the product of this reaction?*

1-Butanol was not obtained as the sodium borohydride was not a strong enough base/reducing agent. This means the reaction would not produce an alcohol (OH) from carboxylic acid (like it should)

The product of this reaction would have been **hydrogen gas**. This is due to the fact that the hydrogen atom interacts with the NaBH4 and these protons form butanoic acid. The gas would therefore be released by the decomposition of the reducing agent.

5. The reagent below is diisobutylaluminum hydride, or DIBAL. Like sodium borohydride, it is a source of nucleophilic hydride. Predict the configurations of each stereocenter in the product of the following reaction (with appropriate work-up) and provide a justification for your choice. Unlike NaBH4, reductions performed with DIBAL require equimolar amounts of DIBAL and substrate. Can you explain this difference?

The R,S stereoisomer is the most stable isomer and will therefore be the major structure for this reaction.



Conclusion:

This lab completed its task of observing the reduction and recrystallization of benzil. A percent yield of 284% (high as the compound had not entirely dried) was achieved. Though there were some sources of error by observing the TLC plates there appeared to be a clean production of hydrobenzoin through the use of oxidation-reduction and recrystallization techniques. There was no or little of the original product in the end result.

References:

Source 1: "Enantiomers", Dr. Ian Hunt, Department of chemistry, University of Calgary (viewed on 10/03/20) from: http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch07/ch7-2-2.html

Source 2: *Experiment 4: Stereochemical Analysis of the Reduction of Benzil*, Department of Chemistry, University of Ottawa (2019)

Appendix:

SAMPLE CALCULATIONS:

$$percent\ yield = \frac{amount\ obtained\ (g)}{theoretical\ amount\ (g)} * 100\%$$

$$percent\ yield = \frac{2.84\ g\ hydrobenzoin}{1.0\ g\ benzil} * 100\%$$

$$= 284\%$$

Theoretical yield = molar mass of product * mol of limiting reagent

$$= 214.26\ g/mol * 0.0047\ mol$$

= 1.01 g

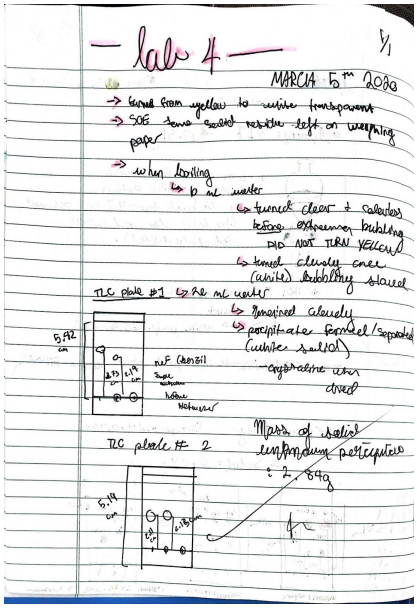
RF calculation: TLC #1 spot 1

Rf= distance travelled by spot / distance of solvent travelled

=2.73/5.42

=0.50

RAW DATA:



TLC PLATES: