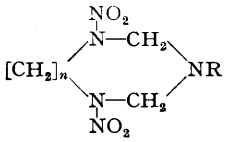
356. *Studies on Nitroamines. Part VI. The Nitration of some Aminomethylnitroamines.*

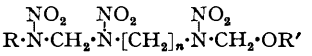
By F. CHAPMAN, P. G. OWSTON, and D. WOODCOCK.

The compounds (I; $n = 1$ or 2; R = alkyl) and (III)—(VI), prepared as described in Part IV of this series, have been nitrated at various temperatures with combinations of 98% nitric acid, acetic acid, acetic anhydride, and ammonium nitrate, and the main reaction products identified.

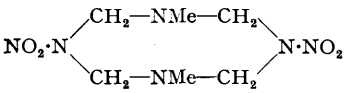
1 : 5-DINITRO-3-ALKYLHEXAHYDRO-1 : 3 : 5-TRIAZINES (I; $n = 1$; R = Me or Et), on treatment with 98% nitric acid at 10°, gave the corresponding linear nitrate esters (II; R = Me or Et; R′ = NO_2), whilst treatment with nitric acid at 50—60° in the presence of acetic acid, acetic anhydride, and ammonium nitrate resulted in the formation of the acetates (II; R = Me or Et; R′ = Ac). These results confirm the structures previously assigned (Part IV) to the initial materials. Nitration of the 3-methyl compound (I; $n = 1$; R = Me) with a mixture of 98% nitric acid and ammonium nitrate at 60—65° or 95—100° gave cyclonite (I; $n = 1$; R = NO_2) as the only identifiable product. A very small amount of cyclonite was also obtained by nitration of the 3-ethyl compound (I; $n = 1$; R = Et) with 98% nitric acid, acetic acid, acetic anhydride, and ammonium nitrate at 55—60°.



(I.)



(II.)

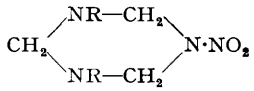


(III.)

The structure of the *nitrate* (II; $n = 1$; R = Et; R′ = NO_2) was confirmed by conversion into the corresponding methyl ether and acetate (R′ = Me or Ac) by boiling methyl alcohol or sodium acetate–acetic acid, respectively.

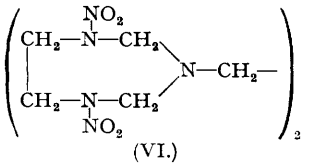
The 1 : 5-dinitro-3-alkyl-1 : 3 : 5-triaza*cyclo*heptanes (I; $n = 2$; R = Me, Et, Pr^i, Bu^n, or *cyclo*hexyl) were nitrated with acetic anhydride and 98% nitric acid at 55° in the presence or absence of ammonium nitrate. Without ammonium nitrate the corresponding linear *compounds* (II; $n = 2$; R = Me, etc.; R′ = Ac) were invariably formed. With ammonium nitrate, compounds of type (II; $n = 2$) may still be the only products which can be isolated, *e.g.*, from (I; $n = 2$; R = Me or Bu^n) the homologue of cyclonite (I; $n = 2$; R = NO_2) may be formed simultaneously, *e.g.*, from (I; $n = 2$; R = Et), or it may be the only product of nitration which can be isolated, *e.g.*, from (I; $n = 2$; R = Pr^i or *cyclo*hexyl).

From these results it seems that compounds of type (I; $n = 1$ or 2; R = alkyl) can readily undergo nitration to give linear compounds (II; $n = 1$ or 2) or ring compounds (I; $n = 1$ or 2; R = NO_2). The evidence available is not sufficient to enable the reaction products to be predicted, but it is noteworthy that cyclonite and its homologue have been isolated only when the nitration mixture contained ammonium nitrate.



(IV; R = *cyclo*hexyl.)

(V.)



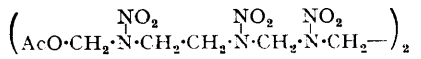
(VI.)

No identifiable product could be obtained by treating the cyclic compound (III) (Chute, Downing, McKay, Myers, and Wright, "Nitrolysis of Hexamine, Part I," *Canadian J. Res.*, in the press) with 98% nitric acid at 10°, but, by use of a mixture of 98% nitric acid, acetic anhydride, and ammonium nitrate at 55—60°, an excellent yield of the acetate (II; $n = 1$; R = Me; R′ = Ac) was obtained.

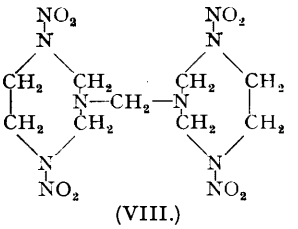
cyclo*Hexylamine nitrate* was the only compound which could be isolated by nitration of (IV) with 98% nitric acid at 10°. 98% Nitric acid, acetic acid, acetic anhydride, and ammonium nitrate at 55—60° gave a 15% yield of cyclonite.

The acetate (II; $n = 1$; R = Me; R′ = Ac) was obtained by nitration of (V) with 98% nitric acid, acetic acid, acetic anhydride, and ammonium nitrate at 50—60°.

The nitration product obtained by treatment of 3 : 3′-ethylenebis-(1 : 5-dinitro-1 : 3 : 5 triaza*cyclo*heptane) (VI) with 98% nitric acid and acetic anhydride was the same, whether or



(VII.)



(VIII.)

not ammonium nitrate was added. Analyses gave results in good agreement with those required for *compound* (VII), as expected by analogy with the behaviour of compounds of type (I; $n = 1$ or 2; R = alkyl) under similar conditions. It is, however, interesting to contrast the behaviour of the compound (VI) with that reported for the corresponding methylene compound (VIII) (Myers and Wright, "Nitrolysis of Hexamine, Part IV," *Canadian J. Res.*, in the press), which on comparable nitration gave a mixture of the linear compound (II; $n = 2$; R = CH_2·OAc; R′ = Ac) and the cyclic compound (I; $n = 2$; R = NO_2).

Experimental.

NN′N″-*Trinitro*(*acetoxymethylaminomethyl*)(*methylaminomethyl*)*amine* (II; $n = 1$; R = Me; R′ = Ac).—(*a*) 1 : 5-Dinitro-3-methylhexahydro-1 : 3 : 5-triazine (I; $n = 1$; R = Me) (1·9 g., 0·01 mol.) was added, simultaneously with a solution of ammonium nitrate (2·4 g.) in 98% nitric acid (3·2 g.), to a mixture of glacial acetic acid (6·9 c.c.) and acetic anhydride (6·5 c.c.) and stirred at 50—60° for ¼ hour. After the addition of water (*ca.* 40 c.c.), a white solid (2·2 g.), m. p. 140—146°, was collected, washed with water, and dried.

(*b*) 1 : 5-Dinitro-3 : 7-dimethyl-1 : 3 : 5 : 7-tetra-aza*cyclo*octane (III) (1·7 g., 0·007 mol.) was treated in the same manner with the appropriately reduced quantities of the other reagents; yield, 3·7 g.; m. p. 134—136°.

(*c*) Methyldi-(*N*-nitro-*N*-methylaminomethyl)amine (V) (1·8 g., 0·009 mol.) was treated similarly with acetic anhydride (4·5 c.c.) and the appropriately reduced quantities of the other reagents; yield, 1·0 g.; m. p. 114—125°.

Crystallisation of each crude product from glacial acetic acid gave rosettes of prisms, m. p. 153—154°, which were shown to be (II; $n = 1$; R = Me; R′ = Ac) (Canadian workers, private communications) by analyses, determinations of mixed m. p., and a comparison of *X*-ray diffraction diagrams.

Treatment of 1 : 5-*Dinitro*-3-*methylhexahydro*-1 : 3 : 5-*triazine* (I; $n = 1$; R = Me) *with Nitric Acid Alone.*—The compound (1·4 g.) was stirred with 98% nitric acid (12 c.c.) for 0·5 hour and poured into dry ether (50 c.c.). The crude gum hardened on trituration with further portions of dry ether, and was converted into (II; $n = 1$; R = Me; R′ = Et) by boiling with fused sodium acetate in acetic acid, cooling, and dilution with water, or into the methyl ether (II; $n = 1$; R = R′ = Me), plates, m. p. 110° [workers at The University of Pennsylvania (private communications) give m. p. 114°], by heating under reflux with excess of methyl alcohol for 2 hours and cooling.

NN′N″-*Trinitro*(*nitroxymethylaminomethyl*)(*ethylaminomethyl*)*amine* (II; $n = 1$; R = Et; R′ = NO_2).—1 : 5-Dinitro-3-ethylhexahydro-1 : 3 : 5-triazine (I; $n = 1$; R = Et) (1·0 g.) was added to 98% nitric acid (10 c.c.), stirred at 10—15° for ½ hour, and then added dropwise to dry ether (50 c.c.) at <15°. The white crystalline *nitrate* (0·91 g.), m. p. 111—114° (decomp.), was collected, washed three times with ether, and dried [Found: C, 19·1; H, 4·4; O·NO_2 (nitron), 20·75, 20·82. $C_5H_{11}O_9N_7$ requires C, 19·2; H, 3·5; O·NO_2, 19·8%].

This nitrate (0·2 g.) was boiled under reflux with methyl alcohol (4 c.c.) for 2 hours, and the resultant solution concentrated and allowed to cool. The crystalline methyl ether (II; $n = 1$; R = Et; R′ = Me) (0·10 g.) was collected, dried, and recrystallised from methyl alcohol; it formed prisms, m. p. 101—102° (Found: C, 25·8; H, 5·0. Calc. for $C_6H_{14}O_7N_6$: C, 25·5; H, 5·0%). Workers at The University of Pennsylvania (private communication) give m. p. 96°.

NN′N″-*Trinitro*(*acetoxymethylaminomethyl*)(*ethylaminomethyl*)*amine* (II; $n = 1$; R = Et; R′ = Ac).—(*a*) 1 : 5-Dinitro-3-ethylhexahydro-1 : 3 : 5-triazine (I; $n = 1$; R = Et) (1·0 g.) was added, simultaneously with a solution of ammonium nitrate (1·2 g.) in 98% nitric acid (1·1 c.c.), to a mixture of glacial acetic acid (3·5 c.c.) and acetic anhydride (3·3 c.c.) stirred at 55—60°. Solid commenced to separate after the addition was complete, and stirring was continued for ½ hour, whereafter water (30 c.c.) was added. The product (0·96 g.), m. p. 114—116°, was collected, washed with water, and dried in a desiccator. Repeated crystallisation from methyl alcohol gave monoclinic prisms, m. p. 132° (workers at The University of Pennsylvania, private communication, give m. p. 133—134°). Cyclonite, m. p. 200—201° (decomp.), was isolated in minute amount from a fraction less soluble in methyl alcohol.

(*b*) The nitrate (II; $n = 1$; R = Et; R′ = NO_2) (0·1 g.) was boiled under reflux for 2 minutes with fused sodium acetate (0·1 g.) in glacial acetic acid (1 c.c.). The solution was cooled, water (1 c.c.) added, and the crystalline precipitate was collected, washed with water, and dried in a vacuum; yield, 0·07 g.; m. p. 131—132°, unaltered by recrystallisation from methyl alcohol.

Nitration of 1-*Nitro*-3 : 5-*di*cyclo*hexylhexahydro*-1 : 3 : 5-*triazine* (IV).—(*a*) *By* 98% *nitric acid.* The compound (1·0 g.) was added to 98% nitric acid (10 c.c.) and stirred at 10—15° for ½ hour and then added dropwise, with stirring, to dry ether (60 c.c.) at <15°. The gum which separated was washed by stirring with fresh ether and dissolved in methyl alcohol; the solution was concentrated and kept at 0° overnight. Recrystallisation, from alcohol–ether, of the precipitate thus obtained, gave cyclo*hexylamine nitrate* as prisms, m. p. 153—154° (decomp.) (Found: C, 43·4; H, 8·4; N, 17·6; O·NO_2 (nitron), 37·4. $C_6H_{14}O_3N_2$ requires C, 44·5; H, 8·6; N, 17·3; O·NO_2, 38·2%). The product was very soluble in water and gave a positive brown-ring test for nitrates, and the odour of *cyclo*hexylamine was observed after warming it with dilute sodium hydroxide.

(*b*) The compound (IV) was heated at 50—60° for ½ hour with ammonium nitrate, nitric acid, acetic acid, and acetic anhydride. The sticky solid precipitated by water yielded cyclonite on crystallisation from acetone.

Nitration of 1 : 5-*Dinitro*-3-*alkyl*-1 : 3 : 5-*triaza*cyclo*heptanes* (I; $n = 2$; R = Me, Et, etc.).—(*a*) *By* 98% *nitric acid and acetic anhydride at* 55°. The *cyclo*heptane (1·0 g.) was dissolved in acetic anhydride (10 c.c.) and warmed to 55° with stirring. 98% Nitric acid (4 c.c.) was then added at such a rate that the temperature remained constant at 55° ± 2°. After 15 minutes, the solution was diluted with water (40 c.c.); the linear nitration product (II; $n = 2$; R′ = Ac; R = Me, Et, etc.) was obtained as a sticky gum, which could be crystallised from methyl alcohol or a mixture of methyl alcohol, acetone, and water. Details of the acetates (II; $n = 2$; R′ = Ac; R = Me, etc.) and the yields obtained from 1 g. of the corresponding compound (I; $n = 2$) are recorded in Table I.

TABLE I.

Compounds, NO_2·NR·CH_2·N(NO_2)·CH_2·CH_2·N(NO_2)·CH_2·OAc.

R.	Crystal form, and solvent.	M. p	Analysis.	Yield.
Me	Clusters of prisms; acetone–methanol	89—91°	Found: C, 27·4; H, 4·5; N, 26·8%. $C_7H_{14}O_8N_6$ requires C, 27·1; H, 4·5; N, 27·1%	0·5 g.
Et	Prisms; acetone–methanol–water	64—67	Found: C, 30·0; H, 5·0; N, 25·3%. $C_8H_{16}O_8N_6$ requires C, 29·6; H, 4·9; N, 25·9%	1·0
Pr^i	Clusters of prisms; acetone–methanol–water	69—72	Found: C, 31·9; H, 5·6; N, 23·6%. $C_9H_{18}O_8N_6$ requires C, 32·0; H, 5·3; N, 24·9%	0·7
Bu^n	Prisms; methanol–water	92—94	Found: C, 33·6; H, 5·9; N, 24·2%. $C_{10}H_{20}O_8N_6$ requires C, 34·1; H, 5·7; N, 23·9%	0·95
*cyclo*Hexyl	Prisms; acetone–methanol–water	63—65	Found: C, 37·8; H, 5·8; N, 22·3%. $C_{12}H_{22}O_8N_6$ requires C, 38·1; H, 5·8; N, 22·2%	0·95

(*b*) *By* 98% *nitric acid, acetic anhydride, and ammonium nitrate at* 55°. The nitrations were carried out as in (*a*), except that a solution of ammonium nitrate (1·7 g.) in 98% nitric acid (2·3 g.) was added instead of pure 98% nitric acid. Details of the nitration products obtained in each case are recorded in Table II, the identities being established by mixed melting points.

TABLE II.

Compound nitrated. (I; $n = 2$), R =	Nitration product(s).	Yield (from 1 g.).
Me	(II; $n = 2$; R = Me; R′ = Ac)	0·3 g.
Et	(II; $n = 2$; R = Et; R′ = Ac)	0·6
	(I; $n = 2$; R = NO_2)	0·2
Pr^i	(I; $n = 2$; R = NO_2)	0·6
Bu^n	(II; $n = 2$; R = Bu^n; R′ = Ac)	0·7
*cyclo*Hexyl	(I; $n = 2$; R = NO_2)	0·4

Nitration of 3 : 3′-*Ethylenebis*-(1 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*heptane*) (VI) *by* 98% *Nitric Acid and Acetic Anhydride.*—The compound (VI) (1 g.) was dissolved in acetic anhydride (150 c.c.) at 55° with stirring. 98% Nitric acid (25 c.c.) was added dropwise, and the temperature maintained at 55°. When the addition of the acid was complete, the *diacetate* (VII) began to separate. The nitration mixture was cooled and the solid collected. By repeated recrystallisation from glacial acetic acid, the product (0·85 g.) was obtained as rosettes of prisms, m. p. 161—162° [Found: C, 27·3; H, 4·1; N, 26·6%; *M*, (Rast), 561, 572; acetyl, 15·1. $C_{14}H_{26}O_{16}N_{12}$ requires C, 27·2; H, 4·2; N, 27·2; *M*, 618; acetyl, 13·9%).

The authors wish to thank Dr. E. Roberts for a pure specimen of the acetate (II; $n = 1$; R = Et; R′ = Ac), and Professor F. J. Llewellyn for determining the *X*-ray diffraction diagrams.

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