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ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal
www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2018, Vol. 34, No.(1):
Pg. 576-579

(Brief Communication)

HMX Synthesis by using RFNA/P_2O_5 as a Novel Nitrolysis System

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http://dx.doi.org/10.13005/ojc/340169

(Received: June 23, 2017; Accepted: October 01, 2017)

ABSTRACT

A novel and efficient approach for the synthesis of octahydro- 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) was achieved through nitrolysis of 1,3,5,7-tetracetyl-1,3,5,7-tetraazacyclooctane (TAT) in the presence of red fuming nitric acid (RFNA) and P_2O_5 . various parameters such as temperature, concentration of nitrating agent, time and mole ratio of RFNA/P_2O_5 has been investigated to develop the optimum conditions. The good yields, high purities, easy work-up and short reaction times are advantages of this method.

Keyword: Octogen(Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), Synthesis,P_2O_5, Nitrolysis.

INTRODUCTION

Nitrolysis is one of the key processes in synthetic chemistry and widely used in industry, nitrolysis process mostly requires concentrated amounts of nitric acid, great number of the energetic materials such as HMX are produced by various nitrolysis processes[1-5]. HMX (1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane), is one of the most powerful high-melting explosives which is useful for military and non-military applications[6,7]. In the past decades various methods for HMX prepration have been reported in the literature, one of the first methods developed by Bachmann in 1951[8] but there are several undesirable features including slow rate of production, poor yield, large amount of hazardous wastes and great amount of by-products such as RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and mixture of cyclic and linear nitramines.

In order to improve HMX production other synthetic approaches involving TAT (1,3,5,7-tetracetyl-1,3,5,7-tetrazacyclooctane), DADN(1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazacyclooctane) or

DANNO (1,5-diacetyl-3-nitro-5-nitroso-1,3,5,7-tetrazacyclooctane) have been proposed, the main precursor for these alternative routes is DAPT (3,7-diacetyl-1,3,5,7-tetraazabicyclo-[3.3.1]-nonane) which could be easily prepared from hexamine and acetic anhydride in good yield.

According to Siele's works[9] DADN gave a better yield in compare to the Bachmann procedure but this synthesis involves use of sulfuric acid and polyphosphoric acid which are not required in the Bachmann process.

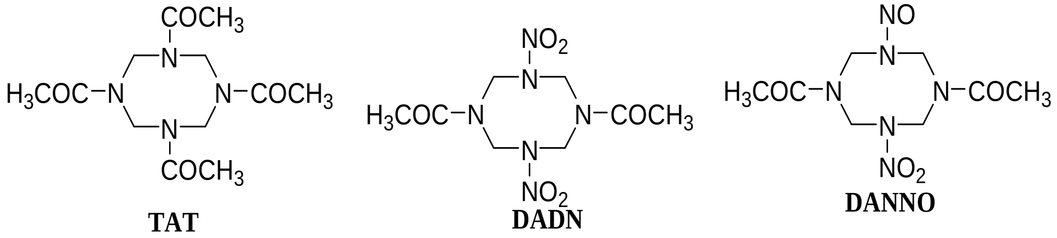

Fig. 1. main precursors for HMX synthesis

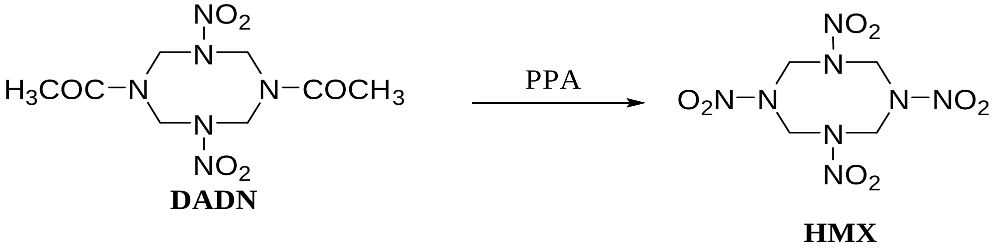

Fig. 2. synthesis of HMX from DADN

TAT is an extremely valuable precursor of HMX which can be easily prepared by acetylation of DAPT in presence of acetic anhydride and anhydrous sodium acetate at 110 °C in high yield.

Nitrolysis of TAT to HMX involving the reaction of TAT with a mixture of nitric acid and phosphorus pentoxide at 75 °C for 15 min crude HMX is obtained in 75-80% yield with impurities such as SOLEX (1-acetyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane) which is the main by-product of this process . In order to improve the yield and purity of the product in the present work we changed the condition of the synthesis and replaced the nitric acid with RFNA, resulted pure product and more than 95% yield. HMX with high purity plays an important role in oil well drilling process and some other important non-military industrial uses.

EXPERIMENTAL

All starting chemicals were purchased from commercial suppliers and without further purification. The melting points are reported without correction.

Instruments

Melting points were determined on an Electrothermal 9100 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, 5µm and mobile phase, MeOH: H_2O).

General procedure for the Nitrolysis of TAT to HMX

The procedure started by stirring RFNA (30 ml) in 5 °C and P_2O_5 (12 g) added gradually to the reaction media while the temperature was fixed at 5 °C, after adding TAT to the solution temperature increased to 75 °C and the mixture stirred for 15 min. at 75 °C. after that the reaction solution was quenched in crushed ice (200 g) and pure HMX precipitated and filtered, washed with water and dried to 0.99 g of HMX, yield 95%, m.p. 275 °C (lit.[10] mp 274-276 °C), ^{1}H NMR (DMSO-d_6, 300 MHz) δ 6.2 (s, all protons); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 64 ; the purity was 100% identified on HPLC.

RESULTS AND DISCUSSION

In this paper we used a novel system for nitrolysis of TAT to HMX with the highest yield compared to other works reported in literatures and the highest purity.

The reaction (Fig. 3) condition where optimized by changing time, temperature and mole ratio of RFNA/P_2O_5, the results are summarized in Table. 1.

According to the results, Low yields of HMX were obtain with lower amount of RFNA or P_2O_5 and lower ratio of RFNA/P_2O_5 made an obvious decline in the result of the reaction respectively 62% and 55%, after finding the optimal molar ratio influence of time and temperature were examined which showed that reducing the time of the reaction to less than 15 min. dropped the yield and increasing the time didn't improve the yield of production.

In order to explain the mechanism of this reaction and the high yield and purity, we can consider the role of two sources of nitration agents (N_2O_5, NO_2^+), first source of nitration agents is

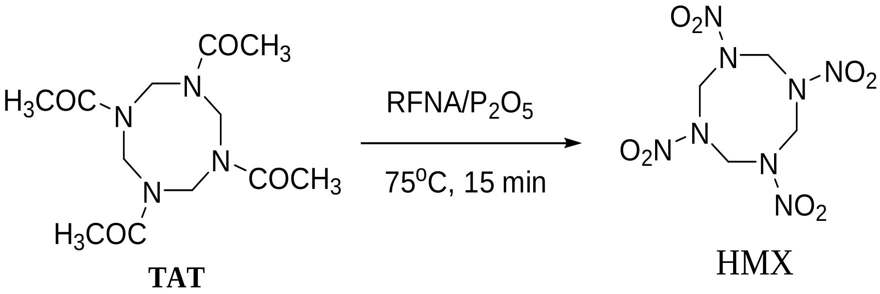

Fig. 3. synthesis of HMX from TAT

Table.1: Finding the optimized condition for HMX nitrolysis

Entry	RFNA	P_2O_5	Temperature(°C)	Time(Min.)	Yield	m.p.
1	30	0	75	15	X	-
2	30	10	75	15	87	265
3	30	14	75	15	88	273
4	30	8	75	15	66	267
5	20	8	75	15	55	274
6	25	10	75	15	62	275
7	30	12	85	15	65	275
8	30	12	60	15	60	262
9	30	12	75	10	65	272
10	25	10	75	25	70	275
11	30	12	75	25	90	267
12	35	14	75	15	67	265
13	30	12	75	15	95	275

P_2O_5 and nitric acid[11] which produce phosphoric acid as a by-product. The second source of producing nitration agents, is N_2O_4 (in RFNA)[12] at presence of the phosphoric acid which is the by-product of the first reaction. This concentrated amounts of nitration agents could turn all of the acetyl groups on TAT to nitrogen dioxide at 75 °C and completes the reaction to the highest yield and purity.

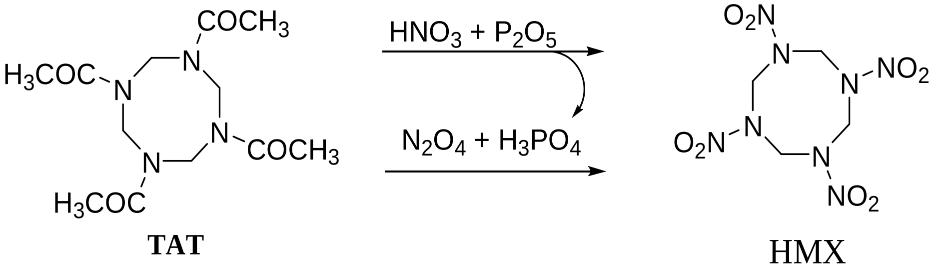

Fig. 4. Two different source of the reagents for TAT nitrolysis

CONCLUSION

In conclusion, the RFNA/P_2O_5 mixture is a powerful and efficient reagent in the ambient time and temperature for nitrolysis of TAT to the valuable HMX, therefore this procedure has the highest yield reported in literatures which is more than 95% of HMX per mole of TAT and pure HMX which means no by-products such as RDX and SOLEX. short reaction time, excellent yield and purity, easy work-up are among the advantages of this procedure.

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