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Syntheses of 2,2,5,5-Tetranitronorbornane and 2,2,7,7-Tetranitronorbornane[1]

Alan P. Marchand,* Rajiv Sharma, and Umesh R. Zope
Department of Chemistry, University of North Texas Denton, Texas 76203-0068
William H. Watson* and Ram P. Kashyap
Department of Chemistry, Texas Christian University Fort Worth, Texas 76129

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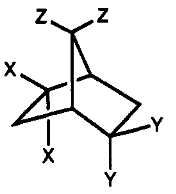
Introduction

Strained polynitro polycyclic compounds are of considerable current interest to U.S. military agencies as a new class of energetic materials.[2-4] As part of an ongoing research program in this area,[2,3] we have undertaken the syntheses of two novel tetranitronorbornanes, i.e., 2,2,5,5- and 2,2,7,7-tetranitronorbornanes (the title compounds, **1** and **2**, respectively). These target molecules were chosen as part of a model study for the eventual synthesis of 2,2,5,5,7,7-hexanitronorbornane, **3**, whose calculated explosive performance characteristics render it of particular interest to our program.[5]



1 (X = Y = NO_2, Z = H)
2 (X = H, Y = Z = NO_2)
3 (X = Y = Z = NO_2)

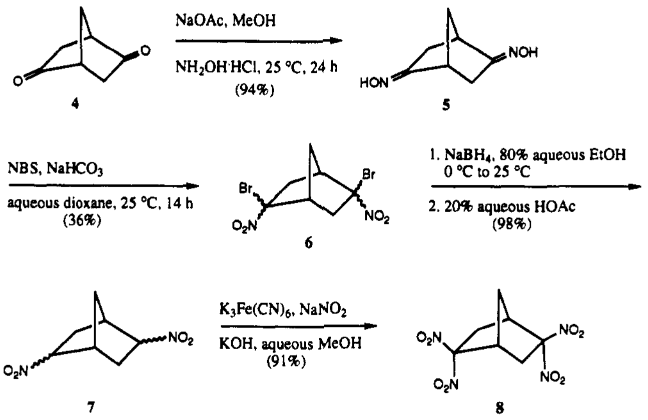
Synthesis of 1

Our multistep synthesis of **1** is shown in Scheme I. Thus, norbornane-2,5-dione (**4**)[6] was converted into the corresponding dioxime, **5**, in 94% yield by using the method described by Corey and co-workers.[7] The oxime functionalities in **5** then were converted into vicinal dinitro groups [i.e., $C(NO_2)_2$] by using a familiar three-step reaction sequence[2a,b] which involves (i) oxidative bromination of the oxime moiety in **5** (to afford **6**, 36-45%),[2a,b] (ii) subsequent $NaBH_4$ promoted reduction of the C-Br bonds in **6** (to afford **7**, 98%),[8] and (iii) oxidative nitration of each of the 2,5-$CH(NO_2)$ groups in **7** (to afford **1**, 91%).[9,10] The structure of **1** was established unequivocally via single-crystal X-ray crystallographic methods (vide infra).[10]

X-ray Structural Analysis of 1

Pertinent X-ray data appear in the supplementary material, including a structure drawing of **1** (see Figure 1 therein). The N(1) and N(3) nitro groups in **1** are twisted out of the planes defined by C(1)-C(2)-N(1) and by C(4)-C(5)-N(3), respectively, by only 3-4°. In contrast, the N(2) and N(4) nitro groups are twisted out of the planes defined by C(3)-C(2)-N(2) and by C(6)-C(5)-N(4), respectively, by ca. 12-13°. This highly symmetric arrangement of atoms appears to be related to the lack of close intermolecular contacts in the crystal and may also reflect a compromise between O···H intramolecular attractions and O···O dipolar repulsions.

Scheme I



Synthesis of 2

The approach which proved to be suitable for preparing **2** (shown in Scheme II) was designed specifically to avoid the intermediacy of norbornane-2,7-dione, as Haller-Bauer cleavage of this strained 1,3-diketone under either acidic or basic conditions was considered to be a potential problem.[11] Indeed, when a solution of 7,7-dimethoxynorbornan-2-one (**10**, an intermediate in the synthesis of **2**) in 10% aqueous sulfuric acid-THF was refluxed for 7 h, Haller-Bauer cleavage indeed occurred concomitant with hydrolysis of the ketal group, thereby affording 3-oxocyclohexanecarboxylic acid (**11**). None of the desired product of simple ketal hydrolysis, i.e., norbornane-2,7-dione, could be isolated from this reaction.

The C=C double bond in 7,7-dimethoxynorborn-5-en-2-ol(**8**)[12] was reduced catalytically by using hydrogen over palladized charcoal, thereby affording **9** (93%). Subsequent oxidation of **9** with pyridinium chlorochromate (PCC) produced **10** (95%), which then was converted into the corresponding oxime (**12**, 92%). The oxime moiety in **12** was converted into a $C(NO_2)_2$ functionality by applying the three-step sequence which had been used previously to transform **5** into **1**.[2a,b] The resulting dimethoxydinitronorbornane, **15**, was subjected to acidic hydrolysis.[13] The ketodinitronorbornane thereby obtained (**16**, 72%)

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[1] Dedicated to Dr. N. R. Ayyangar on the occasion of his 60th birthday.

[2] (a) Marchand, A. P.; Dave, P. R.; Rajapaksa, D.; Arney, B. E., Jr.; Flippen-Anderson, J. L.; Gilardi, R.; George, C. *J. Org. Chem.* **1989**, *54*, 1769. (b) Marchand, A. P.; Arney, B. E., Jr.; Dave, P. R. *Ibid.* **1988**, *53*, 443. (c) Marchand, A. P.; Sharma, G. V. M.; Annapurna, G. S.; Pednekar, P. R. *Ibid.* **1987**, *52*, 4874.

[3] For a review, see: Marchand, A. P. *Tetrahedron* **1988**, *44*, 2377.

[4] Velicky, R. W.; Iyer, S.; Campbell, C.; Sandus, O.; Alster, J.; Marchand, A. P.; Sharma, G. V. M.; Annapurna, G. S. *J. Energ. Mater.* **1988**, *6*, 145.

[5] Jayasuriya, K. Personal communication.

[6] Hawkins, R. T.; Hsu, R. S.; Wood, S. G. *J. Org. Chem.* **1978**, *43*, 4648.

[7] Corey, E. J.; Melvin, L. S., Jr.; Haslanger, M. F. *Tetrahedron Lett.* **1975**, 3117.

[8] Iffland, D. C.; Criner, G. X. *J. Am. Chem. Soc.* **1953**, *75*, 4047.

[9] Kornblum, N.; Singh, H. K.; Kelly, W. J. *J. Org. Chem.* **1983**, *48*, 332.

[10] (a) While this study was in progress, we became aware of the fact that **1** had also been synthesized by Professor George A. Olah and coworkers (Department of Chemistry, University of Southern California) and that the X-ray structure of this compound had been solved by Dr. Richard Gilardi (Laboratory for the Structures of Matter, Naval Research Laboratory). See: Olah, G. A.; Ramaiah, P.; Surya Prakash, G. K.; Gilardi, R. *J. Org. Chem.*, following paper in this issue. We thank Professor Olah and Dr. Gilardi for having shared their results with us prior to publication and for having kindly agreed to simultaneous publication of the results of our parallel studies. (b) See footnote 10 in ref 10a.

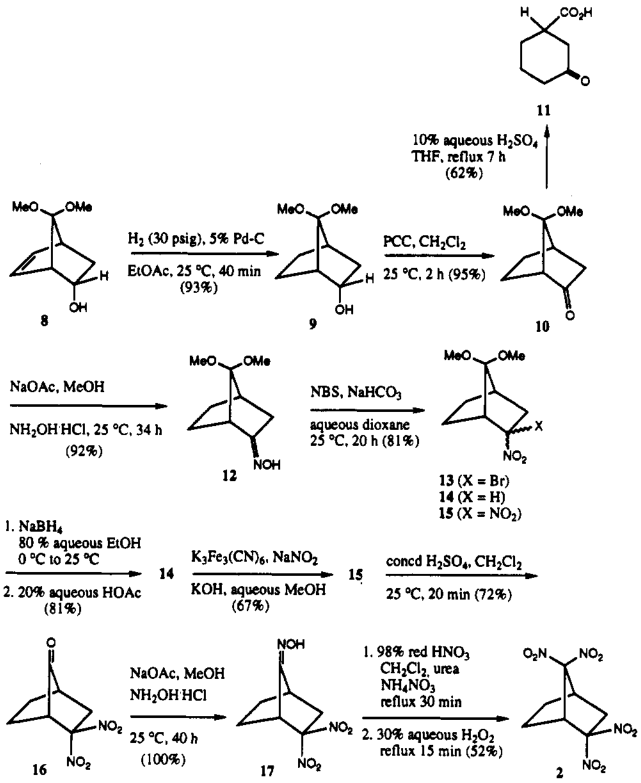
[11] Hamlin, K. E.; Weston, A. W. *Org. React.* **1957**, *9*, 1.

[12] Jung, M. E.; Hudspeth, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 5508.

[13] Scherer, K. V., Jr. *Tetrahedron Lett.* **1966**, 5685.

0022-3263/93/1958-0759$04.00/0

Scheme II



was converted into the corresponding oxime[7] (**17**, 100%), which then was oxidatively nitrated[13] to afford **2** in 52% yield.

Discussion

One feature of the ^1H NMR spectrum of **2** is unusual and merits comment. We observed that the C(1) bridgehead proton in **2** is unusually highly deshielded (δ 4.4). Similar deshielding of the C(3) bridgehead proton in 2,2,4,4-tetranitroadamantane (**18**, δ 4.7) was noted previously by Dave and co-workers.[14a] This unusual deshielding simply may result from the cumulative magnetic anisotropic effects of the adjacent nitro groups in both **2** and **18**. Alternatively, deshielding of the bridgehead proton which is flanked by four NO_2 groups in **2** and in **18** instead may reflect the cumulative electron-withdrawing inductive effect of the nitro substituents in each of these compounds. The source of this unusual deshielding effect upon the C(1) bridgehead proton in **2** is undergoing further investigation in our laboratory.

Experimental Section

Melting points are uncorrected. High-resolution mass spectra were obtained by personnel at the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, NE 68588.

2,5-Dibromo-2,5-dinitronorbornane (6). Norbornane-2,5-dione (**4**)[6] was converted into the corresponding dioxime, **5**, by using the method described by Corey, Melvin, and Haslanger.[7] Thus, to a solution of **4** (10.0 g, 80.6 mmol) and anhydrous NaOAc (15.87 g, 193.5 mmol) in anhydrous MeOH (125 mL) was added portionwise with stirring solid $NH_2OH{\cdot}HCl$ (12.33 g, 177.4 mmol), and the resulting mixture was stirred at rt for 24 h. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. The residue, crude dioxime **5** (11.7 g, 94%), was recrystallized from MeOH. Pure **5** was thereby obtained as a colorless microcrystalline solid: mp 219 °C (lit.[10] mp 214 °C); IR (KBr) 3205 (m), 3138 (sh, m), 3092 (s), 2987 (m), 2897 (s), 2316 (br, s), 955 cm^{-1} (s); ^1H NMR (CD_3OD) δ 1.71 (m, 2 H), 2.23, 2.46 (AB q, with additional doubling of the lowfield half of the AB pattern, J = 17.0, 4.8 Hz, 4 H), 3.00–3.07 (m, 2 H), 10.45 (s, 2 H); ^{13}C NMR (CD_3OD) δ 33.57 (t), 40.40 (d), 42.51 (d), 165.2 (s). The oxime groups in **5** have been shown via X-ray crystallographic analysis to possess the *E,E* configuration.[15]

2,5-Dibromo-2,5-dinitronorbornane (6). To a suspension of NBS (4.45 g, 22.7 mmol) and $NaHCO_3$ (1.90 g, 22.7 mmol) in water (40 mL) was added a solution of **5** (500 mg, 3.25 mmol) in 35% aqueous dioxane (28 mL), and the resulting mixture was stirred at rt for 14 h. Crushed KOH pellets (1.4 g, 25 mmol) were added to the reaction mixture, and the resulting mixture was stirred at rt for an additional 20 min. The reaction mixture then was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extracts were washed with 10% aqueous KOH (20 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. Crude **6** (520 mg, 45%) was thereby obtained as a gummy material that solidified upon standing at rt. This material was recrystallized from EtOAc to afford pure **6** as a colorless microcrystalline solid (402 mg, 36%): mp 137–138 °C; IR (KBr) 1547 (s), 1351 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.4 (m, 2 H), 2.6–2.9 (m, 4 H), 3.2 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.50 (t), 40.89 (t), 51.98 (d), 92.66 (s). Anal. Calcd for $C_7H_8Br_2N_2O_4$: C, 24.44; H, 2.34. Found: C, 24.56; H, 2.33.

2,5-Dinitronorbornane (7). A solution of **6** (1.81 g, 5.26 mmol) in EtOH (70 mL) was cooled externally to 0 °C. To this cooled solution was added dropwise with stirring a solution of $NaBH_4$ (2.20 g, 57.9 mmol) in 80% aqueous EtOH (50 mL) during 15 min. The resulting mixture was stirred at 0 °C for 30 min after the addition of the reducing agent had been completed. The external cold bath was removed, and the reaction mixture was allowed to warm gradually to rt with stirring during 45 min. Dilute (20%) aqueous HOAc then was added dropwise with stirring until all of the precipitated solid material had dissolved; (ca. 2–3 mL of dilute acid was required for this purpose). The resulting clear solution then was concentrated in vacuo, and the residue was partitioned between water (50 mL) and CH_2Cl_2 (50 mL). The layers then were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water (50 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. The residue, a colorless oil (950 mg, 98%), was triturated with EtOAc–hexane. A solid material was thereby obtained, which upon repeated recrystallization from EtOAc–hexane afforded pure **7** as a colorless microcrystalline solid: mp 170–171 °C; IR 1528 (s), 1377 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.7 (m, 2 H), 2.1 (m, 4 H), 3.05 (m, 2 H), 4.85 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.62 (t), 37.78 (t), 41.91 (d), 85.11 (d). The fact that the ^{13}C NMR spectrum of **7** contains only four resonances requires that this compound contain a 2-fold symmetry element. Thus, the two C–NO_2 bonds in **7** must possess either the *exo*-2,*exo*-5 or the *endo*-2,*endo*-5 (and not the *exo*-2,*endo*-5) configuration. We are unable to render an unequivocal choice between the 2-fold-symmetric alternatives on the basis of available NMR spectral data.[10b] Anal. Calcd for $C_7H_{10}N_2O_4$: C, 45.16; H, 5.41. Found: C, 45.50; H, 5.31.

2,2,5,5-Tetranitronorbornane (1).[9] Compound **7** (580 mg, 3.15 mmol) and KOH (1.55 g, 27.7 mmol) were dissolved in 40% aqueous MeOH (20 mL), and the resulting solution was filtered. The filtrate was added to another solution that contained $K_3Fe(CN)_6$ (10.38 g, 31.52 mmol) and $NaNO_2$ (6.09 g, 88.3 mmol) in water (100 mL), and the resulting mixture was stirred at rt for 2 h. CH_2Cl_2 (30 mL) was added, and the resulting mixture was stirred for 1 h. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extracts were washed with water (2 × 25 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. Crude **1** (790 mg, 91%) was thereby obtained as a colorless solid. Recrystallization of this material from CH_2Cl_2–hexane afforded pure **1** as colorless needles: mp 191-192 °C (lit.[10] mp 194 °C); IR (KBr) 1556 (vs), 1351 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.2 (m, 2 H),

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[14] (a) Dave, P. R.; Ferraro, M.; Ammon, H. L.; Choi, C. S. *J. Org. Chem.* **1990**, *55*, 4459. (b) Gilbert, E. E. Personal communication.

[15] Bott, S. G.; Marchand, A. P.; Zope, U. R. Manuscript in preparation.

2.85–3.02 (m, 4 H), 3.69 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.08 (t), 38.69 (t), 46.13 (d), 122.06 (s); MS (70 eV) *m/e* (relative intensity) (no molecular ion), 112 (23.9), 91 (53.0), 79 (67.0), 65 (75.2), 53 (47.0), 39 (100.0). Anal. Calcd for $C_7H_8N_4O_8$: C, 30.44; H, 2.92. Found: C, 30.57; H, 2.95.

***endo*-7,7-Dimethoxynorbornan-2-ol (9).** To a solution of *endo*-7,7-dimethoxynorborn-5-en-2-ol[11] (**8**, 1.20 g, 7.14 mmol) in EtOAc (20 mL) was added a catalytic amount of 5% palladized charcoal (300 mg). The resulting mixture was placed in a Parr shaker apparatus, and hydrogen (30 psig) was introduced. The resulting mixture was shaken at rt for 40 min and then filtered to remove spent catalyst. The filtrate was concentrated in vacuo, and the residue was purified via column chromatography on silica gel by eluting with 20% EtOAc–hexane. Compound **9** (1.13 g, 93%) was thereby obtained as a colorless oil: IR (film) 3648–3099 (s, br), 2944 (s), 2817 (sh, m), 1450 (m), 1323 (m), 1196 (m), 1140 (m), 1104 (m), 1056 (m), 992 (m), 936 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 0.98 (dd, J = 12.7, 3.1 Hz, 1 H), 1.24–1.46 (m, 2 H), 1.55–1.75 (m, 1 H), 1.80–1.99 (m, 2 H), 2.02–2.23 (m, 3 H), 3.04, (s, 3 H), 3.07 (s, 3 H), 4.35 (ddt, J = 9.6, 3.1, 1.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.56 (t), 27.57 (t), 38.45 (t), 38.55 (d), 43.84 (d), 50.12 (q), 50.48 (q), 70.17 (d), 114.1 (s); MS (70 eV) *m/e* (relative intensity) (no molecular ion), 166 (100.0), 142 (9.7), 118 (16.8), 116 (15.4), 102 (53.8), 98 (23.8), 82 (1.1), 80 (11.7), 76 (12.5), 68 (11.0), 59 (12.5), 56 (27.0).

Compound **9** was further characterized as the corresponding 1-naphthylurethane derivative. Recrystallization from CH_2Cl_2–hexane afforded the pure urethane as a colorless microcrystalline solid: mp 149 °C; IR (KBr) 3247 (br, m), 2930 (m), 1684 (s), 1541 (s), 1239 (s), 1085 (s), 774 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.24, 1.35 (AB q, with further doubling of the upfield half of the AB pattern, J = 13.2, 4.8 Hz, and considerable broadening of the lowfield half of the AB pattern, 2 H), 1.52–2.00 (m, 3 H), 2.11 (t, J = 4.4 Hz, 1 H), 2.24–2.43 (m, 1 H), 2.50 (t, J = 4.3 Hz, 1 H), 3.26 (s, 3 H), 3.26 (s, 3 H), 5.21 (ddt, J = 9.8, 4.9, 1.3 Hz, 1 H), 6.94 (br s, 1 H), 7.43, 7.64 (AB q, J = 8.0 Hz, 2 H), 7.52–7.58 (m, 2 H), 7.81–7.93 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 18.57 (t), 27.26 (t), 35.70 (t), 38.03 (d), 42.03 (d), 50.03 (q), 50.52 (q), 74.76 (d), 113.5 (s), 119.2 (d), 120.5 (d), 124.9 (d), 125.7 (d), 125.8 (d), 126.0 (d), 126.8 (s), 128.6 (d), 132.5 (s), 134.0 (s), 154.2 (s). Anal. Calcd for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79. Found: C, 70.41; H, 6.57.

7,7-Dimethoxynorbornan-2-one (10). To a stirred suspension of pyridinium chlorochromate (PCC, 2.78 g, 12.9 mmol) in anhydrous CH_2Cl_2 (20 mL) at rt was added dropwise with stirring a solution of **9** (1.48 g, 8.58 mmol) in anhydrous CH_2Cl_2 (15 mL) during 5 min. After all of the substrate had been added, the resulting mixture was stirred at rt for 2 h. Anhydrous Et_2O (40 mL) was added, and the organic layer was decanted, leaving behind a brown sludge. This process was repeated (3 × 20 mL). The combined ethereal extracts were filtered through a short Florisil column, and the eluate was concentrated in vacuo, thereby affording pure **10** (1.40 g, 95%) as a colorless oil; IR (neat) 1742 (s), 1212 (m), 1090 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.37 (m, 2 H), 1.80 (br s, 1 H), 1.92 (m, 2 H), 2.32 (br m, 1 H), 2.45 (br m, 2 H), 3.18 (s, 3 H), 3.21 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 21.16 (t), 25.64 (t), 38.11 (d), 43.98 (t), 49.93 (q), 52.81 (q), 52.61 (d), 11.72 (s), 213.22 (s).

Compound **10** was further characterized via its corresponding (2,4-dinitrophenyl)hydrazone (2,4-DNPH) derivative. Recrystallization of the 2,4-DNPH derivative from CH_2Cl_2–hexane afforded pure material as orange needles: mp 210–211 °C; IR (KBr) 3316 (m), 1619 (s), 1595 (m), 1412 (s), 1351 (s), 1325 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.34–1.56 (complex m, 2 H), 1.96–2.18 (complex m, 3 H), 2.53–2.71 (complex m, 2 H), 2.92 (d, J = 5.8 Hz, 1 H), 3.25 (s, 3 H), 3.31 (s, 3 H), 7.90, 8.26 (AB q, with further doubling of the lowfield half of the AB pattern, J = 9.0, 4.5 Hz, 2 H), 9.10 (d, J = 4.5 Hz, 1 H), 10.81 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.80 (t), 26.19 (t), 33.82 (t), 38.42 (d), 47.21 (d), 50.51 (q), 51.15 (q), 112.41 (s), 116.37 (d), 123.54 (d), 128.87 (s), 129.92 (d), 137.58 (s), 145.04 (s), 165.74 (s). Anal. Calcd for $C_{15}H_{18}N_4O_6$: C, 51.42; H, 5.18. Found: C, 51.53; H, 5.24.

3-Oxocyclohexanecarboxylic Acid (11). To a solution of **10** (1.40 g, 8.23 mmol) in THF (30 mL) was added 10% aqueous H_2SO_4 (30 mL), and the resulting solution was refluxed for 7 h. The reaction mixture was concentrated in vacuo, and the residue was partitioned between water (15 mL) and CH_2Cl_2 (15 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with water (25 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. A colorless oil (820 mg) was thereby obtained. This material was purified via column chromatography on silica gel by eluting with 20% EtOAc–hexane. Compound **11** (510 mg, 62%) was thereby obtained as a colorless oil. Upon trituration with EtOAc–hexane, this oil solidified. Careful recrystallization of this solid material from EtOAc–hexane afforded pure **11** as a colorless microcrystalline solid: mp 75–76 °C (lit. mp 75–76 °C,[15] mp 76 °C[16]); IR (KBr) 1735 (s), 1681 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.8 (m, 2 H), 2.1 (m, 2 H), 2.3 (m, 2 H), 2.5 (d, J = 6.0 Hz, 2 H), 2.8 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.78 (t), 26.94 (t), 40.34 (t), 42.23 (t), 42.39 (d), 178.99 (s), 210.29 (s).

7,7-Dimethoxynorbornan-2-one Oxime (12).[7] To a stirred solution of **10** (1.32 g, 7.76 mmol) in anhydrous MeOH (20 mL) at rt was added solid NaOAc (700 mg, 8.54 mmol), and the resulting mixture was stirred at rt until all of the solid had dissolved. To the resulting clear solution was added solid $NH_2OH\cdot HCl$ (590 mg, 8.54 mmol), and the resulting mixture was stirred at rt for 34 h. The reaction mixture was filtered, and the residue was washed with MeOH (2 mL). The combined filtrates were concentrated in vacuo, thereby affording crude oxime **12** (1.32 g, 92%). Repeated recrystallization of this material from $CHCl_2$–hexane afforded a single, pure stereoisomer of **12** as a colorless microcrystalline solid: mp 89–92 °C; IR (KBr) 3340 (s), 1676 (w), 1333 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.20–1.55 (m, 2 H), 1.75–2.46 (m, 4 H), 2.52–2.85 (m, 2 H), 3.22 (s, 3 H), 3.25 (s, 3 H), 8.16 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.54 (t), 26.22 (t), 32.79 (t), 37.87 (s), 44.78 (s), 50.28 (q), 51.01 (q), 112.70 (s), 165.07 (s). Anal. Calcd for $C_9H_{15}NO_3$: C, 58.36; H, 8.16. Found: C, 58.49; H, 8.32.

2-Bromo-2-nitro-7,7-dimethoxynorbornane (13). To a stirred suspension of NBS (5.46 g, 30.7 mmol) and $NaHCO_3$ (2.58 g, 30.7 mmol) in water (80 mL) at rt was added with stirring a solution of oxime **12** (1.62 g, 8.76 mmol) in 65% aqueous dioxane (60 mL). The resulting mixture was stirred at rt for 20 h. Solid KOH (1.78, 30.7 mmol) was added, and the reaction mixture was stirred for an additional 20 min. The reaction mixture then was extracted with CH_2Cl_2 (3 × 75 mL). The combined organic extracts were washed sequentially with 10% aqueous KOH (75 mL) and water (75 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. Compound **13** (2.0 g, 81%) was thereby obtained as a colorless oil (mixture of isomers): IR (film) 1550 (s), 1336 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.77–1.92 and 2.00–2.09 (2 m, total 4 H), 2.42–2.76 (m, 5 H), 2.78 (d, J = 16.6 Hz, 1 H), 2.97 and 3.03 (2 dt, J = 4.6, 2.0 Hz, total 2 H), 3.39 and 3.45 (2 q, J = 4.6 Hz, total 1 H), 3.62 (dd, J = 6.0, 2.4 Hz, 1 H), 3.83 (d, J = 16.6 Hz, 1 H), 3.73, 3.93, 3.97, and 4.03 (4 s, total 12 H), 4.00 and 4.16 (2 t, J = 4.6 Hz, total 1 H); ^{13}C NMR ($CDCl_3$) δ 23.48 (t), 23.50 (t), 23.80 (t), 24.92 (t), 39.30 (2 C, d), 43.97 (t), 44.91 (t), 49.32 (d), 49.96 (d), 50.31 (q), 50.53 (q), 50.71 (q), 50.86 (q), 94.52 (s), 96.11 (s), 111.60 (s), 112.82 (s). Anal. Calcd for $C_9H_{14}BrNO_4$: $(M_r + Li)^+$ 288.0266. Found (FAB HRMS): $(M_r + Li)^+$ 288.0257. This material was used as obtained in the next step without further purification.

2-Nitro-7,7-dimethoxynorbornane (14). A solution of **13** (2.00 g, 7.15 mmol) in EtOH (80 mL) was cooled externally to 0 °C. To this cooled solution was added dropwise with stirring a solution of $NaBH_4$ (1.49 g, 39.3 mmol) in 80% aqueous EtOH (80 mL) during 25 min. The resulting mixture was stirred at 0 °C for 30 min after all of the reducing agent had been added. The external cold bath was removed, and the stirred reaction mixture was allowed to warm gradually to rt during 1 h. Workup of the reaction mixture was performed in the manner described previously for the corresponding reduction of **6** (vide supra). The product was purified via flash column chromatography on silica gel by using 1:1 EtOAc–hexane as eluent. Pure **14** (mixture of isomers, 1.16 g, 81%) was thereby obtained as a colorless oil: IR (film) 1544 (s), 1382 (s), 1348 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.16–1.50 (m, 4 H), 1.70–2.05 (m, 4 H), 2.20 (m, 4 H), 2.76 (m, 2 H), 3.05 (d, J = 5.2 Hz, 2 H), 3.12, 3.13, 3.16, and 3.18 (4 s, total 12 H), 4.16 (dd, J = 9.2, 4.1 Hz, 1 H), 4.95 (q, J = 6.2 Hz, 1 H); ^{13}C

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NMR ($CDCl_3$) δ 20.26 (t), 23.62 (t), 25.73 (t), 26.31 (t), 30.92 (t), 32.96 (t), 37.77 (d), 37.90 (d), 42.83 (d), 43.83 (d), 50.28 (q), 50.40 (q), 50.64 (2 C, q), 85.38 (d), 85.47 (d), 112.89 (s), 113.50 (s). Anal. Calcd for $C_9H_{15}NO_4$: $(M_r + Li)^+$ 208.1161. Found (FAB HRMS): $(M_r + Li)^+$ 208.1156.

2,2-Dinitro-7,7-dimethoxynorbornane (15).[9] Compound 14 (1.16 g, 5.77 mmol) was dissolved in a solution of KOH (1.42 g, 25.4 mmol) in 75% aqueous MeOH (50 mL). The resulting solution was filtered, and the filtrate was added to another solution which contained $K_3Fe(CN)_6$ (9.50 g, 28.85 mmol) and $NaNO_2$ (5.57 g, 80.8 mmol) in water (90 mL), and the resulting mixture was stirred at rt for 2.5 h. Methylene chloride (60 mL) was added, and the resulting mixture was stirred for 1.5 h. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were washed with water (2 × 30 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by using 5% EtOAc–hexane as eluent. Pure **15** (950 mg, 67%) was thereby obtained as a colorless oil: IR (film) 1572 (s), 1376 (s), 1331 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.05–1.14 (dq, J = 12.5, 3.8 Hz, 1 H); 1.34–1.44 (dq, J = 10.0, 5.3 Hz, 1 H), 1.80–2.05 (m, 2 H), 2.42 (br m, 1 H), 2.84 (br s, 2 H), 3.12 (s, 3 H), 3.25 (s, 3 H), 3.46 (dd, J = 7.1, 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.81 (t), 23.99 (t), 37.29 (t), 38.78 (d), 47.13 (d), 50.68 (q), 50.90 (q), 113.12 (s); 124.45 (s). Anal. Calcd for $C_9H_{14}N_2O_6$: $(M_r + Li)^+$ 253.1012. Found (FAB HRMS): $(M_r + Li)^+$ 253.0998.

2,2-Dinitronorbornan-7-one (16).[12] To a stirred solution of **12** (950 mg, 3.86 mmol) in CH_2Cl_2 (10 mL) at rt was added concentrated H_2SO_4 (1 mL) dropwise with stirring during 1 min. The resulting mixture was stirred at rt for 20 min and then poured into ice–water (50 mL). Solid $NaHCO_3$ was added until effervescence had ceased. The resulting mixture was poured into a separatory funnel, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (5 × 20 mL). The combined organic layers were washed with water (2 × 20 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. Crude **16** (556 mg, 72%) was thereby obtained as a gummy material that solidified on standing. Recrystallization of this material from EtOAc–hexane afforded pure **16** as a colorless microcrystalline solid: mp 134–135 °C; IR (KBr) 1775 (s), 1561 (s), 1333 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.38–1.72 (m, 2 H), 1.92–2.24 (m, 2 H), 2.49 (t, J = 4.0 Hz, 1 H), 2.62 (dq, J = 16.3, 3.1 Hz, 1 H), 3.14 (d, J = 5.4 Hz, 1 H), 3.23 (d, J = 16.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.58 (t), 20.90 (t), 36.33 (t), 39.08 (d), 47.81 (d), 118.27 (s), 202.64 (s). Anal. Calcd for $C_7H_8N_2O_5$: C, 42.00; H, 4.03. Found: C, 41.89; H, 4.03.

2,2-Dinitronorbornan-7-one Oxime (17).[7] To a solution of **16** (475 mg, 2.37 mmol) in anhydrous MeOH (10 mL) at rt was added with stirring solid NaOAc (214 mg, 2.61 mmol), and the resulting mixture was stirred until all of the solid material had dissolved. To the resulting clear solution was added with stirring solid $NH_2OH{\cdot}HCl$ (182 mg, 2.61 mmol), and the reaction mixture was stirred at rt for 40 h. The reaction mixture was filtered, and the filtrate was washed with MeOH (2 mL). The combined filtrates were concentrated in vacuo, thereby affording crude **17** (mixture of *Z* and *E* isomers, 510 mg, 100%) as a colorless, viscous oil. On standing in a refrigerator, this oil gradually solidified, thereby affording a colorless solid: mp 63–66 °C; IR (KBr) 3245 (s), 1680 (w), 1561 (s), 1376 (m), 1318 cm^{-1} (s). This material was used as obtained in the next step without further purification.

2,2,7,7-Tetranitronorbornane (2).[13] To a refluxing solution of **17** (510 mg, 2.37 mmol) in anhydrous CH_2Cl_2 (40 mL) under argon was added a solution of 98% red HNO_3 (7 mL, excess), urea (100 mg, 1.66 mmol), and NH_4NO_3 (100 mg, 1.33 mmol) in anhydrous CH_2Cl_2 (20 mL) dropwise with stirring during 20 min. The reaction mixture acquired a dark green color during this time. After this addition had been completed, the resulting mixture was refluxed for 0.5 h. After this time, 30% aqueous H_2O_2 (3.5 mL, excess) was added dropwise with stirring during 20 min. The color of the reaction mixture changed gradually from green to blue and finally to pale yellow during the time of addition of the oxidant. Refluxing was continued for 15 min after the addition of H_2O_2 had been completed. Then, the reaction mixture was allowed to cool gradually to rt. The reaction mixture was poured into a separatory funnel, and the layers were separated. The CH_2Cl_2 layer was washed sequentially with cold water (2 × 75 mL), saturated $NaHCO_3$ solution (75 mL), and water (75 mL) and then dried ($MgSO_4$) and filtered. The filtrate was concentrated in vacuo, thereby affording crude **15** as a gummy material. This material was purified via column chromatography on silica gel by using 1:9 EtOAc–hexane as eluent. Pure **2** (338 mg, 52%) was thereby obtained as a colorless microcrystalline solid: mp 213–214 °C; IR (KBr) 1570 (s), 1365 cm^{-1} (s); ^1H NMR ($CDCl_3$) (ddd, J = 15.0, 9.5, 4.7 Hz, 1 H), 1.71–2.08 (m, 2 H), 2.26–2.40 (m, 1 H), 3.33–3.51 (m, 3 H), 4.38 (dd, J = 4.5, 1.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.77 (t), 23.94 (t), 38.21 (t), 43.21 (d), 51.13 (d), 121.26 (s), 126.22 (s); MS (70 eV) *m/e* (relative intensity) 136 (15.7), 126 (21.2), 112 (22.1), 91 (50.1), 79 (87.5), 65 (73.4), 53 (51.0), 39 (100.0). Anal. Calcd for $C_7H_8N_4O_8$: C, 30.44; H, 2.92. Found: C, 30.79; H, 2.88.

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Supplementary Material Available: X-ray experimental procedure, X-ray structure drawing of **1**, tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates and isotropic thermal parameters for **1**, and ^{13}C NMR spectra of **5**, **13**, **14**, and **15** (11 pages). This material is contained in 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.