Synthesis of 1,3,5,7-Tetraazacyclooctane Derivatives (1)

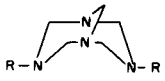
H. Yoshida, G. Sen and B. S. Thyagarajan

Chemistry Department, University of Idaho, Moscow, Idaho 83843

Received April 16, 1973

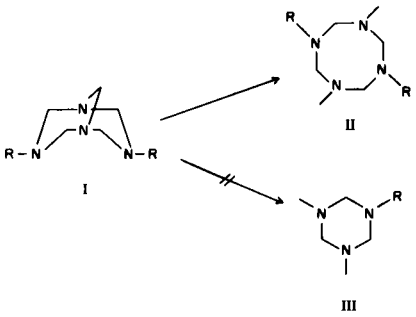
Tetraazaadamantane was converted under mild conditions into 1,3,5,7-tetraazabicyclo[3.3.1]-nonane derivatives. The latter were transformed selectively into 1,3,5,7-tetraazacyclooctane derivatives avoiding the formation of 1,3,5-triazacyclohexane compounds.

Recently, there has been a revival of interest in the chemistry of tetraazabicyclononane derivatives (I) of the following type (2-8).



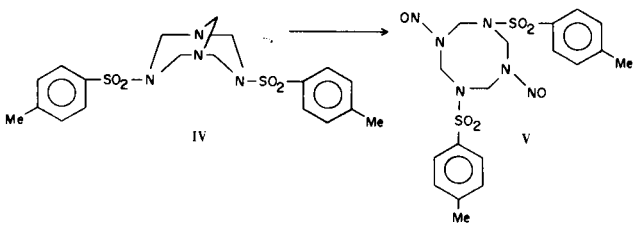
I

The primary interest in these studies was to obtain a tetraazacyclooctane derivative (II) to the exclusion of any triazine products (III), starting with compounds of type I.



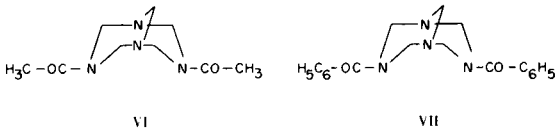
II III

In an earlier publication (2) we described the successful conversion of 3,7-di(*p*-tolylsulfonyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonane (IV) into 1,5-di(*p*-tolylsulfonyl)-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (V) exclusively.

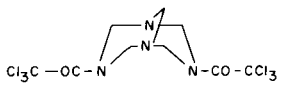


IV V

However, compounds of the type V suffered from the limitation that the arylsulfonyl function could not be readily removed without concomitant cleavage of the ring structure. In the present study, we describe an improvement in this situation by using compounds 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3.3.1]nonane (VI), 3,7-dibenzoyl-1,3,5,7-tetraazabicyclo[3.3.1]nonane (VII) and 3,7-di(trichloroacetyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonane (VIII).

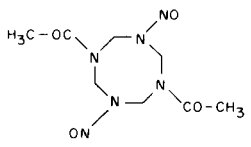


VI VII

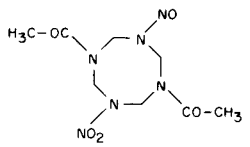


VIII

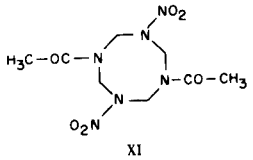
These compounds were obtained by earlier published procedures (5,5a) in yields of 90%, 10% and 5.1%, respectively. The use of dinitrogen tetroxide in the cleavage of bicyclononane derivatives like VI was described by Wright and co-workers (7). These investigators employed a large excess of 98% nitric acid and dinitrogen tetroxide to convert VI to X in yields of 75%. However, the product was described as a photosensitive compound (which we show it is not) and no elemental analyses were given. We reacted VI with dinitrogen tetroxide alone as reagent *and* medium to give a 62% yield of 1,5-diacetyl-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (IX). When acetone or acetic acid was used as solvent in this reaction, yields of IX decreased. However, when the same reaction was carried out in methylene chloride or chloroform, almost instantly a solid precipitate of XII appeared. This solid was extremely hygroscopic and gave a positive nitron test for nitrate ion. An acid-base titration gave a molecular weight of 307. Further treatment of XII with a large excess of 99% nitric acid converted it in good yields into 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (XI) (7). The latter was also formed by reaction of IX with 99% nitric acid.



IX

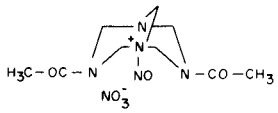


X



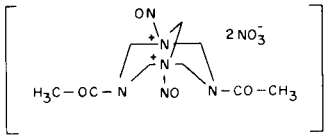
XI

Based on the properties of XII described by us, we suggest the following structure for it:



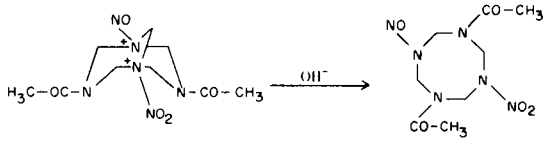
XII

The quaternary salt XII presumably reacts with more dinitrogen tetroxide to give a diquaternary salt XIII which is not isolable. It undergoes hydrolytic cleavage to give the eight-membered ring derivative IX.



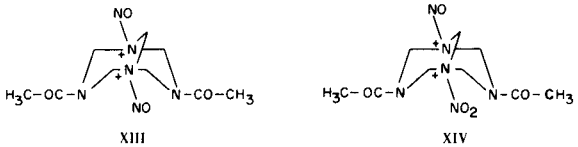
XIII

Interestingly, the decomposition of XIII in water is very slow, taking nearly 12 hours, whereas in aqueous alkali such decomposition occurs much faster. We therefore suggest the possibility of a sequence VI → XII → [XIII] → IX in the entire transformation. While we have isolated XII owing to its extreme insolubility in nonpolar solvents, and characterized it, efforts to trap or identify XIII have proven futile. Despite this difficulty we present in the sequel additional data which strongly support a dication intermediate such as XIII. Treatment of VI with fuming nitric acid afforded a 76% yield of 1,5-diacetyl-3-nitro-7-nitroso-1,3,5,7-tetraazacyclooctane (X). This structure was confirmed, in addition to its elemental analyses and spectral data, by its facile conversion to XI upon treatment with excess 99% nitric acid. While fuming nitric acid and VI gave exclusively X, reaction with a combination of reagents like dinitrogen tetroxide and sulfuric acid or fuming nitric acid and sulfuric acid gave mixtures of XI and X, the latter being the major product. Attempted separation of the two products XI and X was unsuccessful owing to their solubility characteristics but the mixture could readily be converted entirely into XI by further reaction with excess 99% nitric acid. It is well known that fuming nitric acid contains dissolved nitrogen tetroxide (11). It is also known that the system dinitrogen tetroxide and sulfuric acid carries the cations NO^+ and $NO_2{}^+$ (10,9). Thus, with two different cations present, the bicyclononane derivative VI has the opportunity of forming a diquaternary salt XIV analogous to XIII, followed by nucleophilic attack on the bridge methylene to generate the tetraazacyclooctane product X.

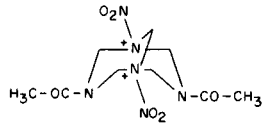


XIV X

In systems like dinitrogen tetroxide and sulfuric acid or fuming nitric acid and sulfuric acid, it is conceivable all the three cations like XIII, XIV and XV are present.

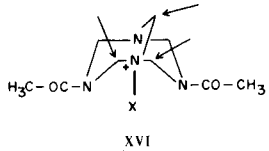


XIII XIV



XV

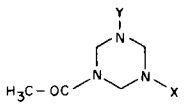
In the presence of excess nitric acid, XIII could be converted into XIV and XV at different rates, while concurrently, nucleophilic attack at the bridge methylene could lead to varying amounts of X and XI. In all of these transformations, it must be emphasized, there was no evidence for the formation of 6-membered ring products at all. Even the very crude reaction mixture showed peaks in the nmr spectrum corresponding only to the tetraazacyclooctanes and none other. This observation adds weight to our postulate that the diquaternary salt is responsible for the selective hydrolytic cleavage.



XVI

A monocation like XVI could suffer attack at other sites as well, as indicated. In the monoquaternary salt, the two methylenes flanking the quaternary nitrogen and

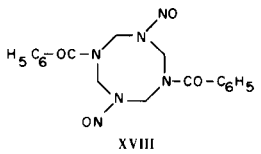
bounded in by the acetamide nitrogens are the most susceptible for nucleophilic attack. Consequently, attack at these sites would rather lead to formation of six-membered ring products (XVII *vide infra*) (12).



XVII

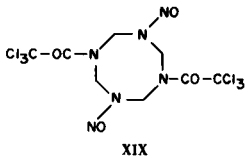
Thus a combination of the two factors *viz.* the reduced basicity (or nucleophilicity) of the 3,7-nitrogens *and* the facile formation of the diquaternary salt, lead to the selective cleavage of the tetraazabicyclo[3.3.1]nonane system to the tetraazacyclooctane products.

The generality of these observations are well demonstrated in the behavior of the bicyclononane derivatives VII and VIII. Reaction of the former with dinitrogen tetroxide gave 1,5-dibenzoyl-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (XVIII).



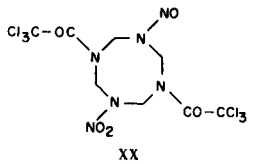
XVIII

Compound VIII under analogous conditions gave 1,5-di(trichloroacetyl)-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (XIX).

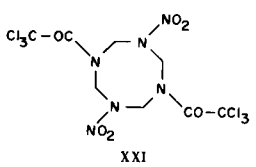


XIX

Reaction of VIII with fuming nitric acid gave 1,5-di(trichloroacetyl)-3-nitro-7-nitroso-1,3,5,7-tetraazacyclooctane (XX) in 82% yield. On further reaction with 99% nitric acid, both XIX and XX gave 1,5-di(trichloroacetyl)-3,7-dinitro-1,3,5,7-tetraazacyclooctane (XXI) in 89% and 91% yields, respectively.

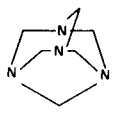


XX

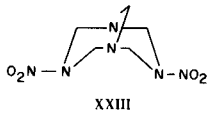


XXI

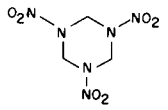
The reactions of 3,7-diacetyl-1,3,5,7-tetraazabicyclo-[3.3.1]nonane thus far described using dinitrogen tetroxide alone or as a solution in sulfuric acid or nitric acid afford the dinitroso derivative IX or the nitro-nitroso derivative X. The latter is then converted by further treatment with 99% nitric acid to the dinitro compound XI. It is therefore to be anticipated that under conditions generating the nitronium ion exclusively, one should directly secure the dinitro derivative XI. In the event, this expectation proved right. Use of metal nitrates and sulfuric acid (10) gave a 73% yield of XI, while a mixture of 70% nitric acid and sulfuric acid (10) gave an even better yield (80%) of the same product. These results again emphasize the selective nature of hydrolytic attack on the bridge methylene carbons. That this result is largely a consequence of masking the nucleophilicity of two of the four nitrogens is exemplified by the contrasting behavior of tetraazaadamantane XXII itself. The latter incorporates four equivalent basic nitrogens and is therefore open to hydrolytic attack at more than one methylene center. When treated with potassium nitrate and sulfuric acid, tetraazaadamantane (XXII) affords a maximum of 25.4% 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (XXIII), and when treated with 99.6% nitric acid, XXII affords a mixture of 1,3,5-trinitro-1,3,5-triazacyclohexane (XXIV) and XXIII (13).



XXII



XXIII



XXIV

EXPERIMENTAL

Melting points are uncorrected. Nmr spectra were recorded on a Varian A-60 spectrometer using tetramethylsilane (TMS) as an internal standard. Mass spectra were determined on a Hitachi-Perkin-Elmer RMU-6E spectrometer.

3,7-Diacetyl-1,3,5,7-tetraazabicyclo[3.3.1]nonane (VI) and 3,7-dibenzoyl-1,3,5,7-tetraazabicyclo[3.3.1]nonane (VII) were prepared according to Gilbert (5,5a).

3,7-Di(trichloroacetyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonane (VIII).

To a stirred solution of 2.8 g. (0.02 mole) of tetraazaadamantane (XXII) and 5.0 g. (0.036 mole) of potassium carbonate in 20 ml. of water was added dropwise 7.2 g. (0.0396 mole) of trichloroacetylchloride over a period of 5 minutes while maintaining the temperature between -5° and 0°. During addition, a white solid separated. After stirring the mixture 5 minutes longer, the solid was filtered and dried. Recrystallization from hot absolute ethanol yielded prisms of VIII, m.p. 212°, yield, 0.43 g. (5.1%).

Anal. Calcd. for $C_9H_{10}Cl_6N_4O_2$: C, 25.80; H, 2.41; N, 13.37. Found: C, 26.07; H, 2.36; N, 13.38.

TABLE I

Reaction of VI with Liquid Dinitrogen Tetroxide to Give IX
(One g. of VI was used in each case).

Experiment No.	Amount of N_2O_4 used (g.)	Solvent (ml.)	Reaction condition	Reaction time	Yield of IX (g.)	% Yield of IX
1	4	-----	room temperature	10 minutes	0.75	62
2	7	-----	ice water cooling	10 minutes	0.45	37
3	7	-----	ice water cooling	20 minutes	0.33	27
4	4	-----	ice water cooling	10 minutes	0.75	62
5	3	AcOH(10)	ice water cooling	2 minutes	0.60	49
6	1.5	AcOH(6)	room temperature	20 seconds	0.72	59
7	1.5	AcOH(6)	ice water cooling	5 minutes	0.49	40
8	1	AcOH(6)	room temperature	30 seconds	0.73	60
9	1.5	Ac_2O(6)	room temperature	2 minutes	0.67	55
10	1	Acetone(11)	ice water cooling	10 minutes	0.55	45
11	0.3	Acetone(16)	ice water cooling	10 minutes	0	0

TABLE II

Nitrolysis of VI With a Solution of Nitric Acid in Sulfuric Acid at 25-30° to Give XI
(Two and twelve one hundredths g. of VI was used in each case)

Experiment No.	% of HNO_3 used	Volume of HNO_3 used (ml.)	Volume of H_2SO_4 (a) used (ml.)	Time for addition (minutes)	Time for Stirring (minutes)	Yield of XI (g)	% Yield of XI	M.p. of XI
1	70	4.2	12	12	60	2.32	80	264-265° dec.
2	70	6	10	12	60	2.13	73.4	265° dec.
3	90	4.2	12	12	60	2.18	75.2	264-265° dec.
4	99	4.2	12	12	48	2.21	76.2	265° dec.
5	99	4.2	12	12	60	2.25	77.6	264-265° dec.
6	99	4.2	12	12	75	2.12	73.1	265° dec.

(a) Specific gravity of sulfuric acid = 1.84.

1,5-Diacetyl-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (IX).

A suspension of 1 g. (0.00472 mole) of VI in 4 g. (0.0434 mole) of liquid dinitrogen tetroxide was stirred at room temperature for 10 minutes. The reaction mixture was then poured into ice water and then neutralized with potassium carbonate. After 12 hours, 0.75 g. (62%) of faint yellow crystals separated out. These were recrystallized from nitromethane to give needles of IX, m.p. 165-167°; M^+ = 258; nmr (δ in DMSO-d_6): 2.18 (6H, Ac), 5.6-6.1 (8H, CH_2).

Anal. Calcd. for $C_8H_{14}N_6O_4$: C, 37.21; H, 5.47; N, 32.54. Found: C, 37.27; H, 5.67; N, 32.39.

The reaction of VI with liquid dinitrogen tetroxide was carried out under different conditions, all of them are summarized in Table I.

Isolation and Investigation of the Monocationic Intermediate (XII).

To a stirred solution of 3.0 g. (0.0142 mole) of VI in 20 ml. of dichloromethane was added dropwise 2 g. (0.0217 mole) of liquid dinitrogen tetroxide while maintaining the temperature between 10 and 11°. The precipitate that appeared immediately was collected by decantation of the solvent and dried in vacuum. It was highly hygroscopic and gave a positive nitron test to show the presence of NO_3^-. Its molecular weight was found to be 307 by acid-base titration using phenolphthalein as indicator, the calculated value for the structure XII being 304.

1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (XI).

To a vigorously stirred solution of 4.2 ml. of 70% nitric acid

TABLE III

Nitrolysis of VI With Potassium Nitrate and/or Sodium Nitrate at 25 to 30° to Give XI
(Two and twelve hundredths g. of VI was used in each case).

Experiment No.	Amount of KNO_3 used (g.)	Amount of $NaNO_3$ used (g.)	Volume of H_2SO_4 (a) used (ml.)	Time for addition (minutes)	Time for stirring (minutes)	Yield of XI (g.)	% Yield of XI	M.p. of XI
1	4.1	0	10	12	60	2	68.9	261° dec.
2	8.2	0	20	12	60	2.1	72.6	261-261.5° dec.
3	8.2	0	20	12	25	1.5	51.7	258.5-259° dec.
4	8.2	0	20	12	75	2.1	72.6	261.5° dec.
5	8.2	0	20	12	90	1.92	66.2	261° dec.
6	8.2	0	20	12	105	1.9	65.5	261.5° dec.
7	4.1	3.4	20	12	60	2.1	72.6	261° dec.
8	0	6.8	20	12	60	2.1	72.6	261° dec.

(a) Specific gravity of sulfuric acid = 1.84.

in 12 ml. of concentrated sulfuric acid (specific gravity = 1.84), 2.12 g. (0.01 mole) of VI was added over a period of 12 minutes, while maintaining the temperature between 25 and 30°. After stirring for one more hour at 25 to 30°, the reaction mixture was poured into 250 ml. of ice water. The solution was made alkaline by adding solid potassium carbonate, the precipitated solid was filtered, washed thoroughly with water and dried, m.p. 264-265° (dec., yield, 2.32 g. (80%). The compound on recrystallization from boiling nitromethane melted at 265° (d) (reported 265.5-266° (7)); nmr (δ in DMSO-d_6): 2.3 (6H, Ac); 5.56 (8H, CH_2).

Anal. Calcd. for $C_8H_{14}N_6O_6$: C, 33.10; H, 4.82; N, 28.96. Found: C, 33.38; H, 4.95; N, 29.11.

The identity of this compound was further confirmed by its conversion to the known 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) by the method due to Wright (7).

Nitrolysis of VI was carried out under different conditions, varying the strength of nitric acid, volume of the acid used and the reaction period. The results are shown in Table II.

Nitrolysis of VI was also effected with sodium nitrate (or potassium nitrate) in sulfuric acid in the same manner as described above. The results are presented in Table III.

1,5-Diacetyl-3-nitro-7-nitroso-1,3,5,7-tetraazacyclooctane (X).

To 20 ml. of red fuming nitric acid was added 2.0 g. (0.00944 mole) of VI over 12 minutes with stirring while maintaining the temperature between 8 and 10°. The whole solid went into solution. The mixture was poured into ice water giving a clean blue solution. The solution was neutralized with potassium carbonate, and the precipitate formed was collected by filtration, washed with water and dried. Recrystallization from nitromethane gave needles of X, m.p. 225-227° (reported 225.2-227.2° (7)), yield, 1.97 g. (76.3%); M^+ = 274; nmr (δ in DMSO-d_6): 2.1-2.3 (6H, Ac); 5.1-6.0 (8H, CH_2).

Anal. Calcd. for $C_8H_{14}N_6O_5$: C, 35.04; H, 5.15; N, 30.64. Found: C, 34.89; H, 5.15; N, 30.42.

The Reaction of VI with Liquid Dinitrogen Tetroxide in Sulfuric Acid.

To a solution of 3 ml. of liquid dinitrogen tetroxide in 10 ml. of concentrated sulfuric acid (specific gravity = 1.84) was added 1.0 g. (0.00472 mole) of VI with stirring and keeping the temperature between 14 and 16°. After stirring for another 15 minutes at 14 to 16° (during this period whole solid went into the solution), the reaction mixture was poured into ice water and the solution neutralized with potassium carbonate to give 1.2 g. of solid, m.p. 243-245°. This product was shown to be a mixture of X (major) and XI from the nmr and mass spectral data. The crude material (0.49 g.) when stirred with excess 99% nitric acid at ice water temperature yielded 0.47 g. of XI giving an overall yield of 84% (calculated on the basis of VI).

The Reaction of VI With a Solution of Red Fuming Nitric Acid in Sulfuric Acid.

To a stirred solution of 25 ml. of red fuming nitric acid in 10 ml. of concentrated sulfuric acid (specific gravity = 1.84) was added 2.0 g. (0.00944 mole) of VI keeping the temperature between 14 and 16°. After stirring for one more minute at 14 to 16°, the reaction mixture was poured into ice water and the solution neutralized with potassium carbonate to give 1.89 g. of a mixture of X (major) and XI.

Conversion of IX and X to XI.

A mixture of IX (0.5 g., 0.00194 mole) and 99% nitric acid (5 ml.) was stirred for 15 minutes at ice water temperature. The reaction mixture was then poured into ice water and solution was made alkaline with potassium carbonate to give 0.56 g. (99%) of XI.

The compound X was similarly treated to yield XI to the extent of 95%.

Attempted Conversion of IX to X.

(a) To a solution of 3 ml. of liquid nitrogen tetroxide in 10 ml. of concentrated sulfuric acid (specific gravity = 1.84), 1 g. (0.00388 mole) of IX was added with stirring over 3 minutes, keeping the temperature between 13 and 17°. The reaction

mixture was stirred for 12 more minutes and quenched by pouring into ice water. Neutralization of the solution with potassium carbonate gave 1.03 g. of solid. The product was identified as XI by mixed m.p. with an authentic sample.

(b) A mixture of IX (0.5 g., 0.00194 mole) and 99% nitric acid (1.5 ml.) was stirred at 10 to 13° for 3 minutes whereby a clear solution was obtained. The whole solution was poured into ice water and neutralized with potassium carbonate to give a solid m.p. 231-243°. This product was identified as a mixture of X (major) and XI, from the nmr and mass spectral data.

1,5-Di(trichloroacetyl)-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (XIX).

A suspension of 0.80 g. (0.00191 mole) of VIII in 5 ml. of liquid dinitrogen tetroxide was stirred in a closed container for 20 hours. The reaction mixture was poured into ice water and the solution was neutralized with potassium carbonate to give a solid precipitate which when recrystallized from nitromethane melted at 234-235°; yield, 0.41 g. (43%); nmr (δ in acetone-d_6): 5.24, 5.88, 6.17, 6.41.

Anal. Calcd. for $C_8H_8Cl_6N_6O_4$: C, 20.65; H, 1.72; N, 18.06. Found: C, 20.53; H, 1.74; N, 18.19.

1,5-Di(trichloroacetyl)-3-nitro-7-nitroso-1,3,5,7-tetraazacyclooctane (XX) Was Prepared Similarly as X.

This compound had m.p. 225-227° (nitromethane), yield, 82%; nmr (δ in acetone-d_6): 5.68, 5.77, 6.15, 6.56.

Anal. Calcd. for $C_8H_8Cl_6N_6O_5$: C, 19.98; H, 1.68; N, 17.48. Found: C, 20.12; H, 1.84; N, 17.23.

The compounds XIX and XX were converted into the corresponding dinitro compound XXI by treatment with 99% nitric acid.

Compound XXI had m.p. 275-278° (nitromethane); nmr (δ in acetone-d_6): 6.05.

Anal. Calcd. for $C_8H_8Cl_6N_6O_6$: C, 19.34; H, 1.62; N, 16.91. Found: C, 19.22; H, 1.56; N, 16.82.

1,5-Dibenzoyl-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (XVIII).

This compound was prepared similarly to IX with the exception that sodium acetate was added to the reaction mixture to reduce the acidity of liquid dinitrogen tetroxide, m.p. 197° (nitromethane), yield, 58%.

Anal. Calcd. for $C_{18}H_{18}N_6O_4$: C, 56.54; H, 4.74; N, 21.98. Found: C, 56.26; H, 4.67; N, 21.94.

3,7-Dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (XXIII).

To a vigorously stirred suspension of 5.1 g. (0.06 mole) of sodium nitrate in 16 ml. of concentrated sulfuric acid (specific gravity = 1.84) was added XXII (2.80 g.) over a period of 20 minutes while maintaining the temperature between 8 and 15°. The reaction mixture was further stirred for another one hour and quenched by pouring into 200 ml. of ice water. The *p*H of the solution was made 6.5 by adding aqueous ammonia solution, whereby 1.11 g. (25.4%) of XXIII precipitated out, m.p. 207-208° dec. (nitromethane) (reported 213°) (14).

Anal. Calcd. for $C_5H_{10}N_6O_4$: C, 27.52; H, 4.58; N, 38.53. Found: C, 27.61; H, 4.56; N, 38.83.

REFERENCES

(1) This work was supported by the U.S. Army Munitions Command, Dover, New Jersey.

(2) H. Yoshida, G. Sen and B. S. Thyagarajan, *J. Heterocyclic Chem.*, 10, 279 (1973).

(3) E. G. Hodge, *J. Org. Chem.*, 37, 320 (1972).

(4) A. Senning, P. Kelly and L. F. Johnson, *Acta Chem. Scand.*, 26, 1663 (1972).

(5) M. Warman, V. I. Siele and E. E. Gilbert, *J. Heterocyclic Chem.*, 10, 97 (1973).

(5a) V. I. Siele and E. E. Gilbert, Private Communication.

(6) H. Tada, *J. Am. Chem. Soc.*, 82, 266 (1960).

(7) E. Aristoff, J. A. Graham, R. H. Meen, G. S. Meyers and G. F. Wright, *Can J. Res.*, 27B, 520 (1949).

(8) J. A. Bell and I. Dunstan, *J. Chem. Soc.*, C, 1559 (1969).

(9) D. J. Millen, *J. Chem. Soc.*, 2600 (1950).

(10) R. J. Gillespie and E. A. Robinson in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press, London and New York, 1965, Chapter, 4, p. 172-174.

(11) F. A. Cotton, G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Second edition 1966, p. 350.

(12) "The monocation isolated as an insoluble solid from dichloromethane was reacted with a variety of nucleophiles like deuterium oxide, deuterium oxide and potassium carbonate, aniline, *n*-butylamine, acetic anhydride and sodium acetate. Under all of these conditions, the product was always an unresolvable complex mixture of a number of products. In no case was a clear cut eight-membered ring product obtainable, in contrast to the case of the dication which gave one single product cleanly which was the tetraazacyclooctane derivative."

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

(14) W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton and L. B. Scott, *J. Am. Chem. Soc.*, 73, 2769 (1951).