

APPLICATION OF SONOCHEMISTRY FOR THE SYNTHESIS OF CAPRIC ALIPHATIC ESTERS

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Abstract

The aim of this study is to demonstrate a simple and rapid "green" method for the ultrasound assisted synthesis of aliphatic esters of capric acid. The spectral characterization of esters was performed by IR and NMR spectroscopies. The impact of ultrasonic irradiation on the reaction in a comparison with the conventional method was analyzed based on the reaction time and the yield of the resulting esters.

Keywords: keywords, keywords, keywords, keywords, keywords, keywords, keywords.

INTRODUCTION

The increased use of resources and the requirements for environmental protection require finding more efficient, environmentally friendly synthesis methods, as well as reducing the waste generated. [1-3]

After the formulation of the 12 principles of "green chemistry", this concept began to be supplemented with new content. Sonochemistry is a modern branch of green chemistry related to the application of ultrasonic waves to chemical processes. [4-6]

The main advantages of sonochemistry are the use of less dangerous chemicals and solvents, reducing energy consumption and increasing the selectivity of the reaction. In this regard, the ultrasonic impact in many cases facilitates the management of chemical reactions, stimulating higher efficiency and effectiveness. [7-9]

Ultrasound affects the reaction mixture not only with the high energy of cavitation, but also induces new reactivity, intensifies diffusion, improves stirring, which ultimately leads to the acceleration of the reaction and sometimes to the formation of unexpected organic compounds. [1, 9]

EXPERIMENTAL PART

Conventional synthesis

In a 300 cm³ Erlenmeyer flask, place 0.5 mol of alcohol, add 2 mmol of conc. H₂SO₄ as a catalyst, after which the weighed amount of 4

mmol fatty acid is added. The flask was connected to a water-cooled reflux condenser and heated to boiling.

After 120 min, the reaction is stopped and the reaction mixture is cooled intensively, with the addition of 100 cm³ of ice-cold dec of water and neutralized with 10% Na₂CO₃. Carry out three extractions with 20 cm³ of diethyl ether each. The extracts are combined and dried with anhydrous Na₂SO₄.

After filtering, the ether and alcohol are distilled under vacuum. The residue is separated and the yield of the ester is determined.

Ultrasonic synthesis

In a 300 cm³ Erlenmeyer flask, place the amount of 0.5 mol alcohol, add 2 mmol conc. H₂SO₄ as a catalyst, after which the weighed amount of 4 mmol fatty acid is added.

The flask was connected to a water-cooled reflux condenser and placed in a Dimoff A-2/2 ultrasonic bath (100 W, 44 kHz). It is treated with ultrasound for 15 min at room temperature.

After completion of the reaction, the reaction mixture was cooled intensively, with the addition of 100 cm³ of ice-cold distilled water and neutralization with 10% Na₂CO₃ was carried out. A triple extraction with 20 cm³ of diethyl ether is carried out. The extracts were combined and dried with anhydrous Na₂SO₄.

After filtration, the ether and the alcohol are distilled off under vacuum. The residue is separated and the yield of the ester is determined.

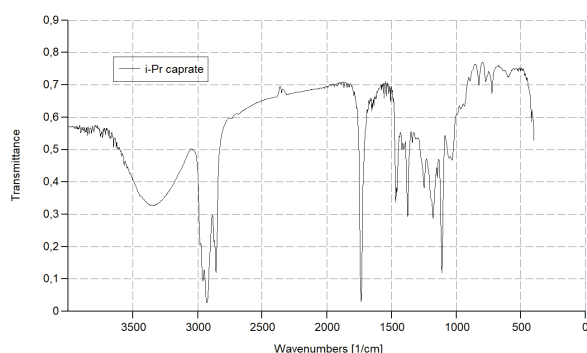
Identification and characterization methods

IR spectra of the investigated substances were recorded on an IR-FT spectrophotometer Nicolet Avatar (Termo Scientific, USA) in a KBr tablet. When recording the spectrum, thirty-two scans were performed in the interval between 4000 and 500 cm^{-1} .

^1H and ^{13}C NMR spectra were recorded on a Bruker Advance II+ 600 MHz instrument. All chemical references are presented in ppm and referenced to the TMS standard.

RESULTS AND DISCUSSION

The synthesis of aliphatic esters of capric acid was carried out by both methods - conventional and by ultrasound. The results of the yield of esters show its increase by 5 to 16 percentage points when applying the US method compared to the conventional one. The largest increase was for *i*-propanol and the smallest for *t*-butanol. Summary data are shown in Table 1.



a.

Fig. 1. IR-FT spectra of synthesized *i*-Pr caprate (a) and *i*-Bu caprate (b)

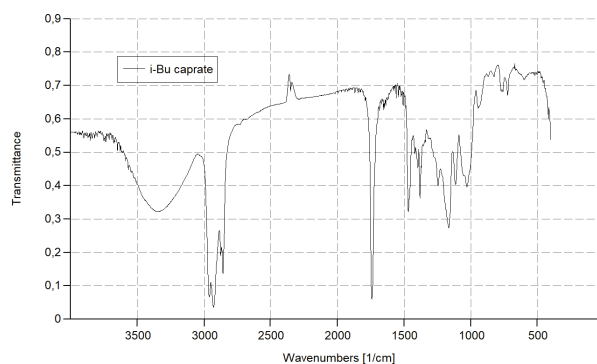
In the ^1H NMR spectra of the *i*-propyl caprate, resonance signals in the interval 4.83-4.90 ppm characteristic of methine protons CH of the *i*-propyl group are observed. Methyl protons from the *i*-propyl group are observed at 1.35-1.39 ppm, and methylene protons from the

Table 1. Reaction time and yield in the synthesis of aliphatic esters of capric acid

Ester	Conventional synthesis		US synthesis	
	Reaction time, min	Yield, %	Reaction time, min	Yield, %
<i>i</i> -Pr caprate	120	60	15	76
<i>n</i> -Bu caprate	120	70	15	82
<i>i</i> -Bu caprate	120	75	15	80
<i>t</i> -Bu caprate	120	80	15	87

Those obtained by US esterification aliphatic esters of capric acid were characterized by IR-FT spectroscopy. Several areas characteristic of esters stand out in the spectra. In the region 600-1500 cm^{-1} are the absorption bands of hydrocarbon chains.

The intense and narrow band in the spectrum at 1743 cm^{-1} due to valence vibrations ($\nu\text{C}=\text{O}$) of the carbonyl group in the ester is very clearly visible. The valence vibrations of the C-H bond are manifested in a band of medium intensity, which is observed in the region of 2930 cm^{-1} . In the case of esters, a band appears at about 2850 cm^{-1} corresponding to $\nu\text{C}-\text{H}_{\text{as}}(\text{CH}_2)$. In addition to them, bands characteristic for C-O-C from the ester group appear - 1270, 1223 cm^{-1} .



b.

aliphatic acid chain - at 0.97-1.0 ppm. Methylene protons are registered in the spectrum at 1.29-2.31 ppm, and the resonance signals for CH_2 protons associated with the $\text{C}=\text{O}$ group are observed at 2.28-2.31 ppm.

Resonance signals for carbonyl carbon atom at 172.83-174.36 ppm. The signals for the C atom of the *t*-butyl group were recorded at 81.62 ppm, and for the carbon atom of the *i*-butyl group at 19.69 ppm. The signals for the carbon atoms from the three methyl groups in *t*-butanol are observed at 28.3 ppm, and those from the fatty acid and *n*-butanol – at 14.02 ppm.

CONCLUSION

Ultrasonic energy was found to accelerate the esterification process of capric acid with aliphatic alcohols. As a result, the reaction time is significantly reduced, and the process is carried out at a low reaction temperature.

With the help of the used spectral methods, it was established that the aliphatic esters of capric acid were obtained, and that, under the selected synthesis conditions, no changes were observed in the molecules of the compounds.

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REFERENCE

- [1]. Mason, T., D. Peters Practical sonochemistry, Horwood Publishing Limited, 2011.
- [2]. Farris, R.D., J. Am. Oil Chem. Soc., 56, 1979, 770A-773A.
- [3]. Piccicuto, S., Blecker, C., Brohee, J.C., Mbampara, A., Lognay, G., Deroanne, C., Paquot, M., Marlier, M. Biotechnol., Agron. Soc. Environ, 5, 2001, 209-219.
- [4]. Vaze, S., Chem. Eng. World, 31, 1996, 115–116.
- [5]. Deshmane, V.G., P.R. Gogate, A.B. Pandit, Ultrasonics Sonochem., 16, 2009, 345.
- [6]. Hanh, H.D., N.T. Dong, K. Okitsu, R. Nishimura, Y. Maeda, Renew., Energy 34, 2009, 766, 780.
- [7]. Pacheco, B., C. Nunes, C. Rockembach, P. Bertelli, M. Mesko, M. Roesch-Ely, S. Moura, Cl. Pereira, Eco-friendly synthesis of esters under ultrasound with p-toluenesulfonic acid as catalyst, Green Chemistry Letters and Reviews, Vol. 7, No. 3, 2014, 265–270
- [8]. Wen, B., Wumanjiang Eli, Qunji Xue, Xin Dong, Weimin Liu, Ultrasound accelerated esterification of palmitic acid with vitamin C, Ultrasonics Sonochemistry 14 (2007) 213-218
- [9]. Hobuss, C., D. Venzke, B. Pacheco, A. Souza, M. Santos, S. Moura, F. Quina, K. Fiametti, J. Oliveira, C. Pereira, Ultrasound-assisted synthesis of aliphatic acid esters at room temperature, Ultrasonics Sonochemistry, 19, 2012, 387-389.