X-ray Analysis. A suitable crystal of **8**, 0.25 × 0.25 × 0.13 mm, was obtained by slow recrystallization from acetonitrile. All data were taken at 22 (1) °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters obtained by refinement of the setting angles for 25 reflections with $11 < 2\theta < 25°$ were $a = 16.930$ (5) Å, $b = 17.248$ (2) Å, $c = 6.974$ (1) Å, $\beta = 100.51$ (1)°, $V = 2002$ (1) Å^3, $d_c = 1.388$ g cm^{-3}, and $Z = 4$. The space group was confirmed as $P2_1/n$ by collection and examination of the systematically absent reflections $h0l$, $h + l$ odd and $0k0$, k odd.

Intensity data were collected out to a limit of $2\theta < 50°$ by the Ω–2θ method at a variable scan rate from 3 to 20° 2θ min^{-1}. The scan range was from 2θ(Mo Kα_1) – 0.5° to 2θ(Mo Kα_2) + 0.5°. three standard reflections were remeasured periodically and showed no significant change. Corrections were made for Lorentz and polarization effects, but no absorption correction was necessary ($\mu = 2.86$ cm^{-1} for Mo Kα).

The structure was solved by direct methods with the program MULTAN79.[9] By use of 216 reflections with $E \geq 1.94$, an E map, calculated with the phase set having the best combined figure of merit, yielded 26 of the 29 non-hydrogen atoms. The remaining three atoms and all hydrogen atoms were located in subsequent difference electron density maps.

Refinement was by full-matrix least squares. The function minimized was

$$\Sigma w(|F_o| - K|F_c|)^2$$

where $w^{-1} = \sigma^2(F_o) + (0.03F_o)^2$. Scattering factors and anomalous dispersion corrections for all atoms were from International Tables for X-ray Crystallography.[10] The agreement indices are $R = \Sigma||F_o| - K|F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - K|F_c|)^2/\Sigma wF_o^2)^{1/2}$. Refinement proceeded smoothly and converged to $R = 0.036$ and $R_w = 0.049$ for the 29 non-hydrogen atoms with anisotropic thermal parameters and 18 hydrogen atoms with isotropic thermal parameters. Of the 3517 reflections measured, 2830 had $I > \sigma(I)$ and were included in the calculations. The estimated standard deviation of an observation of unit weight was 1.24. The final scale factor was 2.364 (6). A final difference electron density map contained residual density between –0.36 and +0.27 e/Å^3 but was featureless.

Registry No. **3**, 70940-99-7; **4**, 70660-17-2; **5**, 93454-57-0; **6**, 93454-58-1; **7**, 93454-59-2; **8**, 93454-60-5; **9**, 93454-61-6; **11**, 93454-62-7; **12**, 93454-63-8; **13**, 93454-64-9; *i*-PrOH, 67-63-0.

Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

(9) Computer programs used for this study were part of the Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975, revision 3B, 1980, except this version of MULTAN is from the 1981 SDP user's group tape exchange.

(10) "International Tables fof X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, Chapter 2.

An Alternate Synthesis of Cyclic 1,3-Dinitramines

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Received April 5, 1984

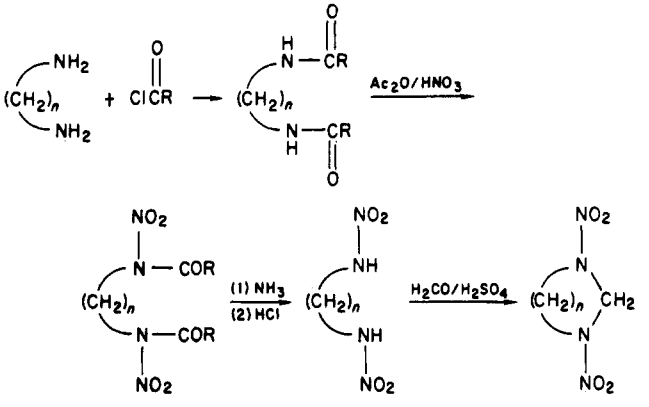
An alternate synthesis for cyclic 1,3-dinitramines has been developed. The new method involves the trapping of an in situ generated cyclic aminal with nitrous acid to generate a cyclic 1,3-dinitrosamine, which is subsequently converted to the cyclic 1,3-dinitramine by treatment with 100% nitric acid or solutions of N_2O_5 in 100% nitric acid. This alternate synthesis is superior for the synthesis of 5- and some 6-membered cyclic 1,3-dinitramines but not for 7-membered compounds.

Introduction

Cyclic 1,3-dinitramines are a potentially important class of energetic materials related to 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX). The first synthesis of a compound of this class was accomplished by Goodman[1] who synthesized 1,3-dinitro-1,3-diazacyclopentane, **1**, from ethylenediamine by the four-step procedure summarized in Scheme I. The same reaction sequence was used by Bell and Dunstan[2] to synthesize both 1,3-dinitro-1,3-diazacyclohexane, **2**, and 1,3-dinitro-1,3-diazacycloheptane, **3**. We have come to refer to this procedure as the "primary nitramine" synthesis of cyclic 1,3-dinitramines.

This procedure, although quite straightforward, suffers from two major problems. First, it requires four discrete steps which means that it is quite time consuming and that the overall yields are frequently not very high. Secondly, when we attempted to apply this procedure to the synthesis of more complicated polynitramines, such as the spirocyclic tetranitramine **4**, the yields for the ring closure step frequently were under 10%. It is well-known that primary nitramines are unstable in strong acid,[3] and it appears that in these cases the ring closure step is slower than the acid-catalyzed decomposition of the primary nitramine reactant.

Scheme I. Primary Nitramine Synthesis of Cyclic 1,3-Dinitramines[a]



[a] $n = 2, 3, 4$.

†Current address: Morton Thiokol Inc., Elkton Division, Elkton, MD 21921.

(1) Goodman, L. *J. Am. Chem. Soc.* **1953**, *75*, 3019.
(2) Bell, J. A.; Dunstan I. *J. Chem. Soc. C* **1966**, 870.
(3) Fridman, A. L.; Ivshin, V. P.; and Novikov, S. S. *Russ. Chem. Rev. (Engl. Transl.)* **1969**, *38*, 640.

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Scheme II. Alternate Synthesis of Cyclic 1,3-Dinitramines via Cyclic 1,3-Dinitrosamines

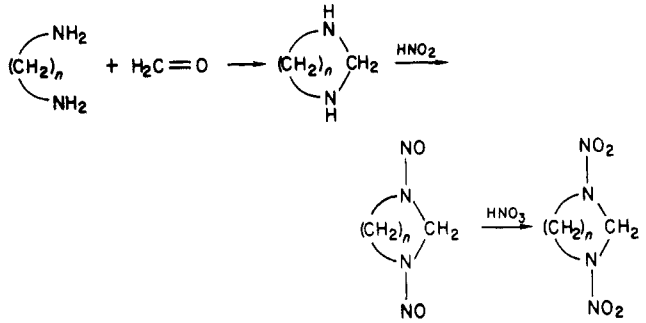
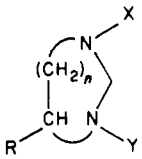
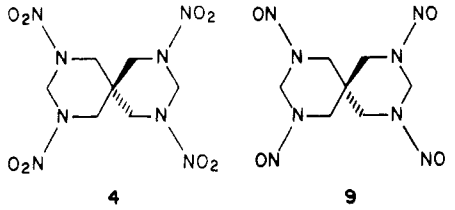


Chart I. Structures of Compounds Studied



	n	R	X	Y		n	R	X	Y
1	1	H	NO_2	NO_2	11	2	CH_3	NO	NO
2	2	H	NO_2	NO_2	12	1	H	NO	NO_2
3	3	H	NO_2	NO_2	13	2	H	NO	NO_2
5	2	H	NO	NO	14	1	CH_3	NO	NO_2
6	2	H	H	H	15	1	CH_3	NO	NO
7	1	H	NO	NO	16	2	CH_3	NO	NO_2
8	3	H	NO	NO	17	2	CH_3	NO	NO
10	1	CH_3	NO	NO	18	1	CH_3	NO	NO_2
					19	2	CH_3	NO	NO_2



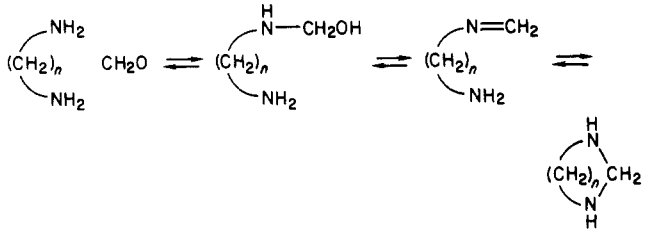
4 9

Because of these problems with the primary nitramine synthesis of cyclic 1,3-dinitramines, we desired to develop an alternate synthesis for this class of compounds which did not suffer from these problems. The route which we chose to explore is summarized in Scheme II. Our reasons for selecting this nitrosamine route were the known conversion of 1,3,5-trinitroso-1,3,5-triazacyclohexane (R-salt) to RDX by Wright and co-workers[4] and our successful conversion of *trans*-1,4,5,8-tetranitroso-1,4,5,8-tetraazadecalin to *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin.[5] The structures of the compounds synthesized in this study are summarized in Chart I.

Results

Since there seemed to be ample precedent for the conversion of nitrosamines to nitramines, we concentrated our initial efforts on the synthesis of cyclic 1,3-dinitrosamines. Examination of the literature showed that only one example of this type of compound was known. Evans[6] had synthesized the $n = 3$ case, **5**, in 20% overall yield starting from 1,3-diaminopropane. This synthesis of **5** was conducted as a two-step procedure. First, the 1,3-diaminopropane was reacted with formaldehyde and the 1,3-diazacyclohexane **6** isolated, and secondly, it was nitrosated

Scheme III. Simplified Scheme for the Reaction of an α,ω-Diamine with Formaldehyde[a]



[a] $n = 2, 3, 4$.

Table I. Yields of 1,3-Dinitroso-1,3-diazacycloalkanes from the Trapping of in Situ Generated 1,3-Diazacycloalkanes

α,ω-diamine	product	yield, %	mp, °C
$H_2N(CH_2)_2NH_2$	7	90	43–44
$H_2N(CH_2)_3NH_2$	5	95	61–63[a]
$H_2N(CH_2)_4NH_2$	8	12	~20
$C(CH_2NH_2)_4$	9	>55	185–186
$H_2NCH_2C(CH_3)HNH_2$	10	93	liquid
$H_2N(CH_2)_2C(CH_3)HNH_2$	11	84	liquid

[a] Lit.[6] mp 61.5–63 °C.

in conventional fashion to give **5**. The main reason for the low overall yield was the very low yield of 28% for the first step. We rationalized that the actual isolation of **11** might not be necessary for the following reasons. In aqueous solution the reaction of an α,ω-diamine with formaldehyde involves a series of equilibria, which are summarized in simplified form in Scheme III. Since Evans had been able to carry out the nitrosation of **6** in aqueous solution, this implied to us that either the equilibrium was established very slowly or that **6** was the thermodynamically favored product of the reaction. In order to determine which of these possibilities was correct, we ran a series of experiments where various α,ω-diamines were allowed to react with 1 equiv of formaldehyde in water for a short period of time. The reaction mixtures were then quenched by adding 2.1 equiv of nitrous acid. After workup, variable yields of the desired cyclic 1,3-dinitrosamines were obtained, as summarized in Table I. One can readily see that good yields of the desired dinitroso compounds are obtained when a five- or six-membered ring is formed but not when a seven-membered ring is formed. This, of course, is in line with the classical work on the relative ease of formation of five-, six-, and seven-membered rings.[7]

Having established that we could synthesize the cyclic 1,3-dinitrosamines, we turned our attention to converting them to the desired cyclic 1,3-dinitramines. Two methods have been developed for converting nitrosamines to nitramines. Emmons showed that pertrifluoroacetic acid would oxidize simple nitrosamines to nitramines.[8] Wright and co-workers found that 98–100% nitric acid would convert R-salt to RDX.[4] This type of reaction has been shown to be a nitrolysis (i.e., NO replaced by NO_2), not an oxidation.[9] This reaction also only works for nitrosamines bearing nitrosamine, nitramine, or dinitro substituents in the β-position.

All attempts to oxidize our cyclic 1,3-dinitrosamines with pertrifluoroacetic acid failed. Fortunately, however, the nitrolysis reactions with nitric acid proved more successful. Somewhat to our surprise, when we ran the reaction of the simple monocyclic 1,3-dinitrosamines with 100% nitric

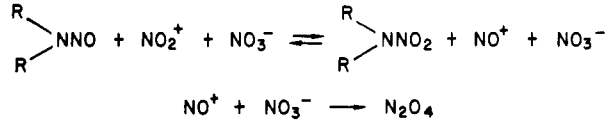
(4) Brockman, F. J.; Downing, D. C.; Wright, G. F. *Can. J. Res. B* **1949**, *27*, 1469.
(5) Willer, R. L. *Propellants, Explos., Pyrotechn.* **1983**, *8*, 65.
(6) Evans, R. F. *Aust. J. Chem.* **1967**, *20*, 1643.
(7) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw Hill Book Co.: New York, **1962**; p 198.
(8) Emmons, W. D. *J. Am. Chem. Soc.* **1954**, *76*, 3468.
(9) Gafurov, R.; Sogomonyan, E. M.; and Eremenko, L. T. *Izv. Akad. Nauk. SSR Shir. Khim. (Engl. Transl.)* **1973**, 2826.

Table II. Products from the Reaction of Cyclic 1,3-Dinitrosamines with 100% HNO_3

1,3-dinitrosoamine	product(s)[a]	yield, %	mp, °C
7	12	80	70–71
5	13	90	72–73
9	4	70	240–245
10	14 and 15	80	liquid
11	16 and 17	85	liquid

[a] New compounds gave satisfactory C, H, and N analysis (±0.3%).

Scheme IV



acid, the products which we initially isolated were the cyclic 1-nitrosamino-3-nitramino compounds **12** and **13** from **7** and **5**, respectively. From the methyl-substituted compounds **10** and **11** mixtures of the two possible nitro-nitroso compounds **14** and **15** and **16** and **17** were isolated. Wright and co-workers made a similar observation in their study of the conversion of R-salt to RDX where they could isolate 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane if the reaction of R-salt with 100% nitric acid was quenched at 0 °C.[4] They found that if the reaction mixture was allowed to warm to room temperature before quenching the product was the completely nitrolyzed RDX. In our case, we found that neither increasing the reaction time nor raising the final reaction temperature resulted in any significant conversion of the nitro-nitroso compounds to the desired dinitramino compounds. However, when the tetranitroso compound **9** was reacted with 100% nitric acid, a good yield of the desired tetranitro compound **4** was obtained. These results are summarized in Table II.

These results suggested to us that a stronger nitrolyzing reagent was needed. We then tried using solutions of N_2O_5 in 100% nitric acid as our nitrolyzing media. The solutions of N_2O_5 were generated by a recently developed electrochemical process.[10] Using the stronger media we were able to isolate good yields of the desired five-membered dinitramines **1** and **18**, but the yields of the six-membered compounds **2** and **19** were very low. The products were, however, still contaminated with some of the nitro-nitroso products. Complete elimination of the nitro-nitroso products could be accomplished by passing a stream of dry nitrogen over the reaction to remove N_2O_4 as it forms during reaction. The N_2O_4 is formed from the reaction of nitrosonium ions with nitrate ions. Removal of the N_2O_4 from the system apparently shifts the equilibrium summarized in Scheme IV. The yields of the nitramines are summarized in Table III. The reason for the low yields of the six-membered compounds **2** and **19** is their decomposition under reaction conditions since an authentic sample of **2** rapidly decomposes when dissolved in 100% HNO_3.

Discussion

The alternate synthesis of cyclic 1,3-dinitramines described in this paper is superior to the conventional primary nitramine synthesis for the synthesis of all five-membered ring and some six-membered ring 1,3-dinitramines studied. It is clearly inferior for seven-membered ring 1,3-dinitramines. Its inferiority for the synthesis of the seven-membered ring compound is clearly due to the fact that the synthesis relies upon the equilibrium between an α,ω-diamine and formaldehyde favoring the cyclic aminal (see Scheme III), which apparently does not occur when a seven-membered ring must be formed. We have in a separate ^{13}C NMR[11] study confirmed that the equilibrium between α,ω-diamines and formaldehyde in water favors the cyclic aminals in those cases where a five- or six-membered ring is formed but not where a seven-membered ring is formed. Our results in this study are consistent with a rapid establishment of the equilibrium between the α,ω-diamine and formaldehyde and a diffusion-controlled nitrosation[12] to give the cyclic 1,3-dinitramines.

Table III. Products from the Reaction of Cyclic 1,3-Dinitrosamines with Solutions of N_2O_5 in 100% Nitric Acid

1,3-dinitrosamine	product[a]	yield, %	mp, °C
7	1	85	132–133 (lit.[1] 132.5–134)
5	2	30	84–86 (lit[2] 84.5–86.5)
9	4	94	240–245
10	18	75	79–80
11	19	>10	77–78

[a] All new compounds gave satisfactory C, H, and N analysis (±0.3%).

The fact that the simple monocyclic cyclic 1,3-dinitrosamines give the cyclic 1-nitroso-3-nitro compounds when treated with 100% nitric acid seems to establish that nitrosamino groups are better at activating nitrosamino groups toward nitrolysis than are nitramino groups. This is in accord with Wright and co-workers'[4] observation that there is a much reduced rate of nitrolysis of the third nitrosamino group in the nitrolysis of R-salt to RDX.

The lower yield of the six-membered compounds as compared to the five-membered compounds in the nitrolysis using the solutions of N_2O_5 in 100% nitric acid seems to be due to the fact that they undergo nitrolysis at a slower rate than the five-membered rings and undergo decomposition faster than the five-membered compounds. That they undergo decomposition faster has been confirmed experimentally.

Experimental Section

Warning! The dinitrosamines described in this paper are either known[13] or suspected carcinogens and should be handled with great care. The dinitramines are energetic materials and should be handled accordingly.

Cyclic 1,3-Dinitrosamines. The α,ω-diamine (0.1 mol) is dissolved in 50 mL of distilled water. This is stirred and 8.2 g of a 37% formaldehyde solution (0.1 mol) is added over 2 min. This solution is stirred for 1 h then 14.5 g of sodium nitrite (0.21 mole) is added. When the sodium nitrite has dissolved, the solution is cooled to <5 °C by means of an ice–water bath and a solution made from 20 g of concentrated hydrochloric acid and 20 g of ice is added in one portion. (**Caution**: In some cases considerable gas evolution occurs at this point). The mixture is stirred for 10 min and the product isolated by either extraction into methylene chloride (3 × 100 mL) (**5**, **7**, **8**, **10**, and **11**) or by filtration (**9**). The solvent is removed at reduced pressure to give the crude product. The results are summarized in Table I.

Reaction of 1,3-Dinitroso-1,3-diazacycloalkanes with 100% Nitric Acid. The dinitrosoamine (10 mmol) is added slowly to 10 mL of well-stirred 100% nitric acid maintained at −35 °C by a dichloroethane–dry ice slush. The dichloroethane–dry ice bath

(10) Harrar, J. E.; Pearson, R. K. *J. Electrochem. Soc.* **1982**, 129.

(11) Willer, R. L.; Moore, D. W., manuscript in preparation.

(12) Casado, J.; Castro, A.; Leis, J. R.; Quintela, M. A. L.; Mosquera, M. *Monatsh. Chem.* **1983**, *114*, 639–646.

(13) Bertram, B.; Habs, M.; Wiessler, M.; Braun, H.; Kretzer, H. *Cancer Lett.* **1979**, *6*, 57–60.

is replaced by an ice–water bath and the solution stirred for 30 min. The ice water bath is removed and the solution stirred for 30 additional min. The reaction is quenched by pouring onto 50 g of crushed ice. After the ice has melted, the aqueous solution is extracted with three 50-mL portions of methylene chloride. The combined methylene chloride extracts are dried over MgSO. The solution is filtered and the solvent removed at reduced pressure to yield the crude products. In the case of **9** the product was collected by vacuum filtration. The results are summarized in Table II.

Reaction of 1,3-Dinitrosamines with N_2O_5 Solutions. The dinitrososamine (10 mmol) is slowly added to 10 mL of a well-stirred solution of 24–30% N_2O_5 in 100% nitric acid maintained at −30 °C by means of a dry ice–dichloroethane slush. The cooling bath is replaced with an ice–water bath, and a stream of dry nitrogen is blown across the surface of the reaction. After 20 min the ice–water bath is removed and the solution stirred for 5 min. The contents are then poured onto 50 g of crushed ice. After the ice has melted, the products are isolated by vacuum filtration and washed with water. The results are summarized in Table III.[14]

Acknowledgment. Financial support of this research was provided by the Naval Weapons Center's Independent Research Funds and the Naval Sea Systems Command Explosive R&D Program, Task No. 61153N-SR02402.

Registry No. **1**, 5754-91-6; **2**, 5754-89-2; **4**, 84606-37-1; **5**, 15973-99-6; **7**, 93000-52-3; **8**, 93000-53-4; **9**, 93000-54-5; **10**, 93000-55-6; **11**, 93000-56-7; **12**, 93000-57-8; **13**, 93000-58-9; **14**, 93000-59-0; **15**, 93000-60-3; **16**, 93000-61-4; **17**, 93000-62-5; **18**, 93000-63-6; **19**, 93000-64-7; $H_2N(CH_2)_2NH_2$, 107-15-3; $H_2N(CH_2)_3NH_2$, 109-76-2; $H_2N(CH_2)_4NH_2$, 110-60-1; $C(CH_2NH_2)_4$, 4742-00-1; $H_2NCH_2C(CH_3)HNH_2$, 78-90-0; $H_2N(CH_2)_2C(CH_3)HNH_2$, 590-88-5; HCHO, 50-00-0; HNO_3, 7697-37-2; N_2O_5, 10102-03-1.

(14) The NMR data for these compounds will be presented elsewhere. Willer, R. L.; Moore, D. W., manuscript in preparation.

Synthesis of *cis*- and *trans*-1,3,5,7-Tetranitro-1,3,5,7-tetraazadecalin

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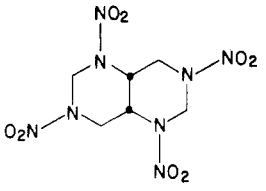
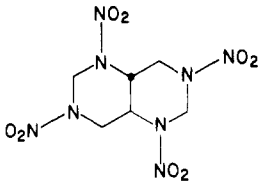
Received April 5, 1984

The synthesis and preliminary characterization of two new polynitramine compounds, *cis*- and *trans*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (**1** and **2**), is described. Also isolated and partially characterized were two byproducts of the synthesis of **1** and **2**, (*R**,*R**)-1,1′,3,3′-tetranitro-4,4′-biimidazolidine (**3**) and (*R**,*S*)-1,1′,3,3′-tetranitro-4,4′-biimidazolidine (**4**).

This paper is a continuation of our work on developing new methodology for the synthesis of polynitramino compounds and establishing the effect of stereochemistry and isomerization on the physical and chemical properties of polynitramino compounds.



1



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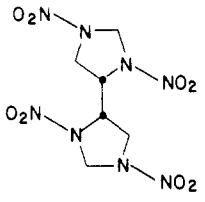

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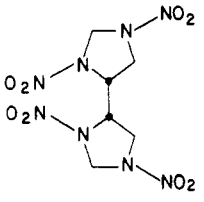
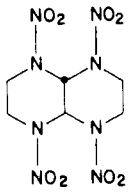


4

Our previous work in this area has resulted in the synthesis of *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin[1] (**5**),



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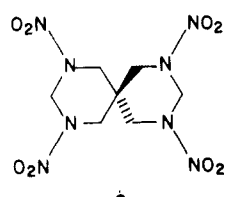

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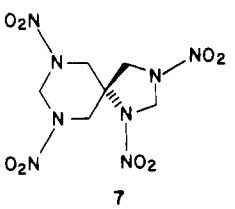

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2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane[2] (**6**), and an improved synthesis of 1,3,7,9-tetranitro-1,3,7,9-tetraazaspiro[4.5]decane[3] (**7**). Compounds **5** and **7** are isomeric (i.e., both $C_6H_{10}N_8O_8$) yet they have very different densities (1.80 g/mL for **5**[1] and 1.70 g/mL for **7**[3]). This large difference prompted us to formulate other structures which are isomeric with **5** and **7**. Two such compounds are **1** and **2**. We felt that these compounds were very attractive synthetic targets because they retain the basic decalin ring structure of **5** while the nitramino substituents are moved around the ring. This would allow determination of the effects of placement of the nitramino groups further away from each other. Since we hoped to be able to synthesize both stereoisomers (cis and trans), we should thus be able to determine the effect of the stereochemistry at the ring junction on the density of these polynitramino compounds.

Our strategy for the synthesis of **1** and **2** was based on our previously developed methodology for the synthesis of polynitramino compounds.[2] This technique involves the trapping of an in situ generated 1,3-diazacycloalkane with nitrous acid to give a 1,3-dinitroso-1,3-diazacycloalkane followed by nitrolysis of the dinitroso compound to the corresponding 1,3-dinitro-1,3-diazacycloalkane with 100% nitric acid or N_2O_5 in 100% nitric acid.[2] A retrosynthetic analysis of **1** and **2** based upon this methodology indicated that the required starting materials were *threo*-1,2,3,4-tetraaminobutane (**8**) for **1** and *erythro*-1,2,3,4-tetraaminobutane (**9**) for **2**. Our strategy for synthesis of unknown **8** and **9** was to start with the corresponding tetra-

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(2) Willer, R. L.; Atkins, R. L. *J. Org. Chem.*, in press.
(3) Willer, R. L., NWC TM 4703, Naval Weapons Center, China Lake, CA, Jan 1982, 10 pages.

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