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Ultrasonically promoted nitrolysis of DAPT to HMX in ionic liquid

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Abstract

The present work aims at developing a new process to synthesize HMX from DAPT using ultrasound in ionic liquid. Reaction has been carried out in ultrasonic bath, effect of various parameters such as presence and absence of ultrasound, volume and type of solvent, temperature, concentration of nitrating agent has been investigated with an aim of obtaining the optimum conditions for the synthesis of HMX. It was observed that ultrasonically promoted nitroylsis of DAPT to HMX has exhibited significant enhancement in yield at ambient condition.

Keywords: Ultrasonic; Ionic liquid; HMX; Nitrolysis

1. Introduction

HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) is one of the most powerful military explosives [1–3]. Just as RDX (cyclotrimelhylene trinitramine), it is prepared from inexpensive chemicals(hexamethylenetetramine and nitric acid). However, it is about five times as costly as RDX. RDX can be made in good yields by several procedures. In contrast, only one method is available for preparing HMX that developed by Bachmann and Sheehan, and this process has a series of undesirable features [4], including high usage of acetic anhydride, slow rate of production and poor yield. Other ways such as TAT (1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane) procedure and DADN (1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane) procedure need three or more steps to produce HMX, and they are not economical or in favor of environment.

In recent years, ultrasound has been employed in various chemical transformations with considerable enhancement in rates and yield, and in several cases facilitates organic transformations at ambient conditions which otherwise require drastic conditions of temperature and pressure, or even unachievable reactions [5–11]. The driving energy is provided by cavitations, the formation and collapse of bubbles, which liberates considerable energy in short time. The use of non-volatile solvents should provide a clue to force less volatile substrates to undergo the cavitational activation. The increasing use of non-aqueous room temperature ionic liquids (IL) for synthetic purposes corresponds to a new trend in Green Chemistry. These liquids have no vapor pressure, which should change considerably the characteristics of cavitation in this bulk [12–14]. For this reason, we envisaged to use the combination of both these concepts to induce new focuses.

One-step reaction from DAPT (3,7-diacetyl-1,3,5,7-tetraazacyclo-[3.3.1]-octane) to HMX can hardly be finished with very low yield (<10%) in common conditions. In this paper, this procedure can be completed with much higher yield by the ultrasonic assistance. The nitration of DAPT was carried out in a room temperature ionic liquid under sonochemical conditions using N_2O_5/HNO_3 as nitrating agent.

2. Experimental

2.1. Chemicals

Dinitrogen pentoxide is prepared by the reaction of N_2O_4 with ozone [15] and stored at −20 °C before use. IL is [BMIM]PF_6^-, which is prepared by a reported method

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[16], and its purity is more than 99.8% (tested by ^{1}H NMR), it is directly used in the ultrasonic nitration. Other chemicals were of research grade and were used as obtained from J&K Co. Ltd.

2.2. Equipments

The experiment was carried out in a round-bottomed flask of 25 ml capacity. Ultrasonic bath was used for irradiation with ultrasound, which was produced by a ultrasonic cleaning bath (KGD-250B) at 40–80 kHz. The ultrasonic cleaner had a rated input power of 120 W. The tank dimensions were 350 mm × 1800 mm × 150 mm with liquid holding capacity of 8.9 l. The reactions were carried out in suspended at the centre of the cleaning bath, 5 cm below the surface of the liquid. The experimental setup is shown in Fig. 1.

^{1}H NMR spectra was recorded on Bruker DRX 300 MHZ.

IR spectra was recorded on MB154SFTIR using KBr pellets.

Mass spectra was recorded on Finnigan TSQ Quantumm ultra AM LC/MS spectrometer.

2.3. Typical procedure for sonochemical nitration

Quantitative IL and 1 g DAPT were placed in a three-neck 25 ml flask, stirred and sonicated in a thermostated ultrasonic cleaning bath at certain temperature. N_2O_5 dissolved in 98% nitric acid was cooled to −10 °C and then decanted into an addition funnel and added to the flask dropwise over a 10 min period. The mixture was stirred for 1 h and the temperature was kept the same. The ultrasonic cleaner was kept on working during the whole reaction. After reaction, the mixture was poured to 100 ml ice water, cooling and crystalling. After filtrating and drying, HMX was obtained and analyzed by LC/MS. IL can be recycled by simple partition (see Table 1).

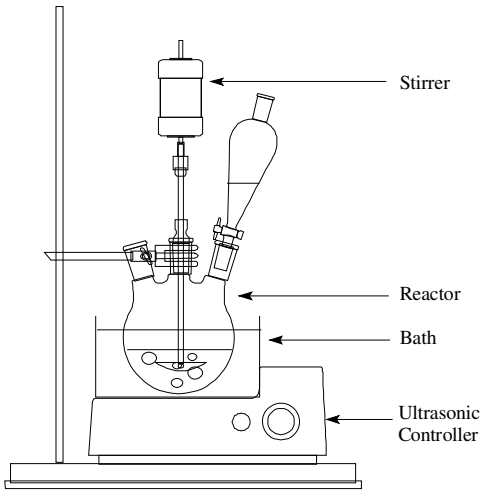

Fig. 1. Experimental setup.

Table 1
Nitration of DAPT under ultrasonic condition

Entry	Solvent	Frequency[a]/ kHz	$n(HNO_3)$:$n(N_2O_5)$: n(DAPT)	Temperature (°C)[b]	Yield (%)[c]
1	None	None	24:3:1	40	9.6
2	None	40	24:3:1	40	34.5
3	5 ml CH_2Cl_2	40	24:3:1	40	31.2
4	5 ml IL	40	24:3:1	40	66.8
5	5 ml IL	30	24:3:1	40	53.5
6	5 ml IL	60	24:3:1	40	47.9
7	5 ml IL	80	24:3:1	40	38.3
8	10 ml IL	40	24:3:1	40	59.4
9	20 ml IL	40	24:3:1	40	51.5
10	5 ml IL	40	24:3:1	60	63.4
11	5 ml IL	40	24:3:1	80	65.1
12	5 ml IL	40	12:1:1	40	24.0
13	5 ml IL	40	12:6:1	40	64.9
14	5 ml IL	40	12:8:1	40	57.2
15	5 ml IL	40	12:3:1	40	46.2
16	5 ml IL	40	36:3:1	40	60.7
17	5 ml IL	40	48:3:1	40	54.3

[a] The power of ultrasound transferred into the reaction depends on the frequency of ultrasound. As the dissipated power cannot be changed on the control panel, it was indirectly varied by adjusting the frequency of ultrasound.

[b] Temperature control is difficult, for the irradiation of ultrasound can lead to temperature rise. In order to keep the temperature invariable, the temperature on the control panel should be set a little lower than appointed temperature, the balance of the evaporation of water and the irradiation of ultrasound can keep the water in steady and needed temperature.

[c] Yield is calculated by DAPT.

3. Results and discussions

High price of HMX is the restriction for its application. DAPT can be gained with a yield of over 100% by acetolysis of hexamine with acetic anhydride in the presence of ammonium acetate. If HMX can directly produced from DAPT, its costs can be reduced a lot.

Initially experiments were carried out in the absence of ultrasound. One-step reaction from DAPT to HMX is almost infeasible. However, in the reactions using N_2O_5/HNO_3 as nitrating agent, the ultrasonically mediated nitrolysis has led to a high yield in an ambient condition. The effects of various operating parameters on the yield of HMX are discussed below.