

# 568. Methylene-nitramines. Part I. The Reaction of Hexamine Dinitrate with Nitric Acid at Low Temperatures.

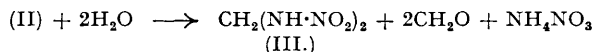
By K. W. DUNNING and W. J. DUNNING.

Dilution of the hexamine dinitrate-nitric acid reaction mixture at low temperatures with ethyl ether and subsequent treatment of the gum so obtained with methyl and ethyl alcohols and water severally leads to 1-alkoxy-3 : 5-dinitro-1 : 3 : 5-triazacyclohexane (IV), 1 : 3-dinitro-1 : 3 : 5-triaza-*n*-pentane 5-nitrate (V), and methylenedi-1-(3 : 5-dinitro-1 : 3 : 5-triazacyclohexane) (VI). Dilution of the reaction mixture with methyl and ethyl alcohol produces mainly 3 : 5-dinitro-1 : 3 : 5-triazacyclohexane nitrate (II). 1-Methoxymethyl-3 : 5-dinitro-1 : 3 : 5-triazacyclohexane (IV; R = Me) has been synthesised from (II), methyl alcohol, and formaldehyde. 1 : 3 : 5-Trinitro-1 : 3 : 5-triazacyclohexane (I) has been synthesised from (V), acetic anhydride, and formaldehyde.

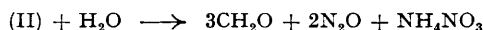
THE final product of the action of nitric acid on hexamine or hexamine dinitrate at 0° is 1 : 3 : 5-trinitro-1 : 3 : 5-triazacyclohexane (hexahydro-1 : 3 : 5-trinitro-*s*-triazine; cyclonite) (I) (Henning, G.P. 104,280, H 20660, 1899; Herz, U.S.P. 1,402,693/1922; Hale, *J. Amer. Chem. Soc.*, 1925, **47**, 2754). Most workers in the field consider that the hexamine molecule undergoes a stepwise degradation to (I), and some evidence for this has accrued from the work of Vroom and Winkler (private communication) who, on treating hexamine dinitrate with 97% nitric acid at -40°, isolated a compound, m. p. 98°, to which they assigned structure (II), 3 : 5-dinitro-1 : 3 : 5-triazacyclohexane nitrate. This gave (I) both with nitric acid and with acetic anhydride.



Dr. J. K. N. Jones also established several other properties of the compound which support structure (II), and has given us permission to quote them. (1) Boiling alcohol decomposes (II) with formation of ammonium nitrate, formaldehyde, hexamine, and methylenedinitramine, the last isolated as the barium salt. Jones assigned structure (III) to methylenedinitramine and this was later confirmed by Brian and Lamberton (*J.*, 1949, 1633), who obtained it by the hydrolysis of methylenebis-*N*-nitroacetamide. (2) Compound (II), titrated with baryta, gave an equivalent weight of 88. It requires an equivalent weight of 80 if it is assumed to hydrolyse to 1 mole of methylenedinitramine (known to be a dibasic acid), one of ammonium nitrate, and 2 moles of formaldehyde :



When an equal volume of acetone was added to the neutral solution, the barium salt of methylenedinitramine slowly separated in 92% yield. (3) In boiling water, (II) liberated three moles of formaldehyde, as would be expected if the six-membered ring were disrupted as follows :

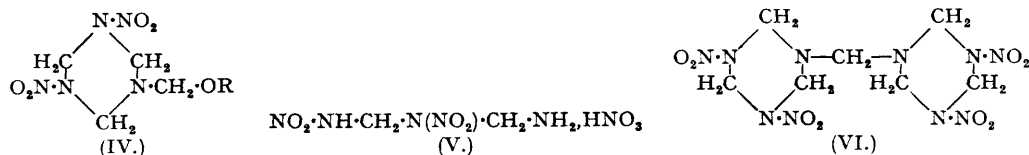


(4) Heating (II) with acetic anhydride containing sodium acetate gave a product, m. p. 156°, which Jones showed to be 1-acetyl-3 : 5-dinitro-1 : 3 : 5-triazacyclohexane. (5) With sodium nitrite (II) yields 3 : 5-dinitro-1-nitroso-1 : 3 : 5-triazacyclohexane.

The question arises whether (II) is a true intermediate, or whether it has been produced by the hydrolysis of some other substance during the addition of water to the reaction mixture. The work described here aimed at isolating the true intermediate, and a suitable method of ending the reaction at any given stage appeared to be the dilution of the reaction mixture with a solvent which was unlikely to react chemically with the intermediate and in which the latter was sparingly soluble. Ether was chosen, since it is miscible with nitric acids containing up to 15% of water.

When the reaction of hexamine dinitrate with 97% aqueous nitric acid at low temperatures was stopped at the appropriate stage by diluting the reaction mixture with cold ether, a white unstable gum (A) separated. This was stabilised by stirring it with cold ethyl alcohol, in which it immediately became granular. Extraction of this white granular residue with ether gave 1-ethoxymethyl-3 : 5-dinitro-1 : 3 : 5-triazacyclohexane (IV; R = Et) in 17% yield.

Structure (IV) was assigned to this compound because (a) an elemental analysis agreed with  $C_6H_{13}O_5N_5$ , (b) boiling dilute hydrochloric acid liberated the theoretical quantity of formaldehyde, (c) a mixture of glacial acetic acid and 70% sulphuric acid liberated an amount of nitrous oxide consistent with two  $>N\cdot NO_2$  groups per molecule [a method first used by Roberts and Watkins (unpublished work) for determination of nitramine groups], (d) 96% nitric acid afforded (I) in 91% yield. Reactions of (IV) or its methyl analogue with acetic anhydride, acetyl chloride, and acetyl nitrate (see Part II) further support this structure.



Evaporation of the solution obtained by stirring the gum with alcohol and subsequent recrystallisation of the residue from 80% aqueous nitric acid gave a substance, for which analysis, the quantity of formaldehyde evolved when the substance was boiled with water, and the yield of barium methylenedinitramine on titration with baryta indicated the structure 1 : 3 : 5-triaza-*n*-pentane 5-nitrate (V). This substance did not give (I) when treated with 96% nitric acid.

Similarly, stirring the gum with methyl alcohol produced (IV; R = Me) and (V) in 24% and 22% yield, respectively.

When stirred with water, gum (A) gave a compound identical with a product obtained in small yield by Dr. J. K. N. Jones (unpublished work) by triturating samples of (II) with barium hydroxide solution. This compound, to which Jones originally assigned structure (IV; R = H) is methylenedi-1 : (3 : 5-dinitro-1 : 3 : 5-triaza-cyclohexane) (VI) (Chute, McKay, Meen, Myers, and Wright, *Canadian J. Res.*, 1949, **27**, B, 489). Professor E. G. Cox kindly determined the molecular weight of the authors' sample by X-ray diffraction measurements obtaining the value 373 [theor. 366 for (VI)]. Also, since structure (IV; R = H) may be regarded as an *N*-substituted formaldehyde-ammonia, closely related to the pyridine and quinoline  $\psi$ -bases, it would be expected to react readily with alcohol to form an ether. The substance, however, was unreactive towards methyl and ethyl alcohols, which further supports structure (VI). Substance (VI) also gave (I) with nitric acid and 1-acetyl-3 : 5-dinitro-1 : 3 : 5-triazacyclohexane with acetic anhydride.

The question at issue is, what intermediate would give a mixture of (IV; R = Et) and (V) with ethyl alcohol for example? The gum might consist mainly of the nitrate ester (IV; R =  $NO_2$ ) which might react with alcohols and with water to give (IV; R = Me or Et) and (VI) respectively, and (V) might conceivably arise by degradation of the triazacyclohexane ring of (IV; R =  $NO_2$ ) in the alcoholic solution. Alternatively, if the gum contained (IV; R = H) one would expect a rapid reaction with ethyl alcohol to give (IV; R = Et). Again, the gum might consist mainly of 3 : 5-dinitro-1 : 3 : 5-triazacyclohexane nitrate (II). Secondary bases condense with formaldehyde and alcohols, yielding the ethers of  $\psi$ -bases (McLeod and Robinson, *J.*, 1921, **119**, 1470), and it therefore seemed possible that (II) might undergo similar condensation with formaldehyde and methyl alcohol; (II) did, in fact, give (IV; R = Me) in 60% yield on treatment with an excess of aqueous formaldehyde and methanol at room temperature (a similar synthesis occurred with ethyl alcohol). (II), added to excess of methyl alcohol without formaldehyde, gave (IV; R = Me) in reduced yield (12%) and (V) in 47% yield. In the latter case (II) was presumably partly degraded to (V), and the formaldehyde liberated by rupture of the triazacyclohexane ring was used in the synthesis of (IV; R = Me).

If gum (A) was stirred with acetic anhydride saturated with sodium acetate at room temperature, the sole product was (I).

Interruption of the low-temperature reaction between aqueous 97% nitric acid and hexamine dinitrate by dilution with ethyl alcohol produced a granular precipitate, consisting of (II) in 55% and (IV; R = Et) in 5% yield. Similarly, with methyl alcohol as diluent, a 50% yield of (II) and a 1% yield of (IV; R = Me) was obtained. The action of a nitric acid-methyl alcohol mixture (95 : 5) on hexamine dinitrate at low temperatures was also studied. The material obtained on diluting the reaction mixture with methyl alcohol was shown to be (II) by comparing its X-ray powder photograph with that of an authentic specimen.

Various attempts have been made to synthesise (I) from suitable fragments. Use of (a) formaldehyde, nitramide, and methylenedinitramine in the presence of 100% nitric acid, or

(b) 1 : 3-dinitro-1 : 3 : 5-triaza-*n*-pentane 5-nitrate (V) and formaldehyde with 100% nitric acid, failed. If, however, (V) was added to a mixture of excess of paraformaldehyde and acetic anhydride, (I) was obtained in 61% yield. It seems that nitric acid is not a sufficiently good condensing agent (or is too destructive) to be effective in synthesising the ring; it may reasonably be assumed that ring synthesis does not occur in the nitric acid medium and that the triazacyclohexane ring occurring in products from the nitrolysis of hexamine with concentrated nitric acid is formed by partial degradation of the hexamine molecule, rather than by complete disintegration and resynthesis.

#### EXPERIMENTAL.

*Termination of the Nitrolysis by Ether.* 1-Ethoxymethyl-3 : 5-dinitro-1 : 3 : 5-triazacyclohexane (IV; R = Et) and 1 : 3-Dinitro-1 : 3 : 5-triaza-*n*-pentane 5-nitrate (V).—Hexamine dinitrate (40 g.) was added with rapid stirring to 97% nitric acid (320 c.c.), supercooled at  $-45^{\circ}$ , in a 1500-c.c. tall-form beaker, in acetone-carbon dioxide. The temperature was then allowed to rise to  $-28.5^{\circ}$  during about 40 seconds, and was kept there for 5 minutes. The reaction mixture was then cooled rapidly to  $-60^{\circ}$  and cooled (*ca.*  $-60^{\circ}$ ) ether (500 c.c.) was added slowly, the temperature being kept below  $-50^{\circ}$ . A white gum (A) separated, from which the ethereal nitric acid was decanted. The gum was then stirred for 20 minutes with cold ether (300 c.c.) to remove the nitric acid, and thus became less gummy and settled at the bottom of the beaker. This material was solid, however, only at low temperatures under ether. At room temperature it rapidly decomposed to a liquid smelling strongly of formaldehyde. A portion was boiled with water, in which it was completely soluble, thus indicating that no 1 : 3 : 5-trinitro-1 : 3 : 5-triazacyclohexane (I) was present. A portion was added to cold water, and the filtrate tested with a solution of iodine in aqueous potassium iodide; a black precipitate of the tetraiodide of hexamine showed that hexamine dinitrate was present.

The ether was then decanted from the gum, and cooled ethyl alcohol (400 c.c.) added, whereupon a white granular precipitate immediately formed. The whole was stirred for 1 hour, the temperature being allowed to rise to  $0^{\circ}$ ; the alcohol was decanted, and the granular residue stirred with more ethyl alcohol (200 c.c.) at  $0^{\circ}$ . After separation of the residue (B) by filtration, the second alcoholic filtrate was added to the first.

Residue (B) contained a trace of hexamine dinitrate, but no (I). It was extracted with warm ether, in which it was readily soluble, from which 6 g. (17% yield) of crystals, m. p.  $115^{\circ}$  (decomp.), were obtained [Found: C, 30.6, 30.7; H, 5.4, 5.6; N, 30.0, 30.4; ammonia-N, 5.7, 5.7;  $\text{CH}_2\text{O}$ , 49.2, 49.2.  $\text{C}_6\text{H}_{13}\text{O}_5\text{N}_5$  (IV; R = Et) requires C, 30.6; H, 5.5; N, 29.8; ammonia N, 6.0;  $\text{CH}_2\text{O}$ , 51.0%]. With 96% nitric acid, the substance gave (I) in 91% yield. In later experiments, the material from the ether-extraction of (B) was further recrystallised from cold acetone-chloroform, the solvent being slowly evaporated in a vacuum-desiccator. Large crystals, m. p.  $118-119^{\circ}$ , were obtained. This compound is very soluble in acetone at room temperature, but slowly decomposes to a white solid, sparingly soluble in acetone which was not investigated further.

The alcohol was slowly removed at the pump (liquid-air traps) from the filtrate remaining after separation of (B). The white residue thus obtained was ground and stirred with cold acetone, washed with ether, and dried in a vacuum-desiccator [7 g.; m. p.  $111^{\circ}$  (decomp.) to a pale green fluorescent liquid]. The residue, easily soluble in water, contained hexamine dinitrate, which in earlier experiments was removed by rapid washing of the residue with ice-water, followed by acetone and ether. The material thus obtained from five experiments melted at  $122^{\circ}$ ,  $125^{\circ}$ ,  $129^{\circ}$ ,  $129^{\circ}$ ,  $129^{\circ}$ , severally, three of the samples being analysed [Found: C, 10.8, 10.8, 10.7; H, 3.6, 3.5, 3.4; N, 38.2, 38.0, 37.3; ammonia-N, 5.7, 5.7;  $\text{CH}_2\text{O}$ , 25.0.  $\text{C}_2\text{H}_5\text{O}_7\text{N}_6$  (V) requires C, 10.5; H, 3.5; N, 36.8; ammonia-N, 6.1;  $\text{CH}_2\text{O}$ , 26.3%].

1 : 3-Dinitro-1 : 3 : 5-triaza-*n*-pentane 5-nitrate (V) was titrated with *N*-sodium hydroxide until neutral to phenolphthalein. A saturated solution of barium chloride was added in slight excess, followed by an equal volume of acetone. The white crystalline precipitate of the barium salt of methylenedinitramine was collected by filtration, washed with water and acetone, dried *in vacuo* at  $20^{\circ}$ , and weighed. The equivalent weight of (V) by titration was 91, and the percentage of methylenedinitramine 58.8%, weighed as barium salt. If alkali yields 1 mole of methylenedinitramine, 1 mole of formaldehyde, and 1 mole of ammonium nitrate, the theoretical percentage of methylenedinitramine is 59.7. When added to 96% nitric acid, (V) did not give (I). In later experiments (V) was purified by dissolution in the least amount of 80% nitric acid and storage in a vacuum-desiccator containing phosphoric oxide and sodium hydroxide. It crystallised as colourless six-sided plates and prisms of the orthorhombic system, m. p.  $129^{\circ}$ . An X-ray powder photograph of this substance was quite different from one of compound (II).

*Treatment of Gum (A) with Methyl Alcohol.* 1-Methoxymethyl-3 : 5-dinitro-1 : 3 : 5-triazacyclohexane (IV; R = Me) and (V).—The experiment described above was repeated up to the washing of the gum with cold ether. Methyl alcohol (400 c.c.) at  $-40^{\circ}$  was then added to the gum and the mixture was stirred for 1 hour, the temperature being allowed to rise to  $0^{\circ}$ . The methyl alcohol was then decanted and residue (B), now granular, was stirred with cold methyl alcohol (200 c.c.) in which it was sparingly soluble. The white powder (B) was collected and dissolved in warm dry acetone. On storage, large crystals (8 g., 24%), m. p.  $134^{\circ}$  (decomp.), were obtained (Found: C, 27.4, 27.3; H, 4.8, 5.0; N, 32.9; 34.5; ammonia-N, 8.4, 6.7; OMe, 14.0, 13.6.  $\text{C}_5\text{H}_{11}\text{O}_5\text{N}_5$  requires C, 27.1; H, 5.0; N, 31.7; ammonia-N, 6.3; OMe, 14.0%). Nitration of this compound gave (I) in 88% yield (see Part II). The methyl-alcoholic solution, consisting of the two portions which had been stirred with the gum, was concentrated in the cold. A crystalline precipitate separated which was washed with acetone and ether and dried *in vacuo*, the yield being 7.5 g. (22%) and the m.p.  $128-129^{\circ}$  (decomp.) not depressed by an authentic specimen of 1 : 3-dinitro-1 : 3 : 5-triaza-*n*-pentane 5-nitrate (V).

*Treatment of Gum (A) with Water.* Methylene-di-1-(3 : 5-dinitro-1 : 3 : 5-triazacyclohexane) (VI).—The experiment described above was repeated up to the washing of the gum with cold ether. Then the gum was stirred rapidly with ice-cold water (200 c.c.) for 15 minutes. The white precipitate, which had become granular, was separated by filtration and stirred with more ice-cold water for 5 minutes. It was then collected, washed twice with ice-cold water, and dried over phosphoric oxide. The dry residue (m. p. 120°) was dissolved in the smallest quantity of dry acetone, and ether-light petroleum (b. p. 60–80°) was added. Clusters of needle-like crystals gradually separated [3 g.; m. p. 136° (decomp.)]; these gave no depression with the compound, m. p. 136°, obtained by Dr. J. K. N. Jones by triturating (II) with barium hydroxide solution. Products from three experiments were analysed [Found: C, 23.2, 23.1, 23.3; H, 3.8, 4.2, 3.6; N, 39.6; ammonia-N, 10.2; OMe, 0. Calc. for  $C_4H_9O_5N_5$  (IV; R = H): C, 23.2; H, 4.4; N, 33.4; ammonia-N, 6.7; OMe, 0%. Calc. for  $C_7H_{14}O_8N_{10}$  (VI): C, 23.0; H, 3.8; N, 38.3; ammonia-N, 7.7; OMe, 0%]. The values for carbon agree with either formula, but those for hydrogen and nitrogen analyses agree better with formula (VI). Also, the molecular-weight determination of a sample of this compound, kindly undertaken by Professor E. G. Cox and Miss M. W. Gougill, shows that structure (VI) is correct, the following results being obtained. Monoclinic:  $a = 9.10$ ,  $b = 24.96$ ;  $c = 47$  Å.;  $\beta = 93^\circ 56'$ . Space group  $P2_1/n$ . Density 1.68 g./c.c., whence four molecules per unit cell.  $M = 373$  (Calc. for  $C_7H_{14}O_8N_{10}$ :  $M$ , 366). It is possible, but improbable, that the molecular weight is 186 (Calc. for  $C_4H_9O_5N_5$ :  $M$ , 207); the difference between 207 and 186 is well outside the experimental error, so this formula is excluded.

*Treatment of (VI) with Methyl Alcohol.*—(VI) (0.126 g.) was added to anhydrous methyl alcohol (1 c.c.) and kept at room temperature for 1 hour. The insoluble portion, collected by filtration, washed with ether (1 c.c.), and dried *in vacuo*, had m. p. 136°, giving no depression when mixed with the original material and a depression of 8° in a 50 : 50 mixture with (IV; R = Me). The product did not contain methoxyl. A similarly unsuccessful attempt was made using ethyl alcohol.

*Treatment of (VI) with Nitric Acid.*—(VI) (0.1603 g.) was added to 98% nitric acid (3 c.c.) at  $-40^\circ$  and the temperature kept at  $-40^\circ$  for 30 minutes. The solution was then allowed to warm to room temperature before being poured into water (200 c.c.). Next morning the precipitate was filtered off, washed with cold water, and dried at 100°. The yield was 0.1553 g. (about 90%), and the m. p. 202–203° undepressed on admixture with an authentic specimen of (I).

*Reaction of (VI) with Acetic Anhydride.*—(VI) (0.30 g.) was heated with acetic anhydride (5 c.c.) at 80° for 4 hours and then poured into water, and the mixture evaporated to dryness on a water-bath. Recrystallisation of the residue from acetone-light petroleum gave crystals, m. p. 156° (no depression with an authentic specimen of 1-acetyl-3 : 5-dinitro-1 : 3 : 5-triazacyclohexane).

*Synthesis of 1-Methoxymethyl-3 : 5-dinitro-1 : 3 : 5-triazacyclohexane (IV; R = Me).*—Methyl alcohol (100 c.c.) and 40% aqueous formaldehyde solution (20 c.c.) at room temperature were rapidly stirred together. 3 : 5-Dinitro-1 : 3 : 5-triazacyclohexane nitrate (II) was added, heat was evolved, and the suspension became crystalline. The mixture was stirred for 5 minutes, filtered, washed three times with methyl alcohol (50 c.c.), then with ether (50 c.c.), and dried in a vacuum-desiccator; the product (17.63 g.) had m. p. 134° [no depression with 1-methoxymethyl-3 : 5-dinitro-1 : 3 : 5-triazacyclohexane (IV; R = Me), m. p. 134°] after recrystallisation from cold acetone-chloroform with slow evaporation in the cold *in vacuo* [Found: C, 27.5; H, 5.0; N, 32.4; ammonia-N, 6.8; OMe, 13.7. Calc. for  $C_5H_{11}O_5N_5$ : C, 27.1; H, 5.0; N, 31.7; ammonia-N, 6.3; OMe, 14.0%].

*Synthesis of (IV; R = Et).*—Aqueous 40% formaldehyde (20 c.c.) was added to ethyl alcohol (100 c.c.) at room temperature. 3 : 5-Dinitro-1 : 3 : 5-triazacyclohexane nitrate (II) was added with rapid stirring. The white crystalline suspension was collected by filtration, washed three times with ethyl alcohol (50 c.c.), and dried *in vacuo* (yield, 21 g.; m. p. 105°). Recrystallisation from cold acetone-chloroform gave large colourless crystals (11.5 g.), m. p. 117–118° not depressed by admixture with an authentic sample of 1-ethoxymethyl-3 : 5-dinitro-1 : 3 : 5-triazacyclohexane (IV; R = Et).

*Reaction of (II) with Methyl alcohol.*—(II) (6.4 g.) was stirred with methyl alcohol (100 c.c.) at room temperature for 45 minutes, nearly all the material dissolving. The solution was filtered and the methyl alcohol removed in the cold *in vacuo*. The white residue was digested with acetone ( $2 \times 25$  c.c.) at room temperature and collected by filtration. It was then washed with ether (25 c.c.) and dried *in vacuo* [yield, 2.9 g. (47%); m. p. 120° (decomp.)]. Recrystallisation from 85% nitric acid at room temperature gave crystals (1.5 g.), m. p. 129° (decomp.) undepressed by 1 : 3-dinitro-1 : 3 : 5-triazacyclohexane 5-nitrate. Evaporation of the acetone filtrate gave crystals (0.7 g., 11.9%), m. p. 134° unchanged when mixed with an authentic specimen of (IV; R = Me).

*Treatment of Gum (A) with Acetic Anhydride, Saturated with Sodium Acetate.*—Hexamine dinitrate (40 g.) in 97% nitric acid (320 c.c.), after 5 minutes at  $-28.5^\circ$ , was diluted with cooled ether, giving a gum which was washed with more ether and stirred for 1½ hours with acetic anhydride (100 c.c.), saturated at room temperature with anhydrous sodium acetate. The white granular product obtained was collected, washed with water, and recrystallised from acetone, and again from ethyl acetate, giving crystals (10 g., 30%), m. p. 202° undepressed by admixture with an authentic specimen of (I).

*Interruption of the Nitrolysis by Dilution with Ethyl Alcohol.*—Hexamine dinitrate (40 g.) was added with rapid stirring to 97% nitric acid (320 c.c.), previously supercooled to  $-45^\circ$ . The temperature was allowed to rise to  $-28.5^\circ$  during 40–60 seconds, and kept there for 5 minutes. The mixture was then rapidly cooled to  $-60^\circ$ , and cooled ethyl alcohol (600 c.c.) added slowly with rapid stirring, the temperature being kept below  $-40^\circ$ . After 30 minutes' stirring, a thick white precipitate (B) gradually separated; it was filtered off, washed with two 50-c.c. portions of cold ethyl alcohol ( $-40^\circ$ ) and dried in a vacuum-desiccator. The product (25 g.), m. p. ca. 94° (collapses at 85°), dissolved completely with decomposition in boiling water, which showed the absence of (I).



(B) was digested with ether at room temperature. Evaporation of the extract yielded a crystalline residue (2 g.), m. p. ca. 105°, which was washed with water and with two 10-c.c. portions of ethyl alcohol, then dissolved in dry acetone at room temperature, and the solution evaporated slowly in a vacuum-desiccator, giving large crystals, m. p. 115° (decomp.) [undepressed by an authentic sample of (IV); R = Et] (Found: C, 30.6; H, 5.6; N, 29.6; ammonia-N, 7.2.  $C_6H_{13}O_5N_5$  requires C, 30.6; H, 5.5; N, 29.8; ammonia-N, 6.0%).

The residue from (B) was digested with ether giving C (20 g.), m. p. 96° (decomp.). A portion of (C), added to acetic anhydride, gave crystals which when recrystallised from acetone had m. p. 199° alone and mixed with (I). A portion of (C) was stirred with ethyl alcohol at room temperature and filtered from a very small amount of insoluble matter. The filtrate was evaporated in the cold in a vacuum-desiccator, leaving a white residue, which, when washed with acetone and ether, dried *in vacuo*, and recrystallised from 80% nitric acid, gave crystals, m. p. 129° (decomp.), forming a yellow green, slightly fluorescent liquid [Found: C, 10.2; H, 3.7; N, 36.4; ammonia-N, 7.1. Calc. for  $C_2H_8O_7N_6$  (V): C, 10.5; H, 3.5; N, 36.8; ammonia-N, 6.1%]. (C) was added to a saturated solution of sodium acetate in acetic anhydride at room temperature and set aside for 3 days. The acetic anhydride was then removed *in vacuo* and the residue extracted with acetone. The material obtained from the acetone solution, after being twice recrystallised from warm ethyl acetate, yielded crystals, m. p. 156° (no depression when mixed with authentic 1-acetyl-3:5-dinitro-1:3:5-triazacyclohexane) (Found: C, 26.7; H, 3.9; N, 32.0; ammonia-N, 6.6. Calc. for  $C_5H_9O_5N_5$ : C, 27.4; H, 4.1; N, 32.0; ammonia-N, 6.4%). These are all characteristic reactions of 3:5-dinitro-1:3:5-triazacyclohexane nitrate (II).

**Dilution of the Nitrolysis Mixture with Methyl Alcohol.**—Hexamine dinitrate (40 g.) was allowed to react with 96% nitric acid (320 c.c.) under the conditions given in the preceding paragraphs. Dilution of the reaction mixture with cooled methyl alcohol (400 c.c.) gave a white granular precipitate after 30 minutes' stirring at -30°. This was filtered off, stirred with acetone (75 c.c.) at -60°, collected, washed with cold ether (100 c.c.), and dried *in vacuo*. The yield of material (B) was 18 g.

The acetone filtrate when evaporated in the cold left a few large crystals in a gummy residue. The crystals were ground with water to remove the gum, which was water-soluble, and crystallised from the smallest amount of acetone at room temperature. The crystals obtained had m. p. 134° and gave no m. p. depression with (IV); R = Me) (Found: C, 27.0; H, 4.2; N, 30.3; ammonia-N, 7.8. Calc. for  $C_5H_{11}O_5N_5$ : C, 27.1; H, 5.0; N, 31.7; ammonia-N, 6.3%).

(B) had m. p. 96° (decomp.) [Found: C, 14.0; H, 3.8; N, 35.0; ammonia-N, 6.9;  $NO_2$ , 26.5;  $CH_2$ , 15.4. Calc. for  $C_2H_8O_7N_6$  (II): C, 15.0; H, 3.3; N, 35.0; ammonia-N, 7.0;  $NO_2$ , 25.9;  $CH_2$ , 17.5%]. A portion of (B) (6 g.) was dissolved in methyl alcohol (100 c.c.) at room temperature with stirring and the alcoholic solution evaporated in the cold *in vacuo*, giving a residue which was washed with acetone (10 c.c.) and ether (20 c.c.) and dried *in vacuo*. The yield was 2 g. and the m. p. 119°. Recrystallisation from 86% nitric acid gave crystals, m. p. 129° (decomp. to a yellow fluorescent liquid), giving no m. p. depression with authentic (V) (Found: C, 10.9; H, 3.8; N, 35.4; ammonia-N, 7.2;  $CH_2$ , 11.1;  $NO_2$ , 27.0. Calc. for  $C_2H_8O_7N_6$ : C, 10.5; H, 3.5; N, 36.8; ammonia-N, 6.1;  $CH_2$ , 12.3;  $NO_2$ , 27.2). A portion of (B) added to acetic anhydride at room temperature, dissolved readily. On removal of the acetic anhydride in the cold, crystals separated which when recrystallised from acetone had m. p. 201°, undepressed by admixture with (I). When (B) was treated with acetic anhydride which had been saturated with sodium acetate at room temperature and the mixture was kept for 4 days, crystals were obtained which when recrystallised from ethyl acetate gave long needles, m. p. 156° undepressed when mixed with 1-acetyl-3:5-dinitro-1:3:5-triazacyclohexane.

**Nitrolysis with Nitric Acid (95%) and Methyl Alcohol (5%).**—Hexamine dinitrate (13.3 g.) was added, with rapid stirring, to the nitric acid-methyl alcohol mixture (100 c.c.), cooled to -55° during 7 seconds. The temperature rose to -45° and was then allowed to reach -40° and kept there for a further 8 minutes. The mixture was then rapidly cooled and methyl alcohol (200 c.c.) added, the temperature of the mixture being kept below -30°. The mixture was cooled to -80°, and, with stirring, the temperature was allowed to reach -30° again, during 30 minutes. A white precipitate separated gradually; this was collected, washed with acetone (2 × 75 c.c.) cooled to -80°, then with ether, and dried in a vacuum-desiccator, to give 3.5 g., m. p. 90°. The precipitate contained some hexamine dinitrate, but no (I) (Found: C, 16.0; H, 3.4. Calc. for  $C_3H_5O_7N_6$ : C, 15.0; H, 3.3%). An X-ray powder photograph of this material was identical with that of 3:5-dinitro-1:3:5-triazacyclohexane nitrate (II).

**Synthesis of 1:3:5-Trinitro-1:3:5-triazacyclohexane (I).**—(V) (1.77 g.) was added to acetic anhydride (10 c.c.) containing paraformaldehyde (1 g.), and the mixture set aside at room temperature for 2 days. Water (30 c.c.) was then added and the mixture kept for an hour. The supernatant liquid was decanted from the residue, the latter being washed with a further 30 c.c. of water, collected by filtration, and dried *in vacuo*. The material was then extracted with acetone (30 c.c.) at room temperature and the solution evaporated to dryness on a water-bath. The crystalline residue (1.05 g.) had m. p. 197° (decomp.). It was recrystallised from warm acetone, giving large crystals (0.5 g.), m. p. 199°. Admixture with an authentic specimen of (I) caused no depression of m. p.; the mixed m. p. with 1-acetyl-3:5-dinitro-1:3:5-triazacyclohexane was 140°. The experiment was repeated under the same conditions except that the temperature of the mixture was kept at 85° for 2 hours and then water was added. Recrystallisation of the residue from acetone gave large crystals, m. p. 202° alone or when mixed with authentic (I).