Nitration of 1,1-Diamino-2,2-dinitroethylenes

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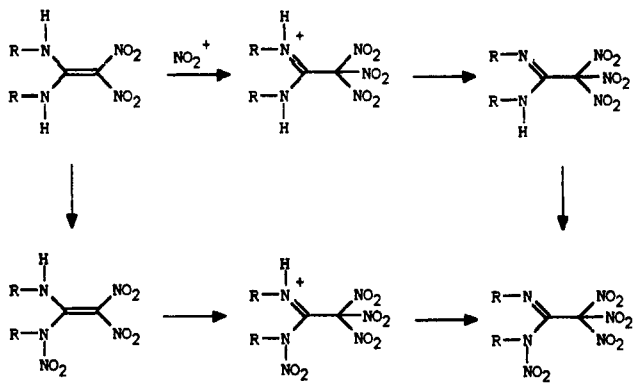
The nitration of 1,1-diamino-2,2-dinitroethylenes, obtained by the reaction of amines with 1,1-diiododinitroethylene, was studied. Reaction of 2-(dinitromethylene)-1,3-diazacyclopentane (**1a**) with nitric acid and trifluoroacetic anhydride in methylene chloride gave 3-nitro-2-(trinitromethyl)-1,3-diazacyclopent-1-ene (**3a**) in high yield. Analogous products **3b–3d** were obtained from 2-(dinitromethylene)-1,3-diazacyclohexane (**1b**), 2-(dinitromethylene)-1,3-diazacycloheptane (**1c**), and 3,9-bis(dinitromethylene)-2,4,8,10-tetraazaspiro[5.5]undecane (**1d**). Nitration of **1a** with nitric acid in sulfuric acid gave the corresponding nitrosamine **2a**. Reductive denitrations of the trinitromethyl compounds **3a**, **3b**, and **3c** with potassium iodide gave salts of the corresponding dinitromethyl compounds **4a**, **4b**, and **4c**. Bromination and chlorination of **4a** afforded 2-(bromodinitromethyl)-3-nitro-1,3-diazacyclopentent-1-ene (**5**) and 2-(chlorodinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene (**6**), respectively. Acidification of the salts **4a**, **4b**, and **4c** gave 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (**7a**), 2-(dinitromethylene)-1-nitro-1,3-diazacyclohexane (**7b**), and 2-(dinitromethylene)-1-nitro-1,3-diazacycloheptane (**7c**), respectively. The nitration of **7a** gave **3a**. Nitrations of the diamino mononitro olefins, 2-(nitromethylene)-1,3-diazacyclopentane (**8a**) and 2-(nitromethylene)-1,3-diazacyclohexane (**8b**), gave **3a** and **3b**. The structures of **3a**, **3d**, **7a**, **7b**, and **7c** were obtained by X-ray crystallography. Olefin twist angles for **7a–7c**, as high as 74.5°, are rationalized on the bases of ring geometry and hydrogen bonding.

There is general interest in the structural properties[1] as well as synthetic applications[2] of nitroolefins and other electronegatively substituted olefins. We have reported the synthesis of tetranitroethylene[3] and 1,2-difluorodinitroethylene[4] by the thermal extrusion of nitrogen tetroxide from hexanitroethane and 1,2-difluoro-1,1,2,2-tetranitroethane, respectively. X-ray crystallography of 1,2-difluoro-1,2-dinitroethylene showed that one of the two nitro groups is out of the plane of the rest of the molecule and that the C–C double bond distance is unusually short at 1.284 Å. Consequently, we resynthesized a compound reported as 1,2-diiodo-1,2-dinitroethylene in 1900[5] and found the material was actually 1,1-diiodo-2,2-dinitroethylene.[6] One of the two nitro groups of this compound was shown to be perpendicular to the ethylene plane. Some addition and substitution reactions of 1,1-diiodo-2,2-dinitroethylene were examined. Amines displaced iodines to give the corresponding diamino dinitro olefins. These olefins were found by crystallography to be twisted, some with olefin twist angles greater than any previously reported, with concomitant bond distance distortions. In the present work, we have examined the nitration of these unusual amines.

The diamine derived from ethylenediamine and 1,1-diiodo-2,2-dinitroethylene, 2-(dinitromethylene)-1,3-diazacyclopentane (**1a**), was nitrated initially using mixed nitric and sulfuric acids as the reaction medium at 0 °C. The product, isolated in 53% yield, was identified as 3-nitroso-2-(trinitromethyl)-1,3-diazacyclopent-1-ene (**2**). The nitration of **1a** with nitric acid and trifluoroacetic anhydride in methylene chloride at 0 °C gave 3-nitro-2-(trinitromethyl)-1,3-diazacyclopent-1-ene (**3a**) in 89% yield. The nitrosamine **2** as also converted to the nitramine **3a** with the latter reagent.

Scheme I



The nitration of other cyclic amines derived from 1,1-diiodo-2,2-dinitro-ethylene and diamines gave similar trinitromethyl derivatives as shown in Table I. Thus, 2-(dinitromethylene)-1,3-diazacyclohexane (**1b**) and 2-(dinitromethylene)-1,3-diazacycloheptane (**1c**) gave 3-nitro-2-(trinitromethyl)-1,3-diazacyclohex-1-ene (**3b**) and 3-nitro-2-(trinitromethyl)-1,3-diazacycloheptene (**3c**), respectively, whereas the spiro starting material derived from pentaerythrityl tetramine, 3,9-bis(dinitromethylene)-2,4,8,10-tetraazaspiro[5.5]undecane (**1d**) gave 3,9-bis(trinitromethyl)-4,10-dinitro-2,4,8,10-tetraazaspiro[5.5]undeca-2,8-diene (**3d**).

Formally, the formation of the trinitromethyl derivatives involves attack of a nitronium ion equivalent on the dinitrovinyl carbon, with loss of a proton on nitrogen, and nitration of the other amine nitrogen. No information is available as to the order of these two steps (Scheme I).

Few examples of the conversion of *gem*-dinitro to trinitromethyl compounds have been reported previously. Salts of terminal *gem*-dinitroalkanes, $R(NO_2)_2^-$, have been reported to react with tetranitromethane to give trinitromethyl derivatives.[7] The direct nitration of benzaldehyde

(1) Politzer, P.; Bar-Adon, R. *J. Am. Chem. Soc.* **1987**, *109*, 3529. Dewar, M. J. S.; Ritchie, J. P.; Alster, J. *J. Org. Chem.* **1985**, *50*, 1031. Penner, G. H. *THEOCHEM* **1986**, *137*, 121–7. Sadova, N. I.; Vilkov, L. V. *Russ. Chem. Rev.* **1982**, *51*, 87–105.

(2) Rappoport, Z.; Topol, A. *J. Org. Chem.* **1989**, *54*, 5967. Barrett, A. G. M.; Graboski, G. G. *Chem. Rev.* **1986**, *86*, 751–762. Perekalin, V. V. *Zh. Org. Khim.* **1985**, *21*, 1111–28.

(3) Tzeng, D.; Baum, K. *J. Org. Chem.* **1983**, *48*, 5384.

(4) Baum, K.; Archibald, T. G.; Tzeng, D. *J. Org. Chem.* **1991**, *56*, 537–539.

(5) Biltz, H.; Kedesdy, E. *Chem. Ber.* **1900**, *33*, 2190.

(6) Baum, K.; Bigelow, S. S.; Nguyen, N. V.; Archibald, T. A.; Gilardi, R.; Flippen-Anderson, J. L.; George, C. *J. Org. Chem.* **1992**, *57*, 235–241.

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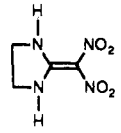
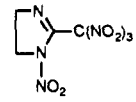
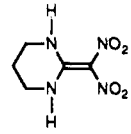
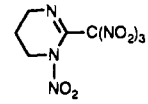
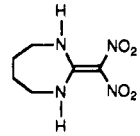
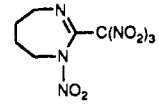
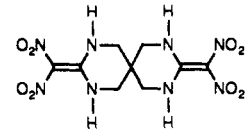
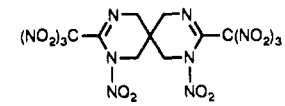
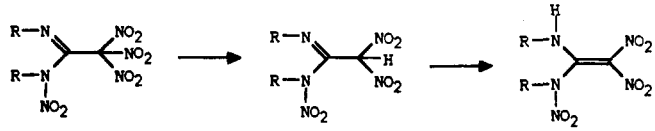
Table I. Nitration Products

starting material	product	yield (%)	mp (°C)
 **1a**	 **3a**	89	112–3 dec
 **1b**	 **3b**	95	106–7
 **1c**	 **3c**	57	80–82
 **1d**	 **3d**	74	152–3 dec

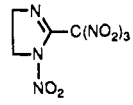
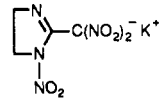
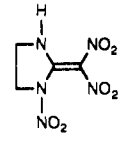
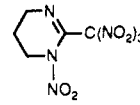
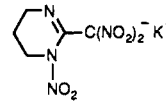
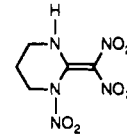
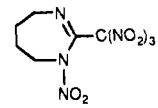
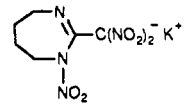
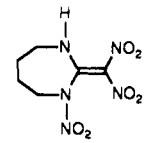
oximes and aryl nitrolic acids gave aryl trinitromethanes[8] (Ponzio reaction), but the reaction failed for aliphatic examples. A multistep nitration leading to a trinitromethyl derivative is the conversion of cyanoacetic acid to cyanotrinitromethane.[9] A sulfur ylide, $Me_2S^+C(NO_2)_2^-$, has been nitrated to give the trinitromethyl derivative, $Me_2S^+C(NO_2)_3$.[10]

The availability of the novel heterocyclic trinitromethyl derivatives **3** prompted us to study their reactions using known trinitromethyl group transformations. For example, reductive denitration of the trinitromethyl groups would be expected to give the dinitromethyl analogues, which are tautomeric with *N*-nitro-1,1-diamino-2,2-dinitro olefins. These materials would be of interest in determining the effect of the lessened electron-supplying ability of the amino groups on the tendency to form twisted ethylene structures.



Reductive denitrations of the trinitromethyl commpounds **3a**, **3b**, and **3c** were carried out using potassium iodide[11] as the reducing agent. The corresponding nitronate salts **4a**, **4b**, and **4c** were obtained in 83–95% yields (Table II). Bromination and chlorination of suspensions of the potassium salt **4a** in methylene chloride afforded 2-(bromodinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene (**5**) and 2-(chlorodinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene (**6**) in 74% and 81% yield, respectively.

Table II. Reductive Denitration

starting material	reductn product	acidificatn product	mp (°C)
 **3a**	 **4a**	 **7a**	121–2
 **3b**	 **4b**	 **7b**	113
 **3c**	 **4c**	 **7c**	115

Acidification of the nitronate salts **4a**, **4b**, and **4c** gave 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (**7a**), 2-(dinitromethylene)-1-nitro-1,3-diazacyclohexane (**7b**), and 2-(dinitromethylene)-1-nitro-1,3-diazacycloheptane (**7c**), respectively (Table II). The melting points of these products, 113–121 °C, are low compared to those of the corresponding 1,1-diamino-2,2-dinitroethylenes (about 200 °C), consistent with the expected reduced charge separation due to the electron-withdrawing substituent on one of the amino groups.

Since the *N*-nitro derivatives are possible intermediates in the transformation of 1,1-diamino-2,2-dinitroethylenes to **3**, the nitration of 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (**7a**) with nitric acid and trifluoroacetic anhydride in methylene chloride was examined. A 91% yield of **3a** was obtained.

The synthesis of 1,1-diamino-2-nitroethylenes by the reduction of amines with thio derivatives of nitroethylene

(7) C. W. Plummer, U.S. Pat 2991315, 1961; 3316311, 1957.
(8) Ponzio G. *Gazz. Chim. Ital.* **1906**, *36*II, 287. Novikov, S. S.; Khmelnitskii, L. I.; Lebedev, O. V. *Izv. Akad. Nauk, Otd. Khim Nauk.* **1960**, 1783.
(9) Parker, C. O.; Emmons, W. D.; Rolewicz, H. A.; McCallum, K. S. *Tetrahedron* **1962**, *17*, 79.
(10) Shevelev, S. A.; Semenov, V. V.; Fainzil'berg, A. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1977**, 2530.
(11) Glover, D. J.; Kamlet, M. J. *J. Org. Chem.* **1961**, *26*, 4734.

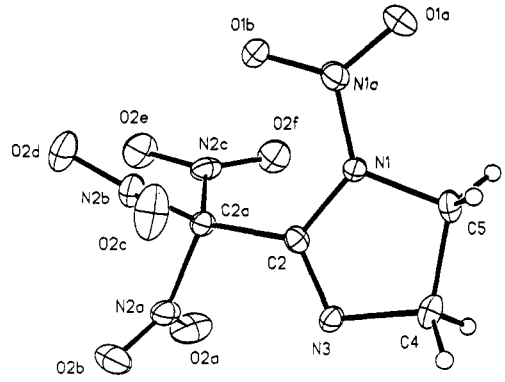


Figure 1. Molecular structure and numbering scheme for 3-nitro-2-(trinitromethyl)-1,3-diazacyclopentene (**3a**).

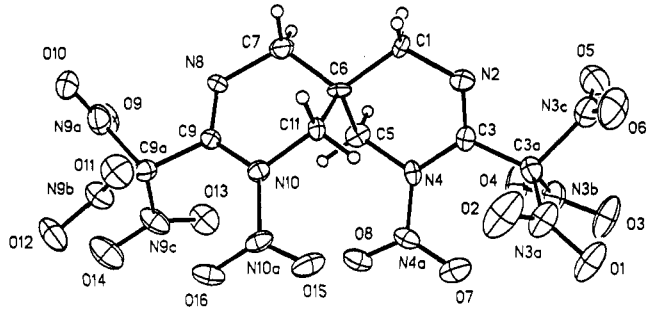
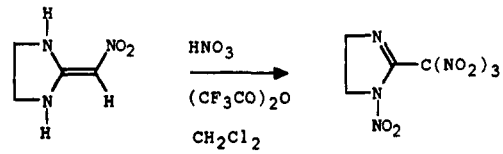


Figure 2. Molecular structure and numbering scheme for 3,9-bis(trinitromethyl)-4,10-dinitro-2,4,8,10-tetraazaspiro[5.5]undec-2,8-diene (**3d**).

has been reported,[12] and by this procedure we prepared 2-(nitromethylene)-1,3-diazacyclopentane (**8a**) and 2-(nitromethylene)-1,3-diazacyclohexane (**8b**). Nitrations of these mononitro olefins with nitric acid and trifluoroacetic anhydride in methylene chloride gave the same trinitromethyl products that were obtained from the corresponding dinitro olefins **3a** and **3b**, although yields were lower (22% and 16%, respectively).



X-ray Crystallography. The structures of **3a** and **3d** were confirmed by single-crystal analysis and are shown in Figures 1 and 2. Their nitramine regions are quite crowded, in each case, by the α-trinitromethyl substitution. In **3a**, the nitramine group and the adjacent five-membered ring are coplanar (to within ±0.04 Å), and the adjacent trinitromethyl group is staggered so that its two nearer nitro groups straddle the nitramine plane fairly symmetrically (see Figure 1). Even in this optimal conformation, several nonbonded distances are significantly less than their corresponding van der Waals[13] (e.g., O1B···N2B = 2.64 Å, O1B···N2C = 2.69, van der Waals O···N = 290 Å), a good indicator of repulsive strain. Further evidence of strain is provided by a comparison of bond angles; those closer to the region of close contact are several degrees larger than angles of a corresponding type that are farther away; e.g., the nitamine bond angle C2–N1–N1A is 127.1(4)° while C5–N1–N1A is 123.5(3)°, and the closer trinitromethyl N–C–N angle is 113.7(3)° while the farther ones are 103.5(3)° and 106.4(3)°. These and other comparisons indicate that each of the crowded nitro groups has tipped 2–4° away from the source of the strain. **3d** contains two such crowded regions with local deviations similar to those cited for **3a**. The two diazacyclohexene rings of **3d** are in half-chair conformations; in the first ring, atoms C1–N4 are coplanar to within 0.03 Å and atoms C5 and C6 are puckered ±0.4 Å to either side of this plane. The second ring is related to the first by an approximate (but close) 2-fold axis of symmetry passing through the spiro atom, C6, and thus displays and identical conformation.

The structures of the reductive denitration products **7a**, **7b**, and **7c**, shown in Figures 3–5, are dissimilar. The structure of **7b** is qualitatively similar to that of its diamino precursor reported in an earlier article.[6] Both display a

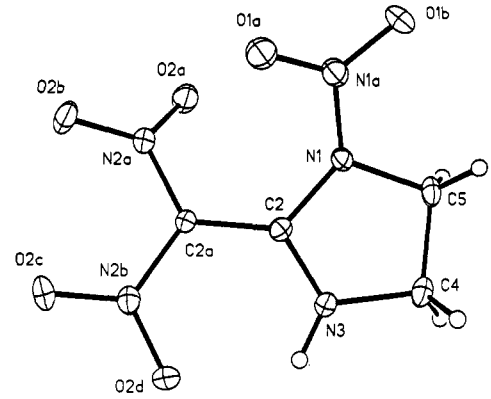


Figure 3. Molecular structure and numbering scheme for 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (**7a**).

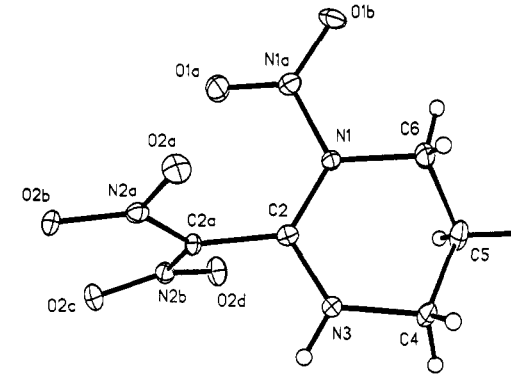


Figure 4. Molecular structure and numbering scheme for 2-(dinitromethylene)-1-nitro-1,3-diazacyclohexane (**7b**).

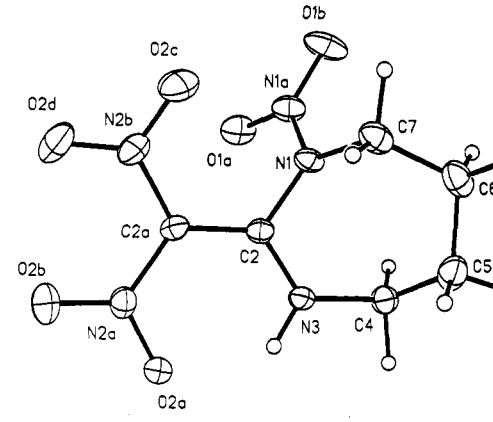


Figure 5. Molecular structure and numbering scheme for 2-(dinitromethylene)-1-nitro-1,3-diazacycloheptane (**7c**).

(12) Freund, E. *Chem. Ber.* **1919**, *52*, 542. Gompper, R.; Schaeffer, H. *Chem. Ber.* **1967**, *100*, 591. Rajappa, S.; Sreenivasan, R.; Advani, B. G. *Ind. J. Chem.* **1977**, *15B*, 297.

(13) Dunitz, J. D. *X-ray Analysis and the Structure of Organic Molecules*; Cornell University Press: Ithaca, NY, and London, 1979.

Table III. Selected Torsion Angles (deg) and Bond Distances (Å) in 7a, 7b, and 7c[a]

atom labels	7a	7b	7c
O1A-N1A-N1-C2	-5.5 (5)	-6.6 (4)	-6.9 (5)
N1A-N1-C2-C2A	34.7 (6)	-8.4 (4)	-66.1 (4)
N1-C2-C2A-N2A	20.5 (5)	-69.7 (4)	-2.7 (5)
C2-C2A-N2A-O2A	28.9 (5)	4.9 (4)	-18.3 (5)
C2-C2A (olefin bond)	1.406 (5)	1.464 (4)	1.394 (5)
C2-N3 (olefin-amine)	1.302 (5)	1.287 (4)	1.303 (5)
C2-N1 (olefin-nitramine)	1.389 (5)	1.373 (4)	1.415 (5)

[a] The torsion angle may be defined for any four-atom string of atoms A-B-C-D. The rotation about the B-C axis needed to bring the A-B and C-D vectors (bonds) into cis-eclipsed conformation is the *torsion angle*. If a clockwise rotation is needed, the torsion angle is *positive* in sign.[13]

massive twist (74.5° for **7b**, 89.0° for **1a**, see ref 6 for definition of twist) about the olefinic or pseudoolefinic bond (C2-C2A in **7a-c**) and show the full pattern of bond shortenings and lengthenings consistent with a fairly complete transformation to a dipolar diene form. The diazacyclohexane ring of **7b** has an envelope conformation; namely, all atoms except C5 are coplanar to within 0.05 Å, and C5 is displaced from this plane by 0.67 Å. This conformation is also displayed by **1a**, perhaps because its geometry is optimal for π-electron delocalization along the nitramine-amine pathway.

7a and **7c** are twisted only 15.2 and 3.2° about their olefin bonds. Both would be severely crowded by full retention of planarity along the segment connecting the nitramine nitro and the proximal dinitromethylene nitro groups (O1A-N1A-N1-C2-C2A-N2A-O2A in **7a**), for there would be four consecutive "cis" configurations along the chain. Both depart substantially from planarity, but in different ways. The individual torsion angles along this crowded segment are given for **7a**, **7b**, and **7c** in Table III. **7a** displays three consecutive torsions in the 20-25° range. Since they are all of the same sign, increasing them jointly has a cumulative effect on the nonbonded distance between the atoms at the ends of the chain, which is O1A···O2A = 2.72 Å. This is just slightly less than the van der Waals distance (O···O, 2.80 Å), generally considered the threshold for significant repulsion. **7b**, as already mentioned, separates the terminal groups by twisting primarily at the "olefin" bond. **7c** shows still another pattern, displaying a torsion of 66.1 (4)° about the ring bond located between the olefin and the nitramine group. This torsion allows the nitramine group to bend well out of the way (the closest nonbonded nitramino-nitro contact is 3.068 Å), while the olefin-amine π-electron network remains relatively planar. This mode of deformation is probably facilitated by the flexibility of the diazacyclohexane ring; it adopts a chairlike conformation that contains a planar N1-C2-N3-C4 segment.

7a-7c each have the potential to form an internal hydrogen bond between the amine, N3-H3, and an oxygen atom from the closer nitro group on C2A that would tend to stabilize the planarity of the olefin/amine region. **7a** and **7c** do participate in such H bonds, although the hydrogen is bifurcated (divided) between an intra- and an intermolecular H bond in both cases. In **7b**, the amine again forms two bifurcated H bonds, but both are intermolecular and serve to link the molecules in continuous chains along the *b* axis of the crystal. Table IV contains geometrical parameters describing the hydrogen bonding.

Experimental Section

NMR spectra were obtained using a Bruker AC 200-MHz spectrometer. Melting points were determined with a DuPont DSC or in open capillary tubes with an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by Gailbraith Laboratories, Inc., Knoxville, TN, or Oneida Research Services, Inc., Whitesboro, NY.

Table IV. Hydrogen Bond Parameters

	acceptor O	symm. op. (on O)	H3···O (Å)	N3···O (Å)	N3-H3···O (deg)
7a	O2D	intramolecular	1.998	2.285	122.7
	O2B	$1-y, {}^1/_2+x, -{}^1/_2+z$	2.229	2.887	131.0
7b	O2B	${}^1/_2-x, {}^1/_2+y, 1-z$	2.099	2.895	151.8
	O2C	${}^1/_2-x, {}^1/_2+y, 1-z$	2.233	2.847	127.5
7c	O2A	intramolecular	1.904	2.574	133.9
	O2A	${}^1/_2-x, {}^1/_2-y, -z$	2.270	2.946	135.7

Polynitro compounds are potentially explosive, and adequate shielding and protection should be used.

3-Nitro-2-(trinitromethyl)-1,3-diazacyclopent-1-ene (3a). To a solution of 4.2 g (20.50 mmol) of trifluoroacetic anhydride in 15 mL of methylene chloride at 0 °C was added 2.0 g (20 mmol) of 90% nitric acid. After 5 min, 0.200 g (1.15 mmol) of 2-(dinitromethylene)-1,3-diazacyclopentane[6] (**1a**) was added portionwise over a 10-min period. The resulting solution was stirred at 0 °C for 1 h, warmed to room temperature, and poured into 100 mL of ice. The organic layer was washed with water (3 × 20 mL) and brine (20 mL) and dried ($MgSO_4$). Solvent was removed under vacuum, and the residue was recrystallized from methylene chloride/hexane to give 0.27 g (89%) of 3-nitro-2-(trinitromethyl)-1,3-diazacyclopent-1-ene (**3a**), a white solid: mp 112-113 °C dec; UV (MeOH) λ_{max} (ϵ) 266 (9400); ^{1}H NMR ($CDCl_3$) δ 4.32-4.52 (m); ^{13}C NMR ($CDCl_3$) δ 50.06, 54.15, 119.93, 143.34; ^{14}N NMR δ 34.7 (J = 4 Hz), 42.2 (J = 24 Hz). Anal. Calcd for $C_4H_4N_6O_8$: C, 18.19; H, 1.53; N, 31.82. Found: C, 18.30; H, 1.50; N, 31.54.

3-Nitro-2-(trinitromethyl)-1,3-diazacyclohex-1-ene (3b). Nitration of 2-(dinitromethylene)-1,3-diazacyclohexane[6] (**1b**) by the above procedure gave 3-nitro-2-(trinitromethyl)-1,3-diazacyclohex-1-ene (**3b**) in 95% yield, a white solid: mp 106-107 °C; ^{1}H NMR ($CDCl_3$) δ 2.20 (q, J = 6 Hz, 2 H), 3.81 (t, J = 6 Hz, 2 H), 4.27 (t, J = 6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.59, 46.31, 47.44, 123.40, 134.85. Anal. Calcd for $C_5H_6N_6O_8$: C, 21.59; H, 2.17; N, 30.22. Found: C, 21.80; H, 2.17; N, 30.28.

3-Nitro-2-(trinitromethyl)-1,3-diazacyclohept-1-ene (3c). 2-(Dinitromethylene)-1,3-diazacycloheptane (**1c**) was nitrated by the above method. Removal of the solvent after the extraction procedure left an oil, which was triturated with methylene chloride/hexane to give 3-nitro-2-(trinitromethyl)-1,3-diazacyclohept-1-ene (**3c**) as a white solid (47% yield): mp 80-82 °C; ^{1}H NMR ($CDCl_3$) δ 1.83-1.97 (m, 4 H), 3.90-4.05 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.55, 23.98, 49.35, 52.74, 122.42, 140.17. Anal. Calcd for $C_6H_8N_6O_8$: C, 24.66; H, 2.67; N, 28.76. Found: C, 24.97; H, 2.78; N, 28.84.

3,9-Bis(trinitromethyl)-4,10-dinitro-2,4,8,10-tetraazaspiro[5.5]undeca-2,8-diene (3d). 3,9-Bis(dinitromethylene)-2,4,8,10-tetraazaspiro[5.5]undecane[6] (**1d**) was nitrated by the above method. The product was recrystallized from acetone/hexane (rather than methylene chloride/hexane) to give 3,9-bis(trinitromethyl)-4,10-dinitro-2,4,8,10-tetraazaspiro[5.5]undeca-2,8-diene (**3d**) as a white solid (74%): mp 152-153 °C dec: ^{1}H NMR (acetone-d_6) δ 4.13 (d, J = 18.5 Hz, 2 H), 4.25 (d, J = 18.5 Hz, 2 H), 4.56 (d, J = 13 Hz, 2 H), 4.75 (d, J = 13 Hz, 2 H); ^{13}C NMR (acetone-d_6) δ 34.51, 51.50, 52.59, 124.52, 135.39. Anal. Calcd for $C_9H_8N_{12}O_{16}$: C, 20.01; H, 1.49; N, 31.11. Found: C, 20.37; H, 1.35; N, 30.71.

3-Nitroso-2-(trinitromethyl)-1,3-diazacyclopent-1-ene (2). A mixture of 3 mL of concentrated sulfuric acid and 2 mL of 90% nitric acid was added to a solution of 0.2 g (1.15 mmol) of 2-(dinitromethylene)-1,3-diazacyclopentane (**1a**) in 8 mL of concentrated sulfuric acid at 0 °C. The solution was stirred at 0 °C for 17 h and then poured onto 50 mL of ice. The product was washed with water and dried to give 0.15 g (53%) of 3-nitroso-2-(trinitromethyl)-1,3-diazacyclopent-1-ene (**2**), a white solid: mp 64-65 °C; ^{1}H NMR ($CDCl_3$) δ 4.11 (t, J = 8 Hz, 2 H), 4.39 (t, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 45.78, 55.22, 120.07, 145.93. Anal. Calcd for $C_4H_4N_6O_7$: C, 19.36; H, 1.63; N, 33.87. Found: C, 19.66; H, 1.67; N, 33.69.

Nitration of 3-Nitroso-2-(trinitromethyl)-1,3-diazacyclopentene (2). 3-Nitroso-2-(trinitromethyl)-1,3-diazacyclopentene

(2) (0.4 g, 1.6 mmol) was added to a mixture of 5 mL of trifluoroacetic hydride and 2 mL of 90% HNO_3 at 0 °C. After the mixture was stirred at 0 °C for 2 h, a white solid precipitated. Ice (10 g) was added, and the mixture was stirred for 30 min and filtered to give 0.3 g (70%) of 3-nitro-2-(trinitromethyl)-1,3-diazacyclopent-1-ene (**3a**) identical with the material described above.

2-(Dinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene Potassium Salt (4a). A solution of 2-(trinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene (**3a**) (0.10 g, 0.38 mmol), potassium iodide (0.2 g, 1.20 mmol), and 18-crown-6 ether (0.1 g) in 5 mL of dry tetrahydrofuran was stirred at room temperature for 16 h. The solid product was isolated by filtration, washed with tetrahydrofuran (10 mL), and recrystallized from water/methanol/ether to give 0.80 g (89%) of 2-(dinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene potassium salt (**4a**), a white solid: mp 205 °C dec; ^1H NMR (DMSO-d_6) δ 3.93 (t, J = 8 Hz, 2 H), 4.16 (t, J = 8 Hz, 2 H); ^{13}C NMR (DMSO-d_6) δ 47.85, 51.35, 125.37, 147.89. Anal. Calcd for $C_4H_4N_5O_6K$: C, 18.70; H, 1.57; N, 27.23. Found: C, 19.02; H, 1.60; N, 27.03.

2-(Dinitromethyl)-3-nitro-1,3-diazacyclohex-1-ene Potassium Salt (4b). By the above procedure (recrystallization omitted), 2-(trinitromethyl)-3-nitro-1,3-diazacyclohex-1-ene (**3b**) gave 2-(dinitromethyl)-3-nitro-1,3-diazacyclohex-1-ene potassium salt (**4b**) (95%), an off-white solid: mp 139 °C (DSC); ^1H NMR (DMSO-d_6) δ 1.93 (p, J = 6 Hz, 2 H), 3.47 (t, J = 6 Hz, 2 H), 3.98 (t, J = 6 Hz, 2 H); ^{13}C NMR (DMSO-d_6) δ 22.01, 44.61, 46.97, 130.28, 141.96. Anal. Calcd for $C_5H_6N_5O_6K$: C, 22.14; H, 2.23; N, 25.82. Found: C, 22.00; H, 2.33; N, 25.59.

2-(Dinitromethyl)-3-nitro-1,3-diazacyclohept-1-ene Potassium Salt (4c). By the above procedure 2-(trinitromethyl)-3-nitro-1,3-diazacyclohept-1-ene (**3c**) gave 2-(dinitromethyl)-3-nitro-1,3-diazacyclohept-1-ene potassium salt (**4c**) (83%), a yellow solid: mp 124 °C (DSC); ^1H NMR (DMSO-d_6) δ 1.61 (p, J = 6 Hz, 2 H), 1.79 (p, J = 6 Hz, 2 H), 3.63 (t, J = 6 Hz, 2 H), 3.93 (t, J = 6 Hz, 2 H). Anal. Calcd for $C_6H_8N_5O_6K$: C, 25.26; H, 2.83; N, 24.55. Found: C, 24.95; H, 2.51; N, 24.33.

2-(Bromodinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene (5). A solution of bromine (1 g, 6.25 mmol) in methylene chloride (10 mL) was added dropwise over a 10-min period to a suspension of 2-(dinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene potassium salt (**4a**) (0.7 g, 2.72 mmol) in of methylene chloride (50 mL) at 0 °C. The reddish solution was stirred at 0 °C for 1 h and then filtered. Solvent was removed from the filtrate, and the residue was recrystallized from methylene chloride/hexane to give 0.60 g (74%) of 2-(bromodinitromethyl)-3-nitro-1,3-diazacyclopentene (**5**), a white solid: mp 106 °C (DSC); ^1H NMR ($CDCl_3$) δ 4.18–4.27 (m, 2 H), 4.36–4.46 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 50.49, 53.30, 112.20, 147.87. Anal. Calcd for $C_4H_4N_5O_6Br$: C, 16.12; H, 1.35; N, 23.50; Br, 26.81. Found: C, 16.47; H, 1.31; N, 23.21; Br, 26.89.

2-(Chlorodinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene (6). Chlorine gas was bubbled through a suspension of 2-(dinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene potassium salt (**3a**) (0.7 g, 2.72 mmol) in 50 mL of methylene chloride for 1 h at 0 °C. The solution was filtered, and the filtrate was stripped of solvent. The residue was recrystallized from methylene chloride/hexane to give 0.56 g (81%) of 2-(chlorodinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene (**6**), a white solid: mp 91.5 °C (DSC); ^1H NMR ($CDCl_3$) δ 4.20–4.29 (m, 2 H), 4.36–4.46 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 50.35, 53.47, 118.79, 147.00. Anal. Calcd for $C_4H_4N_5O_6Cl$: C, 18.95; H, 1.59; N, 27.62; Cl, 13.98. Found: C, 19.15; H, 1.60; N, 27.32; Cl, 13.56.

2-(Dinitromethylene)-1-nitro-1,3-diazacyclopentane (7a). A solution of 2-(dinitromethyl)-3-nitro-1,3-diazacyclopent-1-ene potassium salt (**4a**) (0.1 g, 0.39 mmol) in water (5 mL) was cooled to 0 °C, and concd HCl (1 mL) was added dropwise. After 15 min, the resulting precipitate was washed with water (5 mL) and recrystallized from acetone/hexane to afford 0.08 g (94%) of 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (**7a**), a bright yellow solid: mp 121–122 °C dec; ^1H NMR (DMSO-d_6) δ 3.96 (t, J = 8.5 Hz, 2 H), 4.38 (t, J = 8.5 Hz, 2 H), 11.34 (br s, 1 H); ^{13}C NMR (DMSO-d_6) δ 47.79, 48.91, 127.51, 149.87. Anal. Calcd for $C_4H_5N_5O_6$: C, 21.93: H, 2.30: N, 31.96. Found: C, 21.97; H, 2.10; N, 31.88.

2-(Dinitromethylene)-1-nitro-1,3-diazacyclohexane (7b). A solution of 2-(dinitromethyl)-3-nitro-1,3-diazacyclohex-1-ene potassium salt (**4b**) (2 g, 7.38 mmol) in 15 mL of water was acidified dropwise with 10 mL of 30% HCl at 0 °C. After 15 min, the precipitate was washed with water (3 × 30 mL) and ether (3 × 30 mL). Recrystallization (acetone/hexane) gave 0.2 g (12%) of 2-(dinitromethylene)-1-nitro-1,3-diazacyclohexane (**7b**), a yellow solid: mp 113.3 °C (DSC): ^1H NMR (DMSO-d_6) δ 2.20 (p, J = 6 Hz, 2 H), 3.67 (t, J = 6 Hz, 2 H), 4.29 (t, J = 6 Hz, 2 H), 7.81 (b, 1 H); ^{13}C NMR (DMSO-d_6) δ 20.45, 41.30, 47.44, 126.37, 151.47. Anal. Calcd for $C_5H_7N_5O_6$: C, 25.76; H, 3.03; N, 30.04. Found: C, 25.99; H, 2.97; N, 29.86.

2-(Dinitromethylene)-1-nitro-1,3-diazacycloheptane (7c). A solution of 1.5 g (5.26 mmol) of 2-(dinitromethyl)-3-nitro-1,3-diazacyclohept-1-ene potassium salt (**4c**) in water (50 mL) was acidified with 10 mL of 50% HCl solution at 5 °C. After 15 min, the solid product was washed with cold water (2 × 15 mL) and ether (3 × 20 mL). Recrystallization from acetone/hexane afforded 0.4 g (31%) of 2-(dinitromethylene)-1-nitro-1,3-diazacycloheptane (**7c**), a yellow solid: mp 115.3 °C (DSC): ^1H NMR (DMSO-d_6) δ 1.68 (m, 2 H), 1.85 (m, 2 H), 3.72 (m, 2 H), 4.17 (m, 2 H), 10.30 (b, 1 H); ^{13}C NMR (DMSO-d_6) δ 23.24, 23.67, 45.50, 50.97, 134.74, 149.99. Anal. Calcd for $C_6H_9N_5O_6$: C, 29.16; H, 3.67; N, 28.33. Found: C, 29.46; H, 3.65; N, 28.18.

Nitration of 2-(Dinitromethylene)-1-nitro-1,3-diazacyclopentane (7a). 2-(Dinitromethylene)-1-nitro-1,3-diazacyclopentane (**7a**) (0.2 g, 0.9 mmol) was added at 0 °C to a solution of 100% HNO_3 (2.5 g 40 mmol) and trifluoroacetic anhydride (6 g, 29 mmol) in CH_2Cl_2 (30 mL). The solution was stirred at 0 °C for 2 h, and 50 mL of ice-water was added. The organic layer was washed with water (2 × 50 mL) and brine (50 mL) and dried ($MgSO_4$). Evaporation of solvent gave 0.22 g (91%) of 3-nitro-3-(trinitromethyl)-1,3-diazacyclopent-1-ene (**3a**).

Nitration of 2-(Nitromethylene)-1,3-diazacyclopentane (8a). 2-(Nitromethylene)-1,3-diazacyclopentane (**8a**) (1.00 g, 7.74 mmol) was added to a solution of trifluoroacetic anhydride (32.5 g, 155 mmol) and 90% nitric acid (10 g, 155 mmol) in methylene chloride (100 mL) at 0 °C. The solution was stirred at 0 °C for 1 h and allowed to warm to room temperature overnight. The solution was poured onto 100 mL of ice, and the mixture was stirred for 30 min. The organic layer was then washed with water (2 × 100 mL) and brine (100 mL) and dried (magnesium sulfate). Evaporation of solvent gave a yellow oil which was chromatographed (silica gel, EtOAc/hexane) to give 0.45 g (22%) of 3-nitro-2-(trinitromethyl)-1,3-diazacyclopent-1-ene (**3a**).

Nitration of 2-(Nitromethylene)-1,3-diazacyclohexane (8b). Nitration of 2-(nitromethylene)-1,3-diazacyclohexane (**8b**) (1.00 g, 7 mmol) by the above procedure gave, after column chromatography (silica gel, EtOAc/hexane) and trituration with EtOAc/hexane, 0.31 g (16%) of 3-nitro-2-(trinitromethyl)-1,3-diazacyclohex-1-ene (**3b**) identical with the material described above.

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Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.