569. *Methylene-nitramines. Part II. An Investigation of Some Properties of 1-Alkoxymethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane and of Related Compounds.*

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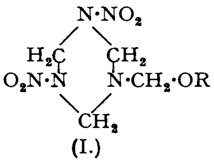
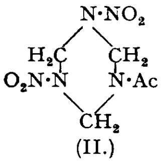
1-Methoxymethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (I; R = Me) yields 1 : 3 : 5-trinitro-1 : 3 : 5-triaza*cyclo*hexane (*A*) with nitric acid, and 1-acetyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (II) with acetic anhydride, but with acetyl chloride and acetyl bromide gives 1-chloromethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (III; X = Cl) and 1-bromomethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (III; X = Br) respectively. The action of acetyl nitrate on (I; R = Me) produces a mixture of (*A*) and 1 : 7-diacetoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane (IV; R = Ac). The reactions of 1-chloromethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane with nitric acid, alcohols, water, acetic anhydride, and acetyl nitrate have been studied.

The ethers (I; R = Me and Et) are converted into 1 : 3 : 5-trinitro-1 : 3 : 5-triaza*cyclo*hexane (hexahydro-1 : 3 : 5-trinitro-*s*-triazine) (*A*) in 89% and 91% yields, respectively, when treated with nitric acid, the triaza*cyclo*hexane ring remaining intact under these conditions; the side chain is by some mechanism replaced by a nitro-group. With acetic anhydride both ethers give 1-acetyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (II). However, with acetyl chloride the main reaction is not an acetylation; the ethers (I; R = Me and Et) dissolve readily in acetyl chloride at room temperature and there is almost immediate precipitation of crystalline 1-chloromethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (III; X = Cl) in 88% yield; 1-acetyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (II) was also isolated in 1% yield. Similar reactions of alkyl ethers and acyl chlorides in the presence of small amounts of zinc chloride or ferric chloride are known (Descudé, *Compt. rend.*, 1901, **132**, 1129; Wedekind and Haeussermann, *Ber.*, 1901, **34**, 2081; Underwood and Wakeman. *J. Amer. Chem. Soc.*, 1930, **52**, 387; Underwood and Toone, *ibid.*, p. 4087; Knoevenagel, *Annalen*, 1914, **402**, 133). Similarly, (I; R = Me) and acetyl bromide give 1-bromomethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (III; X = Br) in 62% yield.


(I.)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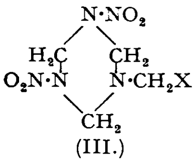
(III.)

(IV.) $R\cdot O\cdot CH_2\cdot N(NO_2)\cdot CH_2\cdot N(NO_2)\cdot CH_2\cdot N(NO_2)\cdot CH_2\cdot OR$

The halogeno-compounds (III; X = Cl and X = Br) both yielded 1 : 3 : 5-trinitro-1 : 3 : 5-triaza*cyclo*hexane (*A*) when allowed to react with 97% nitric acid (in 90·7% and 80% yield, respectively). Excess of methyl or ethyl alcohol converted them into the corresponding ethers (I; R = Me and Et), whereas from both acetic anhydride formed 1-acetyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (II). When (III; X = Cl) was stirred with aqueous sodium acetate, a small yield (5·4%) of methylenedi-1-(3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane) (*B*) was obtained.

It seemed possible at first sight that acetyl nitrate might behave in a similar way to acetyl chloride and yield 1-nitroxymethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (III; $X = O\cdot NO_2$) from (I; $R = CH_3$). However, instead, a mixture of (*A*) and 1 : 7-diacetoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane (IV; R = Ac) was obtained (Carruthers, Bevan, and Woodbury, private communication). Since the solubilities of (*A*) and of (IV; R = Ac) in common solvents are very similar, the two components were separated with difficulty by fractional crystallisation, and the yield of (IV; R = Ac) was very low. Separation was effected by a method discovered by Wright *et al.* (*Canadian J. Res.*, 1949, **27**, *B*, 503) who converted (IV; R = Ac) by 99% nitric acid into 1 : 7-dinitroxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane (IV; $R = NO_2$), which when refluxed with ethyl alcohol forms 1 : 7-diethoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane (IV; R = Et). The latter is soluble in ether, whereas (*A*) is very sparingly soluble and remains unchanged during the operations described.

1-Chloromethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (III; X = Cl), treated with acetyl nitrate and subjected to Wright's procedure, gave (IV; R = Et) in 26% and (*A*) in 1% yield. Methylenedi-1-(3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane) (*B*) gave (*A*) and (IV; R = Et), each in

36% yield. After reaction of acetyl nitrate with hexamine (*A*) was obtained in 17% yield and (IV; R = Ac) was isolated as the ethoxy-derivative in 19% yield. Acetyl nitrate had no action on 1 : 3-dinitro-1 : 3 : 5-triaza-*n*-pentane 5-nitrate.

In an attempt to determine whether the triazaheptane could arise by synthesis, acetyl nitrate was added to a mixture of paraformaldehyde and 3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane nitrate. The only product obtained (72% yield) was (*A*). It appears that the 1 : 7-diacetoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane (IV; R = Ac) arises by the action of acetyl nitrate on substances which contain a triaza*cyclo*hexane ring with an adjacent methylene group in the side chain.

EXPERIMENTAL.

Reactions of 1-*Methoxymethyl*-3 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*hexane* (I; R = Me).—(a) *With nitric acid.* (I; R = Me) (1·50 g.) was added to 99% nitric acid (12 c.c.) at −40°. The mixture was allowed to reach 0° during 10 minutes. It was kept at 0° for a further 30 minutes, and then poured into ice-cold water (75 c.c.) and kept in an ice-bath for 1 hour. The white precipitate, filtered off and dried at 100° (yield, 1·33 g.), had m. p. 203°, giving no m. p. depression with an authentic specimen of (*A*) (Found : C, 16·1; H, 3·5. Calc. for $C_3H_6O_6N_6$: C, 16·2; H, 2·7%).

(b) *With acetic anhydride.* (I; R = Me) (0·76 g.) was added to acetic anhydride (5 c.c.) at room temperature and the solution set aside in an open dish at room temperature for 3 days. Crystals were formed which, washed with ether and dried *in vacuo* (0·26 g.), had m. p. 154°. Recrystallisation from ethyl acetate gave (II) (0·15 g.), m. p. 156° undepressed when mixed with an authentic specimen (Found : C, 27·8; H, 4·1; N, 31·2. Calc. for $C_5H_9O_5N_5$: C, 27·4; H, 4·1; N, 32·0%).

(I; R = Et) (1·5 g.) gave with acetic anhydride (8 c.c.) under similar conditions 0·4 g. of pure (II), m. p. 156° undepressed by admixture with an authentic specimen.

(c) *With acetyl chloride. Isolation of* (III; X = Cl). Finely powdered (I; R = Me) (20 g.) was added slowly to acetyl chloride (120 c.c.) which was stirred at 10° in a closed vessel. The powder dissolved; during 20 minutes' stirring the temperature rose from 10° to 23° and a thick white crystalline precipitate separated. This was collected by sucking the mixture through a large-bore tap in the apparatus on to a sintered filter, an odour of methyl acetate being observed. The precipitate was then washed by sucking acetyl chloride (50 c.c.) through the tap and filter, and the product dried in a vacuum-desiccator. The yield of 1-*chloromethyl*-3 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*hexane* was 18 g. (88%) and the m. p. 147° (Found : C, 21·4, 21·5; H, 4·3, 4·1; N, 30·7, 32·1; Cl, 15·2, 15·6; CH_2, 22·7. $C_4H_8O_4N_5Cl$ requires C, 21·3; H, 3·5; N, 31·0; Cl, 15·7; CH_2, 24·8%). On addition of ether to the acetyl chloride mother-liquor and storage for several days, a few crystals (0·2 g., 1%) of (II) separated, m. p. 156° (Found : C, 27·1; H, 3·8. Calc. for $C_5H_9O_5N_5$: C, 27·4; H, 4·1%).

(d) *With acetyl bromide. Isolation of* (III; X = Br). (I; R = Me) (21 g.) was added slowly with stirring to acetyl bromide (100 g.) at −10°, the mixture being in a closed reaction vessel. The temperature rose rapidly to 10° and a crystalline precipitate separated of 1-*bromomethyl*-3 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*hexane*, which was sucked through a large-bore tap on to a sintered filter. Dry ether was then sucked through the apparatus and through the product. The sintered filter and product were then transferred to a vacuum desiccator. The yield was 16 g. (62%) and the m. p. 127° (decomp.) (Found : C, 17·5, 18·0; H, 2·8, 3·1; Br, 29·7, 29·6, 29·6. $C_4H_8O_4N_5Br$ requires C, 17·8; H, 3·0; Br, 29·6%).

Reactions of (III; X = Cl *or* Br).—(a) *With nitric acid.* The chloro-compound (III; X = Cl) 0·598 g.) was added to 96% nitric acid (8 c.c.) at −20°. The temperature was allowed to reach 10° and kept there for ½ hour. Pouring the solution into water (45 c.c.) gave a white precipitate. The mixture was kept in an ice-bath for an hour, and the precipitate then collected on a sintered filter and dried at 100°. (*A*) (0·545 g., 90·7%), m. p. 204° (decomp.) alone or mixed with an authentic sample, was obtained. Under similar conditions (III; X = Br) (0·415 g.) and 98% nitric acid (6 c.c.) gave (*A*) 0·279 g. (81%), m. p. 204° alone or mixed with an authentic sample. In a duplicate experiment, (III; X = Br) (1·112 g.) gave (*A*) (0·714 g., 78%).

(b) *With methyl and ethyl alcohol.* The chloro-compound (III; X = Cl) (5 g.) was added to methyl alcohol (50 c.c.) at room temperature. Heat was evolved and an immediate crystalline precipitate was obtained. The supernatant liquid was decanted, and the precipitate washed with methyl alcohol (50 c.c.), collected, and recrystallised from acetone–chloroform. The yield was 1·9 g. (38·8%) and the m. p. 134° [no depression with an authentic specimen of (I; R = Me)] (Found : OMe, 13·2. Calc. for $C_5H_{11}O_5N_5$: OMe, 14·0%).

The compound (III; X = Cl) (3 g.) was added at room temperature to ethyl alcohol (30 c.c.). The crystalline precipitate was collected, washed with ethyl alcohol (3 × 10 c.c.), and dissolved in chloroform–acetone at 0° and some of the solvent removed in the cold. Crystals were obtained (0·9 g.), m. p. 115° (decomp.), giving no m. p. depression with an authentic specimen of (I; R = Me) (Found : OEt, 20·6. Calc. for $C_6H_{13}O_5N_5$: OEt, 19·2%).

Addition of (III; X = Br) (2·5 g.) to methyl alcohol (20 c.c.) at room temperature caused the liberation of bromine and the separation of a crystalline precipitate. This was collected, washed with methyl alcohol (2 × 10 c.c.), then with ether (10 c.c.), and recrystallised from warm acetone–chloroform. (I; R = CH_3) (0·6 g.), m. p. 134°, giving no m. p. depression with an authentic sample, was obtained (Found : OMe, 13·1. Calc. for $C_5H_{11}O_5N_5$: OMe, 14·0%).

(c) *With acetic anhydride. Isolation of* (II). The compound (III; X = Cl) (3 g.), added to acetic anhydride (15 c.c.) at room temperature, dissolved in a few minutes. The solution, set aside in an open beaker for four days, gave (II) as large crystals which were washed with methyl alcohol (2 × 10 c.c.), then with dry ether (2 × 10 c.c.) (yield, 2·28 g.). Recrystallisation from warm ethyl acetate gave 1·84 g. (63%) of (II), m. p. 156° undepressed with an authentic specimen (Found : C, 27·5; H, 4·4. Calc. for $C_5H_9O_6N_5$: C, 27·4; H, 4·1%).

Under similar experimental conditions (III; X = Br) (1·5 g.) was added to acetic anhydride (7·5 c.c.) and after recrystallisation from ethyl acetate, crystals (0·54 g.), m. p. 156°, giving no depression with an authentic specimen of (II), were obtained (Found : C, 27·6; H, 4·5%). They gave a depression of 26° with (IV; R = Ac).

(d) *With water, producing methylenedi*-1-(3 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*hexane*) (B). The compound (III; X = Cl) (6 g.) was stirred with aqueous sodium acetate (50 c.c. of water +4 g. of hydrated sodium acetate) at room temperature. The supernatant liquid was decanted, the residue was stirred with water (30 c.c.), filtered, washed with ethyl alcohol (10 c.c.) and then with ether (20 c.c.), and dissolved in acetone at room temperature, and light petroleum (b. p. 40—60°) added. White crystals separated (0·3 g., 5·45%), m. p. 136°, giving no m. p. depression with an authentic specimen of (*B*) (Found : C, 23·0; H, 4·1. Calc. for $C_7H_{14}O_8N_{10}$: C, 23·0; H, 3·8%).

Reaction of (I; R = Me) *with Acetyl Nitrate*.—The ether (I; R = Me) (14 g.) was added to acetyl nitrate (44 g.), cooled in a stoppered flask in solid carbon dioxide. There was no noticeable evolution of heat and the temperature was allowed to rise to −6°. The precipitate was collected, washed with ether, and dried *in vacuo* (12·5 g.). On fractional crystallisation of this mixture from acetone, pure (*A*) (6 g.) was separated, but the other component, suspected of being (IV; R = Ac), could not be obtained free from (*A*). However, on addition of ether to the acetyl nitrate mother-liquor, a small crystalline precipitate of (IV; R = Ac) was obtained, m. p. 152° (Found : C, 26·6; H, 4·3. Calc. for $C_8H_{14}O_{10}N_6$: C, 27·1; H, 3·6%), which, when dissolved in 98% nitric acid, kept thus for 1 hour, and poured into water, gave no precipitate. Destruction by concentrated nitric acid is a property of open-chain derivatives such as (IV), whereas (*A*) remains undecomposed by nitric acid for a very long time. It appeared, therefore, that the small portion of the product which had remained dissolved in the acetyl nitrate was almost pure (IV; R = Ac).

Later experiments were carried out as follows. Acetyl nitrate (49 g.) was cooled in a solid carbon dioxide–acetone bath, and (I; R = Me) (8·5 g.) was added. The reaction mixture was allowed to reach room temperature, then cooled again, and diluted with cold ether (150 c.c.). The precipitate was filtered off, washed with ether, and dried *in vacuo* (10·5 g.). It was then dissolved in 99% nitric acid (30 c.c.) at −40° and the temperature allowed to reach 0°. The mixture was then poured into ice-water (100 c.c.), giving a white precipitate which was collected, washed with cold ethyl alcohol (25 c.c.), and refluxed with absolute ethyl alcohol (100 c.c.) for 1¼ hours. The solution was then cooled in a solid carbon dioxide–acetone bath, and the precipitate which separated was collected and then extracted with ether. The ethereal solution was dried (Na_2SO_4) and filtered, and the filtrate evaporated to dryness on a water-bath. The residue of 1 : 7-diethoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane (IV; R = Et) was recrystallised from warm ethyl alcohol, giving thin plates, m. p. 82° (2·9 g., 23%), undepressed on admixture with an authentic specimen (Found : C, 28·9; H, 5·2; OEt, 26·4. Calc. for $C_8H_{18}O_8N_6$: C, 29·5; H, 5·5; OEt, 27·6%). The residue, insoluble in ether, when washed several times with ether and dried *in vacuo* (yield, 2·5 g., 29·4%), had m. p. 204°, giving no m. p. depression with an authentic specimen of (A).

Reaction of (III; X = Cl) *with Acetyl Nitrate*.—Acetyl nitrate (59 g.) in a stoppered flask was cooled to −60° in a solid carbon dioxide–acetone bath, and (III; X = Cl) (5·4 g.) was added, forming a solution which was allowed to reach room temperature, then cooled again to −60°, and diluted with cold ether (200 c.c.), the flask being kept in the above cooling bath. The precipitate which separated was collected, washed several times with cold ether, and dried *in vacuo* (yield, 8 g.). This mixture of (A) and (IV; R = Ac) was then dissolved in 99% nitric acid (25 c.c.) at −40°, and the temperature allowed to reach 0°. The solution was poured into ice-cold water (100 c.c.), giving a white precipitate which was collected, washed with cold ethyl alcohol (25 c.c.), and then refluxed with absolute ethyl alcohol (50 c.c.) for 1½ hours. The solution obtained was cooled in a solid carbon dioxide bath, the crystalline precipitate collected and then extracted with ether, and the ethereal solution dried (Na_2SO_4). The residue, insoluble in ether, was very small (0·05 g., 0·9%) and had m. p. 204° undepressed on admixture with (A). The ethereal solution was evaporated to dryness and the residue recrystallised from warm ethyl alcohol, giving (IV; R = Et) (2 g., 25·6%), m. p. 82°, undepressed on admixture with an authentic sample (Found : C, 29·4; H, 5·7; OEt, 26·0 Calc. for $C_8H_{18}O_8N_6$: C, 29·5; H, 5·5; OEt, 27·6%).

Reaction between Methylenedi-1-(3 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*hexane*) (B) *and Acetyl Nitrate*.—Acetyl nitrate (35 g.) was cooled in solid carbon dioxide–acetone, and (*B*) (2·5 g.) added. The experiment was then conducted as described in the previous paragraphs. The ether-soluble material thus obtained was recrystallised from alcohol, giving 0·81 g. (36·4%) of (IV; R = Et), m. p. 82° undepressed on admixture with an authentic sample. The residue, (1·1 g., 36·3%), m. p. 203°, insoluble in ether, gave no m. p. depression with a specimen of (*A*).

Reaction of Hexamine with Acetyl Nitrate.—Hexamine (6 g.) was added to cooled acetyl nitrate (94 g.) and treated as above. The ether-soluble component (2·4 g., 18·9%), when recrystallised from ethyl alcohol, gave 1·5 g. of (IV; R = Et), m. p. 82° undepressed on admixture with an authentic sample (Found : C, 29·1; H, 6·0. Calc. for $C_8H_{18}O_8N_6$: C, 29·5; H, 5·5%). The insoluble residue, washed with water and dried *in vacuo*, gave (*A*) (1·8 g.), mixed m. p. 204°.

Reaction of Acetyl Nitrate with 3 : 5-*Dinitro*-1 : 3 : 5-*diaza*cyclo*hexane Nitrate* (C) *and Paraformaldehyde*.—The nitrate (*C*) (6 g.) and paraformaldehyde (1 g.) were added to acetyl nitrate (30 g.) cooled in solid carbon dioxide, and treated as described above. No ether-soluble material was obtained, the sole product being (*A*) (4 g., 72%), m. p. 204°, giving no m. p. depression with an authentic specimen.

1 : 3-*Dinitro*-1 : 3 : 5-*triaza*-n-*pentane* 5-*Nitrate* (D) *and Acetyl Nitrate*.—The nitrate (*D*) (5 g.) was added to acetyl nitrate (33 g.), cooled in solid carbon dioxide, and the mixture then allowed to reach

room temperature. It was cooled again and diluted with cold ether. A precipitate (4·5 g.) was obtained, having m. p. 129° undepressed by admixture with the original substance (Found: C, 11·1; H, 4·0; NO_3', 29. Calc. for $C_2H_8O_7N_6$: C, 10·5; H, 3·5; NO_3', 27·2%). It was completely soluble in cold water.

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[*Received, June* 12*th*, 1950.]