ponents [(*E*)- and (*Z*)-**9d**: each M^+ (*m/z*) 254].

Reactions of 3 and 4 with 9,10-Phenanthrenequinone (eq 3). The stannyl reagent **3** (179 mg, 0.48 mmol) was added to a dichloromethane solution (12 mL) of the quinone (83.2 mg, 0.4 mmol) and BF_3·OEt_2 (170 mg, 1.2 mmol) at −78 °C under N_2. The reaction mixture was warmed to −45 °C and then quenched with a saturated aqueous NaCl solution, followed by the usual workup. The product was isolated by preparative TLC, developing with 1:1 ether/hexane. The R_f 0.65 band contained 103 mg (88%) of γ-adduct **11**, pale yellow prisms: mp 133–135 °C; NMR ($CDCl_3$) δ 0.68, 1.25 (each m, 7 H, $CH_2CH_2CH_3$), 2.20 (m, 1 H, CH), 4.10 (s, 1 H, OH), 4.42–5.00 (m, 2 H, C=CH_2), 5.53 (m, 1 H, CH=C), 7.33–8.00 (m, 8 H, Ar H); IR (KBr) 3490, 2940, 1685, 1600, 1443, 1000, 920, 763, 730 cm^{-1}.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 81.77; H, 7.21.

The reaction with stannyl reagent **4** was performed according to the same procedure described above. Workup afforded **11** (73 mg, 63%).

Reactions of Neryltributylstannane (5) and Geranyltributylstannane (6) with Quinones. A. The stannyl reagent **5** was added to 1,2-naphthoquinone, **1a**, and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general reaction procedure. After acetylation, the product was isolated and purified by preparative TLC (developing twice with 3:2 ether/hexane) to afford **12**: 66% $\Delta^{2'}$-*Z*; a pale yellow oil; NMR (CCl_4) δ 1.60 (s, terminal *trans*-CH_3), 1.66 (s, *cis*-CH_3), 1.74 (s, CH_3 nearest ring), 2.16 (br, CH_2CH_2), 2.23 (s, $OCOCH_3$), 2.35 (s, $OCOCH_3$), 3.75 (d, CH_2, *J* = 8 Hz), 5.42 (m, olefinic H), 7.27–8.15 (m, Ar H); IR ($CHCl_3$) 2950, 2925, 1770, 1605, 1458, 1365, 1187 cm^{-1}.

B. The stannyl reagent **6** was added to **1a** and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general procedure. After acetylation, the product was isolated by preparative TLC (developing twice with 3:2 ether/hexane) to afford **12**: 95% $\Delta^{2'}$-*E*.

C. The stannyl reagent **5** was added to *p*-benzoquinone, **2a**, and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general procedure. After acetylation, the product was isolated and purified by preparative TLC (developing with chloroform) to afford **13**: 68% $\Delta^{2'}$-*Z*; oil; NMR (CCl_4) δ 1.54 (s, terminal *E*-CH_3), 1.60 (s, *Z*-CH_3), 1.71 (s, CH_3 nearest ring), 2.04 (s, CH_2CH_2), 2.13 (s, $OCOCH_3$), 2.15 (s, $OCOCH_3$), 3.12 (d, CH_2, *J* = 7 Hz), 5.05 (m, olefinic H), 6.78 (m, Ar H); IR ($CHCl_3$) 2952, 2920, 1758, 1485, 1365, 1168, 1010 cm^{-1}.

D. The stannyl reagent **6** was added to **2a** and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general procedure. After acetylation, the product was isolated by preparative TLC (developing with chloroform) to afford **13**: 96% $\Delta^{2'}$-*E*; oil.

E. The stannyl reagent **5** was added to 2-methyl-1,4-naphthoquinone, **2d**, and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general procedure. After oxidation with Ag_2O, the product was isolated and purified by preparative TLC, developing twice with 2:3 ether/hexane. The R_f 0.78 band contained vitamin $K_{2(10)}$: 67% $\Delta^{2'}$-*Z*; all spectral data were coincident with the reported values.[2c]

F. The stannyl reagent **6** was added to **2d** and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general procedure. After oxidation with Ag_2O, the product was isolated by preparative TLC, developing with 3:7 ether/hexane. The R_f 0.77 band contained vitamin $K_{2(10)}$: 97% $\Delta^{2'}$-*E*; all spectral data were coincident with the reported values.[1a,2c]

Reactions of 5 and 6 with 9,10-Phenanthrenequinone (eq 4). The stannyl reagent **5** (154 mg, 0.36 mmol) was added to a CH_2Cl_2 (12 mL) of the quinone (62.4 mg, 0.3 mmol) and BF_3·OEt_2 (128 mg, 0.9 mmol) at −78 °C under N_2. The reaction mixture was warmed to −50 °C and then quenched with a saturated aqueous NaCl solution (3 mL), followed by the usual workup. The product was isolated and purified by preparative TLC, developing twice with 1:4 ether/hexane. The R_f 0.70 band contained 56 mg (54%) of **14**: a pale yellow oil; NMR (CCl_4) δ 1.20, 1.48, 1.58, 1.69 (each s, total 9 H, side chain CH_3), 1.87 (br, 4 H, CH_2CH_2), 2.44 (d, 2 H, $ArCH_2$, *J* = 8 Hz), 3.97 (s, 1 H, OH), 4.98 (br m, 2 H, olefinic H), 7.30–8.00 (m, 8 H, Ar H); IR (CCl_4) 3500 (OH), 2960, 2910, 1692, (C=O), 1600, 1450 cm^{-1}.

Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.51; H, 7.71.

The reaction of stannyl reagent **6** (205 mg, 0.48 mmol) with 9,10-phenanthrenequinone (83.2 mg, 0.4 mmol) in the presence of BF_3·OEt_2 (170 mg, 1.2 mmol) was performed according to the same procedure described above. Workup as above afforded **14** (85 mg, 62%).

Directed Alkyl Substitution of the Dodecahedrane Nucleus. The 1,4-Dimethyl, 1,6-Dimethyl, and 1,4,16-Trimethyl Derivatives. Indanododecahedrane by Stepwise Dehydrogenation of a Benzylated Seco Derivative

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A 1:1 mixture of finely divided titanium metal and 5% platinum on alumina catalyzes the dehydrocyclization of secododecahedrane **3** to 1,6-dimethyldodecahedrane (**4**). A small quantity (10–15%) of the monomethyl derivative is coproduced. This demethylation process could be used to synthetic advantage when applied to the trimethyl-substituted secododecahedrane **11**, the synthesis of which is first detailed. Heating **11** with the catalyst system at 200 °C (two passes of 36-h duration) affords 1,3,16-trimethyldodecahedrane (**12**) and the 1,4-dimethyl derivative (**13**). These hydrocarbons were separated by fractional crystallization and characterized spectroscopically. The spectral properties of the three known dimethyldodecahedranes are correlated. A preparation of benzylsecododecahedrane **26** is also detailed. Heating of **26** at 200 °C with the preceding catalyst system leads efficiently to benzyldodecahedrane. Stepwise dehydrogenation has also proven feasible as shown by independent conversion to 2,3-indanododecahedrane at 260 °C. The ready formation of a 1,2-disubstituted dodecahedrane is thereby demonstrated.

Historical documentation of attempts by organic chemists to prepare dodecahedrane is rich and varied.[1] The central importance of the polycyclopentanoid $(CH)_{20}$ array that characterizes this molecule has fostered the development of many creative strategies, only one of which has been sucessful to date. In 1981, we reported acquisition of the 1,16-dimethyl derivative and detailed its three-di-

(1) Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189.

0022-3263/87/1952-1265$01.50/0

Table I. ^{1}H NMR and ^{13}C NMR Data (300-MHz) for the Known Dimethyldodecahedranes

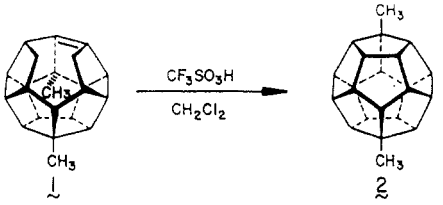
compd	symmetry	proton shifts, δ	carbon shifts, ppm
2[a]	D_{3d}	3.44 (m, 12 H), 2.93 (m, 6 H), 1.19 (s, 6 H)	76.08, 74.57, 67.38, 32.82
4[b]	C_{2v}	3.41 (m, 12 H), 2.90 (m, 6 H), 1.14 (s, 6 H)	75.06, 74.94, 74.85, 67.43, 66.99, 66.66, 66.24, 32.54
13[b]	C_s	3.34 (m, 13 H), 2.98 (m, 2 H), 2.88 (m, 2 H), 2.49 (d, J = 10.6 Hz, 1 H), 1.15 (s, 6 H)	82.57, 75.64, 74.94, 74.51, 67.45, 67.30, 67.01, 66.94, 66.75, 66.51, 66.24, 65.86, 33.12

[a] In C_6D_6 solution (ref 4d). [b] In $CDCl_3$ solution.

mensional structure as determined by X-ray analysis.[2] Disclosures that methyldodecahedrane[3] and the parent hydrocarbon itself[4] had been prepared and characterized soon followed.[5] The exceptional symmetry (I_h, icosahedral) and essentially complete lack of angular strain in dodecahedrane have more recently been confirmed by crystallographic techniques.[6]

One of the more remarkable transformations important to the Paquette approach is a dehydrocyclization to introduce the final carbon–carbon bond. Originally, this was achieved through the agency of hydrogen-presaturated 10% palladium on carbon at elevated temperatures. A more effective protocol, developed subsequently to bypass certain limitations of this process, involves utilization of a mixture of finely divided titanium metal and 5% platinum on alumina as the dehydrogenation agent.[7] This metal combination holds exceptional promise for several reasons. The first is that it is far less scale-limited than its predecessor. The second serviceable aspect is its efficacy toward controlled dehydrogenation. The third is its ability to accomplish demethylation in a regioselective manner.

The latter venture has been motivated by our earlier finding that trifluoromethanesulfonic acid dissolved in methylene chloride acts on 1 to give predominantly the most highly symmetric cyclized product 2.[2b] As noted in

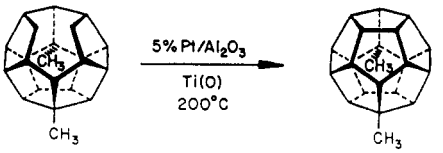


1 2

that report, methyl migration could have operated prior to formation of the final dodecahedrane C–C bond or, somewhat more plausibly, after the C_{20} framework had been assembled. Suitable investigation of this Wagner–Meerwein rearrangement process requires the availability of several dimethyldodecahedranes in addition to 2. A complete account of the synthesis of the 1,4 and 1,6 isomers is provided herein. These developments constitute the first stage of our overall plan to delve into this interesting mechanistic question.

Results

Preparation of Di- and Trimethylated Dodecahedranes. Diimide reduction of 1 in the predescribed manner[2b] provided 3. Dehydrocyclization of this secododecahedrane with an intimate 1:1 mixture of 5% platinum on alumina and zerovalent titanium powder at 200 °C for 8 h in the absence of air afforded 4 in 74% isolated yield.



3 4

Methyldodecahedrane, the end result of single-stage dealkylation, was produced concurrently to the extent of 10–15%. The 300-MHz ^{1}H NMR spectrum of 4 features the expected low-field multiplet attributable to the 12 sterically unperturbed ring hydrogens, a somewhat more shielded six-proton absorption due to those hydrogens flanking the alkyl substituents, and a sharp singlet of area 6 arising from the symmetrically disposed methyl groups (see Table I). When the off-resonance-decoupled ^{13}C NMR spectrum of 4 was seen to consist of eight lines, it was made clearly apparent that the product was of C_{2v} symmetry. Therefore, no alkyl migration transpires as a result of these ring closure conditions.

The partial conversion of 3 to methyldodecahedrane, although not further investigated per se, alerted us to a possible synthetic application of the process. If a trimethylsecododecahedrane could be constructed without undue complication and one of its pendant substituents subsequently excised with good regioselectivity, an otherwise less accessible dimethyl derivative could result. Our attention was directed to 11 in anticipation of a correlation between steric accessibility to the catalyst and rate of alkyl group cleavage. Indeed, formation of 13 by this methodology has proven feasible.

The known methyl octadecahydro-3a,6d,7-trimethyl-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-carboxylate[2b] was treated sequentially with diisobutylaluminum hydride and pyridinium chlorochromate. Aldehyde **5b** was obtained efficiently. Because of its inherent dissymmetry, **5b** exhibits a 21-line (two carbons overlap) ^{13}C NMR spectrum with the aldehyde carbonyl absorption apparent at 204.21 ppm. The presence of this functional group was also evident in its infrared (1712 cm^{-1}) and ^{1}H NMR spectra (δ 9.92 s). In parallel with the behavior of lesser substituted analogues, low-temperature irradiation of **5b** eventuates predominantly in decarbonylation. Notwithstanding, it was possible to realize in 28% combined yield the formation of four stereoisomeric cyclopentanols. Their separation was not attempted. Instead, oxidation was effected to

(2) (a) Paquette, L. A.; Balogh, D. W.; Usha, R.; Kountz, D.; Christoph, G. G. *Science (Washington, D. C.)* **1981**, 211, 575. (b) Paquette, L. A.; Balogh, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 774. (c) Christoph, G. G.; Engel, P.; Usha, R.; Balogh, D. W.; Paquette, L. A. *Ibid.* **1982**, *104*, 784.

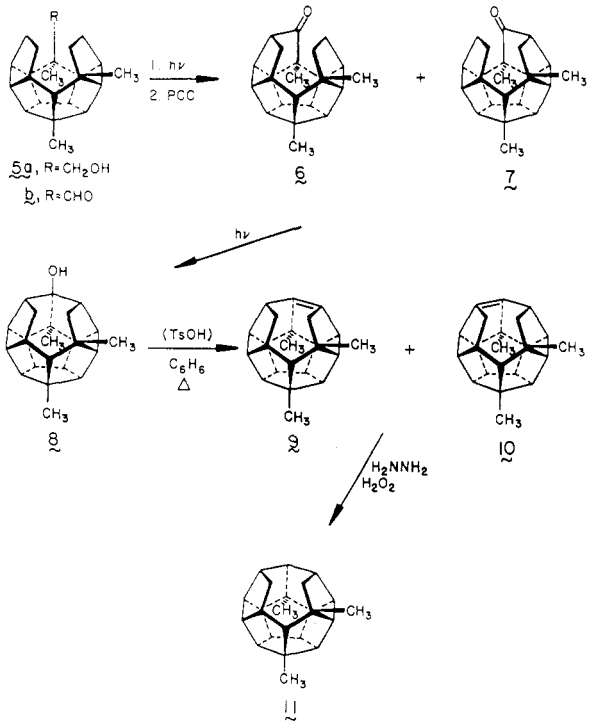
(3) (a) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 4502. (b) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W. *Ibid.* **1883**, *105*, 5541.

(4) (a) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503. (b) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *Ibid.* **1983**, *105*, 5446.

(5) Overviews: (a) Paquette, L. A. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 4495. (b) Paquette, L. A. *Chem. Aust.* **1983**, *50*, 138. (c) Paquette, L. A. In *Strategies and Tactics of Organic Synthesis*; Lindberg, T., Ed.; Academic Press: New York, 1984; pp 175–200.

(6) Gallucci, J. C; Doecke, C. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1986**, *108*, 1343.

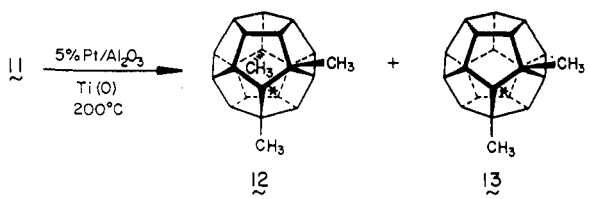
(7) Paquette, L. A.; Miyahara, Y.; Doecke, C. W. *J. Am. Chem. Soc.* **1986**, *108*, 1716.



provide ketones **6** and **7**. ^{1}H NMR analysis of this mixture indicated that one of these two trisecododecahedranes predominated heavily. Its specific substitution plan was not deduced. Rather, the **6**/**7** pair was irradiated as before so as to arrive at the single, homogeneous seco alcohol **8**.

Acid-catalyzed dehydration of **8** in refluxing benzene preceeded smoothly to make available the inseparable mixture of olefins **9** and **10**. The stage was now set for diimide reduction to **11**. By every standard, the methylene groups in **11** experience an enormously heightened level of steric compression.[2c] These factors are reflected in its ^{1}H NMR spectrum wherein the 19 framework hydrogens appear as an extended series of overlapping multiplets in the region from δ 3.8 to 0.5.

The practicalities of preparatively useful dehydrogenative cyclization and regiocontrolled demethylation now surfaced. In actual fact, the experimental conditions first tried proved entirely workable. Thus, heating **11** with the Pt/Ti mixture at 200 °C for 36 h, followed by isolation and reapplication to a new sample of catalyst for a second iteration of the thermal treatment, in fact gives rise to a mixture of **12** and **13**. The optimal method for separation



of these hydrocarbons rests on selective crystallization from benzene–ethanol. With proper solvent partitioning, the more symmetric, less soluble **13** (40%) can be freed of the more soluble trimethyldodecahedrane **12** (23%). The spectral properties of both compounds rigorously define their dodecahedrane nature. As summarized in Table I, **13** displays the 13 carbon signals demanded by its C_s symmetry. Moreover, its ^{1}H NMR spectrum features a doublet due to H* that is shifted to substantially higher field (δ 2.50) from the other protons on the sphere. The lessened ability of eclipsing C–C bonds (relative to C–H bonds) to deshield flanking hydrogen atoms has earlier been demonstrated.[2-4] In **12**, the cumulative influence of *two* methyl groups acting simultaneously on H* should lead to its appearance as a unique signal incrementally displaced by a factor of approximately 2 relative to, for example, those protons immediately surrounding the methyl groups in **2** or **4**. This is indeed the case (Table I). Moreover, this property is shared by H* in **12** and is consequently regarded as a reliable spectral indicator of the 1,4-dimethyl substitution plan. Another striking property of **12** and **13** is their behavior upon mass spectral impact at 70 eV. In a fashion entirely characteristic of **2**, their mass spectra are overwhelmingly dominated by the presence of two intense peaks corresponding to the molecular ion (M^+) and to $M^+ - CH_3$. This dramatic resistance to more extensive fragmentation is not shared by **11** and other secododecahedranes.

The reason for the regioselective demethylation of **12** (or its precursor **11**) appears to reside in the accessibility of the platinum to the C(16)–CH_3 bond. It can be argued that the pair of methyl groups positioned at C(1) and C(4) exert a mutually protective "umbrella" adequate to deter encroachment of Pt into that area of the spherical surface. It can be further postulated that oxidative addition (or other comparable metal insertion process) into either the C(1)–CH_3 or C(4)–CH_3 bond is less ready since a larger group emerges and steric impedance brought on by the nearby methyl rises.[8]

With practical routes to **4** and **13** having been achieved, a remaining issue is their positive identification in mixtures containing **2**, **4**, and **13** and possibly the two additional, still unknown dimethyl isomers. To this time, capillary gas chromatography has not shown signs of being serviceable; coelution is observed. Similarly, ^{1}H NMR cannot be relied upon to provide useful quantitative information because the number of mutually overlapping multiplets is too large. However, it may prove possible to deduce isomer percentages by ^{13}C NMR spectroscopy, provided that appropriate pulse delays are employed. We note (Table I) that methyl absorptions in each of the isomers are adequately separated, this distinction possibly providing a workable solution to this analytical dilemma.

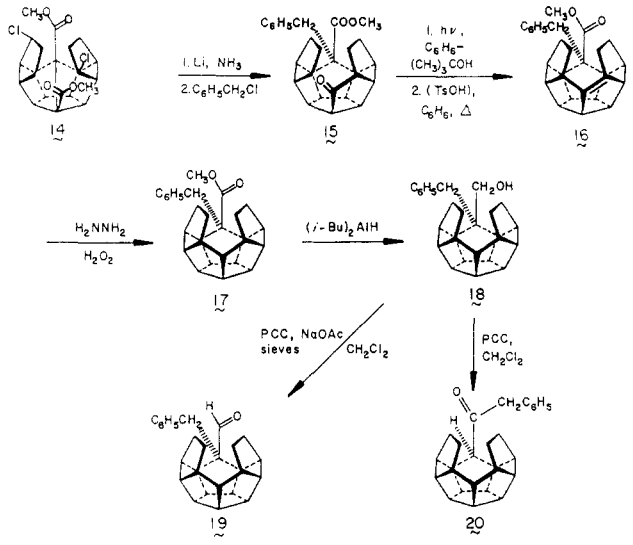
The results of an ongoing investigation that seeks to develop these findings more fully in a mechanistic direction will be disclosed following its successful completion.

Synthesis of Benzyl- and Indanododecahedranes. Reduction of dichloro diester **14** with 6 equiv of lithium metal in liquid ammonia is known to generate a semicyclized dienolate,[9] condensation of which with a limiting amount of electrophile results in kinetically preferred alkylation α to the carbomethoxy group.[3b,8] In the present instance, addition of benzyl chloride (1.5 equiv) to the reactive dianion resulted in immediate fading of the blue color. The major isolated product proved to be the desired keto ester **15** (44%). The use of somewhat more than 1 equiv of the halide was mandated under these circumstances because of competitive stilbene production that consumed some.

With the location of the benzyl group in **15** well-defined by ^{1}H NMR analysis, we next focused our efforts on effecting closure of the more remote surface of the molecular sphere. Irradiation with a 450-W lamp through Pyrex in deoxygenated benzene–*tert*-butyl alcohol (4:1) solution

(8) For the hydrogenolytic removal of methyl and other functional groups from adamantanes, diamantanes, and triamantanes, consult: (a) Maier, W. F.; Grubmuller, P.; Thies, I.; Stein, P. M.; McKervey, M. A.; Schleyer, P. v. R. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 939. (b) Grubmuller, P.; Maier, W. F.; Schleyer, P. v. R.; McKervey, M. A.; Rooney, J. J. *Chem. Ber.* **1980**, *113*, 1989.

(9) Paquette, L. A.; Balogh, D. W.; Ternansky, R. J.; Begley, W. J.; Banwell, M. G. *J. Org. Chem.* **1983**, *48*, 3282.

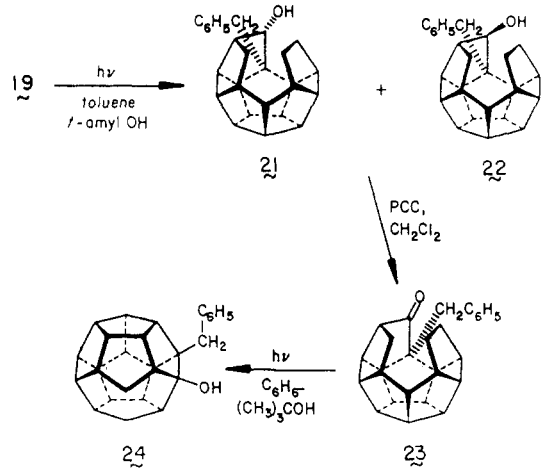


induced photocyclization. Direct dehydration of the tertiary alcohol so formed with *p*-toluenesulfonic acid in benzene gave olefin **16** in 83% overall yield. The structure of the dehydration product must be **16** rather than its more symmetrical isomer since 26 nonequivalent carbon resonances are observed in its ^{13}C NMR spectrum. Subsequent diimide reduction efficiently transformed **16** into **17** with return of planar symmetry as reflected in its simplified ^{13}C NMR spectrum (18 lines).

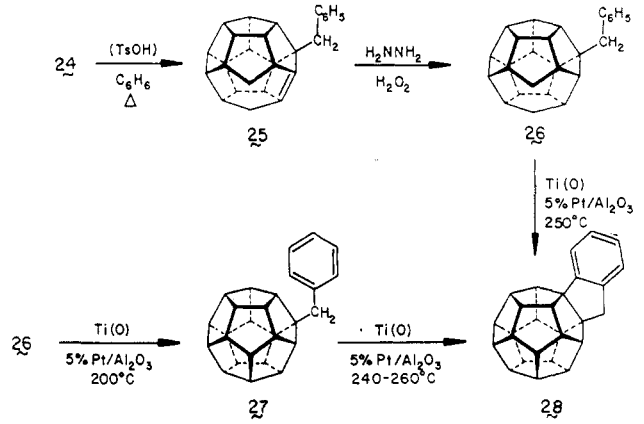
The oxidation level of the carbomethoxy group now had to be adjusted in order to allow implementation of additional framework bond construction. While conversion to alcohol **18** was uneventful, its subsequent oxidation to aldehyde **19** proved highly sensitive to reaction conditions. Many experiments resulted in formation of ill-defined products. Only when pyridinium chlorochromate (PCC) was utilized under buffered (NaOAc) conditions and in the presence of powdered 3 Å molecular sieves could a desirable yield (86%) of **19** be arrived at. By comparison, the use of pyridinium dichromate (PDC) provided **19** in a maximum yield of 54%. The difficulties encountered here appear to have their root cause in the tendency of the benzyl group to undergo 1,2-migration when the carboxaldehyde substituent becomes activated via O-protonation or its equivalent. This reaction course is particularly favored when the oxidation medium is not buffered. For example, PCC in dichloromethane acts on **18** to furnish a ketone tentatively identified as **20**.

As in related examples, the photoactivation of **19** has the potential for engaging three major competing processes: decarbonylation, cyclization, and reduction. The latter option has not proven to be a serious problem. Loss of carbon monoxide, on the other hand, is facile because the α position is fully substituted and tertiary radical production holds thermodynamic appeal. By performing the irradiation of **19** in a 9:1 toluene–*tert*-amyl alcohol solvent system at −60 to −70 °C, this excited-state pathway can be abated to a level that allows the homo-Norrish pathway to be competitive. The epimeric alcohols **21** and **22**, separable by MPLC on silica gel, were obtained in a combined yield of 18%.

Since oxidation of both **21** and **22** results in conversion to **23**, separation of the secondary alcohols ultimately proved unnecessary. The third and final homo-Norrish step proceeded readily to give **24**, dehydration of which led directly to **25** in 84% overall yield. With the acquisition of **25**, diimide reduction was utilized to produce benzylsecododecahedrane **26**. Confirmation that all of the steps had occurred in the chemical sense illustrated in the



formulas as supported by extensive spectral data was secured by X-ray crystal structure analysis of **26** (Figure 1).[10]



The successful conversion of **26** to benzyldodecahedrane (**27**) rests on the availability of an effective transannular dehydrocyclization agent. When an intimate mixture of **20** was heated with hydrogen-presaturated 10% palladium on charcoal (250 °C, 12 h), the catalyst system earlier developed for this purpose,[3,4] the two major resulting products were the parent dodecahedrane hydrocarbon and **28** (relative ratio 40:60). Brief scrutiny of reaction variables indicated that this unacceptable distribution did not improve significantly with alteration of conditions. In contrast, the undesirable features of this important ring closure did not surface when recourse was made alternatively to heating **26** with a 1:1 mixture of 5% platinum on alumina and finely powdered titanium metal. Since experiments conducted with Ti(0) alone led to no chemical change, it is reasonable as expected that the platinum acts as the dehydrogenating agent. Hydrogen is, of course, liberated in this process and hydrogenolysis would be minimized or curtailed if a second metal could absorb this byproduct at elevated temperatures. Zerovalent titanium is well-recognized to be amenable to conversion to a dihydride alloy stable to above 600 °C.[11] For our purposes, finely powdered Ti was required and the material was prepared for us at the Allied Corporation by means of a

(10) Gallucci, J. C., private communication.

(11) (a) Libowitz, G. G. In *Critical Materials Problems in Energy Production*; Stein, C., *Ed.*; Academic Press: New York, 1976; Chapter 28. (b) Libowitz, G. G. *The Solid-State Chemistry of Binary Metal Hydrides*; Benjamin: New York, 1965; p 66. (c) Livanov, V. A.; Bukhanova, A. A.; Kolachev, B. A. *Hydrogen in Titanium*; Israel Program for Scientific Translations: Jerusalem, 1965. (d) Clark, R. J. H. In *Comprehensive Inorganic Chemistry*; 1973; Vol. 3, Chapter 32. (e) Fanelli, A. J.; Maeland, A. J.; Rosan, A. M.; Crissey, R. K. *J. Chem. Soc., Chem. Commun.* **1985**, 8.

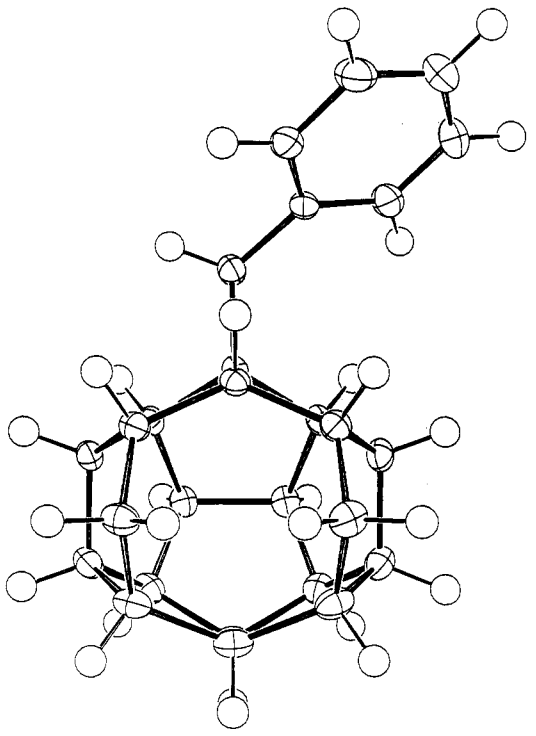


Figure 1. ORTEP drawing of **26**. The hydrogen atoms are drawn with an artificial radius for clarity; the non-hydrogen atoms are presented as 50% probability thermal ellipsoids.

hydriding–dehydriding cycle. The final stage consists of heating TiH_2 (particle size 200 mesh or less) to 600 °C at 10^{-7} torr until all of the hydrogen is evolved. It is imperative that the highly reactive metal so produced be handled under argon at all times to preclude formation of an oxide coating. From the standpoint of chemical efficiency, pure **27** can be easily obtained in high purity at a minimum yield of 64%.

An additional serviceable aspect of this catalyst system is its ability to effect controlled dehydrogenation. Thus, the conversion of **26** to **27** proceeds smoothly at 200 °C for 40 h. At 260 °C, however, additional dehydrocyclization occurs to afford the indano-fused product **28**. This conversion can be realized by commencing either with **26** or **27**. The formation of **28** is particularly notable since it represents a ready means for preparing 1,2-disubstituted dodecahedranes.[7] Such derivatives are normally disadvantaged thermodynamically because of nonbonded steric compression.[12]

The dehydrocyclization of hydrocarbons over heterogeneous platinum catalysts has been extensively studied for small (C_5 and C_6) molecules.[13,14] More recently, attention has turned to homogeneous reactions in an effort to ameliorate reactions conditions.[15,16] An extended Huckel MO analysis of H–H and C–H activation by d^0 metal centers has also just appeared.[17]

A characteristic feature of the influence of hydrogen on the heterogeneous processes, particularly at fairly high partial pressures of H_2, is to suppress reaction because of competitive absorption on the metal surface.[18] We have sought to offset this inhibition by admixing finely divided Ti(0) and allowing for conversion to its dihydride.[11] The ploy has been reasonably effective, although the Pt–Ti system is hardly starved of hydrogen since regioselective hydrogenolytic cleavage is observed in certain examples.[19]

Finally, we do not intend to speculate on whether the ring closure of secododecahedranes proceeds by oxidative addition into the pair of "outside" hydrogens, only the "inside" ones where steric congestion is particularly severe, or a combination of the two. Suffice it to say that rapid H–D exchange processes would cause stereochemical questions of this type to be particularly difficult to answer even if proper isotopic labeling could be accomplished.

Experimental Section

1,6-Dimethyldodecahedrane (4). A 12-mg sample of **3**[2b] was dissolved in benzene (2 mL) and added to 5% platinum on alumina (200 mg, previously dried over P_2O_5 at 110 °C) in a small flask. After solvent evaporation, the powder was transferred to a modified Schlenk-type tube containing 100 mg of active titanium powder under argon. The tube was sealed under vacuum, vigorously shaken for 2 min,[20] and heated in a silicone oil bath at 200 °C for 38 h. The cooled tube was opened and the contents were extracted thoroughly with benzene. The filtered solution gave, after solvent evaporation, 10.7 mg of colorless crystals. purification of this material by reversed phase HPLC (Zorbax ODS, 4.6 × 250 mm, methanol as eluant) returned 8.8 mg (74%) of **4** as colorless meedles, mp 266–268 °C (from ethanol); for ^1H and ^{13}C NMR data, see Table I; MS, m/z calcd (M^+) 288.1978, obsd 288.1981; m/z (relative intensity) 288 (77), 273 (100).

Octadecahydro-3a,6d,7-trimethyl-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-methanol (5a). A solution of the ester[2b] (65 mg, 0.185 mmol) in 5 mL of toluene was cooled to −78 °C and diisobutylaluminum hydride (1 M in hexane, 1 mL, 1.0 mmol) was added. The mixture was stirred at −78 °C for 2 h and allowed to warm to 25 °C for 1 h. After the excess hydride had been quenched with methanol, the reaction mixture was added to 50 mL of methylene chloride and the organic layer was washed with dilute hydrochloric acid, saturated sodium bicarbonate solution, water, and brine. After being dried over magnesium sulfate, the solution was filtered and concentrated in vacuo to give 60 mg of **5a**. Recrystallization from cold ethyl acetate gave analytically pure material, mp 78–79 °C: ^1H NMR (300 MHz, $CDCl_3$) δ 4.20 ($^1/_2$ AB q, J_{AB} = 10.5 Hz, $\Delta\nu_{AB}$ = Hz, 1 H), 4.05 ($^1/_2$ AB q, J_{AB} = 10.5 Hz, $\Delta\nu_{AB}$ = Hz, 1 H), 4.0–0.8 (m, 21 H), 1.39 (s, 3 H), 1.12 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 78.89, 73.1, 68.60, 67.43, 66.22, 65.59 (2C), 65.40, 64.72, 59.13, 58.70, 58.06, 57.00, 52.34, 51.90 (2C), 40.34, 38.16, 35.59, 34.47, 31.12, 30.93, 30.29; MS, m/z calcd (M^+) 324.2453, obsd 324.2461.

Ocdadecahydro-3a,6d,7-trimethyl-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-carboxaldehyde (5b). A solution of alcohol **5a** (60 mg, 0.18 mmol) in 1 mL of methylene chloride was added to a suspension of pyridinium chlorochromate (60 mg, 0.28 mmol) in 5 mL of methylene chloride with stirring under nitrogen. After 1.5 h, ether was added and the organic layer was decanted and washed with dilute hydrochloric acid solution, saturated sodium bicarbonate solution, water, and brine. The solution was dried and filtered. Concentration of the filtrate gave 60 mg (100%) of **5b**

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(20) A WIG-L-BUG apparatus is well-suited to this task.

as a clear oil which crystallized upon standing. Recrystallization from ethyl acetate gave pure aldehyde, mp 96–98 °C: IR (KBr, cm^{-1}) 2905, 2665, 1712, 1450, 1375; ^1H NMR (300 MHz, $CDCl_3$) δ 9.92 (s, 1 H), 4.2–0.8 (m, 20 H), 1.30 (s, 3 H), 1.16 (s, 3 H), 1.10 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 204.21, 78.59, 73.07, 67.06 (2C), 66.45, 65.90, 64.81, 64.21, 64.08, 59.78, 59.47,58.93, 52.37, 51.40, 50.25, 40.72, 35.99, 34.71 (2C), 31.86, 30.83, 29.43; MS, m/z calcd (M^+) 322.2297, obsd 322.2303.

Anal. Calcd for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.75; H, 9.34.

Photolysis of Aldehyde 5b. Octadecahydro-3a,6,7-trimethyl-1,6,7-metheno-1*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalen-2-ol and Its Isomeric Alcohol. Aldehyde **5b** (100 mg) was dissolved in 8 mL of a 9:1 toluene–ethanol solution. The mixture was cooled to −78 °C under nitrogen and irradiated with a 450-W Hanovia lamp through Pyrex. After 2 h, the solution was warmed to 25 °C and the solvent was removed under reduced pressure. Preparative TLC (10% methylene chloride–15% ether–75% hexane) on silica gel gave three bands. The major band (R_f 0.8) was a mixture of decarbonylated materials (50 mg). The other two bands (R_f 0.4 and 0.3) comprised of mixtures of the four expected cyclopentanols (40 mg, 40%); IR (KBr, cm^{-1}) 3400, 2920, 1365, 1083; MS, m/z calcd (M^+) 322.2297, obsd 322.2303. These compounds were directly oxidized.

Octadecahydro-3a,6,7-trimethyl-1,6,7-metheno-2*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalen-2-one (6) and Isomeric Ketone 7. The mixture of four epimeric alcohols (40 mg, 0.12 mmol) was dissolved in 1 mL of dichloromethane and added under nitrogen to a stirred suspension of pyridinium chlorochromate (35 mg, 0.16 mmol) in dichloromethane (5 mL). After 2.5 h, ether (15 mL) was added and the liquid was decanted from the brown salts. The salts were triturated with ether (2×) and the combined ether extracts were washed with dilute hydrochloric acid solution, saturated sodium bicarbonate solution, water, and brine. After being dried over magnesium sulfate, the ether solution was filtered and concentrated in vacuo to give 37 mg (92%) of a pale yellow oil. Preparative TLC on silica gel (10% ether in hexane elution) gave a mixture of the two ketones **6** and **7** (28.5 mg). One isomer apparently predominates (^1H NMR analysis), but the particular isomeric structure could not be assigned to the respective ketone; IR ($CDCl_3$, cm^{-1}) 2925, 1715, 1368; ^1H NMR (200 MHz, $CDCl_3$) δ 3.9–0.6 (m, 19 H), 1.26 (s, 3 H), 1.18 (s, 3 H), 1.14 (s, 3 H); MS, m/z calcd (M^+) 320.2140, obsd 320.2148.

Hexadecahydro-2,6d,7-trimethyl-1,6,2,5-ethanediylidenecyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalen-3b(1*H*)-ol (8). A mixture of isomeric ketones **6** and **7** (10 mg, 0.031 mmol) was dissolved in 3 mL of a solution of benzene (80%) and *tert*-butyl alcohol (20%) and irradiated with a 450-W Hanovia lamp for 16 h through Pyrex. The solvent was removed in vacuo to give a yellow oil which was subjected to preparative TLC on silica gel (elution with 10% ether and 10% dichloromethane in hexane) to give 9 mg (90%) of pure alcohol **8**: IR (KBr, cm^{-1}) 3410, 2940, 1448, 1005; ^1H NMR (200 MHz, $CDCl_3$) δ 4.0–0.8 (m, 19 H), 1.29 (s, 3 H), 1.25 (s, 3 H), 1.17 (s, 3 H); MS, m/z calcd (M^+) 320.2140, obsd 320.2132.

Dehydration of 8. 1,1a,1b,2,3,3c,4,5,5a,6,6a,6b,6c,6d,6e,6f-Hexadecahydro-2,6d,7-trimethyl-1,6,2,5-ethanediylidenecyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene (9) and Isomer 10. To a solution of alcohol **8** (9 mg, 0.028 mmol) in 3 mL of benzene was added one crystal of *p*-toluenesulfonic acid, and the mixture was heated at the reflux temperature for 15 min. The mixture was cooled to 25 °C, added to 20 mL of ether, and washed with saturated sodium bicarbonate solution, water, and brine prior to drying. The solution was filtered and evaporated to dryness under reduced pressure to give 8 mg of a clear oil containing a mixture of isomeric olefins **9** and **10** which could not be separated: ^1H NMR (90 MHz, $CDCl_3$) δ 3.8–0.6 (m, 17 H), 1.21 (s, 9 H); MS, m/z 302.

Hexadecahydro-2,6d,7-trimethyl-1,6,2,5-ethanediylidenecyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene (11). A solution of olefins **9** and **10** (15 mg, 0.05 mmol) was dissolved in 5 mL of ethanol to which 1 mL of ethanol had been added to aid in dissolution. The mixture was cooled to −10 °C and hydrazine (200 μL, 6.25 mmol) was added. Chilled hydrogen peroxide (30%, 680 μL) was added dropwise over a period of 45 min and the resulting solution was stirred for 6 h while being allowed to warm to 25 °C. The reaction mixture was added to water and extracted with pentane (3 × 15 mL). The combined pentane extracts were washed with water (2×) and brine before drying. The solution was filtered and evaporated to dryness in vacuo to give 13 mg (86%) of trimethylsecododecahedrane **11**: ^1H NMR (90 MHz, $CDCl_3$) δ 3.8–0.5 (m, 19 H), 1.26 (s, 3 H), 1.18 (s, 6 H); MS, m/z 304.

Dehydrocyclization of 11. A 15.5-mg sample of **11** was coated onto 200 mg of 5% platinum on alumina by using benzene as solvent. The dried powder was transferred to a modified Schlenk-type containing 100 mg of finely divided titanium under argon. The tube was carefully evacuated and sealed under high vacuum, shaken vigorously for 2 min,[20] and heated in a silicone oil bath at 200 °C for 36 h. The cooled solid mixture was repeatedly extracted with benzene. The concentrated benzene extracts were reapplied to a new batch of catalyst and heated as above at 200 °C for an additional 36 h. Repeated extraction with benzene afforded 11.7 mg of semicrystalline product. A second run was performed in an entirely analogous fashion on 10.2 mg of **11** and 5.6 mg of product was obtained. The combined semisolids were subjected to reverse phase HPLC (Zorbax ODS, 4.6 × 250 mm, methanol as eluent) and subsequently fractionally crystallized from benzene–ethanol. There was isolated 5.9 mg (23%) of the more soluble **12** and 10.3 mg (40%) of the less soluble **13**.

For **12**: colorless needles, mp 208–210 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.52–3.34 (m, 9 H), 3.00–2.87 (m, 7 H), 2.51 (d, J = 10.8 Hz, 1 H), 1.15 (s, 6 H), 1.14 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 82.73, 75,20, 75,18, 75,13, 75,09, 74,74, 67,26, 66.94, 66.85, 66.57, 66.15, 65.99, 33.07, 32.49; MS, m/z calcd (M^+) 302.2079, obsd 302.2029; m/z relative intensity) 302 (93), 287 (100).

For **13**: colorless prisms, mp 315–316 °C; for ^1H and ^{13}C NMR data, see Table I; MS, m/z calcd (M^+) 288.1878, obsd 288.1850; m/z (relative intensity) 288 (88), 273 (100).

Methyl Octadecahydro-7-benzyl-3-oxo-1*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalene-7-carboxylate (15). Lithium metal (100 mg, 14.4 mmol) cut into small pieces was dissolved in cold (−78 °C), freshly distilled liquid ammonia (from sodium, 120 mL). With good mechanical stirring, a solution of **14** (1.00 g, 2.35 mmol) in dry, freshly distilled 1,2-dimethoxyethane (10 mL) was introduced via syringe during 8 min. Stirring was continued for 30 min at −78 °C, at which point benzyl chloride (423 mg, 3.34 mmol) dissolved in 1,2-dimethoxyethane (5 mL) was injected during 15 s. The reaction mixture was stirred at −78 °C for 30 min and at −33 °C for 30 min when it turned a deep pink color. Solid ammonium chloride (1.0 g) was immediately added and the ammonia was allowed to evaporate. The residue was extracted with dichloromethane (3×) and the combined organic layers were washed with water. The dried concentrate was subjected to MPLC on silica gel (elution with ether–dichloromethane–petroleum ether, 1:1:6). There was isolated in order of elution stilbene (99 mg), dibenzylated keto ester, an unknown substance, and finally the desired **15** (430 mg, 44.3%) as colorless prisms, mp 152–153 °C (from ethanol): IR (KBr, cm^{-1}) 2940, 1719, 1452, 1280, 1193, 1094, 719, 702; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 3 H), 7.00 (m, 2 H), 4.0–2.75 (series of m, 13 H), 3.62 (s, 3 H), 2.59 (m, 1 H), 2.16 (m, 1 H), 2.0–1.2 (series of m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 227.29, 174.51, 137.36, 130.13, 127.93, 126.91, 65.19, 62.15, 59.26, 57.22, 55.68, 54.80, 54.57, 54.33, (2C), 53.94, 53.18, 52.45, 50.73, 50.60, 50.53, 35.16, 31.21, 30.94, 30.34, 26.76; MS, m/z calcd ($M^3 - C_6H_5CH_2$) 325.1800, obsd 325.1780.

Anal. Calcd for $C_{28}H_{32}O_3$: C, 80.73; H, 7.74. Found: C, 80.44; H, 7.69.

Methyl 1,1a,1b,2,3,3a,4,5,5a,6,6a,6b,6c,6d,6e,6f-Hexadecahydro-7-benzyl-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-carboxylate (16). A solution of **15** (350 mg, 0.84 mmol) in 10 mL of a *tert*-butyl alcohol–benzene mixture (1:4) contained in a water-jacketed Pyrex photolysis vessel was deoxygenated by bubbling argon through the solution for 30 min. The vessel had previously been rinsed with triethylamine and dried. Irradiation with an external 450-W Hanovia lamp for 23 h resulted in the complete consumption of **15**. The pale yellow solution was evaporated to leave the hydroxy

ester as an oil, which crystallized on standing.

This material was dissolved in benzene (50 mL), treated with *p*-toluenesulfonic acid (40 mg), and heated at the reflux temperature on a Dean–Stark trap for 5 h. The solvent was evaporated and the product was purified by flash chromatography on silica gel (elution with ether–dichloromethane–petroleum ether, 4:4:92). There was isolated 282 mg (83.4%) of **16** as colorless prisms, mp 142–144 °C (from acetone): IR (KBr, cm^{-1}) 2940, 2875, 1705, 1432, 1319, 1260, 1202, 1088, 720, 704; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (m, 3 H), 6.99 (m, 2 H), 3.86 (m, 1 H), 3.61 (br s, 3 H), 3.54 (m, 3 H), 3.20–2.75 (m, 8 H), 2.94 (AB q, J = 12.3 Hz, 2 H), 2.5–1.3 (series of m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 174,52, 140.12, 137.49, 136.90, 130.36, 127.74, 126.85, 72.34, 69.61, 63.31, 63.20, 63.04, 62.70, 59.10, 55.92, 54.16, 52.40, 52.35, 50.30, 48.92, 48.60, 46.90, 30.19, 28.25, 28.20, 24.25; MS, m/z calcd (M^+) 398.2246, obsd 398.2275.

Anal. Calcd for $C_{28}H_{30}O_2$: C, 84.38; H, 7.59. Found: C, 84.24; H, 7.58.

Methyl Octadecahydro-7-benzyl-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-carboxylate (17). A solution of **16** (243 mg, 0.61 mmol) in tetrahydrofuran (5 mL) was diluted with ethanol (25 mL) and cooled to 0 °C under argon. With stirring, this solution was treated with anhydrous hydrazine (1.4 mL) in one portion and 30% hydrogen peroxide (0.52 mL) over a period of 1 h via a syringe. Stirring was continued for an additional hour at 0 °C and then overnight at room temperature. During this time, much of the reduction product precipitated as a white crystalline powder. The reaction mixture was diluted with dichloromethane and water. The aqueous phase was extracted twice with the same solvent and the combined organic layers were washed with water, dried, and concentrated. The product crystallized upon trituration with acetone. The yield of colorless granular crystals was 232 mg (95.1%). Recrystallization from ethanol afforded colorless plates, mp 153–154 °C: IR (KBr, cm^{-1}) 2930, 1734, 1490, 1450, 1429, 1313, 1265, 1188, 1096, 1086, 701; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 3 H), 7.00 (m, 2 H), 3.64 (s, 3 H), 3.8–3.5 (m, 3 H), 3.26 (m, 2 H), 3.20–2.75 (series of m, 9 H), 2.50 (m, 2 H), 2.15 (m, 2 h), 1.95–1.55 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 174.66, 137.61, 130.36, 127.69, 126.75, 70.40, 66.44, 64.22, 64.06, 57.28, 57.12, 54.40, 52.86, 50.73, 50.29, 49.55, 31.24, 30.32; MS, m/z calcd (M^+ – $C_6H_5CH_2$) 309.1854, obsd 309.1850.

Anal. Calcd for $C_{28}H_{32}O_2$: C, 83.96; H, 8.05 Found: C, 83.84; H, 8.01.

Octadecahydro-7-benzyl-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-methanol (18). To a stirred solution of **17** (596 mg, 1.49 mmol) in benzene (20 mL) under an argon atmosphere was added 10 mL of diisobutylaluminum hydride solution (1 N, 10 mmol). The reaction mixture was stirred for 24 h, at which time 10 mL of methanol was slowly introduced. Dichloromethane (20 mL) was immediately introduced, 10% hydrochloric acid (50 mL) was added, and the phases were separated. [Failure to act rapidly allows aluminum salts to precipitate; the solution becomes gelled and redissolution in acid is made difficult.] The aqueous phase was extracted with dichloromethane (3×) and the combined organic layers were washed with water, dried, and filtered through a short column of silica gel. Evaporation of the solvent and trituration of the residue with acetone gave **18** as colorless needles, mp 203–205 °C dec (from acetone): 536 mg (96.7%); IR (KBr, cm^{-1}) 3400, 2930, 1450, 998, 702; IR ($CDCl_3$, cm^{-1}) 3620, 2930, 1494, 1453, 990; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 5 H), 4.15 (s, 2 H), 3.60 (m, 4 H), 2.68 (s, 2 H), 3.3–1.4 (eries of m, 19 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 139.20, 131.40, 127.76, 126.00, 70.54, 67.17, 65.40, 61.59, 59.77, 57.07, 55.77, 52.09, 51.17, 50.44, 49.83, 31.36, 30.78; MS m/z calcd (M^+ – $C_6H_5CH_2$) 281.1905, obsd 281.1910.

Anal. Calcd for $C_{27}H_{32}O$: C, 87.05; H, 8.66. Found: C, 86.91; H, 8.60.

Octadecahydro-7-benzyl-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-carboxaldehyde (19). A. Buffered PCC on Molecular Sieves. A mixture of **18** (230 mg, 0.617 mmol, dry sodium acetate (170 mg), activated, powdered 3-Å molecular sieves (460 mg), and pyridinium chlorochromate (180 mg, dried in vacuo) in dichloromethane (12 mL) was stirred for 40 min at room temperature under argon. The reaction mixture was diluted with ether (5 mL) and petroleum ether (100 mL) filtered through a short column of silica gel (20 × 50 mm) and concentrated. Recrystallization of the residue from acetone gave **19** (197 mg, 86%) as colorless prisms, mp 186–188 °C dec: IR (KBr, cm^{-1}) 2930, 2715, 2665, 1720, 1716, 1706, 1490, 1450; ^1H NMR (300 MHz, $CDCl_3$) δ 9.94 (s, 1 H), 7.25 (m, 3 H), 7.05 (m, 2 H), 3.7–2.8 (series of m, 14 H), 2.74 (s, 2 H), 2.48 (m, 2 H), 2.1–1.55 (series of m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 206.0, 136.6, 130.9, 128.3, 128.0, 126.8, 70.3, 69.2, 68.6, 66.9, 64.8, 57.5, 56.8, 52.7, 52.4, 50.4, 49.8, 31.6, 30.5; MS m/z calcd (M^+) 370.2297, obsd 370.2295.

Anal. Calcd for $C_{27}H_{30}O$: C, 87.52; H, 8.16. Found: C, 86.99; H, 8.12.

B. PDC Oxidation. A mixture of **18** (200 mg, 0.537 mmol) and pyridinium dichromate (350 mg, 0.93 mmol) in dichloromethane (15 mL) was stirred at room temperature for 12 h. Dilution with ether (10 mL) and petroleum ether (20 mL) was followed by filtration through a column of silica gel (15 × 50 mm). Evaporation of the filtrate and recrystallization from acetone afforded 108 mg (54.3%) of **19** as colorless cyrstals.

Oxidation of 18 with Acid-Catalyzed Rearrangement. To a stirred solution of **18** (250 mg, 0.67 mmol) in dichloromethane (8 mL) was added a solution of pyridinium chlorochromate (180 mg) in the same solvent (40 mL) over 30 min. After 1 h, most of **18** had been oxidized as determined by TLC. After 12 h of stirring, the reaction mixture was diluted with petroleum ether (20 mL), filtered through a column of silica gel (18 × 50 mm, elution with dichloromethane–petroleum ether, 1:1), and concentrated. The product was purified by preparative TLC on silica gel to give **20** as a clear colorless oil (163 mg, 65.6%); IR ($CDCl_3$, cm^{-1}) 2960, 1710, 1500, 1460; ^1H NMR (300 MHz, $CDCl_3$) δ 7.5–7.1 (m, 5 H), 3.74 (s, 2 H), 3.7–1.7 (series of m, 23 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 210.43, 134.73, 129.45, 128.53, 126.75, 69.93, 66.49, 65.71, 59.24, 55.58, 54.05, 51.62, 50.98, 50.75, 47.37, 31.85, 29.55; MS, m/z calcd (M^+ – $C_6H_5CH_2$) 279.1749, obsd 279.1703.

Octadecahydro-7-benzyl-1,6,7-metheno-1*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalen-2-ol (21). A solution of **19** (166 mg, 0.45 mmol) in a 9:1 mixture of toluene and *tert*-amyl alcohol (40 mL) contained in a quartz tube was deoxygenated by bubbling nitrogen through it. This tube was placed in a larger quartz tube and cold nitrogen was passed through the outer tube to cool the solution to –60 to –70 °C. The cooled reaction mixture was irradiated in a Rayonet reactor fitted with 3000-Å lamps for 3.75 h. After evaporation of the solvent, the residue was subjected to MPLC on silica gel (elution with ether–dichloromethane–petroleum ether, 1:1:6). In addition to decarbonylated material (81 mg) and several unknown byproducts, there was isolated 17 mg of one epimer (**21** or **22**) and 13.3 mg of the second (combined yield of 18.3%).

For epimer A: IR ($CDCl_3$, cm^{-1}) 3610, 3570, 2940, 1490, 1450, 1098, 1088, 1078; ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 (m, 5 H), 4.30 (d, J = 6.7 Hz, 1 H), 2.78 (d, J = 12.8 Hz, 1 H), 2.68 (d, J = 12.8 Hz, 1 H), 3.35–2.55 (series of m, 15 H), 2.22 (m, 2 H), 1.94 (m, 4 H), 1.60 (s, 1 H); MS, m/z calcd (M^+) 370.2297, obsd 370.2284.

For epimer B: IR ($CDCl_3$, cm^{-1}) 3600, 2940, 1493, 1450, 1080, 1052, 1030, 1015; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 5 H), 4.90 (d, J = 4.2 Hz, 1 H), 2.93 (d, J = 14.9 Hz, 1 H), 2.82 (d, J = 14.9 Hz, 1 H), 3.55–2.6 (series of m, 15 H), 2.50 (m, 2 H), 1.98 (m, 4 H), 1.59 (s, 1 H); MS, m/z calcd (M^+) 370.2297, obsd 370.2330.

Octadecahydro-1-benzyl-2-oxo-1,6,7-metheno-1*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalene (23). To a suspension of pyridinium chlorochromate (50 mg) in dichloromethane (5 mL) was added a solution of the epimeric mixture **21**/**22** (30.3 mg) in 1 mL of the same solvent. The reaction mixture was stirred at room temperature for 4 h, diluted with ether (10 mL), and filtered. The filtrate was washed with dilute hydrochloric acid and water prior to drying. Solvent evaporation left a residue, purification of which by preparative TLC on silica gel (elution with dichloromethane–ether–petroleum ether, 5:7:88) gave 20 mg (66%) of **23** as a colorless oil: IR ($CDCl_3$, cm^{-1}) 2945, 1708, 1490, 1450, 1175, 1140; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 5 H), 3.8–1.6 (series of m, 23 H, 23 H); MS, m/z calcd (M^+) 368.2140, obsd 368.2107.

Hexadecahydro-7-benzyl-1,6,2,5-ethanediylidenecyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]penta-

len-3b(1*H*)-ol (24). A solution of **23** (20 mg) in 8 mL of a mixture of benzene and *tert*-butyl alcohol (4:1) was deoxygenated with nitrogen and irradiated with a 450-W lamp through Pyrex for 5.5 h. The solvent was removed under reduced pressure to leave **24** which was directly dehydrated: IR ($CDCl_3$, cm^{-1}) 3590, 3010, 2930, 1495, 1450, 1015; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.15 (m, 5 H), 3.5–2.9 (series of m, 16 H), 2.83 (s, 2 H), 1.65 (m, 4 H), 1.25 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.30, 130.20, 127.91, 125.55, 98.58, 82.27, 68.98, 68.04, 65.71, 65.65, 64.84, 60.92, 60.27, 52.94, 48.90, 43.41, 32.11; MS, m/z calcd (M^+) 368.2140, obsd 368.2188.

1,1a,1b,2,3,3a,4,5,5a,6,6a,6b,6c,6d,6e,6f-Hexadecahydro-7-benzyl-1,6,2,5-ethanediylidenecyclopenta[3,4]pentaleno-[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene (25). The preceding material was dissolved in benzene (15 mL), *p*-toluenesulfonic acid (2 mg) was added, and the reaction mixture was heated at the reflux temperature for 2 h. Following the evaporation of solvent, **25** was isolated by preparative TLC on silica gel (elution with 5% dichloromethane in petroleum ether). The colorless oil weighed 15.9 mg (84% overall from **23**); ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (m, 5 H), 3.43 (m, 2 H), 2.88 (d, J = 13.0 Hz, 1 H), 2.83 (d, J = 13.0 Hz, 1 H), 3.35–2.75 (series of m, 14 H), 2.57 (m, 1 H), 1.85 (m, 1 H), 1.48 (m, 1 H).

This material was directly saturated.

Octadecahydro-7-benzyl-1,6,2,5-ethanediylidenecyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene (26). A magnetically stirred solution of **25** (15.9 mg) in a cold (0 °C mixture of tetrahydrofuran (1 mL) and ethanol (5 mL) was treated with hydrazine (0.30 mL) in one portion and subsequently with 30% hydrogen peroxide (1.0 mL) over 1 h. Stirring was continued at 0 °C for an additional hour and at room temperature overnight. After the addition of water, the solution was extracted with dichloromethane (4×) and the combined organic layers were washed with water, dried, and filtered through a short column of silica gel. The eluate was concentrated and the residue was recrystallized from acetone to give **26** as colorless prisms, mp 131–132 °C (8.8 mg, 55%): ^1H NMR (300 MHz, $CDCl_3$) δ 7.30–7.15 (m, 5 H), 3.60–3.25 (m, 3 H), 3.20–2.70 (m, 16 H), 2.75 (s, 2 H), 1.46 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.25, 130.04, 127.73, 125.60, 83.50, 69.22, 67.73, 65.92, 65.57, 62.05, 54.36, 52.81, 52.46, 50.00, 49.90, 32.20; MS, m/z calcd ($M^+ - CH_2Ph$) 261.1643, obsd 261.1621.

Benzyldodecahedrane (27). A 12.2-mg sample of **26** was coated onto 200 mg of 5% platinum on alumina (benzene solvent). The solid was dried in a vacuum and admixed under an argon atmosphere with 200 mg of titanium powder in a 6-mm tube that was subsequently sealed. The contents of the glass tube was shaken vigorously for 2 min and heated in an oil bath at 200 °C for 40 h. The product was leached into benzene and the organic solution was filtered through a short column of silica gel and concentrated. There was isolated 7.8 mg (64%) of **27** as colorless crystals, mp 195–200 °C (from benzene–ethanol): ^1H NMR (300 MHz, $CDCl_3$) δ 7.2–7.0 (m, 5 H), 3.24 (br s, 19 H), 2.65 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.30, 129.89, 127.78, 125.53, 72.04, 67.09, 66.99, 66.55, 66.50, 49.19 (quaternary C not observed); MS, m/z calcd (M^+) 350.2034, obsd 350.2084.

2,3-Indanododecahedrane (28). A. Dehydrocyclization of 26. In a drybox (argon atmosphere) was prepared a mixture of finely divided titanium metal (100 mg), 5% platinum on alumina (100 mg), and **26** (4.1 mg). This mixture was placed in a 6-mm glass tube under argon, sealed under vacuum (ca. 30-mm length), and shaken vigorously for 1 min. The tube was heated in an oil bath at 240 °C for 12 h, cooled, and opened. The product was leached from the solid with benzene and analyzed by capillary VPC. This material was coated on a fresh 50 mg of 5% platinum on alumina and dried well under vacuum. This solid was transferred under argon to a tube containing titanium metal powder (50 mg). This tube was sealed under vacuum, well shaken, and heated at 260 °C for 11 h. The product was leached out with benzene, filtered, and evaporated to give **28** as colorless crystals, mp 208–210 °C (from benzene) (2.2 mg, 54;): ^1H NMR (300 MHz, $CDCl_3$) δ 7.24–7.03 (m, 4 H), 3.7–3.2 (series of m, 18 H), 3.24 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 153.60, 141.26, 127.28, 126.12, 123.61, 123.45, 93.97, 84.96, 77.73, 75.44, 67.67, 67.58, 67.37, 66.95, 66.88, 66.75, 66.59, 53.67, 29.69; MS, m/z calcd (M^+) 348.1878, obsd 348.1873.

B. Dehydrocyclization of 27. Benzyldodecahedrane (1.1 mg) was coated onto 100 mg of 5% platinum on alumina by using benzene as solvent. After being dried under vacuum, the solid was transferred under argon to a Schlenk-type tube containing 100 mg of 200-mesh titanium powder. The tube was sealed, well shaken, and heated at 250 °C for 14 h. Workup in the predescribed manner furnished **28** identical by 300 MHz ^1H NMR to the hydrocarbon described above.

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