Found: C, 58.9; H, 5.5; N, 6.3; Cl, 15.7.

α-[3,4-(Methylenedioxy)phenyl]-4-morpholineacetonitrile 4-Oxide (27). To a solution of 12.3 g (0.05 mol) of α-[3,4-(methylenedioxy)phenyl]-4-morpholineacetonitrile in 50 mL of dichloromethane was added 11.2 g (0.055 mol) of *m*-chloroperbenzoic acid in 200 mL of dichloromethane. The exotherm was moderated with a cold water bath. After 18 h of stirring at room temperature, the mixture was filtered and the filtrate washed with 10% sodium sulfite and with saturated $NaHCO_3$ solution. The organic layer was dried ($MgSO_4$) and concentrated to a gum (12.1 g). Trituration with hexane gave 11.4 g (87%) of white crystals, mp 99–101 °C. A 0.50-g sample was recrystallized from acetone-hexane to give 0.40 g of white crystals, mp 104–105 °C.

Anal. Calcd for $C_{13}H_{14}N_2O_4$: C, 59.5; H, 5.4; N, 10.7. Found: C, 59.2; H, 5.7; N, 10.5.

3,4-(Methylenedioxy)benzoic Acid (30). A solution of 2.62 g (0.01 mol) of α-[3,4-(methylenedioxy)phenyl]-4-morpholineacetonitrile 4-oxide in 40 mL of 90% acetic acid was refluxed for 2 h. Cooling and filtering gave 0.52 g (31%) of tan crystals, mp 218–226 °C. The filtrate was diluted with water until turbid. Filtration gave 1.04 g of solid. The solid was heated with acetic acid and filtered from insoluble solid, and the filtrate was diluted with water until turbid. Cooling and filtering gave 0.70 g (42%) of tan crystals, mp 214–217 °C (lit.[12c] mp 229–231 °C). The IR and ^1H NMR spectra were identical with those of authentic piperonylic acid.

4-[3,4-(Methylenedioxy)benzoyl]morpholine (29). A 0.44-g (0.011 mol) sample of sodium hydride (60% in oil) was washed with hexane under argon. To the hydride were added 15 mL of *N,N*-dimethylformamide and a solution of 2.62 g of α-[3,4-(methylenedioxy)phenyl]-4-morpholineacetonitrile 4-oxide in 15 mL of DMF. The solution turned purple and a brown solid precipitated. After 4 h of stirring at room temperature, the solvent was removed under vacuum and the residue was partitioned between dichloromethane and water.

The CH_2Cl_2 layer was washed with saline solution and dried ($MgSO_4$), and the solvent was removed under vacuum. Toluene was added several times and the solvent removed to give 1.91 g (82%) of an amber gum. Bulb-to-bulb distillation of the gum gave 1.75 g (75%) of a pale yellow gum, bp 170–175 °C (0.1 mm) (lit.[15] bp 180–186 °C (0.4 mm)).

Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.3; H, 5.6; N, 6.0. Found: C, 61.4; H, 5.6; N, 6.0.

Acknowledgment. We thank L. M. Brancone and staff for elemental analyses, W. Fulmor and staff for spectral studies, and Dr. R. T. Hargreaves for high-resolution mass spectra.

Registry No. **3**, 71818-91-2; **4**, 71818-92-3; **5**, 15190-10-0; **7**, 1144-74-7; **8**, 1503-49-7; **9**, 41938-65-2; **10**, 71818-93-4; **11**, 3457-46-3; **12**, 33599-26-7; **13**, 71818-94-5; **15**, 71818-95-6; **16**, 71818-96-7; **17**, 71818-97-8; **18**, 71818-98-9; **19**, 17221-37-3; **20**, 19867-89-1; **21**, 71818-99-0; **22**, 71819-00-6; **23**, 71819-01-7; **25**, 21724-87-8; **26**, 71819-02-8; **27**, 71819-03-9; **28**, 19202-04-1; **29**, 63916-59-6; **30**, 94-53-1; 9-ethyl-α-morpholino-3-carbazoleacetonitrile, 71819-04-0; *N*-ethylcarbazole-3-carboxaldehyde, 7570-45-8; morpholine, 110-91-8; potassium cyanide, 151-50-8; 4-methyl-2-morpholino-2-phenylglutaronitrile, 71819-05-1; methacrylonitrile, 126-98-7; 3-benzoyl-2-methylpropionic acid, 1771-65-9; 3-(*p*-chlorobenzoyl)propionitrile, 40394-87-4; 3-(*m*-chlorobenzoyl)propionitrile, 34555-37-8; *p*-fluorobenzonitrile, 1194-02-1; α-phenyl-α-(α,α,α-trifluoro-2-nitro-*p*-tolyl)-4-morpholineacetonitrile, 71818-72-9; 4-chloro-3-nitro-1-(trifluoromethyl)benzene, 121-17-5; *p*-fluoronitrobenzene, 350-46-9; ethyl chloroformate, 541-41-3; *p*-chlorobenzoyl chloride, 122-01-0; ethyl bromoacetate, 105-36-2; 3-phenyl-2-pyrazolin-5-one, 4860-93-9; epibromohydrin, 3132-64-7; epichlorohydrin, 106-89-8; α-[3,4-(methylenedioxy)phenyl]-α-(2,3-epoxypropyl)-4-morpholineacetonitrile, 71818-73-0; α-[3,4-(methylenedioxy)phenyl]-4-morpholineacetonitrile, 37673-10-2; allyl chloride, 107-05-1; α-(4-methoxyphenyl)-4-morpholineacetonitrile, 15190-13-3; α-(4-acetamidophenyl)-4-morpholineacetonitrile, 71818-74-1; α-(1-benzyl-3-indolyl)-4-morpholineacetonitrile, 71818-75-2; α-(2-pyridyl)-4-morpholineacetonitrile, 53813-00-6; α-(4-pyridyl)-4-morpholineacetonitrile, 71818-76-3; α-(3-pyridyl)-4-morpholineacetonitrile, 36740-09-7; acrylonitrile, 107-13-1; ethyl acrylate, 140-88-5; γ-(2-pyridyl)-γ-cyano-4-morpholinebutyronitrile, 71818-77-4; ethyl γ-(2-pyridyl)-γ-cyano-4-morpholinebutanoate, 71818-78-5; ethyl γ-(4-pyridyl)-γ-cyano-4-morpholinebutanoate, 71818-79-6; γ-cyano-γ-(4-methoxyphenyl)-4-morpholinebutyronitrile, 71818-80-9; γ-(4-acetamidophenyl)-γ-cyano-4-morpholinebutyronitrile, 71818-81-0; ethyl γ-cyano-γ-(4-methoxyphenyl)-4-morpholinebutanoate, 71818-82-1; γ-cyano-γ-(4-pyridyl)-4-morpholinebutyronitrile, 71818-83-2; ethyl γ-cyano-γ-(3-pyridyl)-4-morpholinebutanoate hydrochloride, 71818-84-3; ethyl γ-cyano-γ-(2-pyridyl)-4-morpholinebutanoate hydrochloride, 71818-85-4; ethyl γ-cyano-γ-(4-pyridyl)-4-morpholinebutanoate hydrochloride, 71818-86-5; 4-methoxy-γ-oxobenzenebutyronitrile, 55234-56-5; 4-acetamido-γ-oxobenzenebutyronitrile, 71000-25-4; ethyl 4-methoxy-γ-oxobenzenebutanoate, 15118-67-9; γ-oxo-2-pyridinebutyronitrile, 71818-87-6; γ-oxo-4-pyridinebutyronitrile, 49835-53-2; ethyl γ-oxo-3-pyridinebutanoate hydrochloride, 71818-88-7; ethyl γ-oxo-2-pyridinebutanoate hydrochloride, 71818-89-8; ethyl γ-oxo-4-pyridinebutanoate hydrochloride, 71818-90-1.

Construction and Base-Promoted Cyclization of a C_{2v}-Symmetric Diepoxy Tetraquinane Disulfone

Neil J. Hales and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

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A scheme is presented for elaborating dimethyl 2a,3,3a,5a,6,6a,6b,6c-octahydrodicyclopenta[*ch,gh*]pentalene-*endo,endo*-3,6-dicarboxylate (**5**) into a bis-homologated C_{2v}-symmetric diepoxy disulfone (**4**). Although the twofold cyclization of the bis carbanion of **4** could in principle give rise to a functionalized hexaquinane of C_2 symmetry (i.e., **3**), the reaction of **4** with dimsyl anion does not follow this course. Rather, a single α-sulfonyl carbon attacks both epoxides under the basic conditions to deliver a product which contains a newly constructed norbornane ring (i.e., **20**). However, the cyclized material is no longer serviceable for the construction of the dodecahedrane framework.

In connection with investigations aimed at the synthesis of dodecahedrane (**1**), we have considered the possibility that twofold intramolecular cyclization within a centrosymmetric molecule might serve as an efficient means of rapidly enhancing the polyquinane level[1,2] of the structure. Of particular interest to us are those molecules where the nucleophilic and electrophilic centers remain incorporated within the framework to serve later as activated sites conducive to further structural elaboration. The concept is exemplified by the retrosynthetic sequence shown, where

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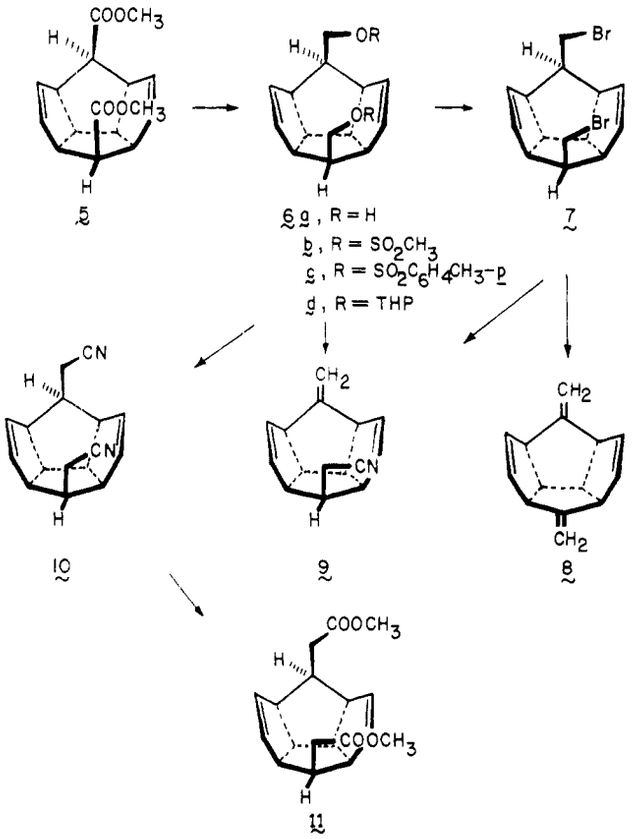
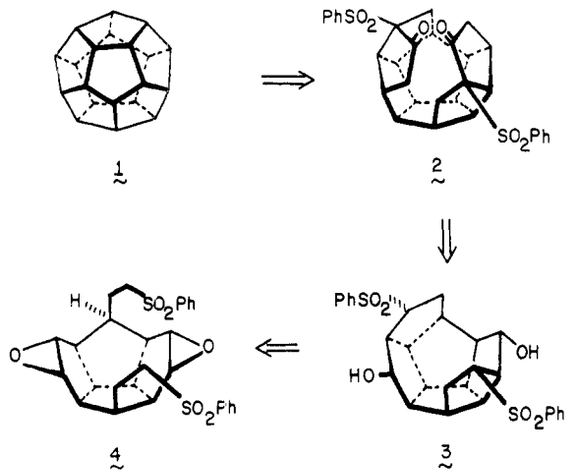
(2) Paquette, L. A. *Fortschr. Chem. Forsch.* **1979**, *79*, 43.

0022-3263/79/1944-4603$01.00/0

Scheme I



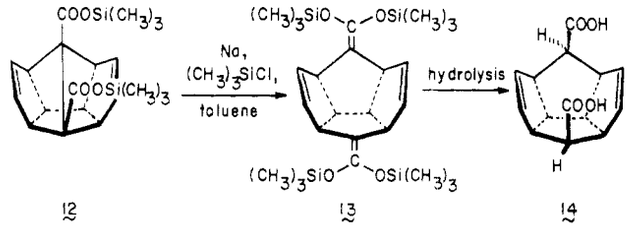
the availability of diepoxy disulfone 4 could in principle permit construction of hexaquinane 3 and octaquinane 2.



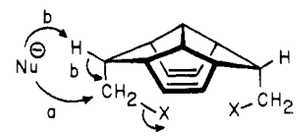
The latter diketone is a functionalized trisecododecahedrane considered to be a possible precursor of the elusive target hydrocarbon (1). We herein describe the preparation of 4 and detail the chemical behavior of the derived bis(α-sulfonyl)carbanion.

Synthesis of Tetraquinane 4. With the preceding considerations in mind, our starting point was the endo,endo diester **5** whose convenient synthesis has been previously described.[3] In structural terms, **5** is seen to be a C_{2v}-symmetric tetraquinane which requires modification of its carbomethoxy groups. Importantly, incursion of epimerization to the more thermodynamically favored exo environment must be avoided. Homologation of an ester via its alcohol constitutes an integral part of standard synthetic practice. However, attempts to adapt such chemistry to **5** are seriously complicated by a competing elimination reaction (Scheme I). Thus, the endo,endo diol **6a** was activated by conversion to its dimesylate (**6b**) and ditosylate (**6c**). Additionally, treatment of bis(tetrahydropyranyl) derivative **6d** with triphenylphosphine dibromide[4] afforded **7**. Perhaps for steric reasons, the latter conversion proved difficult to carry out efficiently. Furthermore, **7** was not prone to undergo S_N2 displacement when exposed to cyanide ion dissolved in dimethyl sulfoxide or hexamethylphosphoramide (HMPA). Instead, double bonds are introduced with formation of the known tetraene **8**[5] and triene nitrile **9**. Attempts to convert **6a** directly to **10** by means of the sodium cyanide, triphenylphosphine, and diethyl azodicarboxylate reagent[6] system also met with failure. While the sulfonate esters **6b** and **6c** have provided the desired **10** and this dinitrile has been converted to diester **11**, the yields are low. Consequently, this route was not deemed sufficiently practical for further pursuit.

Scheme II



That the formation of elimination products is kinetically favored was not unexpected. When the leaving groups adopt that conformation necessary to enable backside nucleophilic displacement to materialize from the less crowded convex surface (path a in A), the molecule simultaneously is electronically aligned for smooth E2 elimination (path b). Only the latter mechanistic alternative leads to relief of nonbonded steric strain.



Recourse was next made to reductive cleavage of bis(trimethylsilyl) ester **12**[7] with sodium and trimethylsilyl chloride in toluene (Scheme II). The resulting ketene acetal **13**, which was formed in high yield, underwent hydrolysis to give a mixture of diacids composed principally of the endo,endo isomer **14**. Due to this unexpected loss of total stereochemical control, the isolated quantities of purified **14** were only moderate.

The availability of **14** was vastly improved when it was recognized that trimethylsilyl iodide[8] is capable of transforming **5** into **14** without epimerization (Scheme III). As much as 35% of the endo,endo monoester is obtained concurrently. The latter may easily be separated from **14** and subsequently converted via its trimethylsilyl derivative to the diacid. As a result, this procedure constitutes a very

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(6) Loibner, H.; Zbiral, E. *Helv. Chim. Acta* **1976**, *59*, 2100.

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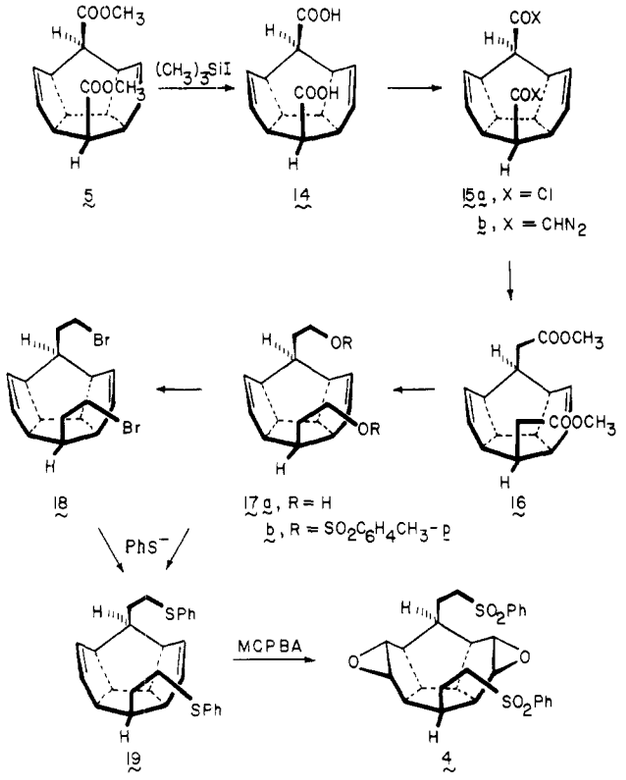
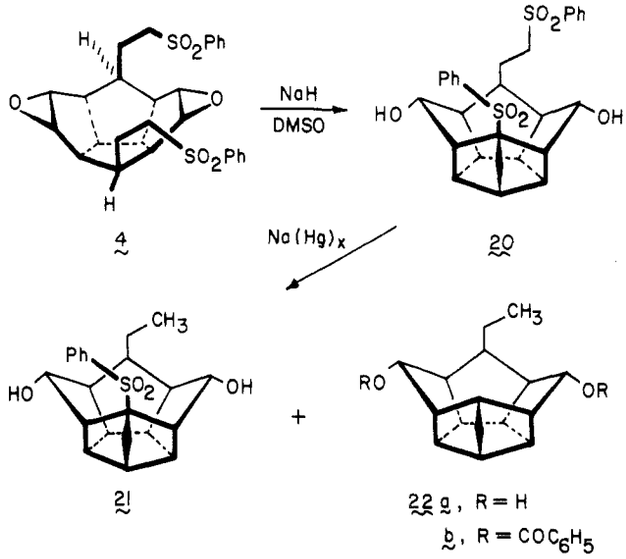
Scheme III



Scheme IV



good synthesis of pivotal intermediate **14**.

Diacid chloride **15a** could be prepared cleanly without epimerization. When added to an excess of ethereal diazomethane, **15a** gave the highly crystalline bis(diazo ketone) **15b** which was isolated in 95% overall yield from **14**. Treatment of **15b** with silver acetate and triethylamine in methanol–tetrahydrofuran effected Wolff rearrangement and afforded the bis-homologated diester **16** in quantitative yield. Sequential reaction of **16** with lithium aluminum hydride and triphenylphosphine–carbon tetrabromide[9] produced **18**. As expected, the substantially diminished steric congestion about the functionalized carbon atoms in ditosylate **17b** and dibromide **18** allows for efficient S_N2 displacement by thiophenoxide. Exhaustive oxidation of the bis(thioether) so formed (**19**) with *m*-chloroperbenzoic acid led stereospecifically to **4**.

In each of the intermediates described in Scheme III, there exists high (C_{2v}) symmetry which is easily recognized by simplification of the ^{13}C NMR spectra (see Experimental Section). This is a definitive asset which permits essentially instant recognition of the success or failure of the twofold chemical reaction required at all stages for the maintenance of symmetry. The synthetic plan is also streamlined, since molecular construction is accomplished concurrently at two sites.

Cyclization of 4. Intramolecular cyclization within **4** was brought about by stirring with an excess of oil-free sodium hydride in dimethyl sulfoxide at room temperature for 2 days. That both epoxide rings had been cleaved in the lone product isolated (63%) was evident in the ^1H NMR spectrum (pyridine-d_5 solution). There is displayed a broad two-proton singlet at δ 6.41 due to the hydroxyl groups and a multiplet of equal area centered at δ 4.97 arising from the associated methines (>CHOH). The ^{13}C NMR spectrum did not correspond to that expected for **3**. Rather, loss of axial symmetry had materialized such that all four of the aromatic carbon resonances were doubled and the alicyclic region consisted of 11 lines. We briefly considered the possibility that an epimer of **3** with the benzenesulfonyl groups in an exo,endo relationship had been produced. Such an eventuality would require that a large number of the alicyclic carbon resonances be fortuitously isochronous, a phenomenon viewed as unlikely. Nonetheless, this particular disposition of the benzenesulfonyl groups could materialize simply if the second cyclization were followed by deprotonation. On subsequent workup, delivery of a proton from the convex surface would enjoy an enormous kinetic advantage.

Reductive desulfonylation[10] of **20** furnished a mixture of the mono- and bis-cleaved compounds assigned structures **21** (50%) and **22a** (17%), respectively (Scheme IV). The major product was a colorless crystalline solid which exhibited ^1H NMR absorptions clearly indicative of the presence of an ethyl group. That the carbon skeleton has underlying planar symmetry was indicated by the 15 ^{13}C NMR signals. Similar features characterize **22b** which was obtained by benzoylation of **22a** (see Experimental Section).

It is of some interest that the conditions utilized by us for the reductive desulfonylation of **20** promoted rapid removal of the primary benzenesulfonyl group at room temperature. On the other hand, the second stage of reduction to give **22a** could be satisfactorily achieved only with much longer reaction times. Although the selective removal of a primary benzenesulfonyl function in the presence of an identical tertiary group has not previously been noted, our findings suggest that such may be accomplished with relative ease and constitute a process of wide scope.

The desired cyclization of **4** to **3** is not observed because of the kinetically more favored reaction wherein a single α-sulfonyl carbon attacks both epoxide rings. Although the cyclizations of epoxy sulfones to generate both cyclopropane[11] and cyclopentane systems[12] have been examined with success recently, the special steric constraints and geometric features contained within **4** cause the initial cyclization to proceed more slowly than the norm. Once progress has been made from the tetraquinane to the

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(12) Fischli, A.; Branca, Q.; Daly, J. *Helv. Chim. Acta* **1976**, *59*, 2443.

pentaquinane framework, the molecule gains inflexibility. The presumption that a second similar cyclization must proceed still more slowly is not unreasonable. Under these circumstances, it is not surprising that transannular bonding can become favored. Because formation of this last carbon–carbon bond generates a norbornyl ring system (front face of **21** and **22** as drawn), product development would not appear to be under thermodynamic control but arises because of those kinetic factors just considered. In addition to representing an interesting chemical change, the base-promoted closure of **4** to **20** represents the first demonstration in our laboratory that a stabilized carbanion contained in a polyquinane framework can be effectively utilized in an intramolecular displacement reaction to generate additional five-membered rings.

Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained with a Varian EM-360 spectrometer; apparent splittings are given in all cases. Carbon spectra were recorded with a Bruker HX-90 spectrometer. Infrared spectra were determined on a Perkin-Elmer Model 467 instrument. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-*endo*,*endo*-bis(hydroxymethyl)dicyclopenta[*cd*,*gh*]pentalene (6a). A solution of **5**[5] (912 mg, 3.3 mmol) in dry ether (10 mL) was added dropwise during 15 min to a stirred suspension of lithium aluminum hydride (750 mg, 19.7 mmol) in dry ether (50 mL) at 5 °C. The reaction mixture was stirred overnight at room temperature, cooled to 0 °C, and treated dropwise with saturated aqueous sodium sulfate solution (12 mL), saturated aqueous ammonium chloride solution (20 mL), and finally 10% hydrochloric acid (to pH 3). The phases were separated and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic solutions were washed with water (10 mL), saturated sodium bicarbonate solution (10 mL), water (10 mL), and brine (10 mL) prior to drying. Solvent evaporation gave 735 mg (100%) of **6a** as a white solid: mp 133–134 °C (from toluene); ν_{max} (KBr) 3300, 2890, 1030, 1005, 750, 735 cm^{-1}; ^{1}H NMR (pyridine-d_5) δ 5.75 (m including s at δ 5.75, 6 H), 4.04 (d, J = 7 Hz, 4 H), 3.67–3.0 (m, 6 H), 2.65 (m, 2 H); m/e calcd 218.1307, osbd 218.1311.

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.00; H, 8.31.

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-*endo*,*endo*-bis(hydroxymethyl)dicyclopenta[*cd*,*gh*]pentalene Bis(methanesulfonate) (6b). A stirred solution of **6a** (202 mg, 0.918 mmol) and triethylamine (303 mg, 3.0 mmol) in dichloromethane (10 mL) was cooled to −10 °C and treated with methanesulfonyl chloride (231 mg, 2.02 mmol) during 5 min. The reaction mixture was maintained at −10 °C for 15 min, transferred to a chilled separatory funnel, and washed in turn with ice water (10 mL), chilled dilute hydrochloric acid (10%, 2 × 5 mL), saturated sodium bicarbonate solution (10 mL), and brine (10 mL). The dried organic phase was evaporated to give 310 mg (93%) of **6b**, a colorless oil which was used without further purification: ν_{max} (CH_2Cl_2) 2950, 2900, 1355, 1170, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.46 (s, 4 H), 4.28 (d, J = 7 Hz, 4 H), 3.85–2.85 (m including s at δ 3.05, 12 H), 2.85–2.15 (m, 2 H); m/e calcd 218.1307, obsd 218.1311.

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-*endo*,*endo*-bis(hydroxymethyl)dicyclopenta[*cd*,*gh*]pentalene Bis(*p*-toluenesulfonate) (6c). A solution of **6a** (191 mg, 0.876 mmol) in dry pyridine (10 mL) was cooled to 0 °C and treated with *p*-toluenesulfonyl chloride (706 mg, 3.70 mmol). The reaction mixture was maintained at 0 °C for 27.5 h, poured into ice water (50 mL), and extracted with ether (4 × 25 mL). The ether extracts were combined, washed with chilled 5% hydrochloric acid (2 × 20 mL) and brine (2 × 20 mL), diluted with dichloromethane (20 mL), and dried at 0 °C. Solvent evaporation afforded 344 mg (75%) of **6c** as a colorless crystalline solid: mp 169–170 °C dec (from ethyl acetate); ν_{max} (CH_2Cl_2) 2950, 2900, 1360, 1140, 1125, 950, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.56 (d, J = 8 Hz, 4 H), 7.25 (d, J = 8 Hz, 4 H), 5.23 (d, J = 7 Hz, 4 H), 4.05 (d, J = 7 Hz, 4 H), 3.62–2.85 (m, 6 H), 2.85–2.15 (m including s at δ 2.47, 8 H).

Anal. Calcd for $C_{28}H_{30}O_6S_2$: C, 63.86; H, 5.74. Found: C, 63.81; H, 5.79.

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-*endo*,*endo*-bis[[(tetrahydropyran-2-yl)oxy]methyl]dicyclopenta[*cd*,*gh*]pentalene (6d). A stirred mixture of **6a** (200 mg, 0.918 mmol) and dihydropyran (193 mg, 2.30 mmol) in dry ether (25 mL) was cooled to 0 °C and treated with trifluoroacetic acid (1 μL). The reaction mixture was sealed under argon for 36 h and then evaporated to leave a white powder shown (^{1}H NMR) to be unreacted **6a**. This material in dichloromethane (40 mL) was treated with dihydropyran (230 mg, 2.74 mmol) and pyridinium tosylate (25 mg, 0.10 mmol) and sealed under argon for 18 h. The reaction mixture was diluted with ether, washed with brine and water (25 mL, 1:1), and dried. Solvent removal left **6d** as a clear colorless oil (quantitative): ν_{max} (CH_2Cl_2) 2960, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.48 and 5.41 (m's, 4 H), 4.57 (m, 2 H), 4.15–3.35 (m, 8 H), 3.35–2.85 (m, 6 H), 2.70–2.10 (m, 2 H), 1.95 (m, 12 H).

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-*endo*,*endo*-bis(bromomethyl)dichloropenta[*cd*,*gh*]pentalene (7). A solution of bromine in dichloromethane [8.25 mL of a solution of bromine (1 mL) in CH_2Cl_2 (10 mL) or 15 mmol] was added to a cold (0 °C) stirred solution of dry triphenylphosphine (3.93 g, 15 mmol) in dichloromethane. A pale yellow solution resulted.

A solution of **6d** (1.92 g, 4.98 mmol) in dichloromethane (10 mL) was added to the above in the cold and stirred at 0 °C for 30 min and then at room temperature for 25 h. The amber reaction mixture was concentrated and the product was chromatographed on basic alumina. Elution with petroleum ether gave 464 mg (24%) of pure **7** as a white solid, mp 120–121 °C (from hexane), followed by 533 mg (28%) of impure **7** (ca. 80% purity). For **7**: ν_{max} (KBr) 3040, 2960, 2900, 1445, 1290, 1260, 1215, 750, 630, 540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.55 (s, 4 H), 3.52 (d, J = 7 Hz, 4 H), 3.38 (m, 6 H), 2.63 (m, 2 H); m/e calcd 341.9620, obsd 341.9625.

Anal. Calcd for $C_{14}H_{16}Br_2$: C, 48.87; H, 4.69. Found: C, 48.94; H, 4.71.

Typical Reaction of 7 with Sodium Cyanide. A stirred solution of **7** (90 mg, 0.26 mmol) in HMPA (10 mL) was treated with sodium cyanide (200 mg, 4.08 mmol) and heated under argon in an oil bath at 115 °C for 112 h. The reaction mixture was diluted with hexane (to 150 mL), washed with brine (3 × 50 mL), and dried. ^{1}H NMR analysis showed no detectable amount of dinitrile **10**. The only identifiable components are **8** and **9** in an approximate ratio of 2:1.

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3-methylene-6-*endo*-(cyanomethyl)dicyclopenta[*cd*,*gh*]pentalene (9): ν_{max} (CH_2Cl_2) 2900, 2240, 1655, 1080, 1000, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.38 (br s, 4 H), 4.85 (s, 2 H), 3.90–3.05 (m, 6 H), 2.43 (br s, 3 H).

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-dimethylenedicyclopenta[*cd*,*gh*]pentalene (8): the spectra are identical with those previously reported;[5] m/e calcd 182.1095, obsd 182.1099.

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-*endo*,*endo*-bis(cyanomethyl)dicyclopenta[*cd*,*gh*]pentalene (10). A. From Dimesylate 6b. A stirred suspension of sodium cyanide (105 mg, 2.14 mmol) in a solution containing **6b** (200 mg, 0.54 mmol) and dimethyl sulfoxide (2 mL) was heated at 90 °C for 27 h under argon. The progress of the reaction was monitored by thin-layer chromatography. The reaction mixture was poured into brine (25 mL) and the product was extracted with hexane (4 × 10 mL). The combined hexane extracts were washed with brine (4 × 10 mL) and dried. Solvent evaporation left a pale yellow crystalline solid (77 mg), the ^{1}H NMR spectrum of which showed it to be a mixture of **9** and **10** in approximately a 1:2.5 ratio. A trace quantity of tetraene **8** was also present. Recrystallization of this material from hexane gave pure **10** (34 mg, 27%) as off-white crystals: mp 107–109.5 °C; ν_{max} (KBr) 3040, 2905, 2240, 1430, 1370, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.50 (s, 4 H), 3.37 (br s, 6 H), 2.46 (br s, 6 H); m/e calcd 236.1313, obsd 236.1319.

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82. Found: C, 81.16; H, 6.85.

The hexane mother liquor was chromatographed on Florisil. Elution with hexane–dichloromethane (1:1) gave 15 mg (15%) of **9** as a clear viscous oil.

B. From Ditosylate 6c. A stirred suspension of sodium cyanide (100 mg, 2.04 mmol) in a solution containing **6c** (200 mg, 0.38 mmol) and dimethyl sulfoxide (2 mL) was heated at 90 °C for 3.5 h under argon. The predescribed workup afforded a pale yellow oil (123 mg) which was purified by filtration through a column of alumina. A trace of tetraene **8** was first eluted followed by a mixture of **9** and **10** (51 mg) in a ratio of 1:5.5 (^{1}H NMR estimate).

Hydrolysis–Esterification of 10. A solution of 80% pure **10** (170 mg) in methanol (10 mL) was treated with aqueous methanolic potassium hydroxide solution [40% (w/v) KOH in 5:3 (v/v) CH_3OH–H_2O, 30 mL] and heated at the reflux temperature for 12 h. The resulting clear pale yellow solution was poured onto ice (150 g) and concentrated hydrochloric acid (30 mL), and the precipitated product was extracted into ether–ethyl acetate (1:1, 2 × 40 mL). These extracts were combined and washed with saturated sodium bicarbonate solution (3 × 25 mL). The alkaline layers were combined, acidified, and extracted with ether–ethyl acetate (1:1, 3 × 25 mL). The organic phases were dried and evaporated to give 179 mg of diacid as a colorless crystalline solid.

This material was dissolved in chloroform–methanol (6:1, 140 mL), treated with 3 drops of concentrated sulfuric acid, and heated at reflux for 12 h. The condensate was returned to the flask via a Soxhlet thimble packed with molecular sieve 3A. The cooled reaction mixture was treated with anhydrous potassium carbonate (10 g), stirred for 10 min, filtered, and evaporated to give a yellow oil which was dissolved in dichloromethane and washed with brine (2 × 25 mL). The organic phase was dried and evaporated to give 190 mg of a crystalline substance judged by ^{1}H NMR to contain ca. 80% of **11**. Pure **11** was subsequently obtained by the Arndt–Eistert homologation sequence.

Bis(trimethylsilyl) 3,3a,3b,4,6a,7a-Hexahydro-3,4,7-metheno-7*H*-cyclopenta[*a*]pentalene-7,8-dicarboxylate (12). A suspension of 3,3a,3b,4,6a,7a-hexahydro-3,4,7-metheno-7*H*-cyclopenta[*a*]pentalene-7,8-dicarboxylic acid[3,5,7] (1.00 g, 4.10 mmol) in dry toluene (50 mL) was stirred under argon and treated with triethylamine (2.06 g, 20.4 mmol) followed by trimethylsilyl chloride (1.78 g, 16.4 mmol). The mixture was heated at reflux for 10 h, cooled, and filtered under argon. The filtrate was evaporated under high vacuum to furnish 1.48 g (93%) of **12** which was utilized without further purification.

Reductive Cleavage of 12. A solution of unpurified **12** (from 4.10 mmol of diacid) in toluene (10 mL) was added under nitrogen to a stirred suspension of sodium sand (3.68 g, 160 mg-atom) in a solution of trimethylsilyl chloride (19.6 g, 180.5 mmol) in toluene 100 mL). The vigorously stirred mixture was heated at reflux for 16 h, allowed to stand at room temperature for 5 h, filtered under nitrogen, and evaporated to dryness to give the ketene acetal **13**: ^{1}H NMR ($CDCl_3$) δ 5.26 (m, 4 H), 4.0–2.85 (m, 6 H), 0.25 (s, 36 H).

This substance was dissolved in toluene (20 mL) and isopropyl alcohol (10 mL) and kept at room temperature for 43 h. Pyridinium tosylate (100 mg) was added and the reaction mixture was maintained at room temperature for an additional 48 h before being poured into ether (100 mL) and extracted with 3% sodium hydroxide solution (3 × 75 mL). The combined basic layers were extracted with ether (2 × 25 mL) before acidification. Extraction with ether followed by drying and evaporation of solvent gave 635 mg (63% overall from diacid) of **14** as a yellowish, oily solid. Trituration with ether afforded purer product as a white crystalline solid with spectral properties identical with those described below.

Trimethylsilyl Iodide Mediated Cleavage of 5.[7] A solution of **5** (6.11 g, 22.3 mmol) and trimethylsilyl iodide (15.4 g, 77.0 mmol) in ethanol-free chloroform (150 mL) was heated at gentle reflux under a nitrogen atmosphere in the dark for 39 h. The pale pink reaction mixture was poured into water (800 mL), shaken vigorously, and basified with sodium bicarbonate to pH 9. The chloroform layer was removed and the aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined chloroform and dichloromethane layers were dried and evaporated to leave 230 mg of unreacted **5**. The water layer was acidified and the precipitated solid was taken up in ethyl acetate–ether (1:1, 1 × 500 mL and 4 × 100 mL). The combined organic phases were washed with brine, dried, and evaporated to furnish a white crystalline solid (5.68 g) identified (^{1}H NMR) as a mixture of **14** and the monomethyl ester (61:39). Trituration of this product with ethyl acetate (25 mL) gave pure **14** (3.65 g) and a pale yellow solid (1.95 g) rich in the monoester. Recrystallization of **14** from ethyl acetate afforded colorless crystals: mp 251–253.5 °C dec; ν_{max} (KBr) 3046, 2956, 2931, 2885, 1708, 1409, 1266, 1217, 758, 745 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 11.83 (br s, 2 H), 5.62 (s, 4 H), 3.58–2.88 (m, 8 H); *m/e* calcd 246.0892, obsd 246.0897.

Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.69; H, 5.73.

3,6-*endo*,*endo*-Bis(diazoacetyl)-2a,3,3a,5a,6,6a,6b,6c-octahydrodicyclopenta[*cd*,*gh*]pentalene (15). A mixture of **14** (3.50 g, 14.2 mmol) and oxalyl chloride (60 mL) was stirred at room temperature for 2.5 h. The excess acid chloride was removed under reduced pressure to leave a white crystalline solid which was dissolved in the minimum volume of dichloromethane and filtered through glass wool. The filtrate was evaporated to leave **15a** as a colorless crystalline solid; ν_{max} (CH_2Cl_2) 1800 cm^{-1}.

This substance dissolved in dichloromethane (24 mL) was added slowly to a solution of diazomethane (ca. 150 mmol) in ether (500 mL) at 0 °C. During the addition, the bis(diazo ketone) began to precipitate from solution. The reaction mixture was allowed to warm to room temperature during 1.25 h and evaporated to dryness under reduced pressure. There was obtained 4.71 g (94.5%) of **15b** as a pale yellow crystalline solid: mp 134 °C dec (from dimethoxyethane–ethyl acetate); ν_{max} (CH_2Cl_2) 2110, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.65 (s, 4 H), 5.28 (s, 2 H), 3.50–2.70 (m, 8 H); *m/e* calcd 294.1167, obsd 294.1123. This material was used without further purification.

Dimethyl 2a,3,3a,5a,6,6a,6b,6c-Octahydrodicyclopenta[*cd*,*gh*]pentalene-3,6-*endo*,*endo*-diacetate (16). A partial solution of **15b** (4.71 g, 13.4 mmol) in tetrahydrofuran (100 mL) and methanol (300 mL) was stirred at 70 °C while a solution of silver acetate (224 mg, 1.34 mmol) in triethylamine (5 mL) and methanol (5 mL) was introduced in ca. 0.5-mL portions during 3 h. An identical solution of silver acetate was added and the reaction mixture was maintained at 50 °C for 18 h. Precipitated solids were removed by filtration through Celite and the filtrate was evaporated. The resulting yellow oil was dissolved in dichloromethane (100 mL) and washed with water (2 × 10 mL), dilute hydrochloric acid (2 × 10 mL), water (10 mL), and brine (10 mL) before drying. Solvent removal left 4.02 g (93%) of **16** which was additionally purified by filtration through a pad of Florisil and recrystallization at −20 °C from hexane–ethyl acetate: ν_{max} (CH_2Cl_2) 2920, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.43 (s, 4 H), 3.63 (s, 6 H), 3.60–2.85 (m, 6 H), 2.46 (br s, 6 H); *m/e* calcd 302.1518, obsd 302.1525.

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-*endo*,*endo*-bis(2-hydroxyethyl)dicyclopenta[*cd*,*gh*]pentalene (17a). A stirred suspension of lithium aluminum hydride (350 mg, 9.21 mmol) in tetrahydrofuran (30 mL) was treated at 0 °C under nitrogen with a solution of **16** (330 mg, 1.09 mmol) in tetrahydrofuran (20 mL) during 5 min. The reaction mixture was stirred at 0 °C for 5 min and then allowed to stand at room temperature overnight. Following the addition of ethyl acetate and powdered Glauber's salt, the reaction mixture was filtered and the filtrate evaporated to give 270 mg (100%) of **17a**: mp 126–128 °C (from ethyl acetate); ^{1}H NMR δ (pyridine-d_5) 6.0–5.2 (br m including s at δ 5.56, 6 H), 3.93 (t, *J* = 6.5 Hz, 4 H), 3.5–2.9 (m, 6 H), 2.6–1.6 (m, 6 H); ^{13}C NMR (pyridine-d_5) 133.6, 61.8, 56.0, 52.7, 42.4, 34.1 ppm; *m/e* calcd 246.1620, obsd 246.1626.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.97; H, 9.03.

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-*endo*,*endo*-bis(2-hydroxyethyl)dicyclopenta[*cd*,*gh*]pentalene Bis(*p*-toluenesulfonate) (17b). A solution of **17a** (380 mg, 1.54 mmol) in pyridine (12 mL) was treated with *p*-toluenesulfonyl chloride (1.473 g, 7.72 mmol) at room temperature. The reaction mixture was maintained under nitrogen at 0 °C for 49 h, poured into ice water (100 mL), and extracted with dichloromethane (1 × 50 mL, 3 × 25 mL). The combined organic layers were washed with 5% hydrochloric acid (2 × 40 mL) and brine (2 × 50 mL) prior to drying and evaporation. There was obtained 695 mg (81%) of **17b** as a colorless crystalline solid: mp 123–124 °C (from ethyl acetate–hexane); ^{1}H NMR ($CDCl_3$) δ 7.80 (d, *J* = 8 Hz, 4 H), 7.33 (d, *J* = 8 Hz, 4 H), 5.35 (s, 4 H), 4.12 (t, *J* = 6 Hz, 4 H), 3.5–2.65 (m, 6 H), 2.43 (s, 6 H), 2.4–1.5 (m, 6 H); ^{13}C NMR ($CDCl_3$) 146.3,

135.1, 134.6, 131.5, 129.5, 71.6, 56.5, 53.7, 42.5, 30.9, 23.2 ppm.

Anal. Calcd for $C_{30}H_{34}O_6S_2$: C, 64.96; H, 6.18. Found: C, 64.77; H, 6.27.

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-*endo*,*endo*-bis(2-bromoethyl)dicyclopenta[*cd*,*gh*]pentalene (18). A stirred suspension of **17a** (100 mg, 0.41 mmol) in a solution of carbon tetrabromide (340 mg, 1.02 mmol) and dichloromethane (10 mL) at 0 °C was treated portionwise with triphenylphosphine (320 mg, 1.22 mmol) during 20 min. After 10 min, the reaction mixture became homogeneous and took on a pale yellow color. The solvent was evaporated under reduced pressure to leave a thick oil which was chromatographed on Florisil. Elution with hexane furnished 100 mg (66%) of **18** as a colorless solid: mp 81–82 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 5.46 (s, 4 H), 3.50 (t, J = 6 Hz, 4 H), 3.35–2.85 (m, 6 H), 2.70–1.95 (m including t (J = 6 Hz) at δ 2.03, 6 H); ^{13}C NMR ($CDCl_3$) 133.12, 54.81, 52.09, 43.60, 33.40, 32.67 ppm; m/e calcd 369.9933, obsd 369.9938.

Anal. Calcd for $C_{16}H_{20}Br_2$: C, 51.64; H, 5.42. Found: C, 51.59; H, 5.39.

2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-*endo*,*endo*-bis[2-(phenylthio)ethyl]dicyclopenta[*cd*,*gh*]pentalene (19). A. From Dibromide 18. A solution of **18** (173 mg, 0.465 mmol) in anhydrous tetrahydrofuran (25 mL) was stirred under nitrogen at room temperature sequentially with thiophenol (536 mg, 4.88 mmol) and potassium *tert*-butoxide (0.5 g, 4.46 mmol). The resultant white slurry was stirred overnight at room temperature before being diluted with ether (100 mL) and washed with brine (25 mL), dilute sodium hydroxide solution (2 × 25 mL), and brine (2 × 25 mL). After drying and evaporation, there was obtained 295 mg of a pale yellow solid which was purified by thick-layer chromatography on silica gel (elution with dichloromethane–hexane (3:7)). Pure bis-sulfide **19** weighed 148 mg (74%): mp 104–105 °C; ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 10 H), 5.42 (s, 4 H), 3.50–2.65 (m, 10 H), 2.65–1.50 (m, 6 H); m/e calcd 430.1789, obsd 430.177.

Anal. Calcd for $C_{28}H_{30}S_2$: C, 78.09; H, 7.02. Found: C, 77.95; H, 7.01.

B. From Diol 17a. A solution of tri-*n*-butylphosphine (447 mg, 2.21 mmol) in dry tetrahydrofuran (10 mL) was treated with *N*-(phenylthio)succinimide (440 mg, 2.13 mmol). A purple color developed. The reagent was stirred at room temperature under nitrogen for 1 min and treated with a solution of **17a** (201 mg, 0.82 mmol) in the same solvent (2 mL). At this point, the color faded to salmon pink. After 24 h at room temperature, the reaction mixture was diluted with ether (100 mL) and washed with water (50 mL), 10% sodium hydroxide solution (3 × 35 mL), and brine (2 × 25 mL) before drying. Solvent removal under reduced pressure left a yellow oil (735 mg). Chromatography on Florisil (hexane elution) gave 147 mg (56%) of **19** as white rosettes, mp 103–104 °C.

C. From Ditosylate 17b. A 500-mg (0.903 mmol) sample of ditosylate **17b** was treated with potassium thiophenoxide as described in section A. The resultant colorless oil (567 mg) was purified by thick-layer chromatography on silica gel. There was isolated 286 mg (73%) of **19**.

3,6-*endo*,*endo*-Bis[2-(benzenesulfonyl)ethyl]-1,2:4,5-*exo*,*exo*-diepoxydodecahydrodicyclopenta[*cd*,*gh*]pentalene (4). A solution of **19** (148 mg, 0.34 mmol) in dichloromethane (15 mL) was stirred with powdered disodium hydrogen phosphate (2.20 g, 15.60 mmol) and treated with *m*-chloroperbenzoic acid (560 mg, 3.24 mmol). The reaction mixture was stirred at room temperature for 40 h, diluted with ethyl acetate, and washed with neutralized ($NaHCO_3$) sodium bisulfite solution (3 × 50 mL) and brine (2 × 50 mL). Drying and solvent evaporation left a white solid (0.3 g) which was purified by thick-layer chromatography on silica gel. Elution with 25% ethyl acetate in dichloromethane afforded 130 mg (72%) of **4** as a colorless crystalline solid: mp 229 °C (from tetrahydrofuran–hexane); ν_{max} (KBr) 3020, 2950, 2920, 2905, 1450, 1310, 1150, 1090, 820, 750, 690, 630, 590, 530, 370 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.0–7.65 (m, 4 H), 7.6–7.3 (m, 6 H), 3.5–3.0 (br s, 6 H), 3.0–2.0 (m, 14 H); ^{13}C NMR (pyridine-d_5) 140.2, 133.9, 129.7, 128.4, 60.9, 57.9, 55.2, 49.4, 44.7, 12.7 ppm; m/e calcd 526.1484, obsd 526.1496.

Anal. Calcd for $C_{28}H_{30}O_6S_2$: C, 63.86; H, 5.74. Found: C, 63.74; H, 5.75.

Base-Promoted Cyclization of 4. A 175-mg (7.29 mmol) sample of sodium hydride which had been washed free of mineral oil was suspended with stirring in dimethyl sulfoxide (6 mL) under nitrogen. This suspension was treated with a solution of **4** (174 mg, 0.33 mmol) in the same solvent (7 mL), and the mixture was stirred at room temperature for 22 h before being syringed into brine (150 mL). Dilution with water to redissolve the precipitated salt was followed by extraction with ethyl acetate–ether (1:1, 100 mL). The aqueous phase was neutralized with solid potassium dihydrogen phosphate and again extracted with ethyl acetate–ether (1:1, 3 × 50 mL). All of the organic layers were combined, washed with brine (3 × 50 mL), dried, and evaporated to give an oily, colorless solid (162 mg). Thick-layer chromatography on silica gel (elution with ethyl acetate) furnished 111 mg (63%) of **20**, a white crystalline solid: mp 240–242 °C (from tetrahydrofuran–hexane); ^{1}H NMR (pyridine-d_5) δ 8.3–7.7 (m, 4 H), 7.7–7.2 (m, 6 H), 6.4 (br s, 2 H), 4.95 (br s, 2 H, $w_{1/2}$ = 5 Hz), 3.7–2.1 (m, 14 H), 1.85 (br s, 2 H, $w_{1/2}$ = 4 Hz); ^{13}C NMR (pyridine-d_5) 140.5, 138.4, 133.9, 133.7, 130.3, 129.6, 129.1, 128.2, 71.6, 71.2, 63.2, 60.2, 57.3, 55.4, 53.2, 49.5, 49.4, 48.0, 23.4 ppm.

Anal. Calcd for $C_{28}H_{30}O_6S_2$: C, 63.86; H, 5.74. Found: C, 63.79; H, 5.82.

Reductive Desulfonylation of 20. A. Complete Reduction. A suspension of disodium hydrogen phosphate (350 mg, 2.46 mmol) in a stirred solution of **20** (105 mg, 0.20 mmol) in methanol (5 mL) was treated at room temperature under nitrogen with 6% sodium amalgam (1 g, 250 mg/30 min). After 30 min, the reaction mixture was diluted to 100 mL with ether, washed with brine (2 × 25 mL), dried, and evaporated. The resultant oily white solid (120 mg) was dissolved in pyridine (4 mL) and treated with benzoyl chloride (242 mg, 1.73 mmol). After 17 h, the stirred reaction mixture was diluted with ethyl acetate–ether (1:1, 100 mL) and washed with brine (50 mL), 5% hydrochloric acid (50 mL and 2 × 25 mL), and brine (2 × 25 mL). The organic phase was dried and concentrated to give a yellow oil (225 mg). Thick-layer chromatography on silica gel (dichloromethane elution) gave 55 mg (61%) of **22b**: mp 165–166 °C (from ethyl acetate–hexane); ^{1}H NMR ($CDCl_3$) δ 8.1–7.8 (m, 4 H), 7.7–7.1 (m, 6 H), 5.50 (br s, 2 H), 3.2–1.2 (series of m's, 15 H), 1.95 (t, J = 8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 165.8, 132.7, 131.1, 129.5, 128.3, 78.3, 58.8, 57.8, 56.6, 52.1, 51.8, 51.3, 45.6, 41.5, 22.5, 13.3 ppm.

Anal. Calcd for $C_{30}H_{30}O_4$: C, 79.27; H, 6.65. Found: C, 79.44; H, 6.66.

B. Partial Reduction. Reduction of **20** (95 mg, 0.181 mmol) with 0.5 g of 6% sodium amalgam in the predescribed manner gave a mixture of **21** and **22a** which were separated by repeated preparative thin-layer chromatography. There was isolated 8 mg (17%) of **22a**: ^{1}H NMR ($CDCl_3$) δ 4.15 (br s, 2 H), 3.15–1.30 (series of m's, 17 H), 1.15 (t, J = 6 Hz, 3 H); ^{13}C NMR (pyridine-d_5) 73.44, 63.05, 61.59, 57.27, 52.41, 52.12, 51.59, 45.96, 42.46, 23.14, 13.67 ppm.

Also obtained was 35 mg (50%) of **21**: ^{1}H NMR ($CDCl_3$) δ 8.05–7.75 (m, 2 H), 7.75–7.35 (m, 3 H), 4.65 (br s, 2 H), 3.15–1.15 (series of m's, 12 H), 1.05 (t, J = 6 Hz, 3 H); ^{13}C NMR (pyridine-d_5) 138.49, 133.83, 130.38, 129.02, 71.93, 71.20, 63.43, 60.23, 57.37, 53.19, 51.98, 49.74, 49.40, 22.99, 13.53 ppm.

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Registry No. 4, 71831-29-3; **5**, 68297-12-1; **6a**, 71831-30-6; **6b**, 71831-31-7; **6c**, 71831-32-8; **6d**, 71831-33-9; **7**, 71831-34-0; **8**, 53283-08-2; **9**, 71831-35-1; **10**, 71831-36-2; **11**, 71831-37-3; **11** diacid, 71831-38-4; **12**, 71831-39-5; **13**, 71831-40-8; **14**, 71831-41-9; **14** monomethyl ester, 71831-42-0; **15a**, 71831-43-1; **15b**, 71849-83-7; **17a**, 71831-44-2; **17b**, 71831-45-3; **18**, 71849-84-8; **19**, 71831-46-4; **20**, 71831-47-5; **21**, 71831-48-6; **22a**, 71831-49-7; **22b**, 71831-50-0; 3,3a,3b,4,6a,7a-hexahydro-3,4,7-metheno-7*H*-cyclopenta[*a*]pentalene-7,8-dicarboxylic acid, 61206-25-5.