(b) **Formation of RDX and HMX.**—The RDX-HMX mixture (8.43 g. or 80%) which was obtained from 3.32 g. of hexamine, 5.4 g. of the tracer ammonium nitrate, 4.48 cc. of 98% nitric acid and 18 cc. of acetic anhydride was dissolved in 50 cc. of warm nitromethane, 100 cc. of water was added and the nitromethane was distilled over a period of two and one-half hours. The resultant mixture of RDX crystals (d. 1.77) and HMX crystals (d. 1.96) was separated into three fractions by repeated fractional centrifugings in a mixture (d. 1.81) of trimethylene dibromide and mineral oil. One fraction consisted of RDX with m.p. 197–200°, which after two recrystallizations from acetone had m.p. 204–205° (cor.) and contained 3.0 atom per cent. of N^{15}. Another fraction was chiefly HMX with m.p. 268–269°, which was raised to 282° (cor.) after two recrystallizations from acetone; atom per cent. N^{15} based on total nitrogen, 1.5%. The recovered ammonium nitrate, which was purified by recrystallization to constant m.p. 168.5–169.5°, contained 3.95 atom per cent. of N^{15} (original tracer salt had 7.5 atom per cent. of N^{15}, based on the two N atoms).

In a run using 6.05 g. of tracer ammonium nitrate and 7.75 cc. of nitric acid only 4.96 g. of RDX was formed. After purification to m.p. 204–205° (cor.) it contained 1.8 atom per cent. of N^{15}.

ANN ARBOR, MICHIGAN RECEIVED DECEMBER 11, 1950

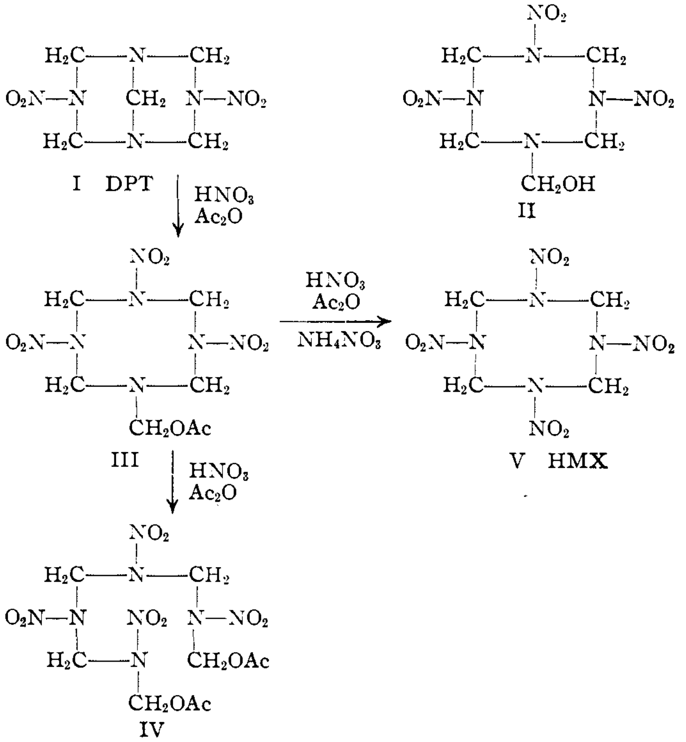
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

1-Acetoxymethyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooöctane and its Reactions. Significance in the Nitrolysis of Hexamethylenetetramine and Related Compounds[1]

BY W. E. BACHMANN AND E. L. JENNER

1-Acetoxymethyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooöctane is formed by nitrolysis and acetylation of 1,5-methylene-3,7-dinitro-1,3,5,7-tetrazacyclooöctane at the bridge methylene group. The compound reacts with nitric acid and acetic anhydride to give a linear tetranitramine and with nitric acid, acetic anhydride and ammonium nitrate to yield the cyclic tetranitramine HMX.

When 1,5-methylene-3,7-dinitro-1,3,5,7-tetrazacyclooöctane (DPT, I), a compound readily prepared by nitrolysis of hexamethylenetetramine,[2] is treated with one equivalent of 98% nitric acid in excess acetic anhydride, 1-acetoxymethyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooöctane (III) precipitates almost immediately from the reaction mixture in well-defined crystals and in good yield (80%). In the reaction, cleavage of the bridge occurs; one of the bridgehead nitrogen atoms acquires a nitro group, the other holds the acetoxymethyl group. The reaction may be considered to involve nitrolysis of I to the methylol derivative II, followed by acetylation of the hydroxy group by the acetic anhydride. III is not soluble in the common organic solvents; when warmed with acetone, acetic anhydride, or with nitromethane it decomposed with the evolution of formaldehyde. The structure of III was established by its analysis, saponification equivalent, and reactions. When warmed with water it decomposed rapidly to water-soluble products, among which was acetic acid but not nitric acid. This result showed that the acetyl group was indeed on the methylol group and that the nitro group was probably present as a nitramine group.



On reaction of III with a mixture of acetic anhydride and nitric acid, scission of the eight-membered ring occurred, and the linear tetranitramine, 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (IV) was produced in good yield. The same type of nitrolysis–acetylation occurred in this reaction as took place in the formation of III. When ammonium nitrate was present in the nitric acid–acetic anhydride mixture, the ring remained intact; the acetoxymethyl group was replaced by a nitro group with the formation of the cyclic tetranitramine HMX (V) in good yield. This result illustrates the marked effect of ammonium nitrate on the course of the reaction. The HMX was accompanied by a small amount of the cyclic trinitramine RDX. The formation of RDX could conceivably result from ring closure of a fragment containing the three trinitramine groups or by a Ross–Schiessler synthesis from the formaldehyde obtainable from the acetoxymethyl group. Information on this point could be obtained by a quantitative estimation of the RDX and by

---

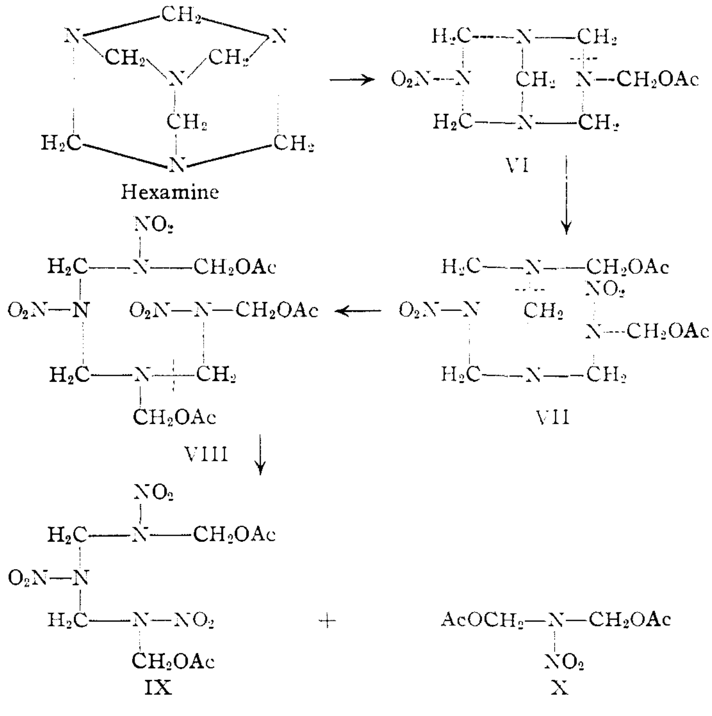
[1] This investigation was carried out under a contract recommended by the NDRC between the OSRD and the Regents of the University of Michigan, 1940–1945. This material has been released by the Security Review Branch of the Department of Defense.

[2] W. S. Chute, D. C. Downing, A. F. McKay, G. S. Myers and G. F Wright, *Can. J. Research*, **B27**, 218 (1949).

the use of ammonium nitrate containing N^{15}.

The formation of III from I, of IV from III, and of V from III are significant in that the reactions demonstrate types of scission and reactions that may occur in the nitrolysis of hexamine and related compounds.[3] All of the reactions involve the introduction of a single nitro group at a time. Wright and co-workers[4] had shown that I was converted into IV by addition of an excess of acetic anhydride and nitric acid, but they had no way of deciding where scission had occurred. The present work, involving as it does the stepwise conversion of I into IV, locates the points of cleavage and also shows the order in which the unsymmetrical cleavage of I occurs: the bridge is broken first and then the eight-membered ring.

On the basis of the scission reaction observed in the steps I→III and III→IV, a plausible formulation can be devised for the formation of the linear diacetoxytrinitramine IX when hexamine is added gradually to a mixture of nitric acid and acetic anhydride. Scission of any one of the bonds of hexamine would give VI. By the application of the single principle that cleavage will occur at bonds (indicated by dotted lines) distant from the nitramine group and nearest to the nitrogen atom holding an acetoxymethyl group VII, VIII and finally IX would be successively formed. The formulation also accounts for bis-(acetoxymethyl)-nitramine (X) which has been isolated by Wright and co-workers,[3] who also proposed a reaction scheme. The proposed scheme in which VII is formed is preferred to one involving cleavage of the bridge of VI to give an eight-membered ring from which IX and X could be obtained. By slight modification the first path could account for the formation of RDX when ammonium nitrate is present.



The reaction III→V shows that an acetoxymethyl group on a nitrogen atom not holding a nitro group can be replaced by a nitro group, a point which may be of importance in the consideration of a mechanism for the formation of RDX from hexamine. On the basis of the available results it is not possible to decide whether III is an intermediate in the production of HMX (V) in the reaction of DPT (I) with acetic anhydride, nitric acid and ammonium nitrate.[4] The yields of HMX obtained directly from DPT and from III appear to be about the same. Wright and co-workers[4] did not report that RDX was present in their product, but its presence is likely judging from the melting point of the product reported by them.

Experimental

1-Acetoxymethyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooöctane (III).—To a swirled suspension of 5 g. of 1,5-methylene-3,7-dinitro-1,3,5,7-tetrazacyclooöctane (I)[5] in 23 cc. of acetic anhydride in a 100-cc. erlenmeyer flask, 1 cc. of 98% nitric acid was added rapidly. The temperature rose and just as the last of I went into solution sugar-like crystals of III precipitated. The product was filtered from the cooled mixture and washed with acetone; yield 5.9 g.; m.p. 152° when placed in a bath at 140° and heated rapidly. A solvent suitable for recrystallization of III has not been found.

Anal. Calcd. for $C_7H_{13}N_7O_8$: C, 26.0; H, 4.0; N, 30.3. Found: C, 26.3; H, 4.3; N, 30.8.

On 2-g. runs in 10 cc. of acetic anhydride with 0.4 cc. of 98% nitric acid, it was possible to filter the solution quickly through a loose cotton plug in a glass funnel as soon as practically all of I had gone into solution; an additional 0.1 cc. of nitric acid was then added to the filtrate. On larger runs it is difficult to get complete reaction and filtration before the onset of crystallization of III. If the preparation is carried out at 60–70°, a smaller yield of an inferior product is obtained.

A clear solution resulted in a few minutes when 1 g. of III and 10 cc. of water were warmed on a steam-bath. Titration of the acidic solution with standard alkali to an end-point with phenolphthalein gave a saponification equivalent of 323 (calculated 340). The solution contained acetate ion but no nitrate ion.

Conversion of III into 1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (IV).—One gram of 1-acetoxymethyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooöctane was added to a mixture of 2 cc. of 98% nitric acid and 5 cc. of acetic anhydride; the temperature was maintained at 20–25° by cooling. After one-half hour the mixture was poured onto ice; yield 1.1 g.; m.p. 180–182°. One recrystallization from acetone gave a first crop of 0.75 g.; m.p. 182–184° alone and when mixed with an authentic specimen of IV.

Conversion of III into HMX.—To a stirred mixture of 30 cc. of acetic acid, 5 cc. of acetic anhydride and 5 g. of ammonium nitrate, which was kept at 65° throughout the reaction, 10 cc. of acetic anhydride, 10 g. of III and a solution of 3.5 g. of ammonium nitrate in 2.9 cc. of 99% nitric acid were added simultaneously and equivalently (three feeds) in the course of ten minutes. After an additional ten minutes of stirring, 100 cc. of water was added, the mixture was cooled, and the colorless solid (10.1 g.) was collected. Di-

---

[3] For parallel reactions see W. J. Chute, A. F. McKay, R. H. Meen, G. S. Myers and G. F Wright, *Can. J. Research*, **B27**, 503 (1949).

[4] A. F. McKay, H. H. Richmond and G. F Wright, *ibid.*, **B27**, 462 (1949).

[5] W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton and L. B. Scott, THIS JOURNAL, **73**, 2769 (1951).

gestion of 3 g. of the solid with hot dilute aqueous ammonia gave 1.79 g. of nearly pure HMX (V); m.p. 278° (safety shield should be used). After heating another 3-g. portion with 50% acetic acid containing 1% of nitric acid on a steam-bath for 15 hours, 2.44 g. remained with m.p. 270°. From this 0.12 g. of pure RDX was isolated as transparent rhombs; m.p. 204–205° (cor.), alone and when mixed with an authentic specimen.

ANN ARBOR, MICH. RECEIVED DECEMBER 11, 1950

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

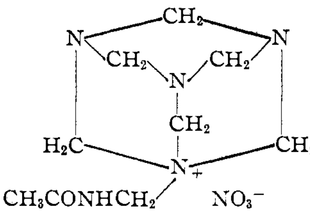
Structure Determination and Synthesis of 1-Acetamidomethylhexamine Nitrate[1]

BY W. E. BACHMANN, E. L. JENNER AND L. B. SCOTT

A compound formed by the action of acetic anhydride on hexamine mononitrate is shown to be 1-acetamidomethylhexamine nitrate. Several new syntheses of the compound are described.

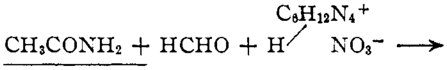
By the action of acetic anhydride on hexamine mononitrate Linstead, Kuehl and Leavitt[2] obtained a beautifully crystalline compound of unknown structure. Later, excellent directions for its preparation were devised by Carmack, Kuehl, Leavitt and Connor,[3] who reported that the empirical formulas $C_9H_{18}N_6O_4$ and $C_{15}H_{30}N_{10}O_7$ agreed best with the analytical values. The presence of a nitrate ion was indicated in the spectrum and the acetate ion was detected in the alkaline hydrolysate of the compound by the color test with lanthanum nitrate.

A determination of the nitrate ion by precipitation with nitron gave us an equivalent weight of 275, which was in agreement with the empirical formula $C_9H_{18}N_6O_4$. Assuming the presence of a hexamine nucleus $C_6H_{12}N_4$, there remained C_3H_6NO after subtraction of the hexamine moiety and a nitrate group. Since C_3H_6NO must contain an acetyl group (to account for the acetic acid produced on hydrolysis), only the grouping CH_3N remained after subtraction of CH_3CO. This could only be $-NHCH_2$ and the group attached to the hexamine molecule must be either $CH_3CONHCH_2-$ or CH_3COCH_2NH-, of which the first appeared to be the logical choice. On the basis of these speculations the compound has the structure (I) of the quaternary salt, 1-acetamidomethylhexamine nitrate

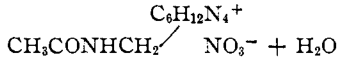


I

If the proposed structure is correct, the compound could probably be prepared from hexamine mononitrate, formaldehyde and acetamide according to the formulation



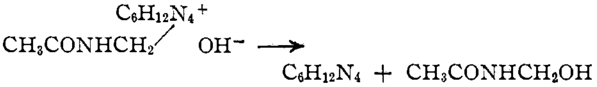
$$CH_3CONH_2 + HCHO + H\overset{C_6H_{12}N_4^+}{\diagup}\ NO_3^- \longrightarrow$$



$$CH_3CONHCH_2\overset{C_6H_{12}N_4^+}{\diagup}\ NO_3^- + H_2O$$

Experiment showed this to be the case; the quaternary salt which crystallized from a solution of acetamide and hexamine mononitrate in formalin was identical in all respects with the compound prepared from acetic anhydride and hexamine mononitrate.

It had been reported that the compound reacted with one equivalent of alkali at room temperature and a second equivalent at elevated temperature. We have investigated the reaction with one equivalent of alkali more closely. In agreement with the structure the aqueous solution of the salt is neutral; when 0.1 *N* sodium hydroxide was added to the aqueous solution of the quaternary salt containing phenolphthalein, a pink color was soon formed. The color faded quickly but reappeared when more alkali was added. More time was required for the fading as more of the compound had reacted. The half-way point was reached in about one-half hour; complete neutralization of one equivalent of alkali required about 12 hours. These results suggested that the quaternary hydroxide was unstable and decomposed in the following manner into hexamine and N-methylolacetamide.



$$CH_3CONHCH_2\overset{C_6H_{12}N_4^+}{\diagup}\ OH^- \longrightarrow C_6H_{12}N_4 + CH_3CONHCH_2OH$$

From the mixture hexamine and sodium nitrate were isolated in good yield. The N-methylolacetamide could not be obtained crystalline; on sublimation of the fraction containing it acetamide was obtained. Clearly the reaction with a second equivalent of alkali at elevated temperature involved the hydrolysis of the acetamide. In agreement with the proposed formula, the compound yielded exactly one mole equivalent of acetic acid on saponification.

The neutralization reaction suggested another synthesis of the quaternary salt, which was realized; namely, the reaction of N-methylolacetamide with hexamine mononitrate. The salt was obtained also from acetamide, paraformaldehyde and hexamine in acetic acid followed by addition of nitric acid; from hexamine mononitrate and acetamide in acetic acid followed by addition of water (the requisite formaldehyde must have been derived from hydrolysis of part of the hexamine); from hex-

---

[1] This investigation was carried out under a contract recommended by the NDRC between the OSRD and the Regents of the University of Michigan, 1940–1945. This material has been released by the Security Review Branch of the Department of Defense.

[2] R. P. Linstead, F. A. Kuehl and J. Leavitt, private communication.

[3] M. Carmack, F. A. Kuehl, J. Leavitt and R. Connor, private communication.