

yielded 6.05 g. of a colorless liquid, b.p. 98–119° (3 mm.), which still contained some chlorine.

A 2.00-g. portion of this distillate was oxidized with 1.20 g. of chromium trioxide in 20 ml. of 90% acetic acid by allowing the solution to stand at room temperature overnight. The excess chromium trioxide was reduced by the addition of methyl alcohol and the organic material was isolated. This material was converted to an oxime by heating it for two hours with a solution of 2.00 g. of hydroxylamine hydrochloride and 8.0 g. of potassium hydroxide in 40 ml. of ethyl alcohol. Most of the alcohol was then removed by evaporation and the suspension was poured into water. The crude oxime (1.00 g.) was separated by filtration. Crystallization from petroleum ether, b.p. 60–68°, containing a little benzene and from dilute methanol produced an analytically pure sample, m.p. 111–111.5°.

*Anal.* Calcd. for  $C_{12}H_{15}NO$ : C, 76.15; H, 7.99. Found: C, 76.11; H, 7.99.

1,1-Dimethyl-2-tetralone was also prepared in 72.8% yield by the methylation of 2-tetralone using methyl iodide and potassium *t*-butoxide in *t*-butyl alcohol. The material so obtained boiled at 142–146° (24 mm.);  $n_D^{25}$  1.5406. An oxime prepared from this ketone melted at 109.5–110° and showed no depression of melting point when mixed with the oxime obtained above. After this work was completed, the preparation of 1,1-dimethyl-2-tetralone by the methylation of 2-tetralone using methyl iodide and sodium hydride in benzene was reported.<sup>8</sup>

1-(3-Chloro-2-butenyl)-2-naphthol.—To a solution of 146.1 g. (1.015 moles) of 2-naphthol in 500 ml. of warm toluene under nitrogen was added 23.3 g. (1.012 moles) of sodium wire in small portions with stirring. The resulting paste was thinned by the addition of 300 ml. of toluene. To the rapidly stirred suspension heated at 100–110° was slowly added 142.5 g. (1.14 moles) of 1,3-dichloro-2-butene over a period of one hour. The mixture was then heated under reflux for five hours. The mixture was diluted with water and the unreacted 2-naphthol (24.1 g.) was removed by extraction of the toluene solution with a 5% sodium hydroxide solution. The toluene was removed by distillation. The residual oil was mixed thoroughly with four times its volume of Claisen alkali<sup>9</sup> and the resulting suspension was extracted thoroughly with petroleum ether. The Claisen alkali was acidified with hydrochloric acid; the red oil which separated was extracted with ether; and the ether solution was dried over magnesium sulfate, then distilled. Distillation under vacuum yielded 114.7 g. of 1-(3-chloro-2-butenyl)-2-naphthol, b.p. 165–175° (1.5 mm.). The distillate, which slowly solidified on standing, was crystallized

(8) Soffer, Stewart, Cavagnol, Gellerson and Bowler, *THIS JOURNAL*, **72**, 3704 (1950).

(9) Claisen, *Ann.*, **418**, 96 (1919); Claisen, Kremers, Roth and Tietze, *ibid.*, **424**, 210 (1925).

from petroleum ether, b.p. 60–68°, and gave 105.3 g. (45.5%) of product, m.p. 65.5–66°. Further crystallization of this substance raised its melting point to 68–68.5°. The compound slowly turns green on standing in air.

*Anal.* Calcd. for  $C_{14}H_{13}ClO$ : C, 72.26; H, 5.63. Found: C, 71.91; H, 5.80.

1-(3-Chloro-2-butenyl)-2-naphthyl benzoate was prepared by treating the naphthol with benzoyl chloride and aqueous sodium hydroxide. After crystallization from methanol it melted at 84–84.5°.

*Anal.* Calcd. for  $C_{21}H_{17}ClO_2$ : C, 74.89; H, 5.08. Found: C, 74.84; H, 5.27.

1-(3-Chloro-2-butenyl)-1-dichloromethyl-2-keto-1,2-dihydronaphthalene (V).—A solution of 60.0 g. (0.26 mole) of 1-(3-chloro-2-butenyl)-2-naphthol and 120 g. of sodium hydroxide in 1200 ml. of water was heated to 76° with stirring. To it was added 240 ml. of chloroform over a period of five hours. The resulting mixture was then heated under gentle reflux for an additional three hours. The chloroform solution was then separated from the aqueous layer; the aqueous layer was extracted with two 50-ml. portions of chloroform; and the chloroform solutions were combined. The chloroform was removed by distillation. The residual oil was mixed with four times its volume of Claisen alkali<sup>9</sup> and the resulting mixture was extracted six times with 25-ml. portions of petroleum ether, b.p. 60–68°. These extracts were combined, dried over magnesium sulfate, then concentrated under reduced pressure. During this concentration the product separated as a light tan solid. In this manner 24.3 g. (35%) of 1-(3-chloro-2-butenyl)-1-dichloromethyl-2-keto-1,2-dihydronaphthalene, m.p. 68–70°, was obtained. The compound is readily crystallized from ethanol.

*Anal.* Calcd. for  $C_{13}H_{13}Cl_2O$ : C, 57.08; H, 4.15. Found: C, 57.40; H, 4.43.

1-Allyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene was prepared in 47% yield from 1-allyl-2-naphthol<sup>10</sup> by a procedure similar to that described above. The product distilled at 126–132° at 1.5 mm. The analytical sample was obtained by refractionating this material, b.p. 122° (0.8 mm.);  $n_D^{25}$  1.6085.

*Anal.* Calcd. for  $C_{14}H_{12}Cl_2O$ : C, 62.94; H, 4.53. Found: C, 63.19; H, 4.69.

**Acknowledgment.**—The authors are indebted to the Research Corporation for a grant in support of this research.

(10) The 1-allyl-2-naphthol used in this preparation was prepared in 40% yield by the direct allylation of 2-naphthol with allyl bromide by a procedure similar to that described for 1-(3-chloro-2-butenyl)-2-naphthol.

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

## Cyclic and Linear Nitramines Formed by Nitrolysis of Hexamine<sup>1</sup>

BY W. E. BACHMANN, W. J. HORTON, E. L. JENNER, N. W. MACNAUGHTON AND L. B. SCOTT

The procedure for the preparation of cyclotrimethylenetrinitramine (RDX) by nitrolysis of hexamine in acetic anhydride in the presence of ammonium nitrate has been improved. In the reaction some of the cyclic tetranitramine, a high explosive with an eight-membered ring, is formed. By suitable modification the reaction mixture can be made to yield a linear trinitramine. The use of isotopic ammonium nitrate in the RDX reaction is described.

Recently we described a new process for preparing the high explosive cyclotrimethylenetrinitramine (I, RDX) by the reaction of hexamethylenetrinitramine (hereinafter called hexamine) with nitric acid, acetic anhydride and ammonium nitrate.<sup>2</sup> It was shown that the product of the

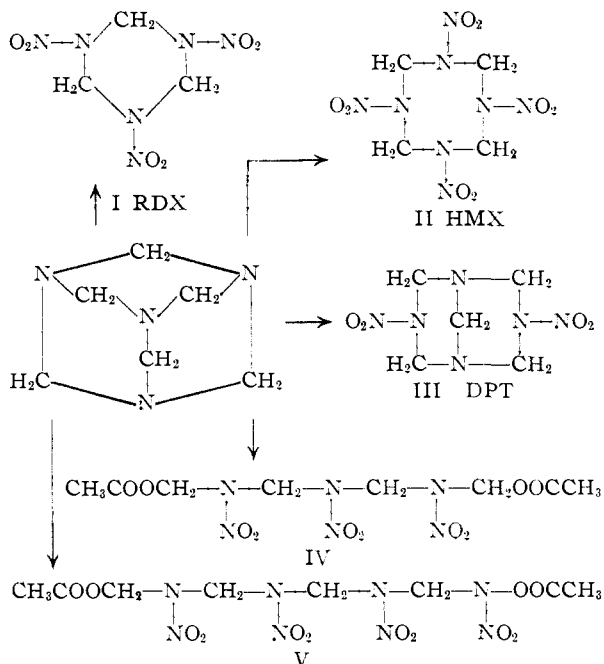
(1) This investigation was carried out under a contract recommended by the NDRC between the OSRD and the Regents of the University of Michigan, 1940–1945. This material has been released by the Security Review Branch of the Department of Defence.

(2) W. E. Bachmann and J. C. Sheehan, *THIS JOURNAL*, **71**, 1842 (1949).

reaction contained a small amount (0–10%) of a high-melting compound which was called HMX. As a result of hundreds of experiments, conditions have been worked out whereby RDX (with some HMX) can be obtained in yields higher than 80%; the highest yield obtained was 90% (based on the formation of two moles of RDX per mole of hexamine).

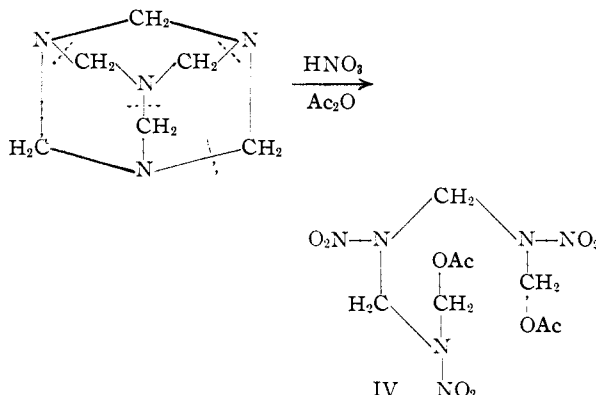
On the basis of analysis (identical with that of RDX), high melting point, and molecular weight we suggested (in 1941) that HMX was 1,3,5,7-

tetranitro-1,3,5,7-tetrazacyclooctane (II), the next higher methylenenitramine homolog of RDX. This structure has been amply confirmed by subsequent investigations, particularly those of Wright and co-workers.<sup>3</sup> The latter investigators prepared HMX by nitrolysis of 1,5-methylene-3,7-dinitro-1,3,5,7-tetrazacyclooctane (III, also called DPT from the name dinitropentamethylenetetramine) by means of nitric acid, acetic anhydride and ammonium nitrate; in the reaction the bridgehead methylene group is eliminated and the two bridgehead nitrogen atoms acquire nitro groups. The DPT was obtained by them by the action of acetic anhydride on hexamine dinitrate at room temperature for two to three days. By a shorter method described in the present work DPT can be made in higher yield, and with this and other modifications HMX can be prepared readily from hexamine in an over-all yield of 28%. The low solubility of HMX in organic solvents makes it possible to remove RDX by recrystallization and to isolate HMX from RDX-HMX mixtures containing only 5% of HMX.



Bachmann and Sheehan<sup>2</sup> found that the nitrolysis reaction took an entirely different course when the same reagents used to make RDX were mixed at 0° and then warmed to 75°. The new compound (m.p. 154–155°) which was produced was shown to be an acetylation as well as nitration product with a molecular weight of about 350. We confirmed the finding<sup>4</sup> that the compound yields two moles of acetic acid on hydrolysis and suggested the following scheme for the formation of a structure (IV)<sup>5</sup> possessing the requisite molecular formula<sup>4</sup> and properties. The formation of the 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane

(IV) involves the scission of four bonds of the hexamine molecule (indicated by dotted lines) and does not necessitate the recombination of fragments.



In the present study it was found that the temperature *per se* does not influence the course of the reaction to any great extent. The reason for the formation of the linear trinitramine IV when hexamine was mixed in the cold with the other reagents was the relative insolubility of the ammonium nitrate at the lower temperatures; as a result a reaction took place between hexamine, nitric acid and acetic anhydride to form IV. If a larger volume of acetic acid was employed so that the ammonium nitrate was in solution at the lower temperatures, then a 67% yield of RDX was obtained instead of IV. Moreover, if hexamine (1 mole) is treated with nitric acid (4 moles) and excess acetic anhydride cold or hot, IV is the chief product and only a small amount of RDX is produced. The latter procedure provided a convenient preparative method in which the linear trinitramine precipitated from the anhydrous reaction mixture in crystalline form.

1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (IV) is the first example of a linear nitramine formed by nitrolysis of hexamine. Wright and co-workers<sup>3b</sup> obtained its methylenenitramine homolog, 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (V) by treatment of DPT with a mixture of nitric acid and acetic anhydride. We have worked out a procedure whereby the linear tetranitramine V can be prepared from hexamine in essentially a one-step operation; the product precipitates from the anhydrous reaction mixture in crystalline form.

In view of the nitrolysis of hexamine to RDX (one mole) by nitric acid alone, it might be expected that if the ammonium nitrate were omitted from the present reaction mixture at least one mole of RDX would be formed. This is not the case. Instead, the reaction takes an entirely different course to yield the linear trinitramine IV as described below, and only small amounts of RDX are produced. The result showed that the ammonium nitrate serves not only as the source of the two nitrogen atoms required for the second mole of RDX but is essential in directing the course of the nitrolysis to form the first mole of RDX. A solution of potassium nitrate (1 mole) in 98% nitric acid (2 moles) has some properties similar

(3) (a) W. J. Chute, D. C. Downing, A. F. McKay, G. S. Myers and G. F. Wright, *Can. J. Research*, **B27**, 218 (1949); (b) A. F. McKay, H. H. Richmond and G. F. Wright, *ibid.*, **B27**, 462 (1949).

(4) E. Roberts, private communication.

(5) The structure is one of two for which Dr. J. R. Johnson, Cornell University, expressed a preference.

to that of a solution of ammonium nitrate (1 mole) in nitric acid (2 moles); the two solutions do not burn the skin as does nitric acid alone, and on cooling they deposit crystals of the trinitrate ( $\text{KNO}_3 \cdot 2\text{HNO}_3$  and  $\text{NH}_4\text{NO}_3 \cdot 2\text{HNO}_3$ , respectively.) However, substitution of the potassium nitrate solution for the corresponding ammonium nitrate solution (which gives high yields of RDX) resulted in the formation of only a trace of RDX.

Some exploratory work was carried out utilizing  $\text{N}_{15}\text{H}_4\text{NO}_3$  in place of ordinary ammonium nitrate in the RDX reaction in order to determine whether the formation of only one or both molecules of RDX and the formation of HMX involved incorporation of amino nitrogen from the ammonium radical of the salt. The situation was complicated, however, by the discovery that interchange between hexamine nitrogen and ammonium nitrogen occurred in a solution of hexamine and tracer ammonium nitrate in acetic acid.

In a normal run (80% yield of RDX-HMX) with the tracer ammonium nitrate, 37% of the amino nitrogens of the RDX and only 15% of the amino nitrogens of the HMX were derived from the ammonium nitrate (by exchange and/or incorporation). When a much larger amount of nitric acid was used so that the yield of RDX was only 47%, only 20% of the amino nitrogens in the RDX came from the ammonium nitrate. In spite of the complications introduced by interchange, apparently the formation of HMX involves less interaction with ammonium nitrate (by exchange or incorporation or both) than does the formation of RDX, and less interaction of the ammonium radical of the salt is involved in the formation of RDX in high nitric acid concentration.

Hexamine can undergo two fundamentally different types of cleavage, leading to (a) compounds containing three amino nitrogen atoms such as RDX and the linear trinitramine, 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, and to (b) compounds with four amino nitrogen atoms as DPT, HMX and the linear tetranitramine, 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane. The first type of cleavage is favored by high acidity and/or high activity of nitrating agent. The second type of cleavage occurs under conditions of low acidity and/or low activity of the nitrating agent, particularly in the initial attack on the hexamine. These results are paralleled by the behavior of hexamine with nitrous acid in aqueous solution. At high acidity the compound with three amino nitrogen atoms (trinitrosotrimethylenetriamine) is the chief product; at comparatively low acidities the four-amino nitrogen compound (dinitrosopentamethylenetetramine) is formed.<sup>8</sup> The gross effects of the activity of the nitrating agent and the ammonium nitrate can be summarized as follows:

Acidity and/or activity of nitrating agent (particularly for initial attack)	Ammonium nitrate	
	Present	Absent
High	RDX	Linear trinitramine <sup>a</sup> (IV)
Low	HMX	Linear tetranitramine <sup>b</sup> (V)

<sup>a</sup> 1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane. <sup>b</sup> 1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane.

(6) W. E. Bachmann and N. C. Deno, *THIS JOURNAL*, **73**, 2777 (1951).

## Experimental

**Preparation of RDX.**—The previously described procedure<sup>2</sup> was improved. The hexamine dinitrate (65 g.) was divided into twenty-six equal portions; a buret containing 145 cc. of acetic anhydride was marked off into twenty-six portions and a buret containing 26 cc. of 98% nitric acid was marked off into twenty-eight equal portions. In the flask a mixture of 50 g. of ammonium nitrate and 30 cc. of acetic acid was warmed to 75°, 30 cc. of acetic anhydride (not from the buret) was added, and then one-fourth portion of the hexamine dinitrate and two portions of the nitric acid from the buret. With the temperature maintained at 74–76° by a water-bath the three reagents were added to the stirred mixture equivalently in the course of fifteen minutes; the remainder of the first portion was counted as the first portion. After an additional fifteen minutes at the same temperature, the mixture was cooled to 60° and filtered; yield of RDX, 81.8 g.; m.p. 201–203° (cor.) with previous softening at 196°. From the filtrate an additional 8–10 g. of RDX (containing a greater proportion of HMX than the first crop) was obtained. Similar results were obtained at 65°.

In a variation of this procedure a solution of ammonium nitrate (55 g.) in 98% nitric acid (75 g. or 50 cc.) was prepared. In one buret 43.3 cc. of this solution was marked off in twenty-seven equal portions; in the other buret 147 cc. of acetic anhydride was marked off into 25 portions; the 65 g. of hexamine dinitrate was divided into twenty-five equal portions. Two of the ammonium nitrate-nitric acid portions (3.2 cc.) were added to 40 g. of ammonium nitrate, 30 cc. of acetic anhydride and 30 cc. of acetic acid in the flask at 75°. The addition of the three reagents to the flask was made as before; yield of RDX 91.3 g. (84%) with an HMX content of 5%.

In a run in which 70% nitric acid was employed (with sufficient additional acetic anhydride to react with the water in the acid) a 76% yield of RDX was obtained. When no acetic anhydride was employed in a run at 75°, no RDX was produced. When only 4% of the normal quantity of nitric acid was used at 75°, a 2% yield of RDX was produced. High yields of RDX were obtained also by the use of propionic anhydride and butyric anhydride in place of acetic anhydride. When chloroacetic anhydride was used under the same conditions, no RDX was formed because this anhydride destroyed the ammonium nitrate with evolution of gas; only by employing a large excess of ammonium nitrate could some RDX (10% yield) be obtained.

**Preparation of 1,5-Methylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DPT, III) from Hexamine.**—The procedure is an extension of an experiment of Baxter, Linstead, Carmack, Kuehl and Leavitt<sup>7</sup> in which smaller quantities of DPT were prepared by mixing instantaneously hexamine, 98% nitric acid and acetic anhydride in acetic acid. Two solutions were prepared: (a) 201.6 g. of hexamine in 330 cc. of acetic acid; and (b) 126 cc. of 98% nitric acid in 360 cc. of acetic anhydride (prepared by the gradual addition of the acid to stirred acetic anhydride which was kept at 15° or lower by means of an ice-water bath; the solution should be used immediately). The two solutions were added from burets continuously and equivalently to 60 cc. of acetic acid which was stirred in a 3-liter, three-necked flask by an efficient mechanical stirrer. The temperature of the mixture was held at 25–30° by a water-bath equipped with an inlet for cold water. The addition required sixty minutes, and the mixture was stirred for an additional thirty minutes at the same temperature. After the addition of 800 cc. of water (warmed to 65°), the DPT was collected on a filter and washed with water; yield 150 g. (48%); m.p. 198° (dec.). The product was used without further purification in the next step. Wright and co-workers<sup>8a</sup> have listed the solvents from which DPT can be recrystallized, but did not report the m.p. of the recrystallized product; their first crop (20% yield) had m.p. 205–206° cor. After recrystallization from nitromethane we have had DPT which melted as high as 213° and 216°.

When a reaction temperature of 65° was employed in the preparation, the yield of product (m.p. above 200°) was reduced to about one-half the usual amount. When all of the acetic acid solution of hexamine was placed in the flask initially and the nitric acid-acetic anhydride mix-

(7) G. Baxter, R. P. Linstead, M. Carmack, F. A. Kuehl and J. Leavitt, private communication.

ture was added gradually, the yield of DPT was less than 20%.

**Preparation of HMX (II) from DPT.**—The method is that of Wright and co-workers<sup>2b</sup>; however, only one-third as much nitric acid-ammonium nitrate was employed, and the method of purification was different. A solution of 44 g. of ammonium nitrate in 47 cc. of 98% nitric acid was allowed to stand until it ceased gassing and became practically colorless. In a 2-l., three-necked flask equipped with a thermometer and mechanical stirrer was placed 100 g. of DPT and 460 cc. of acetic anhydride. Ground-glass connections are preferable to corks and rubber stoppers. If the reaction is conducted in a good hood, connections to the flask are not necessary. When the stirred suspension had been heated to 60° by a water-bath, the nitric acid-ammonium nitrate solution was added over a period of ten minutes; the temperature was kept at 60–65° throughout the reaction. During the first five minutes the reaction was highly exothermic and it was necessary to keep the temperature of the water-bath at 20–30°; during the last five minutes a bath temperature of 40° sufficed. When the addition was half completed, the solution was clear; as addition continued the mixture became milky.

After the addition the mixture was stirred at 60–65° for one hour; HMX began to crystallize in a few minutes. The mixture was allowed to cool to 50° and 450 cc. of cold water was added rapidly to the stirred mixture. There must be no delay in adding the water, for if only a small amount is introduced the temperature rise may be excessive. The temperature of the mixture fell to 40° and then rose to 90°. The mixture was heated on a steam-bath for twelve hours with the flask wrapped in towels to keep the temperature as high as possible. A considerable amount of gas which contained formaldehyde was evolved during this simmer. The crude HMX, which contained 16% of RDX, was filtered from the cooled mixture; weight, 102 g.; m.p. 272–276° (cor.). A filtered solution of the HMX-RDX mixture in 3 liters of hot acetone was concentrated by distillation on a steam-bath to a 400-cc. volume; during the operation much of the HMX crystallized from the hot solution. The slurry was allowed to cool, and the HMX was collected on a filter and washed with acetone; yield 80 g.; m.p. 281–282° (cor.). HMX crystallizes from acetone and from nitromethane in large and colorless bipyramids.

*Anal.* Calcd. for  $C_4H_8N_8O_8$ : C, 16.2; H, 2.73; N, 37.9. Found: C, 16.0; H, 2.68; N, 38.2.

The molecular weight of HMX in acetone was found by the boiling point elevation method of Menzies; calcd., 296; found, 299. As a check the method was applied to RDX; calcd., 222; found, 223.

By the procedure described by Wright<sup>2b</sup> we obtained 8.4 g. of 96% HMX from 10 g. of recrystallized DPT (m.p. 213° (cor.)).

**1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (IV).**—A series of runs were made in which hexamine, nitric acid and acetic anhydride were brought together under various conditions. In (a) is given a procedure in which ease of obtaining a pure compound rather than yield is emphasized. In (b) is given a procedure which employs hexamine dinitrate.

(a) Forty-five cc. of 98% nitric acid was added gradually with stirring to 120 cc. of acetic anhydride (in a three-necked flask equipped with a thermometer and a paddle stirrer) which was kept at 15–20° by means of an ice-bath. A solution of 33.6 g. of hexamine in 55 cc. of glacial acetic acid was added continuously to the stirred mixture at 15–20° in twenty minutes. The resulting mixture was heated in the course of fifteen minutes to 75°; the clear solution was stirred as it cooled to room temperature; at about 70° a few crystals of IV were introduced. After standing at room temperature for twelve hours, the well-formed crystals of IV were collected on a filter and washed with acetic acid. The moist product was dissolved in 100 cc. of hot acetic acid, and the solution after seeding was allowed to cool; yield of colorless plates 43 g. (51%); m.p. 153.5–154.5°.

The original mother liquor contained additional IV and much water-insoluble gum. The whole was disposed of by converting it into water-soluble products by addition of 700 cc. of water followed by simmering on a steam-bath for three to five hours.

By omitting the heating to 70°, a 48-g. first crop was obtained which gave 34 g. of IV with m.p. 154–155° on recrystallization.

(b) To an ice-cold mixture of 60 cc. of acetic anhydride and 13.8 cc. of 98% nitric acid prepared as above was added with stirring 20.8 g. of hexamine dinitrate.<sup>2</sup> Not much heat was evolved and the solid could be added in less than five minutes. The stirred mixture was warmed in the course of one-half hour to 75° and held there for five minutes (some brown fumes). The slow addition of 160 cc. of water precipitated 23 g. of product. Recrystallization of a 15-g. portion from acetone-ethyl acetate yielded 7.6 g.; m.p. 153–154°.

A solution of 5 g. of the crude product in 40 cc. of 70% acetic acid was heated on a steam-bath for twenty-four hours; this treatment destroyed all of IV. Upon evaporation of the solution 0.35 g. of RDX (m.p. 201–204°) was obtained; this corresponds to a 7% yield of RDX in the reaction.

**Degradative Hydrolysis of IV.**—Ten grams (0.028 mole) of IV (m.p. 153.5–154.5°) was heated on a steam-bath with 100 cc. of 85% phosphoric acid under a reflux condenser. A clear solution was obtained in thirty minutes; after twenty-four hours crystals of paraformaldehyde were present in the condenser. After the addition of 100 cc. of water, the solution was distilled; more water was added and the distillation was continued. The acid in the distillate was neutralized and the solution was evaporated to dryness. After treatment with potassium permanganate and filtration from manganese dioxide, the solution was again evaporated, the residue was dissolved in 100 cc. of water, phosphoric acid was added and the solution was distilled. The distillate contained 0.055 mole (calculated, 0.056 mole) of acetic acid; no phosphate, nitrate or halide ions were present. The solution possessed the Duclaux numbers of acetic acid; from the acid, silver acetate was prepared and analyzed, and the known *p*-bromophenacyl derivative of acetic acid was prepared.

**1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (V).**—Twenty cc. of acetic acid was placed in a four-necked 1-l. flask equipped with a thermometer, paddle stirrer and two burets, and the flask was immersed in an ice-bath. A solution of 33.6 g. of hexamine in 55 cc. of acetic acid and a cold freshly-prepared mixture (see above) of 21 cc. of 98% nitric acid and 60 cc. of acetic anhydride were added continuously and equivalently in six minutes to the stirred acetic acid; the temperature of the reaction mixture was kept at 30°. After being stirred at 30° for one-half hour more, the thick mixture was poured into a dry beaker (hood). Acetic anhydride (150 cc.) was added to the uncleaned reaction flask; 40 cc. of 98% nitric acid was added with cooling, and the four-state reaction product (contained in the beaker) was added in three to five minutes; the temperature was kept at 25–30°. Acetic anhydride (50 cc.) was used to transfer the residual material in the beaker into the reaction mixture.

The stirred reaction mixture was heated slowly to 70°; brown fumes were evolved and some solid remained undissolved. The bath was removed and the mixture was stirred as it cooled to room temperature. After two hours the product was collected on a filter and washed with acetic acid; yield 41.2 g.; m.p. 174–177°. Recrystallization from 600 cc. of acetic acid yielded colorless nacreous plates of V; yield 33.1 g. (32%); m.p. 182.5–183.5°.

**Reactions with N<sup>15</sup> in the Ammonium Nitrate.**—The salt (Eastman Kodak Company) contained approximately 15 atom per cent. of N<sup>15</sup> in the ammonium radical. The atom per cent. abundance of N<sup>15</sup> in the ordinary ammonium radical is 0.4%.

(a) **Interchange of Nitrogen in Hexamine and Isotopic Nitrogen in Ammonium Nitrate.**—A clear solution of 0.44 g. of hexamine (atom per cent. of N<sup>15</sup> based on total nitrogen, 0.4%) and 0.5 g. of the isotopic ammonium nitrate in 21 cc. of acetic acid was kept at 65° for fifteen minutes. To the cooled solution was added 0.3 cc. of 98% nitric acid, and the precipitate of hexamine dinitrate was collected by filtration and washed with 10 cc. of cold 10% nitric acid to remove ammonium nitrate. The hexamine was liberated from its salt with dilute alkali, isolated by evaporation of the solution and extraction into chloroform, and purified by recrystallization from absolute ethanol; atom per cent. of N<sup>15</sup> in the hexamine, 1.15%.<sup>8</sup>

(8) We are indebted to Dr. G. F. Wright for obtaining the nitrogen in elemental form (Dumas method) and to Dr. N. Keevil, University of Toronto, for the analyses by the mass spectrograph.

(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<sup>15</sup>. An-

other fraction was chiefly HMX with m.p. 268–269°, which was raised to 282° (cor.) after two recrystallizations from acetone; atom per cent. N<sup>15</sup> 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<sup>15</sup> (original tracer salt had 7.5 atom per cent. of N<sup>15</sup>, 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<sup>15</sup>.

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

## 1-Acetoxyethyl-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane and its Reactions. Significance in the Nitrolysis of Hexamethylenetetramine and Related Compounds<sup>1</sup>

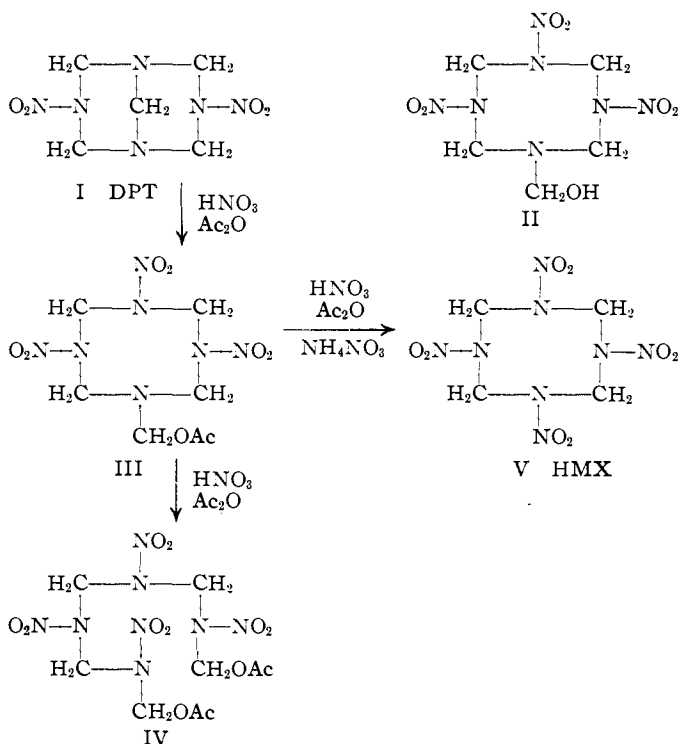
BY W. E. BACHMANN AND E. L. JENNER

1-Acetoxyethyl-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane is formed by nitrolysis and acetylation of 1,5-methylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane 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-tetraazacyclooctane (DPT, I), a compound readily prepared by nitrolysis of hexamethylenetetramine,<sup>2</sup> is treated with one equivalent of 98% nitric acid in excess acetic anhydride, 1-acetoxyethyl-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane (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 acetoxyethyl 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-tetra-nitro-2,4,6,8-tetraazanonane (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 acetoxyethyl 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 ammo-



onium 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-Schiesler synthesis from the formaldehyde obtainable from the acetoxyethyl 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).