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SHORT COMMUNICATION

Preparation of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane from 2,6,8,12-tetraacetyl 2,4,6,8,12-hexaazaisowurtzitane using Various Nitrating Agents

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ABSTRACT

The 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW), a high energy material with cage structure, is considered as the most powerful explosive today. It is usually prepared via nitration with concentrated nitric and sulphuric acid, but this technique pollutes the environment. In this study, HNIW was synthesised by nitration of 2,6,8,12-tetraacetyl 2,4,6,8,12-hexaazaisowurtzitane (TAIW) various nitrating agents. Using this nitrating agent, the reaction eliminated use of concentrated sulphuric acid and was also environmental- friendly. Meanwhile, the effects of reaction temperature, time, and other factors on yield were studied. The structure of the compound was characterised by elemental analysis, Infrared, ^{1}*H*NMR and MS.

Keywords: CL-20, nitration, HNIW, TAIW, synthesis of explosives, propellant compounds

1. INTRODUCTION

The search for new energetic materials as potential replacements for currently used explosive and propellant formulations (used in gun and rocket propellants) is an area of intense investigation in military and industrial applications[1–4]. There are three propellant compounds currently attracting much interest: 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12 hexaazaisowurtzitane (HNIW), also known as CL-20, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, also known as HMX, and hexahydro-1,3,5-trinitro-1,3,5-triazine, also known as RDX. All three nitramine compounds are structurally related to one another. (Fig. 1.)

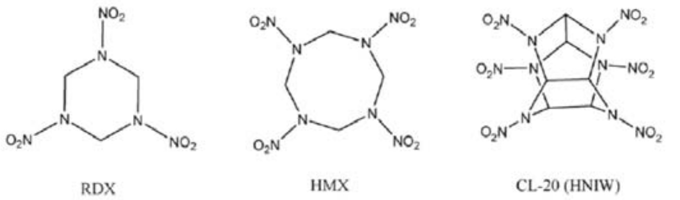

Figure 1. Structures of RDX, HMX and CL-20.

Many reports published on its physical characteristics have been reviewed in a recent article by Nielsen[1], *et al.* All known methods of producing HNIW are based on the same starting material, 2,4,6,8,10,12-hexabenzyl 2,4,6,8,10,12-hexaazaisowurtzitane, which is first reductively acylated to form 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazaisowurtzitane[5]. Synthesis efforts have been made for a number of nitrolysable precursors to CL-20, including isowurtzitane cage substituted with nitroso[5], formyl[6], and acetyl[7], groups. Synthesis of CL-20 from TAIW has appeared as a favourable method, both in terms of process economy and product purity. The High Energy Materials Research Laboratory, Tehran has established a process for the preparation of CL-20 by nitration of TAIW[8]. CL-20 is usually prepared via nitration with concentrated nitric acid and sulphuric acid, but this technique pollutes the environment.

The majority of organic nitration require the use of sulphuric acid or oleum in the nitric acid because sulphuric acid is present as catalyst, solvent, and dehydrating agent. Also, in about 94 per cent sulphuric acid, the nitric acid practically completely ionised to nitryl ion. Utilisation of sulphuric acid produces contaminated and diluted spent acid stream. Nitration of HBIW with harsh or mild nitrating agents results in decomposition of the cage structure[1]. This necessitated the synthesis of easily nitrolysable precursors from HBIW for the synthesis of CL-20. The present study aims to find the explosive and thermal characteristics of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane and considering explained disadvantages associated with nitration in the presence of sulphuric acid prompted the authors to develop an acceptable synthetic procedure and nitration for this material (Scheme 1).

2. EXPERIMENTAL

The melting points were determined on open capillary and were not corrected. IR spectra were recorded by Perkin-Elmer infrared spectrometer using matrix KBr. ^{1}*H*NMR and ^{13}*C*-NMR spectra were recorded on Backer 300 MHz instrument model WG-300 and δ units with reference to tetramethylsilane

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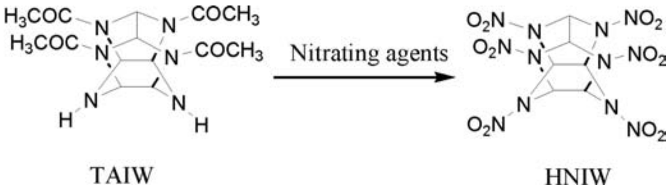

Scheme 1. Nitration of TAIW.

internal standard. Commercially available solvents and reagents were used without further purification. TAIW was prepared according to a published procedure[9].

2.1. Nitration of 2,6,8,12-tetraacetyl 2,4,6,8,10,12-hexaazaisowurtzitane exemplified for N_2O_4

To a solution of TAIW (336 mg, 1 mmol) in 98 per cent nitric acid (10 ml) was added N_2O_4 (0.1 g). Then reaction mixture was heated to 80-85 °C, and maintained at this temperature for 2 h, and then poured into ice/water (10 g) with vigorous stirring, the temperature being kept below 35 °C during the addition. The precipitated product was filtered-off and washed with water (5 times) until neutral washings were obtained. The product was isolated in the hydrated α form after drying to constant weight at 40 °C. HPLC analysis showed that the purity of the 2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane obtained was 99.0 per cent, (420 mg, 97 per cent). The decomposition temperature (240 °C) and FT-IR and NMR spectra were identical to those reported[1].

3. RESULT AND DISCUSSION

In this work, various experiments were carried out on TAIW. After extensive literature search, various nitrating agents were selected (Table 1). Table 1 shows the effect of different nitrating agents on conversion in nitration of TAIW. As seen from the table, use of N_2O_4 for the nitration of TAIW gave high yield towards the other reagents. This is because the nitronium ion concentration was increased in the presences of N_2O_4. On the other hand, silica sulphuric acid (entry 6) was chosen because it is an excellent acid source (a proton source for the *in situ* generation of NO_2^+) under completely heterogeneous conditions). In entry 5 and 8-10 in Table 1, also nitrate salts help to increase the nitronium ion concentration in solution.

Table 1. Nitration of TAIW by various nitrating agents

Entry	Nitrating agent	Temp. (°C)	Time (h)	Yield (%)
1	HNO_3 (98%)	85	3	76
2	HNO_3/H_2SO_4	80	1	96
3	HNO_3/CF_3COOH	85	2	93
4	HNO_3/N_2O_4	80	2	97
5	HNO_3/NH_4NO_3	85	2	91
6	HNO_3 / Silicasulphuric acid	85	3	94
7	HNO_3/AC$_2$O	85	3	89
8	HNO_3/KNO_3	85	2	85
9	$HNO_3/NaNO_2$	85	2	84
10	HNO_3/CAN (Ceric ammonium nitrate)	85	3	87

It is essential to know the operating temperature envelope at which the reaction has a maximum yield and optimum heat generation. Previously, it was reported[8] that the temperature for nitration of TAIW is 76 ± 1 °C. To generate the temperature envelope, nitration was conducted at 65 °C, 70 °C, 80 °C, and 85 °C, and the process was found safe in the temperature range of 80–85 °C and yield was also more. It was observed that beyond 85 °C, formation of NO_x gases increased significantly, which is not desirable. Thus, the approximate temperature envelope for the reaction is 85 °C. Below 80 °C, a reaction takes place but the reaction time is prolonged by an additional 2 h.

To study the effect of strength of nitric acid on the purity and the yield of the product, experiments were carried out with nitric acid having strength of 65 per cent and 98 per cent. As expected, the purity and the yield of the product came down as the strength of the nitric acid was brought down. This is because the nitronium ion concentration and the solubility of partially-nitrated products were reduced as the water content increased in the nitric acid. Maximum yield and purity of CL-20 was obtained with 98 per cent HNO_3. In the presence of catalysts, nitric acid underwent ionisation to generate nitronium (NO_2^+) ions, and TAIW underwent electrophilic substitution reaction at nitrogen atoms by the electrophile NO_2^+ ion to give the nitrated product; i.e., CL-20.

Up to now, the crystal transformation of HNIW is mostly performed using the solvent-non-solvent method. In industry, the system of ethyl acetate-chloroform is widely used to perform the crystal transformation of HNIW, but using the one-pot method from TAIW to prepare ε-HNIW, both operations of hydrolysis-nitration of TAIW and crystal transformation of HNIW occur in one pot with a very high yield and purity of ε-HNIW.

4. CONCLUSIONS

In conclusion, a new process to synthesise HNIW from TAIW with high yield has been developed using different nitrating agents. Operating parameters such as temperature, effect of strength of nitric acid have been optimised to give maximum yield of the desired product. This reaction has wide scope in the nitrolysis of a variety of other nitrogen heterocyclics. Further work is in progress to extrapolate these findings to other organic transformations.

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