43. *Synthesis of Bis-2,2,2-trinitroethylnitrosamine.*

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2,2,2-Trinitroethanol does not undergo the expected Mannich condensation with hydroxylamine or with methylenediamine. The product from the reaction with hydroxylamine is bis-2,2,2-trinitroethylnitrosamine. Methylenediamine decomposes in the presence of trinitroethanol to yield a mixture of ammonium chloride, ammonium nitroform, and bis-2,2,2-trinitroethylamine. When this ternary mixture reacts with acetic anhydride–nitric acid, bis-2,2,2-trinitroethylnitrosamine is formed, instead of the nitramine.

2,2,2-Trinitroethanol undergoes Mannich condensation with ammonia to give bis-2,2,2-trinitroethylamine (I) in high yield.[1] A similar reaction between formaldoxime and a mixture of nitroform and formaldehyde, with the formation of bis-2,2,2-trinitroethylhydroxylamine (II), has also been reported.[2] The condensation of trinitroethanol and methylenediamine was reported[3] to give 1,1,1,7,7,7-hexanitro-3,5-diazaheptane (III) which, upon nitration, was said to yield 1,1,1,3,5,7,7,7-octanitro-3,5-diazaheptane (IV).

We believe, from the present work, that the compounds claimed to be bis-2,2,2-trinitroethylhydroxylamine and 1,1,1,3,5,7,7,7-octanitro-3,5-diazaheptane are in fact the same compound, bis-2,2,2-trinitroethylnitrosamine (V), which has not been previously reported.

[1] Schenk and von der Forst, B.I.O.S. report HEC 5475.

[2] Farago, George Washington University Progress Report No. 12.

[3] Carleton and Frankel, Aerojet Quarterly Progress Report No. 682.

$$\left.\begin{array}{ll} R\cdot CH_2\cdot NH\cdot CH_2\cdot R & (I) \\ R\cdot CH_2\cdot N(OH)\cdot CH_2\cdot R & (II) \\ R\cdot CH_2\cdot NH\cdot CH_2\cdot NH\cdot CH_2\cdot R & (III) \\ R\cdot CH_2\cdot N(NO_2)\cdot CH_2\cdot N(NO_2)\cdot CH_2\cdot R & (IV) \\ R\cdot CH_2\cdot N(NO)\cdot CH_2\cdot R & (V) \end{array}\right\} \quad [R = C(NO_2)_3]$$

Reaction of Formaldoxime and Nitroform.—Formaldoxime and nitroform reacted, with or without formaldehyde, in the presence of sulphuric acid to yield a heavy oil which decomposed spontaneously with evolution of nitrous fumes. After adhering nitroform had been removed from the remaining yellowish solid, the product, m. p. 85·2—86·2°, gave correct analytical results for bis-2,2,2-trinitroethylnitrosamine. The yield was increased markedly by preparing the formaldoxime *in situ* from formaldehyde and hydroxylamine sulphate.

The analytical results (C, 13·0; H, 1·1; N, 30·3; 0, 55·7%; *M*, 375 established the empirical formula as $C_4H_4N_8O_{13}$ which was consistent with its being bis-2,2,2-trinitroethylnitrosamine and not bis-2,2,2-trinitroethylhydroxylamine ($C_4H_5N_7O_{13}$ requires C, 13·4; H, 1·4; N, 27·3; O, 57·9%; *M*, 359).

The presence of an *N*-nitroso-group was established by examination of the ultraviolet (u.v.) spectrum (Fig. 1); in non-polar solvents the spectrum showed fine structure with $\lambda_{max.}$ at 380 mμ, whereas in polar solvents the fine structure was lost and $\lambda_{max.}$ was shifted towards the blue end of the spectrum. This behaviour is characteristic of nitrosamines containing strongly electronegative groups (Fig. 2),[4,5] *e.g.*, bis-trifluoroethylnitrosamine, and also di-(2-bromo-2,2-dinitroethyl)nitrosamine, which was prepared by Klager's method.[6]

The compound was not hydrolysed to the amine by acid nor oxidised by trifluoroperacetic acid. It reacted with nitric acid to yield bis-2,2,2-trinitroethylnitramine.

Bis-2,2,2-trinitroethylnitrosamine was also synthesised by direct nitrosation of the amine (i) by White's [7] method with dinitrogen tetroxide, and (ii) by using sodium nitrite in trifluoroacetic acid–trifluoroacetic anhydride.

It was not possible to determine the mechanism by which the nitrosamine was formed because the intermediate oil was too unstable to permit characterisation; this oil was induced to crystallise at low temperature but the white solid which separated inflamed spontaneously and exploded. The u.v. spectrum of the oil was examined in the 360—400 mμ region; the characteristic fine structure due to the *N*-nitroso-group was not evident until the solution had aged for 3 weeks.

Reaction between Methylenediamine and 2,2,2-Trinitroethanol.—Carleton and Frankel [3] reported the synthesis of 1,1,1,3,5,7,7,7-octanitro-3,5-diazaheptane (IV) from methylenediamine:

$$CH_2(NH\cdot CHO)_2 \xrightarrow{1} CH_2(NH_2\cdot HCl)_2 \xrightarrow{2} \underset{(III)}{CH_2[NH\cdot CH_2\cdot C(NO_2)_3]_2} \xrightarrow{3} \underset{(IV)}{CH_2[N(NO_2)\cdot CH_2\cdot C(NO_2)_3]_2}$$

1, HCl. 2, NaOAc–$C(NO_2)_3\cdot CH_2\cdot OH$. 3, Ac_2O–HNO_3.

By repeating their method a white crystalline solid, having the reported melting point and correct analysis, was obtained. However, the u.v. and infrared (i.r.) spectra * of this compound were identical with those of the compound characterised by us as bis-2,2,2-trinitroethylnitrosamine (Figs. 1—3), and also with those reported by Carleton and Frankel.[3]

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* D.M.S. 11,943.

[4] Haszeldine and Jander, *J.*, 1954, 691.
[5] Haszeldine and Mattinson, *J.*, 1955, 4172.
[6] Klager, *J. Org. Chem.*, 1958, **23**, 1519.
[7] White, *J. Amer. Chem. Soc.*, 1955, **77**, 6008.

Investigation of the intermediate revealed that it was not 1,1,1,7,7,7-hexanitro-3,5-diazaheptane (III) but a mixture of the ammonium salt of nitroform and bis-2,2,2-trinitroethylamine, together with a considerable amount of chloride ion. We also found that the method used by Carleton [3] for the synthesis of methylenediamine dihydrochloride differed from the original method of Knudsen,[8] and it always gave material contaminated with much ammonium chloride.

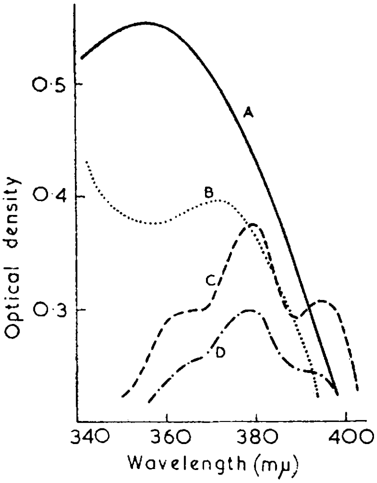

FIG. 1. Ultraviolet spectrum of bis-2,2,2-trinitroethylnitrosamine (V) in A, ethanol; B, acetonitrile; C, carbon tetrachloride; D, chloroform.

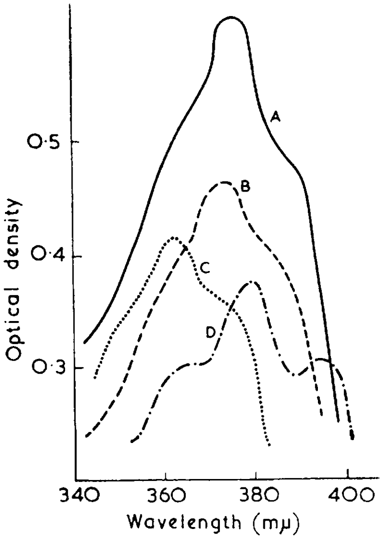

FIG. 2. Ultraviolet spectra of nitrosamines R·N(NO)·R′.

A, $R = R' = CH_2{\cdot}C(NO_2)_2{\cdot}Br$; B, $R = CH_2{\cdot}CF_3$, $R' = CH_2{\cdot}C(NO_2)_3$; C, $R = R' = CH_2{\cdot}CH_3$; D, $R = R' = CH_2{\cdot}C(NO_2)_3$ (V), in A, chloroform; B, methylene chloride; C and D, carbon tetrachloride.

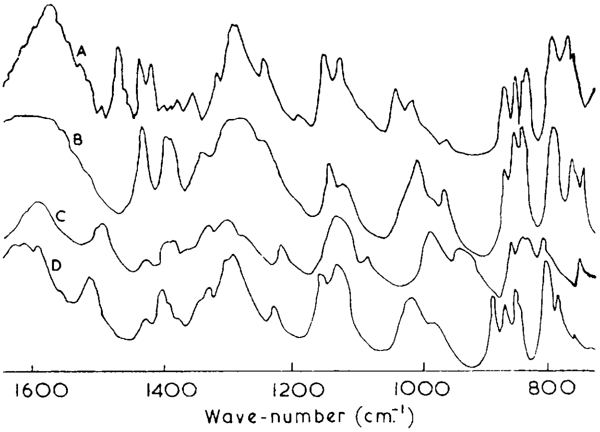

FIG. 3. Infrared spectra of bis-2,2,2-trinitroethylnitrosamine and similar compounds.

A, Bis-2,2,2-trinitroethylamine; B, Bis-2,2,2-nitroethylnitramine; C, Bis-2-bromo-2,2-dinitroethylnitrosamine; D, Bis-2,2,2-trinitroethylnitrosamine (V).

By using Knudsen's method,[8] a pure sample of methylenediamine dihydrochloride was obtained. When this reacted with 2,2,2-trinitroethanol, the product was bis-2,2,2-trinitroethylamine (I). It is therefore apparent that, in aqueous solution and in the presence of 2,2,2-trinitroethanol, the diamine decomposes to yield ammonia which condenses with the 2,2,2-trinitroethanol. This reaction predominates, and prevents Mannich condensation between the alcohol and the diamine.

The nitration of pure bis-2,2,2-trinitroethylamine (I) in acetic anhydride–nitric acid yielded bis-2,2,2-trinitroethylnitramine containing no nitrosamine. It is surprising that the presence of the contaminants resulting from the synthesis used by Carleton and Frankel [3] should cause nitrosation in such a strong nitrating mixture as acetic anhydride–nitric acid. In order to explain this anomaly, a series of mixtures containing bis-2,2,2-trinitroethylamine was nitrated under standard conditions. When the amine was mixed with nitroformate ion and with chloride ion then the nitrosamine was formed in good yield. If either of these ions alone, or other combinations of ions, was used then treatment with acetic anhydride–nitric acid afforded the nitramine. The nitramine was also formed if sodium nitrite was added to the nitrating acid, but the product always contained 20—30% of the nitrosamine. When dinitrogen tetroxide was added to the nitrating acid, however, nitration was completely suppressed and a high yield of pure nitrosamine was obtained.

Although a mixture of acetic anhydride and nitric acid has been used as a nitrating agent for many years, very little is known of the mechanism of its action. That the mixture can also react as a nitrosating agent, in the presence of chloride ion, has been shown by Wright.[9] However, we have shown that chloride ion alone was not sufficient to cause nitrosation of bis-2,2,2-trinitroethylamine.

Since both the nitrosonium and nitronium ion could be present in the nitrating mixture, nitrosation could take place either by preferential destruction of the nitronium ion or by an artificial increase in the amount of nitrosonium ions. Neither of these possibilities was strongly indicated by the experimental evidence. Bis-2,2,2-trinitroethylnitrosamine was very stable towards nitric acid and, once formed, was not oxidised under the reaction conditions employed.

EXPERIMENTAL

Bis-2,2,2-trinitroethyl-nitramine and -nitrosamine were normally identified by i.r. and u.v. spectroscopic methods, as differences in the elemental analyses for various mixtures of the two compounds were so slight as to be comparable with the sensitivity of determination. Each of the compounds could contain significant amounts of the other with very little lowering of the melting point. Molecular weight determinations were by Clark's isothermal distillation method; [10] the solvent used was methylene chloride.

Materials.—The nitric acid used was of 99·7% purity and contained no nitrous acid. It was prepared by distillation from a mixture of equal volumes of conc. sulphuric acid and 98% nitric acid at 30—40 mm. The acid was stored below 0° and had a useful life of 3—4 weeks. The acetic anhydride, b. p. 139—141°, was distilled shortly before use. Nitroform and 2,2,2-trinitroethanol were prepared from tetranitromethane by Marans and Zelinsky's method.[11]

Bis-2,2,2-trinitroethylamine.—To a slurry of 2,2,2-trinitroethanol (15 g.) in water (12 ml.) aqueous ammonia (*d* 0·88, 2·0 ml.) was added dropwise. The mixture was set aside at room temperature and shaken occasionally. After 1 hr. the crystals which had formed were filtered off, and the filtrate was treated with more aqueous ammonia (3—4 drops); this procedure was repeated until crystals no longer formed. The combined precipitates were washed with water until the washings were colourless and then air-dried to afford bis-2,2,2-trinitroethylamine (11·5 g., 81%), m. p. 108° (decomp.). This material was pure enough for most puıposes. A portion was crystallised from chloroform (recovery 85%) to yield the amine, m. p. 111—112°

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[8] Knudsen, *Ber.*, 1914, **47**, 2698.

[9] Wright *et al.*, *Canad. J. Chem.*, 1948, **26**B, 89.

[10] Clark, *Ind. Eng. Chem.*, 1941, **13**, 820.

[11] Marans and Zelinsky, *J. Amer. Chem. Soc.*, 1950, **72**, 5329.

(decomp.) (Found: C, 14·05; H, 1·35; N, 28·60. Calc. for $C_4H_5N_7O_{12}$: C, 14·0; H, 1·45; N, 28·55%). The material slowly decomposed in contact with air.

Attempted Synthesis of Bis-2,2,2-trinitroethylhydroxylamine.—Nitroform (3 g.) was added, dropwise, to a stirred suspension of formaldoxime (0·45 g.) in 60% aqueous sulphuric acid (15 ml.). After 48 hr. at room temperature the yellow oil, which had formed, spontaneously decomposed to give a yellow solid. The solid was washed with water, dried, and crystallised from chloroform (charcoal) to yield crystals of *bis-2,2,2-trinitroethylnitrosamine* (0·3 g., 16%), m. p. 85·2—86·2°, alone and in admixture with a sample prepared by the action of nitrogen tetroxide on the amine (Found: C, 12·95; H, 1·25; N, 29·5%; *M*, 371. $C_4H_4N_8O_{13}$ requires C, 12·9; H, 1·05; N, 30·1%; *M*, 372). By preparing the formaldoxime *in situ* and controlling the decomposition of the intermediate oil by cooling in an ice-bath, the yield of pure material was increased to 36%.

Bis-2,2,2-trinitroethylnitrosamine.—(*a*) Bis-2,2,2-trinitroethylamine (1·7 g.) was mixed with sodium nitrite (0·69 g.). The mixed solids were added, during 15 min., to a mixture of trifluoroacetic acid (25 g.) and trifluoroacetic anhydride (19·5 g.). The mixture was stirred for a further 15 min. and then poured into ice–water. The precipitate (1·45 g., 78%) was washed with water, dried, and shown by i.r. and u.v. spectroscopy to be pure bis-2,2,2-trinitroethylnitrosamine. (*b*) Bis-2,2,2-trinitroethylamine (5·13 g.) was added to a mixture of anhydrous sodium acetate (3·6 g.), glacial acetic acid (40 ml.), and dinitrogen tetroxide (redistilled from P_2O_5; 2·2 ml.). The addition was completed in 10 min. with the temperature maintained at 15—20°. The mixture was allowed to warm to room temperature, during 1 hr., and was then poured into ice–water to yield bis-2,2,2-trinitroethyl nitrosamine (5·2 g., 93%), m. p. 85° (Found: C, 13·1; H, 1·15; N, 30·0%).

Attempted Synthesis of 1,1,1,3,5,7,7,7-Octanitro-3,5-diazaheptane, using Carleton and Frankel's Method.[3]—Methylenediformamide (63·6 g.) was added to stirred concentrated hydrochloric acid (75 ml.) at 12°. The solution was set aside for 12 hr. and the precipitate then filtered off, washed with ice-cold water, and dried. This material (31·1 g.), m. p. 230—240° (decomp.) [lit., 260° (decomp.)] was assumed to be methylenediamine dihydrochloride. A sample (14·8 g.) was dissolved in methanol (430 ml.) and treated with 2,2,2-trinitroethanol (45 g.). Sodium acetate (18·9 g.) in methanol (230 ml.) was then added dropwise, and the solution set aside at room temperature for 18 hr. The solvent was removed under reduced pressure and the residual solid extracted with alcohol and with hot acetone. The extracts were concentrated to give an unstable yellow solid (45 g.), m. p. 102—105°. A portion of this intermediate (20 g.) was added with stirring at 5° to a mixture of 99·7% nitric acid (103 ml.) and acetic anhydride (103 ml.). The mixture was allowed to warm to room temperature during 15 min. and was then poured on to ice. The precipitate was crystallised twice from carbon tetrachloride–light petroleum to afford a crystalline solid (8·1 g.), m. p. 83·9—84·1°, alone and in admixture with bis-2,2,2-trinitroethylnitrosamine (Found: C, 13·05; H, 1·2; N, 30·0%).

Methylenediamine Dihydrochloride.—Methylenediformamide (41·5 g.) was dissolved in conc. hydrochloride acid (270 ml.) and set aside at room temperature until crystals of *methylenediamine dihydrochloride* had separated (30·5 g., 63%), m. p. 260° (decomp.) (Found: C, 10·2; H, 6·85; N, 23·35%; Equiv. 59·0; $CH_8Cl_2N_2$ requires C, 10·1; H, 6·7; N, 23·55%; Equiv. 59·5).

Reaction of Methylenediamine Dihydrochloride with 2,2,2-Trinitroethanol.—The diamine dihydrochloride reacted with 2,2,2-trinitroethanol, as in the previous experiment, to yield bis-2,2,2-trinitroethylamine (16·5 g.), m. p. 101—103°. Examination of the i.r. spectrum showed that the material was substantially pure and that it contained no ammonium nitroform. The intermediate was nitrated in the usual way to give a white solid (7·8 g.), m. p. 80—82°, which was shown by u.v. analysis to contain no nitrosamine. The solid was crystallised from carbon tetrachloride to yield bis-2,2,2-trinitroethylnitramine (3 g.), m. p. 92—93°.

Nitration of Mixtures of Bis-2,2,2-trinitroethylamine with Other Reagents.—Bis-2,2,2-trinitroethylamine was gently mixed with the other reagents using a bone spatula on filter paper. The mixture was then added, in small portions, to a nitrating mixture which had previously been prepared by the dropwise addition of 99·7% nitric acid (8·7 ml.) to acetic anhydride (8·7 ml.). The temperature was kept at 0—5° during the preparation of the nitrating mixture and at 15—20° during the addition, by the use of a carbon dioxide–solvent cooling bath. In an experiment with dinitrogen tetroxide, the reagent was added to the nitrating acid before the addition of the amine. The presence of nitrosamine in the products was shown by the u.v. spectra of solutions (1·5 g./l.) in carbon tetrachloride at 360—400 mμ. Mixtures of the nitrosamine and the nitramine could be accurately analysed by determination of the molecular extinction coefficient at 380 mμ.

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