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Sodium hexametaphosphate/ HNO_3 As a novel system for the synthesis of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) via nitrolysis of 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DADN)

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1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX) has been prepared through efficient nitrolysis of DADN in the presence of sodium hexametaphosphate (SHMP) in fuming HNO_3. Due to the importance of HMX skeleton, designing novel methods for its preparation is still highly desired. To achieve this goal, DADN was selected as starting materials. The low price, good-to-high yields and good-to-excellent purities, easy work-up, and short reaction times are among the advantages of the presented method.

Keywords: HMX, DADN, Nitration, SHMP

INTRODUCTION

Carrying out the organic reactions under nitrolysis condition has attracted much attention due to its importance in explosive chemistry. The nitramine structural motive presents in many explosive compounds displaying a wide range of energetic activities. HMX has proved to be valuable building blocks in explosive chemistry [1]. Meanwhile, HMX is recognized as one of the most attractive nitamine explosives, with wide variety of useful energetic activities such as high-density, high detonation velocity, and great explosion potential [2-5]. In recent years, some explosive skeletons were synthesized through nitrolysis of nitramines in our research group [6-8]. Fuming HNO_3 has been used as a suitable medium for the formation of chemical explosives. Designing new condition based on various agents for the synthesis of explosive skeletons is an interesting subject in organic synthesis. These agents can play different roles both as nitrating and dehydrating agents in fuming HNO_3; Fig 1 shows some examples dehydrating agent important structures

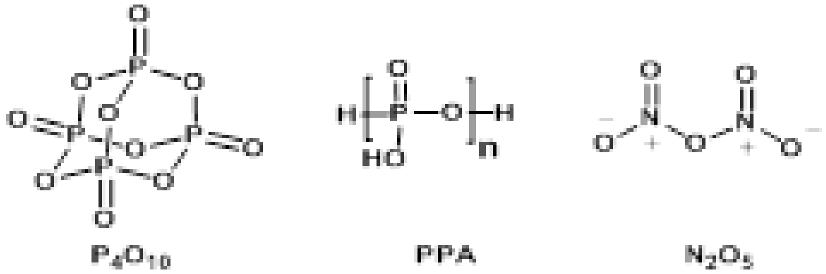

Fig. 1. Left to right, structurs of phosphorus pentoxide, polyphosphoric acid, and nitrogen pentoxide.

Different reagents have been used for the synthesis of HMX [9]. However, most of them suffered from some drawbacks; e.g. high costs, difficult storage and handling and high toxicity. Furthermore, they are among the environmental pollutants because of producing some types of toxic by-product [10-12]. Therefore, development of suitable methods for the synthesis of HMX is an interesting challenge in organic process research.

Sodium hexametaphosphate (SHMP) is known as one of the most food additive that is commonly used as an emulsifying salt in the process of producing cheese (Fig.2) [13]. Also, SHMP is an affordable compound with a great potential as a dehydrating agent which is suitable for nitrolysis of nitramines. Therefore, we have introduced a novel suitable system (HNO3/SHMP) for the nitrolysis of DADN to HMX.

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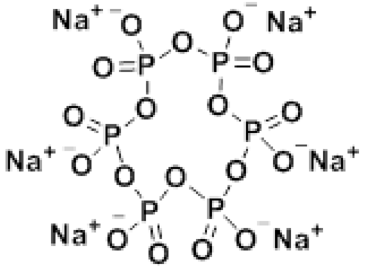

Fig. 2. Structure of sodium hexametaphosphate (SHMP)

In continuation of our previous research works based on the nitrolysis reactions of nitramines to high explosives [6-8] and also high efficient synthesis of HMX [14], we were encouraged to investigate the formation of HMX under new nitrolysis conditions. Herein, we report nitrolysis of DADN via SHMP as a low-price-dehydrating agent for the synthesis of HMX (Fig. 3).

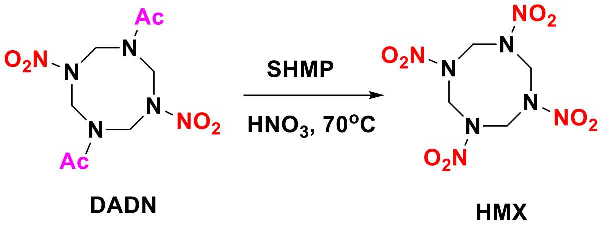

Fig. 3. Synthesis of HMX via nitration of DADN.

EXPERIMENTAL SECTION

Materials. Fuming HNO_3 [98% (v/v)] was used as received from Merck. Also, sodium hexametaphosphate was used as received from Sigma-Aldrich.

Instrumentation. Melting points were determined on an Electrothermal9100 apparatus and were uncorrected. FTIR spectra were obtained on a Perkin-Elmer infrared spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were run on Bruker DRX-300 AVANCE spectrometers at 300 MHz for ^{1}H-NMR, 75 MHz for ^{13}C-NMR. DMSO-d6 was used as solvent. The purification of HMX was done using preparative HPLC (column C18, 5 μm and mobile phase, MeOH: H_2O).

PROCEDURE

Preparation of HMX from DADN

A suspension of DADN (10 g), sodium hexametaphosphate (114.4 g) and 98% fuming nitric acid (170ml) was stirred magnetically at room temperature for 10 minute. Then, the reaction solution was heated to 70ºC and reacted for another 75 min. The reaction solution was quenched in ice-water (2000 g). The obtained precipitate was filtered, and white powder of HMX was obtained (80%), m.p.: 271-273 °C; IR (KBr, cm-1): υ = 3035, 1560, 1462, 1395, 1278, 1202, 1143, 1086, 948, 830, 761, 658, 599, 437; ^{1}H NMR (DMSO-d6, 300 MHz): δ(ppm) = 6.02 (s, 8H, -CH2); ^{13}C NMR (DMSO-d6, 75 MHz): δ(ppm) = 63.3; The purity was 100% identified on HPLC.

RESULTS AND DISCUSSION

In this work, DADN was selected as starting material. At the beginning, DADN was synthesized directly from DAPT [10]. Then DADN was nitrated to HMX by SHMP/HNO3. To achieve the best efficiency, the influence of using amount of SHMP, nitrolysis temperature and time of reaction in the formation of HMX in the presence of fuming HNO_3 was investigated. Optimization results are shown in Tables 1 to 3.

Table 1 Choosing Optimized Amount of SHMP[a]

No	DADN(g)	SHMP(g)	$\frac{SHMP}{DADN}$(mole)	Yield (%)[b]
1	10	83.2	4	17
2	10	114.4	5.5	80
3	10	145.6	7	30
4	10	176.8	8.5	30

[a]Reaction conditions: fuming HNO_3 (98%), Reaction time (75 min), Temperature (70 °C).[b]Isolated Yield.

Table 2 Optimization of Reaction Temperature[a]

No	$\frac{SHMP}{DADN}$(mole)	Temperature(°C)	Yield(%)[b]
1	5.5	40	-
2	5.5	55	58
3	5.5	70	80
4	5.5	85	15

[a]Reaction conditions: fuming HNO3 (98%), Reaction time (75 min), DADN (10g).[b]Isolated Yield.

Table 3 Synthesis of HMX in different reaction time[a]

No	Temperature(°C)	Time (min)	$\frac{SHMP}{DADN}$(mole)	Yield(%)[b]
1	70	45	5.5	17
2	70	60	5.5	30
3	70	75	5.5	80
4	70	90	5.5	42

[a]Reaction conditions: fuming HNO3 (98%), DADN (10g).[b]Isolated Yield.

The results show that the best conditions (80% yeild) for synthesis of HMX by SHMP/HNO_3 is at 70 °C for 75 minutes and with molar ratio 5.5 SHMP/DADN.

CONCLUSIONS

In conclusion, we have developed the efficient nitrolysis of DADN for the synthesis of HMX using an appropriate system. The desired product was formed in good yields (80%) in the presence of $Na_6P_6O_{18}$ as suitable agent in fuming HNO_3. Good-to-excellent yield and purity, short reaction time, easy work-up, existence of other active functional groups and application of this approach in explosive chemistry are among the advantages of this report.

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