SYNTHESIS OF NITROGEN-15 LABELED 1,3,5-TRINITRO-1,3,5-TRIAZACYCLOHEXANE (RDX) AND 1,3,5,7-TETRANITRO-1,3,5,7-TETRAAZACYCLOOCTANE (HMX)

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SUMMARY

Procedures are described for the synthesis of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) fully labeled with nitrogen-15.

Key Words: Nitramines, RDX/HMX, Hexamine, Nitrogen-15, Nitrolysis

INTRODUCTION

Of the compounds which are prominent as energetic materials, the nitramines, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) are especially important because of the central role they occupy in the field of explosives and propellants (1,2). In the course of investigations in these laboratories into the mechanism of decomposition induced by different stimuli (3,4), several single and multiple labeled compounds containing the stable isotopes ^{13}C, ^{15}N, ^{18}O, and ^{2}H were required. This report describes in

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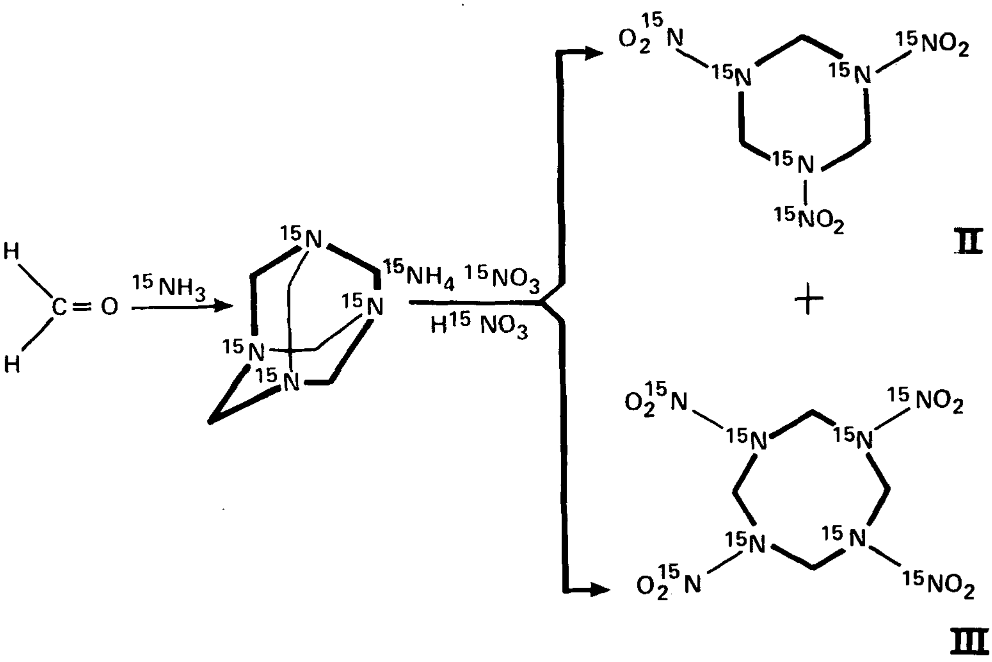
detail the synthetic procedures employed to prepare isotopically double ^{15}N-labeled HMX and RDX by the nitrolysis of hexamethylenetetramine as outlined in Scheme I.

SCHEME I



EXPERIMENTAL

The ^{15}N enriched ammonium nitrate and potassium nitrate used in these procedures were obtained from Stohler Isotope Chemicals and contained nitrogen-15 in 99% abundance. Melting points are uncorrected. ^{1}H-NMR spectra were obtained using a Varian Associates T-60 spectrometer.

Hexamethylenetetramine-^{15}N

Ammonia-^{15}N gas was generated by the dropwise addition of a solution of 5.00 g (0.0658 mole) of ammonium acetate (99% ^{15}N enrichment) in 5.0 mL of water to 20 mL of boiling 30% potassium hydroxide over a 30-minute period. The ammonia-^{15}N was bubbled into 10 mL of a 37% formalin solution and the mixture was allowed to stand at room temperature for 0.5 h. Removal of the excess formaldehyde and water at reduced pressure followed by further drying by repeated azeotropic distillation with benzene gave 2.26 g (99%) of white crystalline hexamethylenetetramine-^{15}N, mp 263°C decomp., consistent with the literature values (5). The ^1H-NMR spectrum ($CDCl_3$) exhibited an unresolved multiplet (5)at δ4.72.

Nitrolysis Mixture

The mixture of $H^{15}NO_3$-$^{15}NH_4{}^{15}NO_3$ used in the nitrolysis step was made up on a vacuum line. The 100% HNO_3 was prepared by the gradual addition over 15 minutes of $K^{15}NO_3$ (5.0 g) to a cooled solution of concentrated H_2SO_4 (10 mL). The mixture was gradually warmed to 45°C in a water bath and the HNO_3 that distilled was collected at liquid nitrogen temperature in a graduated vessel. In a separate section of the cacuum train ammonia gas condensed from a tank and subjected to two freeze-thaw cycles, was dried and purified by passing it through KOH pellets and condensing it on metallic sodium. After several hours of contact the ammonia was distilled and the appropriate volume collected. This was then admitted to the previously prepared 100% HNO_3 through a breakseal to give the nitrolysis mixture having the desired composition.

RDX/HMX-^{15}N (II and III)

To a stirred mixture of glacial acetic acid (15 mL), acetic anhydride (0.25 mL) and paraformaldehyde (0.35 g) maintained at 44°C ± 1 in a 100 mL reaction vessel fitted with three 5-mL pressure-equalized burettes, the following solutions were added simultaneously and uniformly over a 15 minute period: (a) hexamethylenetetramine-^{15}N (2.1 g) in acetic acid (3.5 mL), (b) acetic anhydride (5.5 mL) and (c) a nitrolysis mixture consisting of 1.98 g of 98-100% nitric acid (99% ^{15}N) and 1.72 g of ammonium nitrate-^{15}N (99%). An additional 1.5 mL of acetic anhydride was added and after 15 minutes this was followed by the uniform addition over a 15-minute period of more acetic anhydride (9.0 mL) and nitrolysis mixture [nitric acid-^{15}N (2.98 g) - ammonium nitrate- ^{15}N (2.75 g)] as before.

The reaction mixture was stirred at 44°C for an additional hour, diluted with 8.0 mL of water and heated at reflux for 30 minutes. Addition of 50 g of ice precipitated the crude product which was collected, washed with cold water and allowed to dry to give 4.3 g of an 85:15 mixture of HMX/RDX.

The finely powdered mixture was extracted with ethylene dichloride (100 mL/g of mixture) using a mechanical stirrer to dissolve the RDX. Two recrystallizations of the residue from acetone gave 2.2 g of pure HMX, mp 275°C, lit. (2) mp 276-277°C. The RDX, recovered from the ethylene dichloride extract, was recrystallized twice from 50% aqueous acetone to give 0.6 g of material, mp 205°C, lit. (7) mp 205°C. The ^{1}H-NMR properties of these materials were consistent with the reported (6) values (HMX δ6.04 and RDX δ6.09).

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