

# Derivatization of Alcohols Using (bmim)HSO<sub>4</sub>: A Green Approach for the Undergraduate Chemistry Laboratory

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**Abstract** Alcohol is one of the functional groups detected as part of qualitative organic analysis. The final identification of alcohol involves the preparation of suitable crystalline derivative, usually the 3,5-dinitrobenzoate. According to the standard procedure, 3,5-dinitrobenzoic acid is first converted to 3,5-dinitrobenzoyl chloride by reaction with either phosphorous pentachloride (PCl<sub>5</sub>) or thionyl chloride (SOCl<sub>2</sub>). However, in this reaction, hazardous side products like phosphorous oxychloride (POCl<sub>3</sub>), hydrochloric acid (HCl) and sulphur dioxide (SO<sub>2</sub>) are produced. In the present method, we report the direct and benign conversion of alcohols to the corresponding 3,5-dinitrobenzoates using ionic liquid, (bmim)HSO<sub>4</sub> under microwave irradiation.

**Keywords:** alcohol, qualitative organic analysis, 3,5-dinitrobenzoate, ionic liquid, microwave

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## 1. Introduction

Qualitative analysis of an unknown organic compound for both undergraduate and postgraduate students is an essential part of the chemistry syllabus. This systematic analysis includes preliminary examination, tests for functional groups and preparation of a suitable crystalline derivative. Alcohols, which are mostly liquids, are converted to the corresponding 3,5-dinitrobenzoates and the identification is done through the melting point determination of this derivative. [1,2] The common method of conversion of an alcohol to the 3,5-dinitrobenzoate has the disadvantage of not adhering to the principles of green chemistry. Green chemistry is applying strategies and procedures to reduce or eliminate the usage or production of harmful substances to minimize the damage to the environment. [3] Chemists have begun to create chemical processes that are safer and less polluting by employing the twelve principles of green chemistry. [4,5] Keeping in mind the various principles of green chemistry, there is a need to modify the current method and develop a safe and benign procedure for producing the alcohol derivatives. In the current work, 3,5-dinitrobenzoate derivatives of common alcohols are prepared via a microwave-assisted synthesis using the ionic liquid, (bmim)HSO<sub>4</sub>. In recent years, the use of microwave assisted organic synthesis in the undergraduate laboratory has gained much popularity [6,7]. These reactions provide a green approach to chemical synthesis. Generally, microwave assisted reactions offer numerous key advantages, such as, improved energy efficiency, a shorter reaction time and in many cases, reactions may be

performed under solventless conditions. [8,9] Ionic liquids are commonly known as designer solvents. They are primarily organic salts with melting points below 100°C and therefore are also known as liquid organic salts. Ionic liquids, in general, display physical properties close to fluids or liquids at ambient temperatures and today, they serve as an excellent alternate solvent for organic synthesis. The attractiveness of use of ionic liquids as solvents in organic synthesis has grown substantially during the past years. [10] (bmim)HSO<sub>4</sub> is an acidic ionic liquid which is used for the preparation of 3,5-dinitrobenzoate from alcohol.

## 2. Experimental

Alcohols are routinely transformed to the appropriate 3,5-dinitrobenzoates for characterization. [1,2] Traditionally, 3,5-dinitrobenzoic acid is first converted to the 3,5-dinitrobenzoyl chloride followed by reaction with desired alcohol.

## 3. Conventional Method for Synthesis of 3,5-dinitrobenzoate

Prepared the 3,5-dinitrobenzoyl chloride by combining 1.0 g 3,5-dinitrobenzoic acid with 1.5 g phosphorus pentachloride (PCl<sub>5</sub>) with constant stirring (in a fume cupboard). Next, in a dry boiling tube kept in a heated water bath, the 3,5-dinitrobenzoyl chloride so prepared is mixed with desired alcohol (1 mL). The product is washed with saturated sodium bicarbonate (NaHCO<sub>3</sub>) solution and water, followed by recrystallization with alcohol. The full

procedure generally takes the undergraduate student 45 to 60 minutes to complete.

#### 4. Green Synthesis of 3,5-dinitrobenzoates of Alcohols Using (bmim)HSO<sub>4</sub>

In a clean and dry round bottom flask, equimolar amounts of 3,5-dinitrobenzoic acid and the desired alcohol were combined with 3 mL of the ionic liquid, (bmim)HSO<sub>4</sub>. The mixture was heated under microwave (Milestone Start Synth) irradiation for 3 minutes at 70°C. Added ice cold water to the reaction mixture for precipitating the 3,5-dinitrobenzoate. To eliminate any unreacted 3,5-dinitrobenzoic acid, the precipitated ester was filtered and washed with an aqueous sodium bicarbonate solution. The pure 3,5-dinitrobenzoate derivative was obtained through recrystallization in alcohol. This microwave assisted preparation takes the undergraduate student only 15-20 minutes from start to finish. The various 3,5-dinitrobenzoates were characterized via melting point.

#### 5. Result and Discussion

The microwave assisted preparation of the 3,5-dinitrobenzoate derivatives of alcohols using the ionic liquid, (bmim)HSO<sub>4</sub> [Figure 1] is associated with several advantages, which are highlighted below:

- Toxic chemicals like PCl<sub>5</sub> and SOCl<sub>2</sub> are not used.
- Generation of hazardous by-products such as hydrogen chloride, phosphorous oxychloride and sulphur dioxide are eliminated.
- The above protocol allows the reduction in time and energy. The reaction times are significantly lower in the microwave assisted method compared to conventional two-step process.
- This modified method works for some secondary alcohols as well, though the yields were generally low. Tertiary alcohols however, failed to undergo the microwave assisted reaction.

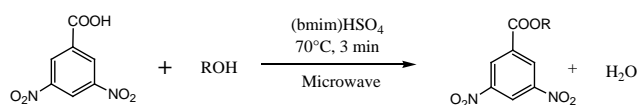


Figure 1. Microwave assisted esterification of alcohol using (bmim)HSO<sub>4</sub>

Table 1. Microwave assisted esterification of alcohol using bmim (HSO<sub>4</sub>)

S. No.	Alcohol*	Yield (%)	Literature Melting Point (°C)	Observed Melting Point (°C)
1	Methanol	40	109	108-109
2	Ethanol	40	93	92-93
3	n-Propanol	35	74	73-74
4	2-Propanol	30	122	122-123
5	n-Butanol	35	63	62-63
6	n-Pentanol	45	62	61-62
7	3-methyl-1-Butanol	45	62	62-64
8	n-Hexanol	40	59	58-59
9	n-Octanol	40	62	62-64
10	n-Decanol	45	57	56-57
11	Benzyl Alcohol	25	112	110-112

\*All the alcohols were freshly distilled.

Various alcohols which are routinely available in the common undergraduate laboratory were used to prepare the 3,5-dinitrobenzoates and identification was through melting point confirmation and listed in Table 1.

Results of this microwave assisted esterification with ionic liquid is overall a greener, cleaner and safer process. The protocol is in accordance with the principles of green chemistry. The procedure proceeds with less chemicals used, generates less waste, is time saving, energy efficient and in general gave better yields.

#### 6. Conclusion

The synthesis of 3,5-dinitro benzoate derivatives of simple alcohols is reported using a simple and environmentally friendly approach. Harmful chemicals are no longer used and undesired by-products are no longer formed. This method works well for most primary and secondary alcohols. The method adheres to the basic green chemistry concepts, making it simple to adopt in an undergraduate chemistry lab.

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#### 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.

#### References

- [1] Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G. and Tatchell, A. R., Vogel's Textbook of Practical Organic Chemistry, 5th Eds., Pearson Education Pte. Ltd., Delhi, India, pp. 1241-1242, 2006.
- [2] Ahluwalia, V. K.; Dhingra, S.; Comprehensive Practical Organic Chemistry: Qualitative Analysis; Universities Press Private Limited: Hyderabad, India, pp 56, 2000.
- [3] Anastas, P.T. and Warner, J.K. Oxford Green Chemistry - Theory and Practice, University Press, 1998.
- [4] Green Chemistry: An Introduction, Sujata Sengupta and Sharda M. Sonkar, Prestige Publication, 2019.
- [5] An Introductory Text on Green Chemistry, Indu Tucker Sidhwani and R.K. Sharma, Wiley Publications, 2020.
- [6] Martin, Eric; Kellen-Yuen, Cynthia (2007). *Microwave-Assisted Organic Synthesis in the Organic Teaching Lab: A Simple, Greener Wittig Reaction*. 84(12), 2004-0.
- [7] Kappe, C. Oliver; Murphree, S. Shaun (2009). *Microwave-Assisted Carbonyl Chemistry for the Undergraduate Laboratory*. 86(2), 227-0.

- [8] A brief review: Microwave assisted organic reaction 1Madhvi A. Surati, 1 Smita Jauhari\*, 2K. R. Desai, Archives of Applied Science Research, 2012, 4 (1): 645-661.
- [9] New Trends in Green Chemistry, Authors: Ahluwalia, V.K., Kidwai, M., 2004, Springer Publications.
- [10] For a short review of ionic liquids: Ionic Liquids: Prospects and Retrospect, Martyn J. Earle, Suhas P. Katdare and Alwar Ramani, in Green Chemistry: Environment Friendly Alternatives, Rashmi Sanghi and M. M. Srivastava, Narosa Publishing House.
- [11] Phosphorus pentachloride CAS No. 10026-13-8 [Online], LOBA Chemie Pvt. Ltd., Mumbai, India <https://www.lobachemie.com/lab-chemical-msds/MSDS-PHOSPHOROUS-PENTACHLORIDE-CASNO-10026-13-5258A-EN.aspx> PDF (accessed on 23 January 2022 at 3.24pm).
- [12] Thionyl chloride CAS No. 7719-09-7 [Online], LOBA Chemie Pvt. Ltd., Mumbai, In <http://obachemie.com/lab-chemical-msds/MSDS-THIONYL-CHLORIDE-CASNO-7719-09-06282-EN.aspx> PDF (accessed on 23 January 2022 at 3.33pm).
- [13] Hydrogen Chloride CAS No. 7647-01-0 [Online], Sigma-Aldrich, Bangalore, India <https://www.sigmaaldrich.com/IN/en/sds/SIGMA/H1758> PDF (accessed on 23 January 2022 at 3.36pm).
- [14] Phosphorus oxychloride CAS No 10025-87-3 [Online], LOBA Chemie Pvt. Ltd., Mumbai, <https://www.lobachemie.com/lab-chemical-msds/MSDS-PHOSPHORUS-OXYCHLORIDE-CASNO-10025-87-05258-EN.aspx> PDF (accessed on 23 January 2022 at 3.38pm).
- [15] Sulphur Dioxide CAS No. 7446-09-05 [Online], Sigma-Aldrich, Bangalore, India <https://www.sigmaaldrich.com/IN/en/sds/aldrich/295698> PDF (accessed on 23 January 2022 at 3.41pm).



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