A CONVENIENT SYNTHESIS OF NITROGEN-15 AND DEUTERIUM LABELLED OCTAHYDRO-1,3,5,7-TETRANITRO-1,3,5,7-TETRAZOCINE (HMX)

M. D. Coburn and D. G. Ott
University of California, Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545

SUMMARY

The preparation of pure octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) labelled with nitrogen-15 and deuterium was accomplished by sequential nitrolysis of appropriately labelled octahydro-1,5-diacetyl-3,7-endomethylene-1,3,5,7-tetrazocine. The latter compounds were obtained from the reaction of acetic anhydride with hexamethylenetetramine that was specifically labelled by the reaction of the appropriate formaldehyde and ammonia.

Key Words: Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, HMX, Deuterium, Nitrogen-15

INTRODUCTION

Isotopically labelled octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), a military high explosive, has been prepared previously (1) by the nitrolysis of hexamethylenetetramine (1) according to the Bachman process (2), which is the current commercial process for HMX manufacture. This method is undesirable for preparing labelled HMX because the product is contaminated with hexahydro-1,3,5-trinitro-*s*-triazine (RDX), which must be removed by fractional crystallization.

DISCUSSION

We found that nitrogen-15 labelled HMX could be obtained pure in good yields according to Scheme 1 (3). Treatment of formaldehyde with ammonia-^{15}N gave 1-$^{15}N_4$, which was allowed to react with acetic anhydride in the presence of ammonium-^{15}N acetate to yield octahydro-1,5-diacetyl-3,7-endomethylene-1,3,5,7-tetrazocine-$^{15}N_4$ (2-$^{15}N_4$). Nitrolysis of 2-$^{15}N_4$ with potassium nitrate-^{15}N in sulfuric acid gave octahydro-1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocine-$^{15}N_6$ (3-$^{15}N_6$), which was converted to HMX-$^{15}N_8$ when heated with nitric acid-^{15}N in

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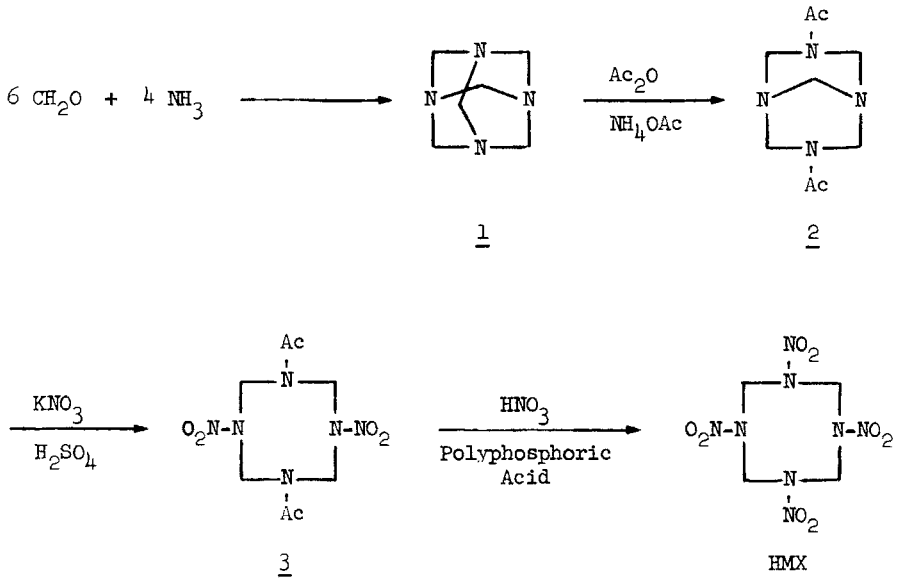
polyphosphoric acid. Ring-labelled HMX-$^{15}N_4$ was obtained when 2-$^{15}N_4$ was subjected to nitrolysis with unlabelled reagents according to the same reaction sequence.

The preparation of HMX-$^{2}H_8$ was accomplished according to Scheme 1 by starting with formaldehyde-$^{2}H_2$ and ammonia. No exchange of hydrogen for deuterium occurred when unlabelled acids were employed in the nitrolysis steps.

Analysis by high pressure liquid chromatography and nuclear magnetic resonance spectroscopy showed all final products to be free of RDX and other impurities.



Scheme 1

EXPERIMENTAL

Hexamethylenetetramine-$^{15}N_4$.-- To a stirred solution of ammonium-^{15}N sulfate (16.75 g, 0.125 mol) in formalin (30 ml, 0.385 mol) and water (15 ml) was added sodium bicarbonate (23.1 g, 0.275 mol) in small portions. The solution was allowed to stand at room temperature overnight and was evaporated to dryness under reduced pressure. The residue was extracted with chloroform (75 ml, then 8 x 20 ml) and the extracts were evaporated to dryness under reduced pressure to afford the product as a white solid (8.73 g, 97% yield).

^{1}H-nmr ($CDCl_3$) δ: 4.69 (q, $J_{^{15}NCH}$ = 1.3 Hz, CH_2).

Octahydro-1,5-diacetyl-3,7-endomethylene-1,3,5,7-tetrazocine-$^{15}N_4$.-- To a well stirred mixture of hexamethylenetetramine-$^{15}N_4$ (8.65 g, 0.06 mol) and ammonium-^{15}N acetate (3.5 g, 0.05 mol) in water (1.6 ml) was added acetic anhydride (16.6 g, 0.016 mol) dropwise at 5-10°C. After stirring at room temperature overnight, the solution of product in acetic acid was used in the next step without purification.

^{1}H-nmr ($CDCl_3$) δ: 2.22 (s, 6H, CH_3); 4.2-5.9 (m, 10H, CH_2).

Octahydro-1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocine-$^{15}N_6$.-- One-half of the above solution of octahydro-1,5-diacetyl-3,7-endomethylene-1,3,5,7-tetrazocine-$^{15}N_4$ (0.03 mol) was added to a solution of potassium nitrate-^{15}N (15.4 g, 0.15 mol) in concentrated sulfuric acid (50 ml) with rapid stirring at 25-30°C. The resulting solution was stirred at 20°C for one hour, then it was poured into ice-water (500 ml). The product, which crystallized slowly overnight, was collected by filtration, washed with water, and dried to yield 6.4 g (76%) of white solid, mp 265°C.

Octahydro-1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocine-$^{15}N_4$.-- This compound was obtained from the remainder of the octahydro-1,5-diacetyl-3,7-endomethylene-1,3,5,7-tetrazocine-$^{15}N_4$ solution using unlabelled potassium nitrate in the above procedure.

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine-$^{15}N_8$.-- To a vigorously

stirred (mechanical stirrer) mixture of nitric acid-^{15}N (22.5 g, 0.35 mol) and polyphosphoric acid (50 g) was added octahydro-1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocine-$^{15}N_6$ (6.4 g, 0.023 mol). The resulting mixture was heated at 60-70°C for one hour, then it was diluted with ice-water (200 ml). The product separated as a white solid that was collected by filtration, washed with water, and dried to yield 5.0 g (74%).

^{1}H-nmr ($CDCl_3$) δ: 6.04 (t, $J_{^{15}NCH}$ = 2.2 Hz, CH_2).

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine-$^{15}N_4$.-- This compound was obtained by nitrolysis of octahydro-1,5diacetyl-3,7-dinitro-1,3,5,7-terazocine-$^{15}N_4$ with unlabelled nitric acid according to the previous procedure.

Hexamethylenetetramine-$^2H_{12}$.-- To a slurry of paraformaldehyde-$^2H_2$ (5.0 g, 0.14 mol) in water (8 ml) was added concentrated ammonium hydroxide (8 ml, 0.12 mol) over a period of one hour at 20-30°C. The solution was stirred overnight and evaporated under reduced pressure. The residue was treated with magnesium sulfate and repeatedly extracted with chloroform (5 x 30 ml). The filtered extracts were evaporated to dryness under reduced pressure to give the product as a white solid (3.53 g, 100% yield).

Octahydro-1,5-diacetyl-3,7-endomethylene-1,3,5,7-tetrazocine-$^2H_{10}$.-- This compound was prepared from hexamethylenetetramine-$^2H_{12}$ according to the procedure described for octahydro-1,5-diacetyl-3,7-endomethylene-1,3,5,7-tetrazocine-$^{15}N_4$.

^{1}H-nmr ($CDCl_3$) δ: 2.22 (s, CH_3).

Octahydro-1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocine-$^2H_8$.-- This compound was prepared from octahydro-1,5-diacetyl-3,7-endomethylene-1,3,5,7-tetrazocine-$^2H_{10}$ according to the procedure described for octahydro-1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocine-$^{15}N_4$.

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine-$^2H_8$.-- This compound was prepared from octahydro-1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocine-$^2H_8$ by nitrolysis according to the procedure described for octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine-$^{15}N_4$.

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