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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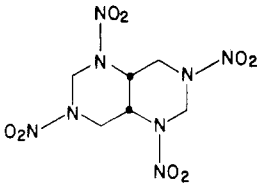
Received April 5, 1984

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.



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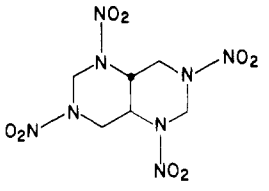

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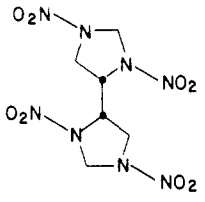

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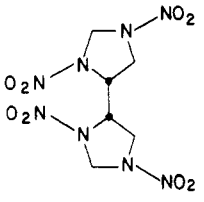

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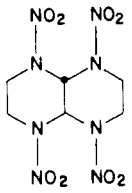
Our previous work in this area has resulted in the synthesis of *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin[1] (**5**),



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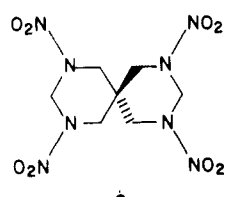

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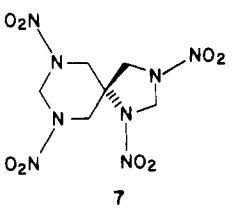

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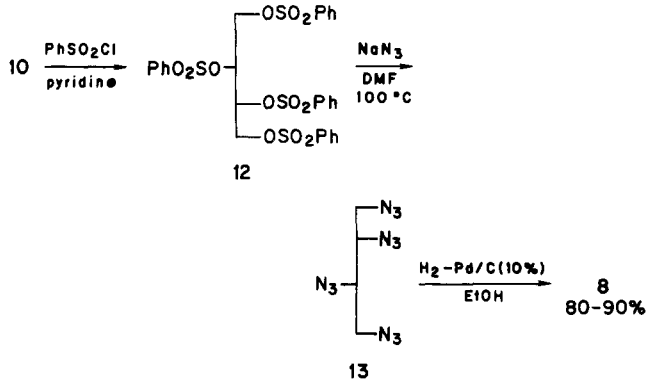
2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane[2] (**6**), and an improved synthesis of 1,3,7,9-tetranitro-1,3,7,9-tetraazaspiro[4.5]decane[3] (**7**). Compounds **5** and **7** are isomeric (i.e., both $C_6H_{10}N_8O_8$) yet they have very different densities (1.80 g/mL for **5**[1] and 1.70 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-

(1) Willer, R. L. *Prop., Explos., Pyrotech.* **1983**, *8*, 65.
(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.

Scheme I. Synthesis of *threo*-1,2,3,4-Tetraaminobutane (10)



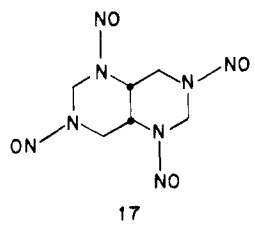
hydroxybutanes (threitol (**10**) and erythritol (**11**). These would be converted to the amines by standard procedures,[4] via the tetrabenzenesulfonate derivatives (benzenesulfonyl chloride in pyridine), tetraazides (sodium azide in dimethyl formamide), and finally reduction of the tetraazide to the tetraamine by catalytic hydrogenation.

Results

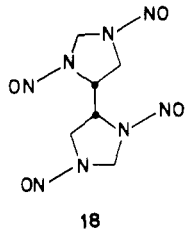
Synthesis. *cis*-1,3,5,7-Tetranitro-1,3,5,7-tetraazadecalin (1). The starting material, threitol (**10**), is commercially available, but quite expensive. We, therefore, chose to synthesize it from diethyl L-tartrate using a procedure adapted from one developed by R. U. Lemieux and J. Howard.[5] Several modifications (detailed in the Experimental Section) were made which both increased the yields and simplified the procedures. An attempted direct reduction of diethyl L-tartrate to L-threitol with $LiAlH_4$ failed.

The conversion of the L-threitol to *threo*-1,2,3,4-tetraaminobutane (**8**) is summarized in Scheme I. The tetraamine was characterized as its tetraacetamide derivative **8b**. Since the tetraamine was a hygroscopic liquid, it was difficult to get exact yield data. The best value for the combined yeild of the displacement step and reduction step was 80–90%. The crude tetramine was used for the following synthetic procedures.

Tetramine **8** was reacted with aqueous formaldehyde and the product was nitrosated in situ to give the tetranitroso derivative in 60–62% overall yield from **12**. The product was an amorphous powder and gave indications that it was a mixture of compounds. This is not unreasonable since there are three different ways for the *threo*-1,2,3,4-tetraaminobutane to cyclize, as summarized in Scheme II. As shown from the results of the nitrolysis, the product is a mixture of the tetranitroso compounds **17** and **18**.



17



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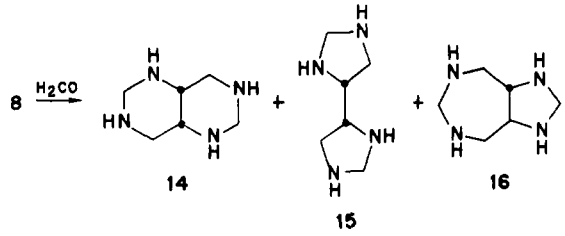
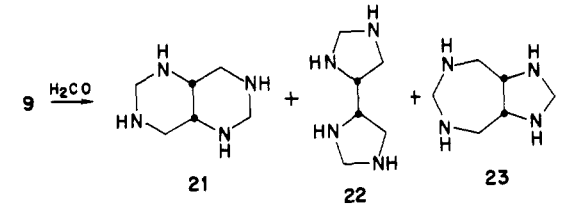
The nitrolysis of the product proceeded in rather poor yield to give a crude product which was clearly a mixture of two compounds according to ^1H NMR spectroscopy.

Scheme II. Possible Products from the Reactions of 10 with 2 mol of Formaldehyde



Scheme III. Possible Products from the Reaction of 9 with Formaldehyde



The major product was isolated in pure form by fractional recrystallization from acetone. This compound has been assigned the *cis*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (**1**) structure based upon its ^1H NMR spectrum which showed an AB pattern for the isolated methylene groups ($C_{2,6}$) with a large chemical shift difference (≈1.9 ppm). This criterion has been used previously to assign structure in the analogous tetraoxadecalin.[5]

The minor product was isolated pure by preparative thin-layer chromatography (TLC) of the mother liquors from the purification of **1**. It was assigned the (*R**,*R**)-1,1′,3,3′-tetranitro-4,4′-biimidazolidine structure (**3**) on the basis of the small chemical shift difference for the protons of the isolated methylene groups (≈0.3 ppm).

The ratio of **1** to **3** was observed to vary considerably depending on the conditions used for the reaction of **8** with formaldehyde. When this reaction was run for a short time in the cold (0–10 °C), the proportion of **3** in the final product was substantial, even to the point where it was the major product. However, if the reaction was run at 50 °C, the ratio of **1**:**3** became approximately 10:1. This would seem to indicate that **15** is the kinetically favored product of the reaction of **8** with formaldehyde while **14** is the thermodynamically favored product. No evidence could be found for the tetranitro compound corresponding to **16** which would be expected to have two AB patterns for its two different isolated methylene groups.

***trans*-1,3,5,7-Tetranitro-1,3,5,7-tetraazadecalin (2).** The conversion of **11** to the desired *meso*-1,2,3,4-tetraaminobutane (**9**) proceeded without complication through the tetrabenzenesulfonate **19** and the tetraazide **20** as in the case of the cis isomer (Scheme I). The details are given in the Experimental Section. The reaction of the tetraamine **9** with formaldehyde could again yield three products as summarized in Scheme III. The reaction was performed essentially as described for the threo isomer. The product was much more tractable than the product from the active isomer, indicating that it was probably mostly one compound. Nitrolysis of this product gave the crude *trans*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (**2**). The product could be recrystallized from DMF/H_2O to yield pure **2**. Again, the assignment of structure was based upon the large (1.5 ppm) chemical shift difference for the protons of the isolate methylene groups ($C_{2,6}$). From the mother liquors of the recrystallization of **2**, another product was isolated by preparative TLC. Small amounts of this product could also be obtained by further diluting the

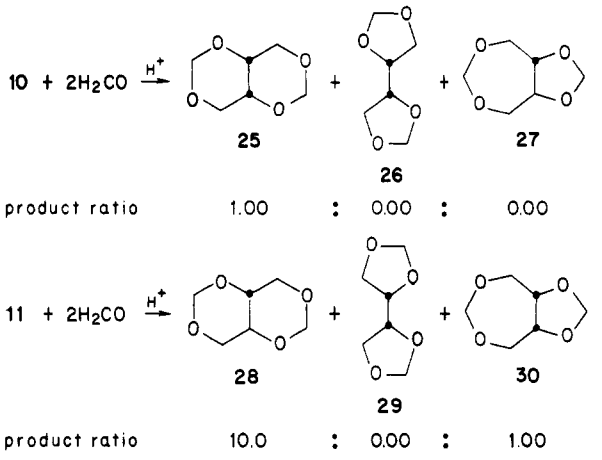
(4) (a) Fleischer, E. B.; et al. *J. Org. Chem.* **1971**, *36*, 3042. (b) Anselme, P. *Org. Prep. Proced.* **1974**, *6*, 103.
(5) Lemieux, R. U.; Howard, J. *Can. J. Chem.* **1963**, *41*, 393.

Table I. Physical and Chemical Properties of 1–4

no.	mp, °C	heat of formn, kcal/mol	density, g/cm^3
1	236–237	+19.4	1.78
2	251–252	+26.5	1.75
3	213–214	+33.0	1.71
4	198–199	nd[a]	nd[a]

[a] nd = not determined.

Scheme IV. Products from the Reaction of Threitol and Erythritol with Formaldehyde



mother liquors and chilling overnight. This product was assigned the (*R**,*S**)-1,1′,3,3′-tetranitro-4,4′-biimidazolidine structure (**4**) on the basis of the small shift difference (0.3 ppm) between the protons of the isolated methylene groups. The ratio of **2** to **4** can be estimated to be 20:1 from the ^{1}H NMR of the crude **2**. Again, no evidence could be found for the existence of any of the tetranitro derivative corresponding to **23**.

Physical and Chemical Properties of 1–4. The physical and chemical properties of compounds 1–4 that have been determined are summarized in Table I.

Discussion

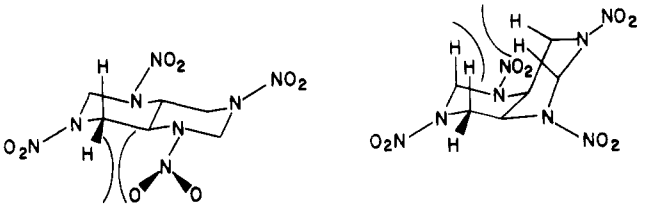
The successful synthesis of **1** and **2** clearly demonstrates that the methodology which we had developed previously for the synthesis of 1,3-dinitro-1,3-diazacycloalkanes is applicable to more complex systems. We now plan to extend this method to even more elaborate structures.

An interesting comparison can be made between this work and similar work on the reaction of threitol and erythritol with formaldehyde.[5-7] As in this work there are three possible products from each reaction as summarized in Scheme IV. In the case of threitol, it has been found that the sole isolated product is *cis*-1,3,5,7-tetraoxadecalin[5] (**25**). We observed that the reaction of *threo*-1,2,3,4-tetraaminobutane (**8**) with formaldehyde gives a mixture of **14** and **15** and that the ratio of **14**:**15** depends upon the reaction conditions. Since the reaction of threitol with formaldehyde was run under conditions which should favor the formation of the thermodynamic product (reflux, acid catalysis), these results compare favorably with ours run at higher temperatures where we obtained a 10:1 mixture of **14** and **15**. The reaction of erythritol with formaldehyde has been found to give an ≈10:1 mixture of the *trans*-1,3,5,7-tetraoxodecalin (**28**), and the 1,3-dioxalano-1,3-dioxepane[6,7] **30**, whereas we obtained a 20:1 mixture of **21** and **22** and none of the 5:7-fused compound **23**. The reasons for these differences in the erythro cases are not clear.

Physical and Chemical Properties. As might be expected, all four compounds have relatively high melting points with both decalins (**1** and **2**) having higher melting points than the biimidazolidines (**3** and **4**). Compound **2** has one of the highest melting points of the known polynitramines.

According to the Holden method,[8] compounds **1**–**4** have the same predicted density of 1.74 g/cm^3. The measured densities vary considerably from this value (see Table I). That **1** has a density greater than that of **2** is in line with the fact that *cis*-decalin has a higher density than *trans*-decalin.[9] That **3** should have such a low density is in accord with the observation that bi compounds tend to have nearly the same densities as their parent compounds because the two rings are forced to be perpendicular to each other.[10-12] We have determined the density of 1,3-dinitroimidazolidine (**31**), the parent compound of **3**, to be 1.68 g/cm^3.

The measured heats of formation (see Table I) of **1**, **2**, and **3** seem to reflect the amount of steric strain present in the molecules as estimated by inspection of molecular models of the compounds. The *trans*-decalin **2** is highly strained because of a very unfavorable interaction between the 1,5 nitro groups and the 4,8 methylene groups. As shown below, this interaction is absent in the *cis*-decalin.



Experimental Section

Caution. The polynitramino compounds described in this paper are impact sensitive, energetic materials and should be treated accordingly.

Densities were determined by gas pycnometry on a Systems, Science, and Software type 6102 gas pycnometer and are the average of three separate determinations or by single-crystal X-ray crystallographs. ^{1}H NMR spectra were recorded on a Varian EM-360 or on a Nicolet WB200 spectrometer. Heats of combustions were determined in a Parr adiabatic bomb calorimeter. IR spectra were recorded on a PE 137 spectrometer. Elemental analysis were determined by Galbraith Laboratories, Knoxville, TN.

Diethyl 2,3-Cyclohexylene-L-tartrate. A solution of diethyl tartrate (206.19 g, 1 mol) and cyclohexanone (147.2 g, 1.5 mol) dissolved in 600 mL of benzene was prepared. To this solution was added 5 g of *p*-toluenesulfonic acid monohydrate. The solution was refluxed and the water collected by means of a Dean–Stark trap. After the water had stopped collecting (16 h), the solution was cooled, washed with 10% NaOH (100 mL), and then dried over $MgSO_4$. The solution was filtered and the solvent removed at reduced pressure. The crude product was vacuum distilled to give 175.6 g of product (0.61 mol, 61%); bp 124–126 °C (0.15 mm) (lit.[5] bp 142 °C (10 mm)).

L-Threitol (10). Diethyl 2,3-*O*-cyclohexylenetartrate (57.2 g, 0.2 mol) was dissolved in 100 mL of dry tetrahydrofuran (THF).

(6) (a) Burden, I. J.; Stoddart, J. Fraser. *J. Chem. Soc., Perkin Trans 1* **1975**, 666–674. (b) Burden, I. J.; Stoddart, J. Fraser. *J. Chem. Soc., Chem. Commun.* **1974**, 863–864.

(7) Jensen, R. B.; et al. *Acta Chem. Scand., Ser. B* **1975**, *29B* 373–378.

(8) Cichra, D. A.; Holden, J. R.; Dickinson, C. NSWC Report TR79-273, Naval Surface Weapons Center, Silver Spring, MD, 1980; 39.

(9) "Handbook of Chemistry and Physics"; 45th ed.; Weast, Robert C., Ed.; The Chemical Rubber Co.: Cleveland, OH, 1964, C281.

(10) Dobratz, B. M. LLNL Report No. UCRL-52997, Lawrence Livermore National Laboratory, Livermore, CA, March 1981.

(11) Nielsen, A. T.; et al. NWC TP 6212, Naval Weapons Center, China Lake, CA, April 1981, 22 pp.

(12) C. Coon, SRI International, unpublished communications.

This solution was added dropwise over a 1-h period to a well-stirred slurry of 14.0 g of lithium tetrahydroaluminate and 400 mL of dry THF. The reaction mixture was stirred for two additional hours; then the reaction was worked up by the careful addition of water (14 mL), 15% NaOH (14 mL), and more water (28 mL). The resulting slurry was filtered and the solid material reslurried with 200 mL of hot THF and refiltered. The combined THF solutions were concentrated at reduced pressure to yield the crude 2,3-*O*-cyclohexylene-L-threitol. The IR and NMR spectra of the crude product indicated it was very pure. Water (200 mL) and 1 mL of concentrated hydrochloric acid were added to the crude product. This mixture was heated and the cyclohexanone/water azetrope distilled off over a 1-h period. The solution was cooled and extracted with 100 mL of diethyl ether. The aqueous phase was concentrated at reduced pressure to yield a thick oil which crystallized upon the addition of absolute alcohol. The alcohol was removed at reduced pressure to yield the crude L-threitol, 20.42 g (0.18 mol, 90%). A small sample was recrystallized from 95% EtOH to give needles; mp 86–87 °C (lit.[5] mp 86–88 °C).

L-Threitol Tetrabenzenesulfonate (12). L-Threitol (12.2 g, 0.1 mol) was dissolved in 200 mL of dry pyridine. This solution was cooled (salt–ice bath), and benzenesulfonyl chloride (75 mL, 0.6 mol) was added dropwise over a 1-h period. The cooling bath was removed and the mixture was stirred at room temperature for 4 h. The solution was poured onto a mixture of 300 g of ice and 100 mL of concentrated HCl. The product oiled out. The aqueous layer was decanted from the oil. The oil was dissolved in a hot mixture of methanol (300 mL) and acetone (50 mL). The volume of the solution was reduced to 200 mL and the product allowed to crystallize. The product was collected and dried. The yield was 60.2 g (0.088 mol, 88%): mp 112–114 °C; ^{1}H NMR ($CDCl_3$) δ 4.20 (m, 4 H, $H_{1,4}$), 4.90 (m, 2 H, $H_{2,3}$), 7.2–8.0 (m, 20 H, C_6H_5).

Anal. Calcd for $C_{28}H_{26}O_{12}S_4$: C, 49.26; H, 3.81. Found: C, 49.18; H, 4.00.

***threo*-1,2,3,4-Tetraazidobutane (13).** L-Threitol tetrabenzenesulfonate (20.46 g, 0.03 mol), sodium azide (10 g, 0.15 mol), and dry DMF (200 mL) were placed in a 500-mL flask. This solution was stirred at 100 °C for 4 h and then cooled to 10 °C and diluted with 250 mL of H_2O. The H_2O/DMF solution was extracted with ether (4 × 100 mL) and the combined ether extracts both extracted with water (2 × 50 mL). The ether solution was dried over $MgSO_4$ and filtered, and the ether was removed at reduced pressure to give crude *threo*-1,2,3,4-tetraazidobutane. The products contained a fair amount of DMF so no yield data could be obtained. No attempt has been made to purify the product because of the known hazards of polyazido compounds: ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 6 H).

***threo*-1,2,3,4-Tetraaminobutane (8).** The crude tetraazide was dissolved in 120 mL of 95% ethanol in a 500-mL Parr bottle, and 1 g of 10% Pd/C was added. This mixture was hydrogenated at 55 psi with the tank shut off. Every hour the bottle was vented and fresh hydrogen was introduced. After 4 h the solution was filtered and the solvent removed at reduced pressure to yield crude *threo*-1,2,3,4-tetraaminobutane. A small portion of this reacted with acetic anhydride to give the tetraacetamide derivative; mp 242–244 °C.

Anal. Calcd for $C_{12}H_{22}N_4O_4$: C, 50.33; H, 7.74; N, 19.57. Found: C, 49.94; H, 7.92; N, 19.17.

***cis*-1,3,5,7-Tetranitroso-1,3,5,7-tetraazadecalin (17) and (*R**,*R**)-1,1′,3,3′-Tetranitroso-4,4′-biimidazolidine (18).** The crude **8** was dissolved in 30 mL of distilled water, and 5.0 g of 37% aqueous formaldehyde solution was added dropwise over a 5-min period. The mixture was stirred at 50 °C for 1 h. The solution was cooled to 5 °C, and sodium nitrite (8.4 g, 0.12 mol) was added. When the sodium nitrite had completely dissolved, 60 mL of 2 N HCl was added in one portion. The product precipitated and was collected and washed well with water. After drying the product weighed 4.61–4.80 g (0.018–0.019 mol, 60–62%).

***cis*-1,3,5,7-Tetranitro-1,3,5,7-tetraazadecalin (1) and (*R**,*R**)-1,1′,3,3′-Tetranitro-4,4′-biimidazolidine (3).** The crude product from the previous step was ground into a fine powder. A 3-g portion (0.012 mol) was then added over a 10-min period to 45 mL of well stirred 100% nitric acid which was maintained at −30 °C by means of a dichloroethane–dry ice slush. After the addition was complete, the dichloroethane bath was removed and replaced with an ice–water bath. The solution was stirred at 0 °C for 20 min; then the ice–water bath was removed and replaced with a 40 °C hot water bath. The mixture was stirred at 40 °C for 15 min and then poured onto 200 g of ice. After the ice had melted, the quench solution was diluted to 500 mL. The crude product was collected by vacuum filtration. A second crop could be collected by allowing the mother liquor to stand overnight. The first crop of crude product weighed 2.26–2.46 g after drying, the second crop 0.75 g. The total yield of crude product is approximately 3.02 g (0.009 mol, 80%). Depending upon the conditions used for the reaction of **10** with formaldehyde, the ratio of **1**:**3** varies from 5:1 to ≈1:1 as determined by the intensity of the $H_{2,6}$ protons.

Separation of 1 and 3. Mixtures Rich in 1. The entire crude product (≈3.0 g) was dissolved in acetone and filtered to remove insoluble materials. The solution was concentrated to 15 mL, and a seed crystal of pure **1** was added. The solution was allowed to evaporate slowly until the volume of liquid was ≈5 mL. The liquid was removed by means of a pipette, and the crystals were washed twice with 10 mL of ethyl acetate and dried in vacuum to give 1.80 g of pure **1**, mp 234–235 °C; ^{1}H NMR ($(CD_3)_2CO$) δ 4.28 (m, 2 H, $H_{4,8}$a), 4.90 (m, 2 H, $H_{4,8}$e), 5.17 (*AB*, J_{AB} = 15 Hz, 2 H, $H_{2,6}$a), 5.57 (m, 2 H, $H_{9,10}$), 7.06 (*AB*, J_{AB} = 15 Hz, 2 H, $H_{2,6}$e).

Anal. Calcd for $C_6H_{10}N_8O_8$: C, 22.36; H, 3.12; N, 34.78. Found: C, 22.60; H, 3.20; N, 34.83.

Mixtures Rich in 3. The crude product was dissolved in 20 mL of acetone and filtered to remove insoluble materials. The solution was warmed to reflux, and water was added dropwise until the solution remained turbid. More acetone was added, and the solution was allowed to cool. The product was collected and washed with acetone. The pure **3** melts at 213–214 °C: ^{1}H NMR ($(CD_3)_2CO$) δ 4.40 (m, 2 H, $H_{3,5'}$), 4.60 (m, 2 H, $H_{5,5'}$), 5.55 (m, 2 H, $H_{4,4'}$), 5.65 (*AB*, J_{AB} = 9.2 Hz, 2 H, $H_{2,2'}$), 5.92 (*AB*, J_{AB} = 9.2 Hz, 2 H, $H_{2,2'}$).

Anal. Calcd for $C_6H_{10}N_8O_8$: C, 22.36; H, 3.13; N, 34.78. Found: C, 22.67; H, 3.12; N, 35.01.

Mixture of 1 and 3. In addition, small amounts of mixtures of **1** and **3** can be separated by preparative TLC using 2-mm silica gel plates and a 50:50 THF–hexane solvent system. The R_fs of **1** and **3** approximately 0.2 and 0.7, respectively.

***meso*-Erythritol Tetrabenzenesulfonate (19).** *meso*-Erythritol (12.2 g, 0.1 mol) was reacted with benzene sulfonyl chloride as described for the threo isomer to give the desired product. It weighed 60.2 g (0.088 mol, 88%): mp 184–185.5 °C; ^{1}H NMR (Me_2SO-d_6) δ 4.30 (m, 4 H, $H_{1,4}$), 5.25 (m, 2 H, $H_{1,4}$), 7.8–8.1 (m, 20 H, C_6H_5).

Anal. Calcd for $C_{28}H_{26}O_{24}S_4$: C, 49.27; H, 3.81. Found: C, 49.46; H, 3.91.

***erythro*-1,2,3,4-Tetraazidobutane (20).** Erythritol tetrabenzenesulfonate (20.4 g, 0.03 mol) was reacted with sodium azide in DMF as described for the threo isomer to give the *erythro*-1,2,3,4-tetraazidobutane: ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 6 H).

***meso*-1,2,3,4-Tetraaminobutane (9).** The crude tetraazidobutane was converted to the tetraamine as described for the *d,l* isomer. A small portion was reacted with acetic anhydride to give the tetraacetamide with mp 310–311 °C.

Anal. Calcd for $C_{12}H_{22}N_4O_4$: C, 50.33; H, 7.75; N, 19.57. Found: C, 50.29; H, 7.65; N, 19.51.

***trans*-1,3,5,7-Tetranitroso-1,3,5,7-tetraazadecalin (24).** The crude *erythro*-1,2,3,4-tetraaminobutane was dissolved in 30 mL of water, and this solution was cooled to 5 °C. Thirty-seven percent aqueous formaldehyde (4.06 g, 0.06 mol) was then added dropwise with stirring. The cooling bath was removed and the mixture stirred at 50 °C for 1 h. Sodium nitrite (8.28 g, 0.12 mol) was added to the solution. When the sodium nitrite had completely dissolved, the solution was cooled to 5 °C, and a solution of 11.5 g of concentrated hydrochloric acid diluted to 50 mL was added. A precipitate formed almost immediately. After 10 min of stirring, the product was collected by vacuum filtration and washed well with water. After drying, the product weighed 2.62 g (0.010 mol, 33%). The material could be recrystallized from DMF/H_2O to give light yellow platelets with mp 200–202 °C dec.

***trans*-1,3,5,7-Tetranitro-1,3,5,7-tetraazadecalin (2).** Fifteen milliliters of 100% nitric acid was placed in a 50-mL Erlenmeyer flask. A magnetic stirring bar was added and the contents cooled

to −30 °C by means of a dichloroethane–dry ice slush. *trans*-1,3,5,7-Tetranitroso-1,3,5,7-tetraazadecalin was added to this solution over 10 min. The dichloroethane–dry ice bath was replaced with an ice–water bath. After being stirred at 0 °C for 30 min, the mixture was stirred at 50 °C for 10 min. The solution was then poured onto 30 g of ice. After the ice had melted, the product was collected by vacuum filtration and was washed well with water. After drying, the crude product weighed 0.66 g. It was purified by dissolving in warm DMF (60 °C) and by adding water until turbid. After cooling to 0 °C, the crystals were collected. The puridied product weighed 0.41–0.45 g and melted at 252–254 °C: ^{1}H NMR (Me_2SO-d_6) δ 4.10 (m, 2 H, $H_{4,8}$a), 4.50 (m, 2 H, $H_{4,8}$e), 4.89 (m, 2 H, $H_{9,10}$), 5.42 (*AB*, J_{AB} = 15 Hz, 2 H, $H_{2,6}$a), 6.81 (*AB*, J_{AB} = 15 Hz, 2 H, $H_{2,6}$e).

Anal. Calcd for $C_6H_{10}N_8O_8$: C, 22.36; H, 3.13; N, 34.78. Found: C, 22.62; H, 3.21; N, 34.62.

***meso*-(*R**,*S**)-1,1′,3,3′-Tetranitro-4,4′-biimidazolidine (4).** By diluting the mother liquors from the recrystallization of **2** with water, an impure material could be isolated. This material was purified by preparative TLC (silica gel G_1/THF–hexane) to give pure **4**: mp 198–199 °C; ^{1}H NMR (Me_2SO-d_6) δ 4.10 (m, 2 H, $H_{5,5'}$), 4.43 (m, 2 H, $H_{5,5'}$), 5.26 (m, 2 H, $H_{4,4'}$), 5.45 (*AB*, J_{AB} = 8.6 Hz, 2 H, $H_{2,2'}$), 5.68 (*AB*, J_{AB} = 8.6 Hz, 2 H, $H_{2,2'}$).

Anal. Calcd for $C_6H_{10}N_8O_8$: C, 27.36; H, 3.13; N, 34.78. Found: C, 27.52; H, 3.22; N, 34.82.

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Registry No. (±)-**1**, 92937-59-2; **2**, 92902-06-2; (±)-**3**, 92902-01-7; *meso*-**4**, 92902-07-3; (±)-**8**, 92901-97-8; (±)-**8** (tetraacetamide deriv), 92901-98-9; *meso*-**9**, 92902-03-9; *meso*-**9** (tetraacetamide deriv), 92902-04-0; **10**, 2319-57-5; **12**, 92901-95-6; (±)-**13**, 92901-96-7; (±)-**14**, 92902-08-4; (±)-**15**, 92902-09-5; (±)-**17**, 92901-99-0; (±)-**18**, 92902-00-6; *meso*-**19**, 92998-69-1; *meso*-**20**, 92902-02-8; **21**, 92902-10-8; *meso*-**22**, 92902-11-9; **24**, 92902-05-1; **31**, 5754-91-6; diethyl 2,3-cyclohexylidene-L-tartrate, 61045-33-8; diethyl tartrate, 87-91-2; cyclohexanone, 108-94-1; 2,3-*O*-cyclohexylidene-L-threitol, 60989-82-4; benzenesulfonyl chloride, 98-09-9; *meso*-erythritol, 149-32-6.

The Use of Carbon–Carbon Connectivity in the Structure Determination of Marmelerin, a Novel Benzofuran Sesquiterpene from *Croton sonderianus*

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The essential oil of *Croton sonderianus* Muell. Arg. (Euphorbiaceae) contains α- and β-pinene, camphene, myrcene, limonene, γ-terpinene, camphor, terpinen-4-ol, copaene, β-elemene, α-gurjunene, cyperene, β-caryophyllene, thujopsene, *trans*-β-farnesene, γ- and δ-cadinene, γ-muurolene, palustrol, guayazulene, and a new benzofuran sesquiterpene named marmelerin (**1**), dihydro-1,2,5,8-tetramethyl-6*H*-indeno[5,4-*b*]furan, whose structure was established by means of a two-dimensional ^{13}C INADEQUATE experiment.

Croton sonderianus Muell. Arg. is a shrub widespread in the Brazilian Northeast and known in the region as "marmeleiro preto". The bark is used in folk medicine for treatment of gastric diseases. Hexane or benzene extracts of its heartwood and roots have shown antifungal and antibacterial activity against *Saccharomyces cerevisiae*, *Helminthosporium* sp., *Trichophyton mentagrophytes*, *Polyporus sanguineus*, *Bacillus subtilis*, *Staphylococcus aureus*, and *Mycobacterium smegmatis*. From the benzene extract of the heartwood was isolated a new clerodane diterpene possessing a spirolactone ring system and named sonderianin whose structure and stereochemistry were determined by X-ray crystallography,[1] a known coumarin, and two new cleisthantane diterpenes.[2]

The leaves produce an essential oil which was analyzed by open tubular glass capillary chromatography coupled to a mass spectral–computer system allowing the identification of α- and β-pinene, camphene, myrcene, limonene, γ-terpinene, camphor, terpinen-4-ol, copaene, β-elemene, α-gurjunene, cyperene, β-caryophyllene, thujopsene, *trans*-β-farnesene, γ- and δ-cadinene, γ-muurolene, and palustrol.[3,4] Herein we are reporting the isolation of guayazulene and a novel benzofuran sesquiterpene from the residue of the fractionally distilled essential oil as well as from the nonpolar fraction of the hexanic extract of roots of the shrub.

Results and Discussion

Fractional distillation of the essential oil gave a residual fraction (bp 260–265 °C (15 mmHg)) which after column chromatography over silica gel produced two pure liquid

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