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Synthesis of Halogenated Glyoximes

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SYNTHESIS OF HALOGENATED GLYOXIMES

by

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ABSTRACT

Dr. Huang is a chemical engineering professor at the University of Alabama. He is interested in using alpha-Halogenated glyoximes to better understand impurity incorporation of organic additives. Various alpha-Halogenated glyoximes are being synthesized for his study. In this project, bromodimethylglyoxime is being synthesized. This is a two-step reaction. The first reaction converts diacetlymonoxime to bromodimethylglyoxalmonoxime through bromination. The product is then reacted with hydroxylammonium chloride to form bromodimethylglyoxime. Ultimately, there has been success in forming bromodimethylglyoxalmonoxime. For this reaction, solvent ratios of methanol must be proportional to literature values. However, there have been difficulties in converting bromomonoxime to bromodimethylglyoxime. There are issues separating the organic and inorganic components. There is a mass fraction collected from the reaction that contains a mixture including hexane and potentially a ketone oxime intermediate. The next course of action is to purify and identify the intermediate.

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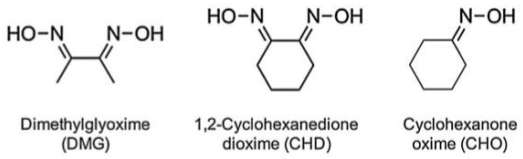
INTRODUCTION

Electrochemical deposition is the process where a coating of metal is deposited on a semiconductor through electrolysis. This technique is commonly used to link components in integrated circuits. Copper is typically used in electroplating due to its low resistance and superior fill characteristics. However, elements such as cobalt, with a short electron mean free path, have become materials of interest because they are insensitive to scaling, preventing an exponential increase in resistivity.

When filling nano trenches, electrochemical deposition should occur primarily at the bottom of the trench to ensure effective interconnects. Filling of trenches can be altered by using organic additives. Accelerators promote deposition while suppressors inhibit it. Suppressors are typically preferred in low concentration at the bottom of trenches to allow filling and are increased at the top. This distribution creates a bottom up effect where deposition is fast at the bottom and suppressed at the top. As a result, finding a proper suppressant determines the efficacy of a trench. Oxime molecules have shown a suppressing effect on cobalt electrodeposition. Our research involves the synthesis of halogenated glyoximes, which can provide potential methods of controlling electrochemical deposition of cobalt and understanding



impurity incorporation in metal films.

Figure I: depicts the molecular structures of dimelthlyglyoxime (DMG), cyclohexanedione dioxime (CHD), and cyclohexanone oxime (CHO). Glyoximes contanin a 1,2 double oxime.

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A proposed mechanism of suppression includes surface adsorption of a chelating species at a low potential. Once the ligand complex is reduced at a higher potential, the surface coverage of the chelate decreases, resulting in the breakdown of suppression. With no suppressive additive, cobalt is reduced, $Co^{2+} + 2e^- \rightarrow Co$. When a glyoxime additive is introduced, a ligand complex is formed in the form, $Co^{2+}+2L^- \rightarrow CoL_2$. [3]The complex interferes with cobalt reduction, suppressing deposition until a higher potential can be reached. At this stage, the complex is reduced, $CoL_2 +2e^- \rightarrow Co + 2L^-$, and dissociates, allowing deposition to resume. Glyoximes are able to form a more stable chelate with Co due to the two adjacent oxime groups. This will lead to stronger adsorption and amplify suppression effects. Glyoximes were found to have a faster suppression speed than mono-oximes..

Halogenated glyoximes may provide a better understanding of additive incorporation. In interconnects, copper exhibits annealing behavior, resulting in large grains. The large grains create a lower resistivity and improve the reliability of interconnects.[2] Impurities can inhibit the annealing behavior of metal films, thus increasing the resistance and inefficiency of the interconnects. Elemental impurities that have been studied for these effects include carbon, oxygen, sulfur, and chlorine for copper. Oxygen, sulfur, and chlorine inhibited the resistance drop and resulted in limited copper grain growth. [2]Chlorine had the greatest inhibition effect while oxygen had the least inhibition. The listed elements provide a limited account of impurity incorporation. It is not understood how organic molecules incorporate into films. To better understand the contributions, a halogenated glyoxime can be synthesized and studied for film incorporation. If the glyoxime includes elements with known impurity incorporation effects such as chlorine and nitrogen, these elements can be accounted for, and contributions from other

constituents can be examined. Understanding the components that produce these effects will determine how much additive is incorporated into the film.

Summary: Synthesis of halogenated glyoximes can provide effective suppressants for electrochemical deposition. Interconnects prefer filling at the bottom of trenches. Therefore, when glyoximes are added to the bulk solution, electrodeposition is accelerated at the bottom and suppressed at the top to create a bottom up effect. Glyoximes enhance suppression effects of electrodeposition by forming a stable ligand complex. The chelate binds free Co^{2+} and prevents its reduction to cobalt metal. Furthermore, halogenated glyoximes can give insight on the impurity incorporation of organic additives. The addition of a halogen group such as chlorine provides an element with studied impurity incorporation effects. As a result, it can be accounted for, allowing other components to be analyzed. Ultimately through this method, a better understanding of how additives contribute to film contamination can be formed.

METHODS

IThe objective of this project was to synthesize various alpha halogenated glyoximes. The first compound attempted was bromdimethylglyoxime. The procedure was adapted from a German scientific journal, *Chemisches Berichte.* The synthesis is a two-step reaction. In the first

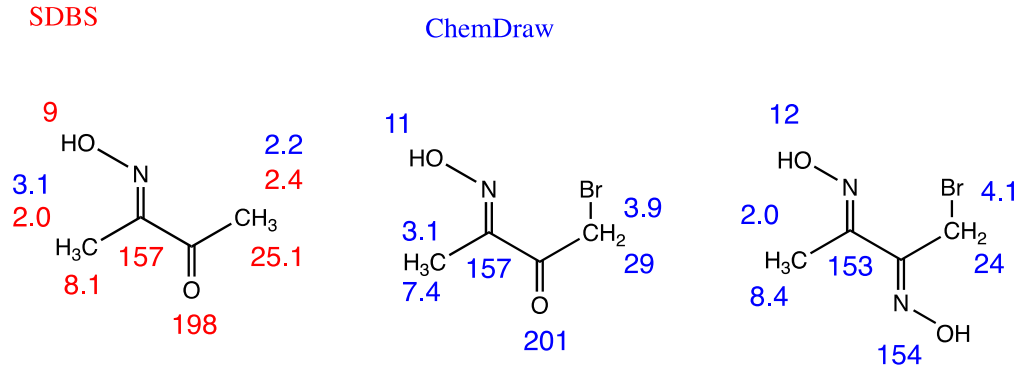

Figure II: details the chemical shifts of bromodimethylglyoxalmonoxime and bromodimethylglyoxime

reaction, diacetyl monoxime is brominated to form bromodimethylglyoxalmonoxime, a lachrymator. Subsequently,the bromomonoxime is converted to bromodimethylglyoxime through the addition of hydroxylammonium chloride. Figure Two provides the expected chemical shifts in the SDS database and Chemdraw for the products produced.

For the first reaction, the literature calls for 0.197 mol of diacetyl monoxime to be dissolved in 20 mL of methanol. The solution is then cooled to 0° C and reacted with 0.203 mol of liquid bromine. Ideally, the solution should foam, and a yellow oil should form. When the oil is iced, crystals should precipitate out of the solution. To purify the product, the crystals are placed in a hydraulic press and crystallized in hot benzene. In the second reaction, the literature calls for 0.200 mol of the bromodimethylglyoxalmonoxime to be dissolved in 120 mL of ethanol. The solution is then combined with 0.3 mol of hydroxylammonium chloride and 0.151 mol of sodium carbonate. Over time, carbon dioxide should evolve and reaction should be shaken for eight hours at room temperature, and the mixture becomes a reddish color. Once the time has allotted, the mixture is filtered, and the filtrand is washed with ethanol. The ethanol solution is then evaporated in a vacuum, and the resulting dioxime is recrystallized in 600 mL of boiling benzene. Figure Three provides an overview of the two reactions. The experimental procedures were altered from literature. Ultimately, three procedures have been attempted for this synthesis.

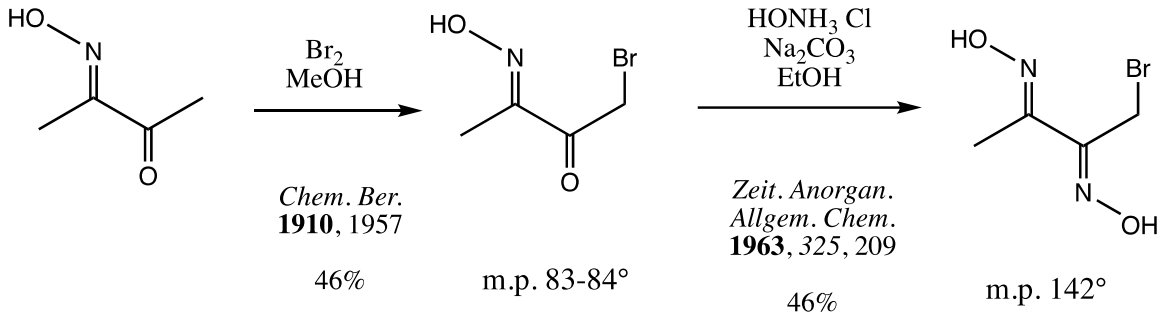

Figure III provides an overview of the two reactions in the synthesis.

In the first attempt, the bromodimethylglyoxalmonoxime would be isolated first and then reacted to form the bromodimethylglyoxime. The proportions for reaction one were cut by 1/100 to limit the effects of the lachrymator, and the purification process was modified from the literature. However , the volume of methanol was not reduced by the same factor to make the reaction easier to work with on such a small scale. In the first attempt to synthesize bromodimethylglyoxalmonoxime, 1.97 mmol of diacetyl monoxime was dissolved in 5 ml of methanol. The solution was chilled to 0° C, and 2.027 mmol of bromine was added. Immediately, the solution turned an orange and brown hue. Drops of sodium thiosulfate was added until excess bromine was reacted, and the solution turned the expected yellow color. The solution was iced for ten minutes to facilitate crystal formation. There were traces of granules in the solution, but it did not precipitate as expected. Therefore, an extraction was performed to isolate the product. The solution was dissolved in methylene chloride. Two layers did form because of the ice added previously in the solution to form crystals. The organic and aqueous layers were separated using a separatory funnel. The organic layer was rotovapped, and the residue was weighed for a mass. There was a mass, and the substance weighed 0.1759 grams. The theoretical yield was 0.356 grams, and the percent yield was 49.4%. A NMR could not be taken because the product was not soluble in chloroform D or DMSO. An IR was taken. Based

on the IR and solubility properties, it was determined that reaction did not form the bromodimethylglyoxalmonoxime, and the procedure was modified.

The second attempt would perform the two reactions consecutively . As a result, different precautions had to be taken when performing the reactions. HCl is produced as a byproduct of reaction one and could react with and consume the sodium carbonate in reaction two. To account for this interference, the expected HCl was calculated and that much molar excess was added to the required carbonate needed in reaction two. Based on the scale used in reaction one, 1.97 mmol of HCl is produced. The reaction that proceeds between HCl and Na_2CO_3 is $2HCl+Na_2CO_3$. As a result, 0.988 mmol of sodium carbonate would be needed to fully react with the HCl and should be added to the amount needed in reaction two. The procedure for reaction one as described above was repeated. However, once the bromomonoxime formed, 2.97 mmol of hydroxyl ammonium chloride and 2.5 mmol of sodium bicarbonate were added to the solution. The solution was stirred vigorously overnight. Subsequently, the methanol solution was rotovapped, and the mass collected was 0.25 g, a 64% yield. The solid would not dissolve in D chloroform or DMSO-d6. The product was added to 200 mL boiling water and filtered. The solution was placed in a crystallizing dish and allowed to evaporate to a few mL over a course of many days. After five months, the liquid had completely evaporated leaving traces of orange granules. Granules were not soluble in methanol when the bromodimethylgloyxime should be soluble in solvent. The crystals were thought to be the inorganic product that was formed as a byproduct of reaction two, NaCl. The crystals were ground and washed with methanol to collect any potential product that was trapped inside the crystal. The solution was rotovapped and the mass recorded was 0.1823 g, a 47.4% yield. An IR was taken of the crystals. The solubility of

the product and the interpretation of the spectra fortified the conclusion that the product was not bromodimethylglyoxime.

In the third attempt, the procedure was performed at a 1/10 scale instead of 1/100. Moreover, the literature proportions of monoxime and methanol were maintained to facilitate the solid formation of the product. Therefore, 19.7 mmol of diacetyl monoxime was dissolved in 2 ml of methanol. The solution was cooled to 0° C and reacted with 20.27 mmol of bromine. This time a solid did form from solution. To eliminate the HCl formed in reaction, the solid was dissolved in CH_2Cl_2 and washed with water. The organic layer was retrieved, dried with $MgSO_4$, and rotovapped. The mass of the product was 1.703 g, a percent yield of 47.8. A proton and carbon NMR was taken in chloroform-d. Based on the shifts, it was determined that bromodimethylglyoxalmonoxime was likely produced and could be used for the second reaction. For the second reaction, the bromodimethylglyoxime is formed. There was 8.53 mmol of bromodimethylglyoxalmonoxime available. The ratios of the reactions were maintained from the literature. Therefore, 8.53 mmol of the product was dissolved in 5.12 mL of ethanol. Subsequently, 12.7 mmol of hydroxyl ammonium chloride and 6.43 mmol of sodium carbonate were added. The solution was stirred overnight, and the inorganic solid was filtered. The organic solution was rotvapped, and the resulting mass was 1.0483 g, a 63.01%. The product was a red gel. The next course of action was purification. Originally, the product was to be dissolved in methylene chloride and washed with water. However, the gel was extremely hygroscopic and would adhere to every surface. Consequently, it would not dissolve in the dichloromethane. Bromodimethylglyoxime should be soluble in ether, but the product would not dissolve. An NMR was taken of the product, and it suggested that purification was needed in order to analyze the product's characteristics. The literature states that the bromodimethylglyoxime should be

recrystallized in benzene for purification. A crystallization test was performed for benzene. The product was insoluble in both room temperature and warm benzene. Various solvents were tested for crystallization including chloroform, ethyl acetate, and methylene chloride. The product was partially soluble in chloroform and ethyl acetate at room temperature, but a portion of the solid never dissolved even at higher temperatures. The insoluble component of the ethyl acetate solution was also insoluble in methylene chloride. The ratio of ethyl acetate soluble and insoluble components of the product was 0.4818 to 0.3277. Based on this ratio, the product was 59.5% soluble in ethyl acetate. A TLC was taken of the ethyl acetate soluble component using ethyl acetate as the developing solvent. The product separated into three components on the TLC plate. The separation indicated that column chromatography could be used to purify the product with the solvent. Column chromatography was performed on the product using ethyl acetate as the eluting solvent. A total of 25 fractions were collected. The ethyl acetate was rotovapped, and the masses were recorded for each fraction. From the maximum fractions, carbon and proton NMR's were taken and analyzed.

RESULTS AND DISCUSSION

The three synthesis procedures varied in proportions and the products isolated. The first attempt performed the bromination of diacetylmonoxime with a scale of 1/100 but maintained a minimum solvent volume for convenience. The product did not precipitate upon reaction as anticipated from the literature. Moreover, the product retrieved did not dissolve in chloroform d or DMSO to take an NMR, but an IR was taken. The spectrum had the expected peaks for carbonyl, alcohol, and oxime group. However, the peaks were not very prominent, suggesting that it was not the desired product bromodimethylglyoxalmonoxime, and could not proceed to the next reaction. In the second procedure, the objective was to react the diacetylmonoxime

directly to bromodimethylglyoxime. The crystals formed were methanol insoluble and unable to dissolve in the chloroform d or DMSO for NMR. It was postulated that the desired product polymerized. Potentially, the OH group on the oxime performed an S_N2 reaction on the bromine. The IR was taken and can be seen in Figure 3.

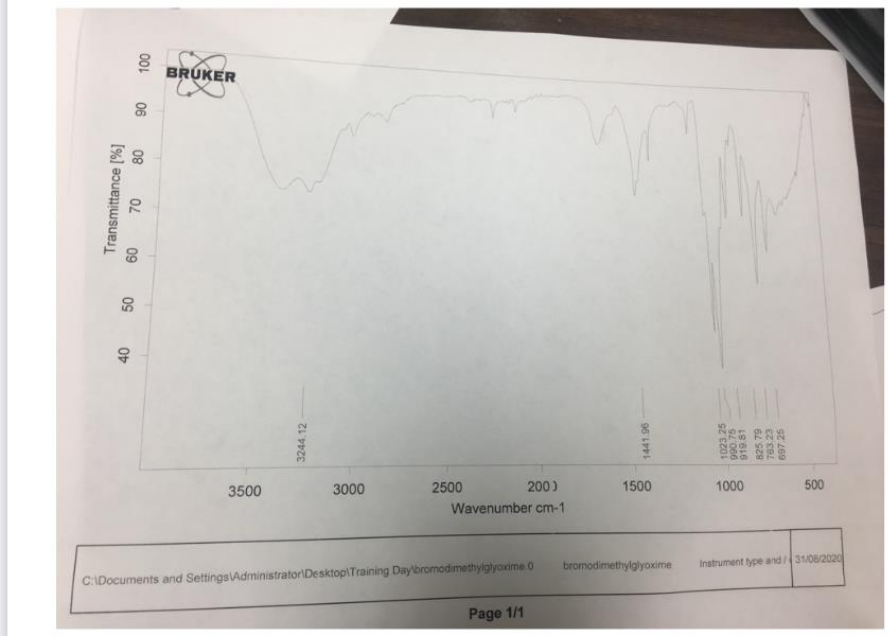

Figure IV The IR spectra taken of the crystals of the product from the second procedure.

The expected frequencies for bromodimethylglyoxime would be 3300 for the OH group, 1570 for the C=N group, 1100-1259 for the N-O, and 600-700 for the C-Br. The polymerized alternative of the product would have the same frequencies but C-Br vibration would be replaced with C-O vibration at 1050-1150 and a less prominent OH peak. Based on the IR taken, there is the broad OH peak at 3300 range and a small peak at the C=N at 1570. However, there are minimal peaks for the C-Br, N-O, and C-O stretches. These factors in addition to the product being insoluble in organic solvents lead to the conclusion that it was not the desired product. For the third procedure, the reactions are performed seperately once again. However, the scaling was

increased to 1/10 proportions from literature were extended to the solvent, methanol. With these changes, the first reaction proceeded in the expected fashion. Upon the addition of bromine, the solid immediately precipitated, and the collected solvent could now dissolve in chloroform d for the NMR. A proton and carbon NMR was taken and can be seen in figure 4 and 5.

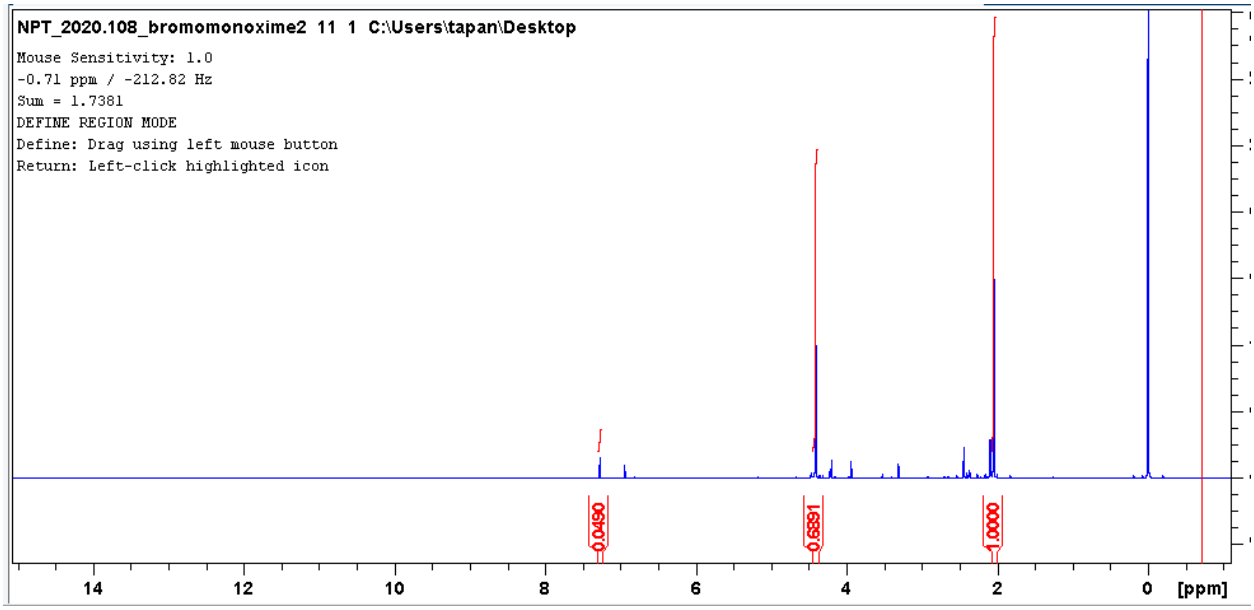

Figure V: is the proton spectra of the crude product for procedure 3 reaction one.

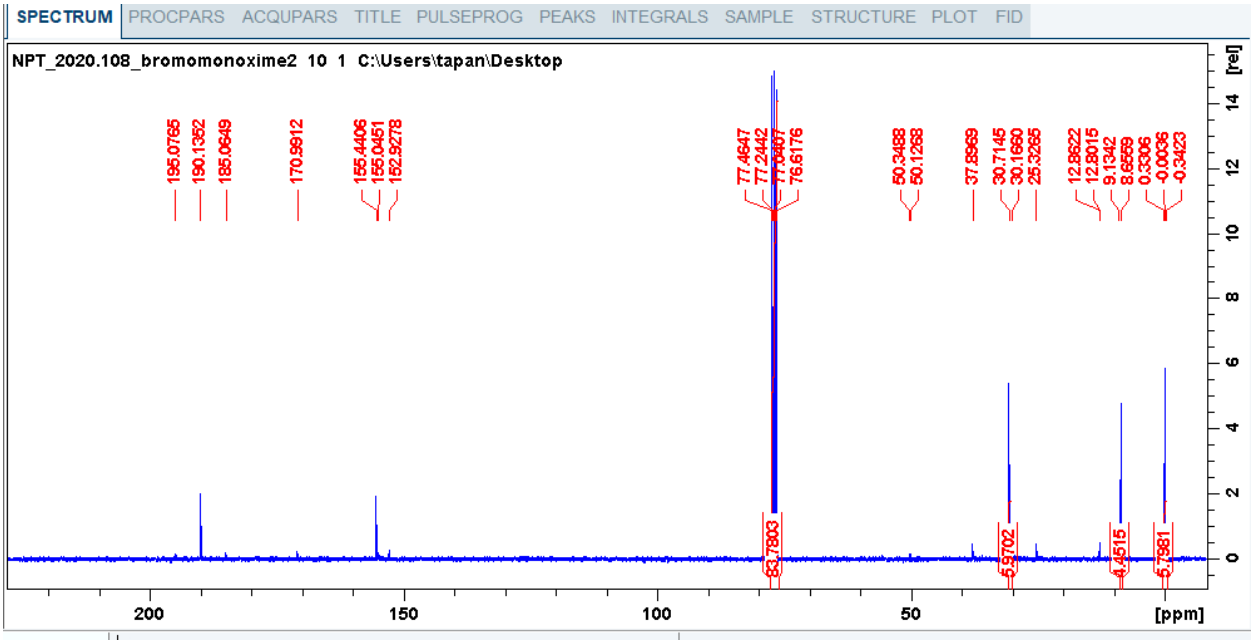

Figure VI: is the carbon spectra of the crude product for procedure 3 reaction one.

For the starting material, distinct shifts include the methyl groups at 2.0 and 2.3 ppm. In the carbon NMR, the methyl group adjacent to the ketone has a shift at 25 ppm. In the experimental NMR, there is peak at 2.0 ppm, but the carbon NMR has a minimal peak at 25 ppm, suggesting that the starting material has reacted. For the bromodimethylglyoxalmonoxime, the predicted proton shifts include 3.1 and 3.9 ppm for the methyl groups. There is a shift at 4.4 ppm that could be the CH_2-Br shifts, and there is a shift at 2.0 ppm. Although ChemDraw predicts a shift at 3.1 ppm for the methyl alpha to the oxime, the actual shift is measured at 2.0 ppm for the SDS database. There is broad peak that extends from 8 to 9 ppm that could be indicative of the oxime group. In the carbon NMR, there are shifts at 190 and 155 ppm that can correspond to the predicted carbonyl and C=N group shifts at 201 and 157ppm. The CH_2-Br is predicted at 29, and there is shift at 30 ppm. For the methyl group, there is a peak at 9 ppm that correlates to the expect shift at 7ppm. Based on these factors, it was concluded that the desired product ,2, was produced and could be used for the next reaction. This suggests that the solvent ratios contribute to the success and ease of the bromination of diacetyl monoxime.

For the second reaction, an NMR was taken of the crude product collected and can be seen in Figure 7.

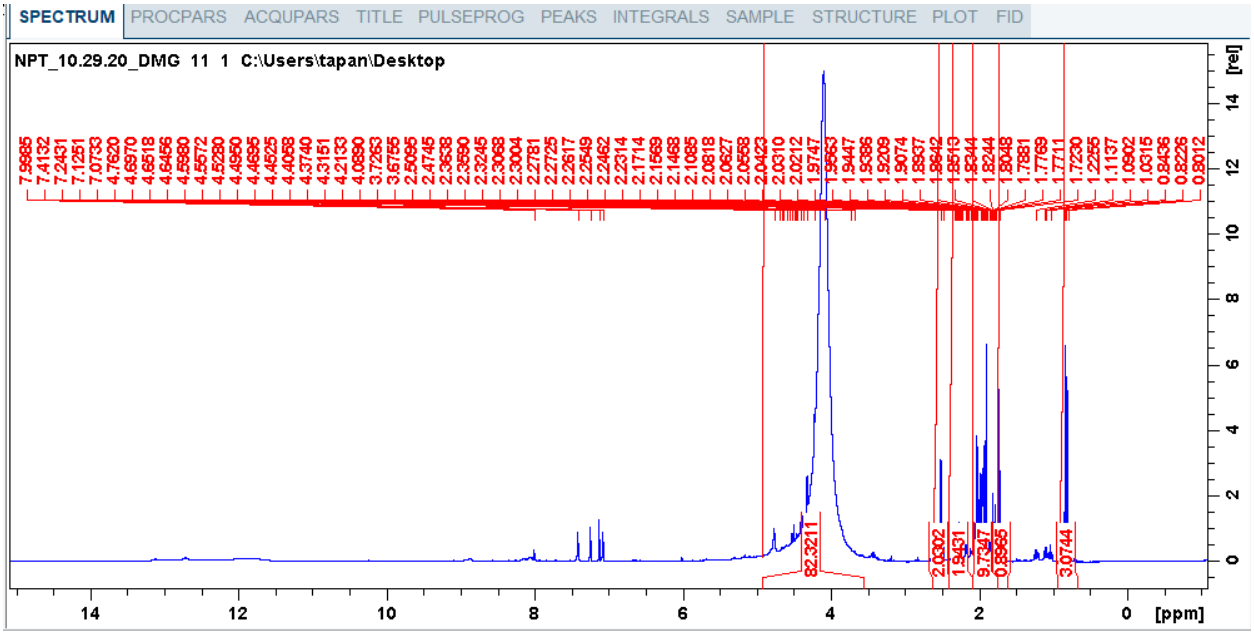

Figure VII: is the proton spectra of the crude product from procedure three reaction two.

The spectrum displayed convolution of peaks and was not readily discerned for chemical shifts and functional group assignments. It was postulated that the product could have formed an array of stereoisomers that were producing various signals. As a result, the product was placed in chromatography column, and the mass fractions collected. The mass per fraction plot can be seen in Figure 8. It should be noted that scale would fluctuate and read less mass than the original flask for some fractions. As a result, these fractions were recorded as a zero mass.

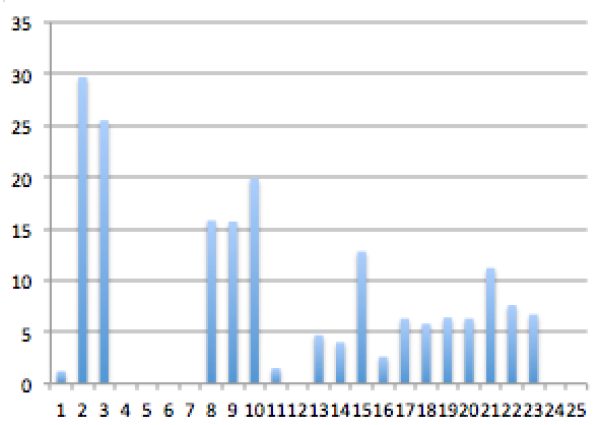

Figure VIII: Mass(mg) versus Fraction

Fractions 2, 10, 15, and 21 were the maxima of the masses, and the NMR's were taken of the fractions. The proton and carbon NMR's for the fractions can be seen in Figure 9, 10, 11, 12, 13, 14, 15, and 16. Fraction 2 was dissolved in chloroform d while 10, 15, and 21 were dissolved in DMSO.

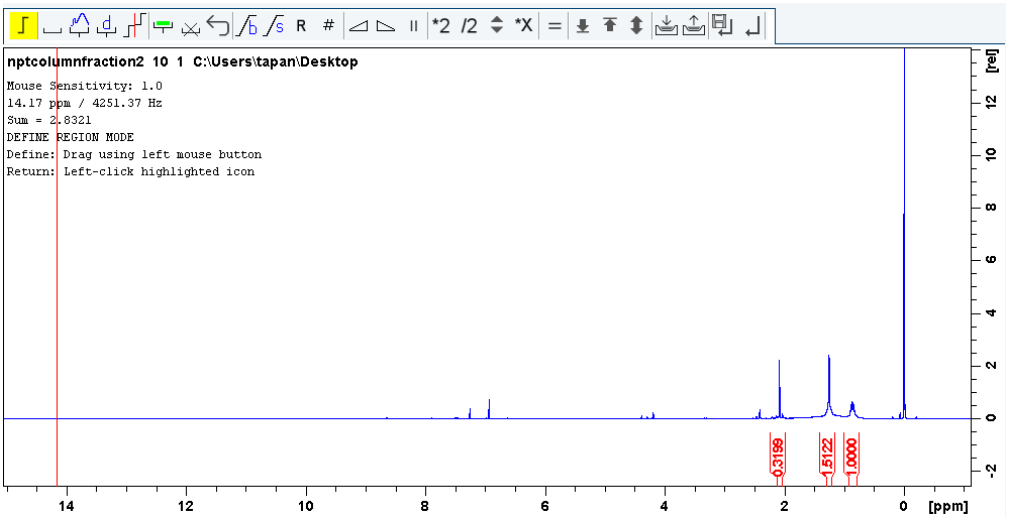

Figure IX: is the proton NMR of fraction 2

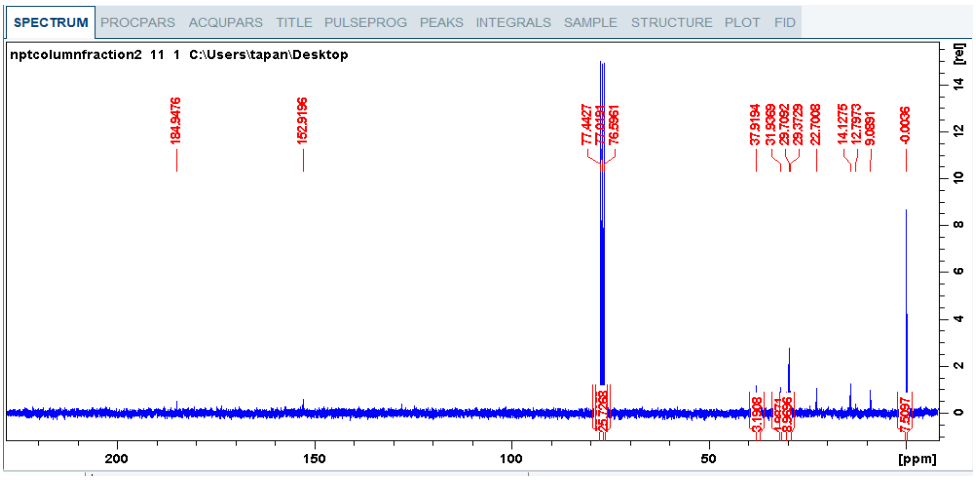

Figure X: is the carbon NMR of fraction 2 for reaction 2

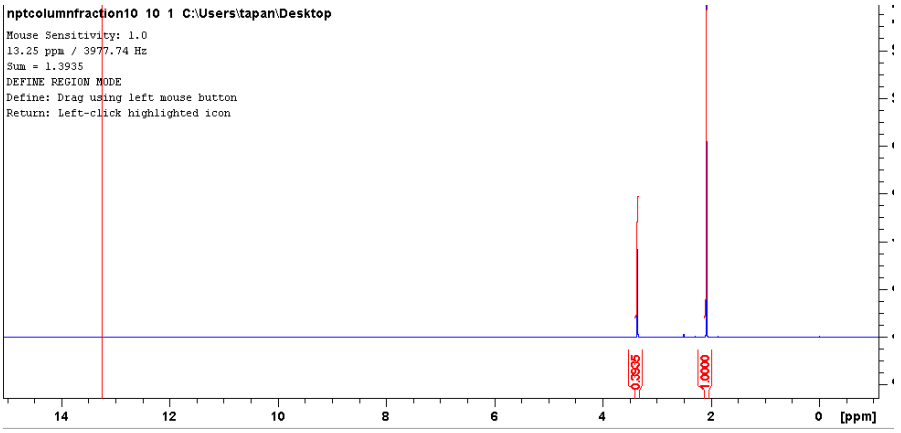

Figure XI: is the proton NMR of fraction 10 for reaction 2

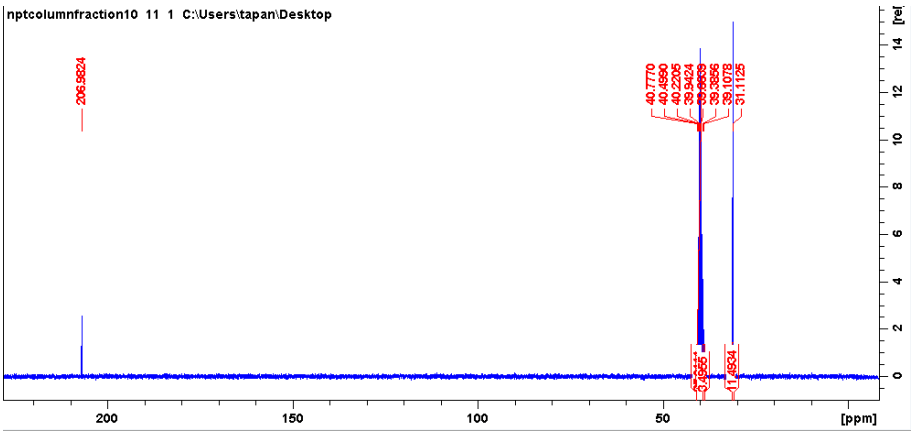

Figure: XII is the carbon NMR of fraction 10 for reaction 2

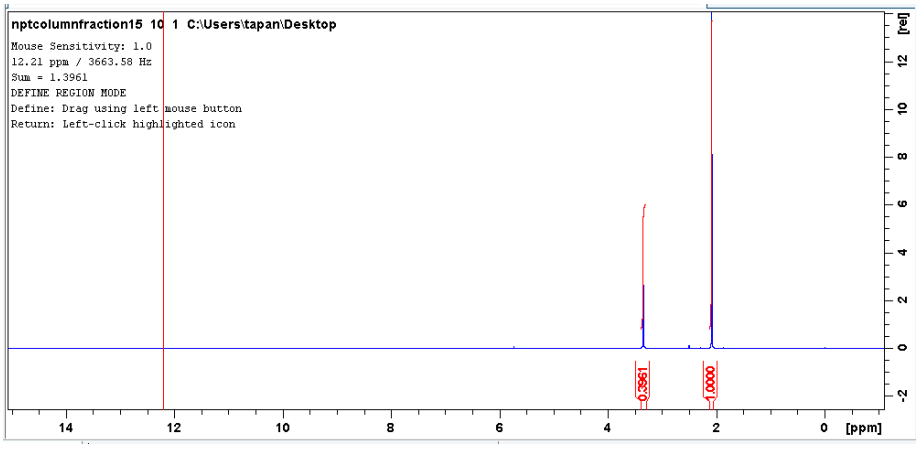

Figure XII: is the proton NMR of fraction 15 for reaction 2

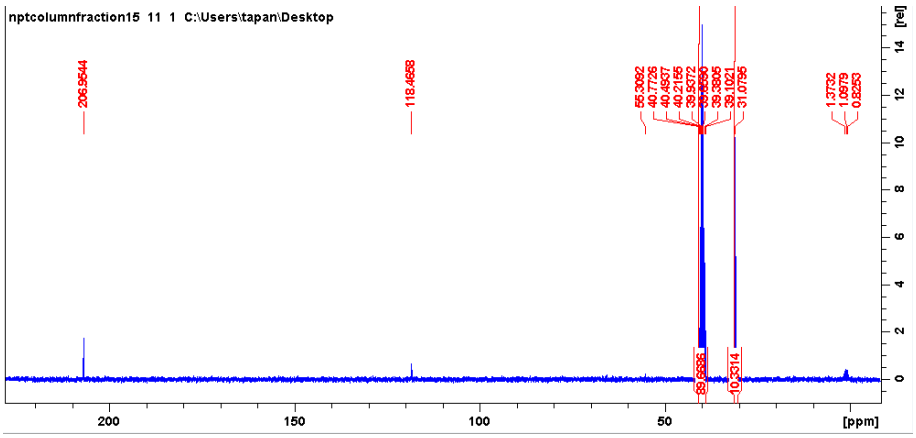

Figure XIV: is the carbon NMR of fraction 15 for reaction 2.

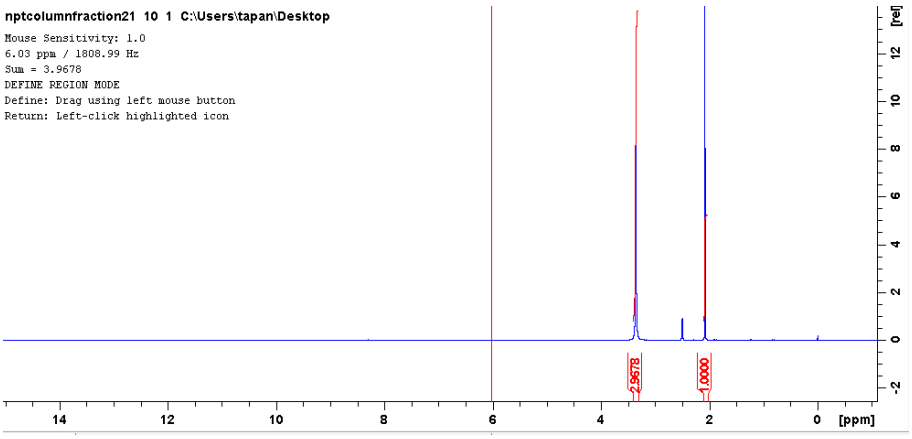

Figure XV: is the proton NMR of fraction 21 for reaction 2

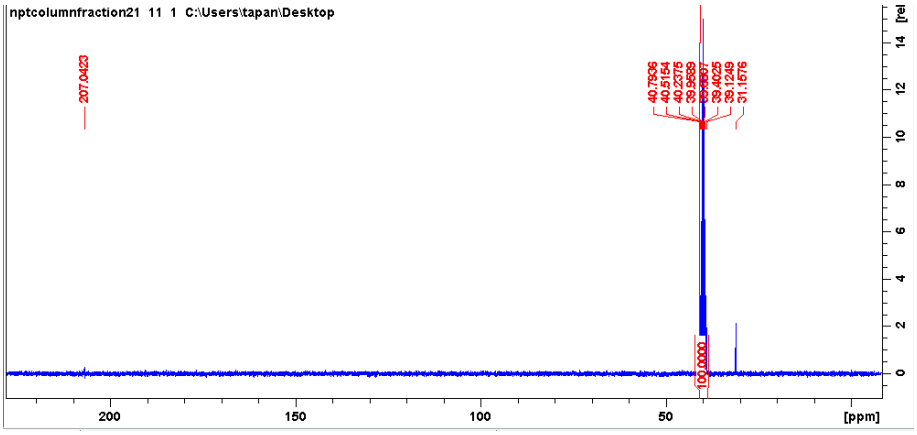

Figure XVI: is the carbon NMR of fraction 21.

Fractions 10, 15, and 21 have the same proton NMR. The shifts at 2.1 and 2.5 ppm are acetone and DMSO respectively. There is a shift at 3.4 ppm that could potentially be water. The carbon spectra are the same for fractions 10 and 21. There are shifts at 207 and 40 ppm that are acetone and DMSO, but no other signals. For fraction 15, the carbon spectrum also has acetone and DMSO shifts. In addition, there is a peak in the alkene region at 118 ppm. Ultimately, the spectra for these fractions suggest inorganic products or components that are not indicative of the desired product. However, fraction 2 seems to contain a mixture. There are 5 peaks in 20-40 regions that would be expected for the CH_2-Br group. There is carbonyl shift at 184 ppm and C=N-OH at 153 ppm. These shifts are different from the starting diacetyl monoxime which has its ketone shift at 198 and its oxime shift at 157 ppm. At the same time, the fraction is not the bromodimethylglyoxime because of the carbonyl shift. The proton NMR contains the expected methyl shift at 2.0 ppm and a trace signal at 4.0 ppm that could be CH_2-Br. The shifts at 0.9 and 1.3 are indicative of hexane, and are also exhibited in the carbon spectra at 14, 23, and 32 ppm. The second fraction could contain a ketone oxime intermediate from the reaction.

CONCLUSION

alpha-Halogenated glyoximes are being synthesized for Dr. Huang at the University of the Alabama. Halogenated glyoximes serve as effective suppressants for electrochemical deposition and provide insight in impurity incorporation of organic additives. In this project, bromodimethylglyoxime is being synthesized. This is a two-step reaction. The first reaction converts diacetlymonoxime to bromodimethylglyoxalmonoxime through bromination. The product is then reacted with hydroxylammonium chloride to form bromodimethylglyoxime. Ultimately, there is a viable procedure to form bromodimethylglyoxalmonoxime. For this reaction, solvent ratios must be proportional to the recommended values in the literature to

facilitate product formation. However, there have been difficulties in converting bromomonoxime to bromodimethylglyoxime. Isolating the organic product from the inorganic components is a primary issue. There is a mass fraction from the reaction that contains a mixture. One of the components has characteristics of a ketone oxime intermediate. In the future, the fraction should be purified in order to isolate the intermediate and identify the compound.

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