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N-Nitropyridinium Nitrate: An Efficient Nitrating Agent for the Synthesis of 2-[Butyl(nitro)amino]ethyl Nitrate (n-BuNENA)

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Abstract: The present investigation focused on the synthesis of 2-[butyl(nitro)amino]ethyl nitrate (n-BuNENA), by the nitration of *N*-butylethanolamine. For this purpose, various nitrating agents were studied and *N*-nitropyridinium nitrate was found to be a good nitrating agent. Short reaction time, ease of handling, performance of the reaction in one step and good yield are the main aspects of the present method. It also lead to 75% yield, which is a higher yield than by other methods. The purity of the product was evaluated by HPLC analysis, and its identity was confirmed by IR and ^{1}H NMR spectroscopy.

Keywords: 2-[butyl(nitro)amino]ethyl nitrate (n-BuNENA), zeolite, *N*-nitropyridinium nitrate, plasticizer, energetic material

1 Introduction

Energetic materials are generally organic compounds containing nitro, azido and hydrazino groups [1]. In the last three decades, some types of high energy materials, such as thermally stable explosives, high performance explosives and energetic plasticizers have been reported in the literature for future space applications [2-4]. The search for promising high-energy materials during the last two decade has led to the discovery of a vast number of energetic oxidizers, fuels and explosives for possible use as an energetic ingredient in propellant/explosive formulations. Among these types of materials, plasticizers containing nitro and nitrato groups are considered to be one of the practical ways to improve the physical and energetic level of solid propellants [5, 6]. Nitroxyethylnitramine (NENA) plasticizers were a new family of energetic plasticizers which were originally discovered in the 1940s [7] and have emerged recently because they generate low molecular weight combustion gases and their starting materials are commercially available at low cost. The basic objectives of developing energetic binders and plasticizers are to enhance the thermal stability and energy content, to improve the oxygen balance of a formulation, to reduce the glass transition temperature and the brittle-ductile transition temperature, and to improve other mechanical properties of the propellant matrix and the burning behaviour of the propellant [8]. 2-[Butyl(nitro)amino] ethyl nitrate (n-BuNENA) is currently being combined with hydroxyterminated polyethers (HTPEs) to develop propellant formulations that meet insensitive munitions (IM) requirements. This compound is currently prepared by nitration of *N*-butylethanolamine [9-11] and involves a zinc chloride-catalyzed, secondary amine nitration using acetic anhydride/nitric acid [12, 13]. The replacement of amino and hydroxyl hydrogens with a nitro group via direct nitration is an important route to N- and O-nitro derivatives. For this purpose various nitrating agents have been developed for the nitration of organic compounds [14, 15].

There are some problems with the synthesis of n-BuNENA from *N*-butylethanolamine which are listed below. The nitric acid-acetic anhydride nitrating system carries some warnings of the explosion hazards associated with the use of mixtures of fuming (97%) nitric acid and acetic anhydride [16]. At the end of the process, a large amount of spent acid is obtained, which, in batch processes, is usually neutralised and/or has to be recycled by complicated techniques. Furthermore, the separation of the products from the acidic solution is a difficult and energy consuming process, that normally implies a basic aqueous work-up. Acetic anhydride/nitric acid has been reported in the previous methods as a nitrating agent. This reagent has generated some byproducts and caused a reduction in the yield of the reaction. Acetic anhydride also has several disadvantages. Acetic anhydride is a restricted chemical due to its potential use in illegal narcotics production and not readily available in many countries. Moreover, acetic anhydride is an irritant and combustible liquid and its vapour is harmful. The substance can be absorbed into the body by inhalation of its vapour and by ingestion. However, the present methods suffer from further disadvantages, such as the use of corrosive and dangerous reagents, harsh reaction conditions and the reaction has been performed in a two step process that is not appropriate from both economic and environmental points of view [17]. *N*-Nitropyridinium nitrate is one of the good nitrating agents, and has been reported in the literature for various nitration reactions [18, 19]. Accordingly, and in continuation of our studies on high energy compounds [20], we decided to study the synthesis of n-BuNENA by the nitration of *N*-butylethanolamine using *N*-nitropyridinium nitrate as the nitrating agent.

2 Experimental

2.1 Materials and instruments

Nitric acid, pyridine and pyrazole were purchased from Merck, *N*-butylethanolamine from Aldrich, acetonitrile from Fluka, dichloromethane and hexane from Dr. Mojalali Company, dinitrogen tetraoxide, zeolites and acetic anhydride from Pingxiang Xiangfeng Company. Dinitrogen pentoxide [21] and ionic liquid [22] were synthesized and *N*-nitropyridinium nitrate was prepared according to a literature method [23]. IR spectra were recorded on a Perkin Elmer FT-IR Spectrometer, usually as a neat sample. ^{1}H NMR spectra were recorded on a Bruker-AC 250 MHz instrument with a pulse Fourier Transform (FT) system, at ambient temperature using tetramethylsilane (TMS) as the internal standard. The purity of n-BuNENA was checked by high performance liquid chromatography (HPLC) using a C8-micro-BP column, a mobile phase of methanol-water (70:30) adjusted to pH 3, a flow rate of 1 mL/min and a UV detector at 230 nm.

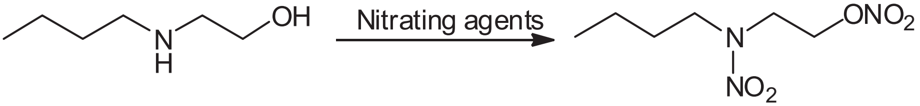
2.2 Procedure

N-Nitropyridinium nitrate (3.74 g, 0.02 mol) and *N*-butylethanolamine (1.17 g, 0.01 mol) were added to acetonitrile (10 mL) at 0 °C in a three-necked round-bottom flask (50 mL) equipped with a thermometer under a nitrogen atmosphere and the reaction mixture was stirred for 1 h. The completion of the reaction was monitored by HPLC (Figure 1). The mixture was poured onto ice (30 g) and stirred for 5 min. The mixture was then extracted with dichloromethane (2 × 10 mL) and the combined extracts were dried over magnesium sulfate. The solution was concentrated by rotary evaporation and n-BuNENA was obtained in 75% yield, as a yellow oil of purity 95%. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.97 (t, $J = 7.3$ Hz, 3 H), 1.38 (m, 2 H), 1.68 (m, 2 H), 3.78 (t, $J = 7.5$ Hz, 2 H), 4.05 (t, $J = 4.9$ Hz, 2 H), 4.77 (t, $J = 4.9$ Hz, 2 H). IR (neat, cm^{-1}): 2963, 2939 and 2876 (CH), 1640 (O-NO_2), 1516 and 1273 (N-NO_2), 847 (N-O). EI-MS (70 ev) m/s: 207 (M^+), 199, 182, 166, 147, 129, 117, 105, 91, 77, 57, 43.

For the measurement of the purity of the prepared n-BuNENA, a 100 ppm standard solution of pure n-BuNENA was prepared as the stock solution and other solutions were prepared from the stock solution by dilution, to obtain the calibration curve. Then the solution of n-BuNENA from a reaction mixture was injected into the HPLC instrument and the purity was obtained from the calibration curve.

3 Results and Discussion

In order to optimize the reaction conditions, we carried out the nitration of *N*-butylethanolamine with various nitrating agents and at different temperatures (Scheme 1).



Scheme 1. Synthesis of n-BuNENA from *N*-butylethanolamine.

The best results were obtained when we used *N*-nitropyridinium nitrate as the nitrating agent. The results are summarized in Table 1.

Table 1. Comparison of various nitrating agents for the synthesis of n-BuNENA from *N*-butylethanoleamine

Entry	Nitrating agent	Time [h]	Temp. [°C]	Yield [%]
1	HNO_3, Ac_2O-$ZnCl_2$	2	0	70
2	*N*-nitropyrazole, BF_3	1.5	0	70
3	HNO_3, Ac_2O-Zeolite LaY	2	0	50
4	HNO_3, Ac_2O, Zeolite HZSM-5	2	0	41
5	N_2O_5	1	0	51
6	N_2O_5, NaF	1	0	70
7	N_2O_5, Zeolite HZSM-5	1	0	50
8	HNO_3 / KNO_3 / $BF_3{\cdot}OEt_2$	1	0	Trace
9	IL TEABS / N_2O_4 / $BF_3{\cdot}OEt_2$ *	1	0	-
10	***N*-nitropyridinium nitrate**	**1**	**0**	**75**
11	*N*-nitropyridinium nitrate	0.5	0	40
12	*N*-nitropyridinium nitrate	2	0	75
13	*N*-nitropyridinium nitrate	1	60	trace
14	*N*-nitropyridinium nitrate	1	r.t	35
15	*N*-nitropyridinium nitrate	1	10	58
16	*N*-nitropyridinium nitrate	1	−10	70

* Ionic Liquid Tri N Ethyl Ammonium Butane Sulfonate

According to Table 1, the best result was obtained when we used *N*-nitropyridinium nitrate as the nitrating agent and the purity of the product obtained was 95% by HPLC analysis (Figure 1).

Although *N*-nitropyrazole can be used in this reaction (entry 2), the use of BF_3 and a slightly lower yield in comparison to the use of *N*-nitropyridinium nitrate are the main disadvantages. Increasing the temperature led to lower yields probably related to the lower stability of the nitronium ion at higher temperatures and adverse reactions in the mixture (entry 13-15). Decreasing the temperature below 0 °C failed to improve the yield (entry 16).

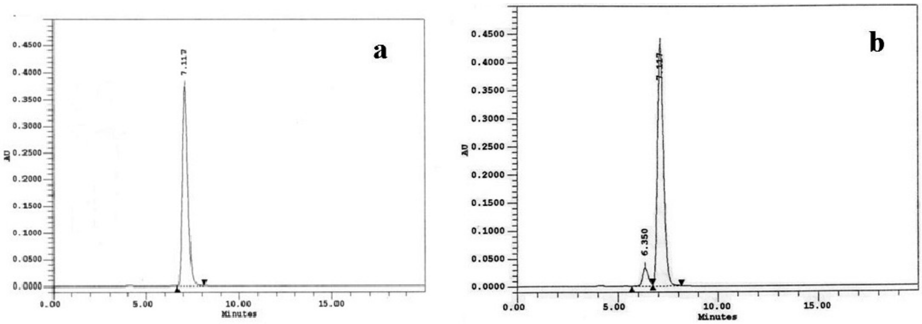
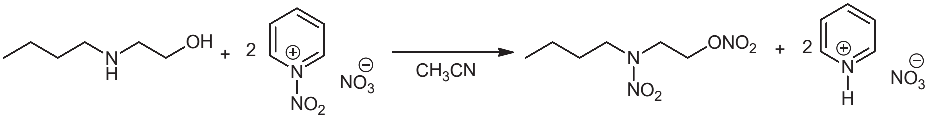


Figure 1. (a) Chromatogram of pure n-BuNENA, and (b) Chromatogram of synthesized n-BuNENA.

The advantages of this method are that it avoids using acetic anhydride and reaction times are shorter. Moreover, the yields are higher in comparison to previous methods. The use of *N*-nitropyridinium nitrate as an organic nitrating agent and ease of handling are the main aspects of the present method [19] (Scheme 2).



Scheme 2. Reaction of *N*-butylethanolamine with *N*-nitropyridinium nitrate.

The by-product in this method is *N*-hydropyridinium nitrate which can be easily separated from the product during extraction of reaction mixture.

4 Conclusions

In this paper, we have presented a powerful and efficient method for the synthesis of n-BuNENA. The reaction was performed at 0 °C for 1 h using

N-nitropyridinium nitrate as an organic nitrating agent. Ease of work-up, short reaction time and performing the reaction in a single step are the main advantages of this method. Moreover we found that *N*-nitropyridinium nitrate is a good nitrating agent for use in organic solvents due to its high solubility and is a more suitable nitrating agent in non-aqueous solvents. Due to the importance of n-BuNENA, the synthesis of this compound can be still considered in the future.

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