Regiospecific Oxidation of Binor S and Acid-Catalyzed Rearrangement of the Product to the First Example of a Pentacyclo[6.6.0.0^{5,14}.0^{7,12}.0^{9,13}]tetradecane

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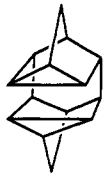
Dimethyldioxirane has been found to oxidize the head-to-head dimer of norbornadiene (binor-S) regiospecifically, giving first the 1-ol and then the 1,9-diol of heptacyclo[8.4.0.0^{2,7}.0^{3,5}.0^{4,8}.0^{9,13}.0^{12,14}]tetradecane. Reaction of the 1-ol with boron trifluoride etherate induces gross rearrangement and leads in good yield to (±)-pentacyclo-[6.6.0.0^{5,14}.0^{7,12}.0^{9,13}]tetradec-2-en-6-one, the first reported member of this new ring system.

The head-to-head dimer of norbornadiene, "binor S" (1) was first reported in 1966[1] and was later prepared in nearly quantitative yield by dimerization of norbornadiene with a variety of transition metal catalysts.[2] This heptacyclic $C_{14}H_{16}$ hydrocarbon consists of two nortricyclane subunits, each of which contains one 3-membered ring and three 5-membered rings. X-ray analysis of a binor S derivative has confirmed that the "inside" edges of the cyclopropane rings are held in close proximity.[3] As there is a close structural similarity between binor S and the isomeric D_{2h} bishomohexaprismane (2), a potential precursor for hexaprismane (3),[4] we selected binor S as a material worth further investigation. Surprisingly, very little chemistry of this compound has been reported, although it was first synthesized almost 25 years ago.[5]



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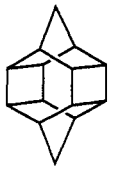

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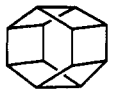

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Functionalization of hydrocarbons is an active area, but still in a developmental stage.[6] Many oxidizing systems, stoichiometric as well as catalytic, have been reported. Recently several reports have appeared about dimethyldioxirane, an extraordinary oxidant.[7] Most important for our purposes here, Murray and co-workers discovered that dimethyldioxirane inserts an oxygen atom into C–H bonds.[8] Tertiary C–H is more prone to oxidation than the secondary and primary counterparts. Dimethyldioxirane can be generated easily by slow addition of potassium peroxymonosulfate to a mixture of sodium bicarbonate, acetone, and water. It can be isolated as a dilute solution in acetone by entrainment-distillation or it can be used in situ.[7f]

We have found that treatment of binor S in methylene chloride with dimethyldioxirane forming on site in acetone/water gives a good yield (98%) of an alcohol along with a trace of its acetate derivative.[9] In a typical laboratory-scale reaction, binor S could be functionalized in gram quantities, and 6–10 g of the product could be obtained readily in a day. The structure of the product was established spectroscopically. The electron impact mass spectrum gave a formula of $C_{14}H_{16}O$ (m/z = 200), confirmed by combustion analysis. The IR spectrum showed strong O–H stretching absorption. Both the ^1H and ^{13}C NMR spectra showed that the compound has no symmetry element. In the CMR spectrum, 14 resonances are apparent. The six well-resolved methine carbon signals in the high-field region of the ^{13}C NMR spectrum (22.7, 19.0, 17.0, 16.8, 16.1, 15.4 ppm), with C–H coupling constants greater than 172 Hz, are assignable to unfunctionalized cyclopropane carbons and lead us to favor structure 4. This assignment was confirmed by analysis of the 2D

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(9) This acetate could be converted to alcohol 4 by $LiAlH_4$ reduction, and the conversion reversed by acetylation.

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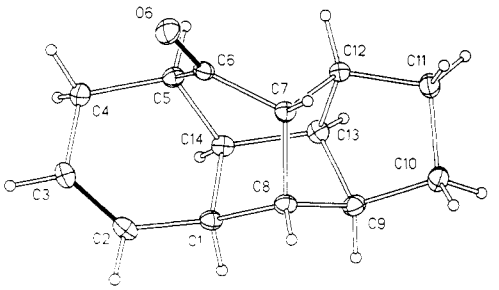
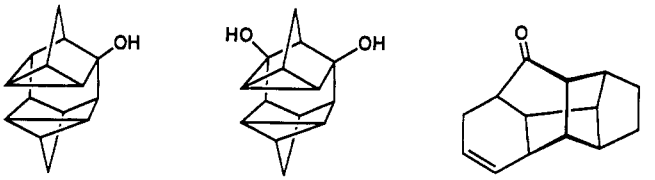


Figure 1. The molecular structure and numbering scheme for pentacyclo[6.6.0.0^{5,14}.0^{7,12}.0^{9,13}]tetradec-2-en-6-one (**6**).

NMR spectra. Further oxidation of the compound **4** with dimethyldioxirane in acetone solution gave a symmetrical diol as the major isolable product. Assignment of structure **5** was straightforward given the analytical details and the symmetry evident from the number of carbon signals (10) in the ^{13}C spectrum of the compound. This identification reinforces our assignment of structure **4**.



4 **5** **6**

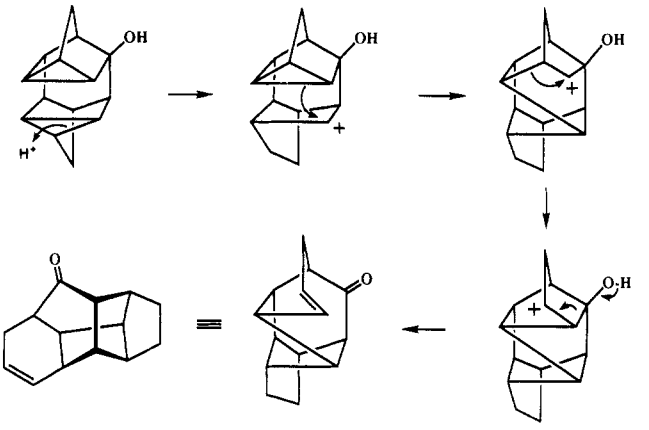
When **4** was treated with boron trifluoride etherate in CH_2Cl_2, it rearranged smoothly to one major product, isolated pure in 59% yield. The EI mass spectrum established the molecular formula as $C_{14}H_{16}O$, the same as the starting material. The IR spectrum showed a strong carbonyl absorption at 1715 cm^{-1}. ^1H and ^{13}C NMR spectroscopy established that the compound is not symmetric and contains three CH_2 groups, two olefinic CH groups, one carbonyl carbon, and eight CH groups. Other finer details of the structure could be gained from COSY, HETCOR, and 2D-INADEQUATE spectra, but the structure was established unambiguously as **6** only by X-ray analysis (Figure 1). The central portion of this molecule, a tricyclononane cage, is composed of two 5- and two 6-membered carbon rings fused into a strained cage. The five smallest bond angles, which range from 92.8 to 98.9°, are all between ring bonds in the 5-membered rings. The longest bond, C7–C8, is 1.573 (3) Å, and is probably lengthened by the same "cage closure" strain that leads to the angle contractions. As expected both enantiomers are present in the crystal. No doubt this interesting complex ring system will soon be put to fruitful use elsewhere.

There can be many conceivable pathways for the formation of **6**. We presume the rearrangement of **4** to **6** is initiated by cleavage of one of the cyclopropane bond away from the facing second cyclopropyl ring (Scheme I) analogous to the known silver ion induced (i.e., cationic) rearrangement of binor S.[5c] Currently we are exploring possible ways to alter the rearrangement pattern.

Experimental Section

Flash column chromatography was done on Merck grade 60 silica gel (230–400 mesh). Low-resolution EI mass spectra were recorded on a GC–MS spectrometer operating at 70 eV. NMR spectra were run in chloroform-*d* unless otherwise stated: ^1H NMR at 400 MHz and referenced to internal tetramethylsilane (0.00 ppm); ^{13}C NMR at 100 MHz and referenced to the central line of the solvent. Proton chemical shifts are reported to a precision of ±0.02 ppm; carbon chemical shifts, to ±0.1 ppm. Infrared spectra were recorded at 2-cm^{-1} resolution.

Scheme I



(±)-Heptacyclo[8.4.0.0^{2,7}.0^{3,5}.0^{4,8}.0^{9,13}.0^{12,14}]tetradecan-1-ol (4). Oxone (Dupont trademark, Aldrich, $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, 600 g) dissolved in water (800 mL) was added slowly over 2 h to a cooled (ice bath), well-stirred mixture of binor S (20 g, recrystallized from ethanol–ether), acetone (300 mL), dichloromethane (200 mL), sodium bicarbonate (280 g), and water (300 mL). After the addition, the reaction mixture was allowed to reach room temperature and was stirred for 12 h further. The solids were removed by filtration and washed with dichloromethane (2 × 200 mL). The filtrate and wash were transferred to a separatory funnel, and the dichloromethane layer was separated. This phase was washed with water and brine and then dried (Na_2SO_4). Evaporation of the solvent at reduced pressure left a solid, which was chromatographed on silica gel. Elution with pentane gave starting material (12.2 g). Elution with diethyl ether–pentane (3:7) first gave the acetate of **4** (650 mg, 2%);[9] further elution gave alcohol **4** as a white, crystalline solid (7.7 g, 98% based on consumed starting material): mp 153–154 °C; IR (KBr) ν 3332, 3270, 3070, 3058, 2928, 2905, 2857, 1296, 1101, 1083, 799, 789 cm^{-1}; ^1H NMR δ 1.94 (br s, 2 H), 1.90 (br s, 1 H), 1.83 (br s, 1 H), 1.78 (d, J = 9 Hz, 1 H), 1.61 (br s, 1 H), 1.51 (br s, 1 H), 1.44 (d, J = 11 Hz, 1 H), 1.37 (q, J = 10 Hz, 2 H), 1.29 (m, 1 H), 1.26 (m, 1 h), 1.22 (t, J = 5.8 Hz, 1 H), 1.17 (m, 2 H), 1.12 ppm (t, J = 5.6 Hz, 1 H); ^{13}C NMR δ 83.2 (s), 49.8 (d, J = 136 Hz), 39.7 (d, J = 137 Hz), 39.6 (d, J = 137 Hz), 38.0 (d, J = 146 Hz), 33.0 (t, J = 131 Hz), 32.1 (d, J = 146 Hz), 31.3 (t, J = 132 Hz), 22.7 (d, J = 175 Hz), 19.0 (d, J = 175 Hz), 17.0 (d, J = 175 Hz), 16.8 (d, J = 174 Hz), 16.1 (d, J = 172 Hz), 15.4 ppm (d, J = 174 Hz); m/z 200 (20), 134 (100), 118 (65), 82 (30). Anal. Calcd for $C_{14}H_{16}O$: C, 83.95; H, 8.05. Found: C, 84.05; H, 7.96.

Heptacyclo[8.4.0.0^{2,7}.0^{3,5}.0^{4,8}.0^{9,13}.0^{12,14}]tetradecane-1,9-diol (5). An acetone solution of dimethyldioxirane (10 mL, 0.07 M, 0.7 mmol) was added to alcohol **4** (100 mg, 0.50 mmol), and the solution was stirred at room temperature in the dark for 14 h. The volatiles were evaporated under reduced pressure, and the residual solid was chromatographed on a silica gel column. Elution with diethyl ether gave starting material (48 mg). Further elution with ether–methanol (9:1) gave diol **3** (42 mg, 75% based on consumed starting material): mp 210–215°C dec; IR (KBr) ν 3327, 3270, 2922, 2905, 1116, 1054, 802 cm^{-1}; ^1H NMR (CD_3OD) δ 1.99 (br s, 1 H), 1.84 (m, 2 H), 1.82 (m, 2 H), 1.50 (m, 1 H), 1.38 (m, 2 H), 1.35 (m, 3 H), 1.30 (br d, J = 5.2 Hz, 2 H), 1.22 (t, J = 5 Hz, 1 H) ppm; ^{13}C NMR (CD_3OD) δ 81.5 (s), 51.6 (d, J = 136 Hz), 45.4 (d, J = 148 Hz), 33.7 (t, J = 133 Hz), 32.8 (d, J = 147 Hz), 29.8 (t, J = 133 Hz), 26.2 (d, J = 176 Hz), 17.8 (d, J = 176 Hz), 17.4 (d, J = 174 Hz), 16.7 ppm (d, J = 174 Hz); m/e 216 (P^+, 5), 183 (5), 165 (7), 150 (100), 133 (40), 91 (55). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.74; H, 7.45. Found: C, 77.59; H, 7.37.

(±)-Pentacyclo[6.6.0.0^{5,14}.0^{7,12}.0^{9,13}]tetradec-2-en-6-one (6). Boron trifluoride etherate (100 mg) was added to a solution of alcohol **4** (1 g) in dry dichloromethane (50 mL) under argon. The mixture was refluxed for 14 h, cooled, poured into water, and extracted with dichloromethane (3 × 30 mL). The extract was washed with water and brine and then dried (Na_2SO_4). Evaporation of the solvent in vacuo afforded a viscous oil. Column chromatography on silica gel with 1:9 diethyl ether–pentane gave

6 as a white, crystalline solid (590 mg, 59%). Crystallization from ether–dichloromethane gave colorless rectangular prisms: mp 104–105 °C; IR (KBr) ν 3027, 2940, 2866, 1715, 1424, 1194, 1172, 878, 789, 723, 700 cm^{-1}; ^{1}H NMR δ 5.75 (m, 1 H), 5.50 (m, 1 H), 2.60 (m, 1 H), 2.54 (m, 1 H), 2.46 (br, 1 H), 2.39 (m, 1 H), 2.30 (m, 2 H), 2.23 (m, 1 H), 2.11 (m, 2 H), 2.06 (m, 1 H), 1.7–1.4 ppm (complex, 4 H); ^{13}C NMR δ 217.7 (s), 129.7 (d, J = 158 J Hz), 127.1 (d, J = 156 Hz), 53.2 (d, J = 145 Hz), 49.9 (d, J = 141 Hz), 47.8 (d, J = 144 Hz), 46.6 (d, J = 138 Hz), 45.3 (d, J = 144 Hz), 45.1 (d, J = 138 Hz), 43.1 (d, J = 132 Hz), 33.9 (d, J = 137 Hz), 27.9 (t, J = 130 Hz), 27.4 (t, J = 131 Hz), 23.1 ppm (t, J = 131 Hz); m/e 200 (P$^+$, 100). Anal. Calcd for $C_{14}H_{16}O$: C, 83.95; H, 8.05. Found: C, 84.19; H, 7.96.

Single-crystal X-ray diffraction analysis of (±)-pentacyclo[6.6.0.0^{5,14}.0^{7,12}.0^{9,13}]tetradec-2-en-6-one (6): $C_{14}H_{16}O$, FW = 200.3, tetragonal space group $I4$, a = 17.708 (3), c = 6.360 (1) Å, V = 1994.5 (6) Å^3, Z = 8, ρ_{calc} = 1.334 mg mm^{-3}, λ(Mo Kα) = 0.710 73 Å, μ = 0.076 mm^{-1}, F(000) = 864, T = 223 K. A clear, colorless, 0.16 × 0.27 × 0.48 mm crystal in the shape of a lath was used for data collection on an automated Siemens R3m/V diffractometer equipped with an incident beam monochromator. Lattice parameters were determined from 25 centered reflections within 20.8 ≤ 2θ ≤ 30.2°. The lattice parameters were determined from 25 centered reflections within 20.8 ≤ 2θ ≤ 30.2°. The data collection range of hkl was: $-1 \le h \le 19$, $0 \le k \le 19$, $0 \le l \le 6$ with $[(\sin\theta)/\lambda]_{max}$ = 0.538. Three standards, monitored after every 97 reflections, exhibited random variations with deviations up to ±2.0% during the data collection. A set of 863 reflections was collected in the $\theta/2\theta$ scan mode, with scan width $[2\theta(K_{\alpha1}) - 0.45]$ to $[2\theta(K_{\alpha2}) + 0.45]$° and ω scan rate (a function of count rate) from 5.0°/min to 30.0°/min. There were 813 *unique* reflections, and 777 were observed with $F_o > 3\sigma(F_o)$. The structure was solved and refined with the aid of the SHELXTL system of programs.[10] The full-matrix least-squares refinement varied 201 parameters namely atom coordinates and anisotropic thermal parameters for all non-H atoms, atom coordinates, and isotropic thermal parameters for the hydrogen atoms. Final residuals were R = 0.024 and R_w = 0.029 with final difference Fourier excursions of 0.13 and −0.14 e Å^{-3}.

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Registry No. 1, 13002-57-8; 4, 130011-60-8; 4 (acetate isomer), 129986-79-4; 5, 130011-61-9; 6, 129986-80-7.

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

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On the Mechanism of Lewis Acid Mediated Nucleophilic Substitution Reactions of Acetals[1]

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Lewis acid mediated nucleophilic substitution of acetals can occur by direct displacement (S_N2) or oxocarbenium ion (S_N1) mechanisms. With acyclic acetals, stereoselectivity increases with increasing steric bulk of the alkoxy group and with increasing polarity of the reaction medium. The enhanced stereoselectivity observed with acetals of secondary and tertiary alcohols is explained by perturbation of the approach trajectory of the nucleophilic alkene as it attacks the oxocarbenium ion. Highest stereoselectivity is seen in the reaction of 2-(1-phenylethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (**4**) with enol silane **5**; only one diastereomeric product (**9s**) is obtained, even in the relatively nonpolar solvent CH_2Cl_2. The $TiCl_4$-mediated reactions of cyclic acetals **18c**, **18t**, **25**, and **28** with silyl enol ether **5** show that in these systems the substitution does not occur by the S_N2 mechanism.

Introduction

The Lewis acid mediated reaction of acetals with nucleophiles such as silyl enol ethers and allylsilanes is a powerful method for carbon–carbon bond formation[3] and has proven to be highly stereoselective in many cases.[4] Detailed mechanistic studies are scarce, although some mechanistic rationales have been put forward for these and related reactions.[3o,4a,c,5-9] Recent communications from Denmark and co-workers provide strong evidence for a mechanistic divergence in an intramolecular version of the reaction[10] and give information pertaining to the structures

(1) Paper 52 in the series Acyclic Stereoselection. For paper 51, see: Mori, I.; Bartlett, P. A.; Heathcock, C. H. *J. Org. Chem.* **1990**, *55*, 5966.

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