Chemistry of Nitramines. Part III.[1] Cyclic Nitramines Derived from Trimethylenedinitramine

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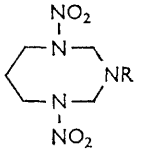
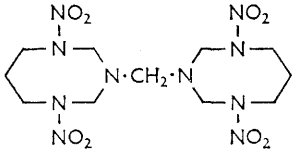
Cyclic nitramines have been prepared by Mannich reactions of trimethylenedinitramine with formaldehyde and various alkylamines or ammonia, and by condensation of tri- or tetra-methylenedinitramine with formaldehyde in sulphuric acid. Reactions of some of the products with nitric and nitrous acid are described.

PREPARATION and some properties of alkoxymethyl derivatives of 1,5-dinitro-1,3,5-triazacyclo-octane (Ia) and (Ib) were described in the preceding Paper.[1] The only other derivatives reported previously are *N*-methyl (Ic), *N*-cyclohexyl (Ig), and *N*-nitro (Ij) compounds, prepared by Chapman and his co-workers.[2]



(Ia: R = CH_2·OMe) (Ig: R = cyclo-C_6H_{11})
(Ib: R = CH_2·OEt) (Ih: R = H)
(Ic: R = Me) (Ii: R = COMe)
(Id: R = Et) (Ij: R = NO_2)
(Ie: R = Pr^i) (Ik: R = NO)
(If: R = Bu^n)



(II)

We have performed reactions between trimethylenedinitramine and formaldehyde in the presence of several primary amines or ammonia; condensation products so obtained have been treated with nitric and nitrous acid to furnish the nitramine (Ij) and nitrosamine (Ik). New, cyclic nitramines have been prepared by condensation of formaldehyde with trimethylenedinitramine or with tetramethylenedinitramine in sulphuric acid.

Alkylamines reacted with trimethylenedinitramine and aqueous formaldehyde to give corresponding 3-alkyl-1,5-dinitro-1,3,5-triazacyclo-octanes (Ic—g). Comparison of melting points with those recorded by earlier workers [2] was unsatisfactory because the products showed poor melting behaviour. However, elemental analyses of the compounds and determination of molecular weight of the n-butyl derivative (If) confirmed that the condensation products are best represented by structure (I).

Condensation of ammonia with trimethylenedinitramine and formaldehyde gave two products, separated by fractional crystallisation from acetone. Elemental composition suggests that the less soluble compound is 3,3′-methylenebis-(1,5-dinitro-1,3,5-triazacyclo-octane) (II), a bicyclic nitramine analogous to the Mannich condensation product obtained from ethylenedinitramine, formaldehyde, and ammonia.[3] Confirmatory evidence was provided by nitrolysis to yield 1,3,5-trinitro-1,3,5-triazacyclo-octane (Ij), and by reaction with nitrous acid giving 1,5-dinitro-3-nitroso-1,3,5-triazacyclo-octane (Ik). Designation of the acetone-soluble product as 1,5-dinitro-1,3,5-triazacyclo-octane (Ih) on the basis of i.r. spectrum, elemental composition, and molecular weight was confirmed by salt formation, *p*-nitrobenzoylation, acetylation, nitration, and nitrosation. Attempted alkylation, using methyl iodide–silver oxide in dimethylformamide, failed.

In forming a secondary amine with formaldehyde and ammonia, trimethylenedinitramine differs significantly from ethylenedinitramine. There were no indications that a corresponding secondary amine is a stable end-product from condensations involving the latter; only high-molecular-weight bicyclic nitramines were obtained.[3]

Reactions with Nitric Acid.—Addition of the crude Mannich condensation product from trimethylenedinitramine, formaldehyde, and ammonia to nitric acid gave a good yield of 1,3,5-trinitro-1,3,5-triazacyclo-octane (Ij), characterised by analysis and molecular-weight determination. The trinitramine was also prepared by treating the separate constituents of the mixture (Ih) and (II) with nitric acid or nitric acid–acetic anhydride.

Reaction mixtures obtained by adding the bicyclic nitramine (II) to nitric acid were diluted with ether or methanol, but, in contrast to the results of earlier work on lower homologues,[3] variation in the work-up procedure did not influence the nature of the product; only the trinitramine (Ij) was isolated in each case. Evidently the nitroxymethyl compound, if present in the reaction mixture, is too unstable to survive treatement with ether or methanol.

The presence of acetic anhydride during nitrolysis of the bicyclic nitramine (II) did not lead to an additional product. Under similar conditions, lower homologues, *viz.*, methylenebis-(3,5-dinitro-1,3,5-triazacyclohexane) [4] and 3,3′-methylenebis-(1,5-dinitro-1,3,5-triazacyclo-heptane),[5] are converted into corresponding cyclic nitramines together with linear diacetates, 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and 1,8-diacetoxy-2,4,7-trinitro-2,4,7-triazaoctane, respectively.

Alkyl derivatives of 1,5-dinitro-1,3,5-triazacyclo-

[1] Part II, preceding Paper.
[2] (*a*) F. Chapman, *J. Chem. Soc.*, 1949, 1631; (*b*) F. Chapman, P. G. Owston, and D. Woodcock, *ibid.*, p. 1638.
[3] Part I, J. A. Bell and I. Dunstan, *J. Chem. Soc.* (*C*), 1966, 862.
[4] W. J. Chute, A. F. McKay, R. H. Meen, G. S. Myers, and G. F. Wright, *Canad. J. Res.*, 1949, **27***B*, 503.
[5] G. S. Myers and G. F. Wright, *Canad. J. Res.*, 1949, **27***B*, 489.

octane reacted with nitric acid–acid anhydride, but no identifiable products were isolated. A low yield of the trinitramine (Ij) was obtained by the action of nitric acid–acetic anhydride–ammonium nitrate on the *N*-cyclohexyl compound (Ig). More extensive nitrolysis studies of corresponding six- and seven-membered-ring compounds are described by Chapman and his co-workers.[6]

Reactions with Nitrous Acid.—High yields of 1,5-dinitro-3-nitroso-1,3,5-triazacyclo-octane (Ik) were obtained by the action of sodium nitrite–sulphuric acid on the ethyl ether (Id), the amine (Ih), the bicyclic nitramine (II), or the crude, Mannich reaction product (Ih) and (II). Although the *N*-alkyl derivatives were aldehyde in concentrated sulphuric acid to give 1,3-dinitro-1,3-diazacyclopentane.[9] Higher homologues of this compound, *viz.*, 1,3-dinitro-1,3-diazacyclo-hexane and -heptane, were obtained by similar condensations using trimethylenedinitramine and tetramethylenedinitramine, respectively. Each product underwent a solid-phase change, becoming isotropic, before melting.

Nuclear Magnetic Resonance Spectra.—The spectra of cyclic nitramines and nitrosamines prepared during this work, are relatively simple (Table 1). Poor solubility of some compounds led to low-intensity spectra and prevented satisfactory integration of peak areas, but, in general, spectra were in accord with the proposed

TABLE 1

N.m.r. spectra of cyclic nitramines and nitrosamines

Compound	τ-values			
	$H_2C(N{\cdot}NO{-})(N{\cdot}NO_2{-})$	$H_2C(N{\cdot}NO_2{-})_2$	$H_2C(N{\cdot}NO_2{-})(C\leqslant)$	$H_2C(C\leqslant)_2$
1,3-Dinitro-1,3-diazacyclopentane		4·47	5·83	
1,3-Dinitro-1,3-diazacyclohexane* (a)		4·10	6·00 (triplet)	—
1,3-Dinitro-1,3-diazacyclohexane* (b)		4·25	6·08 (,,)	8·14 (quintet)
1,3,5-Trinitro-1,3,5-triazacyclohexane		3·86		
1,3-Dinitro-1,3-diazacycloheptane		4·00	6·14	8·17 (,,)
1,3,5-Trinitro-1,3,5-triazacycloheptane		3·96	5·74	
1,5-Dinitro-3-nitroso-1,3,5-triazacycloheptane	3·72, 4·24		5·69	
1,3,5-Trinitro-1,3,5-triazacyclo-octane* (a)		4·02	5·96 (triplet)	—
1,3,5-Trinitro-1,3,5-triazacyclo-octane* (b)		4·16	—	ca. 8·0 (weak)
1,3,5,7-Tetranitro-1,3,5,7-tetra-azacyclo-octane		3·65		
1,5-Dinitro-3-nitroso-1,3,5-triazacyclo-octane* (a)	3·72, 4·32		5·93 (multiplet)	—
1,5-Dinitro-3-nitroso-1,3,5-triazacyclo-octane* (b)	3·90, 4·50		—	7·95 (multiplet)

* Spectra measured in (a) dimethyl sulphoxide, (b) nitromethane, with benzene (τ 2·74) as internal standard; peaks were of low intensity owing to poor solubility.

attacked by the reagent, only methyl and n-butyl compounds gave the nitrosamine (Ik); yields were low. Failure to recover starting material or nitrosamine suggests that reaction may involve cleavage of an N–C bond in the ring, followed by degradation of linear fragments.

Presence of a nitroso group was confirmed by oxidising the product (Ik) to the trinitramine (Ij) with hydrogen peroxide–nitric acid, a reagent used by Wright and his co-workers [7] to oxidise the analogous six-membered-ring nitrosamine.

Ultraviolet (u.v.) spectra of seven-[1] and eight-membered-ring dinitronitrosamines (Ik) show a strong maximum at lower wavelength and a weak absorption band nearer the visible. Jones and Thorn [8] reported a similar u.v. spectrum for a lower homologue, 1,5-dinitro-3-nitroso-1,3,5-triazacyclohexane, attributing the strong maximum to both groups and the weaker absorption to *N*-nitroso.

Condensation of Dinitramines with Formaldehyde.—Ethylenedinitramine undergoes condensation with formstructures. It is of interest that protons in the α-methylene group of the nitrosamines show two resonance peaks due to the *cis* and *trans* configurations of the nitroso group.[10]

EXPERIMENTAL

General methods of analysis and identification were described previously.[3]

N-Alkyl Derivatives of 1,5-Dinitro-1,3,5-triazacyclo-octane.—Trimethylenedinitramine (0·03 mole) was dissolved in 40% aqueous formaldehyde (0·12 mole) at 40°, then the solution was cooled (10°) and treated with the amine (0·06 mole), added dropwise with stirring. Addition of water (20 ml.) during the reaction facilitated stirring; methyl- and ethyl-amine were added as 30% aqueous solutions. After 5 min., *N-alkyl derivatives* (Table 2) were collected, washed with water, and dried.

3,3'-Methylenebis-(1,5-dinitro-1,3,5-triazacyclo-octane) (II) *and 1,5-Dinitro-1,3,5-triazacyclo-octane* (Ih).—Concentrated ammonia solution (0·8 mole) was added dropwise to a stirred solution of trimethylenedinitramine (32·8 g., 0·2 mole) in 40% aqueous formaldehyde (1·6 mole) and acetone

[6] F. Chapman, P. G. Owston, and D. Woodcock, *J. Chem. Soc.*, 1949, 1647.

[7] F. J. Brockman, D. C. Downing, and G. F. Wright, *Canad. J. Res.*, 1949, **27***B*, 469.

[8] R. N. Jones and G. D. Thorn, *Canad. J. Res.*, 1949, **27***B*, 828.

[9] L. Goodman, *J. Amer. Chem. Soc.*, 1953, **75**, 3019.

[10] G. J. Karabatsos and R. A. Taller, *J. Amer. Chem. Soc.*, 1964, **86**, 4373.

(30 ml.). Addition complete (15 min.), the mixture was diluted with water, and insoluble material was collected; removal of acetone from the filtrate, under diminished pressure, gave a second crop. The insoluble residue obtained by washing the crude product (32·6 g.) with hot acetone was percolated with acetone, to yield the *bicyclic nitramine* (II) (12·5 g., 30%) as plates, m. p. 181—183° (Found: C, 31·4; H, 5·5; N, 33·5; basic N, 6·6. $C_{11}H_{22}N_{10}O_8$ requires C, 31·3; H, 5·25; N, 33·2; basic N, 6·6%).

TABLE 2

N-Alkyl derivatives of 1,5-dinitro-1,3,5-triazacyclo-octane

R in RNH_2	Product	Yield (%)	Form	Solvent	M.p.	
Me	(Ic)	67	Plates	Me_2CO–Pet	125—136°	(lit.,[2b] 141–143)
Et	(Id)	50	,,	MeOH	114—120	
Pr^i	(Ie)	31	,,	,,	109—116	
Bu^n	(If)	74	,,	Me_2CO–Pet	80—95·5[a]	
cyclo-C_6H_{11}...	(Ig)	52	Needles	MeOH	114—121	(lit.,[2b] 144—145[b])

	Found (%)					Required (%)			
Compound	C	H	N	*M*	Formula	C	H	N	*M*
(Ic)	33·1	6·0	32·1		$C_6H_{13}N_5O_4$	32·9	6·0	32·0	
(Id)	36·2	6·5	30·1		$C_7H_{15}N_5O_4$	36·0	6·5	30·0	
(Ie)	38·9	7·3	29·2		$C_8H_{17}N_5O_4$	38·9	6·9	28·3	
(If)	41·0	7·4	27·1	270	$C_9H_{19}N_5O_4$	41·4	7·3	26·8	261
(Ig)	45·9	7·4	24·3		$C_{11}H_{21}N_5O_4$	46·0	7·4	24·4	

[a] Solid-phase change (giving needles) at 79°. [b] Decomp.

Careful addition of light petroleum to the solution of the acetone-soluble portion of the crude product gave the *amine* (Ih) (12·7 g., 31%) as laths, m. p. 146—149° (Found: C, 29·1; H, 5·4; N, 35·2. $C_5H_{11}N_5O_4$ requires C, 29·3; H, 5·4; N, 34·1; basic N, 6·8%; *M*, 205), $\nu_{max.}$ 3310 (N–H) cm.$^{-1}$ Recrystallisation (from acetone) yielded plates, m. p. 148·5—150° (Found: C, 29·65; H, 5·65; N, 34·9; basic N, 6·85%; *M*, 205·5), $\nu_{max.}$ 3410 (N–H) cm.$^{-1}$ In acetone, both crystal forms gave identical i.r. spectra.

Reactions of 1,5-*Dinitro*-1,3,5-*triazacyclo-octane* (Ih).—p-*Nitrobenzoylation and acetylation.* By conventional methods, the amine was converted into the N-p-*nitrobenzoyl derivative*, laths (from acetone–light petroleum), m. p. 242—243·5° (Found: C, 40·7; H, 4·2; N, 23·3. $C_{12}H_{14}N_6O_7$ requires C, 40·7; H, 4·0; N, 23·7%), $\nu_{max.}$ 1680 (C=O) cm.$^{-1}$, and the N-*acetyl derivative*, plates (from acetone–light petroleum), m. p. 196—197° (Found: C, 33·8; H, 5·4; N, 28·6. $C_7H_{13}N_5O_5$ requires C, 34·0; H, 5·3; N, 28·3%), $\nu_{max.}$ 1680 (C=O) cm.$^{-1}$

Hydrochloride of 1,5-*dinitro*-1,3,5-*triazacyclo-octane.* Hydrogen chloride was passed into a cooled solution of the amine (Ih) in acetone, to yield the *salt* as a white solid, m. p. 66—70° (Found: C, 24·6; H, 6·3; N, 28·3. $C_5H_{12}ClN_5O_4$ requires C, 24·9; H, 5·0; N, 30·0%). Attempted recrystallisation (from methanol–benzene) gave an oil.

1,3,5-*Trinitro*-1,3,5-*triazacyclo-octane* (Ij).—The amine (Ih) was treated with nitric acid in the usual manner,[3] to furnish the trinitramine (Ij) (69%), needles (from acetone–light petroleum), m. p. 170—172° (lit.,[2a] 164—166°) (Found: C, 24·5; H, 4·1; N, 33·7%; *M*, 247·5. Calc. for $C_5H_{10}N_6O_6$: C, 24·0; H, 4·0; N, 33·6%; *M*, 250), $\lambda_{max.}$ (MeOH) 234 mμ (ε 15,400), crystal density 1·708 g./c.c. When nitric acid–acetic anhydride was used the yield was 72%. The trinitramine was also prepared by the action of nitric acid or nitric acid–acetic anhydride on the bicyclic nitramine (II) (yields were 40 and 27%, respectively).

Oils, showing carbonyl absorption, were obtained by nitrolysis of 3-methyl- (Ic) and 3-n-butyl-1,5-dinitro-1,3,5-triazacyclo-octane (If) in nitric acid–acetic anhydride at 40°. Under similar conditions in presence of ammonium nitrate, the 3-cyclohexyl derivative (Ig) afforded the trinitramine (Ij) (5%).

1,5-*Dinitro*-3-*nitroso*-1,3,5-*triazacyclo-octane* (Ik).—Each substrate was added to a mixture of sodium nitrite, sulphuric acid, and water,[3] to yield the *nitrosamine* (Ik), needles (from acetone–ethanol), m. p. 187—187·5° (Found: C, 25·7; H, 4·4; N, 35·4%; *M*, 236. $C_5H_{10}N_6O_5$ requires C, 25·6; H, 4·3; N, 35·9%; *M*, 234), $\lambda_{max.}$ (MeOH) 237, (Me_2CO) 376 mμ (ε 14,100 and 52). The nitrosamine was prepared from the following derivatives of 1,5-dinitro-1,3,5-triazacyclo-octane (% yield in parentheses): amine (Ih) (72), bicyclic nitramine (II) (85), 3-ethoxymethyl- (Ib) (86), 3-methyl- (Ic) (9), and 3-n-butyl- (If) (1); no water-insoluble products were obtained from 3-ethyl- (Id), 3-isopropyl- (Ie), and 3-cyclohexyl-derivatives (Ig).

Oxidation of the nitrosamine with cold hydrogen peroxide-nitric acid [7] afforded the trinitramine (92%).

1,3-*Dinitro*-1,3-*diazacyclohexane*.— Trimethylenedinitramine (16·4 g.) was added to a stirred, cooled (0°) solution of paraformaldehyde (6 g.) in 87% sulphuric acid (250 ml.), following Goodman's directions.[9] After 10 min. the mixture was poured on ice, giving the *dinitramine* (14·5 g., 83%) as a white solid which crystallised from ether (percolation) forming plates, m. p. 84·5—86·5° with solid-phase change (birefringent to isotropic) at 77—78° (Found: C, 27·4; H, 4·9; N, 31·9%; *M*, 178·5. $C_4H_8N_4O_4$ requires C, 27·3; H, 4·6; N, 31·8%; *M*, 176), $\lambda_{max.}$ (MeOH) 241 mμ (ε 8900), crystal density 1·580 g./c.c.

1,3-*Dinitro*-1,3-*diazacycloheptane*.—Treatment of tetramethylenedinitramine [11] with paraformaldehyde–sulphuric acid, in a similar manner, furnished the homologous *dinitramine* (84%), plates (from ether), m. p. 108° with solid-phase change (birefringent to isotropic) at 102·5—103° (Found: C, 31·8; H, 5·5; N, 29·3%; *M*, 195. $C_5H_{10}N_4O_4$ requires C, 31·6; H, 5·3; N, 29·5%; *M*, 190), $\lambda_{max.}$ (MeOH) 239 mμ (ε 13,260).

N.m.r. Spectra.—These were measured in dimethyl sulphoxide solution (20% w/v) on a Perkin-Elmer R10 spectrometer operating at 60 Mc./sec.; chemical shifts from tetramethylsilane are shown in Table 1.

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ESSEX. [5/859 *Received, August 9th*, 1965]

[11] M. P. J. Dekkers, *Rec. Trav. chim.*, 1890, **9**, 96.