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Functional Group Manipulation along the Perimeter of a Hemispherical Molecule. Synthesis of Dihydro- and Tetrahydro-C_{16}-hexaquinacene

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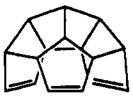
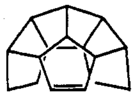
The synthesis of tetrahydro-C_{16}-hexaquinacene (**2**) was successfully achieved by reduction of enedione **4** to **5a** and subsequent exposure of this enediol to diphenyl disulfide and tri-*n*-butylphosphine in refluxing tetrahydrofuran. The resulting bis(phenylthio) derivative **6** underwent smooth reductive desulfurization with lithium in liquid ammonia. The structural assignment to **2** so obtained was confirmed X-ray crystallographic analysis. When routes to the dihydro analogue **3** based upon saturated diol **8** and unsaturated alcohol **12** were found to be less than satisfactory, recourse was again made to **6**. In this instance, oxidation was first accomplished with 1 equiv of *m*-chloroperbenzoic acid, after which thermolysis produced **14**. Dissolving metal reduction then gave **3**, the C_s symmetry of which was clearly apparent from its spectral properties.

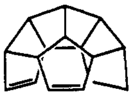
In the course of earlier work dealing with the chemistry of functionalized C_{16}-hexaquinacenes,[2] we noted that restrictions in utilization of the pendant groups were numerous. The heightened proximity effects and transannular compression at play in hemispherical systems related to **1**[3] clearly exert considerable impact on the course of otherwise conventional chemical reactions. We have more recently investigated possible approaches to tetrahydro- (**2**) and dihydro-C_{16}-hexaquinacenes (**3**) for the ulterior purpose of assessing by thermochemical means[4] the possible existence of homoconjugative ground-state character in **1**.[5] Herein we detail successful approaches to these partially saturated congeners of **1**. The schemes skirt around the stringent limitations in reactivity brought on by the inherently rigid topography of this group of molecules.



1



2



3

Results and Discussion

The Tetrahydro Derivative. The conversion of diketone **4** to **1** by way of ditosylate **5b** had previously been shown to be a particularly serviceable route to **1**.[3] Recrystallization of the crude triene from isooctane allows for convenient acquisition of the triene in a state of 100% purity as judged by capillary gas chromatography (Scheme I).

Our willingness to consider **5b** as a direct precursor of **2** was predicated on the knowledge that the reducing agent would be required to deliver hydride from the relatively unhindered exterior of the molecule. However, all attempts to displace the tosylate groups with a variety of hydride sources (e.g., lithium triethylborohydride, lithium aluminum hydride, etc.) were to no avail. Nor could the carbon–oxygen bonds in **5b** be cleaved satisfactorily by dissolving metal reduction.[6] Attempts to transform diol **5a** into **2** by the free-radical deoxygenation scheme developed by Barton[7] gave unidentified tin-containing materials.

Table I. Crystallographic Details for 2

formula	$C_{16}H_{20}$
formula wt.	212.33
space group	$P2_1/n$
a, Å	7.554 (2)
b, Å	22.685 (2)
c, Å	7.592 (2)
β, deg	119.41 (1)
vol, Å^3	1133
Z	4
density (calcd), g/cm^3	1.24
cryst size	0.25 mm × 0.35 mm × 0.54 mm
radiation	Mo Kα with graphite monochromator
linear abs coeff, cm^{-1}	0.65
temp, °C	22
2θ limits, deg	$4 \leq 2\theta \leq 55$
scan speed	4°/min in ω with maximum total of 4 scans/ref
background time/scan time	0.5
scan range	$(1.15 + 0.35 \tan \theta)°$ in ω
data collected	$+h, +k, \pm l$
unique data	2687
unique data with $F_o^2 > 3\sigma(F_o^2)$	1033
final no. of variables	145
$R(F)^a$	0.074
$R_w(F)^b$	0.086
error in observation of unit wt, e	3.06

$^a R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w = 1/\sigma^2(F_o)$.

Table II. Least-Squares Refinements for 2 as a Function of the Double-Bond Location

	model with C7=C8	model with C10=C11	model with C15=C16
bond lengths			
C7=C8	1.37 (1)	1.37 (1)	1.38 (1)
C10=C11	1.41 (1)	1.40 (1)	1.41 (1)
C15=C16	1.38 (1)	1.38 (1)	1.38 (1)
R factor	0.078	0.084	0.079

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[1] NSERC (Canada) Postdoctoral Fellow, 1987–1989.

[2] Osborn, M. E.; Kuroda, S.; Muthard, J. L.; Kramer, J. D.; Engel, P.; Paquette, L. A. *J. Org. Chem.* **1981**, *46*, 3379.

[3] (a) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1978**, *100*, 1600. (b) Christoph, G. G.; Muthard, J. L.; Paquette, L. A.; Böhm, M. C.; Gleiter, R. *Ibid.* **1978**, *100*, 7782. (c) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *Ibid.* **1979**, *101*, 6991.

[4] The results of these studies will be reported independently by Professor Donald W. Rogers (Long Island University).

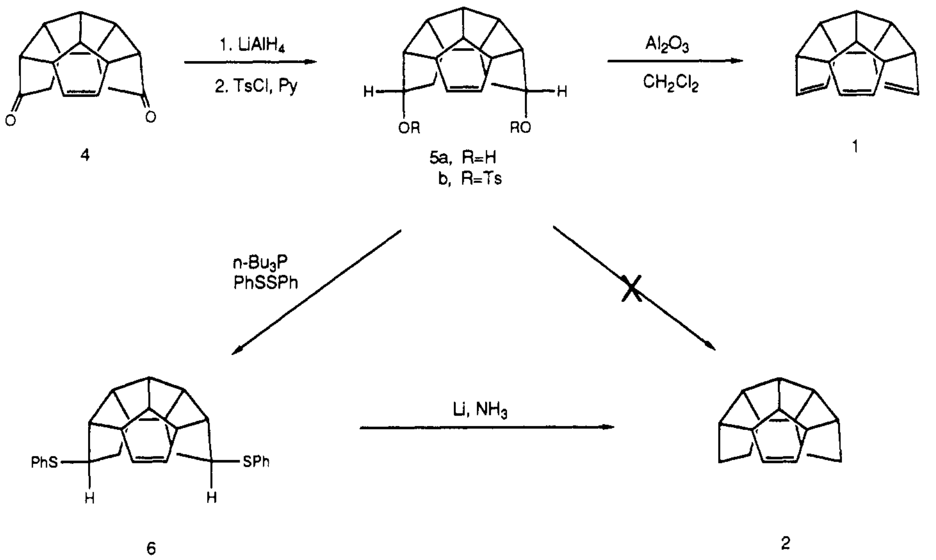
[5] Triquinacene has recently been scrutinized in this fashion: Liebman, J. F.; Paquette, L. A.; Peterson, J. R.; Rogers, D. W. *J. Am. Chem. Soc.* **1986**, *108*, 8267. See also: Miller, M. A.; Schulman, J. M.; Disch, R. L. *Ibid.* **1988**, *110*, 7681.

[6] (a) Carnahan, J. C., Jr.; Closson, W. D. *Tetrahedron Lett.* **1972**, 3447. (b) Closson, W. D.; Wriede, P.; Bank, S. *J. Am. Chem. Soc.* **1966**, *88*, 1581. (c) Kovacs, J.; Ghatak, U. R. *J. Org. Chem.* **1966**, *31*, 119.

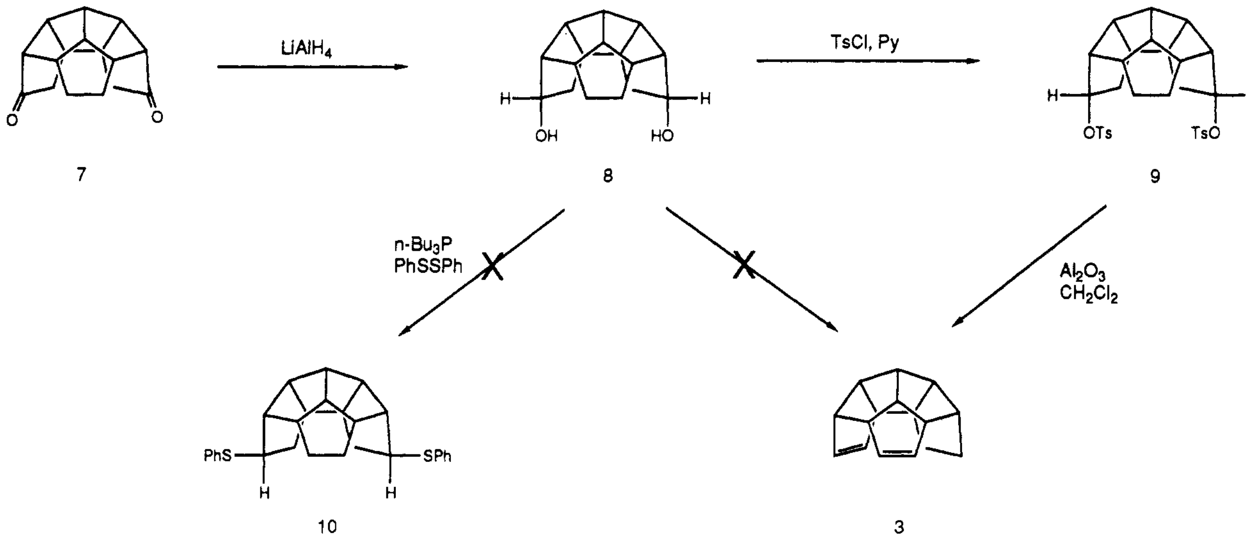
[7] Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574.

0022-3263/89/1954-5039$01.50/0

Scheme I



Scheme II



These complications prompted us to treat **5a** instead with diphenyl disulfide and tri-*n*-butylphosphine in refluxing tetrahydrofuran.[8] These reaction conditions delivered **6** in 88% yield. With the phenylthio substituents now on the exo surface, **6** could be efficiently reduced with lithium in liquid ammonia[9] to **2** (88%). The structural assignment to **2**, initially arrived at on the basis of its spectral properties, was confirmed by single-crystal X-ray analysis (Figure 1, Table I). During the course of full-matrix least-squares refinements, the position of the double bond was not obvious. So, in turn, the double bond with the appropriate sp^2 hydrogen atoms was arbitrarily placed at each of the possible three locations, C7–C8, C10–C11, and C15–C16, and each model was refined to convergence. The results summarized in Table II were obtained. It appears that the location of the double bond is disordered in the lattice with respect to these three positions and that possibly it is located slightly less than one-third of the time at what would correspond to the C10–C11 position. Since the superimposed positions of the atoms in a carbon–carbon double bond (C=C) cannot be resolved from those in a carbon–carbon single bond (C–C), the anisotropic thermal ellipsoids of these atoms are apt to look peculiar, as they do here. Also a difference electron density map, which was calculated after one anisotropic refinement, revealed electron density peaks that had the proper geometry for sp^2 type hydrogens bonded to C7, C8, C10, C11, C15, and C16. Hydrogens of the sp^3 type could also be located for all of the other carbon atoms in the molecule. Ultimately, the disorder was modeled in terms of a 3-fold nature by assigning sp^2 hydrogens to each pair of carbons (C7–C8, C10–C11, or C15–C16) one-third of the time and sp^3 hydrogens to each pair two-thirds of the time.

The Dihydro Derivative. On the basis of the chemistry outlined in Scheme I, we thought that dihydro ditosylate **9** might exhibit an accentuated tendency for elimination on activated alumina[10] because of two additional hydrogen atoms within the molecular cavity. To test

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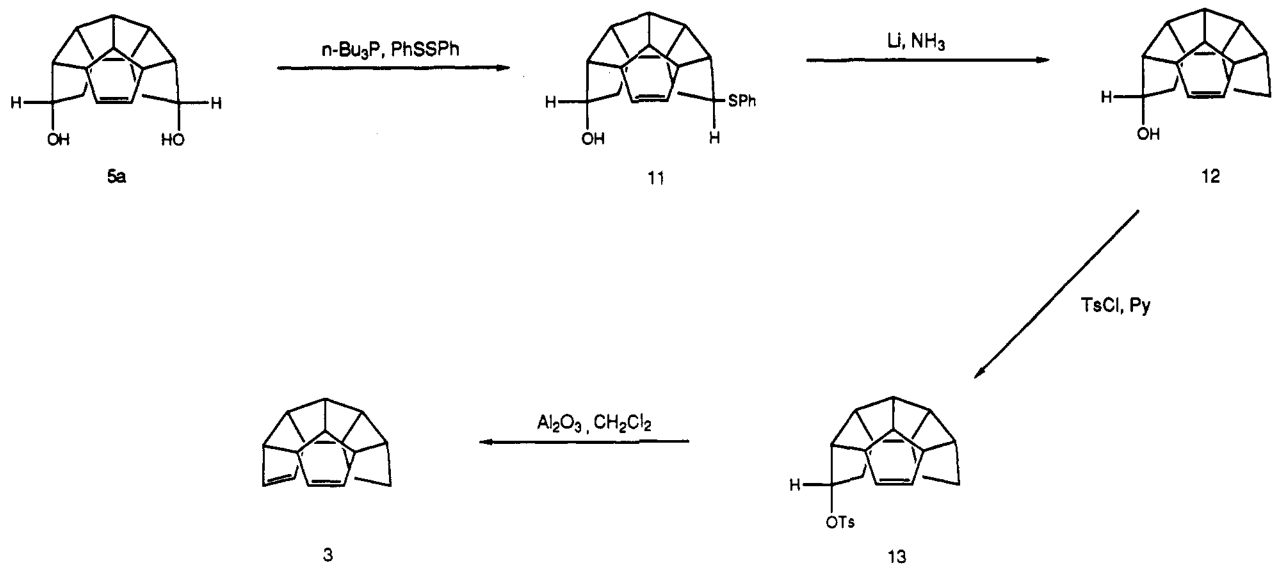
[8] (a) Hanessian, S.; Tyler, P. C.; Demailly, G.; Chapleur, Y. *J. Am. Chem. Soc.* **1981**, *103*, 6243. (b) Marshall, J. A.; Cleary, D. G. *J. Org. Chem.* **1986**, *51*, 858. (c) Cleary, D. G. *Synth. Commun.* **1989**, *19*, 737.

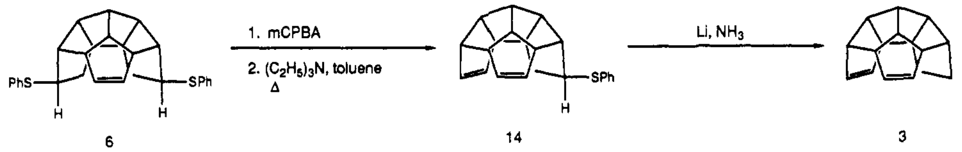
[9] (a) Kodama, M.; Matsuki, Y.; Itô, S. *Tetrahedron Lett.* **1976**, 1121; **1975**, 3065. (b) Dauben, W. G.; Saugier, R. K.; Fleischhauer, I. *J. Org. Chem.* **1985**, *50*, 3767. (c) Sakurai, K.; Kitahara, T.; Mori, K. *Tetrahedron* **1988**, *44*, 6581.

[10] Posner, G. H.; Gurria, G. M.; Babiak, K. H. *J. Org. Chem.* **1977**, *42*, 3173, and additional references cited therein.

Scheme III



Scheme IV



this hypothesis, 4 was subjected to sequential catalytic hydrogenation, hydride reduction, and tosylation (Scheme II). While 9 was indeed subsequently transformed into 3, the elimination reaction presented complications. Capillary gas chromatography indicated 3 to constitute approximately 30% of a five-component mixture. Repeated recrystallization of this impure material increased the percentage of the diene to only the 45% level. Also, chromatography on silver nitrate impregnated silica gel[11] under the best circumstances afforded a three-component mixture containing, of course, 3. By GC-MS, both impurities were determined to possess the same molecular weight as 3, reflecting the likely possibility that they were products of framework rearrangement. The poor yield and low purity demanded that an alternative protocol be developed.

Diol 8 proved to be surprisingly unreactive to the tri-*n*-butylphosphine/diphenyl disulfide reagent combination, thereby precluding convenient access to 10. Methods to dehydrate 8 were also examined, but with a similar lack of success. Thus, decomposition or the return of starting material was encountered when 8 was exposed to such reagents as Martin's sulfurane,[12] thionyl chloride, or phosphorus oxychloride in pyridine, *p*-toluenesulfonic acid on silica gel, and the like. The highly attenuated reactivity of this diol is attributed to severe steric congestion.

For this reason, we returned to enediol **5a** and noted that suitable modification of those conditions earlier applied for its conversion into 6 could be modified to give hydroxy sulfide 11 (Scheme III). Metal–ammonia reduction of 11 generated the monounsaturated alcohol 12. Application of the predescribed C_{16}-hexaquinacene protocol to 12 did lead successfully via 13 to analytically pure 3. To our disappointment, however, this process was not amenable to scale-up. The yield of the **5a** → 11 step drops from approximately 70% (based on recovered starting material) to only 15% when performed above the 50-mg level. This feature was considered unacceptable and the route was ultimately abandoned.

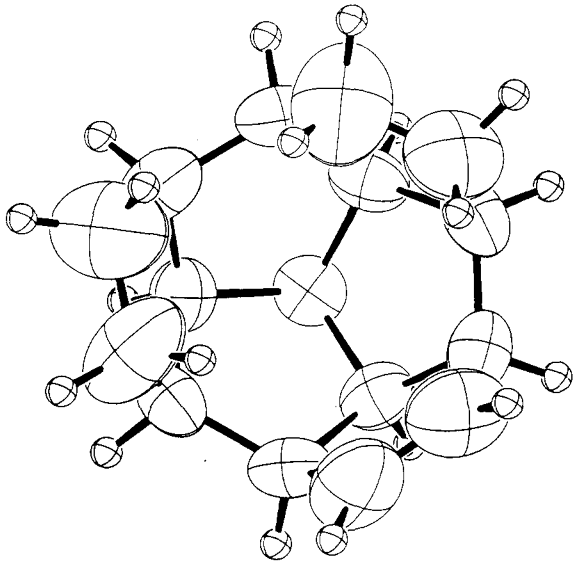


Figure 1. ORTEP drawing of **2**. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. The hydrogen atoms are drawn with an artificial radius. Only one of the three possible locations for the double bond in the unit cell is shown here.

Diene 3 was ultimately obtained in reasonable amounts by the sequence shown in Scheme IV. The discovery was made that the bis(phenylthio) derivative 6 could be selectively oxidized with *m*-chloroperoxybenzoic acid to the monosulfoxide. Thermolysis of the latter in toluene containing triethylamine produced diene sulfide 14, thereby setting the stage for conversion to 3 by reduction with

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[11] Goering, H.; Closson, W. D.; Olson, A. C. *J. Am. Chem. Soc.* **1961**, *83*, 3507.

[12] Martin, J. C. *Aldrichimica Acta* **1985**, *18*, 81.

lithium in liquid ammonia. Capillary gas chromatographic analysis of the crude reduction product revealed the material to be a three-component mixture, with **3** comprising 60% of the total. Analytically pure diene could be routinely obtained by sequential recrystallization from methanol, chromatography on silver nitrate impregnated silica gel, and sublimation. In line with the symmetry inherent to **3**, its ^1H NMR spectrum is characterized by a singlet for the four vinyl protons and its ^{13}C NMR spectrum is comprised of only nine signals.

In summary, the target hydrocarbons **2** and **3** have been prepared from **4** in two and five steps, respectively. Both routes rely on the ready acquisition of **6** and differ notably in the manner in which the pair of phenylthio functionalities are removed from this pivotal intermediate.

Experimental Section[13]

***exo,exo*-1,9-Bis(phenylthio)-2,2a,3,4,4a,4b,5,7a,7b,7c-decahydro-3,4,5-[1]-propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]-pentalene (6).** To a solution of **5a**[3] (1.0 g, 4.1 mmol) in tetrahydrofuran (50 mL) was added diphenyl disulfide (8.9 g, 41 mmol) and tri-*n*-butylphosphine (10.2 mL, 41 mmol). The reaction mixture was heated at gentle reflux for 5 days, cooled, and freed of solvent in vacuo. Chromatography of the residue on silica gel (elution with 5% ethyl acetate in petroleum ether) and trituration of the resulting solid with petroleum ether afforded 1.54 g (88%) of **6** as a white solid, mp 154.5–155 °C (from ethyl acetate): IR ($CHCl_3$, cm^{-1}) 3080, 3060, 3040, 3000, 2940, 2860, 1585, 1482, 1443, 1321, 1315, 1305, 1295, 1270, 1098, 1075, 1032, 990, 865, 698, 675; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 7.1 Hz, 4 H), 7.23 (m, 6 H), 5.54 (s, 2 H), 3.76 (m, 2 H), 3.53 (m, 2 H), 3.26 (t, J = 10.4 Hz, 2 H), 2.95 (q, J = 10.6 Hz, 2 H), 2.87 (m, 2 H), 2.76 (dt, J = 10.4, 2.8 Hz, 2 H), 2.03 (dt, J = 14.1, 7.8 Hz, 2 H), 1.67 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 136.60, 132.17, 130.97, 128.76, 126.33, 63.24, 61.28, 56.18, 55.44, 52.92, 52.68, 46.66, 36.25 ppm; MS, m/z (M^+) calcd 428.1632, obsd 428.1654.

Anal. Calcd for $C_{28}H_{28}S_2\cdot 0.5CH_3COOCH_2CH_3$: C, 76.43; H, 6.81. Found: C, 76.23; H, 6.51.

Tetrahydro-C_{16}-hexaquinacene (2). To a solution of lithium metal (0.5 g, 70 mmol) in 100 mL of liquid ammonia (freshly distilled from sodium) at −78 °C was added a solution of **6** (1.54 g, 3.5 mmol) and *tert*-butyl alcohol (1.6 mL, 17.5 mmol) in 30 mL of dry tetrahydrofuran via cannula. The reaction mixture was stirred at −78 °C for 2 h and at −33 °C for 30 min before being quenched with methanol (15 mL) at the lower temperature. The ammonia was allowed to evaporate, the residue was treated with saturated ammonium chloride solution, and the product was extracted into dichloromethane (4×). The combined organic layers were dried and evaporated, and the residue was purified by chromatography on silica gel impregnated with silver nitrate (10%) (elution with petroleum ether). There was isolated 670 mg (88%) of **2** as a white solid, mp 179–180 °C (from dichloromethane): IR ($CHCl_3$, cm^{-1}) 3040, 2930, 2910, 2860, 1465, 1450, 1365, 1285, 1020, 1005, 915, 865; ^1H NMR (300 MHz, $CDCl_3$) δ 5.59 (s, 2 H), 3.46 (q, J = 9.8 Hz, 1 H), 3.24 (dq, J = 3.1, 3.1 Hz, 4 H), 2.92 (q, J = 10.3 Hz, 1 H), 2.70 (m, 2 H), 2.56 (m, 2 H), 1.85 (m, 2 H), 1.62 (m, 4 H), 1.45 (m, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) 131.90, 64.75, 61.66, 55.86, 53.43, 49.48, 48.09, 31.79, 28.86 ppm; m/z (M^+) calcd 212.1565, obsd 212.1545.

Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.60; H, 9.53.

X-ray Crystallographic Analysis of 2. Crystals of **2** are cloudy and colorless. However, upon cutting one with a razor blade, the interior appeared clear. Examination of the diffraction pattern on a Rigaku AFC5 diffractometer indicated a monoclinic crystal system with systematic absences $h01$, $h + 1$, $2n + 1$, and $0k0$, $k = 2n + 1$. The space group was uniquely determined as $P2_1/n$. At room temperature, the cell constants α = 7.554 (2) Å, b = 22.685 (2) Å, c = 7.592 (2) Å, and β = 119.41 (1)° are based on a least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 22–29° with Mo Kα radiation. The unit cell is metrically pseudohexagonal.

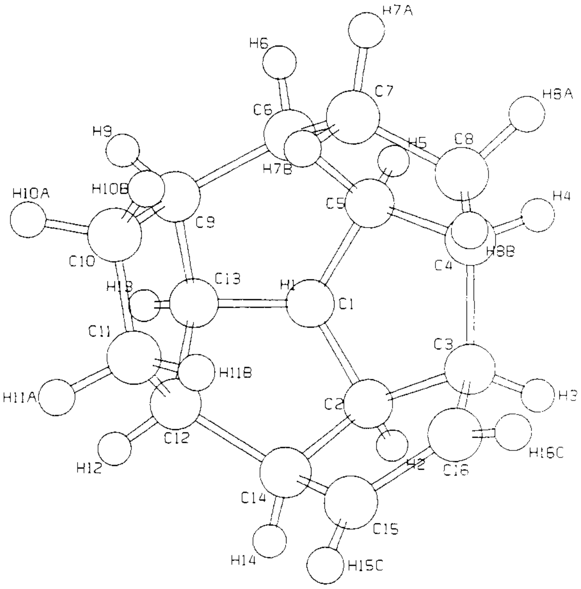

Figure 2. Arbitrary numbering scheme for **2**.

Intensities were measured by the ω-2θ scan method. Six standard reflections were measured every 150 reflections and indicated that the crystal had decayed in a linear fashion during data collection. The intensities of these standard reflections had decreased by an average value of 15%. A linear decay correction was applied to the data during data reduction. All calculations were done with the TEXSAN package of crystallographic programs.[14]

The structure was solved by the direct methods program MITHRIL,[15] and all of the carbon atoms appeared on the electron density map. The hydrogens were included as fixed contributions in their calculated positions with C–H = 0.98 Å. The final refinement cycle for the 1033 intensities with $F_o^2 \dagger 3\sigma(F_o^2)$ and the 145 variables yield agreement indices of R = 0.074 and R_w = 0.086. The final difference electron density map contains maximum and minimum peak heights of 0.33 and −0.25 e/Å^3. Scattering factors were obtained from the usual sources.[16] The arbitrary numbering scheme employed is shown in Figure 2.

Hydrogenation of 4. A 250-mL flask was charged with **4** (3.00 g, 12.5 mmol), 5% palladium on carbon (2.0 g), and ethyl acetate (75 mL). The mixture was magnetically stirred under at atmosphere of hydrogen until hydrogen uptake ceased (ca. 3 h), filtered through Celite, and evaporated to leave a white solid (3.18 g). Recrystallization from ethyl acetate afforded pure **7** (2.80 g, 93%), mp 237.5–240 °C: IR (C_6D_6, cm^{-1}) 1725; ^1H NMR (300 MHz, C_6D_6) δ 3.12–2.95 (m, 2 H), 2.95–2.78 (m, 2 H), 2.60–2.35 (m, 6 H), 2.13–1.87 (m, 4 H), 1.70–1.40 (m, 4 H); ^{13}C NMR (75 MHz, C_6D_6) 219.99, 63.10, 59.53, 58.37, 56.85, 49.75, 43.37, 43.02, 30.56 ppm; MS, m/z (M^+) calcd 242.1307, obsd 242.1297.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.21; H, 7.50.

Hydride Reduction of 7. To a solution of **7** (1.0 g, 4.13 mmol) in 125 mL of dry tetrahydrofuran was added 3.2 g (82.6 mmol) of lithium aluminum hydride. The reaction mixture was heated at gentle reflux for 17 h, cooled to 0 °C, and quenched with 3.2 mL of water, 3.2 mL of 15% sodium hydroxide solution, and 10 mL of water. Anhydrous magnesium sulfate was introduced, and

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[13] The purity of all title compounds was judged to be ≥95% by GC, TLC, and $^1H/^{13}C$ NMR spectral determinations. In those instances where solvent of crystallization is present in the samples, the solvent signals are not reported in the NMR spectra.

[14] TEXSAN, TEXRAY Structure Analysis package, version 2.1, Molecular Structure Corporation, College Station, TX 1987.

[15] Gilmore, C. J. MITHRIL: A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data, University of Glasgow, Scotland, 1983.

[16] Scattering factor for the carbon atom is from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 71. The scattering factor for the hydrogen atom is from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

the voluminous white precipitate was separated by filtration and leached extensively with dichloromethane. The combined filtrates were evaporated to leave 1.1 g (100%) of **8**, mp 209–211 °C (from methanol): IR (Nujol, cm^{-1}) 3180, 2920, 2840, 1460, 1375, 1365, 1350, 1285, 1260, 1170, 1100, 1090, 1070, 1045, 1000, 985; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.50–4.39 (m, 2 H), 3.53–3.37 (m, 2 H), 3.17–2.96 (m, 2 H), 2.82–2.52 (m, 4 H), 2.00–1.90 (m, 2 H), 1.87–1.73 (m, 2 H), 1.59 (br s, 2 H), 1.40–1.15 (m, 4 H), 0.94–0.78 (m, 2 H); MS, *m/z* (M^+) calcd 246.1620, obsd 246.1633.

Anal. Calcd for $C_{16}H_{22}O_2{\cdot}0.5CH_3OH$: C, 75.66; H, 9.22. Found: C, 75.57; H, 9.28.

Ditosylate 9. A solution of **8** (1.0 g, 4.06 mol) in pyridine (40 mL) was treated with *p*-toluenesulfonyl chloride (4.0 g, 16.3 mmol), stirred at room temperature for 2 days, and poured into 10% hydrochloric acid. The product was extracted into dichloromethane (4×), and the combined organic layers were dried and concentrated. The crude product was chromatographed on silica gel (elution with 50% ethyl acetate in petroleum ether) to give **9** (2.0 g, 88%) as a white solid, mp 147.5–148 °C (from methanol): IR ($CHCl_3$, cm^{-1}) 3040, 3020, 2950, 2875, 1600, 1495, 1480, 1450, 1405, 1360, 1310, 1295, 1190, 1180, 1100, 1025, 980, 965, 955, 925, 905, 870, 840, 820; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 4 H), 7.32 (d, *J* = 8.2 Hz, 4 H), 4.89 (dt, *J* = 10.5, 8.0 Hz, 2 H), 3.27 (m, 2 H), 3.01 (m, 4 H), 2.67 (m, 2 H), 2.53 (m, 2 H), 2.44 (s, 6 H), 2.30 (m, 2 H), 2.03 (m, 2 H), 1.90 (m, 2 H), 1.68 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 144.43, 134.15, 129.66, 127.68, 85.21, 66.08, 60.15, 56.33, 51.32, 48.37, 42.42, 33.51, 30.21, 21.61 ppm; MS, *m/z* (M^+) calcd 554.1797, obsd 554.1786.

Anal. Calcd for $C_{30}H_{34}O_6S_2$: C, 64.96, H, 6.18. Found: C, 64.84; H, 6.36.

***exo*-9-(Phenylthio)-2,2a,3,4,4a,4b,5,7a,7b,7c-decahydro-3,4,5-[1]-propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]pentalen-1-*endo*-ol (11).** To a solution of **5a** (1.22 g, 5.0 mmol) in dry tetrahydrofuran (50 mL) was added diphenyl disulfide (10.9 g, 50.0 mmol) and tri-*n*-butylphosphine (12.4 mL, 50.0 mmol). The reaction mixture was heated at gentle reflux for 16 h, cooled to room temperature, and freed of solvent in vacuo. Silica gel chromatography of the residue (elution with 30% ethyl acetate in petroleum ether) afforded 272 mg of **6**, 79 mg of **11**, and 7 mg of recovered **5a**.

For **11**: ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.31 (m, 5 H), 6.15 (m, 1 H), 5.51 (m, 1 H), 4.48 (m, 1 H), 3.95 (m, 1 H), 3.65–2.10 (m, 9 H), 2.00–1.45 (m, 5 H).

Reductive Desulfurization of 11. Into a cold (−78 °C) solution of lithium metal (5.0 mg, 0.77 mmol) in 10 mL of dry ammonia (freshly distilled from sodium) was transfered via cannula a solution of **11** (26 mg, 0.077 mmol) and *tert*-butyl alcohol (0.020 mL, 0.19 mmol) in 3 mL of tetrahydrofuran. The reaction mixture was stirred for 2 h at −78 °C and for 30 min at −33 °C. The predescribed workup was followed by chromatography on silica gel (elution with 50% ethyl acetate in petroleum ether). There was isolated 9.4 mg (53%) of **12** as a white solid, mp 124.5–125.5 °C (from methanol): ^{1}H NMR (80 MHz, $CDCl_3$) δ 6.10 (m, 1 H), 5.60 (m, 1 H), 4.30 (m, 1 H), 3.75–2.20 (series of m, 9 H), 2.10–1.40 (series of m, 7 H); MS, *m/z* (M^+) calcd 228.1514, obsd 228.1539.

The tosylate of **12**, viz. **13**, was prepared conventionally and isolated as a pale yellow oil in quantitative yield: ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 5.83 (m, 1 H), 5.58 (m, 1 H), 4.85 (m, 1 H), 3.55–2.30 (series of m, 9 H), 2.45 (s, 3 H), 2.25–1.35 (series of m, 7 H).

Controlled Oxidation of 6. To a cold (−23 °C), magnetically stirred solution of **6** (1.25 g, 2.92 mmol) in chloroform (50 mL) was added *m*-chloroperoxybenzoic acid (510 mg, 2.92 mmol), and the mixture was stirred for 14 h before being poured into saturated sodium bicarbonate solution. The aqueous suspension was extracted with dichloromethane (4×), and the combined organic phases were dried and evaporated. Silica gel chromatography of the residue (elution with 50% ethyl acetate in petroleum ether) returned 628 mg of unreacted **6** and furnished 464 mg (72% based on recovered **6**) of monosulfoxide as a white solid that was used directly: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (m, 2 H), 7.48 (m, 3 H), 7.28 (m, 5 H), 5.55 (m, 1 H), 4.82 (m, 1 H), 3.65 (br s, 1 H), 2.20 (m, 1 H), 2.00 (m, 1 H), 1.75 (m, 2 H), 1.55 (m, 1 H); MS, *m/z* ($M^+ - C_6H_5SOH$) calcd 318.1442, obsd 318.1421.

Diene Sulfide 14. The preceding monosulfoxide (590 mg, 1.33 mmol) was dissolved in toluene (50 mL), treated with triethylamine (0.30 mL, 1.99 mmol), and heated at gentle reflux for 24 h. After solvent removal in vacuo, the residue was chromatographed on silica gel impregnated with 10% silver nitrate (elution with ethyl acetate). There was isolated 466 mg of **14** as a colorless syrup that was directly reduced; MS, *m/z* (M^+) calcd 318.1442, obsd 318.1425.

Dihydro-C_{16}-hexaquinacene (3). A. Double Elimination within 9. A solution of the ditosylate (0.90 g, 1.62 mmol) in dry dichloromethane (40 mL) was treated with activated alumina (8.0 g) and stirred at room temperature for 30 min. The solvent was removed on a rotary evaporator and finally under a high vacuum. While under a nitrogen atmosphere, 50 mL of toluene was added, and heating at the reflux temperature was maintained for 46 h. After cooling, the alumina was removed by filtration and washed with dichloromethane. The solvents were evaporated, and the residue was filtered through alumina (30 g) with petroleum ether elution. Recrystallization of the purified product from methanol gave **3** (201 mg, 59%) as a white solid, mp 165–167 °C.

B. Elimination of *p*-Toluenesulfonic Acid from 13. A mixture of **13** (35 mg, 0.091 mmol) and activated alumina (300 mg) in dry toluene (3 mL) was stirred at room temperature for 2.5 days, filtered, and evaporated. Chromatography as above gave **3** (8.5 mg, 44%) as a white solid having spectra identical with the samples prepared in A and C.

C. Reductive Desulfurization of 14. A cold (−78 °C) solution of lithium wire (170 mg, 24.6 mmol) in dry liquid ammonia (50 mL, freshly distilled from sodium) was treated with a solution of **14** (780 mg, 2.46 mmol) and *tert*-butyl alcohol (1.2 mL, 12.3 mmol) in 5 mL of dry tetrahydrofuran via cannula. Workup as in part A gave a crude product that was combined with similar material acquired from runs starting with 657 mg and 450 mg of **14** (crude yield per run was approximately 75%). Repeated recrystallizations from methanol and chromatography on 15% silver nitrate impregnated silica gel followed by sublimation at 110 °C and 0.5 Torr gave **3** that was virtually solvate free, mp 194 °C (dec): IR ($CHCl_3$, cm^{-1}) 3050, 3010, 2940, 2885, 1605, 1465, 1450, 1365, 1355, 1290, 1280, 1010, 995, 840, 805; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.43 (s, 4 H), 3.50 (m, 2 H), 3.28 (m, 5 H), 2.97 (d, *J* = 10.7 Hz, 1 H), 2.55 (m, 2 H), 1.62 (m, 2 H), 1.36 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 131.66, 131.56, 63.24, 61.51, 56.17, 54.84, 52.92, 47.77, 30.45 ppm; MS, *m/z* (M^+) calcd 210.1408, obsd 210.1390.

Anal. Calcd for $C_{16}H_{20}{\cdot}0.1\ CH_3OH$: C, 90.56; H, 8.69. Found: C, 90.68; H, 8.67.

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Supplementary Material Available: Tables of final positional, anisotropic thermal, calculated positional parameters, intramolecular distances, and bond angles for **2** (5 pages). Ordering information is given on any current masthead page.