Nitration and Nitrosation Reactions of 7-Nitro-1,3,5-Triaza-adamantane and Derivatives

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Nitration and nitrosation reactions of 7-nitro-1,3,5-triaza-adamantane and some derivatives are described. The products are *N*-nitro- and *N*-nitroso-amines, respectively. The reactions are considered to be related to those of hexamethylenetetramine and its derivatives.

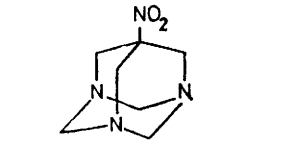
RECENTLY the reactions of 7-nitro-1,3,5-triaza-adamantane (I) to give other 7-substituted 1,3,5-triaza-adamantanes [1-5] and some 1,3,7-triazabicyclo[3.3.1]-nonane derivatives [3] have been reported. In studies related to the nitrolysis of hexamine,[6] we have investigated some nitration and nitrosation reactions of 7-nitro-1,3,5-triaza-adamantane (I), and report the results of these preliminary investigations.

The reaction of an aqueous solution of 7-nitro-1,3,5-triaza-adamantane (I) with concentrated nitric acid at 0—5 °C gives the mononitrate (IIa). The reaction of compound (1) with methyl iodide in refluxing methanol, followed by treatment with powdered silver nitrate, produces 1-methyl-7-nitro-3,5-diaza-1-azonia-adamantane nitrate (IIb).

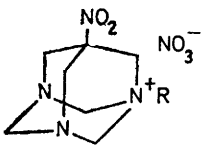
If compound (I) is added to fuming nitric acid below −40 °C, and then cold ethanol or water is slowly added

[1] N. W. Gabel, U.S.P. 3,301,854/1967.
[2] E. B. Hodge and C. D. Hurd, Ger. Offen. 1,956,234/1970.
[3] E. B. Hodge, *J. Org. Chem.*, 1972, **37**, 320.
[4] V. Galik, M. Safar, Z. Kafka, and S. Landa, *Coll. Czech. Chem. Comm.*, 1975, **40**, 442.
[5] A. T. Nielsen, *J. Heterocyclic. Chem.*, 1975, **12**, 161.
[6] A. R. Farminer, Ph.D. Thesis, University of Surrey, 1974.

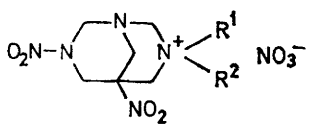
dropwise below −30 °C, a white precipitate forms after a few minutes, then redissolves. After completion of the addition, when the solution is left at room temperature, a white precipitate settles out. This product is considered to be 5,7-dinitro-1,7-diaza-3-azoniabicyclo-[3.3.1]nonane nitrate (IIIa). Treatment of the nitrate (IIIa) with nitric acid–ammonium nitrate at room



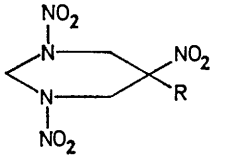
(I)



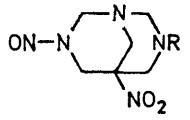
(II) a; R = H
b; R = Me



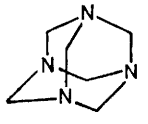
(III) a; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = CH_2OH$



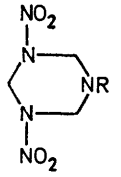
(IV) a; $R = CH_2NH_3^+ NO_3^-$
b; $R = CH_2O{\cdot}NO_2$
c; $R = CH_2OMe$
d; $R = CH_2{\cdot}OAc$
e; R = H
f; $R = CH_2NH^+(CH_2OH)_2 NO_3^-$
g; $R = CH_2NH_2^+CH_2OH NO_3^-$



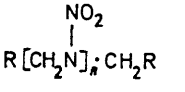
(V) a; R = NO
b; $R = NO_2$



(VI)



(VII) a; $R = NO_2$
b; R = NO
c; $R = H_2^+ NO_3^-$



(VIII) a; $R = O{\cdot}NO_2$
b; R = OMe
c; R = OAc

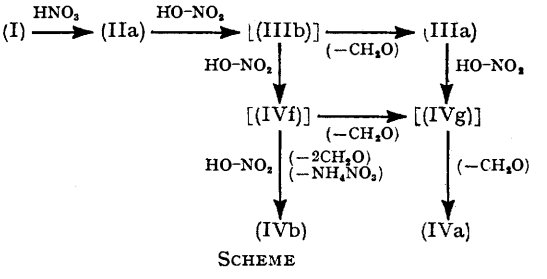
temperature for 60 h, followed by addition of the mixture to ice–water, gives 5-ammoniomethyl-1,3,5-trinitro-1,3-diazacyclohexane nitrate (IVa). This compound is also obtained as the only product, in higher yield, from the reaction of compound (I) with nitric acid–ammonium nitrate under similar conditions. Addition of compound (I) to an excess of fuming nitric acid at 0—10 °C with stirring and cooling, followed by addition of the mixture to crushed ice, gives 1,3,5-trinitro-5-nitro-oxymethyl-1,3-diazacyclohexane (IVb). At lower addition temperatures mixtures containing (IVa and b) are obtained, as revealed by the ^1H n.m.r. analysis.

The reaction of 7-nitro-1,3,5-triaza-adamantane with aqueous sodium nitrite under acidic conditions at *ca.* 0—10 °C produces 5-nitro-3,7-dinitroso-1,3,7-triazabicyclo[3.3.1]nonane (Va). Under similar conditions the compound (IIIa) gives 3,5-dinitro-7-nitroso-1,3,7-triazabicyclo[3.3.1]nonane (Vb). Addition of aqueous sodium nitrite to a cold 7-nitro-1,3,5-triaza-adamantane nitration mixture produces an intense yellow colouration, which appears to indicate the formation of an *N*-nitroso-amine. However, attempted isolation of this product in air resulted only in its decomposition.

The reaction of compound (IVb) with boiling methanol or boiling sodium acetate–acetic acid does not give the expected methoxymethyl (IVc) or acetoxymethyl (IVd) derivative; instead only starting material can be recovered. Although compound (IVa) may be recrystallised from methanol or ethanol, refluxing with water gives (IVe), which can be isolated from the cooled solution.

From the reaction characteristics and the nature of the products formed it is possible to formulate several reaction schemes for the nitration of 7-nitro-1,3,5-triaza-adamantane (I). The complexity of the products (IIIa), (IVa), and (IVb) suggests that these reactions involve a stepwise scission process, since it is difficult to envisage their formation from fragments. A possible set of reaction pathways is illustrated in the Scheme. It is considered that the route (I) ⟶ (IIa) ⟶⟶ (IIIa) ⟶⟶ (IVa) is possible for the nitration of (I) in nitric acid–ammonium nitrate. However, the reaction of (I) with an excess of fuming nitric acid probably does not involve the formation of (IIIa), but rather proceeds *via* an intermediate such as (IIIb).

The nitration and nitrosation reactions of 7-nitro-1,3,5-triaza-adamantane (I) show obvious parallels with those of hexamine (VI),[7-9] although differences are also shown.[9,10] Whereas the products of nitration of (I) are predominantly 1,3,5-trinitro-1,3-diazacyclohexanes (IV), those of hexamine under similar conditions are



SCHEME

1,3-dinitrohexahydro-*s*-triazines (VII) or linear *N*-nitro-amines (VIII; $n = 3$ or 4).[9] The reaction of (VIIIa; $n = 4$) with boiling methanol or boiling sodium acetate–acetic acid gives the methoxymethyl (VIIIb; $n = 4$) and acetoxymethyl (VIIIc; $n = 4$) derivatives, respectively.[11]

These differences in reactivity are presumably related

[7] T. Urbanski, 'Chemistry and Technology of Explosives,' vol. 3, Pergamon, Oxford, 1967.
[8] G. F. Wright, 'The Chemistry of the Nitro and Nitroso Groups,' Part 1, ed. H. Feuer, Wiley, New York, 1969, ch. 9.
[9] J. A. Bell and I. Dunstan, *J. Chem. Soc.* (*C*), 1969, 1559.
[10] W. E. Bachmann and N. C. Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 2777.
[11] J. A. Bell and I. Dunstan, *J. Chem. Soc.* (*C*), 1969, 1556.

to the greater stability of 7-nitro-1,3,5-triaza-adamantane (I) than of hexamine (VI): the latter reacts violently with nitric acid at room temperature, whereas the former does not. The stability shown by 7-nitro-1,3,5-triaza-adamantane and its nitration products may be due to the presence of the C–NO_2 grouping. There are sufficient similarities between these nitration reactions of 7-nitro-1,3,5-triaza-adamantane and comparable reactions of hexamine to suggest that the mechanisms may be comparable, and thus to support the view that such reactions involve a stepwise scission process.[11]

EXPERIMENTAL

Nitric acid–ammonium nitrate solvent was supplied by E.R.D.E., Waltham Abbey. ^{1}H N.m.r. spectra were recorded [solvent $(CD_3)_2SO$ containing Me_4Si] with a Varian HA-100 instrument operating at 100 MHz. ^{13}C N.m.r. spectra [solvent $(CD_3)_2SO$ containing Me_4Si, in 10 mm o.d. n.m.r tubes] were recorded with a Bruker WH-90 FT instrument operating at 22.64 MHz, with broad band proton decoupling for all samples. I.r. spectra (Nujol mulls) were recorded with a Perkin-Elmer 457 instrument. M.p.s were determined with an Electrothermal apparatus.

7-Nitro-1,3,5-triaza-adamantane (I).—This compound, prepared by the modified method of Hodge [3] from nitromethane, paraformaldehyde, and ammonium acetate in refluxing ethanol, recrystallised from water (charcoal) to give white needles, m.p. 290—310 °C (Found: C, 45.4; H, 6.7; N, 30.3. Calc. for $C_7H_{12}N_4O_2$: C, 45.6; H, 6.5; N, 30.4%), $\nu_{max.}$ 1 550s cm^{-1} (C–NO_2), m.p. and ^{1}H n.m.r. data in agreement with those of other workers.[3-5] Treatment of an aqueous solution of (I) (2 g in 50 ml) with cold (5 °C) concentrated nitric acid, added dropwise with stirring, gives the nitrate (IIa), m.p. 209—210 °C (lit.,[4] 204 °C) (Found: C, 34.8; H, 5.3; N, 29.1. Calc. for $C_7H_{13}N_5O_5$: C, 34.0; H, 5.3; N, 28.3%), δ_H 4.03 (s, N·CH_2·C), 4.49 and 4.79 (dd, *J* 12 Hz, N·CH_2·N), and 6.9 vbr (NH^+). Reaction of (I) (7 g) with methyl iodide (10 g) in refluxing methanol (125 ml) for 1 h followed by treatment with powdered silver nitrate (11 g) gives *1-methyl-7-nitro-3,5-diaza-1-azonia-adamantane nitrate* (IIb) (4 g, 40%) on cooling the filtrate; white platelets, m.p. (from methanol) 239—240 °C (Found: C, 36.6; H, 5.8; N, 27.0. $C_8H_{15}N_5O_5$ requires C, 36.8; H, 5.8; N, 26.8%), δ_H 2.82 (s, N^+·CH_3), 3.78 and 3.92 (dd, *J* 12 Hz, N·CH_2·C), 4.24 (N^+·CH_2·C), 4.34 (s, N·CH_2·N), and 4.73 and 5.01 (dd, *J* 11 Hz, N^+·CH_2·N), δ_C 45.2 (N^+·CH_3), 54.8 (N·CH_2·C), 60.2 (N^+·CH_2·C), 68.0 (N·CH_2·N), 72.6 (C·NO_2), and 78.6 (N^+·CH_2·N).

5,7-Dinitro-1,7-diaza-3-azoniabicyclo[3.3.1]*nonane Nitrate* (IIIa).—Compound (I) (1 g) was added to fuming nitric acid (95%; 16 ml) below −40 °C (solid CO_2–acetone bath) with stirring. Cold ethanol (75 ml) (or cold water) was added dropwise, with the temperature kept below −30 °C. The precipitate which first appeared redissolved on further addition. When set aside at room temperature the mixture deposited *compound* (IIIa) (0.8 g, 53%), white needles, m.p. (from ethanol) 170—171 °C (Found: C, 25.6; H, 4.4; N, 30.0; nitrate,[12] 21.5. $C_6H_{12}N_6O_7$ requires C, 25.7; H, 4.3; N, 30.0; nitrate, 22.1%), $\nu_{max.}$ 2 200—3 000 br and 1 610 m (NH_2^+), and 1 745w cm^{-1} (NO_3^-), δ_H 3.2—5.4 (mm, CH_2) and 8.0 vbr (NH_2^+), δ_C 46.3 (C·CH_2·NH_2^+), 50.6 [C·CH_2·N(NO_2)], 52.1 (C·CH_2·N), 62.7 (N·CH_2·NH_2^+), 67.5 [N·CH_2·N(NO_2)], and 75.4 (C·NO_2).

5-Ammoniomethyl-1,3,5-trinitro-1,3-diazacyclohexane Nitrate (IVa).—Compound (I) (1 g) dissolved in nitric acid–ammonium nitrate (20 ml), was left for 60 h, then added to an excess of ice–water to give the product (IVa) (1.3 g, 76%). Compound (IIIa) (1 g) under the same conditions also gives (IVa) (0.5 g, 45%), white *platelets*, m.p (from ethanol) 145—149 °C (Found: C, 19.6; H, 3.8; N, 31.2; nitrate,[12] 19.1. $C_5H_{11}N_7O_9$ requires C, 19.2; H, 3.5; N, 31.3; nitrate 19.8%), δ_H 3.65 (s, CH_2·NH_3^+), 4.17 and 5.47 [dd, *J* 16 Hz, C·CH_2·N(NO_2)], 5.08 and 7.10 (dd, *J* 15 Hz, N·CH_2·N), and 8.44br (s, NH_3^+), δ_C 40.7 (CH_2·NH_3^+), 48.8 [C·CH_2·N(NO_2)], 58.7 (N·CH_2·N), and 81.7 (C·NO_2).

5-Nitro-oxymethyl-1,3,5-trinitro-1,3-diazacyclohexane (IVb).—Compound (I) (1 g) was added to nitric acid (95%; 16 ml) at 0—10 °C (ice-bath) with stirring. The solution was stirred at this temperature for 0.5 h, then added to an excess of ice–water; a white precipitate was deposited. The mixture required stirring for a further 1 h to stabilise the *product* (IVb) (0.45 g, 28%), m.p. (from methanol) 129—130 °C (Found: C, 20.3; H, 2.9; N, 27.8. $C_5H_8N_6O_9$ requires C, 20.3; H, 2.7; N, 28.4%), $\nu_{max.}$ 1 660s cm^{-1} (ONO_2), δ_H 5.17 and 6.95 (dd, *J* 14 Hz, N·CH_2·N), 4.29 and 5.33 [dd, *J* 16 Hz, C·CH_2·N(NO_2)], and 5.18 (s, CH_2·ONO_2), δ_C 48.3 [C·CH_2·N(NO_2)], 59.4 (N·CH_2·N), 70.5 (CH_2·ONO_2), and 82.6 (C·NO_2).

1,3,5-Trinitro-1,3-diazacyclohexane (IVe).—Compound (IVa) (0.5 g) was refluxed for 1.5 h in water. The solution was then filtered hot and left to cool, to give compound (IVe) (0.2 g, 57%), white *platelets*, m.p. 137—140 °C (Found: C, 21.9; H, 3.1; N, 31.6. $C_4H_7N_5O_6$ requires C, 21.7; H, 3.2; N, 31.7%), δ_H 5.49 and 6.79 (dd, *J* 14 Hz, N·CH_2·N), 5.20 (d) and 4.37 [dd, *J* 15 Hz, C·CH_2·N(NO_2)], and 5.35 (m, CH), δ_C 47.2 [C·CH_2·N(NO_2)], 60.0 (N·CH_2·N), and 75.6 (C·NO_2).

5-Nitro-3,7-dinitroso-1,3,7-triazabicyclo[3.3.1]*nonane* (Va).—Compound (I) (1 g) was dissolved in glacial acetic acid (20 ml) and then water (180 ml) was added. The solution was cooled to 5 °C (ice-bath) and cold aqueous sodium nitrite (2 g in 50 ml) was added. After *ca.* 0.25 h a precipitate of (Va) (1.0 g, 80%) had been deposited. Compound (Va) was also prepared (72% yield) from the reaction of aqueous sodium nitrite (2 g in 50 ml) with a solution of (I) (1 g) in ice–water (250 ml) containing concentrated hydrochloric acid (10 ml). Compound (Va) may be prepared by the slow addition of (I) (1 g) to a stirred solution of sodium nitrite (2 g) in dilute sulphuric acid (10 ml) and water (10 ml) at 10 °C (ice-bath), followed by addition of the resulting mixture to an excess of ice–water; yield 0.7 g (56%). The product may be recrystallised from methanol to give yellowish *needles*, m.p. 207—209 °C (Found: C, 31.3; H, 4.4; N, 36.9. $C_6H_{10}N_6O_4$ requires C, 31.3; H, 4.4; N, 36.5%).

3,5-Dinitro-7-nitroso-1,3,7-triazabicylo[3.3.1]*nonane* (Vb).—Compound (IIIa) (1 g) was gradually added to a solution of sodium nitrite (2 g) in dilute sulphuric acid (10 ml) and water (10 ml) at 10 °C (ice-bath) with stirring, to give compound (Vb) (0.4 g, 45%), white *needles*, m.p. (from ethanol) 194—196 °C (Found: C, 29.4; H, 3.9; N, 33.9. $C_6H_{10}N_6O_5$ requires C, 29.3; H, 4.1; N, 34.2%).

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[12] W. C. Cope and J. Barab, *J. Amer. Chem. Soc.*, 1917, **39**, 504.