



Organic CHEMISTRY

An Indian Journal

Full Paper

OCAIJ, 10(2), 2014 [69-72]

Bi (NO₃)₃/ HNO₃: An efficient nitrating agent for synthesis of 2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane from 2, 6, 8, 12-tetraacety-4, 10-lidiformyl-2, 4, 6, 8, 10, 12-isowurtzitane

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ABSTRACT

2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane (HNIW), more commonly called CL-20, is a novel high-density cyclic nitramine, synthesized for use as an energetic component in propellant formulations. It is usually prepared via nitration of precursors with concentrated nitric and sulfuric acid. we report in this work for the first time synthesis of CL-20 from nitration of 2, 6, 8, 12-tetraacety-4, 10-lidiformyl-2, 4, 6, 8, 10, 12-isowurtzitane (TADFIW) by various nitrating agents and mild reaction condition. By the use of this nitrating agent, the reaction eliminated the use of concentrated sulfuric acid and was environmental friendly. Meanwhile, the effects of reaction temperature, time and other factors on yield were studied. The structure of the compound was characterized by elemental analysis, IR, ¹H NMR and MS. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Nitrating Agents;
CL-20;
TADFIW;
Energetic materials.

INTRODUCTION

2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW), more commonly called CL-20, is a novel high-density cyclic nitramine, synthesized for use as an energetic component in propellant formulations^[1]. It meets stringent munitions sensitivity requirements and has a higher energy content than the conventionally used cyclotetramethylenetetranitramine (HMX) and cyclotrimethylenetrinitramine (RDX)^[2,3]. CL-20 has recently shifted to commercial production and is now in exploratory and advanced development^[4].

The molecular structures of CL-20, RDX and HMX are shown in Figure 1.

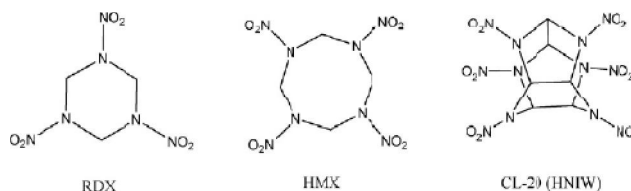
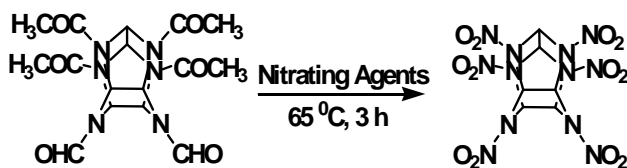


Figure1 : Structures of RDX, HMX and CL-20

The basic structure of CL-20 consists of a rigid isowurtzitane cage with a nitro group attached to each of the six bridging nitrogen atoms within the cage. CL-20 has a higher molecular weight, heat of formation,

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number of N-NO₂ bonds, and density (2.044 g/cm³ for the ϵ -polymorph) than RDX and HMX^[5]. In contrast to the aforementioned nitramines that have no C-C bonds in their structures, CL-20 bears three slightly elongated C-C bonds^[6]. It can exist in four stable polymorphic forms ($\alpha, \beta, \gamma, \epsilon$) under ambient conditions, the structures and densities of which have been established by X-ray crystallography^[3]. Among these, the ϵ -polymorph is preferred for its highest crystal density and stability at ambient conditions^[7]. 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^[8]. Synthesis efforts have been made for a number of nitrolysable precursors to CL-20 including isowurtzitane cage substituted with nitroso^[8], formyl^[9], and acetyl^[10], 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 (American scientists) has established a process for the preparation of CL-20 by nitration of TAIW^[11]. CL-20 is usually prepared via nitration with concentrated nitric and sulfuric acid, but this technique pollutes the environment. The majority of organic nitration requires the use of sulfuric acid or oleum in the nitric acid because sulfuric acid is present as catalyst, solvent and dehydrating agent. Also, in about 94% sulfuric acid, the nitric acid practically completely ionized to nitryl ion. Utilization of sulfuric acid produce 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. In this paper, we thus describe a new Method for synthesis of CL-20 from TADFIW by various nitrating agents (Scheme 1).



Scheme 1 : Nitration of TADFIW

RESULT AND DISCUSSION

In this work, various experiments were carried out on TADFIW. After extensive literature search various nitrating agents have been selected (TABLE 1). TABLE 1 shows the effect of different nitrating agent on conversion in nitration of TADFIW. As seen from the table use of Bi (NO₃)₃ for the nitration of TADFIW gave high yield towards the other reagents. This is because the nitronium ion concentration increased in presences of Bi (NO₃)₃. On the other hand we chose silica sulfuric acid (entry 5) because it is an excellent acid source (a proton source for the *in situ* generation of NO₂⁺) under completely heterogeneous conditions). In entry 4 and 7-10, also nitrates salt help to increase the nitronium ion concentration in solution.

TABLE 1 : Nitration of TADFIW by various nitrating agents

Entry	Nitrating Agent	Temp. (°C)	Time (h:min)	Yield (%)
1	HNO ₃ (98%)	70	3	72
2	HNO ₃ /H ₂ SO ₄	70	4	84.5
3	HNO ₃ / Bi (NO ₃) ₃	65	3	91
4	HNO ₃ /NH ₄ NO ₃	70	3	90
5	HNO ₃ / silica sulfuric acid	65	3	86
6	HNO ₃ /AC ₂ O	65	3	73
7	HNO ₃ /KNO ₃	65	3	76
8	HNO ₃ /NaNO ₂	70	3	68
9	HNO ₃ /CAN (Ceric Ammonium Nitrate)	70	3	85
10	HNO ₃ / Sr (NO ₃) ₂	65	3	86

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^[12] that the temperature for nitration of TADFIW is 85-95 °C. In order to generate the temperature envelope, nitration was conducted at 60, 65, 70, 75, 80, and 85 °C, and the process was found safe in the temperature range of 65-70 °C and yield was also greater. It was observed that beyond 70 °C, formation of NO_x gases increased significantly, which is not desirable. Thus, the approximate temperature envelope for the reaction is 65 °C.

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 and 98%. As expected, the purity and the yield of the prod-

uct 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 reduced as the water content increased in the nitric acid. Maximum yield and purity of CL-20 was obtained with 98% HNO_3 .

In the presence of catalysts, nitric acid underwent ionization to generate nitronium (NO_2^+) ions, and TADFIW underwent electrophilic substitution reaction at nitrogen atoms by the electrophile NO_2^+ ion to give the nitrated product; i.e., CL-20.

EXPERIMENTAL

Melting points were determined on open capillary and are not corrected. IR spectra were recorded by Perkin-Elmer infrared spectrometer using matrix KBr. ^1H NMR and ^{13}C NMR spectra were recorded on Backer 300 MHz instrument model WG-300 and δ units with reference to tetramethylsilane internal standard. Commercially available solvents and reagents were used without further purification. TADFIW was prepared according to a published procedure^[13].

Nitration of TADFIW by various nitrating agents

0.4 g (1 mmol) TADFIW was added gradually to a cooled mixture of 98% nitric acid (10 mL) and Bismuth Nitrate (0.1 g). Then reaction mixture was heated to 65 °C, maintained at this temperature for 2 h and then the mixture cooled to 35 °C and paused into 10 g ice / water with vigorous stirring. The precipitated product was filtered off and washed with Water (4 times) until neutral washings were obtained. The product was drying to constant weight at 40 °C. HPLC analysis showed that the purity of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane obtained was 99.5%. The decomposition temperature (240 °C) and FT-IR and NMR Spectra were identical to those reported^[1].

CONCLUSION

In conclusion, we have found a new and efficient method for synthesis of CL-20 from TADFIW with high yield and high purity ($\geq 99\%$) and our research shows the $\text{HNO}_3/\text{Bi}(\text{NO}_3)_3$ is the good nitrating agent

Between nitrating agents Table 1 for synthesis of CL-20 from TADFIW. Our optimized nitration reaction conditions is at 65 °C for 3 h, and the title compound can reach to 91 % in yield and high purity. Operating parameters such as temperature, effect of strength nitric acid have been optimized 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.

ACKNOWLEDGEMENT

We are grateful for the financial support from the Research Council of Malek Ashtar University of Technology and Chemistry Department of Zanjan University.

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