**Sodium Borohydride Reduction of Benzil**

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**Introduction**:

In this experiment, the complex metal hydride sodium borohydride (NaBH4) serves as a source of a hydride ion (H-). It reduces aldehydes to 1**°** alcohols and ketones to 2**°** alcohols. Sodium borohydride reactions are relatively slow and often have low regioselectivity.1 Sodium borohydride is preferred over lithium aluminum hydride for experimentation in this lab because litium aluminum hydride can react with slightly acidic hydrogen atoms to produce highly flammable hydrogen gas, which could readily explode.2 It is also more expensive than sodium borohydride. The two main techniques used in this lab are recrystallization and melting point.

To identify a particular compound, the melting point can be used by comparison to reported literature values. Recrystallization is used once the hydrobenzoin is formed and compared to the literature values provided. Recrystallization involves dissolving a solid compound in a solvent, and as the solution cools, it slowly crystallizes out. It is important to find a suitable solvent. Once the compound is precipitated from the solution, suction filtration is used to pull the liquid away from the crystals. 2

Melting point is when the solid phase and liquid phase are at equilibrium. A Mel-Temp apparatus with a capillary tube inserted in a slot surrounded by a heating block is used to determine the melting point. To monitor the temperature in the Mel-Temp, a thermometer is inserted into a designated slot next to the capillary tube containing the solid. When unsure of the melting point, an approximate melting point can be determined by heating the sample at a rapid increase of temperature, which would be about 10**°**C per minute. While heating rapidly, one must watch the sample through a magnified eyepiece to observe when the melting occurs. A new capillary tube needs to be used for each measurement of melting point. To find a more accurate melting range, the sample can be heated to around 15**°**C below the melting point, then heated at about 1**°**C per minute. Monitor the sample through the eyepiece and record the first sight of melting of the sample and the temperature when the sample is fully melted.2

LiAlH4 is more powerful and more expensive than NaBH4. Water and simple alcohols can accompany NaBH4 to do the intended reaction. A hydride ion is transferred from the borohydride anion to an electrophilic carbonyl carbon. All four of the hydrogen atoms from BH4- can be transferred in the previously stated manner. The initially formed tetraalkylborate salt decomposes in water or dilute acid to give a product containing an alcohol.

**Table 1: Table of Reagents:**

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| --- | --- | --- | --- | --- | --- |
| Name | Chemical Formula | Molecular Weight (g/mol) | Melting Point (°C) | Boiling Point (°C) | Density (g/cm3) |
| Benzil | C14H10O2 | 210.23 | 94-96 | 346-348 | 1.23 |
| Sodium Borohydride | NaBH4 | 37.83 | 400 | 500 | 1.0740 |
| Water | H2O | 18.015 | 0 | 100 | 1 |
| Ethanol | C2H6O | 46.07 | -114 | 78.37 | 0.789 |
| Hydrobenzoin (S,S or R,R) | C14H14O2 | 214.27 | 148.5-149.5 |  |  |
| Hydrobezoin (meso) | C14H14O2 | 214.27 | 137-139 |  |  |
| Hydrobenzoin (racemic) | C14H14O2 | 214.27 | 122-123 |  |  |

**Reaction:**

Below is the reaction between sodium borohydride and benzil in ethanol, then water to form hydrobenzoin.



**Procedure**:

In a small Erlenmeyer flask, 0.051 g of Benzil was dissolved in 0.73 mL of ethanol. Then the flask was placed in the hot water bath for a couple of minutes in order for the benzyl to dissolve completely. After it dissolved, the flask was taken out of the hot water bath and let cool to room temperature. Then 0.014 g of sodium borohydride was added to the flask and the flask was swirled in order to fully mix the reactants. After 10 minutes, 0.5mL of de-ionized water was added to the mixture. Ethanol was added throughout the reaction to maintain the overall volume. The flask was then placed in the hot water bath until the mixture reached its boiling point. The mixture was then removed from the water bath and hot water was added drop wise until the product crystalized and the solution became cloudy. The solution was allowed to cool to room temperature, and then was placed in an ice bath to completely recrystallize the product. The crystals were collected using suction filtration and washed with a small amount of cold water. They were left to dry while on suction. The mass and melting point range of the dry product was measured and recorded.

**Results:**

The reduction of benzil yielded 0.025 g of hydrobenzoin product, and the melting point of the product was measured and found to be 134.4 - 135.4°C. The limiting reagent in the reaction was found to be benzil, and the theoretical yield was calculated using stoichiometry. The theoretical yield was found to be 0.05198 g. Using equation #1 the percent yield was calculated and found to be 48.1%.

Equation 1: Percent Yield

**Discussion**:

The percent yield for this experiment is fairly high; however, further heating to dissolve the benzil and allowing for complete recrystallization may have produced an increase in the percent yield. Comparing the melting point of the hydrobenzoin product to established values produced that the product is a mixture of meso and racemic chair conformations-- with the major product being the meso product. This is congruent with the expected results due to the flipping of a phenyl group when boron binds to an oxygen. This can be seen in mechanism shown in figure 1. A further possibility of error and a decreased percent yield may have resulted from the inability to remove the crystalized hydrobenzoin product from the reaction flask.

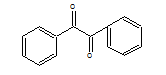
**Conclusion**:

0.025 g of hydrobenzoin product was obtained from the reaction, resulting in a 48.1% yield. Using established melting points, the conformation of the product was decided to be a mixture of meso and racemic with the major product being meso. An increased percent yield may have been obtained by allowing for further dissolution of benzil and recrystallization of hydrobenzoin.

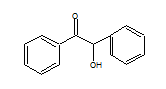
**Questions:**

1. Reduction of just one of the carbonyl groups of benzil gives a compound called benzoin. Draw the structure and give the IUPAC names of benzil, benzoin, and hydrobenzoin.

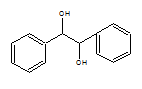
**Benzil: 1,2-diphenylethane-1,2-dione**

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**Benzoin: 2-hydroxy-1,2-di(phenyl)ethanone**

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**Hydrobenzoin: 1,2-diphenylethane-1,2-diol**

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1. Calculate the weight of sodium borohydride needed to reduce 1.00 g of benzil to hydrobenzoin.

**References**:

1 Naimi-Jamal, M. R., Mokhtari, J., Dekamin, M. G., & Kaupp, G. (2009, June 5). Sodium Tetraalkoxyborates: Intermediates for the Quantitative Reduction of Aldehydes and Ketones to Alcohols through Ball Milling with NaBH4. *European Journal of Organic Chemistry*, *2009*(21). Retrieved February 7, 2014, from http://onlinelibrary.wiley.com/doi/10.1002/ejoc.200900352/abstract

2 Sweeting, L. M. (1998). Reducing Agents. In *Towson*. Retrieved February 7, 2014, from http://pages.towson.edu/ladon/orgrxs/reagent/reducers.htm

3 Hill, R., & Barbaro, J. (2005). *Experiments in Organic Chemistry* (3rd ed., pp. T2-E14). N.p.: Contemporary Publishing Company of Raleigh, Inc.