product containing β-pinene/α-pinene, 87:13. Use of additional base led to a decrease in the α-pinene present in the product. Indeed, a reaction mixture from a 1:1.5 ratio of α-pinene to base gave a product with <1% α-pinene. Both (+)- and (−)-β-pinene were synthesized from the corresponding (+)- and (−)-α-pinene, respectively. Data on products obtained with their isomeric and optical purities are summarized in Table I.

Recommended Procedure for Conversion of (+)-α-Pinene to (+)-β-Pinene. All glassware was dried at 150 °C for at least 5 h, and reactions were carried under a static nitrogen atmosphere.[17] To a stirred suspension of *n*-BuLi (100 mL, 2.5 M, 250 mmol) in hexane and *t*-BuOK (28 g, 250 mmol) was added (+)-α-pinene (27.2 g, 200 mmol, 96.6% ee) slowly at −78 °C. After the addition was complete, the reaction mixture was warmed slowly to room temperature and stirred at that temperature for 48 h. The reaction mixture was then cooled to −78 °C, and trimethyl borate (67 g, 650 mmol) in 50 mL of dry ether was added slowly with efficient stirring[18] (^{11}B NMR indicated a peak at δ +3, confirming the formation of the "ate" complex). Then the mixture was slowly warmed to room temperature and stirred for 1 h. Hydrolysis was achieved by adding 100 mL, 10% hydrochloric acid and stirring for 1 h,[19] or 100 mL of water and stirring for 3 h. The organic layer was separated, and the aqueous layer was extracted with hexane (3 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was distilled (55 °C/12 mmHg) to furnish (+)-β-pinene, 23.3 g (86%), isomeric purity >98%. A careful distillation of a small prior fraction through an efficient column readily removes the minor amount of the α-pinene produced in the reaction (bp α-pinene, 156 °C; β-pinene, 165 °C). After preparative GC on a TPC column, 99.7% GC pure (+)-β-pinene was obtained: $[\alpha]^{23}_D$ +23.1° (neat).

By utilizing 1.5 equiv of metalating agent, β-pinene was obtained in ≥99% isomeric purity and 80% yield (Table I).

Rotation of 100% β-Pinene. As reported above, the rotation we achieved with β-pinene prepared from high optical purity α-pinene is $[\alpha]^{23}_D$ +23.1° (neat). This compares with the highest value previously reported for β-pinene made from (+)-10-camphenesulfonyl chloride,[12] $[\alpha]^{25}_D$ +22.8°. Both borane isomerization of α-pinene and recrystallization of tri-*cis*-myrtenylborane[10] gave products with $[\alpha]^{23}_D$ of +22.7° and −22.8°. Earlier, Lucas had reported a rotation of $[\alpha]^{25}_D$ −22.7°.[20] Even though our observed value is higher than those of all previous workers, it would be foolhardy to claim it must be optically purer. The presence of trace amounts of materials with high rotations can result in minor variations of the observed rotation, which confuse the situation.

Acknowledgment. We thank the National Institutes of Health (Grant GM 10937-24) and the Dow Chemical Co. for support of this research program.

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(18) The reaction of methyl borate with the potassium salt **2** is exothermic, and the reaction temperature must be kept at −78 °C. If the addition of methyl borate is too fast or the stirring is not efficient, local overheating occurs, leading to lower yields of β-pinene and increased amounts of a nonvolatile residue.

(19) Stirring the reaction mixture containing the dilute acid results in the formation of products exhibiting a longer retention time on GC analysis than that of β-pinene. Hence, a shorter stirring time is recommended during the hydrolysis by dilute hydrochloric acid.

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Mono-α-functionalization of 2,9-Dimethyl-1,10-phenanthroline[1a]

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Received August 10, 1988

There exists considerable interest in 1,10-phenanthroline and its derivatives (especially neocuproine) because of their biological activity,[2,3] complexation properties,[4-6] inclusion in novel macrocycles,[7] and other applications.[8] Moreover, there are very few literature reports of monofunctionalized derivatives of 2,9-dimethyl-1,10-phenanthroline (**1**), which may have important fungistatic properties[9,10] and offer a viable route to the inclusion of metal ions at selected sites on monoclonal antibodies.[11] This paper describes the monofunctionalization of **1** via mono-*N*-oxide formation (and subsequent Boekelheide rearrangement) and provides insight, via a single-crystal X-ray structure of **2**·2H_2O, into the existence of the proposed 1,10-phenanthroline bis(*N*-oxide).[12-14]

Direct alkyl functionalization of **1** by free-radical halogenation using either *N*-chloro-(NCS)[15,16] or *N*-bromosuccinimide(NBS)[17] under diverse reaction conditions[18] did not yield the monohalo product **6** in significant amounts (2%). Therefore, a more circuitous procedure using the intermediary *N*-oxide was employed, since the mono-*N*-oxide **2** can serve as an appropriate intermediate for the synthesis of unsymmetrical neocuproine derivatives. Mono-*N*-oxide **2** was readily obtained (68%) by oxidation of **1** with 30% hydrogen peroxide in glacial acetic acid[19-22]

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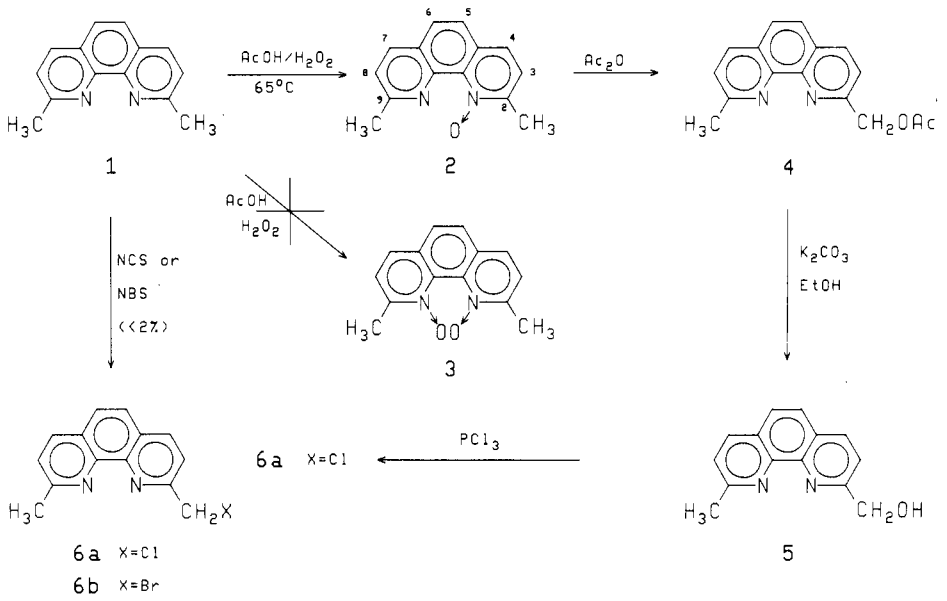
(22) Reaction of **1** with *m*-chloroperbenzoic acid[10] gave low yields of **2**.

0022-3263/89/1954-1766$01.50/0

Scheme I



at 65 °C (Scheme I). The reaction temperature was very critical to the generation of oxide **2** since temperatures ≥ 70 °C or ≤ 60 °C diminished the yields due to formation of side products[23] or recovery of unchanged **1**, respectively. The ^{1}H NMR spectrum of oxide **2** displayed an unsymmetrical 10-line pattern in the aromatic region [H5 (δ 7.69) and H6 (δ 7.71) should both be doublets, but, because of the small $\Delta\delta$, the outer peaks of the second-order coupling were not visible] as well as two singlets at δ 2.78 and 2.94 for the methyl groups. Likewise the ^{13}C NMR spectrum showed an 11-line pattern (5C and 6C signals appeared together at δ 122.9) for the aromatic region and two methyl carbons at δ 25.3 and 18.7. Because of the enhanced reactivity of **2**, acetic anhydride was added at 0 °C and subsequently refluxed to give ester **4**. Alternatively, in order to control the reaction, acetic anhydride was added to a CH_2Cl_2 solution of **2** at 25 °C; CH_2Cl_2 was then removed in vacuo, and the reaction mixture was refluxed. In the ^{1}H NMR spectrum of **4**, the singlets at δ 5.67, 2.93, and 2.20 are indicative of oxymethylene, heteroarylmethyl, and acetate moieties, respectively. Transesterification of **1** with anhydrous potassium carbonate in absolute ethanol gave an excellent yield of alcohol **5**, which on standing decomposed to insoluble material (H_2O, $CHCl_3$, Me_2SO) and was thus used immediately. Phosphorus trichloride in $CHCl_3$ smoothly transformed **5** into the chloromethyl derivative **6** whereas reaction with PBr_3 usually caused reduction to give 2,9-dimethyl-1,10-phenanthroline (**1**) in yields up to 60%! *Care must be exercised in handling* ***6****, since it can be extremely irritating to the skin and mucous membranes.* The ^{1}H NMR spectrum of **6** showed singlets at δ 2.97 and 5.12 for methyl and chloromethyl groups, respectively.

A literature survey revealed that researchers have claimed to have synthesized 1,10-phenanthroline bis(*N*-oxide) by treatment of the parent heterocycle with peracetic acid.[14,24,25] However, in our hands, all attempts to obtain the bis(*N*-oxide) **3**, even under the most exhaustive conditions, resulted in the diminished formation of **2** and oxidized side products.[23] In order to ascertain the steric interactions between the methyl group(s), N-electrons, and oxygen atom as well as to gain insight into the reality of bis(*N*-oxide) formation, a single-crystal X-ray analysis of **2** was undertaken.

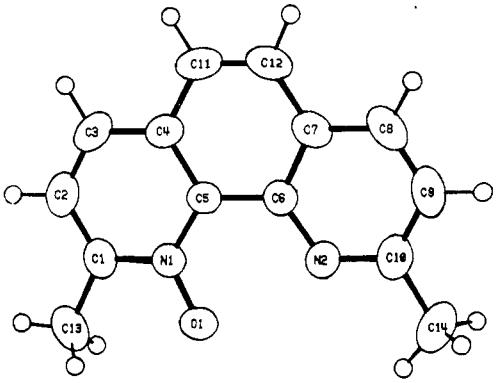


Figure 1. ORTEP drawing of **2**.

Disorder of the oxygen atom exists in the crystal of oxide **2** as depicted in Figure 1; only the major population (68%) is shown. The site of minor population, O1′, lies 1.936 Å from O1. This distance is more than 1 Å shorter than the sum of van der Waal's radii (2.80 Å),[26] precluding the possibility that the crystal contains bis(*N*-oxide). Severe distortions from planarity of the phenanthroline ring would be necessary in order to allow a reasonable nonbonded contact between the two oxygen atoms on the same molecule. The 14 atoms of the phenanthroline ring system are nearly coplanar with a maximum deviation of 0.072 (2) Å (N1) and an average deviation of 0.037 Å and may be described as a bowed, anticlinal distortion such that the anticline crest lies along a line from C1 to C8. *N*-Oxide oxygen O1 lies 0.134 (3) Å out of this plane, while methyl

(23) One of the major products isolated, when the reaction temperature was >70 °C, was 6,6′-dimethyl-3,3′-diformyl-2,2′-bipyridine *N*-oxide: ^{1}H NMR δ 2.34 (s, C*H*$_3$, 3 H), 2.69 (s, C*H*$_3$, 3 H), 7.41 (d, 3-pyr*H*,*J* = 8.6 Hz, 1 H), 7.60 (d, 3′-pyr*H*, *J* = 9.2 Hz, 1 H), 7.71 (d, 4′-pyr*H*,*J* = 9.2 Hz, 1 H), 8.05 (d, 4-pyr*H*,*J* = 8.6 Hz, 1 H), 9.84 and 9.85 (2 s, C*H*O, 2 H); ^{13}C NMR δ 18.6 and 24.4 (*C*H$_3$), 124.0, 124.8, 125.4, 127.2, 128.02, 133.32 (3,3′,4,4′,5,5′-pyr*C*), 186.8 (*C*=O); primed positions designate the *N*-oxide ring.

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C atoms lie 0.093 (3) Å (C13) and −0.149 (4) Å (C14) out of the plane. The N1–C5–C6–N2 torsion angle is 4.6 (4)°. Bond distances within **2** are normal including the N1–O1 distance [1.284 (2) Å]. Alternate aromatic bond lengths are predicted considering the resonance contributors, with shortest distances C1–N1 and C10–N2 (average 1.344 Å) and C2–C3, C8–C9, and C11–C12 (average 1.351 Å).

In the crystal, dimethylphenanthroline *N*-oxide molecules are linked via H-bonding to water molecules. The *N*-oxide oxygen atoms accept H-bonds to form bridges between centrosymmetric, almost square arrays of water molecules. The O···O distances range 2.658 (4)–2.922 (2) Å between water and *N*-oxide, and the H_2O square has 2.887 (2) Å side dimension.

Therefore, due partially to the contribution of the methyl substituents, it can be concluded that the bis(*N*-oxide) of 2,9-dimethyl-1,10-phenanthroline (**3**) will be difficult to obtain by a direct peracid oxidation even at elevated temperatures because of the electronic and steric constraints imposed by the juxtaposition of the two oxygen atoms.[12,13] Recently, Wenkert and Woodward[27] were unable to duplicate the previously reported synthesis of 1,10-phenanthroline bis(*N*-oxide), even under extremely harsh conditions. An alternative structure for the reported 1,10-phenanthroline di-*N*-oxide is 3,3′-diformyl-2,2′-bipyridine,[23] which has the same molecular formula (and, thus, the same analytical data) as the proposed di-*N*-oxide; analytical data were the main structural proof of the di-*N*-oxide.[14,24,25] Work is in progress to indirectly generate the bis(*N*-oxide) via the nonplanar 5,6-dihydro-1,10-phenanthroline[28,29] derivatives, which can be subsequently aromatized.

Experimental Section

General Comments. All melting points were taken in capillary tubes with a Gallenkamp melting point apparatus Model MFB-595 and are uncorrected. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution with Me_4Si, as an internal standard (δ = 0 ppm), and were recorded on an IBM NR/80 spectrometer. Mass spectral (MS) data (70 eV) (assignment, relative intensity) were determined by Mr. H. Land on a Hewlett-Packard HP 5985 GC/mass spectrometer. Infrared spectra were obtained on a IBM IR/38 Fourier transform spectrometer. Elemental analyses were obtained from M-H-W Laboratories, Phoenix, AZ.

2,9-Dimethyl-1,10-phenanthroline *N*-Oxide Dihydrate (2). A stirred solution of neocuproine (**1**) (Aldrich; 1.0 g, 4.8 mmol) in glacial AcOH (7 mL) and H_2O_2 (2 mL, 30%) was heated to 65 °C; after 1.5 and 3 h, additional H_2O_2 (2 mL) was added. After 4.5 h, the solution was cooled to 25 °C, diluted with water (15 mL), and concentrated in vacuo; this dilution/concentration sequence was repeated three times. The residue was neutralized with saturated aqueous Na_2CO_3 and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and concentrated in vacuo to afford a yellowish-brown solid, which was column chromatographed (silica gel; CH_2Cl_2) to give (68%) yellow crystals of *N*-oxide **2**·$2H_2O$: 804 mg; mp 131–132 °C dec; ^1H NMR δ 2.78 (s, 2-phenCH_3, 3 H), 2.94 (s, 9-phenCH_3, 3 H), 7.51 (d, 3-phen*H*, J = 8.1 Hz, 1 H), 7.53 (d, 8-phen*H*, J = 8.2 Hz, 1 H), 7.67 (d, 4-phen*H*, J = 8.1 Hz, 1 H), 7.69 (s, 5-phen*H*, 1 H), 7.71 (s, 6-phen*H*, 1 H), 8.13 (d, 7-phen*H*, J = 8.2 Hz, 1 H); ^{13}C NMR δ 18.7 (2-CH_3), 25.3 (9-CH_3), 122.9 (5, 6*C*), 123.5 (8*C*), 125.1 (3*C*), 126.4 (4b*C*), 127.5 (4*C*), 131.3 (4a*C*), 135.4 (7*C*), 137.5 (10a*C*), 141.8 (10b*C*), 149.6 (2*C*), 158.2 (9*C*); MS m/e 224 (M^+, 87), 208 (M^+ − O, 60), 207 (M^+ − OH, 100), 193 (M^+ − CH_3O, 9), 180 (M^+ − C_2H_4O, 17); IR (neat) 3389 b, 1350 s, 857, 739 cm^{-1}.

2-(Acetoxymethyl)-9-methyl-1,10-phenanthroline (4). After distilled Ac_2O (2 mL) was added to a solution of **2** (700 mg, 2.7 mmol) in CH_2Cl_2, the CH_2Cl_2 was removed in vacuo and the solution was refluxed for 1 h. The mixture was concentrated in vacuo, and the residue was dissolved in $CHCl_3$, washed with saturated aqueous Na_2CO_3, dried with anhydrous $MgSO_4$, and again concentrated in vacuo. The crude residue was eluted through a short Al_2O_3 column with CH_2Cl_2/EtOAc (50:50). The eluent was concentrated to afford (90%) **4** as an orange oil: 645 mg; ^1H NMR δ 2.20 (s, CO_2CH_3, 3 H), 2.93 (s, 9-phenCH_3, 3 H), 5.67 (s, 2-phenCH_2, 2 H), 7.46 (d, 3-phen*H*, J = 8.3 Hz, 1 H), 7.66 (d, 8-phen*H*, J = 8.3 Hz, 1 H), 7.67 (s, 5,6-phen*H*, 2 H), 8.08 (d, 4-phen*H*, J = 8.3 Hz, 1 H), 8.21 (d, 7-phen*H*, J = 8.3 Hz, 1 H); ^{13}C NMR δ 20.1 ($COCH_3$), 24.9 (CH_3), 67.0 (CH_2), 123.0 (8*C*), 124.6 (3*C*), 125.6 (6*C*), 125.8 (5*C*), 126.2 (4b*C*), 127.4 (4a*C*), 135.6 (4*C*), 136.2 (7*C*), 144.4 (10a*C*), 144.5 (10b*C*), 155.6 (2*C*), 158.6 (9*C*), 169.7 (*C*=O); MS m/e 266 (M^+, 8), 223 (M^+ − $COCH_3$, 100), 207 (M^+ − $OCOCH_3$, 3), 193 (M^+ − $CH_2CO_2CH_3$, 11); IR (neat) 1744 s, 1229, 855, 754 cm^{-1}.

2-(Hydroxymethyl)-9-methyl-1,10-phenanthroline Hemihydrate (5). A suspension of **4** (700 mg, 2.6 mmol) and anhydrous K_2CO_3 (600 mg) in anhydrous EtOH (10 mL) was stirred for 4 h. The mixture was concentrated in vacuo, and the residue was triturated with CH_2Cl_2. The organic extract was concentrated in vacuo to give (86%) **5** as a yellow, hygroscopic powder: 530 mg; mp 153–158 °C; ^1H NMR δ 2.83 (s, 9-phenCH_3, 3 H), 5.12 (s, 2-phenCH_2, 2 H), 7.49 (d, 8-phen*H*,J = 8.2 Hz, 1 H), 7.57 (d, 3-phen*H*,J = 8.2 Hz, 1 H), 7.76 (s, 5,6-phen*H*, 2 H), 8.15 (d, 7-phen*H*,J = 8.2 Hz, 1 H), 8.23 (d, 4-phen*H*,J = 8.2 Hz, 1 H); ^{13}C NMR δ 24.8 (CH_3), 65.0 (CH_2), 119.9 (3*C*), 123.0 (8*C*), 124.9 (6*C*), 125.2 (5*C*), 126.3 (4b*C*), 127.2 (4a*C*), 135.8 (7*C*), 135.9 (4*C*), 144.1 (10a*C*), 144.6 (10b*C*), 158.5 (9*C*), 160.5 (2*C*); IR (neat) 3247 b, 1065, 853, 733 cm^{-1}. Anal. Calcd for $C_{14}H_{12}N_2O\cdot{}^1/_2H_2O$: C, 72.09; H, 5.62; N, 12.01. Found: C, 72.45; H, 5.42; N, 11.80.

2-(Chloromethyl)-9-methyl-1,10-phenanthroline Monohydrate (6). To a stirred solution of **5** (450 mg, 1.9 mmol) in $CHCl_3$ (20 mL) was added PCl_3 (2 mL) in $CHCl_3$ (5 mL). The mixture was refluxed for 1 h and then concentrated in vacuo to afford a viscous oil, which was carefully neutralized with aqueous Na_2CO_3 (10%). The light yellow precipitate was filtered, washed with cold water, dried in vacuo, and recrystallized from C_6H_{12} to afford (72%) **6** as a white solid: 360 mg; mp 111–114 °C; ^1H NMR δ 2.95 (s, 9-phenCH_3, 1 H), 5.11 (s, 2-phenCH_2, 2 H), 7.52 (d, 8-phen*H*,J = 8.2 Hz, 1 H), 7.76 (s, 5,6-phen*H*, 2 H), 7.90 (d, 3-phen*H*,J = 8.4 Hz, 1 H), 8.15 (d, 7-phen*H*,J = 8.2 Hz, 1 H), 8.29 (d, 4-phen*H*,J = 8.4 Hz, 1 H); ^{13}C NMR δ 25.8 (CH_3), 47.4 (CH_2), 122.5 (3*C*), 123.4 (8*C*), 125.3 (6*C*), 126.6 (5*C*), 126.8 (4b*C*), 128.3 (4a*C*), 136.2 (7*C*), 137.4 (4*C*), 144.8 (10a*C*), 145.1 (10b*C*), 157.4 (2*C*), 159.2 (9*C*); IR (KBr) 851, 705, 627 cm^{-1}. Anal. Calcd for $C_{14}H_{11}N_2Cl\cdot H_2O$: C, 64.50; H, 5.03; N, 10.74. Found: C, 64.06; H, 4.79; N, 10.59.

Reduction of 5 with PBr_3. To a stirred solution of **5** (450 mg, 2 mmol) in $CHCl_3$ (20 mL) was added PBr_3 (2 mL) in $CHCl_3$ (5 mL). The mixture was refluxed for 1 h and then concentrated in vacuo to afford a viscous oil, which was carefully neutralized with aqueous Na_2CO_3 (10%). The light yellow precipitate was filtered, washed with cold water, dried in vacuo, and passed through a short silica gel column with $CHCl_3$ to afford (60%) **1** (as determined by ^1H NMR) as the major product.

X-ray Experimental. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Crystal data are as follows: $C_{14}H_{12}N_2O\cdot 2H_2O$, FW = 260.3, triclinic space group $P\bar{1}$, a = 7.068 (2) Å, b = 9.292 (2) Å, c = 11.365 (3) Å, α = 67.45 (2)°, β = 72.48 (2)°, γ = 85.48 (2)°, V = 656.8 (3) Å^3, Z = 2, T = 298 K, D_c = 1.316 g cm^{-3}. One hemisphere of data with $1° < \theta < 28°$ was collected by $\omega - 2\theta$ scans of variable rate, 0.53–4.0 deg min^{-1}. Data reduction included corrections for background, Lorentz, and polarization effects. Of 3163 unique data, 2047 had $I > 1\sigma(I)$ and were used in the refinement. The structure was solved using MULTAN and refined by full-matrix least-squares methods based on F with weights $w = \sigma^{-2}(F_o)$, treating C, N, and O atoms anisotropically. The *N*-oxide oxygen was found to be statistically disordered with unequal probability on the two N atoms. Populations of 68% on N1 and 32% on N2 were assigned, judged from relative electron densities. Hydrogen atoms were located in difference maps and included as fixed contributions.

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H atoms on water molecule O2W were not located and assumed to be disordered. Final $R = 0.066$, $R_w = 0.082$ for 2047 data and 182 variables. Maximum residual electron density is 0.33 e A^{-3}.

Acknowledgment. We wish to thank the National Institutes of Health and the LSU Center for Energy Studies for partial support of this work and Professor Randy Thummel for his timely comments.

Registry No. 1, 484-11-7; 2, 118896-77-8; 4, 118896-78-9; 5, 118896-79-0; 6, 118896-80-3.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters for $2 \cdot 2H_2O$ (4 pages). Ordering information is given on any current masthead page.

Synthesis of 4,4,8,8,11,11-Hexanitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane

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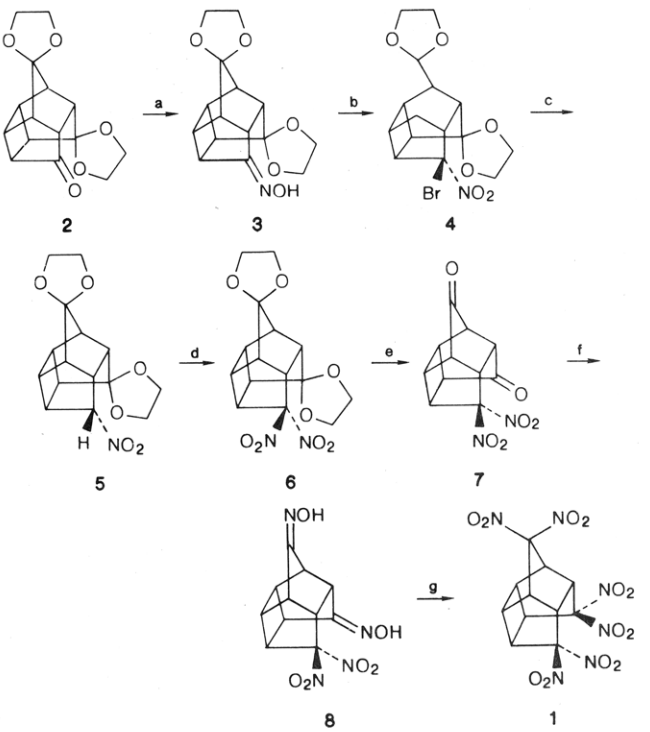
Received November 8, 1988

There is considerable current interst in the synthesis and chemistry of polynitropolycyclic "cage" molecules.[1,2] Compounds of this type are of interest as a new class of energetic materials.[2] Additionally, these compounds are of theoretical interest; the cumulative effects of increasing NO_2 substitution upon the structure, thermodynamic stability, and chemical reactivity of carbocyclic cage systems can be probed through studies of the physical and chemical properties of individual compounds in a series of increasingly NO_2 substituted cage molecules.

As part of a continuing effort to synthesize new polynitropolycyclic systems[1] and in accordance with our long-standing interest in the synthesis and chemistry of novel, substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes (PCU),[3] we now report our synthesis of the title compound, **1**. Compound **1** is isomeric with D_3-hexanitrotrishomocubane, whose synthesis was reported recently.[1i] To our knowledge, **1** is the most highly NO_2 substituted PCU derivative to have been synthesized.[1c,j]

Scheme I[a]



[a] (a) $NH_2OH \cdot HCl$, K_2CO_3, EtOH, reflux 24 h (79%); (b) NBS, dioxane, room temperature, overnight (62%); (c) $NaBH_4$, 60% aqueous EtOH, 0 °C → room temperature, 1 h (84%); (d) $K_3Fe(CN)_6$, $NaNO_2$, aqueous MeOH, room temperature, 2 h (83%); (e) concentrated H_2SO_4, CH_2Cl_2, room temperature, 24 h (50%); (f) $NH_2OH \cdot HCl$, NaOAc, MeOH, reflux 2 h (75%); (g) 98% red nitric acid, NH_4NO_3, urea, dry CH_2Cl_2, reflux 0.5 h, then 30% aqueous H_2O_2, reflux 15 min (19%).

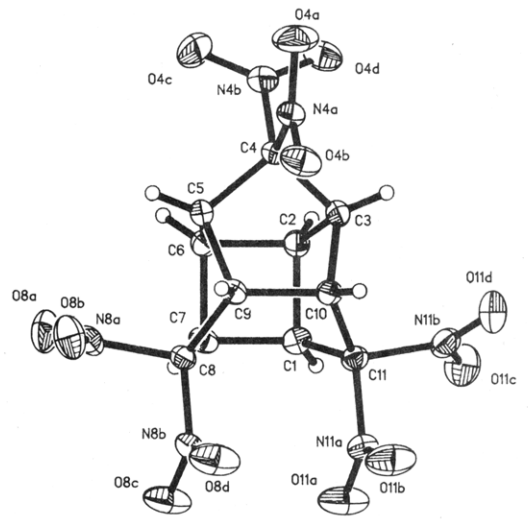


Figure 1. X-ray structure drawing of **1**.

Recently, we demonstrated that NO_2 groups could be introduced conveniently into the 8- and 11-positions of the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane ring system via oxidative nitration of the corresponding 8,11-dioxime.[1j] Hence, our strategy simply was to functionalize the 4-position of the PCU ring system with a masked carbonyl group, which ultimately would be converted into a $C(NO_2)_2$ group.

Our synthesis of **1** that begins with the readily available 4,4:11,11-bis(ethylenedioxy)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecan-9-one (**2**)[1i] is shown in Scheme I. Initially, **2** was converted into the corresponding oxime, **3**. The oximino

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