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Effect of Amines on *O*-Benzyl Group Hydrogenolysis

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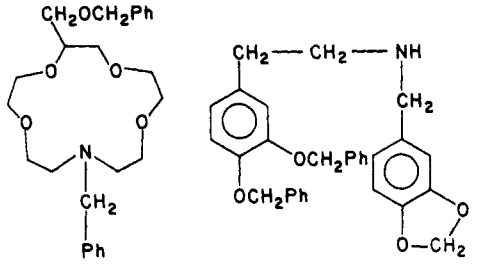
During a recent investigation of preparative routes to functionalized aza crown ethers,[1] we observed exclusive *N*-benzyl group cleavage when monoaza crown **1** reacted with hydrogen in the presence of palladium on activated carbon (Pd/C) catalyst. Since it is generally assumed that O-debenzylation takes place with greater ease than does removal of an *N*-benzyl group,[2,3] this result was totally unexpected. Also, selective cleavage of the *O*-benzyl groups in **2** and **3** has been reported.[4,5] To determine the causative factor for the unusual hydrogenolysis selectivity found with **1**, the present study was undertaken.



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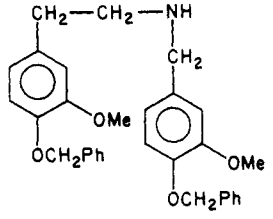

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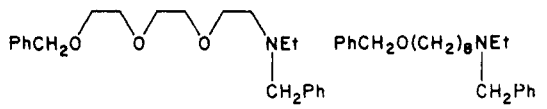
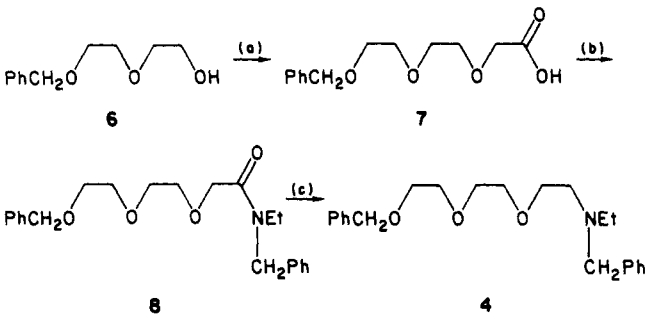
Initially it was thought that the cyclic structure and/or multiethereal linkages of aza crown **1** might be responsible for the unexpected debenzylation selectivity. Therefore, acyclic model compounds **4** and **5** were synthesized (Schemes I and II, respectively). When solutions of **4** and **5** in 95% ethanol were shaken with Pd/C catalyst under



4 **5**

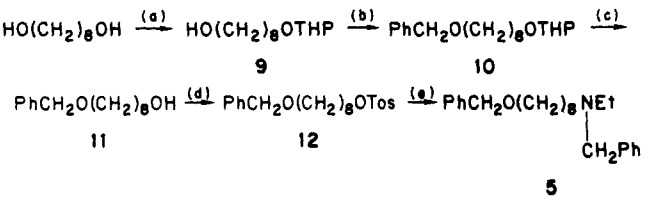
45 psi of hydrogen at room temperature for 20–24 h, only the corresponding products of N-debenzylation **13** and **14** were isolated in yields of 60% and 100%, respectively.

Scheme I[a]

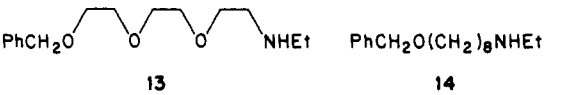


[a] (a) $ClCH_2CO_2H$, *t*-BuOK; (b) $SOCl_2$, then $PhCH_2NHEt$; (c) $LiAlH_4$.

Scheme II[a]



[a] (a) DHP, H^+; (b) $PhCH_2Br$, NaH; (c) H^+; (d) TosCl, pyridine; (e) $PhCH_2NHEt$, Na_2CO_3.



13 **14**

These results suggested that it was not the cyclic polyether structure but the presence of amine functions in **4** and **5** which was inhibiting O-debenzylation under conditions that provided complete cleavage of the *N*-benzyl groups.

To further probe the influence of amines upon potential O-debenzylation processes,[6] benzyl *n*-nonyl ether (**15**) was utilized as the model compound. When a solution of **15** in 95% ethanol was shaken with Pd/C catalyst under 45 psi of hydrogen at room temperature for 20–24 h, complete O-debenzylation was observed. However, when the reaction was conducted under the same conditions but in the presence of 5 mol % of *n*-butylamine or *N*-benzylethylamine, **15** was totally recovered. That such inhibition of O-debenzylation is confined to the more basic nonaromatic amines was established with pyridine. Under the standard conditions, complete cleavage of the *O*-benzyl group in **15** was found in the presence of 5 mol % or even an equimolar amount of pyridine.

The apparent contradiction between our results and the reported O-debenzylations of **2** and **3** which contain amine functions was resolved by studying the reaction of benzyl phenyl ether (**16**) with hydrogen under the standard conditions. In the presence of 5 mol % or 100 mol % of *n*-butylamine, the hydrogenation of **16** proceeded smoothly and gave a quantitative yield of phenol. Thus, the inhibition of O-debenzylation by nonaromatic amines does not extend from alkyl benzyl ethers to aryl benzyl ethers.

We next explored the synthetically attractive possibility that amines might be used to retain an *O*-benzyl group

(1) Son, B.; Czech, B.; Bartsch, R. A. *Synthesis*, in press.
(2) Freifelder, M. "Practical Catalytic Hydrogenation"; Wiley: New York, 1971; pp 431–432.
(3) Rylander, P. N. "Catalytic Hydrogenation in Organic Synthesis"; Academic Press: New York, 1979, p 280.
(4) Forbes, E. J. *J. Chem. Soc.* **1955**, 3926.
(5) Kirby, G. W.; Tiwari, H. P. *J. Chem. Soc.* **1966**, 676.
(6) Scattered hints that the presence of an amino group in a compound may make *O*-debenzylation of the compound more difficult appear in the literature.[7,8]
(7) Hartung, W. H.; Simonoff, R. "Organic Reactions"; Wiley: New York, 1953; Vol. 7, p 263.
(8) Birkhofer, L. *Chem. Ber.* **1942**, *75*, 429.

0022-3263/84/1949-4076$01.50/0

while hydrogenation took place in a different part of a molecule. For this purpose, alkenyl benzyl ether **17** was synthesized. Reaction of **17** with hydrogen under the standard conditions, but in the presence of 5 mol % of *n*-butylamine, gave a quantitative yield of benzyl *n*-undecyl ether (**18**),

$$\underset{\mathbf{17}}{PhCH_2O(CH_2)_9CH{=}CH_2} \xrightarrow[95\%\ EtOH]{H_2,\ Pd/C} \underset{\mathbf{18}}{PhCH_2O(CH_2)_{10}CH_3} \quad (1)$$

the hydrogenation product with an intact *O*-benzyl group. Such use of amines to modify the reactivity of *O*-benzyl groups has exciting potential in the practice of synthetic organic chemistry.

Experimental Section

IR spectra were obtained with a Nicolet MX-S spectrometer and are recorded in reciprocal centimeters. ^1H NMR spectra were recorded with Varian EM-360A or EM360 spectrometers in deuteriochloroform, and chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. Elemental analysis was performed by Galbraith Laboratories, Inc. of Knoxville, TN. Unless specified otherwise reagent grade reactants and solvents were obtained from chemical suppliers and used as received. THF was purified by distillation from $LiAlH_4$ under nitrogen.

10-Phenyl-3,6,9-trioxadecanoic Acid (7). To a solution of 7-phenyl-3,6-dioxaheptanol[9] (12.0 g, 61 mmol) in *tert*-butyl alcohol (250 mL) was added potassium *tert*-butoxide (17.2 g, 0.15 m) under nitrogen. After 1 h of stirring the mixture was brought to reflux and a solution of chloroacetic acid (7.2 g, 76 mmol) in *tert*-butyl alcohol (25 mL) was added dropwise. The mixture was refluxed overnight, the solvent was removed in vacuo, and the residue was extracted with ether, acidified with 6 N HCl, and extracted repeatedly with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and the crude product which was obtained after evaporation of the solvent in vacuo was vacuum distilled, yielding 7.7 g (50%) of **7** as a very viscous, pale yellow oil: bp 172–174 °C (0.25 mm); IR (neat) 3650–2300 (COOH), 1759 (C=O), 1120 (C—O); ^1H NMR 3.69 (d, 8), 4.16 (s, 2), 4.56 (s, 2), 7.31 (s, 5). Satisfactory elemental analysis of this extremely hygroscopic compound could not be obtained.

***N*-Benzyl-*N*-ethyl-10-phenyl-3,6,9-trioxadecanamide (8).** A mixture of **7** (7.6 g, 30 mmol) and thionyl chloride (5.4 g, 45 mmol) was heated at 80 °C for 5 h. Excess thionyl chloride was removed in vacuo to give the crude acid chloride, which was dissolved in dry benzene (15 mL) and added dropwise to a solution of *N*-benzylethylamine (8.1 g, 60 mmol) in 100 mL of dry benzene. The mixture was stirred overnight at room temperature, water (80 mL) was added, and the organic layer was separated and washed with 10% HCl (2 × 50 mL) and then water. After drying over $MgSO_4$, filtration, and evaporation of the solvent in vacuo, the crude product was obtained. This material was purified by column chromatography on alumina with ethyl acetate as eluent to give 8.0 g (72%) of **8** as a colorless, viscous liquid: IR (neat) 1651 (C=O), 1109 (C—O); ^1H NMR 1.08 (t, 3), 2.95–3.85 (m, 10), 4.23 (br s, 2), 4.51 (br s, 4), 7.28 (br s, 10). Anal. Calcd for $C_{22}H_{29}NO_4$: C, 71.13; H, 7.87. Found: C, 71.04; H, 7.93.

***N*-Benzyl-*N*-ethyl-(10-phenyl-3,6,9-trioxadecyl)amine (4).** To a suspension of $LiAlH_4$ (1.2 g, 32 mmol) in THF (30 mL) was added dropwise a solution of **8** (7.2 g, 19 mmol) in THF (40 mL), and the mixture was refluxed with stirring for 4 h and then allowed to stand overnight at room temperature. Aqueous 10% KOH (2.5 mL) was added dropwise with cooling, and the precipitated solid was filtered and transferred back into the reaction flask and boiled for 15 min with 50 mL of THF. Filtration was repeated, the filtrates were combined, and the solvent was removed in vacuo. The crude product was chromatographed on a short alumina column with ethyl acetate as eluent to give 5.25 g (76%) of **4** as a colorless liquid: IR (neat) 1109 (C—O); ^1H NMR 1.02 (t, 3), 2.4–2.9 (m, 4), 3.4–3.8 (m, 12), 4.51 (s, 2), 7.28 (br s, 10). Anal. Calcd for $C_{22}H_{31}NO_3$: C, 73.91; H, 8.74. Found: C, 73.81; H, 8.82.

Monotetrahydropyranyl Ether of 1,8-Octanediol (9). Dihydropyran (16.5 g, 0.19 mol) was added dropwise with stirring to a solution of 1,8-octanediol (25.0 g, 0.16 mol) in 200 mL of glyme containing a catalytic amount of concentrated HCl. After 3 h of stirring, tribenzylamine was added to neutralize the catalyst. Filtration, followed by evaporation of the solvent gave the crude product which was vacuum distilled. A fraction of 13.6 g (bp 130–140 °C (0.15 mm)) was collected and passed through an alumina column using petroleum ether–ethyl acetate (5:1) as eluent to give pure **9** (12.4 g, 34%) as a colorless viscous liquid: IR (neat) 3420 (O–H), 1138, 1120 (C–O); ^1H NMR ($CDCl_3 + D_2O$) 1.1–2.1 (m, 18), 3.1–4.2 (m, 6), 4.55 (br s, 1). Anal. Calcd for $C_{13}H_{26}O_3$: C, 67.79; H, 11.38. Found: C, 67.60, H, 11.26.

8-(Benzyloxy)octyl 2-Tetrahydropyranyl Ether (10). Sodium hydride (50% dispersion in mineral oil, 3.2 g, 67 mmol) was washed with *n*-pentane under nitrogen and suspended in THF (10 mL). To this suspension a solution of **9** (10.5 g, 45 mmol) in THF (30 mL) was added dropwise. After 1 h of stirring at 50 °C, benzyl bromide (7.8 g, 45 mmol) was added and the mixture was refluxed overnight. The solvent was removed in vacuo and water (50 mL) was added. The resultant mixture was extracted with ether (3 × 20 mL), and the combined extracts were dried ($MgSO_4$) and evaporated in vacuo. The crude product was vacuum distilled to give 12.8 g (89%) (bp 176–178 °C (0.75 mm)) of **10** as a colorless, viscous liquid: IR (neat) 1120 (C–O); ^1H NMR 1.1–2.1 (m, 18), 3.1–4.1 (m, 6), 4.50 (br s, 3), 7.31 (s, 5). Anal. Calcd for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06. Found: C, 74.73; H, 10.14.

8-(Benzyloxy)octanol (11). A solution of **10** (12.1 g, 38 mmol) in 150 mL of a CH_2Cl_2–CH_3OH (1:1) mixture containing 2.5 mL of concentrated HCl was stirred at room temperature for 1 h. Then 15 g of $NaHCO_3$ was added to neutralize the catalyst. Filtration, followed by evaporation of the solvent in vacuo gave the crude product which was vacuum distilled to yield 8.4 g (95%) (bp 145–147 °C (0.9 mm)) of pure **11** as a colorless viscous liquid: IR (neat) 3380 (O–H), 1099 (C–O); ^1H NMR 1.2–2.5 (m, 13), 3.3–3.8 (m, 4), 4.47 (s, 2), 7.30 (s, 5). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found C, 75.99; H, 10.38.

1-(Benzyloxy)-8-(tosyloxy)octane (12). A solution of **11** (7.8 g, 33 mmol) in pyridine (40 mL) was cooled to −10 °C and a solution of tosyl chloride (8.8 g, 46 mmol) in pyridine (20 mL) was added dropwise. The reaction mixture was kept in a refrigerator overnight and poured over ice, and ice-cold 6 N HCl was added. Subsequent extraction with CH_2Cl_2 (2 × 20 mL), drying ($MgSO_4$), filtration, and evaporation of the solvent in vacuo produced 12.0 g (93%) of the product which contained only trace impurities. An analytical sample was obtained by column chromatography (alumina and petroleum ether–ethyl acetate, 20:1) as a colorless viscous liquid: IR (neat) 1361, 1188, 1178 [S(=O)$_2$], 1097 (C—O); ^1H NMR 1.1–2.0 (m, 12), 2.42 (s, 3), 3.43 (t, 2), 4.00 (t, 2), 4.46 (s, 2), 7.26 (s, 5), 7.47 (q, 4). Anal. Calcd for $C_{22}H_{30}SO_4$: C, 67.66; H, 7.74. Found: C, 67.94; H, 7.97.

***N*-Benzyl-*N*-ethyl[8-(benzyloxy)octyl]amine (5).** The crude tosylate **12** (10.0 g, 26 mmol) and *N*-benzylethylamine (3.5 g, 26 mmol) were dissolved in dry CH_3CN (100 mL) and anhydrous Na_2CO_3 (6.0 g) was added. The mixture was refluxed for 4 days. The solvent was removed in vacuo, CH_2Cl_2 (30 mL) was added, and the solid was filtered. Evaporation of the solvent in vacuo gave the crude product which was passed through an alumina column with petroleum ether–ethyl acetate (50:1) as eluent to afford 7.5 g (83%) of **5** as a colorless, viscous liquid: IR (neat) 1454 (CH_2N), 1101 (C–O); ^1H NMR 0.98 (t, 3), 1.1–1.8 (m, 12), 2.2–2.7 (m, 4), 3.42 (t, 2), 3.52 (s, 2), 4.46 (s, 2), 7.28 (s, 5). Anal. Calcd for $C_{24}H_{35}NO$: C, 81.53; H, 9.98. Found: C, 81.78; H, 9.93.

***N*-Ethyl(10-phenyl-3,6,9-trioxadecyl)amine (13).** A mixture of **4** (0.70 g, 2.0 mmol) and Pd/C (10%, 70 mg) in 10 mL of 95% ethanol was shaken in a Parr hydrogenator under 45 psi of hydrogen at room temperature for 20 h. The catalyst was filtered and the solvent was removed in vacuo. The residue was passed through a short alumina column with ethyl acetate and ethyl acetate–methanol (5:1) as eluents to give 0.32 g (60%) of **13** as a colorless liquid: IR (neat) 3315 (N–H), 1109 (C–O); ^1H NMR 1.07 (t, 3) 1.97 (br s, 1), 2.4–2.9 (m, 4), 3.3–4.8 (m, 10), 4.50 (s, 2), 7.26 (s, 5). Anal. Calcd for $C_{15}H_{25}NO_3$: C, 67.38; H, 9.42. Found: C, 67.13; H, 9.46.

(9) Johnson, H. *J. Pharm. Sci.* **1975**, *64*, 693.

[8-(Benzyloxy)octyl]ethylamine (14). The amine 5 (1.8 g, 5 mmol) was hydrogenated under the conditions described in the preparation of 13 to yield after workup 1.35 g (100%) of a colorless, viscous liquid which showed a tendency to crystallize during storage: IR (neat) 3280 (N-H), 1454 (CH_2N), 1107 (C-O); ^1H NMR 1.12 (t, 3), 1.2-1.8 (m, 13), 2.5-2.8 (m, 4), 3.46 (t, 2), 4.48 (s, 2), 7.30 (s, 5). Anal. Calcd for $C_{17}H_{29}NO$: C, 77.51; H, 11.09. Found: C, 77.36; H, 11.28.

Benzyl *n*-Nonyl Ether (15). Sodium hydride (50% dispersion in mineral oil, 1.8 g, 75 mmol) was suspended in THF (10 mL) under nitrogen and a solution of 1-nonanol (7.2 g, 50 mmol) in THF (15 mL) was added dropwise. After stirring at 60 °C for 1 h, benzyl bromide (8.55 g, 50 mmol) was added, and the mixture was refluxed overnight. The solvent was removed in vacuo, water (20 mL) was added, and the mixture was acidified with 6 N HCl. Extraction with chloroform (3 × 10 mL), drying over $MgSO_4$ followed by filtration, and evaporation of the solvent in vacuo afforded the crude product which was vacuum distilled (bp 127-129 °C (0.2 mm)) to give 8.8 g (75%) of benzyl *n*-nonyl ether as a colorless liquid: IR (neat) 1103 (C-O); ^1H NMR 0.65-1.95 (m, 17 H), 3.43 (t, 2 H), 4.46 (s, 2 H), 7.27 (s, 5 H). Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 82.24; H, 11.16.

Benzyl Phenyl Ether (16). Phenol (2.35 g, 25 mmol), benzyl bromide (12.8 g, 75 mmol), and tri-*n*-butylhexadecylphosphonium bromide (1.3 g, 2.5 mmol) were dissolved in CH_2Cl_2 (125 mL) and a solution of NaOH (1.5 g, 37.5 mmol) in 125 mL of water was added. The mixture was stirred vigorously for 3 days at room temperature. The organic layer was separated and dried ($MgSO_4$). Following removal of the solvent in vacuo, the residue was dissolved in ether and passed through a short silica gel column to remove the catalyst. The solvent was evaporated in vacuo and the residue was vacuum distilled to give 4.15 g (90%) of a colorless viscous oil (bp 88 °C (0.25 mm)) which crystallized during storage, mp 39.5-40 °C (lit.[10-12] mp 38-39 °C).

11-(Benzyloxy)-1-undecene (17) was prepared by modifying a reported procedure.[13] Sodium hydride (50% dispersion in mineral oil, 9.6 g, 0.20 mol) was washed with *n*-pentane and suspended in THF (70 mL). A solution of 10-undecen-1-ol (25.0 g, 0.15 mol) in THF (40 mL) was added dropwise under nitrogen. After stirring at 60 °C for 1 h, a solution of benzyl bromide (34.2 g, 0.20 mol) in THF (40 mL) was added and the mixture was refluxed overnight. The solvent was then evaporated in vacuo and CH_2Cl_2 (50 mL) was added. After filtration and washing the filtered material with CH_2Cl_2, the solvent was evaporated in vacuo and the residue was vacuum distilled to give 34.7 g (91%) of the product, bp 119-121 °C (0.3 mm) (153-155 °C (1 mm)).[13]

Benzyl *n*-Undecyl Ether (18). Benzyl *n*-undecenyl ether (17) (0.52 g, 2.0 mmol) was dissolved in 95% ethanol (5 mL) and Pd/C (10%, 50 mg) and 3 drops of *n*-butylamine were added. The mixture was shaken under 45 psi of hydrogen at room temperature overnight. After filtration of the catalyst and evaporation of the solvent and the amine in vacuo, 18 (0.50 g, 95%) was obtained as a colorless liquid: IR (neat) 1103 (C-O); ^1H NMR 0.7-2.0 (m, 19), 3.47 (t, 2), 4.48 (s, 2), 7.28 (s, 5). Anal. Calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.64; H, 11.65.

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Registry No. 4, 91842-55-6; 5, 91842-58-9; 6, 2050-25-1; 7, 91842-53-4; 8, 91842-54-5; 9, 51326-52-4; 10, 91842-56-7; 11, 31600-54-1; 12, 91842-57-8; 13, 91842-59-0; 14, 91842-60-3; 15, 91842-61-4; 16, 946-80-5; 17, 81518-75-4; 18, 91842-62-5; DHP, 110-87-2; $ClCH_2CO_2H$, 79-11-8; $PhCH_2NHEt$, 14321-27-8; $HO(CH_2)_8OH$, 629-41-4; $PhCh_2Br$, 100-39-0; Pd, 7440-05-3; 1-nonanol, 143-08-8; phenol, 108-95-2; tri-*n*-butylhexadecylphosphonium bromide, 14937-45-2; 10-undecen-1-ol, 112-43-6; *n*-butylamine, 109-73-9.

(10) Kornblum, N.; Seltzer, R.; Haberfield, P. *J. Am. Chem. Soc.* **1963**, *85*, 1148.
(11) McKillop, A.; Fiaud, J.-C.; Hug, R. P. *Tetrahedron* **1974**, *30*, 1379.
(12) D'Incan, E.; Viout, P. *Tetrahedron* **1975**, *31*, 159.
(13) Anelli, P. L.; Czech, B.; Montanari, F.; Quici, S. *J. Am. Chem. Soc.* **1984**, *106*, 861.

Synthesis of 5,5,9,9-Tetranitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane

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There is considerable current interest in the synthesis and chemistry of strained energetic compounds; polynitropolycyclic "cage" systems are potential members of this important class.[1-4] However, relatively few nitro-containing cage compounds have been synthesized.[1-4] We now report the synthesis of the title compound (1) in ten stereocontrolled steps (see Scheme I). To our knowledge, compound 1 is only the second polynitrobishomocubane to have been synthesized.[4]

The key intermediate in our synthesis of 1 is bishomocubanedione 7. This compound has been synthesized by Paquette and co-workers[5] via a multistep procedure, one step of which involves transoximation of *endo*-dicyclopentadienone dioxime.[6] However, we experienced some difficulty when we attempted to carry out the transoximation procedure. In our hands, only partial transoximation of *endo*-dicyclopentadienone dioxime occurred; accordingly, a gross mixture of several products was obtained. The desired *endo*-dicylopentadienone could be isolated via tedious column chromatographic separation from the product mixture in only 35% yield.

Our alternative approach to 7 is shown in Scheme I. An attempted shortcut to cage dioxime 8 by photocyclization of *endo*-dicyclopentadienone dioxime[6a] failed. Starting material could not be recovered, and no useful products resulted from photolyses attempted under a variety of conditions. Once cage dioxime 8 was in hand, we relied upon published procedures to effect conversion of the oxime functionalities first to nitro groups[7,8] and then to geminal dinitro groups.[9] The required tetranitrobishomocubane 1 proved to be accessible in good overall yield from readily available, inexpensive starting materials (i.e., cyclopentanone and ethylene glycol) by using the route indicated in Scheme I.

Experimental Section

Melting points and boiling points are uncorrected. Proton NMR spectra (60 MHz) were recorded on a Hitachi-Perkin-Elmer Model R-24B NMR spectrometer. ^{13}C NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer. In all cases, signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer Model 1330 infrared spectrophotometer. Mass spectra were obtained with a Hewlett-Packard Model 5970A GC/MS system operating at 70 eV. Elemental microanalyses were per-

(1) Sollott, G. P.; Gilbert, E. E. *J. Org. Chem.* **1980**, *45*, 5405.
(2) (a) Eaton, P. E.; Ravi Shankar, B. K.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J. J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185. (b) Griffin, G. W.; Umrigar, P. P.; Vaz, C. J. "Abstracts of Papers", 187th National Meeting of the American Chemical Society, St. Louis, MO, April 1984, American Chemical Society: Washington, DC, 1984; ORGN 181.
(3) See "The Chemistry of Functional Groups, Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives"; Patai, S., Ed.; Wiley: New York, 1982.
(4) Marchand, A. P.; Suri, S. C. *J. Org. Chem.* **1984**, *49*, 2041.
(5) Paquette, L. A.; Davis, R. F.; James, D. R. *Tetrahedron Lett.* **1974**, 1615.
(6) (a) Doering, W. v. E.; DePuy, C. H. *J. Am. Chem. Soc.* **1953**, *75*, 5955. (b) DePuy, C. H.; Ponder, B. W. *J. Am. Chem. Soc.* **1959**, *81*, 4629.
(7) Nielsen, A. T. *J. Org. Chem.* **1962**, *27*, 1993.
(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.

0022-3263/84/1949-4078$01.50/0