Chinese Chemical Letters 25 (2014) 423–426

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

An efficient method to synthesize TNAD by the nitration of 1,4,5,8-tetraazabicyclo-[4,4,0]-decane with N_2O_5 and acidic ionic liquids

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ARTICLE INFO

Article history:
Received 12 August 2013
Received in revised form 9 December 2013
Accepted 10 December 2013
Available online 24 December 2013

Keywords:
1,4,5,8-Tetraazabicyclo-[4,4,0]-decane
N_2O_5
Inert solvent
Acidic ionic liquids
TNAD

ABSTRACT

An experimental study was carried out on the direct nitration of 1,4,5,8-tetraaza-bicyclo-[4,4,0]-decane to synthesize 1,4,5,8-tetranitro-1,4,5,8-tetraazabicyclo-[4,4,0]-decane (TNAD) with N_2O_5 catalyzed by acidic ionic liquids. Various ionic liquids, such as [HMim]X, $[(CH_2)_4SO_3HMim]X$ and [Capl]X ($X^- = p\text{TSO}^-$, NO_3^-, HSO_4^-), and various parameters such as equivalents of ionic liquid, molar ratio of N_2O_5 to the starting material, reaction time and temperature, and solvent were investigated. Ionic liquid $[(CH_2)_4SO_3HMim]HSO_4$ showed better catalytic activity. In the presence of 3% molar ratio of $[(CH_2)_4SO_3HMim]HSO_4$ ionic liquid to the staring material, the yield of 1,4,5,8-tetranitro-1,4,5,8-tetraazabicyclo-[4,4,0]-decane was improved by 6.2% compared to the system without ionic liquid.

1. Introduction

Cyclic nitramines constitute an important class of highly energetic materials whose synthesis and properties have been extensively studied. 1,4,5,8-Tetranitro-1,4,5,8-tetraazabicyclo-[4,4,0]-decane was first synthesized by Willer [1] and it is an energetic compound used as a main ingredient in composite explosives and propellants. TNAD can yield a lower pressure exponent than that of RDX and HMX, the rate of change in space of the temperature gradient is negligible for these propellants and the rate of mass diffusion is believed to be smaller compared with the rate of mass convection [2,3]. The compatibility of TNAD with other energetic components and inert materials is one of the most stringent aspects of TNAD [4]. In practical applications, it is responsible for releasing the reactivity in these compounds when detonated [5].

The synthesis of TNAD using conventional reagents involved the nitrolysis of 1,4,5,8-tetranitroso-1,4,5,8-tetraazabicyclo-[4,4,0]-decane [1,6,7] and the nitration of 1,4,5,8 -tetraazabicyclo-[4,4,0]-decane with HNO_3/Ac_2O as the nitrating reagents [8]. However, the yields of nitrolysis reactions are below 60% and the sequence involves more than two steps. The yield of the first step of the nitrolysis is very high, but the disposal is difficult because it generates HCl. The yield of the second step is low and all nitrolyses employ HNO_3 or H_2SO_4 as solvent. The yields can be improved in the presence of HNO_3–Ac_2O, but this reaction requires a large excess of nitric acid and acetic anhydride in more than 2 h, which adds considerable expense. Also the high reaction temperature makes the reaction dangerous. In short, these methods inevitably showed some weaknesses such as poor yield, environmental pollution, low reaction rate, and inconvenient waste disposal.

In recent years, various cleaner nitration approaches have been explored. N_2O_5 employed as a green nitrating reagent had been studied for several years. Millar *et al.* [9] introduced N_2O_5 in an inert solvent into the synthesis of nitramines and nitrate esters. Talawer *et al.* [10] succeeded in finding several N_2O_5–inert solvents as green and mild systems. Zhi *et al.* [11] reported that PEG200-DAIL with N_2O_5 could increase the yield of HMX significantly. Cheng *et al.* [12] improved the yield of RDX by 10.5% using ionic liquid as a catalyst.

The past few years have witnessed a growing interest in ionic liquids (ILs) as solvent and catalyst for certain organic reactions. In the presence of ionic liquids, the conversions of the nitration of aromatic compounds have a significant improvement [13–17].

Here we combined the advantage of acidic ionic liquid with N_2O_5-inert solvents. We attempted nitration of 1,4,5,8-tetrazabicyclo-[4,4,0]-decane using the green nitrating agent, dinitration pentoxide, in the presence of acidic ionic liquids. In this reaction, the temperature is lower, there is no acidic waste and the solvent can be used repeatedly. The results are presented in this letter.

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1001-8417/$ – see front matter
http://dx.doi.org/10.1016/j.cclet.2013.12.015

2. Experimental

All chemicals were purchased from commercial sources and used for the reaction without further purification. The melting points were obtained with a WRS-1B Digital Melting Apparatus. The IR spectra were recorded on a Nexus 870FT-IR spectrometer and expressed in cm^{-1}. ^{1}H NMR was recorded on a Bruker DRX 500 MHz spectrometer.

2.1. Preparation of N_2O_5 [18]

P_2O_5 was added slowly to a distillation flask containing freshly distilled nitric acid (100%) and reaction temperature should be kept below 10 °C. Slow distillation affords N_2O_5 with the liberation of nitrogen oxides. The collected N_2O_5 was a white/yellow solid. The product was warmed slowly to 10 °C so that any liquid nitrogen oxides were discarded. It is important that the N_2O_5 used is free of nitrogen oxides. Caution: N_2O_5 is highly corrosive and liberates toxic nitrogen oxide. Small amounts can be quickly neutralized with copious amount of water.

2.2. Preparation of acidic ionic liquids

[HMim]X (X^- = pTSO$^-$, NO_3^-, HSO_4^-) were synthesized according to the procedures reported by Lu *et al.* [12].

[HMim]pTSO: ^{1}H NMR (500 MHz, D_2O, TMS): δ 2.21 (s, 3H), 3.69 (s, 3H), 7.17 (d, 2H), 7.20 (d, 2H), 7.54 (s, 2H), 8.31 (s, 1H). [HMim]NO_3: ^{1}H NMR (500 MHz, D_2O, TMS): δ 3.80 (s, 3H), 7.46 (s, 2H), 8.70 (s, 1H). [HMim]HSO_4: ^{1}H NMR (500 MHz, D_2O, TMS): δ 3.69 (s, 3H), 7.21 (s, 2H), 8.43 (s, 1H).

[$(CH_2)_4SO_3$HMim]X (X^- = pTSO$^-$, NO_3^-, HSO_4^-) were synthesized according to the procedures reported by Qi *et al.* [19].

[$(CH_2)_4SO_3$HMim]HSO_4: ^{1}H NMR (500 MHz, D_2O, TMS): δ 1.46 (m, 2H), 1.51 (t, 2H), 2.11 (s, 3H), 2.69 (t, 2H), 3.60 (s, 3H), 7.08 (d, 1H), 7.18 (d, 2H), 7.42 (d, 2H), 8.40 (s, 1H). [$(CH_2)_4SO_3$HMim]pTSO: ^{1}H NMR (500 MHz, D_2O, TMS): δ 2.03 (s, 3H) 2.13 (m, 2H), 2.76 (t, 2H), 3.75 (s, 3H), 4.12 (t, 2H) 7.15 (d, 2H), 7.21 (d, 2H) 7.38 (s, 2H), 8.34 (s, 1H).

[Capl]X (X^- = pTSO$^-$, NO_3^-, HSO_4^-) were synthesized according to the procedures reported by Cheng *et al.* [20].

[Capl]pTSO: ^{1}H NMR (500 MHz, D_2O, TMS): δ 1.61–1.77 (m, 6H), 2.41 (s, 3H), 2.49 (t, 2H), 3.26 (t, 2H), 7.38 (d, 2H), 7.71 (d, 2H). [Capl]NO_3: ^{1}H NMR (500 MHz, D_2O, TMS): δ 1.41–1.61 (m, 6H), 2.34 (t, 2H), 3.10 (t, 2H). [Capl]HSO_4: ^{1}H NMR (500 MHz, D_2O, TMS): δ 1.37–1.57 (m, 6H), 2.16 (t, 2H), 3.02 (t, 2H).

2.3. Preparation of 1,4,5,8-tetraazabicyclo-[4,4,0]-decane [8]

This compound was obtained as a white powder, mp 205–207.6 °C [lit. [8]: 210–230 °C]. IR (KBr, cm^{-1}): ν 3160(s), 2940(s), 2890(s), 2800(s), 1490(m), 1340(m), 1310(w), 1150(s), 950(s), 860(s).

2.4. General procedure for the synthesis of TNAD catalyzed by acidic ionic liquids

To a cold (0 °C) vigorously stirred solution of N_2O_5 (30 mmol) and CH_2Cl_2 (30 mL), an indicated amount of ionic liquid was added. A given amount of 1,4,5,8-tetraazabicyclo-[4,4,0]-decane was added in portions to keep the temperature below 5 °C. The reaction was carried out at 25 °C for 60 min, and then the mixture was cooled to 20 °C and poured into 50 g of ice water. The solid product was collected by filtration and rinsed with water, the pure product was obtained after recrystallization from DMSO and dried in vacuum. Mp 231.5–232.3 °C; IR (KBr, cm^{-1}): ν 3040(w), 2960(w), 1550(s), 1280(s), 1060(m); ^{1}H NMR (500 MHz, DMSO, TMS): δ 6.5 (s, 2H), 4.4 (m, 4H), 2.5 (m, 4H). ^{13}C NMR (125 MHz, DMSO, TMS): δ 46.9, 69.9.

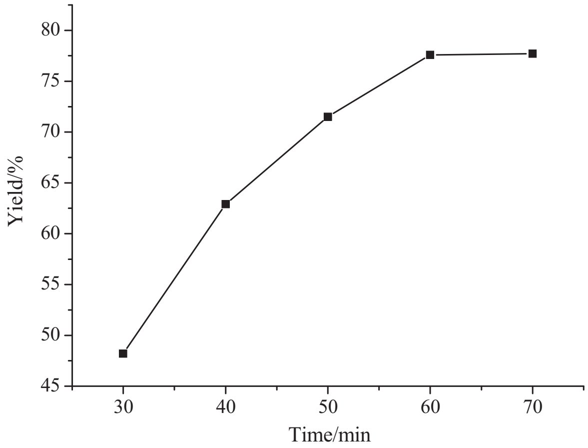


Fig. 1. The effect of reaction time on the nitration. Reaction conditions: n(1,4,5,8-tetraazabicyclo-[4,4,0]-decane)/n(N_2O_5) = 1:6, N_2O_5/CH_2Cl_2 (30 mmol/30 mL), 25 °C.

3. Results and discussion

In our initial study, the nitration of 1,4,5,8-tetraazabicyclo-[4,4,0]-decane (prepared according to [8]) using N_2O_5 in inert solvent in the range of reaction temperatures, reaction times, molar ratios and solvents were examined.

It can be seen from Fig. 1 that the yield of TNAD increased and the reaction rate decreased gradually with time. Most of the reaction was occurred in 50 min. The yield was 77.6% and did not change after 60 min.

Subsequently the effect of reaction temperature on nitration was explored and the results are shown in Table 1. When the reaction temperature was 0 °C, only 15.8% yield was obtained in 60 min and the yield increased as the reaction temperature increased from 0 °C to 25 °C. Continuing to rise the reaction temperature had an adverse effect on the yield. The reason may be higher temperature made the N_2O_5 decomposed more rapidly.

The effect of molar ratio of N_2O_5 to 1,4,5,8-tetraazabicyclo-[4,4,0]-decane was investigated and the results are summarized in Table 2. It was observed that the yields were improved significantly as the amount of N_2O_5 increased. The reason was that N_2O_5 could produce more NO_2^+, which was a good nitrating agent that can improve the yield of TNAD. However, excessive N_2O_5 resulted in lower yield. That may be because of that fact that higher concentration N_2O_5 cleaved the cyclic structure of the product.

Table 3 shows the results of the nitration of 1,4,5,8-tetrazabicyclo-[4,4,0]-decane using N_2O_5 in various inert solvents. It was observed that the yields were improved significantly in more polar solvents. The reason was that polar solvent could

Table 1
Effect of reaction temperature on the nitration.[a]

No.	T (°C)	Yield (%)	Purity (%)
1	0	15.8	99.7
2	15	46.9	99.2
3	25	77.6	99.4
4	35	73.4	99.5
5	45	70.5	99.4

[a] Reaction conditions: n(1,4,5,8-tetraazabicyclo-[4,4,0]-decane)/n(N_2O_5) = 1:6, N_2O_5/CH_2Cl_2 (30 mmol/30 mL), 60 min.

Table 2
Effect of molar ratio on the nitration.[a]

No.	$n(N_2O_5)$:n(1,4,5,8-tetraazabicyclo-[4,4,0]-decane)	Yield (%)	Purity (%)
1	4:1	37.3	99.3
2	5:1	62.1	99.5
3	6:1	77.6	99.8
4	7:1	69.3	99.4
5	8:1	67.6	99.4

[a] Reaction conditions: N_2O_5/CH_2Cl_2 (30 mmol/30 mL), 60 min, 25 °C.

Table 3
Effect of solvent on the nitration.[a]

No.	Solvent	Yield (%)	Purity (%)
1	CH_3NO_2	83.2	99.5
2	$CHCl_3$	79.5	99.6
3	CH_2Cl_2	77.6	99.2
4	CCl_4	71.4	99.8

[a] Reaction conditions: n(1,4,5,8-tetraazabicyclo-[4,4,0]-decane)/$n(N_2O_5)$ = 1:6, 30 mmol N_2O_5, solvent 30 mL, 25 °C, 60 min.

promote the production of NO_2^+ from N_2O_5. The yield of TNAD reached 83.2% in the presence of CH_3NO_2.

Numerous papers have reported that strong acidic catalysts could promote the formation of electrophilic nitronium ions (NO_2^+) from N_2O_5 [21,22]. The effect of the amount of ionic liquid on the nitration of 1,4,5,8-tetrazabicyclo-[4,4,0]-decane was investigated using $[(CH_2)_4SO_3HMim]HSO_4$ in the range of 1%–5% mol ratio to 1,4,5,8-tetrazabicyclo-[4,4,0]-decane, and the results are shown in Fig. 2. It was observed that the yield could be increased to 89.4%, however, further increasing the $[(CH_2)_4SO_3HMim]HSO_4$ loading would decrease the yield. The reason may be that an appropriate acidity was necessary for the nitration reaction. It is important to emphasize that ILs must be used dry to provide the yield achieved.

Then the reaction was compared in several IL systems. Based on the data in Table 4, the conclusion could be drawn that all ILs have catalytic activity in the nitration. Compared to the system without ILs, the yield of TNAD increased by 3.0%–6.2% under the mild conditions indicated in Table 4. The IL $[(CH_2)_4SO_3HMim]X$ showed better catalytic activity than other ILs. This might be related to the acidity of the cations (Scheme 1).

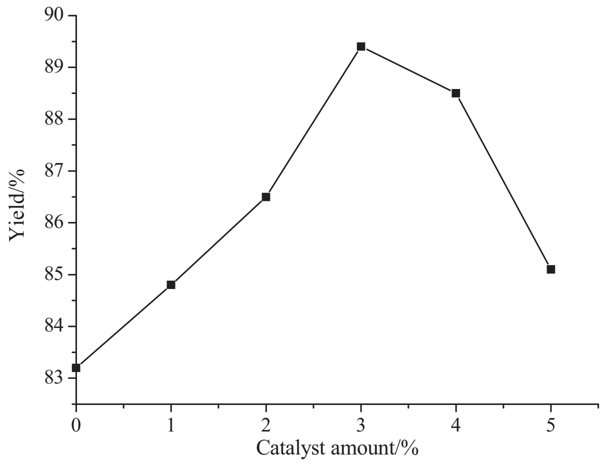


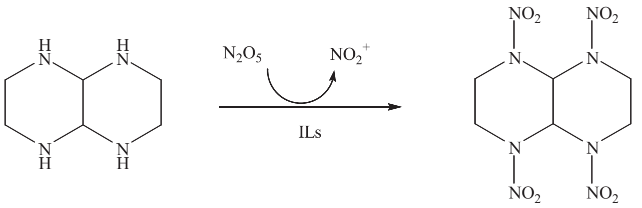
Fig. 2. Effect of the equivalents of ionic liquid on the nitration. Reaction conditions: n(1,4,5,8-tetraazabicyclo-[4,4,0]-decane)/$n(N_2O_5)$ = 1:6, 60 min, 25 °C, N_2O_5/CH_3NO_2 (30 mmol/30 mL).

Table 4
Nitration of 1,4,5,8-tetraazabicyclo-[4,4,0]-decane in various ILs.[a]

No.	IL[b]	Yield (%)	Purity (%)
1	$[HMim]HSO_4$	89.1	99.4
2	$[HMim]NO_3$	88.4	99.6
3	[HMim]*p*TSO	87.3	99.2
4	$[(CH_2)_4SO_3HMim]HSO_4$	89.4	99.3
5	$[(CH_2)_4SO_3HMim]NO_3$	88.8	99.3
6	$[(CH_2)_4SO_3HMim]$*p*TSO	87.9	99.5
7	$[Capl]HSO_4$	88.3	99.4
8	$[Capl]NO_3$	87.6	99.8
9	[Capl]*p*TSO	86.2	99.5

[a] Reaction conditions: n(1,4,5,8-tetraazabicyclo-[4,4,0]-decane)/$n(N_2O_5)$ = 1:6, 60 min, 25 °C, N_2O_5/CH_3NO_2 (30 mmol/30 mL).

[b] The catalyst amount is 3% molar ratio to 1,4,5,8-tetrazabicyclo-[4,4,0]-decane.



Scheme 1. Possible mechanism for electrophilic nitration.

4. Conclusion

In conclusion, a new efficient process to synthesize TNAD from 1,4,5,8-tetraazabicyclo-[4,4,0]-decane in 89.4% yield was successfully developed using N_2O_5 and $[(CH_2)_4SO_3HMim]HSO_4$ in CH_3NO_2. The combination of IL and N_2O_5 seems to be a useful nitrating system. However, the nitration of other nitrogen heterocyclic compounds using this mild reaction system should be further studied.

Acknowledgment

We are grateful for the financial support from the Nature Science Foundation of Jiangsu Province (No. BK2011697).

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