

Reaction of Hexamine and Hexamine Dinitrate with Nitric Acid and Trifluoroacetic Anhydride in Liquid Sulfur Dioxide

RUSSELL REED, JR.

Received October 1, 1957

The action of nitric acid or mixtures of nitric acid and acetic or trifluoroacetic anhydride upon hexamine¹⁻³ or hexamine dinitrate³⁻⁷ has been studied. However, the action of mixtures of nitric acid and trifluoroacetic anhydride upon hexamine (I) dissolved in sulfur dioxide has not been investigated. Liquid sulfur dioxide was found to dissolve large quantities of I; treatment of this solution with a mixture of nitric acid and trifluoroacetic anhydride resulted in the formation of 1-trifluoroacetyl-3,5-dinitro-1,3,5-triazacyclohexane (II) in good yield. This nitramine has not been previously reported and apparently is not formed when hexamine is treated with nitric acid-trifluoroacetic anhydride mixtures.⁸ The structure of the trifluoroacetyl derivative (II) was confirmed by its formation from 3,5-dinitro-3,5-diazapiperidinium nitrate (PCX) and trifluoroacetic anhydride as well as by the titration of II with 0.1*N* alkali. Three moles of sodium hydroxide were consumed per mole of II with the formation of one mole each of disodium methylenedinitramine and sodium trifluoroacetate and, presumably, two moles of formaldehyde although the latter was not determined in a quantitative manner. The trifluoroacetyl compound (II) was inert to a mixture of nitric acid and trifluoroacetic anhydride although II "fumed-off" after being boiled in 99% nitric acid for ten minutes; ammonium nitrate was the only product isolated.

The action of trifluoroacetic anhydride upon a suspension of hexamethylenetetraammonium dinitrate (HADN) in liquid sulfur dioxide at -30° resulted in the formation of a pasty material (III) which was unstable and could not be obtained as a solid. However, when III was treated with methyl or ethyl alcohols there was obtained the 1-methoxymethyl- (IV) and 1-ethoxymethyl-3,5-dinitro-

1,3,5-triazacyclohexane (V), respectively, as well as small quantities of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and of II. The same products were obtained when the solvent sulfur dioxide was omitted in the nitrolyses but the subsequent isolation of IV and V was difficult because of the presence of pasty, amorphous solids. These compounds had been reported by Dunning and Dunning⁹ to result from the action of the alcohols upon the unstable oil which they obtained by allowing nitric acid to react with hexamine at low temperatures. Wright and co-workers³ obtained the ethoxy derivative V by the action of ethanol upon 1-acetoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (VI) (see below).

In the present work it was found that hot alcoholic solutions of IV and V produced 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT).² The other products of this rearrangement have not been determined. A mixture of trifluoroacetic acid and trifluoroacetic anhydride which contained a small amount of nitric acid converted the methyl derivative IV to the 1-trifluoroacetoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (VII), a crystalline solid which, however, slowly evolved trifluoroacetic acid upon standing. Aqueous sodium hydroxide rapidly degraded VII with the formation of disodium methylenedinitramine, sodium trifluoroacetate, and formaldehyde. The ester VII was also isolated when a sulfur dioxide suspension of HADN was treated with a mixture of trifluoroacetic anhydride, nitric and trifluoroacetic acids. Methanol rapidly transformed the ester VII to the unstable 1-hydroxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (VIII), which was reconverted to VII by the action of trifluoroacetic anhydride. When a 2:1 mixture of nitric acid and trifluoroacetic anhydride was allowed to react with VII, there was isolated 1-nitroxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (IX), a crystalline solid which slowly decomposed on storage; IX is a sensitive and brisant explosive. Sodium acetate in acetic acid readily converted IX to the acetate VI which Wright³ had prepared by the acetolysis of methylene-bis-1-[3,5-dinitro-1,3,5-triazacyclohexane].

The formation of only a small amount of the trifluoroacetyl derivative II in the nitrolysis of HADN may be due to the reluctance of this salt to undergo trifluoroacetylation as compared to hexamine. The nitrogen-trifluoroacetyl linkage once formed is not nitrolyzed (as was demonstrated by the inertness of II to nitric acid-trifluoroacetic anhydride mixtures) and would therefore be expected in the product. Liquid sulfur dioxide has also been employed successfully in other nitrolyses.¹⁰

(1) G. C. Hale, *J. Am. Chem. Soc.*, **47**, 2754 (1925).

(2) W. J. Chute, D. C. Downing, A. F. McKay, G. S. Myers, and G. F. Wright, *Can. J. Res.*, **B 27**, 218 (1949).

(3) W. J. Chute, A. F. McKay, R. H. Meen, G. S. Myers, and G. F. Wright, *Can. J. Res.*, **B 27**, 503 (1949).

(4) A. Henning, German Patent 104,280 (1899).

(5) E. Herz, Swiss Patent 88,759 (1920); *Chem. Zentr.*, **92**, IV, 926 (1921).

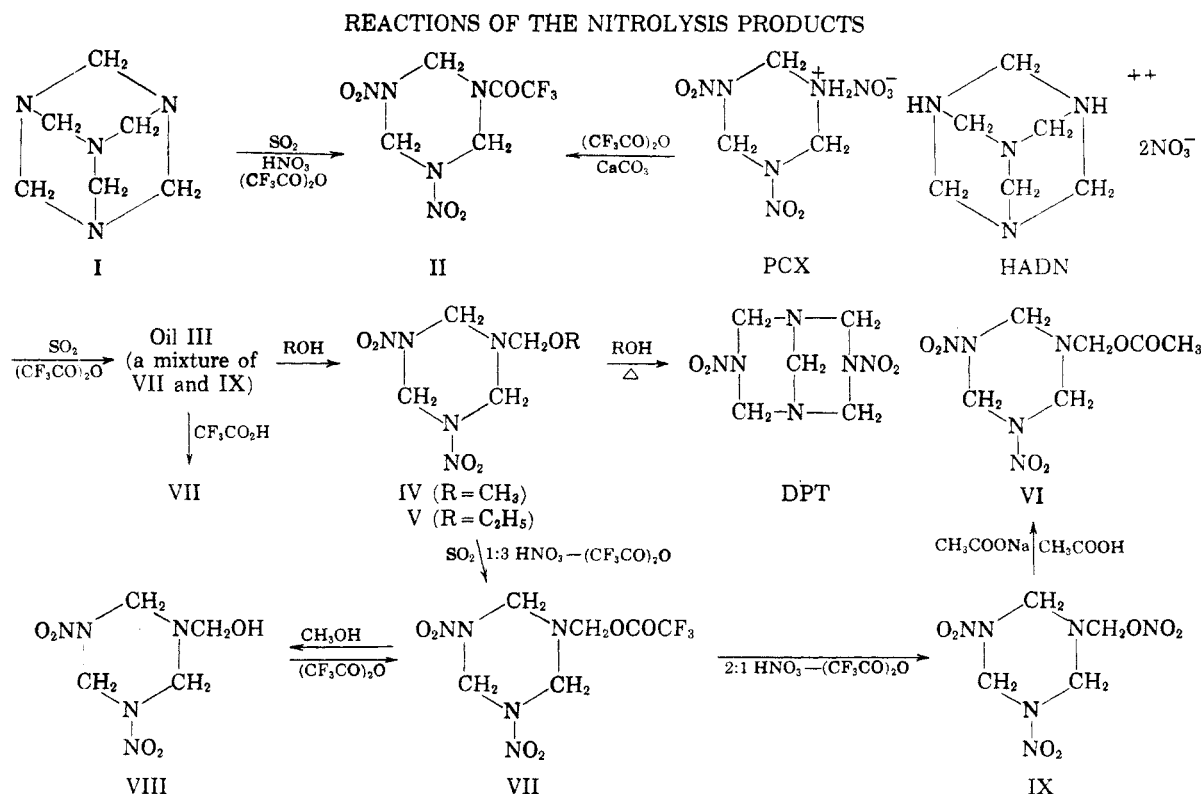
(6) W. E. Bachmann and J. C. Sheehan, *J. Am. Chem. Soc.*, **71**, 1842 (1949).

(7) W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton, and L. B. Scott, *J. Am. Chem. Soc.*, **73**, 2772 (1951).

(8) R. Reed, *J. Am. Chem. Soc.*, **78**, 801 (1956).

(9) K. W. Dunning and W. J. Dunning, *J. Chem. Soc.*, 2920 (1950).

(10) To be reported at a later date.



1-Trifluoroacetyl-3,5-dinitro-1,3,5-triazacyclohexane (II). A solution containing 8.00 g. (0.0572 mole) of hexamine and 43 ml. (0.311 mole) of trifluoroacetic anhydride in 150 ml. of sulfur dioxide maintained at -50° was treated with 15 ml. (0.357 mole) of colorless 99.7% nitric acid. After standing 30 min. at -50° , the sulfur dioxide was removed under reduced pressure leaving a clear colorless oil. The oil was poured into 100 ml. of ice water to produce II as a sticky solid which was dissolved in acetone and the solution slowly poured onto ice to yield 13.3 g. (85%)¹² of II as an easily filterable solid, m.p. $129-131^{\circ}$. Recrystallization from ethylene chloride gave 11.1 g., m.p. $130-131^{\circ}$; the slow addition of water to a solution of recrystallized II in 99% nitric acid produced fine needles, m.p. $131-132^{\circ}$.

Anal. Calcd. for $C_6H_{10}F_3N_3O_5$: C, 21.99; H, 2.21; N, 25.64. Found: C, 22.21; H, 2.45; N, 25.59.

An acetone solution of II was titrated with 0.1N standard sodium hydroxide using a Beckman Model H2 pH meter. The end point occurred at a pH of 11.1 (in 50% by volume aqueous acetone); neut. equiv. 91 (calcd. 91.0 for 3 equiv. per mole of II). The titrated solution was evaporated and then extracted with ether; evaporation of the ether left crystalline sodium trifluoroacetate, identified by a comparison of its X-ray powder pattern with that of an authentic sample. The residue of the titrated solution was acidified with *N* hydrochloric acid and shaken with 25 ml. of ether; evaporation of the ether gave crystals of methylenedinitramine, m.p. $101-102.5^{\circ}$ (reported¹³ 101°) identified by a comparison of the infrared spectrum with that of an authentic sample. When a solution of II in 99% nitric acid was boiled

(11) All melting points are corrected. The combustion analyses were performed by Mr. Everett Bens of this laboratory.

(12) All yields were calculated upon the assumption that 1 mole of hexamine (I), or of HADN, produced 1 mole of product.

(13) R. C. Brian and A. H. Lamberton, *J. Chem. Soc.*, 1633 (1949).

for 10-20 min. a fume-off occurred; ammonium nitrate was the sole product isolated from the nitric acid residue. Benzylamine and II gave a crystalline addition compound, m.p. 115° (gas evol.).

Anal. Calcd. for $C_{12}H_{16}F_3N_6O_5$: C, 37.90; H, 3.98; N, 22.10. Found: C, 37.77; H, 4.18; N, 22.05.

Recrystallization from warm 1:1 methylene chloride-ethylene chloride decomposed the compound and gave crystals of II, m.p. $125-127^{\circ}$.

Formation of 1-trifluoroacetyl-3,5-dinitro-1,3,5-triazacyclohexane (II) from 3,5-dinitro-3,5-diazapiperidinium nitrate (PCX) and trifluoroacetic anhydride. A mixture of 1.00 g. (0.00417 mole) of PCX,¹⁴ 1.0 g. (0.010 mole) of calcium carbonate and 20 ml. of trifluoroacetic anhydride was refluxed for 20 hr. and filtered. Evaporation of the filtrate left 0.20 g. (18%) of crude II as a crystalline residue, m.p. $120-125^{\circ}$; recrystallization from 0.5 ml. of methanol yielded 0.13 g. of II, m.p. $130-131^{\circ}$, identified by a comparison of its infrared spectrum with that of II prepared from hexamine. Extraction of the calcium carbonate precipitate with 5.0 ml. of boiling acetone resulted in the isolation of 0.36 g. of crystalline 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), m.p. $202-203^{\circ}$ (dec.), identified by a comparison of its infrared spectrum with that of authentic material.

1-Methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (IV). A suspension of 10.0 g. (0.0376 mole) of hexamethylenetetraammonium dinitrate in 75 ml. of sulfur dioxide maintained at -30° was treated with 40.0 g. (0.187 mole) of trifluoroacetic anhydride. After standing 3 min., the salt dissolved. The clear colorless solution was then evaporated at reduced pressure (water aspirator) to yield an oily residue which upon treatment with 30 ml. of methanol rapidly precipitated 5.05 g. (61%) of IV as fine needles, m.p. 136° (gas evol.); m.p. $137.5-138.0^{\circ}$ (reported⁹ 134°) after recrystallization from a large volume of ethyl ether. The mother liquor from crude IV was evaporated to a volume of 5.0 ml. and allowed to stand several days at 3° . There was deposited 1.03 g. (10%) of (II) m.p. $130-131^{\circ}$, identified by a com-

(14) A. Vroom and C. Winkler, private communication.

parison of its infrared spectrum with that of the sample prepared from hexamine. The mixture melting point of II prepared from hexamine and that of II from HADN was not depressed.

When HADN was treated with a 20-molar excess of trifluoroacetic anhydride the salt slowly dissolved. After standing 2 hr. the clear solution was evaporated at reduced pressure to yield a colorless oil which did not become solid upon trituration with ether. The oil was dissolved in methanol and the solution was cooled to 0°. The 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (IV) soon crystallized; yield 63%.

A solution of 0.30 g. of IV in 99.5% nitric acid was poured onto ice to yield 0.20 g. (67%) of RDX, m.p. 201–202° (dec.).

When a solution of IV was refluxed in methanol or ethanol for 2 hr. and the solution allowed to stand 20 hr. at room temperature, there was produced a crystalline precipitate of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DPT) m.p. 207–208° (dec.) (reported² 208°) which was identified by a comparison of the infrared spectrum with authentic material.

1-Ethoxy-3,5-dinitro-1,3,5-triazacyclohexane (V) was prepared in the same manner as IV using absolute ethanol; yield 58%; m.p. 117–118° (after recrystallization from ethyl ether) (reported² 117°). The dropwise addition of water to an acetone solution of 1.0 g. (0.43 mole) of V precipitated 0.75 g. (81%) of crystalline DPT, m.p. 208° (dec.), which was identified by a comparison of the infrared spectrum and X-ray powder pattern with those of authentic material. Refluxing an ethanol solution of V for 3 hr. also gave DPT on cooling.

1-Trifluoroacetoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (VII). To a suspension of 10.0 g. (0.376 mole) of HADN in a solution containing 150 ml. of liquid sulfur dioxide and 42.0 g. (0.20 mole) of trifluoroacetic anhydride which was maintained at –60° was added 3.16 ml. of colorless 99.7% nitric acid. The solution was warmed to –45°; after 3 min. all of the HADN had dissolved. The mixture was allowed to stand a total of 10 min. at –45° and then evaporated under reduced pressure. When the volume of liquid had been reduced by one half, crystals began to form. A small quantity of the solid was removed and identified as RDX by a comparison of its infrared spectrum with that of authentic material. Complete evaporation of the solvent left a crystalline solid, 11.7 g., m.p. 120–150° (dec.), which was dissolved in 100 ml. hot ethylene chloride to yield, on cooling, 2.14 g. (26%) of RDX, m.p. 203–204° (dec.). The mother liquor was evaporated to a volume of 20 ml. and cooled to 0° which caused the crystallization of 5.60 g. (49%) of crude VII, m.p. 132–140° (dec.); m.p. 153–154° (dec.) after five recrystallizations from ethylene dichloride containing 2% of trifluoroacetic acid. The infrared spectrum of VII exhibited absorption maxima at 5.60 (trifluoroacetate carbonyl), 6.25, 7.91 (nitramino), 8.8, 10.6, 11.96, 13.05 μ ; the nitroxy absorption at 5.9–6.1 μ was absent.

Anal. Calcd. for $C_6H_8F_3N_5O_6$: C, 23.77; H, 2.66; N, 23.10. Found: C, 23.59; H, 2.71; N, 22.93.

The trifluoroacetyl derivative VII was obtained in 53%

yield when the methoxy derivative IV was nitrolyzed as above.

The trifluoroacetate VII was insoluble in water but soluble in 50% aqueous acetone; the latter solution was acidic to Congo red test paper. Aqueous alkali rapidly attacked VII with the formation of the calculated amount of sodium trifluoroacetate and disodium methylenedinitramine (which upon acidification yielded methylenedinitramine in 75% yield. A solution of VII in 1:1 acetone-methanol was heated for 5 min. and then cooled to 0°. A crystalline precipitate of 1-hydroxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (VIII) was obtained, m.p. 130–134° (dec.), which decomposed after standing several hours. VIII exhibited an absorption at 2.95 μ (OH) in the infrared. The m.p. was raised to 136–137° (dec.) after recrystallization from methylene chloride. Trifluoroacetic anhydride converted VIII to the trifluoroacetate VII in 30% yield.

1-Nitroxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (IX). To 15 ml. of 99.7% nitric acid at –10° was added 2.49 g. (0.0100 mole) of the trifluoroacetate (VII). The mixture was immediately poured into 100 ml. of ether, maintained at –70°, which resulted in the formation of a pasty solid that solidified upon scratching with a glass rod. Filtration gave 1.98 g. (79%) m.p. 120–130° of the crude nitrate ester IX. Four recrystallizations from methylene chloride raised the m.p. to 150–151° (violent dec.); prominent infrared absorption maxima: 5.95–6.00 (nitroxy), 6.25, 7.98–8.0 μ (nitramino). When IX was allowed to stand in cold water in which it was initially insoluble, there was formed after 3 days a gelatinous precipitate which could not be crystallized; the solution was acidic and gave a positive test for nitrate (nitron reagent).

Anal. Calcd. for $C_6H_8N_5O_7$: C, 19.05; H, 3.20; N, 33.33. Found: C, 19.30; H, 3.05; N, 33.71.

From the mother liquors of IX there was isolated a compound which was presumably the nitrate salt of IX, m.p. 145–147° (dec.). The salt was initially soluble in water to yield an acid solution; a gelatinous precipitate soon formed from which no pure substances were isolated. The solution gave a positive test for nitrate. A mixture m.p. of IX and the nitrate salt was depressed to 120–130° (dec.).

Anal. Calcd. for $C_6H_8N_7O_{10}$: C, 15.24; H, 2.88; N, 31.11. Found: C, 14.98; H, 2.80; N, 31.30.

1-Acetoxyethyl-3,5-dinitro-1,3,5-triazacyclohexane (VI). To a solution of 3.00 g. of fused sodium acetate in 10 ml. of acetic acid was added 2.52 g. (0.0100 mole) of the nitrate ester IX. After standing 16 hr., the solution had deposited large crystals. Filtration yielded 1.70 g. (68%) of the acetate VI, m.p. 149–150° (dec.); m.p. 151–152° (dec.) (reported² 143.7–144.7°) after two recrystallizations from methylene chloride; prominent infrared absorption maxima: 5.72 (acetate carbonyl), 6.35, 7.8–8.2 (nitramino), 8.43, 8.92, 9.84, 10.52, 10.77, 11.73, and 13.15 μ .

Anal. Calcd. for $C_6H_{11}N_5O_6$: C, 28.92; H, 4.45; N, 28.11. Found: C, 28.76; H, 4.38; N, 28.00.

RESEARCH DEPARTMENT, CHEMISTRY DIVISION
ORGANIC CHEMISTRY BRANCH
U. S. NAVAL ORDNANCE TEST STATION
CHINA LAKE, CALIF.