354. *Studies on Nitroamines. Part IV. The Reaction of Nitroamines with Formaldehyde and Primary or Secondary Amines.*

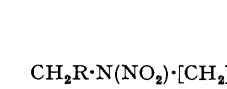
By F. Chapman, P. G. Owston, and D. Woodcock.

A series of compounds (III; R = Me) and (V; R = *cyclo*hexyl or CH_2Ph) has been prepared from methylenedinitroamine, formaldehyde, and the appropriate base, the nitroamine acting in each case as a precursor of nitroamine (II; R = H). Under aqueous conditions, substances (IV; $n = 1$; R = Me, Et, or CH_2Ph) can be isolated, whilst there is evidence of the formation of (IV; $n = 1$; R = H) when ammonia is used. Compounds of type (IV) derived from ethylene- and trimethylene-dinitroamine are also described.

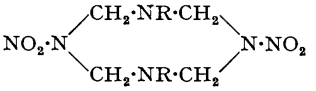
In the preceding paper it was shown that compounds of type (I; R = morpholino; $n = 2$, 3, or 4) are formed from morpholine and the corresponding *N*-hydroxymethylnitroamine, but in the case of methylenedinitroamine the product obtained under aqueous or anhydrous conditions was (II; R = morpholinomethyl).

The reaction between methylenedinitroamine and other bases has now been examined. When a solution of methylenedinitroamine in ethyl acetate is treated with dry gaseous formaldehyde and then with an alcoholic solution of methylamine, the resultant product (III; R = Me) is identical with that obtained from nitroamine by Chute, Downing, McKay, Myers, and Wright ("Nitrolysis of Hexamine, Part I," *Canadian J. Res.*, in the press), and no methylenedinitroamine was regenerated on hydrolysis. On the other hand, the *product* from experiments in which 40% aqueous formaldehyde was used gave a theoretical yield of methylene-

dinitroamine (isolated as the insoluble barium salt); this hydrolysis and elementary analysis indicated that this latter product is (IV; $n = 1$; R = Me), and this was supported by synthesis from *NN'*-bishydroxymethylmethylenedinitroamine (I; $n = 1$; R = OH) and methylamine.


(I.)


(II.)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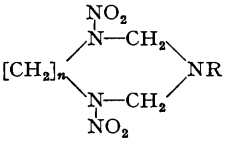
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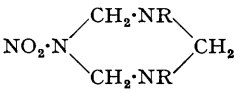
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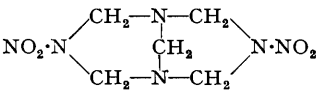

(VI.)

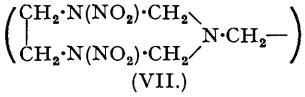
From methylenedinitroamine and *cyclo*hexylamine only one product, identical with that of Chute *et al.* (*loc. cit.*) (V; R = *cyclo*hexyl) could be isolated, whereas, when benzylamine was employed, a mixture of (IV; $n = 1$; R = benzyl) and (V; R = benzyl) was formed in proportions which depended on the conditions; the former component was obtained in 30% and 1—2% yield under aqueous and anhydrous conditions, respectively, but the eight-membered-ring compound (III; R = benzyl) was not obtained.

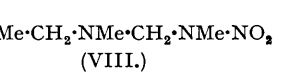
The isolation of compounds of types (II), (III), and (V) in which the grouping $\cdot CH_2 \cdot N(NO_2) \cdot CH_2 \cdot$ is derived from methylenedinitroamine, provides further evidence that the latter can act as a precursor of nitroamine.

It has been shown (Part VII) that the main product of the reaction, in aqueous solution, of methylenedinitroamine, formaldehyde, and ammonium ions, at pH 5—6 is 3 : 7-dinitro-1 : 3 : 5 : 7-tetra-aza*bicyclo*[3 : 3 : 1]nonane (VI). In the present investigation, treatment of a solution of methylenedinitroamine in anhydrous ether with a saturated solution of gaseous formaldehyde and ammonia in the same solvent gave a gummy product which probably contained (IV; $n = 1$; R = H) because its acetyl derivative (IV; $n = 1$; R = Ac) (Aristoff, Graham, Myers, and Wright, "Nitrolysis of Hexamine, Part VI," *Canadian J. Res.*, in the press; also Roberts, private communication) was isolated after boiling with acetyl chloride.

Of secondary amines investigated, other than morpholine, diethylamine and piperidine gave ill-defined products with methylenedinitroamine and formaldehyde.

The 1 : 5-dinitro-3-alkyl-1 : 3 : 5-triaza*cyclo*heptanes (IV; $n = 2$; R = *ethyl*, iso*propyl*, *butyl*, and cyclo*hexyl*) were prepared from ethylenedinitroamine and, unlike the corresponding derivatives of nitroamide and methylenedinitroamine, were stable in hot organic solvents. 3 : 3'-*Ethylenebis*-(1 : 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*heptane*) (VII), prepared similarly from ethylenedinitroamine and ethylenediamine, is an extremely insoluble compound.


(VII.)


(VIII.)

Under anhydrous conditions, trimethylenedinitroamine reacts with methylamine or *cyclo*hexylamine in the presence of formaldehyde to give *compounds* (IV; $n = 3$; R = Me and *cyclo*hexyl, respectively). The former product is more stable than the corresponding methylenedinitroamine derivative (IV; $n = 1$; R = Me), whilst the compound (IV; $n = 1$; R = *cyclo*hexyl) has not so far been obtained.

Methylnitroamine, formaldehyde, and methylamine under aqueous conditions yield the *compound* (VIII). A number of salts, prepared from methylenedinitroamine and organic bases for the purposes of comparison, are described in the experimental section.

Experimental.

1 : 5-*Dinitro*-3 : 7-*dimethyl*-1 : 3 : 5 : 7-*tetra-aza*cyclo*octane* (III; R = Me).—A solution of methylene dinitroamine (0·5 g.) in ethyl acetate (1 c.c.) was saturated with dry gaseous formaldehyde at 0°, and a 33% solution of methylamine in ethyl alcohol (0·9 c.c., 2 mols.) added with stirring. The solid (0·35 g.), m. p. 125—126° (decomp.), which separated, was collected, washed with ether, and dried in a vacuum (Found: C, 31·0; H, 6·0; N, 35·0; CH_2O, 49·1. Calc. for $C_6H_{14}O_4N_6$: C, 30·8; H, 6·0; N, 35·8; CH_2O, 51·2%). The solid was sparingly soluble in cold water, evolving formaldehyde on warming, and soluble in 2N-hydrochloric acid. Methylenedinitroamine could not be isolated after hydrolysis

with cold barium hydroxide solution, and admixture with the compound, m. p. 124° (decomp.), as prepared by Wright (*loc. cit.*) from nitroamine, gave no depression in m. p.

1-*Nitro*-3 : 5-*dibenzylhexahydro*-1 : 3 : 5-*triazine* (V; R = CH_2Ph).—This was prepared as above, using benzylamine (0·8 c.c.) instead of methylamine. After the mixture had been kept overnight at 0°, the white solid (0·63 g.), m. p. 109—115° (decomp.), was collected, dried in a vacuum, and crystallised from cold acetone. A small amount of material, m. p. 130—131° (decomp.), undepressed by admixture with the compound (IV; n = 1; R = CH_2Ph) described below, separated first, and addition of water to the mother-liquors gave a white solid which crystallised from a small amount of acetone in small needles, m. p. 108—110° (decomp.) (Found: C, 65·6; H, 6·3; N, 18·1. Calc. for $C_{17}H_{20}O_2N_4$: C, 65·4; H, 6·5; N, 18·0%), undepressed by admixture with compound (V; R = CH_2Ph) obtained from nitroamine.

1-*Nitro*-3 : 5-*di*cyclo*hexylhexahydro*-1 : 3 : 5-*triazine* (V; R = *cyclo*hexyl).—A solution of methylenedinitroamine (0·7 g.) in ethyl acetate (1·5 c.c.) was saturated with dry gaseous formaldehyde at 0°, and *cyclo*hexylamine (1·0 g., 2 mols.) added. After 0·5 hour the solid (1·0 g.), m. p. 99—101° (decomp.), was collected; it crystallised from ether–light petroleum (b. p. 40—60°) in colourless rectangular prisms, m. p. 101—102° (decomp.) (Found: C, 61·0; H, 9·2; N, 18·6. Calc. for $C_{15}H_{26}O_2N_4$: C, 60·9; H, 9·5; N, 18·9%). The same compound was obtained using excess of 40% aqueous formaldehyde, and neither substance depressed the m. p. of a product, m. p. 99° (decomp.), prepared by Wright's method (*loc. cit.*).

1 : 5-*Dinitro*-3-*benzylhexahydro*-1 : 3 : 5-*triazine* (IV; n = 1; R = CH_2Ph).—Methylenedinitroamine (0·5 g.) was dissolved in 40% aqueous formaldehyde (1·5 c.c., 5 mols.), the solution cooled to 0°, and benzylamine (0·8 c.c., 2 mols.) added dropwise with shaking. After 18 hours at 0°, the white solid *triazine* (1·28 g.), m. p. 104—114° (decomp.), was collected and dried in a vacuum. Crystallisation from cold acetone gave rectangular prisms (0·2 g.), m. p. 127—130° (decomp.) (Found: C, 45·3, 45·2; H, 4·8, 4·9; N, 26·6, 26·4. $C_{10}H_{13}O_4N_5$ requires C, 45·0; H, 4·9; N, 26·2%). Addition of water to the mother-liquors gave a white solid which crystallised from cold acetone in needles, m. p. 107—110° (decomp.), undepressed by admixture with (V; R = CH_2Ph) prepared as described above.

1 : 5-*Dinitro*-3-*methylhexahydro*-1 : 3 : 5-*triazine* (IV; n = 1; R = Me).—(*a*) A solution of methylenedinitroamine (1·0 g.) in 40% aqueous formaldehyde (1 c.c., 3 mols.) was cooled to 0°, and a 33% ethyl-alcoholic solution of methylamine (0·9 c.c., 1 mol.) was quickly added with shaking. After 1 hour at 0°, the crystalline *triazine* (0·6 g.), m. p. 100—104° (decomp.), was collected, washed with cold water, and dried in a vacuum [Found: C, 26·0; H, 4·8; N, 35·4; potential methylenedinitroamine (see Part VII), 70·5, 71·2. $C_4H_9O_5N_4$ requires C, 25·2; H, 4·7; N, 36·7; potential methylenedinitroamine, 71·2%). (*b*) A solution of *NN'*-bishydroxymethylmethylenedinitroamine (0·15 g.) in ethyl acetate (0·5 c.c.) was cooled to 0°, and a 33% ethyl-alcoholic solution of methylamine (0·1 c.c., 1 mol.) added. After 2 hours at 0°, large colourless rhombs (0·08 g.), m. p. 98—99° (decomp.), undepressed by admixture with product (*a*) above, were collected, washed with ether, and dried in a vacuum.

1 : 5-*Dinitro*-3-*ethylhexahydro*-1 : 3 : 5-*triazine* (IV; n = 1; R = Et).—A solution of methylenedinitroamine (1·0 g.) in 40% aqueous formaldehyde (1·0 c.c., 3 mols.) was cooled to <0°, and ethylamine (0·25 c.c., 1 mol.) added dropwise with shaking. The white crystalline *product* (1·0 g.), m. p. 88—89° (decomp.), was collected and dried in a vacuum (Found: C, 29·4; H, 5·3; N. 34·1; potential methylenedinitroamine, 65·5. $C_5H_9O_4N_5$ requires C, 29·3; H, 5·4; N, 34·1; methylenedinitroamine, 66·3%). It was soluble in cold water, but decomposed rapidly when warmed. Hydrolysis with barium hydroxide yielded methylenedinitroamine.

1 : 5-*Dinitro*-3-*acetylhexahydro*-1 : 3 : 5-*triazine* (IV; n = 1; R = Ac).—Anhydrous ammonia in ether (2 c.c.; 1 mol.-equiv. of NH_3), prepared by saturation at −10°, was added cautiously with stirring to a solution of methylenedinitroamine (0·5 g.) in ethyl acetate (1 c.c.) which had been previously treated at 0° with excess of dry gaseous formaldehyde. The sticky white solid (*A*) obtained by decanting the solvent was heated under reflux for 0·5 hour with an excess of acetyl chloride, the solution cooled, and the insoluble material (*B*) collected. The filtrate was evaporated to dryness; the residual oil, crystallised twice from methyl alcohol, gave prismatic plates, m. p. 156° (decomp.), not depressed by admixture with an authentic specimen of (IV; n = 1; R = Ac) (Aristoff *et al.* and Roberts, *locc. cit.*). *X*-Ray diffraction diagrams of this product and of Roberts's compound were identical. Product (*B*) which was the only product obtained when the above reaction was carried out entirely in ethereal solution, was insoluble in water and failed to melt below 360°, though partly subliming. Done in methyl alcohol, the reaction yielded an intractable amorphous material which gradually sublimed at >220°. An attempt to prepare the nitrate of the base (IV; R = H) by treating the substance (*A*) with 55% nitric acid failed.

Methylbis-(N-*nitro*-N-*methylaminomethylamine*) (VIII).—A 33% aqueous solution of methylamine (1·4 c.c., 1 mol.) was added dropwise, with shaking, to a solution of methylnitroamine (2·0 g.) in 40% aqueous formaldehyde (2·0 c.c., 2 mols.) at <0°. The oil which separated from the clear solution gradually solidified (1·42 g.) and was collected, washed with water, and dried in a vacuum; from the mother-liquors the *product* was obtained in large colourless hexagonal prisms, m. p. 62—63° (Found: C, 29·2; H, 6·3; N, 32·9. $C_5H_{13}O_4N_5$ requires C, 29·3; H, 6·3; N, 33·8%).

1 : 5-*Dinitro*-3-*methyl*-1 : 3 : 5-*triaza*cyclo*octane* (IV; n = 3; R = Me).—A solution of trimethylenedinitroamine (0·5 g.) in ethyl acetate (0·5 c.c.) was saturated at −10° with dry gaseous formaldehyde, and 33% ethyl alcoholic methylamine (0·75 c.c., 2 mols.) was added slowly with shaking. The 1 : 3 : 5-*triaza*cyclo*octane* (0·62 g.), m. p. 141—143°, was collected and dried in a vacuum (Found: C, 33·0; H, 5·9; N, 32·1; CH_2O, 30·0, 30·7. $C_6H_{13}O_4N_5$ requires C, 32·8; H, 5·9; N, 31·9; CH_2O, 27·4%).

1 : 5-*Dinitro*-3-cyclo*hexyl*-1 : 3 : 5-*triaza*cyclo*octane* (IV; n = 3; R = cyclo*hexyl*).—The preceding experiment was repeated using *cyclo*hexylamine (0·3 g., 1 mol.), and the *product* (0·4 g.) was collected, washed with ether, and dried in a vacuum. Recrystallisation from methyl alcohol gave rosettes of prisms, m. p. 144—145° (decomp.) (Found: C, 46·0; H, 7·1; N, 26·4. $C_{11}H_{21}O_4N_5$ requires C, 46·0; H, 7·3; N, 24·4%).

1 : 5-*Dinitro*-3-*alkyl*-1 : 3 : 5-*triaza*cyclo*heptanes* (IV; n = 2; R = alkyl).—These *compounds* were

prepared by Wright's method (*loc. cit.*) described for the 3-methyl compound; data below include the yield from ethylenedinitroamine (1·0 g.). 3-Ethyl: rectangular plates (1·0 g.), m. p. 140—142°(from ethyl acetate) (Found: C, 32·9; H, 5·1; N, 33·1. $C_6H_{13}O_4N_5$ requires C, 33·0; H, 5·9; N, 32·0%). 3-*iso*Propyl: minute prisms (0·7 g.), m. p. 107—108° (from ethyl alcohol or ethyl acetate) (Found: C, 36·2; H, 6·1; N, 28·7. $C_7H_{13}O_4N_5$ requires C, 36·1; H, 6·4; N, 27·4%). 3-*n*-Butyl: long prisms (1·1 g.), m. p. 106—107° (from carbon tetrachloride–acetone) (Found: C, 38·3; H, 6·8; N, 27·8. $C_8H_{17}O_4N_5$ requires C, 38·3; H, 6·9; N, 28·4%). *cyclo*Hexyl: clusters of prisms (0·5 g.), m. p. 127° (from ethyl acetate) (Found: C, 44·2; H, 7·1; N, 26·2. $C_{10}H_{19}O_4N_5$ requires C, 44·0; H, 7·0; N, 25·6%).

3 : 3′-*Ethylenebis*-(1′: 5-*dinitro*-1 : 3 : 5-*triaza*cyclo*heptane*) (VII).—This *compound* (1·3 g.), prepared similarly from ethylenedinitroamine (1·0 g.) and ethylenediamine hydrate (0·3 g.), was microcrystalline, had m. p. 205—207° (decomp.), was insoluble in the usual organic solvents, and was purified by washing with sodium hydrogen carbonate solution, water, and finally acetone (Found: C, 29·9; H, 4·9; N, 33·2. $C_{10}H_{20}O_8N_{10}$ requires C, 29·4; H, 4·9; N, 34·3%).

Salts of Methylenedinitroamine.—(*a*) To a cold solution of methylenedinitroamine (0·5 g.) in ethyl acetate (1 c.c.) 33% methylamine in ethyl alcohol (0·9 c.c., 2 mols.) was added. After 0·5 hour at 0°, the very hygroscopic *dimethylamine* salt was collected, recrystallised from methyl alcohol containing a little methylamine, washed with anhydrous ether, and dried in a desiccator, after which it had m. p. 120° (decomp.) (Found: C, 19·0; H, 7·0; N, 39·1. $C_3H_{12}O_4N_6$ requires C, 18·2; H, 7·1; N, 42·4%).

(*b*) The *dicyclohexylamine* salt, similarly prepared from *cyclo*hexylamine (0·85 c.c., 2 mols.), had m. p. 99—100° (decomp.) after recrystallisation from methyl alcohol (Found: C, 46·6; H, 8·9; N, 24·1. $C_{13}H_{30}O_4N_6$ requires C, 46·8; H, 9·0; N, 25·2%).

(*c*) The *dibenzylamine* salt, similarly prepared from benzylamine, crystallised from methyl alcohol containing a trace of benzylamine in aggregates of stout prisms, m. p. 112° (decomp.) (Found: C, 51·8; H, 6·2; N, 24·0. $C_{15}H_{22}O_4N_6$ requires C, 51·4; H, 6·4; N, 24·0%).

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