570. *Methylene-nitramines. Part III.*

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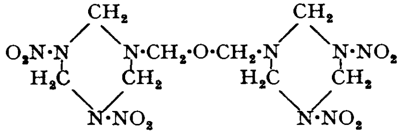
The action of 100% nitric acid at low temperatures on 1-methoxymethyl- and 1-chloromethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane has been investigated. In both cases, when the reaction mixture was diluted with ether, di-(3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexylmethyl) ether (I) was obtained, or, on dilution with water, 3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane nitrate.

The action of absolute nitric acid on 1-methoxymethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (hexahydro-1-methoxymethyl-3 : 5-dinitro-*s*-triazine) (*A*) at −31° was studied with a view to isolating products which might indicate the mechanism of attack of nitric acid on such a molecule. In order to exclude, or at least minimise, the possibility of hydrolytic reactions, dry ether was used as diluent. The time of reaction was varied from 10 to 30 minutes. The products obtained with a reaction time of 10—12 minutes contained a high proportion of nitrate and were unstable in air. On the other hand, a reaction time of 15 minutes gave a product which contained little or no nitrate and was stable in air. Further increase in the time of reaction produced very unstable substances containing some nitrate. The results were not completely reproducible, the nitrate content varying somewhat in duplicate experiments, but it seemed that 15 minutes was the optimum for production of a relatively stable substance, almost free from nitrate.

The products dissolved completely, with decomposition, in boiling water, showing the absence of 1 : 3 : 5-trinitro-1 : 3 : 5-triaza*cyclo*hexane (*B*). In some of the products there was a small impurity of unchanged (*A*), estimated by the methoxyl content of the product. An attempt was made to take *X*-ray powder photographs of the products. Only the products from the 15-minutes reaction were stable enough to exist in air for the requisite length of time. These products were micro-crystalline and gave a definite series of lines. Reaction times of 10 minutes and 30 minutes gave products which decomposed in about half-an-hour in air, forming a liquid. By coating these materials with collodion and exposing them for a long time, a few faint lines were obtained, which corresponded to those of the stable product from the 15-minutes experiment.

The reaction products showed a varying reactivity towards methyl alcohol, the stable product being unreactive, whereas the unstable products reacted readily, forming (*A*). Although the stable product was sparingly soluble in acetone, it could be recrystallised from slightly warmed dry acetone and chloroform, giving crystals which decomposed at 150° with formation of a white sublimate. It was identified as di-(3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexylmethyl) ether, (I) (see Experimental section).



(I.)

Comparison of the *X*-ray photograph of the recrystallised compound with that of methylene-di-1-(3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane) showed that they were different. Professors Hodgkin and Cox independently determined the molecular weight by the *X*-ray diffraction pattern from a single crystal. Their results are in good agreement: 394 and 399 (Calc. for $C_8H_{16}O_9N_{10}$: 396).

Substance (I) gave 1 : 3 : 5-trinitro-1 : 3 : 5-triaza*cyclo*hexane (*B*) in 94% yield when treated with 96% nitric acid. Since, in the experience of the authors, only substances in which the triaza*cyclo*hexane ring is already present give (*B*) with nitric acid of this strength, this was taken as evidence that the triaza*cyclo*hexane ring was present in (I). Confirmation was obtained by the reaction of (I) with acetic anhydride, producing 1-acetyl-3 : 5-dinitro-1 : 3 : 5 triaza*cyclo*hexane. Acetyl nitrate and (I) gave, in addition to (*B*), a product which on further treatment (see Part II) was converted into the more easily separable 1 : 7-diethoxy-2 : 4 : 6-

trinitro-2 : 4 : 6-triazaheptane. It was concluded that the first substance was 1 : 7-diacetoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane, indicating that a methylene group was attached to the triaza*cyclo*hexane ring in the original substance.

Products from experiments with reaction times other than 15 minutes were stirred with acetone at room temperature. White residues were obtained, analyses of which agreed fairly well with that of (I). This, together with the presence in the *X*-ray photographs of faint lines identical with those of (I), suggests that these unstable products were mixtures of (I) and a more labile compound containing nitrate. In an attempt to show whether or not the latter had a methylene group attached to the triaza*cyclo*hexane ring, the behaviour of the unstable products with acetyl nitrate was studied. The results, however, were not conclusive because the amount of 1 : 7-diethoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane finally obtained could have been accounted for theoretically by the quantity of compound (I) already known to be present in the mixture. With nitric acid at 0° these unstable products gave (*B*) in good yield, hence the products from these experiments contain the triaza*cyclo*hexane ring. This nitrate-containing compound is evidently not 3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane nitrate since the latter is sufficiently stable in air to give an *X*-ray powder photograph.

Although no detailed experiments were carried out at these low temperatures for reaction times longer than 30 minutes, it was noted that in one experiment, when the reaction time was 50 minutes, (*B*) was present in the product.

1-Chloromethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (*C*) was allowed to react similarly with absolute nitric acid. Under each of three sets of conditions, the product isolated was almost pure (I), as shown by analysis and an *X*-ray powder photograph. The unstable nitrate-containing products were not formed.

(*A*) was then allowed to react as above with absolute nitric acid but water was used to stop the reaction. The product was noticeably denser than when ether was used. An elementary analysis was in fair agreement with that of 3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane nitrate. The product, when treated with acetyl nitrate, gave (*B*) in good yield, but no trace of 1 : 7-diacetoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane, indicating that no methylene group was attached to the triaza*cyclo*hexane ring. Finally, an *X*-ray powder photograph of the product was identical with that of 3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane nitrate. A possible origin of the latter is hydrolysis of 1-nitroxymethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane by the added water. Similarly, when the reaction between 1-chloromethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane and absolute nitric acid was interrupted by diluting the reaction mixture with water, a white precipitate separated which was almost certainly crude 3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane nitrate.

When methylenedi-1-(3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane) was similarly treated with absolute nitric acid and the reaction mixture diluted with ether, it gave a product containing 60% of 1 : 3 : 5-trinitro-1 : 3 : 5-triaza*cyclo*hexane (*B*). In contrast with the absence of (*B*) in the nitrolysis products from compounds (*A*) and (*C*), its presence in this case supports the formula suggested for this compound in Part I, since the fission of one of the bonds in the system $>N\cdot CH_2\cdot N<$ must lead to immediate formation of (*B*).

Thus neither 3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane nitrate nor the ether (I) is a true intermediate in the nitrolysis of (*A*) and (*C*), but they arise by the interaction of the diluents, water and ether respectively, with the true intermediate.

EXPERIMENTAL.

Reaction of 1-*Methoxymethyl*-3 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*hexane* (A) *with Nitric Acid.*—Experiment 1a recorded below is typical of the series, though the time of reaction was varied (Table I).

Freshly distilled 100% nitric acid (90 c.c.), in a tall-form beaker with a Perspex cover, was stirred and cooled in a solid carbon dioxide–acetone bath until the temperature was –40°. 1-Methoxymethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (*A*) (9 g.) was added with rapid stirring. The temperature was allowed to reach –31° and kept there. After 10 minutes, measured from the beginning of the addition of (*A*), the cooling bath was raised round the beaker, and dry ether (250 c.c.) previously cooled to –80° was added during about 10 minutes, the temperature of the resulting mixture being kept below –30°. A copious precipitate separated and was collected on a sintered-glass filter, covered to prevent condensation of moisture. It was then washed with cold ether (3 × 50 c.c.) and ether at room temperature (50 c.c.) and dried in a vacuum-desiccator (yield, 5·8 g.) (Found : C, 16·9; H, 3·5; NO_3', 22·0, 22·3; OMe, 1·5; CH_2, 16·6%).

Chemical and Physical Properties of the Reaction Products from the Series of Experiments 1a *to* 7b.—(i) *Treatment with boiling water.* A portion of the precipitate obtained in Expt. 1a was boiled with water in which it dissolved completely with decomposition, indicating that no 1 : 3 : 5-trinitro-1 : 3 : 5-triaza*cyclo*hexane (B) was present, since (*B*) is very sparingly soluble in, and is unattacked by, boiling water. By the same test the products of experiments 1b—7b also contained no (*B*).

(ii) *Reactivity with methyl alcohol.* The treatment of product from Expt. 1a is typical. A portion of the precipitate (1·97 g.) was added to methyl alcohol (20 c.c.) at room temperature and set aside for 10 minutes. The insoluble material was collected and dried in a vacuum-desiccator (yield, 1·0 g.) (Found : OMe, 13·1%). Recrystallisation from acetone gave (0·61 g.), m. p. 134° alone and when mixed with an authentic specimen of 1-methoxymethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (*A*). (For the results of a similar treatment of the products from the other experiments, see Table I.)

TABLE I.

Action of 100% *nitric acid at low temperatures on* 1-*methoxymethyl*-3 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*hexane.*

9 g. were treated with 100% nitric acid (90 c.c.) at — 31°. The reaction was arrested by addition of dry ether (250 c.c.).

Expt. no.	Time of reaction (min.).	Wt. of ppt. (g.).	Analysis of ppt.					Analysis of the residue sparingly soluble in $COMe_2$:		% OMe in crude product obtained by treating the ppt. with MeOH.
			C, %.	H, %.	NO_3', %.	CH_2, %.	OMe, %.	C, %.	H, %.	
1a	10	5·8	16·9	3·5	22·0 22·3	16·6	1·5	24·9	3·5	13·1
1b	10	6·3	22·0	4·5	7·7	—	2·5	—	—	—
1c	10	6·5	19·5	4·5	10·3	—	0	—	—	11·0
2	12	6·0	20·3	4·2	16·2	—	0	—	—	—
3	14	7·1	22·3	3·9	9·5	—	2·6	—	—	—
4a	15	6·5	24·2	4·4	0 0	20·9 20·6	2	24·4	4·3	2
4b	15	6·0	21·3	4·2	3·8	—	0	—	—	0
5	18	5·8	18·9	4·0	6·3	—	4·5	—	—	—
6	21	6	20·2	3·8	12·0	18·9	0·5	—	—	—
7a	30	5·8	20·1	3·8	9·9 8·8	—	—	24·7	4·3	—
7b	30	5·8	19·1	4·5	5·0	—	—	—	—	10·8

Further Investigations of the Products from Expts. 4*a and* 4*b*.—A portion (3·0 g.) of the precipitate from Expt. 4a was stirred with acetone (25 c.c.) at room temperature, the solvent decanted, and the residue stirred with acetone (3 × 10 c.c.), then with ether, and the residue (1·5 g.) dried *in vacuo* (Found : C, 24·4; H, 4·3%). An *X*-ray powder photograph of this residue showed the same lines as those of the original precipitate.

The substance was dissolved with warming in dry acetone, and chloroform was added until the solution became slightly cloudy. On storage, small, well-defined crystals of *di*-(3 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*hexylmethyl*) *ether* were obtained (Found : C, 24·5; H, 4·2. $C_8H_{16}O_9N_{10}$ requires C, 24·2; H, 4·0%) ; single crystals began to disintegrate at 129° ; at 150° there was no melting, but extensive decomposition occurred with formation of a white sublimate. An *X*-ray powder photograph of the recrystallised material was identical with that of the material before recrystallisation and different from that of methylenedi-1-(3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane). Professor E. G. Cox and Dr. J. O. Warwicker very kindly undertook a molecular-weight determination and report : " The crystals were monoclinic. $a = 10·53$; $b = 20·56$; $c = 7·47$ A. ; $\beta = 96° 15'$. Space-group $P2_1/m$ (nearly $P2_1/n$). *d* 1·65, whence four molecules per unit cell. Hence $M = 399$ (Calc. for $C_8H_{16}O_9N_{10}$: 396). It is possible, but improbable, that the molecular weight is 200 or 798."

Mrs. Hodgkin and Miss P. Cowan report : " Unit cell dimensions : $a = 10·52$; $b = 20·54$; $c = 7·43$ A. ; $\beta = 97°$. *d* 1·644. From these figures, the unit-cell molecular weight is, by calculation, 1576, *i.e.*, four times 394."

Treatment of the Ether (I) *with Acetyl Nitrate.*—The ether (1·3 g.) was added to acetyl nitrate (14 g.), cooled in solid carbon dioxide–acetone, and the mixture then allowed to reach room temperature. Cooled ether (50 c.c.) was added and the white precipitate collected, washed with ether, dried *in vacuo*, and dissolved in 99% nitric acid (12 c.c.) at —40°, and the temperature allowed to reach 0°. Water (50 c.c.) was added and the precipitate was collected, washed with cold ethyl alcohol (10 c.c.), and then refluxed with absolute ethyl alcohol (40 c.c.) for 1 hour. The alcoholic solution was cooled and the crystalline precipitate was collected and extracted with ether. The ether-insoluble portion of the precipitate weighed 0·44 g. [30·2%; if 2 moles of (*B*) are obtained from one of (I)] and had m. p. 204°, giving no depression when mixed with an authentic specimen of (*B*). The ethereal extract, after evaporation, gave a residue (0·54 g.) [25·3%, assuming 2 moles of 1 : 7-diethoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane are obtained from one of (I)], m. p. 80°, which on recrystallisation from ethyl alcohol gave 1 : 7-diethoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane (0·4 g.), m. p. 82° undepressed on admixture with authentic material.

Treatment of the Ether (I) *with Nitric Acid.*—The ether (0·1318 g.) was added to 96% nitric acid (2 c.c.) at 0° and the reaction mixture kept at 0° for 20 minutes. Distilled water (24 c.c.) was added. The white precipitate, collected, washed with water, and dried at 100°, had m. p. 199° (0·139 g., 94·4%).

Treatment of the Ether with Acetic Anhydride.—The ether (0·2 g.) was added to acetic anhydride (5 c.c.) at room temperature and the mixture set aside. After several days, the crystals which separated were washed with ether and dried *in vacuo* (0·16 g., 72%; m. p. 150°). Recrystallisation from ethyl acetate, gave 1-acetyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (0·098 g.), m. p. 156° (mixed m. p.).

Further Properties of the Unstable Products containing Nitrate (*see Table I*).—*Treatment with acetone.* A portion (3 g.) of the precipitate from Expt. 1a was stirred with acetone (25 c.c.) at room temperature and the acetone decanted from the white insoluble residue, which was then stirred with a further two 10-c.c. portions of acetone. The residual ether (I) was washed with ether and dried in a vacuum-desiccator (0·8 g.) (Found : C, 24·9; H, 3·5%). The precipitate from Expt. 7a was treated similarly and gave a similar white residue (see Table I).

Treatment with acetyl nitrate. The products from Expt. 1b and 2 were treated with acetyl nitrate under similar conditions to those described above for compound (I). 5·9 g. of product from Expt. 1b gave 1·3 g. of 1 : 7-diethoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane and 1·3 g. of (*B*). 5·6 g. of product from Expt. 1c gave 1·0 g. of diethoxy-compound and 0·6 g. of (*B*).

Treatment with nitric acid. The product (0·3376 g.) from Expt. 1c was treated with 100% nitric acid (3·4 c.c.) under conditions similar to those described above for (I). 1 : 3 : 5-Trinitro-1 : 3 : 5-triaza*cyclo*hexane (*B*) (0·240 g., 71 wt.-%), m. p. 198°, was obtained. Recrystallisation from acetone gave (0·1 g.), m. p. 204° undepressed by an authentic specimen of (*B*). A similar experiment with the precipitate (0·771 g.) from Expt. 7b gave material (0·320 g., 41·5 wt.-%) of m. p. 204°, giving no m. p. depression with (*B*).

Reaction of 1-*Chloromethyl*-3 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*hexane* (C) *with* 100% *Nitric Acid.*—Three experiments were carried out (see Table II). Expt. 1 is described as typical. The compound (*C*) (9 g.) was added to rapidly stirred absolute nitric acid (90 c.c.) at −40°. The temperature was allowed to reach −31° and was kept there for 6 minutes, including the time taken in the addition. The mixture was slowly diluted with cold sodium-dried ether (250 c.c.), the temperature being kept below −30°. The reaction vessel had a Perspex cover to prevent condensation of atmospheric moisture on the mixture. The precipitate which separated was washed three times with cold sodium-dried ether, and once with dried ether at room temperature. The yield was 4 g. and the m. p. 100° (decomp.) (Found : C, 22·3; H, 4·5; N, 33·0; NO_3', 2·9; Cl, 0%).

TABLE II.

Reaction of 1-*chloromethyl*-3 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*hexane* (C) *with* 100% *nitric acid* (*reaction terminated by ether*).

							Analysis of ppt.					
Expt. no.	Wt. of (*C*) (g.).	Vol. of HNO_3 (c.c.).	Temp.	Time (mins.).	Ether added, c.c.	Yield (g.).	C, %.	H, %.	N, %.	NO_3', %.	Cl, %.	M. p.
1	9	90	−31°	6	250	4·0	22·3	4·5	33·0	2·9	0	100°
2	9	90	−36	10	250	6·3	22·4	4·3	35·2	0	0	100
3	18	120	−36	4	250	9·0	24·4	4·2	34·8	0	0	130
4	6	60	−31	10	100	3·5	15·8	3·7	—	24·6	0	—

An *X*-ray powder photograph of the original precipitate, which was stable to an 18-hours exposure in air, was identical with that produced by the nitrolysis of (*A*), thus showing that the precipitate was compound (I). The original precipitate dissolved completely in boiling water, which showed the absence of (*B*).

A portion (0·6 g.) of the original preciptate was added to methyl alcohol (10 c.c.) at room temperature and the whole kept for ½ hour. The supernatant liquid was decanted and the insoluble residue washed with methyl alcohol (10 c.c.), then acetone, and finally ether, and dried in a vacuum-desiccator, the yield being 0·09 g. and the m. p. 130° (decomp.) (Found : C, 24·4; H, 4·0; N, 38·3; OMe, 0%). Hence the original precipitate, shown by *X*-ray photographs to be compound (I), is unreactive towards methyl alcohol.

Reaction of (A) *with Nitric Acid. Dilution of the Reaction Mixture with Water.*—The reaction between (*A*) (9 g.) and absolute nitric acid (90 c.c.) was carried out as recorded in Table I, being allowed to proceed for 12 minutes. The mixture was then diluted with water, the temperature of the resulting mixture being kept at −20°. The white precipitate of 3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane nitrate was collected on a sintered-glass filter, washed with acetone (2 × 25 c.c.) cooled to −50°, then with ether (25 c.c.), and dried in a vacuum-desiccator (yield, 6·8 g.) (Found : C, 15·5; H, 3·5; OMe, 0·9; NO_3', 26·5. Calc. for $C_3H_8O_7N_6$: C, 15·0; H, 3·3; NO_3', 25·8%). The methoxyl content of the precipitate indicated the presence of a little unchanged (*A*). An *X*-ray powder photograph of the precipitate confirmed its structure. With acetyl nitrate (50 g.) the precipitate (6·8 g.) gave (*B*) (4·8 g.), m. p. 204°, but no trace of ether-soluble material after the Wright separation (see Part II), a proof of the absence of a methylene group attached to the triaza*cyclo*hexane ring.

Reaction of (C) *with Nitric acid. Dilution of the Reaction Mixture with Water.*—The compound (*C*) (6 g.) was added to 100% nitric acid (10 c.c.) at −40° (see Table II). The product (3·5 g.) was obtained on dilution of the reaction mixture with water and appears to be crude 3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane nitrate (Found : C, 15·8; H, 3·7; NO_3, 24·6%).

Reaction of Nitric Acid with Methylenedi-1-(3 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*hexane*).—This compound (8 g.) was added to 100% nitric acid (80 c.c.) at −40°. The temperature was allowed to rise to −31° (which took 1 minute) and kept there for a further 9 minutes. Pre-cooled ether (250 c.c.) was added, the temperature being kept below −30°. The precipitate was washed with cold ether and dried in a vacuum-desiccator (yield, 6·3 g.) (Found : C, 18·2; H, 3·3; NO_3', 13·4%). A portion of the precipitate (1·25 g.) was recrystallised from acetone, giving large crystals (0·735 g.), m. p. 203° alone or when mixed with an authentic sample of (B).

The elementary analyses quoted in these papers were performed by Miss P. M. Garwood and Drs. Weiler and Strauss.

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