351. *Studies on Nitroamines. Part I. The Nitration of Some Methylenediamines.*

By F. Chapman.

The compounds (I), (IV; $R = R' = Me$ or $CH_2{\cdot}CH_2{\cdot}O{\cdot}NO_2$, and $R = Me$, $R' = Ph$), and (V; $n = 2$, 3, or 4; R = morpholino or piperidino) have been prepared and nitrated with combinations of 98% nitric acid, acetic acid, acetic anhydride, and ammonium nitrate at various temperatures.

The research presented in this and the succeeding seven papers was carried out at the request of the Scientific Advisory Council of the Ministry of Supply during 1943—1945 under the direction of Professor R. D. Haworth, F.R.S. It was designed, in view of the increasing importance of nitroamines as explosives, to extend our knowledge of these compounds, and to throw light upon the reactions leading to the production of cyclonite (1 : 3 : 5-trinitrohexahydro-1 : 3 : 5-triazine) (III; $n = 1$) from hexamethylenetetramine.

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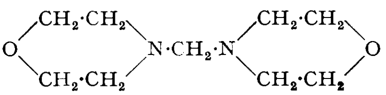
By nitration of substituted methylenediamines of the type $R_2N{\cdot}CH_2{\cdot}NR_2$, it was hoped that information might be obtained on the mode of nitrolysis of hexamethylenetetramine.

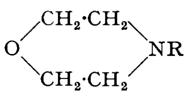
Addition of methylenebismorpholine (I) to 98% nitric acid at 0° gave morpholine nitrate in only 37% yield, calculated on the basis of one molecule of methylenebismorpholine yielding two molecules of morpholine nitrate. This suggested that nitrolysis gave equimolecular amounts of morpholine nitrate and morpholinomethyl nitrate (II; $R = CH_2{\cdot}O{\cdot}NO_2$). This view was supported by the absence of formaldehyde from the nitration liquors, but morpholinomethyl nitrate could not be isolated.

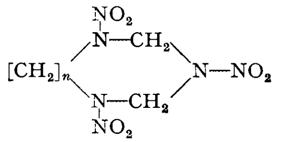
Morpholine nitrate was also formed on treatment of (I) with 98% nitric acid and acetic anhydride at 0°; when the reaction mixture was warmed to 40° or when nitration was effected with a mixture of 98% nitric acid, acetic acid, and acetic anhydride at 55°, 4-nitrosomorpholine (II; R = NO) was obtained. Presumably the nitrosation is due to the reduction of nitric acid by formaldehyde liberated during the reaction.

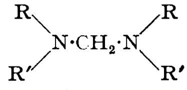
Nitration of (I) with 98% nitric acid, acetic anhydride, and ammonium nitrate at 55° resulted in the formation of cyclonite (III; $n = 1$) and 4-nitromorpholine (II; $R = NO_2$) (Chute *et al.*, *Canadian J. Res.*, 1948, **26**, *B*, 114). Cyclonite probably arises from the combination of the liberated formaldehyde with ammonium nitrate, followed by nitration. This reaction is facilitated by the presence of ammonium nitrate, since the small yields obtained by Chute *et al.* (*loc. cit.*) without a (chloride) catalyst were increased to 47% by the addition of this salt.

The nitration of tetramethylmethylenediamine (IV; $R = R' = Me$) (Henry, *Bull. Acad. roy. Belg.*, 1893, [iii], **26**, 203) with 98% nitric acid in presence of acetic anhydride and ammonium nitrate at 55° or 75° yielded dimethylnitroamine and cyclonite, and threw little light on nitrolysis.


(I.)

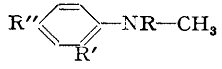

(II.)


(III.)


(IV.)

$CH_2R{\cdot}N(NO_2){\cdot}[CH_2]_n{\cdot}N(NO_2){\cdot}CH_2R$

(V.)


(VI.)

Bismorpholinomethylethylenedinitroamine (V; $n = 2$; R = morpholino) (see Part III), nitrated with 98% nitric acid, acetic anhydride, and ammonium nitrate at 55—60°, yielded 1 : 3 : 5-trinitro-1 : 3 : 5-triaza*cyclo*heptane (III; $n = 2$; Myers and Wright, "Nitrolysis of Hexamine, Part IV," *Canadian J. Res.*, in the press) and 4-nitromorpholine. 1 : 3 : 5-Trinitro-1 : 3 : 5-triaza*cyclo*heptane and 1-nitropiperidine were prepared similarly from bispiperidinomethylethylenedinitroamine (Franchimont, *Rec. Trav. chim.*, 1910, **29**, 306). In the same way, nitration of bismorpholinomethyltrimethylenedinitroamine (V; $n = 3$; R = morpholino) (see Part III) gave 4-nitromorpholine and 1 : 3 : 5-*trinitro*-1 : 3 : 5-*triaza*cyclo*octane* (III; $n = 3$). On the other hand, nitration of bismorpholinomethyltetramethylenedinitroamine (V; $n = 4$; R = morpholino) (see Part III) gave 4-nitromorpholine and a water-insoluble oil which could not be identified.

Nitration of methylenebismonomethylaniline (IV; R = Me, R′ = Ph) (von Braun, *Ber.*, 1908, **41**, 2147) at 0°, with a mixture of 98% nitric acid and acetic anhydride, gave a small yield of 2 : 4 : *N*-trinitro-*N*-methylaniline (VI; R = R′ = R″ = NO_2), but at 55°, with a mixture of 98% nitric acid, acetic anhydride, and ammonium nitrate, *p* : *N*-dinitro-*N*-methylaniline (VI; R = R″ = NO_2, R′ = H) was produced.

Methylenebis-(2 : 2′-*dinitroxydiethylamine*) (IV; R = R′ = $CH_2{\cdot}CH_2{\cdot}O{\cdot}NO_2$) proved quite stable to nitration and was recovered after treatment with 98% nitric acid at 25° or 45° or with a mixture of 98% nitric acid, acetic anhydride, and acetic acid at 55°.

EXPERIMENTAL.

Methylenebismorpholine (I).—Morpholine (17·7 c.c.) was added gradually, with cooling, to a slight excess of 40% formaldehyde (8 c.c.). After the mixture had been heated on a water-bath for 0·5 hour, anhydrous potassium carbonate was added until the water was absorbed. The resultant oil was decanted and distilled. *Methylenebismorpholine* (16·2 g.) was obtained as a colourless liquid, b. p. 110—112°/10 mm. (Found: equiv., by titration with 0·1N-hydrochloric acid, 95·2, 94·8, 94·8. $C_9H_{18}O_2N_2$ requires equiv., 93).

Methylenebis-(2 : 2′-*dinitroxydiethylamine*) (IV; R = R′ = $CH_2{\cdot}CH_2{\cdot}O{\cdot}NO_2$).—Dinitroxydiethylamine nitrate (2·6 g.) prepared by the method of Chute *et al.* (*Canad. J. Res.*, 1948, **26**, *B*, 89) was dissolved in hot water (10 c.c.), and dilute sodium hydroxide solution added until the mixture was alkaline to phenolphthalein. The dinitroxydiethylamine so liberated was extracted with ether (2 × 10 c.c.), the ether extract dried, and the ether removed. The impure residue (1·7 g.) (which showed a tendency to explode if heated alone on a water-bath) was treated with 40% formaldehyde solution (1·0 c.c.), and the mixture heated on the water-bath for 2 hours. The solution so obtained was cooled, and *methylenebis*-(2 : 2′-*dinitroxydiethylamine*) precipitated by addition of methyl alcohol, collected, and dried. After recrystallisation from aqueous methyl alcohol it was obtained as minute prisms (0·6 g.), m. p. 170° (decomp.) (Found: C, 27·3; H, 4·8; N, 20·0. $C_9H_{18}O_{12}N_6$ requires C, 26·9; H, 4·5; N, 20·9%).

Nitration of the Methylenediamines.—In general this was carried out under some or all of the following conditions.

(a) *Using* 98% *nitric acid at* 0°. The methylenediamine (1 g.) was added slowly to well-stirred 98% nitric acid (1·6 g.) at 0°.

(b) *Using* 98% *nitric acid, acetic anhydride, and acetic acid at* 50—60°. The methylenediamine (1 g.) was added slowly and simultaneously with a mixture of 98% nitric acid (1·3 g.) and acetic anhydride (2·4 g.) to a mixture of acetic acid (2·5 g.) and acetic anhydride (2·4 g.) at the appropriate temperature.

(c) *Using* 98% *nitric acid, acetic anhydride, and ammonium nitrate at* 50—60°. The methylenediamine (1 g.) was added slowly and simultaneously with a solution of ammonium nitrate (1·6 g.) in 98% nitric acid (2·2 g.) to acetic anhydride (8 g.) at 50—60°.

Compounds obtained from 1 *G. of the Methylenediamine.*

Compound nitrated.	Conditions.	Product(s).
Methylenebismorpholine (I)	*a*	Morpholine nitrate (0·4 g.).
	b	4-Nitrosomorpholine (0·3 g.).
	c	4-Nitromorpholine (II; R = NO_2) (0·2 g.) and cyclonite (0·04 g.).
Methylenebisdimethylamine (IV; R = R′ = Me)	*c*	Dimethylnitroamine (0·2 g.) and cyclonite (0·05 g.).
NN′-Bismorpholinomethylethylenedinitroamine (V; $n = 2$; R = morpholino)	*c*	1 : 3 : 5-Trinitro-1 : 3 : 5-triaza*cyclo*heptane (III; $n = 2$) (0·5 g.) and 4-nitromorpholine (0·2 g.).
NN′-Bismorpholinomethyltrimethylenedinitroamine (V; $n = 3$, R = morpholino)	*c*	1 : 3 : 5-*Trinitro*-1 : 3 : 5-*triaza*cyclo*octane* (III; $n = 3$) (0·4 g.) * and 4-nitromorpholine (0·3 g.).
NN′-Bismorpholinomethyltetramethylenedinitroamine (V; $n = 4$, R = morpholino)	*c*	4-Nitromorpholine (<0·1 g.).
Methylenebismonomethylaniline (IV; R = Me, R′ = Ph)	*b*	2 : 4 : *N*-Trinitro-*N*-methylaniline (VI; R = R′ = R″ = NO_2) (0·07 g.).
	c	*p* : *N*-Dinitro-*N*-methylaniline (VI; R = R″ = NO_2, R′ = H) (0·15 g.).
Methylenebis-(2 : 2′-dinitroxydiethylamine) (IV; R = R′ = $CH_2{\cdot}CH_2{\cdot}O{\cdot}NO_2$)	*a* and *b*	Initial material (0·8 g.) recovered by addition to ether.

Except for (III; $n = 3$), compounds were identified by mixed melting point with authentic specimens.

* M. p. 164—166° (Found: C, 24·0; H, 3·9; N, 33·8. $C_8H_{10}O_6N_6$ requires C, 24·0, H, 4·0; N, 33·6%).

In all cases the solids which separated during the addition of the methylenediamine were collected, washed, generally with cold acetone, and crystallised. The nitration mixture was then diluted with a large volume of water, and any solids which then separated were collected, washed, dried, and crystallised. The dilute nitration liquors were then extracted with chloroform (10 × 10 c.c.), the chloroform extract was washed with saturated sodium hydrogen carbonate solution, dried, and evaporated. The residue was distilled at 0·5 mm. and crystallised.

This procedure was not adopted with compound (IV; $R = R' = CH_2{\cdot}CH_2{\cdot}O{\cdot}NO_2$). After nitration of this under conditions (*a*) or (*b*), the nitration mixture was cooled if necessary, and then added slowly with stirring to ice-cold ether.

Results are detailed in the annexed Table.

Conversion of Morpholine Nitrate into 4-Nitromorpholine (II; $R = NO_2$) *by Acetic Anhydride and Ammonium Nitrate.*—98% Nitric acid (1 c.c.) was added slowly, with stirring, to acetic anhydride (43·4 g.); ammonium nitrate (13 g.), followed by morpholine nitrate (6·4 g.), were then added, the temperature was raised to 65° during 0·5 hour, and maintained at 65° for a further 1 hour. After cooling, the solution was poured on crushed ice (200 g.) and extracted with chloroform (10 × 10 c.c.). The extract was washed with saturated sodium hydrogen carbonate solution and dried, and the solvent removed. The oily residue was distilled, to give 4-nitromorpholine (2·9 g.), b. p. 84°/1·3 mm., which crystallised from alcohol in prisms (2·7 g.), m. p. 52—53°.

Identification of p : N-*Dinitro*-N-*methylaniline* (VII; $R = R'' = NO_2$, $R' = H$) *by Conversion into* 2 : 4-*Dinitro*-N-*methylaniline* (VII; $R = H$, $R' = R'' = NO_2$).—*p* : *N*-Dinitro-*N*-methylaniline (0·1 g.) was added gradually to concentrated sulphuric acid (1 c.c.) and set aside overnight. The solution was poured into water (10 c.c.) and made slightly alkaline. The bright-yellow precipitate of 2 : 4-dinitro-*N*-methylaniline was collected and crystallised from aqueous acetone as aggregates of minute prisms (0·07 g.), m. p. 175°, undepressed by admixture with an authentic specimen.

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