Green Method of Derivatization of Alcohols: Microwave Assisted Synthesis of 3,5-Dinitrobenzoates

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Abstract

Qualitative organic analysis is an integral component of laboratory training of chemistry students all over the world. Though this training imparts necessary skills to the students to meet the challenges of a career in research and development, the standard procedures followed for qualitative analysis do not adhere to the principles of green chemistry. Continuing with our efforts of adopting green methodologies in the undergraduate and postgraduate chemistry laboratories, we are now reporting the green method of synthesis of 3,5-dinitrobenzoates of alcohols. Conventionally, the 3,5-dinitrobenzoate derivatives of alcohols are prepared by reacting the alcohol with 3,5-dinitrobenzoyl chloride, which itself is prepared by treating the corresponding 3,5-dinitrobenzoic acid with PCl_5 or $SOCl_2$ and results in the formation of harmful by products such as $POCl_3$, HCl and SO_2. In the present green method, under microwave assisted conditions, the alcohol is directly treated with the 3,5-dinitrobenzoic acid in presence of a few drops of concentrated sulphuric acid.

Keywords: Qualitative organic analysis, derivatisation, 3,5 dinitrobenzoate, green methodology, microwave

Introduction:

Both the undergraduate and postgraduate chemistry laboratory curriculum of most universities include the qualitative analysis of an unknown organic compound. Through the standard procedures of preliminary testing, functional group identification and the preparation of a suitable derivative, students are systematically able to analyse the organic compound. Traditionally, an alcohol is successfully identified by converting it into its corresponding esters, such as 3,5-dinitrobenzoates [1, 2]. The traditional procedure for preparing the 3,5-

dinitrobenzoates, has the disadvantage of not adhering to principles of green chemistry. Green chemistry is the practice of adopting techniques and procedures to reduce or eliminate the use or manufacture of harmful substances that are hazardous to human health [3]. By applying the twelve principles of green chemistry, chemists have begun to successfully develop chemical processes which are safer and prevent pollution [4, 5]. Our department has also been adopting greener practices in the laboratory [6]. The goal of this project is to provide a green approach to the traditional method of preparation derivatives of alcohol. In this present work, a microwave assisted synthesis of the 3,5-dinitroderivatives of common alcohols is reported following the principles of green chemistry.

Experimental

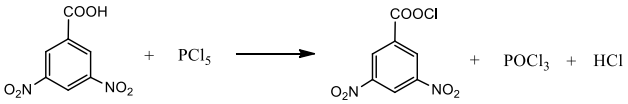
An unknown organic compound is characterized by (i) preliminary tests (ii) functional group tests and finally preparation of a pure crystalline derivative of a definite melting point. For the characterization of alcohols, they are routinely converted to the corresponding 3,5-dinitrobenzoates (Furniss et al. 2006; Ahluwalia and Dhingra 2000). Conventionally, these derivatives are obtained by first conversion of the 3,5-dinitrobenzoic acid to its acid chloride upon reaction with phosphorus pentachloride or with thionyl chloride, followed by the subsequent reaction of the formed acid chloride with the alcohol.

Conventional Method to synthesize 3,5-dinitrobenzoates of alcohols:

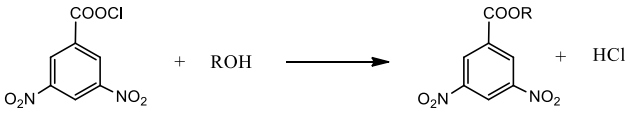
The 3,5-dinitrobenzoyl chloride is first prepared by mixing 1.0 g of 3,5-dinitrobenzoic acid with 1.5 g Phosphorus pentachloride (PCl_5) in a dry boiling tube (in a fume cupboard). The mixture is continuously stirred to obtain a liquid. The crude acid chloride so obtained is now stirred with the given alcohol (1 mL) in a dry boiling tube on a warm water bath. The prepared crude product is poured into ice-cold water, washed with. sodium bicarbonate solution and recrystallized using the appropriate solvent. The time taken to complete the entire procedure is 45 - 60 minutes.

Reaction involved:

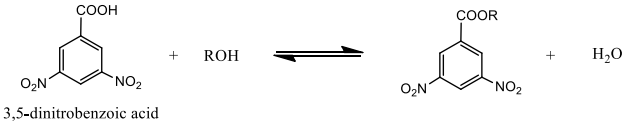
(i) Step 1: Conversion of 3,5-dinitrobenzoic acid to corresponding acid chloride



(ii) Step 2: Conversion of acid chloride to the ester by reaction with alcohol



The reagents (phosphorus pentachloride and Thionyl Chloride) and the side products i.e. hydrogen chloride, phosphorous oxychloride and sulphur dioxide are toxic and hazardous [7, 8, 9, 10, 11]. The direct reaction of alcohol with 3,5-dinitrobenzoic acid is slow and reversible and hence the product cannot be obtained in good purity and yield.



3,5-dinitrobenzoic acid

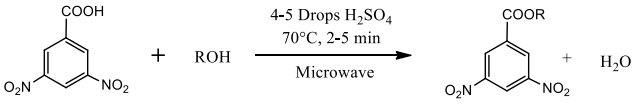
In the present study, we are reporting the microwave assisted preparation of the aforementioned derivatives.

Green strategy to synthesize 3,5-dinitrobenzoates of alcohols through a microwave assisted reaction:

In a clean, dry round bottomed flask mixed 1 g of 3,5-dinitrobenzoic acid with 1 mL of the given alcohol and added 1-2 drops of concentrated sulphuric acid. The mixture was heated in microwave (Milestone Start Synth) for 2 - 5 minutes at 70°C. The reaction mixture was poured into ice cold water resulting in the precipitation of the desired 3,5-dinitrobenzoate. The precipitated ester is filtered and washed aqueous sodium bicarbonate solution to remove any unreacted 3,5-dinitrobenzoic acid. Finally, the desired solid ester product is recrystallized to afford the pure derivative. The total time required to complete the entire procedure is 15-20 minutes.

Reaction Involved:

Microwave assisted esterification of alcohol



Result and Discussion

A safe, energy and time efficient method has been developed for the derivatization of alcohols. Use of harmful chemicals and formation of undesirable by products has been eliminated. The method works well for most primary alcohols, except benzyl and furfuryl alcohols. (Table 1) These alcohols probably undergo dehydration in presence of sulphuric acid and thus produce a charred mass instead. Reactions of secondary and tertiary alcohols afforded the products with poor yield.

Table 1: Microwave Assisted Synthesis of 3,5-Dinitrobenzoate Derivative of Alcohols

S. No.	Alcohol	Yield (%)	Observed Melting Point (°C)	Literature Melting Point (°C)
1	Ethanol	45-50	91-92	93
2	Methanol	45-50	108-109	109

3	Isoamyl alcohol	50-55	61-62	62
4	Amyl alcohol	45-50	47-48	46
5	n-Hexanol	45-50	57-58	58
6	n-Butanol	35-45	63-64	63
7	n-Octanol	40-45	61-62	62
8	n-Decanol	50-55	57-58	57

Overall, the modified green method has the following advantages:

(i) The use of toxic and hazardous chemicals is eliminated, thus reducing the students' exposure to these otherwise harsh chemicals.

(ii) The method is cost effective, especially for the undergraduate laboratory setting.

(iii) The method is time and energy efficient. 16 students were able to perform the reaction in less than 10 minutes, whereas conventionally the student would require approximately one hour each to perform the entire synthesis/experiment.

(iv) The method is simple and safe.

Thus, we have successfully reported the green conversion of the common primary alcohols to their corresponding 3,5-dinitrobenzoate derivatives.

Conclusion

A simple and green method to the synthesis of 3,5-dinitrobenzoate derivatives of simple alcohols is reported. The method is safer and follows the basic principles of green chemistry and can therefore be easily implemented in the undergraduate chemistry laboratory.

ACKNOWLEDGEMENTS

We are thankful to Dr Sunita Dhingra, Associate Professor (Retd.), Department of Chemistry, Miranda House for the guidance and support of the present work. We are thankful to the Principal, Miranda House, for the permission and encouragement to pursue the present study. We also thank our undergraduate students and the laboratory staff for their help in the completion of this project.

Declaration

The manuscript has been prepared through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors declare that they have no conflicts of interest.

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