A Three-Step Synthesis of Azo Dye

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Abstract

Organol brown azo dye was synthesized and altered with functional group conversions to see the effect it would have on its color. This allowed for the testing of what reactions can be used to create new variations of azo dyes. Azo dyes are organic compounds that have a R-N=N-R functional group, and are commonly used in dyeing materials like clothing. In total three steps were completed to synthesize and alter organol brown azo dye. In order to create organol brown dye 1-napthol was reacted with analine, sodium nitrate, and silica gel. The second step converted the alcohol functional group of organol brown into a ketoester functional group. The final step of this process converted an alpha hydrogen on the keto-ester to a bromine using a photoreaction. After each step changes in UV max were recorded to see how alterations in the dye affected color. The final step was attempted using hexane instead of chloroform in order to make this process greener. This change was more cost efficient, equally effective, and less hazardous to humans and the environment. The information collected in this study will be useful for finding new ways to create azo dyes using more green processes.

Introduction of Azo Dye

Azo dyes were one of the earliest forms of chemistry used and are still commonly found in products such as textiles and paints. Throughout history, the use of dye in clothes to make colors richer was a symbol of wealth. The diazonium intermediate allows for the addition of many functional groups, which change the properties of the dye and in turn change the color of the dye. While it is possible to create many functional groups from the diazonium compound, we chose to create the organol brown dye, which dyes several materials orange. A diazonium compoud was synthesized from an amine, water and silica gel. 1-Naphthol was used with the diazonium compound to synthesize Organol Brown dye. A beta ketoester was added onto the compound using ethyl acetoacetate in order to make a ring structure consisting of a double bond and an ester. Chloroform, N-bromosuccinimide (NBS) and a catalytic amount of benzoyl peroxide was added to add a bromine onto the ring structure without compromising the double bond. In order to make this three step synthesis green, it was intended to use hexane in place of chloroform. Hexane is more cost effective and less hazardous to the environment than chloroform.

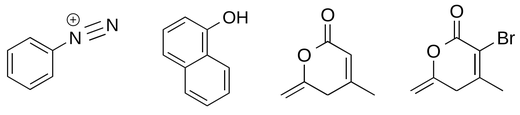


Figure 1. Functional groups used in three step synthesis of Azo dye

Background on Green Chemistry Step

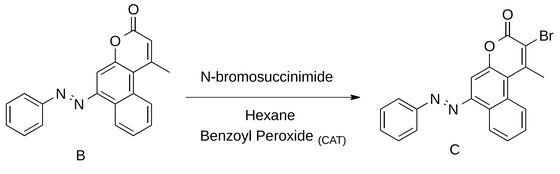
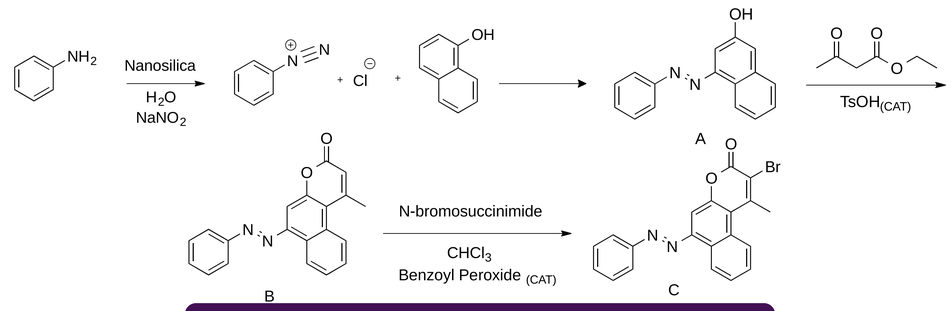


Figure 2. Proposed green step using hexane

Hexane is an alkane consisting of a six-carbon chain, mainly used because it is cheap, relatively safe, unreactive, and is an easily evaporated non-polar solvent. N-hexane is commonly used as a special-purpose solvent and cleaning agent (degreaser) in the textile industry. N-hexane is also commonly used in the printing industry as a cleaner and as a component of some inks and rotogravure printers.

Synthetic Scheme



IR, UV, and NMR Data

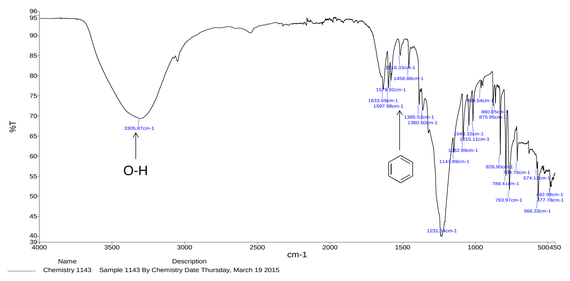


Figure 3. IR analysis of product A

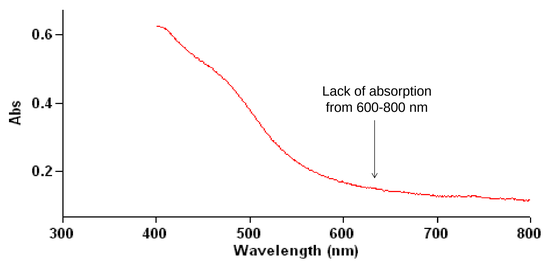


Figure 4. UV-Vis analysis of product A

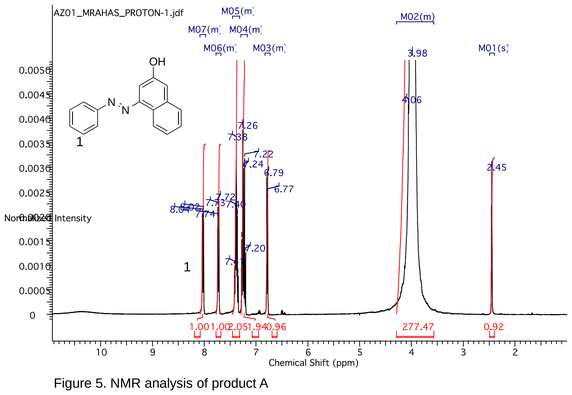


Figure 5. NMR analysis of product A

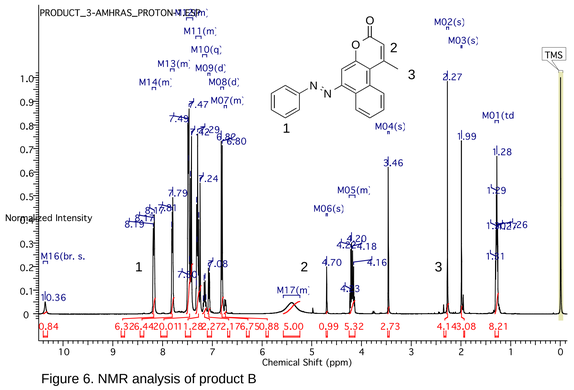


Figure 6. NMR analysis of product B

Green Chemistry Comparison Table

Comparison Parameters	Chloroform	Hexane
Hazards	Hazardous in case of skin contact, eye, ingestion, inhalation irritant. Mutagenic for mammalian somatic cells, bacteria, and yeast. Toxic to kidneys, liver, and heart. Chronic exposure to the substance can produce target organs damage. Carcinogen.	Hazardous in case of skin contact, eye, ingestion, and inhalation irritant. Mutagenic for bacteria and yeast. Chronic exposure to the substance can produce target organs damage and is toxic to peripheral nervous system.
Cost for solvent	$8.50	$3.26
Percent Yield	73%	Not Determined
Reaction Time, Temp	10 hours, 70˚ C	10 hours, 70˚ C
Product Purity, byproducts	Minimal Impurities	Minimal Impurities
Waste produced	Chloroform	Hexane

Discussion

The first two steps in the three step synthesis of Azo dye were completed successfully. The first goal in this project was to synthesize compound A, which was completed. This can be determined using a combination of IR, UV-Vis, and NMR analysis. This is shown by figures 3, 4, and 5. The IR data shows a broad band representing an alcohol group. Two to three bands are visible between 1450-1600 cm^{-1}, which indicates the presence of a benzene ring. The UV-Vis data shows absorption from approximately 400-600 nm which would indicate that violet, blue, green, and yellow light was absorbed, while orange and red light was reflected. This means that the compound is an orange-red dye. The NMR data for compound A is shown in figure 5. Approximately 5 peaks were observed from 7-9 ppm, which indicated multiple aromatic rings. The synthesis of compound B was also successful. This is shown by the NMR data in figure 6. Six peaks shown between 7-9 ppm indicated multiple aromatic rings. A singlet at approximately 5.5 ppm indicated that a Csp2H was present in the molecule. Another singlet was observed between 1 and 3 ppm, which indicated a methyl group was added. While the product was formed, unknown impurities were found because peaks at approximately 1-3 ppm indicated the presence of an unknown byproduct. Compound C was not formed. This can be confirmed by NMR data because the data for compound C was identical to that of compound B, which indicated no reaction occurred. If this experiment was done differently, more analysis using IR would have been done. Additionally, step three would have been repeated in order to successfully synthesize compound C. Furthermore, the green step would have been included in this experiment. Using hexane as a solvent instead of chloroform would have resulted in a greener product.

Conclusion

Overall, the two of the three steps were completed successfully. The third step was not successful and the green step was not completed. This was determined using the NMR analysis.

Future Directions

- Use products B and C to dye more fabric.
- Use hexane in step 3 instead of chloroform.
- Do an IR analysis on products B and C.
- Try this three step synthesis using another azo dye.

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Acknowledgements

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