(27.4 g, 0.477 mol). The flask was then equipped with a reflux condenser topped with a three-way stopcock having a vertical tubulation capped with a septum through which solvents and reagents could be introduced with a syringe fitted with a long needle. By evacuation through the other tubulation of the stopcock, the apparatus was placed under vacuum (≤0.1 Torr) for 1–2 h to remove the bulk of the mineral oil. The flask was then filled with nitrogen, anhydrous tetrahydrofuran (850 mL; distilled from sodium benzophenone ketyl) was added, and the mixture was heated at reflux for 18 h. The mixture was cooled to 0 °C, chloromethyl methyl sulfide (35.2 mL, 0.420 mol) was added dropwise over 25 min, and the mixture was stirred for 1 h at 0 °C and for 1 h at 25 °C. Iodomethane (30.6 mL, 0.492 mol) was added over 5 min, the mixture was stirred for another 15 h at 25 °C, the volatile components were removed under vacuum (≤0.1 Torr), the vacuum was relieved with nitrogen, and the stopcock was removed from atop the condenser, thus exposing the mixture to the air. A solution of sodium tetrafluoroborate (277 g, 2.52 mol) in water (1200 mL) was prepared and was heated to 95 °C. Most of the solution (1000 mL) was slowly poured down the condenser into the flask while the reaction mixture was being stirred. The mixture was suctioned filtered through a preheated (hot water) 350-mL, medium-frit, sintered glass Büchner funnel containing a layer of diatomaceous earth and a layer of sand. The flask and the filter were rinsed with the remaining hot sodium tetrafluoroborate solution, and the combined filtrates were cooled slowly to 0 °C and placed in a freezer at ca. −10 °C for 1–3 h. The product was collected on a Büchner funnel, washed with cold water (150 mL) and cold ether (1500 mL), and dried in a stream of air overnight to give 89.2 g (62.4% overall yield) of 1 as amber-colored, flakelike crystals, identical with the previously reported compound.[2]

(η^5-1,2,3,4,5-Pentamethylcyclopentadienyl)dicarbonyl-[(dimethylsulfonio)methyl]iron Tetrafluoroborate (2). Freshly cut potassium (0.15 g, 3.9 mmol) was cleaned by melting in warm, anhydrous THF (10 mL) under an argon atmosphere. After the potassium was cooled to 25 °C, the solvent was replaced by fresh THF (30 mL), $\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2Fe\}_2$ (0.84 g, 1.7 mmol) was added, and the argon atmosphere was reestablished. The slurry was heated in an oil bath at 65–70 °C while being vigorously stirred for 4 h, after which only a small amount of particulate potassium remained. The red solution was cooled in an ice bath, and $ClCH_2SCH_3$ (0.33 mL, 3.9 mmol) was slowly added via syringe. The mixture was stirred for 45 min in the ice bath and for an additional hour at 25 °C. Iodomethane (1 mL, 16 mmol) was added, and the mixture was stirred at 25 °C for 16 h. The solvent was removed on the rotary evaporator from the resulting yellow slurry. The residue was taken up in a hot solution of $NaBF_4$ (1 g, 9 mmol) and water (40 mL), and the mixture was filtered to remove a dark oily substance. The product crystallized upon cooling, giving 1.1–1.2 g (92–100%) of 2 as yellow-orange crystals: mp 152–156 °C; IR (KBr) 1997 and 1945 (CO str) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.85 (s, 6 H), 2.14 (s, 2 H), 1.80 (s, 15 H).

Standard Procedure for Cyclopropanation of Alkenes. 1,1-Diphenylcyclopropane. Into a 5-mL round-bottom flask were placed a magnetic stirring bar, reagent 1 or 2 (2.00 mmol), and 1,1-diphenylethylene (0.180 g, 1.00 mmol). The flask was fitted with a reflux condenser, atop of which was placed a stopcock, and a nitrogen atmosphere was established within the apparatus. Nitromethane (0.50 mL)[9] was added, and the mixture was heated at reflux (oil bath temperature 116 °C) for up to 4 h while being stirred. The reaction mixture was cooled, and the product was isolated with hexane as a workup solvent and ferric chloride to destroy ferrocene as reported previously.[2b] Obtained was 0.167–0.173 g (86–89%) of 1,1-diphenylcyclopropane.[2b]

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Registry No. 1, 72120-26-4; 2, 120120-19-6; $[\eta^5\text{-}C_5H_5(CO)_2Fe]_2$, 12154-95-9; $\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2Fe\}_2$, 35344-11-7; $ClCH_2SCH_3$, 2373-51-5; 1,1-diphenylethene, 530-48-3; 1,1-diphenylcyclopropane, 3282-18-6.

(9) The nitromethane (Eastman Kodak) was dried first over anhydrous $MgSO_4$ and then over anhydrous $CaSO_4$ overnight. The solvent was filtered into a flask containing activated 3-Å molecular sieves and was heated at 60 °C for 8 h while being stirred. The nitromethane was distilled from the powdered molecular sieves under reduced pressure (bp 58 °C, 150 Torr; Lit.[10] bp 58 °C, 160 Torr) directly into a flask containing additional 3-Å molecular sieves. The purified solvent was stored in the dark. When "wet" nitromethane from commercial sources is used directly as a reaction solvent, the percent conversions of alkenes to cyclopropanes are reduced substantially. **CAUTION**: Distillations of nitromethane and reactions using this solvent at elevated temperature should be conducted behind a safety shield.

(10) Smith, S. G.; Fainberg, H. H.; Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 618.

1-Amino-3,5,7-trinitroadamantane: An Unexpected Oxidation Product of 1,3,5,7-Tetraaminoadamantane. An Improved Synthesis of 1,3,5,7-Tetranitroadamantane

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Recent investigations in our laboratories have focused on the synthesis of strained polycyclic hydrocarbons possessing multiple nitro groups in order to establish their potential as useful energetic materials.[1] Many of the currently available methods for the preparation of these molecules introduce the requisite nitrogens as amino groups, which are subsequently oxidized.[2] The often modest yields obtained from the oxidations, using classical oxidizing agents,[2] has prompted us to devise new strategies for effecting the amino to nitro conversion.

It has recently been demonstrated that a biphasic system of ethyl acetate or dichloromethane and water containing sodium percarbonate (SPC), sodium bicarbonate, and *N,N,N',N'*-tetraacetylethylenediamine (TAED) oxidized primary amines to the corresponding *C*-nitroso compounds in good to excellent yields via the agency of in situ generated peroxyacetic acid.[3,4] This observation and the well-known fact that *C*-nitroso monomers are smoothly converted to nitro compounds on treatment with ozone[5] suggested that this two-step sequence might serve as a useful method to accomplish the desired amine to nitro oxidation (Scheme I).

1-Aminoadamantane (**1a**) was selected as a model compound because 1-nitrosoadamantane maintains a favorable equilibrium concentration of its monomeric form **1b** in solution as judged by the presence of the intense blue color characteristic of aliphatic nitroso monomers. It appears that the dissociation of the nitroso dimer **1c** into its mo-

(1) Sollott, G. P.; Alster, J.; Gilbert, E. E.; Sandus, O.; Slagg, N. J. *Energ. Mater.* **1986**, *4*, 5.

(2) (a) Sollott, G. P.; Gilbert, E. E. *J. Org. Chem.* **1980**, *45*, 5405. (b) Eaton, P. E.; Ravi Shankar, G. J.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185. (c) Marchand, A. P.; Dave, P. R.; Satyanarayana, N.; Arney, B. E., Jr. *J. Org. Chem.* **1988**, *53*, 1088.

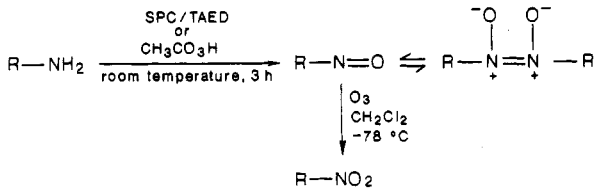
(3) Zajac, W. W.; Walters, T. R.; Woods, J. M. *Synthesis* **1988**, 808.

(4) Dankowski, M.; Kuzel, P.; Lieser, T. *Chim. Oggi.* **1986**, *10*, 60.

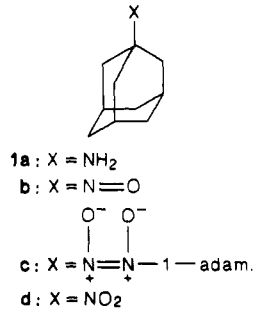
(5) Bailey, P. S. In Ozonation in Organic Chemistry, *Organic Chemistry*; Wasserman, H. H., Ed.; Academic Press: New York, 1982; Vol. 39-II, p 196.

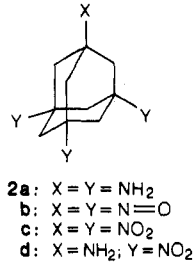
0022-3263/89/1954-2468$01.50/0

Scheme I



nomeric form is essential for the success of the ozonation. Consequently, the ozonation was conducted with use of alternating periods of low-temperature ozonation and room-temperature monomer–dimer equilibration. When no blue color attributable to the nitroso monomer was detected following the equilibration period, 1-nitroadamantane (**1d**) was isolated in 95% yield.





This sequence of reactions was then applied to 1,3,5,7-tetraaminoadamantane (**2a**). Initially, a 62% yield of 1,3,5,7-tetranitroadamantane (**2c**) was obtained, but a substantial lengthening of the SPC-TAED reaction period, from 3 to 65 h, resulted in the isolation of a 91% yield of **2c** following ozonation. The reaction has been successfully carried out on a 15 mM scale (5 g) with only a modest decrease in yield to 83%. This represents a significant improvement over the 48% yield of 1,3,5,7-tetranitroadamantane (**2c**) obtained from the permanganate oxidation[2a] of 1,3,5,7-tetraaminoadamantane (**2a**).

To characterize 1,3,5,7-tetranitrosoadamantane (**2b**), the expected product of the initial reaction, the crude reaction mixture obtained from the SPC-TAED oxidation was subjected to preparative thin-layer chromatography. The fact that the isolated product was not the expected 1,3,5,7-tetranitrosoadamantane (**2b**) was indicated when the molecular ion was determined by FAB mass spectrometry to be m/z 286 instead of the m/z 252 anticipated for **2b**. The molecular ion at m/z 286 was supported by the elemental analysis data, which was consistent with the formula $C_{10}H_{14}N_4O_6$ (MW = 286). The reason for the oxygen excess, relative to **2b** ($C_{10}H_{12}N_4O_4$), was readily apparent from the infrared spectrum with the appearance of absorptions at 1540 (vs), 1457 (w), 1363 (s), and 1232 (w) cm^{-1}, indicative of the presence of at least one nitro group.

The ^1H and ^{13}C NMR spectra indicated C_{3v} symmetry. The only molecule consistent with all of the spectroscopic and analysis data was 1-amino-3,5,7-trinitroadamantane (**2d**). This result was unexpected due to the absence of any discernible bands in the N–H stretching region of the infrared spectrum. The structure was subsequently verified by single-crystal X-ray analysis.[6]

A series of reactions were conducted in order to compare the results of the above SPC-TAED oxidations with those employing peroxyacetic acid obtained from a commercial source as a 35% solution in dilute acetic acid. The reactions of the peroxyacetic acid were examined at three different pHs. These were pH = 2, the pH of the aqueous phase following the addition of the commercially available reagent, pH = 11, the pH of the aqueous layer in the SPC-TAED reaction mixtures, and pH = 8, an intermediate value selected to obviate the shortcomings encountered at the other two pHs (vide infra).

The yield of 1-nitroadamantane (**1d**) isolated from the acidic reaction (pH = 2) was only 16% following ozonation. The yields of **1d** obtained under the basic reaction conditions were 91% and 94% following ozonation for the pH = 11 and pH = 8 oxidations, respectively.

The dramatic decrease in the yield of 1-nitroadamantane under the acidic conditions is thought to result from the protonation of the amine by the acetic acid component of the commercially available reagent and the undesired partitioning of the resulting ammonium acetate into the aqueous layer of the biphasic solvent system.

Although the yields of 1-nitroadamantane (**1d**) were comparable when either the SPC-TAED or basic peroxyacetic acid and ozone oxidations were coupled, an analysis of the crude reaction mixtures isolated after peracid treatment revealed some distinct differences. These differences were regarding the amount of 1-nitroadamantane (**1d**) present in these reaction mixtures prior to ozonation. Thus, while no **1d** was detected in the crude product mixture isolated from the SPC-TAED reaction, **1d** was present in the basic peroxyacetic acid reaction products to the extent of 10% and 32% at pHs 11 and 8, respectively.

These differences correlate with the concentration of peroxyacetic acid attained in the organic phase of each of the biphasic reaction mixtures. The lowest concentration is expected for the SPC-TAED oxidation as the pH of 11 measured for this reaction mixture, due to the presence of a substantial concentration of sodium carbonate from the SPC, is considerably greater than the peroxyacetic acid pK_a of 8.2. Thus, this situation strongly favors the rapid deprotonation of the peroxyacetic acid as it is generated and the attendant partitioning of resulting sodium peroxyacetate into the aqueous phase, thereby restricting the concentration of the free peroxyacid attained in the organic phase. Additionally, the concentration is being limited further by the slow rate of generation of the peroxy acid. The recovery of substantial amounts of TAED from some reaction mixtures suggests that the maximum stoichiometrically allowed amount of peroxyacetic acid is not being generated, and consequently its maximum concentration is not achieved in the normal (3 h) reaction period. The partitioning of the peroxyacetic acid and peroxyacetate anion is the only consideration for the buffered peroxyacetic acid reactions since the maximum amount of the peracid is introduced into the reaction mixture directly. The reaction that is buffered at a pH of 8 will have a much higher equilibrium concentration of peroxyacetic acid versus peroxyacetate, relative to the pH = 11 reaction, and hence a proportionally higher concentration of the oxidant in the organic phase. In fact, the pH 8 buffered peroxyacetic acid reaction was used to synthesize 1-nitroadamantane (**1d**) directly from the amine **1a** in 93% yield.

It should be noted that the SPC-TAED oxidations have been observed to proceed only very slowly at the reduced pH of 8. This reduction in rate is believed to be due to the much lower concentration of the hydroperoxide anion, which is necessary to generate the peracid from the TAED, at the lower pH.

The basic peroxyacetic acid–ozone oxidation sequence was then applied to 1,3,5,7-tetraaminoadamantane (**2a**).

(6) Gilardi, R.; et al. Manuscript in preparation.

The yields of 1,3,5,7-tetranitroadamantane (**2c**) were comparable to those obtained for the SPC-TAED sequence, being 89% and 84% for the reactions buffered at pH = 8 and pH = 11, respectively.

The 1-amino-3,5,7-trinitroadamantane (**2d**) could be isolated only in much lower yields from the basic peroxyacetic acid oxidations because the majority of the amorphous blue solid obtained when the solvent was removed could not be redissolved. The material that did dissolve was determined to be a mixture of **2c** and **2d**. The peroxyacetic acid is thus capable of oxidizing the tetraamine **2a** directly to **2c**. The rate of the overall transformation is slow, and substantial yields (73%) of **2c** can be isolated only after prolonged (>72 h) reaction periods.

These results suggest that peroxyacetic acid is capable of oxidizing 1-aminoadamantane (**1a**) and 1,3,5,7-tetraaminoadamantane (**2a**) to the corresponding nitro compounds **1d** and **2c**, respectively. The rates for the overall transformations are slow but are found to increase with increasing peroxyacetic acid concentrations. This study has also demonstrated that the course of the peroxyacetic acid oxidation of 1,3,5,7-tetraaminoadamantane **2a** is greatly influenced by the presence of the other amino groups on the cage. Thus, while 1-aminoadamantane (**1a**) is cleanly converted to 1-nitrosoadamantane (**1b**) and **1c** by using the SPC-TAED method, three of the amino groups of 1,3,5,7-tetraaminoadamantane are oxidized to nitro at an unprecedented rate while leaving one of the amino groups suprisingly unreacted. The oxidation of the final amino group presents something of a contradiction in that it displays greatly reduced reactivity toward the peroxyacetic acid but enhanced reactivity toward ozone, undergoing an unprecedented near-quantitative oxidation to a nitro group during low-temperature ozonation in solution.[7]

The isolation of 1-amino-3,5,7-trinitroadamantane in good yield by using the SPC-TAED method suggests that this oxidation system may prove useful for effecting selective oxidations in other polyamines. However, the surprising reactivity of the polyamino cage compound relative to its monofunctional counterpart implies that great care must be taken when extrapolating oxidation results to new cage systems.

Experimental Section

Melting points were determined by using a Thomas-Hoover apparatus or Fisher-Johns hot stage and are uncorrected. The FAB mass spectrum was obtained on a VG-7070E using a thioglycerol matrix and argon atoms with an acceleration current of 1 mA at 7 kV. Ozonations were performed with a Welsbach T-408 ozone generator with an oxygen pressure of 6 psi, applied voltage of 90 V and an ozone–oxygen flow rate of 1.25 L/min.

SPC-TAED/Ozone Oxidation of 1-Aminoadamantane (1a). 1-Aminoadamantane (**1a**) (5.0g, 33.1 mmol) was added to a biphasic mixture of dichloromethane (250 mL) and water (250 mL) containing *N,N,N',N'*-tetraacetylethylenediamine (18.86 g, 82.7 mmol, 2.5 equiv; this provides for the formation of 5.0 equiv of peroxyacetic acid), sodium percarbonate (51.81 g, 33.0 mmol, 10 equiv), and sodium bicarbonate (15.0 g, 17.8 mmol). The mixture was stirred at room temperature for 4.5 h, during which time an intense blue color formed in the organic layer. The organic layer was separated, and the aqueous fraction was extracted with dichloromethane (3 × 150 mL). The combined organic layers were washed sequentially with water (2 × 150 mL) and a saturated sodium chloride solution (2 × 100 mL) and dried (anhydrous sodium sulfate). The drying agent was removed by filtration, and the filtrate was concentrated in vacuo to a final volume of 100 mL. The intense blue solution was ozonized for 1 h at −78 °C, after which time a white precipitate had formed and the blue color of the reaction had changed from that of the nitroso monomer to that of condensed ozone. The excess ozone was purged with an oxygen stream, and the reaction mixture was permitted to warm to room temperature. The equilibrium between the monomeric and dimeric forms of the nitroso compound was fully reestablished after 2 h, and the reaction mixture was again subjected to an ozone/oxygen stream at −78 °C for 1 h. This alternation of periods of ozonation and equilibration was continued until no blue color attributable to the nitroso monomer could be detected following the equilibration period (four cycles total). The solvent was removed in vacuo, and the residue was recrystallized from ethanol, thereby affording 5.7 g (95%) of 1-nitroadamantane (**1d**) as a colorless waxy solid: mp 156–158 °C (lit.[8] mp 157–160 °C).

Peroxyacetic Acid/Ozone Oxidation of 1-Aminoadamantane (1a) (pH = 2). 1-Aminoadamantane **1a** (0.20g, 1.32 mmol) was dissolved in a biphasic mixture of dichloromethane (50 mL) and distilled water (50 mL). The peroxyacetic acid solution (1.44 g of a 35% solution in dilute acetic acid, 6.61 mmol, 5 equiv) was added, and the reaction mixture was stirred for 3 h at room temperature. The organic layer was separated, and the aqueous phase was washed with dichloromethane (3 × 50 mL). The combined organic layers were washed sequentially with water (2 × 100 mL) and brine (1 × 100 mL) and dried (anhydrous sodium sulfate). The drying agent was removed by filtration, and the filtrate was reduced by rotary evaporation to a final volume of 50 mL. The blue solution was cooled to −78 °C and subjected to an ozone/oxygen stream for 1 h. The solution was purged of excess ozone with a stream of oxygen and permitted to warm to room temperature. No blue color attributable to the nitroso monomer **1b** was detected after 2 h at room temperature so the solvent was removed in vacuo. The white solid obtained was subjected to preparative thin-layer chromatography (silica gel, chloroform). Isolation of the material from the band at R_f = 0.78 provided 38.3 mg (16%) of 1-nitroadamantane (**1d**).

Peroxyacetic Acid/Ozone Oxidation of 1-Aminoadamantane (1a) (pH = 8). The procedure used was identical with the preceding one except that a saturated sodium bicarbonate solution (50 mL) replaced the water used in the initial biphasic solvent system and the peroxyacetic acid solution was added in small portions to minimize foaming. The band at R_f = 0.80 provided 225 mg (94%) of 1-nitroadamantane (**1d**) under these conditions.

Peroxyacetic Acid/Ozone Oxidation of 1-Aminoadamantane (1a) (pH = 11). The procedure used was identical with that of the pH = 8 reaction except that sodium carbonate (3.00 g, 28.3 mmol) was added after the addition of the peroxyacetic acid solution to raise the pH to ~11. The yield of 1-nitroadamantane (**1d**) isolated after chromatography was 218 mg (91%) under these conditions.

Peroxyacetic Acid Oxidation of 1-Aminoadamantane (1a) (pH = 8). 1-Aminoadamantane (**1a**) (0.20 g, 1.32 mmol) was added to a biphasic mixture of dichloromethane (50 mL) and a saturated sodium bicarbonate solution (50 mL). The peroxyacetic acid solution (2.87 g, 13.2 mmol, 10 equiv) was cautiously added, and the reaction mixture was stirred at room temperature until the blue color of the monomeric nitroso intermediate **1b** could no longer be detected (6–8 h). The reaction mixture was worked up as described above. The yield of 1-nitroadamantane (**1d**) isolated after chromatography was 223 mg (93%) under these conditions.

SPC-TAED Oxidation of 1,3,5,7-Tetraaminoadamantane (2a). The tetrahydrochloride of 1,3,5,7-tetraaminoadamantane (**2a**) (0.35 g, 1.0 mmol) was added to a well-stirred biphasic system of dichloromethane (25 mL) and water (25 mL) containing *N,N,N',N'*-tetraacetylethylenediamine (2.28 g, 10.0 mmol), sodium percarbonate (6.28 g, 40 mmol), and sodium bicarbonate (2.30 g, 27.4 mmol). Stirring was continued for 3 h at room temperature, after which time the green reaction mixture was transferred to a separatory funnel. The organic layer was washed sequentially with water (3 × 25 mL) and a saturated sodium chloride solution (2 × 25 mL) and dried (anhydrous sodium sulfate), and the solvent

(7) Bailey, P. S. In Ozonation in Organic Chemistry, *Organic Chemistry*; Wasserman, H. H., Ed.; Academic Press: New York, 1982; Vol. 39-II, p 175.

(8) Belanger, P. M.; Grech-Belanger, O. *Can. J. Pharm. Sci.* **1977**, *12*, 99.

was removed in vacuo to provide a slightly green amorphous solid. Analytical TLC (silica gel, 35% ethyl acetate/petroleum ether) indicated the presence of two major bands at R_f = 0.40 and R_f = 0.25. The top band was identified as *N,N,N',N'*-tetraacetylethylenediamine, so the crude mixture was redissolved in dichloromethane (50 mL) and extracted with 3.0 M hydrochloric acid (3 × 25 mL). The combined acid extracts were back-washed with dichloromethane (2 × 50 mL) and then neutralized by the careful addition of a saturated sodium bicarbonate solution. The now slightly basic solution was extracted with dichloromethane (6 × 25 mL), and the combined organic layers were washed with water (2 × 25 mL) and a saturated sodium chloride solution (2 × 25 mL) and dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation, and the white solid was subjected to preparative thin-layer chromatography (silica gel, 50% ethyl acetate/petroleum ether). Isolation of the material from the large prominent band at R_f = 0.32 provided 0.21 g (70%) of 1-amino-3,5,7-trinitroadamantane (**2d**). This material was then crystallized slowly from ethyl acetate–hexane to provide colorless needles: mp 200 °C (sealed tube with dec); IR (thin film) 1540 (vs), 1457 (w), 1363 (s), 1232 (w), 734 (w); ^{1}H NMR (acetone-d_6) δ 2.40 (s, 6 H), 2.84 (br s, NH_2), 2.94 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 41.3 (t), 46.7 (t), 52.8 (s), 85.9 (s); mass spectrum (FAB), *m/e* 287 (M + H), 257, 181, 145 (100). Anal. Calcd for $C_{10}H_{14}N_4O_6$: C, 41.96; H, 4.93; N, 19.57. Found: C, 42.44; H, 5.01; N, 19.35.

SPC-TAED/Ozone Oxidation of 1,3,5,7-Tetraaminoadamantane (2a). The tetrahydrochloride of 1,3,5,7-tetraaminoadamantane (**2a**) (0.35 g, 1.0 mmol) was added to a well-stirred biphasic system of ethyl acetate (25 mL) and water (25 mL) containing *N,N,N',N'*-tetraacetylethylenediamine (2.28 g, 10.0 mmol), sodium percarbonate (6.28 g, 40.0 mmol), and sodium bicarbonate (2.30 g, 27.4 mmol). The reaction was stirred for 65 h at room temperature. The blue reaction mixture was transferred to a separatory funnel, and water (100 mL) was added to facilitate the formation of distinct layers. The organic layer was reserved, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with water (2 × 50 mL) and brine (2 × 50 mL) and then dried (anhydrous magnesium sulfate). The drying agent was removed by gravity filtration, and the filtrate was concentrated to a volume of 75 mL. The green solution was cooled to −78 °C and subjected to an ozone–oxygen stream for 1 h. The solvent was removed in vacuo, and the white solid was subjected to preparative thin-layer chromatography (silica gel, 35% ethyl acetate/petroleum ether). The band at R_f = 0.72 was taken and provided 0.29 g (91%) of 1,3,5,7-tetranitroadamantane (**2c**) as ascertained by comparison to an authentic sample. The ^{1}H and ^{13}C NMR spectra were additionally recorded with use of acetone-d_6 in place of dimethyl-d_6 sulfoxide to facilitate sample recovery: mp 348–352 °C (lit.[2a] mp 361–363 °C); ^{1}H NMR (acetone-d_6) δ 3.16 (s, 12 H); ^{13}C NMR (acetone-d_6) δ 41.0 (t), 85.2 (s).

Peroxyacetic Acid/Ozone Oxidation of 1,3,5,7-Tetraaminoadamantane (2a) (pH = 8). The tetrahydrochloride of 1,3,5,7-tetraaminoadamantane (**2a**) (0.35 g, 1.0 mmol) was added to a biphasic mixture of dichloromethane (50 mL), a saturated sodium bicarbonate solution (50 mL), and solid sodium bicarbonate (2.5 g, 29.8 mmol). The peroxyacetic acid solution (4.44 g of a 35% solution, 20.5 mmol, 20 equiv) was added slowly to minimize foaming, and the reaction mixture was stirred vigorously for 3 h at room temperature. The organic layer was separated, and the aqueous phase was washed with dichloromethane (3 × 50 mL). The combined organic layers were washed sequentially with a 1 M sodium hydroxide solution (2 × 100 mL), distilled water (1 × 100 mL), and brine (1 × 100 mL) and dried (anhydrous sodium sulfate). The drying agent was removed by filtration, and the filtrate was reduced to a final volume of 50 mL on a rotary evaporator. The faintly blue solution was cooled (−78 °C) and ozonized for 1 h. The solvent was removed, and the colorless amorphous solid obtained was subjected to preparative thin-layer chromatography (silica gel, chloroform). Isolation of the material from the band at R_f = 0.64 provided 0.28 g (89%) of 1,3,5,7-tetranitroadamantane (**2c**).

Peroxyacetic Acid/Ozone Oxidation of 1,3,5,7-Tetraaminoadamantane (2a) (pH = 11). The procedure used was identical with that of the pH = 8 reaction except that sodium carbonate (7.00 g, 66.0 mmol) was added to the mixture following the addition of the peroxyacetic acid solution to raise the pH of the aqueous layer to ~11. The yield of 1,3,5,7-tetranitroadamantane (**2c**) obtained under these conditions was 0.26 g (84%).

Peroxyacetic Acid Oxidation of 1,3,5,7-Tetraaminoadamantane (2a) (pH = 8). The tetrahydrochloride of 1,3,5,7-tetraaminoadamantane (**2a**) (0.35 g, 1.0 mmol) was added to a mixture of dichloromethane (50 mL), saturated sodium bicarbonate solution, and solid sodium bicarbonate (2.50 g, 29.8 mmol). The peroxyacetic acid solution (4.44 g of a 35% solution, 20.5 mmol, 20 equiv) was slowly added, and the reaction mixture was stirred vigorously for 26 h at room temperature. Additional portions of the peroxyacetic acid solution (4.44 g, 20.5 mmol, 20 equiv) and sodium bicarbonate (5.00 g, 59.5 mmol) were carefully added. The vigorous stirring was continued for 48 h. The organic layer was separated, and the aqueous phase was washed with dichloromethane (3 × 50 mL). The combined organic layers were washed sequentially with a 1 M sodium hydroxide solution (2 × 100 mL) and distilled water (1 × 100 mL) and dried (anhydrous sodium sulfate). The drying agent was removed by filtration, the filtrate was concentrated in vacuo, and the residue was subjected to preparative thin-layer chromatography (silica gel, chloroform). The band at R_f = 0.59 provided 0.23 g (73%) of 1,3,5,7-tetranitroadamantane (**2c**).

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Registry No. **1a**, 768-94-5; **1d**, 7575-82-8; **2a**, 21336-47-0; **2c**, 75476-36-7; **2d**, 119694-48-3; *N,N,N',N'*-tetraacetylethylenediamine, 10543-57-4; sodium percarbonate, 3313-92-6; peroxyacetic acid, 79-21-0.

Synthesis of Enantiomerically Pure γ-(Menthyloxy)butenolides and (*R*)- and (*S*)-2-Methyl-1,4-butanediol

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Chiral butenolides have played a pivotal role in the construction of various natural products.[1] Recently Hanessian and co-workers[2] demonstrated the use of chiral butenolides derived from L-glutamic acid, D-ribonolactone, and D-mannitol as versatile templates for the stereocontrolled synthesis of acyclic structural units containing vicinal or remote substitution patterns. Highly diastereoselective cycloadditions of D-ribonolactone-derived butenolides[3] and related pyranosides[4] have been reported. Enzymatically prepared chiral mono- and bicyclic lactones were elegantly exploited in natural product synthesis.[5]

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