World Journal of Chemical Education, 2024, Vol. 12, No. 2, 45-48
Available online at http://pubs.sciepub.com/wjce/12/2/1
Published by Science and Education Publishing
DOI:10.12691/wjce-12-2-1

Incorporating Green Chemistry into Undergraduate Organic Chemistry Laboratory: Synthesis of Banana Oil

Weihua Wang*, Prabin Rai

Department of Biology and Chemistry, Southern University and A&M College, Baton Rouge, LA 70813, United States
*Corresponding author: Weihua_Wang@subr.edu

Received March 01, 2024; Revised April 02, 2024; Accepted April 09, 2024

Abstract The traditional laboratory of synthesis of banana oil via Fisher esterification was modified to provide a practical integration of green chemistry concepts and principles into undergraduate organic chemistry laboratory at Southern University and A&M College-Baton Rouge campus (SUBR). Besides the traditional method described in our laboratory manual, two more modified methods for the synthesis of banana oil were added. Six out of the 12 principles of green chemistry were introduced. This laboratory offered students an opportunity to do a comparative study of the greenness and efficiency of different synthetic methods for the synthesis of banana oil and practice applying green chemistry principles into organic synthesis. The modified method II was found to be the greenest and most efficient synthetic method with least waste produced, highest atom economy and yield, environmentally benign chemicals, reduced hazardous risk, improved energy efficiency and enhanced accident prevention. Calculations of E-factor and percent atom economy were introduced. The comparison of experimental percent atom economy and percent yield was also included.

Keywords: *green chemistry, organic chemistry laboratory, banana oil, Fisher Esterification, organic synthesis*

Cite This Article: Weihua Wang, and Prabin Rai, "Incorporating Green Chemistry into Undergraduate Organic Chemistry Laboratory: Synthesis of Banana Oil." *World Journal of Chemical Education*, vol. 12, no. 2 (2024): 45-48. doi: 10.12691/wjce-12-2-1.

1. Introduction

Due to the global awareness of environmental issues such as pollution, climate change, waste disposal, and resource depletion, etc., green chemistry has become a powerful strategy to solve the issues [1]. Green chemistry, first described by Anastas and Warner in 1998, is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances [2]. It's outlined with a framework of 12 principles (Table 1). The aim of green chemistry is to help scientists think about how to reduce chemical-related impact on human health and the environment. The scope of green chemistry principles goes beyond concerns of chemical toxicities and includes waste production, energy efficiency, accident prevention, etc. in the life cycle of a chemical product.

Green chemistry is not designed just for industrial settings. Introducing green chemistry into teachings at college/university level can have great beneficial effects as well [3]. Many chemistry departments from colleges/universities all over the world have incorporated green chemistry into their chemistry curricula [4]. By introducing green chemistry into chemistry courses, the next generation of chemists are trained to always keep safety and sustainability in mind and minimize the risk of chemical products and processes to human health and the environment. Teaching students how to apply the principles of green chemistry at the start of their college education will help them build a solid foundation of green chemistry and create a sustainable future for society.

The undergraduate organic chemistry laboratory is an excellent place for students to get hands-on experience with chemical reactions. Therefore, introducing green chemistry concepts/principles into undergraduate organic chemistry laboratories is of great importance. Students can get an opportunity to get first-hand experience on how to apply green chemistry principles into syntheses of chemical products and design greener alternatives. Since the Chemistry program at SUBR signed on to the Green Chemistry Commitment in 2021 [5], we have been working on incorporating green chemistry into our chemistry lecture and laboratory curricula.

Organic esters with low molecular weights are an important family of compounds that are extensively used in artificial flavorings, perfumes, drugs, etc. The synthesis of esters still has broad applications in industry [6,7,8]. Synthesis of banana oil is a typical experiment in undergraduate organic chemistry laboratory to practice the synthesis of esters via Fisher esterification method. The traditional way to prepare banana oil involves heating acetic acid with isopentyl alcohol in the presence of an acid catalyst (Figure 1).

We believe the laboratory of the synthesis of banana oil is a great example to introduce green chemistry concepts/principles to students. The issue with the traditional Fisher esterification method for the synthesis of banana oil is that the reaction is reversible with an equilibrium constant slightly favoring the products. To get a decent yield of the ester product, excess amount of acetic acid is often used because acetic acid is cheaper and easier to be separated from the reaction mixture compared to isopentyl alcohol. On the other hand, the reaction is rather slow due to the poor electrophilicity of the carboxyl group. Therefore, a catalytic amount of concentrated sulfuric acid is commonly used.

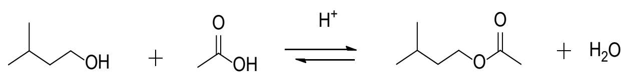

Figure 1. Synthesis of Banana oil with Acetic Acid

Table 1. Twelve Principles of Green Chemistry [2]

Principles	Description
Waste Prevention	It is better to prevent waste than to treat or clean up waste after it has been created.
Atom Economy	Synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product.
Less Hazardous Chemical Syntheses	Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
Design Safer Chemicals	Chemical products should be designed to preserve efficacy of function while reducing toxicity.
Safer Solvents and Auxiliaries	The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.
Design for Energy Efficiency	Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
Use of Renewable Feedstocks	A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
Reduce Derivatives	Unnecessary derivatizations, such as use of blocking groups, protection/deprotection, and other temporary modifications of physical/chemical processes should be minimized or avoided if possible, because such steps require additional reagents and can generate additional waste.
Catalysis	Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
Design for Degradation	Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
Real-Time Analysis for Pollution Prevention	Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
Inherently Safer Chemistry for Accident Prevention	Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

To introduce green chemistry principles, besides the traditional method that had been used in our teaching laboratories [9], two more modified methods were developed. The first modification involves the replacement of the corrosive and hazardous sulfuric acid with a solid catalyst Amberlyst-15. Amberlyst-15 is a polystyrene based ion exchange resin with a strong sulfonic group (Figure 2). It is environmentally benign, safe to handle, inexpensive and recyclable. Because of the above-mentioned advantages, Amberlyst-15 has been used as a great catalyst in various organic synthesis processes [10,11,12]. Through this modification, the following four green chemistry principles are introduced: waste prevention, less hazardous chemical syntheses, catalysis, and inherently safer chemistry for accident prevention.

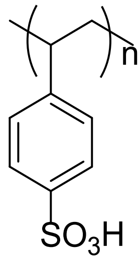

Figure 2. Structure of Amberlyst-15

Another modification is to utilize a more efficient method by using acetic anhydride rather than acetic acid (Figure 3). This reaction is irreversible and more efficient due to higher reactivity of acetic anhydride. It can be carried out at room temperature.

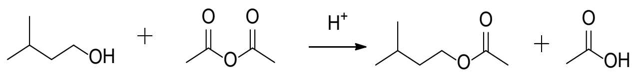

Figure 3. Synthesis of Banana Oil with Acetic Anhydride

The purpose of this modification is to help students understand the following principles of green chemistry: atom economy and design for energy efficiency by changing reagents and reaction conditions.

In addition, during this modified laboratory, the calculations of E-factor (environmental factor) [13], percent atom economy, experimental percent atom economy, and percent yield for each reaction are included to help students better understand the greenness and efficiency of the reactions.

2. Experimental

2.1. Chemicals

The following chemicals were used in this laboratory. Acetic acid, isopentyl alcohol, acetic anhydride, concentrated sulfuric acid, anhydrous calcium chloride, and sodium bicarbonate were purchased from Sigma-Aldrich. Amberlyst-15 was purchased from Thermo Fisher Scientific. All chemicals were used as received without further purification.

2.2. Methods

2.2.1. Traditional Method

16 mL of isopentyl alcohol, 17 mL of glacial acetic acid, 20 drops (~0.5 g) of concentrated sulfuric acid and one boiling chip were added into a 100 ml round-bottom flask. The mixture was heated under reflux for one hour. After the completion of the reaction, the reaction mixture was cooled to near room temperature and transferred to a 125 mL separatory funnel. The reaction mixture was then washed with 5% $NaHCO_3$ solution in 5mL portions

until the pH of the aqueous layer became neutral. The aqueous layers were drained in a container. The total amount of aqueous layers was recorded to calculate the E-factor. The organic layer was dried over anhydrous $CaCl_2$ (1.0 g) and purified by simple distillation. The liquid that distilled between 134°C ~142 °C was collected and its volume was measured.

2.2.2. Modified Method I

The procedure for this modified method is the same as that for the traditional method described in 2.2.1 except that 0.5 g of Amberlyst-15 was used to replace the concentrated sulfuric acid. After the completion of the reaction, Amberlyst-15 was collected and recycled by washing with acetone.

2.2.3. Modified Method II

16 mL of isopentyl alcohol, 15 mL of acetic anhydride, and 0.5 g of Amberlyst-15 were added into a 100 ml Erlenmeyer flask. The mixture was stirred at room temperature for 1 hour. After the completion of the reaction, the reaction mixture was transferred to a 125 mL separatory funnel. Amberlyst-15 was collected and recycled by washing with acetone. Just as in the previous procedures, the reaction mixture was washed with 5% $NaHCO_3$ solution until the pH of the aqueous layer became neutral. The total amount of aqueous solutions was recorded for the calculation of the E-factor. The organic layer was dried over anhydrous $CaCl_2$ and purified by simple distillation. The fraction between 134°C ~142°C was collected and its volume was measured.

2.3. Safety

Proper personal protective equipment (lab coat, safety goggles and gloves) is always required during the lab.

All chemicals should be handled under the fume hood. Acetic acid causes severe skin burns and its vapors are highly irritating to the eyes and respiratory tract. Isopentyl alcohol can irritate the skin, eyes, and respiratory tract. Concentrated sulfuric acid is extremely corrosive, can cause serious burns, and should be handled with extreme caution. Acetic anhydride can cause severe damage to skin and eyes. It reacts violently with water.

3. Results and Discussion

The laboratory of synthesis of banana oil was modified to introduce the concepts and principles of green chemistry to undergraduate organic chemistry laboratory at our university. By conducting an experiment and collaborating with other students, students will obtain first-hand experience on how to apply green chemistry principles to organic synthesis. The design of three different synthetic methods enables students to do a comparative study of the greenness and efficiency of different synthetic reactions. For a section of 18 students, the students can be divided into three groups (6 students in a group). Each group will carry out one synthetic method. Within each group, two students will work as lab partners to perform one synthesis. In this way, each synthetic method will be performed three times. At the end of the laboratory, students will exchange the data and do a comparative study of the greenness and efficiency among these three different synthetic methods and eventually choose which one of the three methods is the greenest and most efficient for the synthesis of banana oil.

Table 2. Comparative Study of the Greenness of Different Synthetic Methods for the Synthesis of Banana Oil

Principles of Green Chemistry	Traditional Method	Modified Method I	Modified Method II
Prevention of Waste	50 mL of aqueous waste produced (E-factor: 3.27)	55 mL of aqueous waste produced (E-factor: 4.80)	45 mL of aqueous waste produced (E-factor: 2.78)
Atom Economy (excess amount of reactant included)	62.4%	62.4%	65.9%
Less Hazardous Chemical Syntheses	Extremely corrosive and destructive H_2SO_4 is used	Nontoxic and environmental benign Amberlyst-15 is used	Nontoxic and environmental benign Amberlyst-15 is used
Design for Energy Efficiency	Reaction is carried out under reflux for 1 hour	Reaction is carried out under reflux for 1 hour	Reaction is performed at room temperature for 1 hour
Catalysis	Nonrecyclable catalyst	Recyclable catalyst	Recyclable catalyst
Inherently Safer Chemistry for Accident Prevention	H_2SO_4 has a potential to cause accident	Safer chemicals	Safer chemicals

Table 2 shows the results of the comparative study of three synthetic methods based on the green chemistry principles that were introduced. When calculating percent atom economy, the excess amount of acetic acid/ acetic anhydride was included as well. After the completion of the experiment, experimental percent atom economy was calculated by using the actual yield of the product. While the percent yield of a reaction is only concerned with the amount of the desired product that was isolated (relative to the theoretical amount of the product), experimental percent atom economy takes all used reagents (including the excess amount of reagent) into account. Therefore, experimental percent atom economy provides more accurate information for the efficiency of a reaction. Table 3 shows the experimental percent atom economy and the percent yield for each of the three synthetic methods.

Table 3. Experimental Percent Atom Economy and Percent Yield

Synthetic Methods	Experimental % Atom Economy	% Yield
Traditional Method	49.8%	79.4%
Modified Method I	37.3%	59.4%
Modified Method II	55.4%	84.1%

As seen from the results in Table 2 and Table 3, modified method II is the greenest and most efficient method among the three synthetic methods. It uses safer and environmentally benign chemicals and produces the least amount of waste. It has the highest atom economy, as well as reduced hazardous risk, improved energy efficiency, and enhanced accident prevention. It also generates the highest yield. Through this comparative study, students can have a better understanding of the factors that affect the greenness and efficiency of a chemical reaction. On the other hand, this modified laboratory enhances the collaboration among students, which is an additional benefit.

4. Conclusion

Implementing green chemistry into undergraduate organic chemistry laboratories is of great importance. It offers students an opportunity to get first-hand experience on how to apply the principles of green chemistry into organic synthesis. Synthesis of banana oil is a typical experiment carried out in undergraduate organic chemistry teaching laboratory. The traditional laboratory procedure was modified in order to incorporate the concepts/principles of green chemistry. Two more synthetic methods were added to compare the greenness and efficiency of different synthetic methods for the synthesis of banana oil. Six out of the 12 principles of green chemistry were applied in this laboratory: waste prevention, atom economy, less hazardous chemical syntheses, design for energy efficiency, catalysis, and accident prevention. The modified method II was found to be the greenest and most efficient way to synthesize banana oil with least waste produced, highest atom economy and yield, environmental benign chemicals, reduced hazardous risk, improved energy efficiency and enhanced accident prevention. Moreover, this modified laboratory enhances the collaboration among students, which is an added benefit.

ACKNOWLEDGEMENTS

The authors would like to thank the Department of Biology and Chemistry at Southern University and A&M College-Baton Rouge campus, and Beyond Benign for the financial support for this project.

References

[1] Tundo, P., and Griguol, E., “Green chemistry for sustainable development,” *Chem. Int.*, 2018, 40 (1), 18−24.

[2] Anastas, P. T., and Warner, J. C, *Green Chemistry: Theory and Practice*; Oxford University Press, New York, 1998.

[3] Bodner, G. M., “2. The quadruple bottom line: the advantages of incorporating Green Chemistry into the undergraduate chemistry major”. *Green Chemical Processes: Developments in Research and Education*, edited by Mark Anthony Benvenuto, Berlin, Boston: De Gruyter, 2017, pp. 7-28.

[4] O’Neil, N. J., Scott, S., Relph, R., and Ponnusamy, E., “Approaches to incorporating green chemistry and safety into laboratory culture,” *J. Chem. Educ.*, 2021, 98, 84-91.

[5] Beyond Benign, Green Chemistry Commitment, https://www.beyondbenign.org/he-whos-committed/.

[6] Zare, M., Golmakani, M. T., and Niakousari, M., “Lipase synthesis of isoamyl acetate using different acyl donors: comparison of novel esterification techniques,” *Lebensm. Wiss. Technol.*, 2019, 101, 214–219.

[7] Azudin, N. Y., Sangaran, S., and Shukor, S. R. A., “Non-enzymatic synthesis route for production of isoamyl acetate in a solvent-free system using miniaturized intensified reactor,” *J. Environ. Chem. Eng.*, 2020, 8, 103186.

[8] Li, Z. Y., Tao, H. Y., and Yang, R. Z., “Preparation of isoamyl acetate by reaction-distillation using ionic liquid as catalyst,” *Adv. Mater. Res.* 2012, 550–553, 164–169.

[9] Burton, S., and Claville, M. *Catalyst: General Organic Chemistry Laboratory 220&221*, Southern University and A&M College.

[10] Harmer, M. A. *Industrial Processes Using Solid Acid Catalysts, in Handbook of Green Chemistry and Technology*; J. H. Clark, D. J. Macquarris, eds.; Blackwell Publishers London., 2002.

[11] Pande, M. A., and Samant S. D. “Amberlyst-15 catalyzed acetylation of phenols and alcohols under solvent free conditions,” *Recyclable Catalysis*, 2012, 1, 6-9.

[12] Pal, R., Sarkar, T., and Khasnobis, S., “Amberlyst-15 in organic synthesis,” *ARKIVOC*. 2012, (i) 570-609.

[13] Sheldon, R. A., “The E factor: fifteen years on,” *Green Chem.,* 2007, 9, 1273-1283.