tional Institute of Health (Grant AI-11490) made possible this research. We are grateful to Dr. Ole Mols for his assistance in recording the high-field NMR spectra.

Registry No. 4, 71342-50-2; **5b**, 82390-84-9; **6**, 86289-31-8; **7**, 80317-84-6; **8**, 86289-32-9; **9a**, 86289-33-0; **9b**, 86289-34-1; **10**, 86289-35-2; **11**, 86307-78-0; **12**, 82390-85-0; **13**, 86289-36-3; **14**, 82390-86-1; **15**, 86289-37-4; **16**, 82390-87-2; **17**, 86289-38-5; **18**, 82390-88-3; **19**, 86289-39-6; **20**, 82390-89-4; **21**, 82390-90-7; **23**, 82390-91-8; A, 86307-79-1.

Total Synthesis of Dodecahedrane

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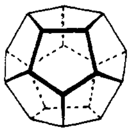
Abstract: The chemical transliteration of Plato's universe—the dodecahedrane—has been synthesized in 23 steps. The key stages of the sequence starting from dichloro diester **2** involve the following: (a) reduction–monoalkylation of **2** using chloromethyl phenyl ether to give **7**; (b) photocyclization of aldehyde **12** without interference from the geminal side chain; (c) retro-aldol cleavage of keto aldehyde **15**; and (d) catalytic dehydrogenation of **19**. The single-peak nature of the ^1H and ^{13}C NMR spectra of **1** conforms to its ultrahigh (I_h) symmetry. The spherical hydrocarbon exhibits three infrared-active and eight Raman-active bands. The unique physical behavior of **1** upon heating to temperatures above 400 °C is detailed.

For centuries, the dodecahedron has been esteemed as the most complex and aesthetically pleasing of the perfect solids of antiquity. In more recent times, scientists have come to regard its molecular transliteration, dodecahedrane ($C_{20}H_{20}$, **1**), as the "Mount Everest of Alicyclic Chemistry".[3] Thus, history did early place before any interested organic chemist the formidable challenge of synthesizing a uniquely symmetric (I_h) hydrocarbon composed exclusively of (12) five-membered rings whose construction could hardly fail to excite interest and curiosity. The problem of defining suitable synthetic protocols for arrival at **1**, which was first given attention 20 years ago in Woodward's laboratory,[4,5] has only recently been successfully resolved at Ohio State.[6,7] Herein, we provide details of the manner in which this achievement was realized.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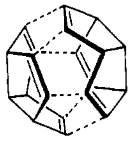
From the first, we looked upon any *convergent* approach to dodecahedrane as plagued with the onerous burden of properly aligning the pair of structural components involved. This complication is most acute when two unconnected segments must be properly conjoined as in the dimerization of triquinacene (A)[4] or the "capping" of peristylane (B).[8] However, highly disadvantageous steric and entropic factors persist subsequent to installation of an interconnective C–C bond as in C.[9,10] Thus, *x*-ray analysis has clearly revealed the two triquinane rings in *dl*- and *meso*-bivalvane to be as mutually distal as possible.[11]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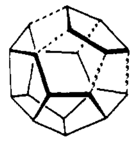
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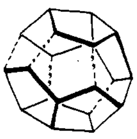
C

Consequently, our design was to employ a *serial* synthesis that, however, would be significantly abbreviated by taking advantage of the enormous symmetry of the target molecule. Indeed, it was our original intent to arrive at **1** by deploying individual laboratory steps fewer than or equal to the number of constituent carbon atoms. Relevantly, certain restrictions exist on the symmetry level of the intermediates. While planar symmetric (i.e., C_s) and twofold axially symmetric (i.e., C_2) molecules were considered quite serviceable,[12] adherence to threefold axial symmetry must deliver a C_{19} precursor and ultimately require introduction of a discrete "CH" unit.[13] Consequently, we opted for the direct construction of C_{20} precursors to **1** that fulfill the first set of criteria.

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(12) Along this line of reasoning, C_{2v} structures would also be admissible to a point. Once a reasonably advanced stage of framework construction had been maintained, one would be forced to lower the symmetry level in order to arrive ultimately at the I_h species in question.

(13) A molecule that could be adapted to this protocol is C_{16}-hexaquinacene [Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1978**, *100*, 1600; **1979**, *101*, 6991]. However, various schemes to rapidly lessen the symmetry level of certain derived intermediates have also been given attention [Osborn, M. E.; Kuroda, S.; Muthard, J. L.; Kramer, J. D.; Engel, P.; Paquette, L. A. *J. Org. Chem.* **1981**, *46*, 3379]. Also, Professor Jack Baldwin (Oxford University) has recently informed us of an approach being developed in his laboratory to access **1** via intermediates having threefold axial symmetry.

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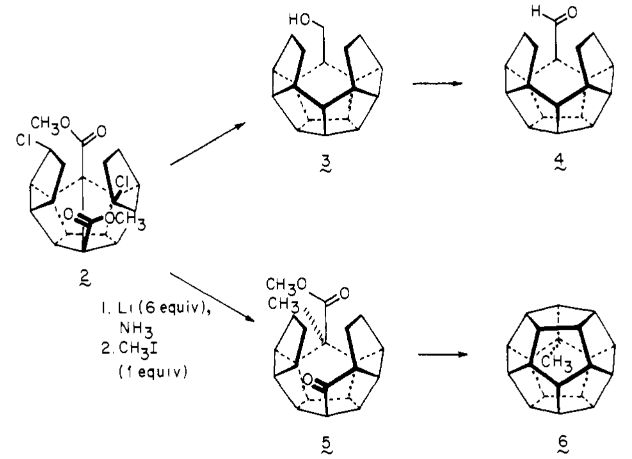
Previously, the attainment of dichloro diester **2** in a minimum of nine steps was described.[14] Its subsequent four-step conversion to triseco alcohol **3** has also been reported.[6,15] Were **3** to be capable of straightforward oxidation to C_s-aldehyde **4**, our original goal of extreme brevity would have been easily met. As matters turned out, however, the nonbonded steric strain in **4** causes it to be highly sensitive to air oxidation.[6,15] So labile did **4** prove to be that it was not further considered as a utilitarian precursor to **1**.

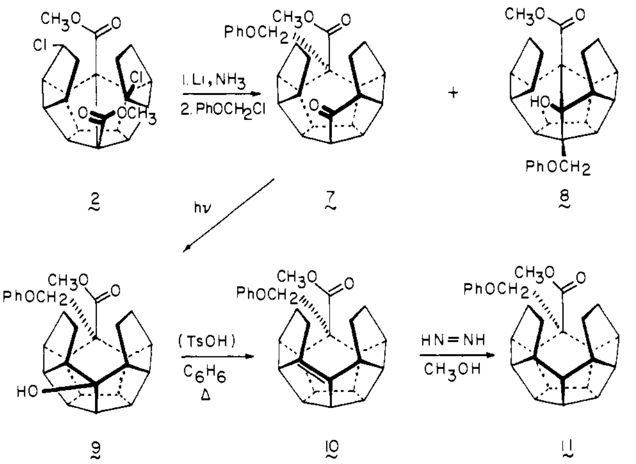


These considerations dictated that a blocking group procedure be implemented, despite the additional steps that this course of action would necessarily introduce. In order to set the stage for this somewhat more extensive operation, a procedure for the regiocontrolled reductive monomethylation of **2** to generate **5** was developed.[16] The expectation that the carbomethoxy group of **5** could be usefully "stitched" into the alicyclic framework was also fulfilled by the successful acquisition of methyldodecahedrane (**6**) in eleven additional steps.[16]

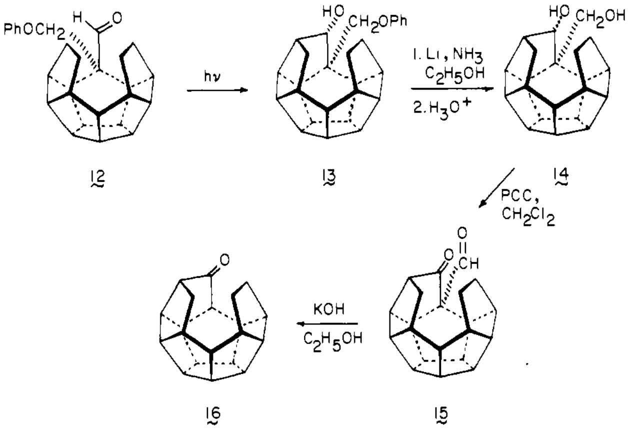
A suitably functionalized analogue of **5** became, for obvious reasons, our choice of pivotal intermediate on the pathway to **1**. Specifically, the plan was to follow the reaction sequence **2** → **5**, but with replacement of the methyl group with a substituent that would effectively deter enolization of the carboxaldehyde functionality at the triseco level, yet prove readily removable at a later stage. The point of departure was necessarily introduction of the blocking group via S_N2 methodology at the tetraseco phase of construction. Subsequently, the pendant side chain must survive the steps involved in fabricating the framework bond on the opposite molecular surface as well as the processes involved during adjustment of the oxidation level of the carbomethoxy group. Most importantly, this blocking group should not accentuate photodecarbonylation of the triseco aldehyde nor engage in capture of its photoexcited carbonyl group.

Following due consideration, the decision was made to utilize phenoxymethyl as the side chian, taking advantage of the anticipated electrophilic properties of chloromethyl phenyl ether.[17] The expectation was that its removal could be subsequently achieved via tandem Birch reduction of the phenyl ring and retro-aldol methodology. When **2** was subjected to dissolving metal reduction and the resultant dianion was treated with 1 equiv of this reagent, the desired tetraseco keto ester **7** was indeed produced (48%) alongside the anticipated transannular hydroxy ester **8** (22%). When irradiated in a dry, deoxygenated benzene–*tert*-butyl alcohol (4:1) solvent system containing small quantities of triethylamine to buffer against acidity, **7** underwent very efficient homo-Norrish cyclization[18] to furnish **9** (90%). Once again, rigid molecular topology and proper C=O- - -H distance and encounter angle for intramolecular hydrogen abstraction[19,20] via a six-membered transition state combined to promote high-yield conversion to photoproduct.

The tertiary carbinol **9** was smoothly dehydrated to **10** and reduced with diimide to provide **11** in 85% overall yield. As in the methyl example, the aldehyde **12** (92%) was arrived at by sequential diisobutylaluminum hydride reduction and pyridinium chlorochromate oxidation. Cyclopentanol **13** was readily procured by irradiation of **12** in deoxygenated toluene–ethanol (9:1) at −78 °C. That the phenoxymethyl residue did avoid entanglement with proximate functionality and fail to enhance competitive photodecarbonylation during photocyclization was evidenced by the relatively good yield of isolated product (36%).



At this point, the risk of complications due to enolization α to an aldehydic carbonyl site was behind us and it became appropriate to direct our attention to the removal of the phenoxymethyl side chain that had served us so well. Birch reduction of **13** delivered a dihydrobenzene product, aqueous acid hydrolysis of which furnished **14** in 99% yield. This diol underwent efficient oxidation to β-keto aldehyde **15** in the presence of pyridinium chlorochromate. Completion of the deblocking sequence was accomplished by a reverse Claisen reaction of **15** in alkaline solution, providing diseco ketone **16** in 37% overall yield.



With the acquisition of **16**, we had reached a point where installation of the penultimate framework bond could be realized

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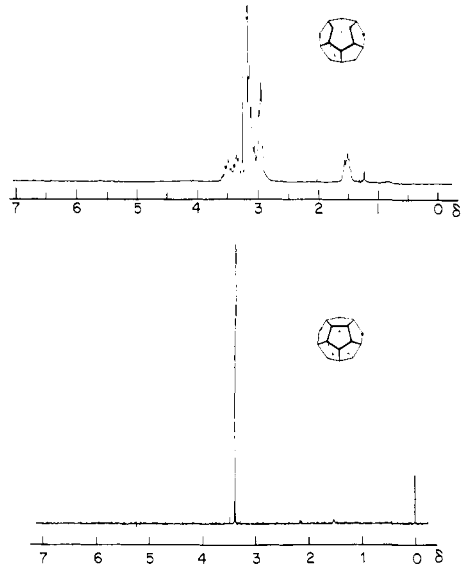
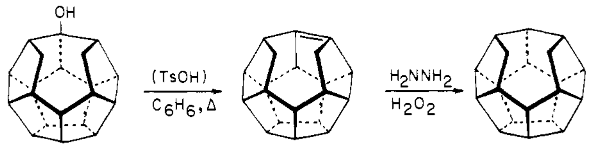


Figure 1. 200-MHz ^1H NMR spectra of secododecahedrane (**19**) (top) and dodecahedrane (**1**) (bottom) recorded in $CDCl_3$ solution.

by again making recourse to photochemistry. In the event, the desired cyclization proceeded without complication to give **17**, which we were able to dehydrate conventionally. Hydrocarbon **18** represents an isomer of dodecahedrane that could potentially rearrange to this species under suitable conditions. As in the case of its monomethyl homolog, however, treatment of **18** with trifluoromethanesulfonic acid in dichloromethane solution led to uncontrolled carbocationic rearrangement.[16] Attempts to effect the desired isomerization with other agents ($BF_3 \cdot OEt_2$; heat; $ClRh(PPh_3)_3$; $RhCl_3 \cdot 3H_2O$; HF; $HClO_4$; and FSO_3H) were also uniformly unsuccessful.



17 **18** **19**

The known tendency of photoexcited olefins to undergo rearrangement[21] led us to speculate that dodecahedrane might well be formed by such a process. Furthermore, the ultraviolet spectrum of **18**, which is characterized by a maximum at 210 nm, suggested that photoexcitation of this strained olefin might well be possible. In actuality, irradiation of **18** in hexane solution through quartz with a 450-W Hanovia lamp led to rapid formation of a product mixture consisting of two major components (VPC analysis). Although these substances remain as yet unidentified,[22] dodecahedrane was clearly not present (^1H NMR analysis).

With these points established, recourse was made to the methodology developed to install the final bond in methyldodecahedrane.[16] Following diimide reduction to provide **19**, the saturated hydrocarbon was heated with hydrogen-presaturated 10% palladium on carbon at 250 °C for ≥4.5 h. Under these conditions, dehydrogenative conversion to **1** occurred with 40–50% efficiency. Although several byproducts also resulted, dodecahedrane was readily separated from the reaction mixture by recrystallization from benzene in 34% yield.

In line with expectation, the ^1H and ^{13}C NMR spectra of **1** (in $CDCl_3$) are characterized by singlets, the former at δ 3.38 and the latter at 66.93 ppm. To allow suitable comparison, the 200-MHz proton spectra of **1** and its secododecahedrane precursor **19** are illustrated in Figure 1. Two aspects of these data are noteworthy. Firstly, the excessive steric compression to which the two internal methylene protons are subjected[23] (estimated to be on the order of 80 kcal/mol[24]) causes them to be substantially shielded (δ 1.6–1.4) relative to their external methylene and methine counterparts (δ 3.5–2.9).[25] Secondly, the relatively low-field chemical shift of the dodecahedryl protons, which suggests that at least one tensor of the proton spin is strongly accented, is not unique to the fully spherical molecule but is seen in all topologically related compounds that have acquired reasonable levels of conformational rigidity. Although the theory of chemical shifts is not yet fully developed, the various possible contributory factors (and remaining questions) enunciated by Boaz[26] for symmetrical, saturated hydrocarbons having no internal rotation may well apply here. The ^{13}C–H coupling constant of 134.9 Hz is somewhat larger than the values earlier calculated by Mislow[27] (128.1 Hz) and Schulman[28] (125.3 Hz) from the estimated amount of s character in the C–H bond. However, the observed J compares quite favorably with those previously determined for 1,16-dimethyldodecahedrane (131.2, 135.0 Hz).[6,20]

The vibrational frequencies exhibited by **1** (120 identity operations) agree fully with a highly rigid network of interlinked methine units. Only three infrared-active bands are observed at 2945, 1298, and 728 cm^{-1}; the eight Raman frequencies appear at 2954, 2938, 1324, 1164, 1092, 840, 676, and 480 cm^{-1}. In general, these findings compare reasonably well with values calculated by Ermer using a force-field program.[29]

As presently obtained, dodecahedrane happens to be optically isotropic, having crystallized in the cubic system as quite well-formed octahedra and cubeoctahedra. This would imply that **1**, in this phase, almost certainly possesses a face-centered-cubic unit cell.[30] By means of a standard microcrystallographic technique, the refractive index of dodecahedrane was determined to be $n_c = 1.670$, $n_D = 1.674$, and $n_F = 1.685$. These values were confirmed by a second technique that yields an optical dispersion curve. Any crystal dynamics calculation would, consequently, have to yield this result and, along with a density measurement, must furnish acceptable values for the unit-cell parameters, etc., especially under the constraints of observed crystal morphology.

A most interesting identity between dodecahedrane's refractive index and one of the key indices of 1,16-dimethyldodecahedrane (**20**) has been noted. The latter hydrocarbon crystallizes in the orthorhombic system ($\alpha = 1.674$ Å, $\gamma = 1.677$ Å) and is weakly anisotropic.[23] The value for α and the n_D of dodecahedrane is the same! This suggests that **1** has a crystal structure very much like that of the 1,16-dimethyl derivative. Upon removal of the distortions present in the b–c plane of the unit cell for **20**, one should arrive at the crystal structure of **1**. In our opinion, no reorientation other than intramolecular distance reductions in the b–c plane will occur on going from **20** to **1**.

Because dodecahedrane showed no visible evidence of melting upon being slowly heated in sealed capillaries up to 450 °C (at which point a brown coloration was obvious), a special microscope hot stage was built and calibrated. With this apparatus, the melting point of **1** was determined to be 430 ± 10 °C, the relatively low precision being forced upon us by the quite rapid rate of heating that was required to achieve the measurement. At these temperatures and atmospheric pressure, dodecahedrane sublimes very rapidly. Nonetheless, a very fleeting liquid phase was ob-

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(22) Currently work is under way to separate and characterize these photoproducts. The results will be reported elsewhere.

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(29) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1977**, *6*, 411. The calculated values are: (a) IR 2898, 1310, 760 cm^{-1}; (b) Raman 289, 2895, 1300, 1166, 1101, 846, 732, 395 cm^{-1}.

(30) An X-ray crystallographic analysis of dodecahedrane is currently in progress.

served. During the heating process, at temperatures not far below the melting point, at least one solid–solid phase transition took place. The dodecahedrane crystals cracked, cracked again, and then a third time until they were so full of fractures that an opaque white appearance was taken on (transition temperature $\sim$410 °C). Because a phase transition from cubic to tetragonal, hexagonal, or orthorhombic would likely not strain the crystal enough to cause such fracturing, our present belief is that the phase transition is to monoclinic or triclinic. Whatever the situation, the melting point behavior of **1** is quite amazing for its molecular weight.

In summary, the total synthesis of dodecahedrane has been achieved in 23 steps from cyclopentadienide anion. What of the future? We intend, of course to address some of the many questions relating to dodecahedrane's potentially distinctive physical and chemical properties. Knowledge of the fundamental nature of spherical organic molecules will thereby be advanced. The magnitude of the challenges to be met must not be underestimated, since the present limitations on our supply of **1** are rather restrictive.

Experimental Section

Proton magnetic resonance spectra were obtained with Varian EM-390, Bruker WP-200, and Bruker WM-300 spectrometers; apparent splittings are given in all cases. ^{13}C NMR spectra were recorded on Bruker WP-80, WP-200, and WM-300 spectrometers. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. The Raman spectrum was obtained on a Spectra Physics Model 164 instrument equipped with an argon laser. Elemental analysis were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Methyl Octadecahydro-7-(phenoxymethyl)-3-oxo-1*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalene-7-carboxylate (7) and Methyl Hexadecahydro-9-hydroxy-8-(phenoxymethyl)-1,4,8-methenodipentaleno[1,2,3-*cd*:1′,2′,3′-*gh*]pentalene-4(1*H*)-carboxylate (8). To 120 mL of liquid ammonia (freshly distilled from sodium) cooled to −78 °C was added 100 mg (14.4 mmol) of lithium wire. After the lithium had dissolved, a solution of **2** (1.0 g, 2.36 mmol) in anhydrous tetrahydrofuran (10 mL) was added dropwise until approximately 95% of the diester had been added. After 0.5 h at −78 °C, the remainder of **2** was added dropwise (the final addition should be discontinued at the point where the deep blue color begins to dissipate). A solution of chloromethyl phenyl ether[17] (336 mg, 2.36 mmol) in 5 mL of dry tetrahydrofuran was immediately added at a rapid dropwise rate. After 15 min, solid ammonium chloride (ca. 1.0 %) was added, and the ammonia was evaporated under a stream of argon. The residue was added to dichloromethane (500 mL) and washed with water (2×) and brine. Concentration of the dried organic phase left a clear oil that was subjected to preparative TLC on silica gel (10% dichloromethane–20% ether–70% hexane elution). Two major bands were observed.

(a) $R_f = 0.3$—there was isolated 489 mg (48%) of **7**: mp 153–154.5 °C (from ethyl acetate); IR (KBr, cm^{-1}) 2920, 1735, 1720, 1595, 1238, 745, 680; ^{1}H NMR (CDCl$_3$) δ 7.4–6.7 (m, 5 H), 4.2–1.1 (series of m, 22 H), 3.81 ($^1/_2$AB q, J = 9 Hz, 1 H), 3.79 ($^1/_2$AB q, J = 9 Hz, 1 H), 3.68 (s, 3 H); ^{13}C NMR (ppm, CDCl$_3$) 226.97, 173.44, 158.82, 129.44, 121.25, 115.06, 79.07, 65.24, 61.48, 59.29 (2 C), 57.41, 54.74, 54.31, 54.07, 52.98, 52.80, 51.83, 51.16, 50.73 (2 C), 35.20, 31.19, 31.01, 30.34, 27.73; *m/e* (M$^+$) 432.

Anal. Calcd for C$_{28}$H$_{32}$O$_4$: C, 77.75; H, 7.45. Found: C, 77.83; H, 7.51.

(b) $R_f = 0.5$—there was obtained 224 mg (22%) of **8**: mp 132–133.5 °C from ethyl acetate); IR (KBr, Cm^{-1}) 3480, 2920, 1700, 1598, 1496, 1246, 742, 682; ^{1}H NMR (CDCl$_3$) δ 7.4–6.6 (m, 5 H), 5.29 (s, 1 H), 4.23 ($^1/_2$AB q, J = 11 Hz, 1 H), 4.10 ($^1/_2$AB q, J = 11 Hz, 1 H), 3.67 (s, 3 H), 3.4–0.9 (series of m, 21 H); ^{13}C NMR (ppm, CDCl$_3$) 178.56, 159.73, 129.33, 120.30, 144.82, 82.48, 67.53, 62.82, 62.93, 60.01, 57.09, 56.90 (2 C), 53.79, 53.11, 51.56, 50.54, 49.42, 48.74, 48.35, 48.21, 32.72, 27.19, 26.07, 25.54, 24.18; *m/e* calcd (M$^+$) 432.2300, obsd 432.2310.

Anal. Calcd for C$_{28}$H$_{32}$O$_4$: C, 77.75; H, 7.45. Found: C, 77.78; H, 7.55.

Methyl Octadecahydro-3b-hydroxy-7-(phenoxymethyl)-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-carboxylate (9). A solution of 7 (260 mg, 0.6 mmol) in 20 mL of a dry deoxygenated benzene–*tert*-butyl alcohol solvent system (4:1) containing 2 drops of triethylamine was irradiated with a 450-W Hanovia lamp through Pyrex for 18 h under a nitrogen atmosphere. The resulting solution was concentrated in vacuo to yield the crude product as a crystalline solid. Recrystallization from benzene–ether provided 234 mg (90%) of **9**: mp 122–124 °C; IR (KBr, cm^{-1}) 3420, 2930, 1725, 1595, 1491, 1235; ^{1}H NMR (CDCl$_3$) δ 7.5–6.6 (m, 5 H), 4.0–0.9 (series of m, 22 H), 3.78 (s, 2 H), 3.67 (s, 3 H); ^{13}C NMR (ppm, CDCl$_3$) 173.68, 158.82, 129.38, 121.13, 115.06, 97.95, 79.92, 79.13, 64.81, 64.14 (2 C), 63.24, 55.34, 53.89, 51.10, 50.79, 31.92, 29.98; *m/e* calcd (M$^+$) 432.2300, obsd 432.2310.

Methyl 1,1a,1b,2,3,3a,4,5,5a,6,6a,6b,6c,6d,6e,6f-Hexadecahydro-7-(phenoxymethyl)-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-carboxylate (10). A solution of **9** (250 mg, 0.58 mmol) and *p*-toluenesulfonic acid (10 mg) in 25 mL of dry benzene was heated to 70 °C under argon for 8 h. The solvent was evaporated in vacuo to give the crude product as a crystalline solid. Recrystallization from ethyl acetate provided pure **10** (223 mg, 93%): mp 155.5–157 °C; IR (KBr, cm^{-1}) 2940, 1728, 1601, 1241, 1221, 1111, 745, 683; ^{1}H NMR (CDCl$_3$) δ 7.4–6.6 (m, 5 H), 4.1–1.1 (series of m, 20 H), 3.82 ($^1/_2$AB q, J = 7.5 Hz, 1 H), 3.69 ($^1/_2$AB q, J = 7.5 Hz, 1 H), 3.60 (s, 3 H); ^{13}C NMR (ppm, CDCl$_3$) 173.71, 158.90, 139.92, 137.10, 129.38, 121.13, 115.16, 80.25, 72.39, 69.62, 63.50, 63.16, 62.58 (2 C), 55.39, 53.40, 52.67, (2 C), 51.02, 48.89, 48.55, 47.04, 30.24, 29.18, 28.30, 24.32; *m/e* calcd (M$^+$) 414.2195, obsd 414.2210.

Methyl Octadecahydro-7-(phenoxymethyl)-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-carboxylate (11). To a cold (0 °C) solution of **10** (240 mg, 0.58 mmol) in 35 mL of an ethanol–tetrahydrofuran mixture (2.5:1) was added anhydrous hydrazine (97%, 1.6 mL). Hydrogen peroxide (30%, 5.7 mL) was introduced dropwise to the cooled reaction mixture over a period of 1 h with stirring. After the addition was complete, the cooling bath was removed and the reaction mixture was stirred overnight at 25 °C, diluted with dichloromethane (200 mL), and washed with water (2×) and brine. The organic phase was dried, filtered, and concentrated in vacuo to afford the product as a crystalline solid. Recrystallization from ethyl acetate give pure **11** (220 mg, 91%): mp 162–164 °C; IR (KBr, cm^{-1}) 2941, 1731, 1496, 1241, 748; ^{1}H NMR (CDCl$_3$) δ 7.4–6.6 (m, 5 H), 4.0–0.8 (series of m, 22 H), 3.78 (s, 2 H), 3.64 (s, 3 H); ^{13}C NMR (ppm, CDCl$_3$) 173.85, 158.95, 129.38, 121.03, 115.16, 79.09, 70.40, 66.46, 64.23, 63.40, 57.38, 54.96, 52.92, 51.07, 50.64, 49.71, 31.36, 30.39; *m/e* calcd (M$^+$) 416.2351, obsd 416.2362.

Anal. Calcd for C$_{28}$H$_{32}$O$_3$: C, 80.73; H, 7.74. Found: C, 80.57; H, 7.65.

Octadecahydro-7-(phenoxymethyl)-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-methanol. A solution of **11** (220 mg, 0.53 mmol) in anhydrous benzene (10 mL) was stirred at room temperature while diisobutylaluminum hydride (2.65 mL of 1 M in hexane, 2.65 mmol) was introduced. The reaction mixture was stirred at 25 °C for 12 h under argon, treated dropwise with methanol to destroy excess hydride, and poured into dichloromethane (200 mL). The organic layer was washed with dilute hydrochloric acid (2×), water, and brine prior to drying. Solvent evaporation left 200 mg (97%) of the carbinol as a crystalline solid: mp 92–94 °C; IR (KBr, cm^{-1}) 3400, 2930, 1599, 1497, 1240, 746, 685; ^{1}H NMR (CDCl$_3$) δ 7.4–6.7 (m, 5 H), 4.33 (s, 2 H), 4.0–1.1 (series of m, 23 H), 3.60 (s, 2 H); ^{13}C NMR (ppm, CDCl$_3$) 159.05, 129.48, 120.98, 114.92, 78.21, 70.54, 67.00, 64.86, 61.61, 61.22, 57.58, 53.55, 51.85, 51.56, 50.98, 31.60, 30.88; *m/e* calcd (M$^+$) 388.2402, obsd 388.2411.

Octadecahydro-7-(phenoxymethyl)-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-carboxaldehyde (12). A solution of the preceding carbinol (200 mg, 0.52 mmol) in 5 mL of dichloromethane was added to a suspension of pyridinium chlorochromate (200 mg, 0.93 mmol) in 10 mL of the same solvent with stirring under argon. After 1.5 h, ether was added and the organic layer was decanted. The residual salts were washed with ether (2×), and the combined organic solutions were washed with dilute hydrochloric acid, saturated sodium bicarbonate solution (2×), water, and brine. Following drying and solvent evaporation, the crude product was filtered through a short silica gel column (10% ether in hexane elution) to give 191 mg (95%) of **12**: 159–161 °C (from ethyl acetate); IR (KBr, cm^{-1}) 2930, 1710, 1492, 1263, 738, 679; ^{1}H NMR (CDCl$_3$) δ 10.17 (s, 1 H), 7.4–6.6 (m, 5 H), 3.9–1.1 (series of m, 22 H), 3.68 (s, 2 H); ^{13}C NMR (ppm, CDCl$_3$) 206.15, 158.82, 129.50, 114.88, 78.65, 66.88, 64.69, 57.73, 54.80, 52.61, 50.25, 49.88, 31.98, 30.58 (3 signals not observed); *m/e* calcd (M$^+$) 386.2246, obsd 386.2237.

Octadecahydro-7f-(phenoxymethyl)-1,6,7-metheno-1*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalen-2-ol (13). A cold (−78 °C) solution of **12** (195 mg, 0.51 mmol) in 20 mL of a deoxygenated 9:1 toluene–ethanol solvent system was irradiated under nitrogen with a 450-W Hanovia lamp through Pyrex. After a 5-h reaction period, the solution was allowed to warm to 25 °C and the solvent was removed under reduced pressure. Preparative TLC on silica gel (elution with 10% dichloromethane–15% ether–75% hexane) gave three bands. At $R_f = 0.8$, a mixture of decarbonylated materials (45 mg) was obtained. The R_f

= 0.6 band comprised alcohol **13** (70 mg, 36%) as an oil: IR (neat, cm^{-1}) 3580, 2930, 1600, 1495, 1233, 743, 681; ^{1}H NMR (CDCl$_3$) δ 7.4–6.6 (m, 5 H), 4.41 (d, J = 6 Hz, 1 H), 4.1–1.0 (series of m, 22 H), 3.78 ($^1/_2$AB q, J = 9 Hz, 1 H) 3.62 ($^1/_2$AB q, J = 9 Hz, 1 H); ^{13}C NMR (ppm, CDCl$_3$) 159.14, 129.58, 121.23, 114.92, 85.49, 84.43, 68.74, 67.87, 67.00, 66.41, 63.11, 62.63, 60.73, 59.23, 57.00, 55.30, 53.55, 53.21, 52.63, 50.34, 32.58, 32.33, 31.75 (2 signals not observed); *m/e* calcd (M$^+$) 386.2246, obsd 386.2253. The R_f = 0.5 band proved to be the precursor alcohol (42 mg, 21%) formed by photoreduction.

Birch Reduction of 13. A solution of **13** (325 mg, 0.84 mmol) in dry tetrahydrofuran (10 mL) was added to 50 mL of liquid ammonia (freshly distilled from sodium). Additional tetrahydrofuran was added as required to ensure complete dissolution of the alcohol. The solution was allowed to reflux gently under argon as lithium wire (118 mg, 16.8 mmol) was added in small pieces over 5 min. After an additional 15 min, absolute ethanol (1 mL) in 1 mL of dry tetrahydrofuran was added dropwise over a 30-min period. (Additional ethanol should be added as required to completely discharge the blue color.) The ammonia was evaporated under a stream of argon and the residue was diluted with water and extracted with dichloromethane (3×). The combined organic portions were washed with water and brine. Concentration of the dried organic phase left the product as a white foam (328 mg, 100%) that was used directly in the next step: IR (CDCl$_3$, cm^{-1}) 3550, 2900, 1685, 1180, 1165, 900, 720; ^{1}H (CDCl$_3$) δ 5.6 (s, 2 H), 4.7–4.5 (br s, 1 H), 4.3–4.2 (m, 1 H), 3.6–2.1 (series of m, 28 H).

Octadecahydro-2-hydroxy-1,6,7-metheno-1*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalene-1-methanol (14). A solution of the Birch product (135 mg, 0.35 mmol) in 20 mL of tetrahydrofuran was treated with 3 M hydrochloric acid (1 mL). The resulting solution was stirred at 25 °C for 3 h and poured into dichloromethane (30 mL). The solution was washed with water and saturated sodium bicarbonate solution (2×) prior to drying. Solvent evaporation left 107 mg (99%) of **14** as a crystalline solid that softens at 172 °C, then first melts at 256.5–257 °C, and finally decomposes at 264–265.5 °C: IR (KBr, cm^{-1}) 3380, 2920, 1040; ^{1}H NMR (CDCl$_3$) δ 4.35 (d, J = 6 Hz, 1 H), 3.8–1.7 (series of m, 25 H); ^{13}C NMR (ppm, CDCl$_3$) 86.12, 80.01, 68.74, 67.77, 66.99, 66.37, 63.02, 62.48, 60.39, 62.48, 60.39, 59.18, 56.99, 55.25, 53.60, 53.11, 52.82, 50.34, 32.62, 32.28, 31.70 (2 signals not observed); *m/e* calcd (M$^+$) 310.1933, obsd 310.1941.

Octadecahydro-2-oxo-1,6,7-metheno-1*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalene-1-carboxaldehyde (15). A solution of **14** (107 mg, 0.34 mmol) in 2 mL of dichloromethane was added to a suspension of pyridinium chlorochromate (298 mg, 1.38 mmol) in 10 mL of the same solvent with stirring under argon. After 4 h, ether was added and the organic layer was decanted. The residual salts were washed with ether (3×), and the combined organic solutions were washed with dilute hydrochloric acid (2×), saturated sodium bicarbonate solution (2×), water and brine. Following drying and solvent evaporation, the crude product was filtered through a short silica gel column (25% ether in hexane elution) to give 81 mg (77%) of **15** as a white solid that was used directly: IR (CDCl$_3$, cm^{-1}) 2940, 1730, 1700, 1450; ^{1}H NMR (CDCl$_3$) δ 9.50 (s, 1 H), 4.2–1.2 (series of m, 22 H).

Octadecahydro-1,6,7-metheno-2*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalen-2-one (16). A suspension of **15** (70 mg, 0.23 mmol) in 6 mL of absolute ethanol was treated with tetrahydrofuran until dissolution occurred. To the resulting solution was added potassium hydroxide (15 mg, 0.26 mmol) dissolved in 6 mL of absolute ethanol. After the solution was stirred under argon at 25 °C for 5 h, water was added and the solution was extracted with dichloromethane (3×). The combined organic extracts were washed with water (2×) and brine prior to drying and solvent evaporation. Purification by preparative TLC (10% dichloromethane–40% ether–50% hexane elution) yielded 31 mg (48%) of **16**, which decomposes above 226 °C without melting (from ether): IR (KBr, cm^{-1}) 2920, 1710, 1445, 690; ^{1}H NMR (CDCl$_3$) δ 3.9–1.4 (series of m, 22 H); ^{13}C NMR (ppm, CDCl$_3$) 228.57, 69.66, 68.65, 67.87, 67.35, 65.30, 61.22, 59.31, 59.23, 58.36, 57.90, 55.88, 54.43, 52.41, 52.15, 50.90, 49.69, 37.18, 31.43, 27.44; *m/e* calcd (M$^+$) 278.1671, obsd 278.1685.

Hexadecahydro-1,6,2,5-ethanediylidenecyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalen-3b(1*H*)-ol (17). A solution of **16** (28 mg, 0.1 mmol) in 10 mL of a deoxygenated benzene–*tert*-butyl alcohol solvent system (4:1) containing 2 drops of triethylamne was irradiated with a 450-W Hanovia lamp through Pyrex for 10 h under a nitrogen atmosphere. The solvent was removed in vacuo to give 28 mg (100%) of **17** as a crystalline solid: mp >350 °C; IR (KBr, cm^{-1}) 3320, 2920, 1000, 990; ^{1}H NMR (CDCl$_3$) δ 3.6–2.8 (m, 18 H), 1.8–1.3 (m, 4 H); ^{13}C NMR (ppm, CDCl$_3$) 98.02, 79.47, 69.38, 68.41, 65.98, 64.18, 64.08, 60.73, 60.06, 53.11, 48.98, 31.99; *m/e* calcd (M$^+$) 278.1671, obsd 278.1680.

1,1a,1b,2,3,3a,4,5,5a,6,6a,6b,6c,6d,6e,6f-Hexadecahydro-1,6,2,5-ethanediylidenecyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]-pentalene (18). A solution of **17** (31 mg, 0.11 mmol) in 15 mL of dry benzene was treated with a few crystals of *p*-toluenesulfonic acid and heated to reflux for 1.25 h. The cooled solution was diluted with dichloromethane and washed with saturated sodium bicarbonate solution (2×) and water. Drying and solvent removal yielded 29 mg (100%) of **18**, which could be recrystallized from hexane: mp >350 °C; IR (KBr, cm^{-1}) 3020, 2920, 1485, 1440, 750, 690; ^{1}H NMR (CDCl$_3$) δ 4.0–2.7 (series of m, 16 H), 2.1–1.2 (series of m, 4 H); ^{13}C NMR (ppm, CDCl$_3$) 142.44, 141.18, 70.74, 67.72, 67.19, 66.71, 65.78, 64.13, 62.92, 61.03, 60.35, 59.08, 58.74, 56.75, 52.53, 51.95, 50.54, 48.21, 33.11, 30.29; UV (isooctane) max 210 nm (ϵ 7670); *m/e* calcd (M$^+$) 260.1565, obsd 260.1571.

Octadecahydro-1,6,2,5-ethanediylidenecyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene (19). To a cold (0 °C) solution of **18** (29 mg, 0.11 mmol) in 14 mL of an ethanol–tetrahydrofuran mixture (5:1) was added anhydrous hydrazine (97%, 450 μL). Hydrogen peroxide (30%, 1.52 mL) was introduced dropwise to the cooled reaction mixture over a period of 45 min with stirring. Following the addition, the reaction mixture was allowed to warm to 25 °C, and stirring was maintained overnight. The reaction mixture was diluted with dichloromethane and washed with water (2×) and brine prior to drying and solvent evaporation. Preparative TLC (5% dichloromethane in hexane elution) afforded 19 mg (66%) of **19** as a crystalline solid: mp >360 °C; IR (KBr, cm^{-1}) 3030, 2940, 2860, 1490, 1450, 700; ^{1}H NMR (CDCl$_3$) δ 3.5–2.9 (series of m, 20 H), 1.6–1.4 (m, 2 H); ^{13}C NMR (ppm, CDCl$_3$) 69.56, 68.25, 65.91, 61.90, 52.86, 49.89, 31.91; *m/e* calcd (M$^+$) 262.1721, obsd 262.1729.

Undecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]eicosane (Dodecahedrane, 1). An intimate mixture of **19** (1 mg, 0.004 mmol) and 10% palladium on carbon (ca. 100 mg) was placed in a stainless steel reactor and flushed with argon. The catalyst bed was then saturated with hydrogen gas (50 psi) and the reactor sealed. The reaction vessel was lowered into a molten salt bath maintained at 250 °C. After 4.5 h, the reactor was removed and allowed to cool. The contents were placed on a short silica gel column and washed with hexane to provide 1 mg of the product mixture that contained 40–50% of **1** (NMR analysis). A total of 4.5 mg of **19** was treated in this way. From the combined reaction mixtures, 1.5 mg of **1** (34%) was obtained by crystallization from benzene: IR (KBr, cm^{-1}) 2945, 1298, 728; Raman (cm^{-1}) 2954, 2938, 1324, 1164, 1092, 840, 676, 480; ^{1}H NMR (CDCl$_3$) δ 3.38 (s); ^{13}C NMR (ppm, CDCl$_3$) 66.93, (d, J_{CH} = 134.9 Hz); *m/e* calcd (M$^+$) 260.1565, obsd 260.1571.

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