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Silica Sulfuric Acid/HNO_3 as a Novel Heterogeneous System for the Nitrolysis of DADN to HMX under Mild Conditions

Yadollah Bayat* and Mohammad Mahdi Ahari Mostafavi

Department of Chemistry, Malek Ashtar University of Technology, P.O. Box 16765-3454, Tehran, Iran
**E-mail: y_bayat@mut.ac.ir*
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1,5-Diacetyl-3,7-dinitro-l,3,5,7-tetraazacyclooctane (DADN) is a key intermediate in the preparation of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), one of the most powerful high-melting explosives. The present investigation focuses on nitrolysis of DADN to HMX by developing a new nitrolysis process involving the use of nitric acid catalyzed by Silica Sulfuric Acid (SSA). In order to optimize the process parameters for synthesis of HMX to obtain higher yield and purity, a study was carried out with variation of some parametric conditions like time, mole ratio of SSA and nitric. This method gave us green and mild conditions for nitration reaction.

Key Words : HMX, DADN, Silica sulfuric acid, Nitrolysis, Nitration

Introduction

1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX), also referred to as octogen or cyclotetramethylenetetranitramine, is a highly energetic material that is useful in variouse explosives and propellants for military and non-military applications.[1-3] HMX is recognized as one of the most powerful nitramine explosive, and is used as the benchmark for all other explosives, but its application is limited owing to high cost.

Some procedures are described for preparing HMX from hexamine (HA). The first known process for the manufacture of HMX was developed in 1951 as conventional Bachmann process taking a continuous nitration process through HA without using H_2SO_4 or polyphosphoric acid.[4] This process involves nitrolysis of hexamethylenetetramine (hexamine) with mixture of nitric acid and excess amount of acetic anhydride. This process typically gives the products with a mixture of cyclic and linear nitramines. Also in this process a great amount of another explosive, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is produced. After optimizing of this process the maximum reported yield of HMX per mole of hexamine feed is about 60-65%.[5]

Because of the inefficiencies in the Bachmann process and the large amounts of hazardous waste matrials producted, this process encountered with some difficulties in large-scale production. For improving of these problems another synthetic routs involving various intermediates for making HMX have been proposed. Some intermediates that have been use to produced HMX are 3,7-dinitro-1,3,5,7-tetraazabicyclo (3,3,1) nonane (DPT),[6-9] 1,3,5,7-tetraacetyl 1,3,5,7-tetraazacyclooctane (TAT),[10] *etc*. One of these intermediate involving 1,5-diacetyl-3',7-dinitro-l,3,5,7-tetraazacyclooctane (DADN) gives a better yield of HMX than the established Bachmann process. But this conversion involves the use of sulfuric and polyphosphoric acids, which are not required in the Bachmann approach.

The synthetic routes for preparing HMX from DADN involves the acetylation of hexamine **1** to diacetylpentamethylenetetraamine, 3,7-diacetyl-1,3,5,7 tetraazabicyclo (3,3,l) nonane (**2**) (DAPT) and nitrolysis of DAPT to DADN **3**, and finally nitrolysis of DADN to HMX **4** (see Fig. 1).

Also hexamine could be converted to DADN in a "one-pot" operation without isolating DAPT in 93% yield using an aqueous nitric-sulfuric acid mixture.[11]

There are several reports in the literature for conversion of DADN to HMX utilizing nitric acid with polyphosphoric acid, phosphorus pentoxide, trifluoroacetic anhydride, and nitrogen pentoxide, *etc*.[12] However, each of these procedures have shown some drawbacks, such as environmental pollution and tedious workup. Also in these processes a large excess of polyphosphoric acids required because the formation of water (*in situ*) as by-product slows the reaction down by diluting the acid. At the end of these processes, a large amount of spent acid is obtained which, in the end of process, is usually neutralized and disposed of, or recycled by complex techniques. Also utilizing of these reagents (similar P_2O_5) is limited somewhat by its tendency to form a protective viscous coating that inhibits further dehydration by unspent material. Hence, there is a clear need for a simple and practical methodology for the nitrolysis of DADN to HMX. In this work we use silica sulfuric acid (SSA) that is an efficient solid acidic source and as alternative munlti-purpose acid catalyst, which has been developed for different

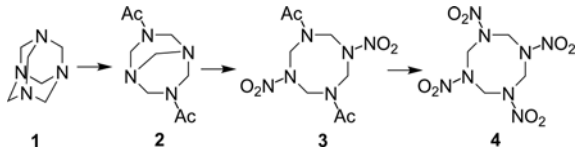


Figure 1. synthetic routes for preparing of HMX from DADN intermediate.

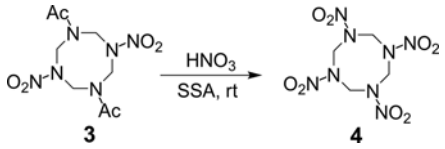
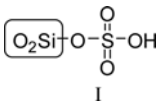


Figure 2. Synthesis of HMX from DADN.

organic transformations.[13,14]

Found that silica gel reacts with chlorosulfonic acid to give silica sulfuric acid (I).



It is interesting to note that the reaction is easy, clean and without any needed work-up procedure because HCl gas is evolved from the reaction vessel immediately. We also found that silica sulfuric acid (I) is an excellent candidate for polyphosphoric acids replacement in this reaction.

We wish here to report a mild and efficient method for synthesis HMX with silica sulfuric acid and nitric acid for conversion of DADN to HMX in room temperature without any impurity of RDX (Fig. 2).

Experimental

TLC experiments were performed on pre-coated silicagel plates using acetone/hexane (1:3) as the eluent. Melting points are reported without correction. All starting chemicals were purchased from commercial suppliers and used without further purification. The silica sulfuric acid was prepared according to published procedures.[15]

General Procedure for the Nitrolysis of DADN to HMX. A suspension of DADN **3** (0.29 g, 1 mmol), silica sulfuric acid (1.2 g, 3.15 mmol) and 100% fuming nitric acid (1 mL, 24 mmol) was stirred magnetically at room temperature. The reaction was completed after 1 hour and the mixture filtered and poured on ice (100 gr). The product precipitated with dilution with another 200 mL water. The product was filtered, washed with water and dried to give HMX, 0.26 g, 90%, mp 276-278 °C (lit.[11] mp 274-276 °C), ^{1}H NMR (DMSO-d_6) δ 6.03 (s, all protons).

Results and Discussion

In this paper we would like to report a simple and convenient method for the effective and mild conversion of DADN **3** to HMX **4** under heterogeneous conditions. We optimized the conditions by examining the reaction Figure 2 involving DADN, SSA and nitric acid to afford the appropriate HMX **4**. In the initial experiments, we screened amounts of SSA for their ability to catalyze the reactions (Table 1). For this purpose we tried to find best amount of catalyst with changing of SSA in constant conditions.

Also to optimize the protocol, we performed the reaction in different amounts of nitric acid that the results shown in Table 2.

Table 1. Synthesis of HMX catalyzed by different amounts of SSA[a]

Entry	SSA gr (mmol)	Yield[b] (%)
1	0.5 (1.31)	60
2	1 (2.63)	80
3	1.2 (3.15)	90
4	1.5 (3.94)	87
5	2 (5.26)	84

[a]Reaction conditions: fuming nitric acid (100%, 1 mL), DADN (1 mmol) reaction time (2 h). [b]Isolated yield.

Table 2. Choosing optimized amounts of nitric acid[a]

Entry	Fuming nitric acid (mL)	Yield (%)
1	0.5	55
2	0.8	83
3	1	90
4	1.5	85
5	2	78

[a]Reaction conditions: fuming nitric acid (100%), DADN (1 mmol), reaction time (2 h)

Table 3. Comparison of last methods and present work

Entry	Reagent (gr)	Nitric acid (gr)	Temp °C	Time	Yield (%)
1	PPA[b] (4.68)	2	60-70	60	100
2	P_2O_5 (2.44)	7.2	50	50	100
3	N_2O_5 (0.37)	1.8	50	60	82
present work	SSA (1.2)	1.54[a]	rt	60	90

[a]Fuming nitric acid. [b]Polyphosphoric acid

Our results show that using 1.2 gr SSA (3.15 mmol) and 1 mL (24 mmol) of fuming nitric acid is the best ratio for giving the best yield. Also this system had previously been found to give good yields in the preparation of HMX without any RDX.

Also as shown in Table 3, in previous works the large excesses of nitric acid were needed to obtain complete nitrolysis of the acetyl groups. In present work, to conversion of 0.29 gr of DADN to HMX, requires 1.54 gr of 100% fuming nitric acid that it decreased in comparing with other methods.

Another valuable point of this method is that the reaction

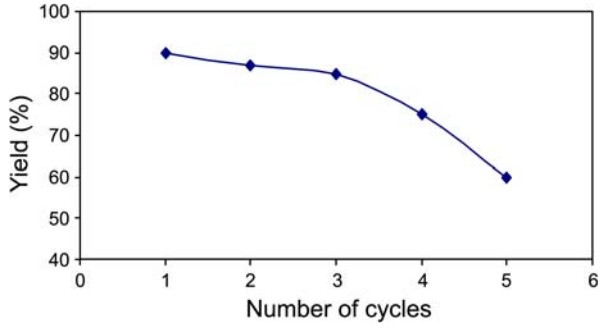


Figure 3. Efficient recycling of the SSA.

proceeds under heterogeneous conditions and also the silica gel can be recovered.

The SSA was recovered and reused in the subsequent reactions at least 3 times without significant loss of activity as shown in 5 consecutive reactions (Fig. 3).

Conclusion

In conclusion, silica sulfuric acid is a good proton source in terms of convenience, cheapness, easy production, insolubility to all organic solvents. Found that the SSA is a good candidate for polyphosphoric acids replacement. Also it recovered and reused in the subsequent reactions as heterogeneous catalyst. We found that this method was very efficient, and the HMX were prepared in high yields in ambient temperature and short time without any RDX impurity. Also the cheapness and availability of the reagents, easy procedure and free work-up make this method attractive for the large-scale operations.

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