

Diels–Alder Reaction Using a Solar Irradiation Heat Source Designed for Undergraduate Organic Chemistry Laboratories

Shikha Amin,[†] Ashley Barnes,[†] Courtney Buckner,[†] Jordan Jones,[†] Mattie Monroe,[†] Leon Nurmomade,[†] Taylor Pinto,[†] Samuel Starkey,[†] Brian M. Agee,[‡] David J. Crouse,[†] and Daniel J. Swartling*,[†]

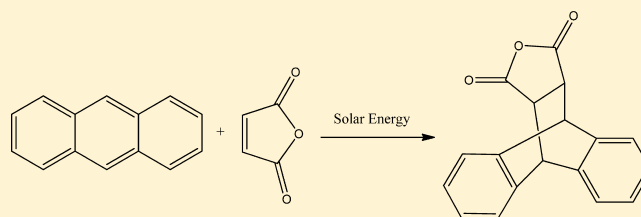
[†]Department of Chemistry, Tennessee Technological University, Cookeville, Tennessee 38505, United States

[‡]School of Environmental Studies, Tennessee Technological University, Cookeville, Tennessee 38505, United States

S Supporting Information

ABSTRACT: Recently proposed solar reflectors developed from satellite dishes have the ability to be incorporated into student laboratory procedures to eliminate electricity use while demonstrating green chemistry techniques at the same time. There have been recent attempts to make chemical synthesis procedures more environmentally friendly. As a result, demand to incorporate more green chemistry techniques into student laboratories has increased. Electricity use is one area of environmental concern because fossil fuels are used for the majority of electrical energy in the United States. An effective means for minimizing the amount of electricity needed to drive chemical reactions to completion is proposed through the use of solar parabolic reflectors. A comparative study is conducted using an electrical and solar heat source on the Diels–Alder cycloaddition reaction of maleic anhydride and anthracene. This reaction is chosen as the test reaction due to its widespread use among many undergraduate chemistry programs. Analysis of the products is performed by NMR spectroscopy.

KEYWORDS: Green Chemistry, Organic Chemistry, Second-Year Undergraduate, High School/Introductory Chemistry, Hands-On Learning/Manipulatives



INTRODUCTION

The main objective of green chemistry is to attempt to make chemicals and processes more sustainable in the environment by developing a cleaner, more environmentally friendly process.¹ To many scientists, this is a tremendous challenge because there is no established method that ensures a truly green process is being implemented. Therefore, generally, only small changes to a setup of synthetic chemical procedures are made in order to reduce hazard levels and alleviate waste generation. One area of environmental concern is the electricity needed to perform a reaction. In the United States, most of the electricity is generated from fossil fuels. The use of fossil fuels has some form of environmental impact associated with them. Nearly two-thirds of the total greenhouse gas emissions in the United States result from the use of fossil fuels for energy.² Furthermore, 1.3 billion people globally live without electricity and do not have the capability to perform the simplest of tasks that require electricity.³

Fossil fuel consumption continues to rise in several countries. In 2009, China consumed 1,537 million tons oil equivalent (9.6% higher than their consumption level in 2008).⁴ The United States has seen a rise in the use of natural gas as the country had a 3.5% increase in natural gas production in 2009.⁴ At the end of 2009, global reserves of natural gas were 6,621 trillion cubic feet.⁴ If global production continues to increase at 1.2% per year, reserves would last approximately 63 years.⁴

As a solution to the electrical use problem, solar-based energy generation processes to perform chemical reactions have been published, engineered, and implemented in various parts of the United States.^{5,6} Recently, to perform chemical reactions, the development of a solar reflector was described that can be used to perform high-temperature chemical reactions using only directed solar irradiation as the heat source.⁷ A solar reflector was designed using a recycled satellite dish and given reflective properties by covering the dish surface with metalized Mylar tape. A Friedel–Crafts acylation reaction was performed for a period of 3 h using directed solar irradiation as the sole thermal heat source to heat to the solvent reflux temperature (88–90 °C). The desired product was obtained in good yield and verified via NMR spectroscopy and GC/MS.

The Diels–Alder cycloaddition is one of the centerpiece reactions in synthetic organic chemistry. This reaction typically involves the formation of bonds through a concerted shift of electrons in a cyclic manner.⁸ The most common incarnation is the formation of an alicyclic compound containing only carbon atoms from the reaction of an electron rich diene (with four π electrons) with an electron poor dienophile (with another set of two π electrons).⁹ This particular reaction is covered in great detail in most undergraduate and graduate organic chemistry textbooks.¹⁰ Furthermore, the Diels–Alder reaction has been one of the most relevant and most popular reactions for

Published: March 11, 2015

undergraduate students for years as evidenced by publications within this *Journal*.^{11–15}

The synthesis of 9,10-dihydroanthraceno-9,10-endo- α,β -succinic anhydride through the Diels–Alder reaction of anthracene and maleic anhydride is a reaction that is performed annually in numerous undergraduate organic chemistry programs.^{16–20} Because this reaction consists of a total of six electrons (four π electrons from the diene, and two π electrons from the dienophile), this reaction typically occurs thermally, that is, only with heat. The original procedure for this laboratory exercise²¹ exhibits features that make it a premier candidate for a reaction that can be molded into a good undergraduate experiment in green chemistry:

1. The reaction requires thermal heating in order to be performed.
2. It is not necessary to run water through a condenser due to the use of a high-boiling solvent.
3. The starting materials display low toxicity.
4. Diels–Alder cycloaddition reactions are notorious for remarkable atom economy.²²

In order to improve upon the green features of this chemical reaction, alterations were made to the original synthetic pathway.²¹ A comparative study of conventional and solar procedures was conducted during the summer 2014 and fall 2014 by students in a second-year undergraduate organic chemistry course and by first-year chemistry majors in general chemistry courses. The pedagogic goal of this student exercise is to demonstrate one of the 12 Principles of Green Chemistry²³ to undergraduate students. The principle that is being demonstrated is the sixth principle: Design for Energy Efficiency. By performing this exercise, students see that alternative energy sources for heating procedures can be incorporated into synthetic reactions to produce statistically equivalent product yields.

■ EXPERIMENT

Students work individually. Anthracene (337 mmol, 0.600 g) and maleic anhydride (306 mmol, 0.300 g) are dissolved in xylene (6.00 mL) in a 10 mL round-bottom flask. Round bottom flasks used in the solar experiments are painted black approximately halfway up the flask using VHT Flame Proof paint, which can withstand intermittent temperatures up to 1093 °C (Figure 1).

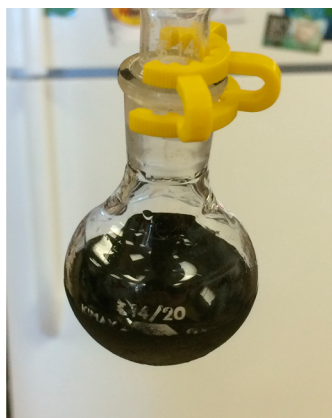


Figure 1. Close-up of painted flask.

The round-bottom flask is connected to a condenser fitted with a drying tube containing calcium chloride. For the electrical experiment, the apparatus is secured in an aluminum heating block on a hot plate, a stir bar is added, and the mixture is heated to reflux (Figure 2). For the solar experiment, the



Figure 2. In-lab experiment reaction setup using hot plate.

flask is attached to the solar reflector in the place that the feed horn of the satellite dish was located to reflect sunlight as a focused beam of solar energy toward the bottom of the flask (Figure 3); no stir bar is added because the natural reflux of the solvent provides enough mixing for the reaction to be successful.⁶



Figure 3. Solar experiment reaction setup using solar reflector.

Each reaction is refluxed for 30 min, at which point the reaction mixture is cooled in an ice bath for up to 1 h to allow the product to crystallize. The product is collected, washed with cold xylene, and air-dried, at which point product evaluation is performed by ¹H NMR analysis and FTIR spectroscopy (see the Supporting Information).

HAZARDS

This experiment does not contain any safety risks that are out of the ordinary. However, proper precautions should be applied when handling any of the reagents and solvents used in the experiment. Maleic anhydride is a skin irritant whose contact should be avoided. Xylene is a flammable liquid, irritant, and must be dispensed using proper personal protective equipment and while working in a fume hood. Anthracene, deuterated-chloroform, and the reaction product (9,10-dihydroanthraceno-9,10-endo- α,β -succinic anhydride) are skin irritants whose contact with skin should be avoided.

RESULTS AND DISCUSSION

Students obtained an 80.8% (average) yield of 9,10-dihydroanthraceno-9,10-endo- α,β -succinic anhydride when the Diels–Alder cycloaddition reaction of anthracene and maleic anhydride was performed with the solar reflector in 22 attempts. The round-bottom flasks were painted black in order to prevent photochemical side reactions and to allow for a more efficient heating process. By painting the flask black, the black paint absorbs the heat energy from the sun at a more efficient rate and sunlight is not allowed to pass directly through the glass. Because a high-boiling solvent (xylene) was used for the reaction, running water was deemed unnecessary. The comparative study using an electric heat source had an average yield of 80.0% yield for 26 students (Table 1). All

Table 1. Percent Yield Comparison Between Electricity Vs Solar Heat Source of 9,10-Dihydroanthraceno-9,10-endo- α,β -succinic Anhydride

Heat Source	Student Attempts	Average Percent Yield (%)	Range (%)
Electricity	26	80	56.6–95.2
Solar	22	80.8	63.5–97.0

experiments were run in duplicate. Seasonal variations did not affect the results obtained and as long as sunlight was present. The solar heat source can be used as a heating source for this chemical reaction at any outside temperature as long as enough sunlight is present to provide at least 500 W/m² solar irradiation (Table 2). The undergraduate students performing

Table 2. 9,10-Dihydroanthraceno-9,10-endo- α,β -succinic Anhydride Yield Comparison between Varying Levels of Solar Irradiation

Parameters	13-Jul-14	8-Aug-14	24-Aug-14	9-Sep-14
Outside Conditions	Sunny	Sunny	Cloudy	Partly Cloudy
Average Solar Irradiation	958 W/m ²	953 W/m ²	420 W/m ²	620 W/m ²
Time To Begin Reflux	2 min	2 min	Did not reflux	4 min
Student Attempts	4	6	2	6
Percent Yield	82.60%	79.00%	0.00%	76.00%

the reactions were of various levels of chemical experience. Students were either currently enrolled in an introductory undergraduate organic chemistry course or were first-year chemistry majors that were enrolled in a general chemistry course. There were no differences in the expectations for students at different levels in their academic career. All students (first- and second-year) were trained to use NMR spectroscopy

and FTIR spectroscopy, took both spectra themselves, and analyzed their samples with the help of faculty and staff. NMR and IR spectra provided in the Supporting Information are representative student obtained spectra.

Students analyzed the product samples through melting point analysis of the product and spectroscopy. Melting point analysis provided evidence that both solar and electrical heating sources for all students produced the desired product. An average melting point of 258–260 °C was obtained by students for their product for both heating methods. By comparing the melting point to the literature value¹⁶ for all starting materials and product, students concluded that they synthesized the desired. Furthermore, students observed that NMR spectra and the FTIR spectra of the product showed no difference between the solar reflector and the conventional procedure.

Through the use of NMR and FTIR spectra, students were able to analyze their products. With help from faculty and staff, students determined the chemical structure of the compound that was produced through peak patterns and integration in the NMR spectra. Through comparison of NMR and FTIR spectra of starting materials to the product, students were clearly able to see that a new compound had been synthesized based upon the appearance/disappearance of peaks/stretches in the various spectra.

By comparing the solar results with results from the reactions performed in the laboratory, students were able to observe that was no statistical difference in the performance of the reaction based upon heating source. Thus, students were able to conclude that the sun is a viable alternative heating source for the Diels–Alder reaction.

CONCLUSION

A solar heat source was used successfully in place of an electrically based heating source to synthesize the product from a well-known, high-temperature reaction with yields that were comparable to the same scale reaction performed using an electric heating source. A solar heat source is a viable option for the replacement of electric heating sources and can be used as a teaching tool for students eager to learn new developmental methods of green chemistry. Through the use of a solar heat source, students used a waste-free source of renewable energy with none of the carbon waste from using electricity. By comparing their results to the results obtained in the laboratory, students fulfilled the pedagogic goal of this project by observing that there was statistically no difference in yield between either heat sources and the same product was synthesized using either heating method. Thus, students were able to come to the conclusion that the sun was a viable heating alternative for the Diels–Alder reaction. Currently, more complex chemical reactions are being conducted using the solar reflector heat source.

ASSOCIATED CONTENT

Supporting Information

Experiment handout and instructor notes. This material is available via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: dswart@tntech.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We wish to thank Tennessee Technological University for funding this research and the Summer 2014 CHEM 3020 Organic Chemistry class at Tennessee Technological University for providing the in-lab reaction data.

■ REFERENCES

- (1) Woodhouse, E.; Breyman, S. Green Chemistry as a Social Movement. *Sci. Technol. Human Values* **2005**, 30 (2), 199–222.
- (2) Pryor, S. C.; Barthelmie, R. J. Assessing Climate Change Impacts on the Near-Term Stability of the Wind Energy Resource Over the United States. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, 108 (20), 8167–8171.
- (3) International Energy Agency. <http://www.worldenergyoutlook.org/resources/energydevelopment/energyaccessdatabase/> (accessed Jun 2014).
- (4) Institute for Energy Research. http://instituteforenergyresearch.org/analysis/in-2009-u-s-led-the-rest-of-the-world-in-increases-of-oil-and-natural-gas-production-china-recorded-the-greatest-increase-in-energy-consumption-and-emissions/#_edn17 (accessed Jun 2014).
- (5) Monroe, L.; Swartling, D. J. Using solar energy in the green synthesis of deep eutectic solvents. At 243rd ACS National Meeting, San Diego, CA, March 25–29, 2012; American Chemical Society: Washington, DC, 2012; CHED-1124.
- (6) Schiel, C.; Oelgemoller, M.; Ortner, J.; Mattay, J. Green Photochemistry: The Solar-Chemical Photo-Friedel-Crafts Acylation of Quinones. *Green Chem.* **2001**, 3 (5), 224–228.
- (7) Agee, B. M.; Mullins, G.; Swartling, D. J. Friedel-Crafts Acylation Using Solar Irradiation. *ACS Sustainable Chem. Eng.* **2013**, 1 (12), 1580–1583.
- (8) Diels, O.; Alder, K. Synthesen in der hydroaromatischen Reihe; I. Mitteilung: Anlagerungen von “Di-en”-kohlenwasserstoffen. *Justus Liebigs Ann. Chem.* **1928**, 460, 98–122.
- (9) Diels, O.; Alder, K. Synthesen in der hydroaromatischen Reihe, V. Mitteilung: Über Δ^4 -Tetrahydro-*o*-phthalsäure. *Ber. Dtsch. Chem. Ges. A* **1929**, 62 (8), 2087–2090.
- (10) See, for example (a) Carey, A.; Giuliano, R. Conjugation in Alkadienes and Allylic Systems. *Organic Chemistry*, 8th ed.; McGraw Hill: New York, 2011; pp 388–427. (b) Carey, A.; Sundberg, R. Concerted Pericyclic Reactions. *Advanced Organic Chemistry, Part A: Structure and Mechanisms*, 4th ed; Kluwer Academic/Plenum Publishers: New York, 2000; pp 605–662.
- (11) Sheppard, W. J. A Diels–Alder Reaction Experiment. *J. Chem. Educ.* **1963**, 40 (1), 40–41.
- (12) Kellett, J. C., Jr. A Diels–Alder Student Preparation. *J. Chem. Educ.* **1963**, 40 (10), 543.
- (13) Marchand, A. P.; Vidyasagar, V.; Buckner, M. B.; Holman, P. O. Lewis Acid Catalysis of a Diels–Alder Cycloaddition: An Undergraduate Organic Experiment. *J. Chem. Educ.* **1987**, 64 (7), 642–644.
- (14) Sauvage, X.; Delaude, L. The Synthesis of *N*-Benzyl-2-azanorbornene via Aqueous Hetero Diels–Alder Reaction. An Undergraduate Project in Organic Synthesis and Structural Analysis. *J. Chem. Educ.* **2008**, 85 (11), 1538–1540.
- (15) Coleman, W. F. Diels–Alder Reactions and the Structure of Transition States. *J. Chem. Educ.* **2010**, 87 (11), 1278–1279.
- (16) Wade, Jr., L. G. *Modular Laboratory Program in Chemistry*; Chemical Education Resources: Palmyra, PA, 1998.
- (17) Crouse, D. J. *Chemistry 3010/3020 2014–2015 Lab Manual*; Tennessee Technological University: Cookeville, TN, 2014.
- (18) Student Notes: Diels–Alder Reaction with Maleic Anhydride and Anthracene. <http://home.hiram.edu/chemistry/organic/Student%20Notes-diels%20alder.pdf> (accessed Jun 2014).
- (19) Mount Holyoke College: Organic Chemistry II Laboratory Experiments, Spring 2008. https://www.mtholyoke.edu/courses/menunez/Chm302OrgIIWeb/chem302_labman_sp08.pdf (accessed Jun 2014).
- (20) Chemistry 365 – Minnesota State University Moorhead: Organic Chemistry II Lab Manual. <http://web.mnstate.edu/jasperse/Chem365/Diels-Alder.pdf> (accessed June 2014).
- (21) Hill, R. K.; Barbaro, J. *Experiments in Organic Chemistry*, 2nd ed.; Contemporary Publishing Company: Raleigh, 2000.
- (22) Trost, B. M. The atom economy — A Search for Synthetic Efficiency. *Science* **1991**, 254 (5037), 1471–1477.
- (23) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford Press: New York, 1998.