Ethylene bromide (182 μL, 2.116 mmol) was added, and the mixture was heated to reflux for 1.5 h. To the resulting solution was added 156 mg (3.99 mmol) of potassium metal, and the mixture was heated at the reflux temperature for 4 h. To the resulting grayish black precipitate was added dichloro diester **52** (75 mg, 0.176 mmol) in one portion. The mixture was then heated at reflux for 15.5 h. The reaction mixture was slowly poured into a cold (0 °C) saturated aqueous ammonium chloride solution. Following the addition of 50 mL of water, the aqueous mixture was extracted with dichloromethane (4 × 30 mL). The combined extracts were washed with water (1 × 30 mL) and brine (1 × 30 mL) before drying. Removal of solvent afforded 86 mg of a yellow solid which was subjected to preparative TLC on silica gel (40% ether–hexane elution). The only identifiable material isolated (R_f 0.4) was **57** (22 mg, 35%), slightly contaminated with the monochloride reduction product.

Acknowledgment. This investigation was supported in part by grants from the National Institutes of Health (AI-11490) and Eli Lilly and Co. We are also grateful to Dr. David Schneider for some early experiments, Dr. Charles Cottrell for ^{13}C NMR measurements, R. Weisenberger for mass spectral data, and Dr. Kurt Loening (Chemical Abstracts Service) for relevant nomenclature.

Registry No. 7, 61223-90-3; **8**, 61223-91-4; **9a**, 53282-97-6; **9b**, 61206-25-5; **10b**, 61231-15-0; **12**, 61206-31-3; **13**, 61206-28-8; **14**, 61206-26-6; **15**, 61206-27-7; **16**, 61231-13-8; **17**, 61231-14-9; **18**, 71341-97-4; **19**, 71341-98-5; **20**, 71341-99-6; **21**, 71425-92-8; **22**, 61206-30-2; **23**, 71393-20-9; **27**, 71342-00-2; **28**, 71392-35-3; **29**, 71342-01-3; **30**, 71369-94-3; **32**, 71425-98-4; **34a**, 71342-02-4; **34b**, 71369-92-1; **40**, 71342-03-5; **41**, 71342-04-6; **42a**, 71342-53-5; **42b**, 71342-54-6; **43**, 71342-55-7; **44**, 71342-56-8; **45**, 71342-57-9; **46**, 71342-58-0; **47**, 71393-21-0; **48**, 71393-22-1; **50**, 71342-48-8; **51**, 71342-49-9; **52**, 71342-50-2; **53**, 71342-51-3; **57**, 71342-52-4; chromic acid, 13530-68-2; dimethyl decahydro-1,5-dihydroxy-3,4,7-metheno-7*H*-cyclopenta[*a*]pentalene-7,8-dicarboxylate, 71342-59-1; dimethyl decahydro-1,6-dihydroxy-3,4,7-metheno-7*H*-cyclopenta[*a*]pentalene-7,8-dicarboxylate, 71342-60-4; cyclopropyldiphenylsulfonium tetrafluoroborate, 33462-81-6; allyltrimethylsilane, 762-72-1; methyl iodide, 74-88-4.

Topologically Spherical Molecules. Rearrangement Reactions of Functionalized C_2-Symmetric Hexaquinane Systems and Synthesis of (C_2)-Dioxa-C_{20}-octaquinane, a Heterocyclic Trisecododecahedrane

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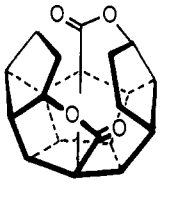
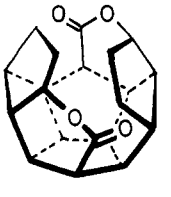
A scheme is described which culminates in an efficient synthesis of (C_2)-dioxa-C_{20}-octaquinane (**3**). Because all of the intermediates employed show a marked tendency to undergo symmetry-destroying transannular reactions, the strategy involved uncovering those transformations which would not trigger these unwanted processes. Lithium aluminum hydride reduction of dilactone **1** or diketo diester **6** gave dilactol **5a**, dissolution of which in thionyl chloride provided the highly reactive α-chloro ether **9**. This substance is particularly prone to 1,2 Wagner–Meerwein shift of its internal σ bond since considerable nonbonded steric strain is thereby relieved. Nevertheless, **9** did undergo successful 1,4-reduction in liquid ammonia with generation of bis(dihydropyran) **15**. Both **15** and its doubly cyclopropanated congener **35** are shown to be particularly prone to transannular bonding. In contrast, the derived diepoxide **39** experienced ring contraction under comparable electrophilic conditions and provided dialdehyde **41**. Decarbonylation of the latter intermediate under rather specific conditions afforded **3**.

Molecules whose carbon skeletons take on a high degree of convex polyhedral topology are of considerable interest, though they remain little-studied at the present time. The preceding paper described a ready solution to the problem of incorporating 20 carbon atoms into six fused five-membered rings with strict control of all-cis stereochemistry at the ten ring junctions and maintenance of a C_2 axis of symmetry.[2] Certain features of the chemical reactivity of dilactones **1** and **2** were disclosed, the weight of evidence being sufficient to justify the deployment of new conceptual schemes to arrive ultimately at our target molecule, the pentagonal dodecahedrane.[3] The purpose of the present study was elucidation of synthetic pathways which would ultimately permit efficient transformation of



1



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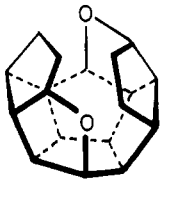

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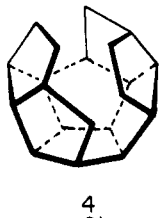


4

existing hexaquinanes such as **1** and **2** into higher order polyquinanes.[4] Such new studies are detailed, and the

(1) (a) Postdoctoral Fellow of the Science Research Council, 1975–1977. (b) National Science Foundation Graduate Fellow, 1972–1975.

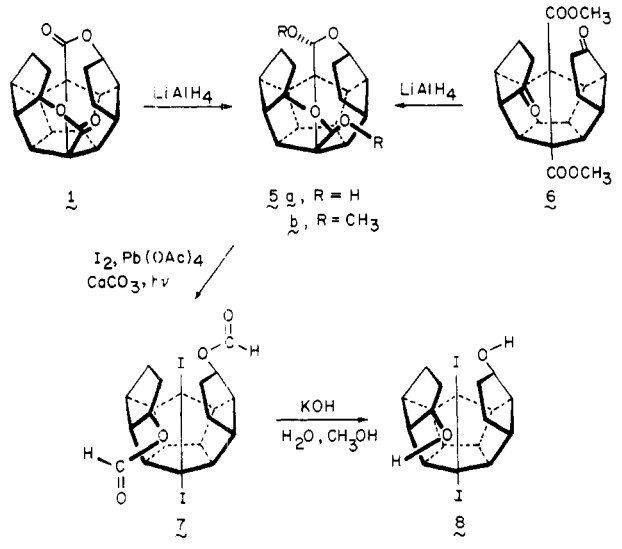
(2) Paquette, L. A.; Wyvratt, M. J.; Schallner, O.; Muthard, J. L.; Begley, W. J.; Blankenship, R. M.; Balogh, D., previous paper in this issue.

(3) For an earlier synopsis of a portion of this study, see: Paquette, L. A. *Pure Appl. Chem.* **1978**, *50*, 1291.

0022-3263/79/1944-3630$01.00/0

successful preparation of the heterocyclic system **3**, the most advanced polyquinane structure known to this time, is described.[5] Through replacement of two methylene groups in the somewhat more sterically crowded and yet unknown trisecododecahedrane **4** by a pair of oxygen atoms, we have gained support for the belief that this highly spherical hydrocarbon should be amenable to conventional synthesis.

Utilitarian Role of "Closed" Dilactol 5a. Challenged by the necessity of avoiding exposure of "open" dilactone **2** to acidic and basic reagents because of its propensity for transannular cyclization, we gave special attention to those chemical modifications of **1** which would maintain the two doubly oxygenated carbon atoms at the aldehyde oxidation level. To this end, **1** was treated with lithium aluminum hydride at 0 °C in tetrahydrofuran and converted to dilactol **5a** in 90% yield. Neither sodium borohydride nor



1 5 a, R = H; b, R = CH3 6 7 8

diisobutylaluminum hydride produced **5a** cleanly. However, a more expeditious route to **5a** was uncovered in the direct $LiAlH_4$ reduction of diketo diester **6**.[2] The tetrol derivative which could result from the ring-opened hydroxy aldehyde form of **5a** was not formed under these conditions (however, see later).

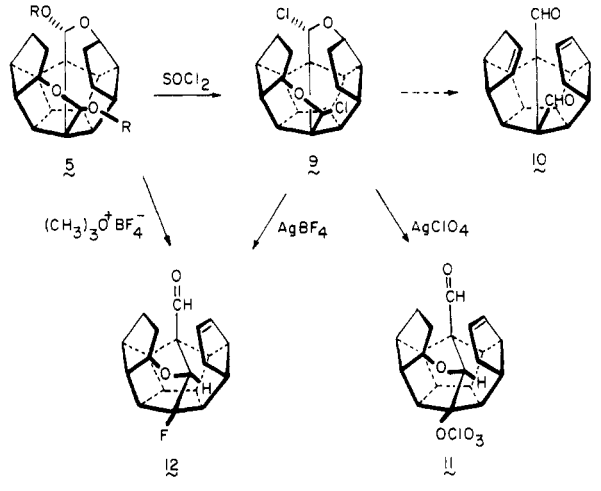
The assignment of stereochemistry to **5a** whose hemiacetal proton absorption is seen at δ 5.96 follows from the chemical transformations to be described, its appreciable lack of solubility, and its stability to catalytic quantities of acid in refluxing aqueous tetrahydrofuran solution. Thus, the isolated dilactol is the product of thermodynamic control and must result from rapid equilibration of its endo,endo isomer during workup and/or isolation.

The conversion of **5a** into methyl acetal **5b** was easily achieved in acidic methanol. The appearance of a single methoxyl absorption at δ 3.41 in the ^1H NMR spectrum, along with an 11-line ^{13}C NMR spectrum, clearly points to retention of C_2 symmetry. By saturation of a dichloromethane solution of **5b** with anhydrous hydrogen bromide and subsequent aqueous hydrolysis, reconversion to **5a** was realized.

When oxidized in the presence of iodine and lead tetraacetate, the dilactol underwent fragmentation to deliver the bis(iodo formate) **7**. The reaction conditions which were applied to **5a** are those known[6] to be suitable for insertion of an OH group into a suitably positioned unactivated C–H bond. Due to the exo orientation of the hydroxyl groups in **5a**, however, proximity factors are grossly inadequate, and free-radical β fragmentation (assumed) operates instead. Through saponification, **7** was transformed to the C_{18} iodo alcohol **8**, thus completing a three-step sequence for extrusion of the carbonyl groups in **1**, should that prove desirable at some later stage.

Upon dissolution of **5a** or **5b** in freshly distilled thionyl chloride, there resulted quantitative conversion to **9** with preservation of the aldehyde oxidation level. As expected, this chloro ether, whose axial symmetry was substantiated by its ten-line ^{13}C NMR spectrum, proved to be moisture sensitive. Its treatment with water or prolonged exposure to the atmosphere returned **5a**; methanolysis gave **5b**. Our original purpose in preparing this intermediate was to capitalize on the inherent stability of oxonium ions and perhaps thereby induce ring opening to diene dialdehyde **10**. Little were we aware of the fact that **9** would, through reaction with silver salts, enter into an unwanted rearrangement process.

Thus, exposure of a benzene solution of **9** to 2 equiv of silver perchlorate afforded a highly crystalline substance whose spectroscopic properties were not consistent with those expected for the desired product **10**. For example,



5 9 10 12 11

only a single aldehyde proton and two vinylic hydrogens were in evidence; further, two widely different >CHO– absorptions were clearly present, and the ^{13}C NMR spectrum denoted the loss of symmetry. Spin-decoupling studies suggested the substance to be **11**, this assignment being later confirmed by an X-ray crystal structure analysis.[7] The study by Engel and Nowacki established further the fully covalent character of the C–O bond to perchlorate, despite its attachment to a fully substituted carbon atom. As far as we are aware, **11** represents the lone example of a stable *tertiary* perchlorate which has no special electronic factors to safeguard its existence!

(4) A review of polyquinane chemistry may be found in: Paquette, L. A. *Fortschr. Chem. Forsch.* **1979**, *79*, 43.

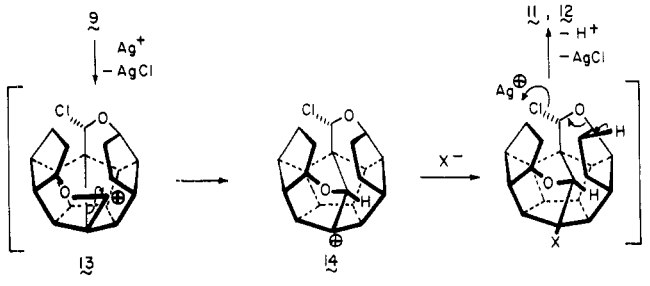
(5) A preliminary account of this synthesis has appeared: Balogh, D.; Begley, W. J.; Bremner, D.; Wyvratt, M. J.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 749.

(6) Cainelli, G.; Mihailovic, M. L.; Arigoni, D.; Jeger, O. *Helv. Chim. Acta* **1959**, *42*, 1124. Meystre, C.; Heusler, K.; Kalvoda, J.; Wieland, P.; Anner, G.; Wettstein, A. *Ibid.* **1962**, *45*, 1317. Heusler, K.; Kalvoda, J.; Meystre, C.; Anner, G.; Wettstein, A. *Ibid.* **1962**, *45*, 2161. Heusler, K.; Kalvoda, J. *Angew. Chem.* **1964**, *76*, 518; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 525. Mihailovic, M. L.; Cekovic, Z. *Synthesis* **1970**, 209. Baggeley, K. H.; Norin, T.; Sundin, S. *Acta Chem. Scand.* **1968**, *22*, 1709. Mihailovic, M. L.; Cekovic, Z.; Stankovic, J.; Pavlovic, N.; Konstantinovic, S.; Djokic-Mazinjanin, S. *Helv. Chim. Acta* **1973**, *56*, 3056. Mihailovic, M. L.; Bosnjak, J.; Cekovic, Z. *Ibid.* **1974**, *57*, 1015. *Ibid.* **1976**, *59*, 475. For reviews by the Yugoslavian group, consult: Mihailovic, M. L.; Partch, R. E. *Sel. Org. Transform.* **1972**, *2*, 97. Mihailovic, M. L. *Lect. Heterocycl. Chem.* **1976**, *3*, 111.

(7) Engel, P.; Nowacki, W. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1977**, 4.

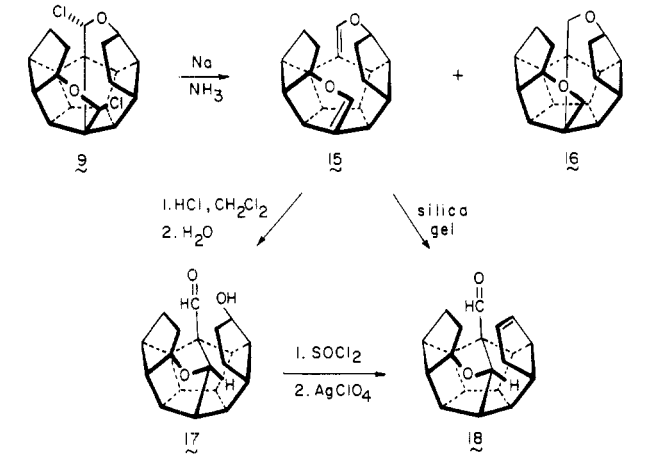
Analogous treatment of **9** with dry silver tetrafluoroborate afforded **12**, a compound also obtained through reaction of **5b** with trimethyloxonium fluoroborate. The ^{1}H NMR spectrum of **12** is very similar to that obtained for **11**, except that the signal assigned to the inner ether hydrogen which appears at δ 4.96 has a larger splitting constant (J = 7 Hz) than its counterpart in **11** (2.5 Hz). An examination of molecular models of **12** indicates the dihedral angle between this hydrogen atom and fluorine to be in the range 60° < ϕ > 90°. Literature precedent indicates that such a hydrogen should be split by 0–5 Hz for ϕ = 60° and by 10–25 Hz for ϕ = 180°.[8] The observed splitting in **12** is accordingly consistent with these data. In addition, when the fluorine signal was saturated, the doublet originally observed collapsed to a broad singlet.

Although the precise timing of these rearrangements has not been unequivocally established, it appears plausible that departure of the first chloride ion is accompanied by a 1,2-shift of the central bond (with relief of substantial steric strain) to generate a tertiary cationic center (see **14**)



which captures the sole anion available to it in solution. Only subsequently is the desired fragmentation believed to occur in the other half of the molecule.

Reductive Central-Bond Cleavage. The Pivotal Bis(dihydropyran) 15. The turn of events culminating in the isolation of **11** and **12** obviously did not conform to our single-minded goal of maintaining axial symmetry. The complication was neatly circumvented by reductive cleavage of the 1,4-dichloride part structure of **9**. In the laboratory, treatment of **9** with sodium in liquid ammonia at −33 °C afforded a mixture consisting of **15** (93%) and **16** (7%). Column chromatography on silica gel permitted



the isolation of pure bis(dihydropyran) in 77% yield. Its ^{1}H NMR spectrum exhibits the characteristic absorptions of an enol ether (broad singlet at δ 6.22 and a multiplet at δ 4.56–4.20), and its ^{13}C NMR spectrum shows ten lines. In the case of **16**, the ether methylene protons appear as

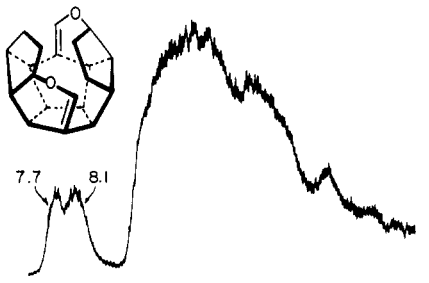
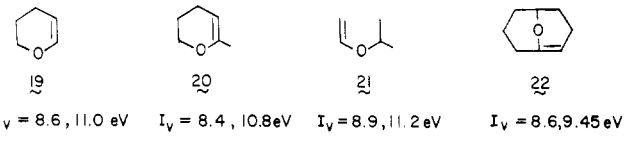


Figure 1. Photoelectron spectrum of **15** (courtesy of Professor Rolf Gleiter).

an expected AB quartet. The difference in the chemical shifts of the inner and outer hydrogens is sufficiently large (1.3 ppm) that the appearance of the signal approached that of an AX system. Steric deshielding of this magnitude had previously been encountered in **5** and **9**. The possibility exists that the markedly lessened solvation experienced by the hydrogens situated inside the cavity may also contribute to the observed downfield shifting.

Vinyl ethers are relatively simple electronically, having only two high-lying occupied molecular orbitals, $\pi - n_\sigma$ and $n_\sigma + \pi$. As a result, the low-energy part of their photoelectron spectra generally exhibits a pair of well-spaced and easily identifiable bands.[9] Alkyl substituents are recognized to affect ionization energies, as reflected, for example, in the behavior of dihydropyrans **19** and **20**. The



fact that both bands are equally shifted has been construed as an indication that the two orbitals under observation are approximately 50:50 mixtures of π and n_σ. In comparison, the photoelectron spectrum (Figure 1) of **15** reveals the same two ionization energies to be exceptionally low lying (see **21** and **22** also), a result which is presumably attributable to extensive "through-space" conjugative interaction. The magnitude of this shift is particularly striking since introduction of a second oxygen atom into a ring system is known to increase the mean ionization energy by 0.6–0.7 eV relative to the parent compound. The relationship of 1,4-dioxane, I_v (n_σ) = 10.05 eV, to tetrahydrofuran, I_v (n_σ) = 9.5 eV, is illustrative.[10]

To gain an appreciation of the ease with which **15** can enter into transannular bonding, we treated a solution of the bis(dihydropyran) in dry methylene chloride with anhydrous hydrogen chloride at −78 °C. An α-chloro ether was indeed obtained, but its evident ease of hydrolysis in moist air prompted the use of an aqueous workup prior to characterization. The hydroxy aldehyde **17** was isolated in high yield. Molecular models indicated the lactol form of this molecule not to be as thermodynamicaly stable as the ring-opened carbonyl derivative, because of prevailing steric constraints and geometric factors. Nonetheless, **17** was found to be capable of reconversion to the cyclized α-chloro ether when stirred with thionyl chloride.

With certain batches of silica gel, bis(dihydropyran) **15** was converted efficiently to unsaturated aldehyde **18**, particularly if allowed to reside on the column for some time. The previously mentioned α-chloro ether also gave **18** when allowed to react with silver perchlorate in benzene, although in inferior yield. The ^{1}H NMR spectra of **17** and

(8) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Germany, 1969; p 348.

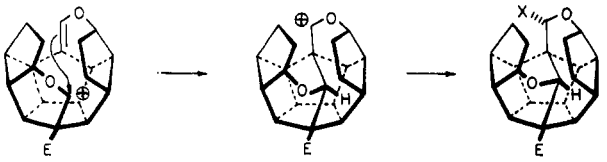
(9) Batich, C.; Heilbronner, E.; Quinn, C. B.; Wiseman, J. R. *Helv. Chim. Acta* **1976**, *59*, 512.

(10) Sweigart, D. A.; Turner, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 5599.

18 are in full agreement with the structural assignments (see Experimental Section).

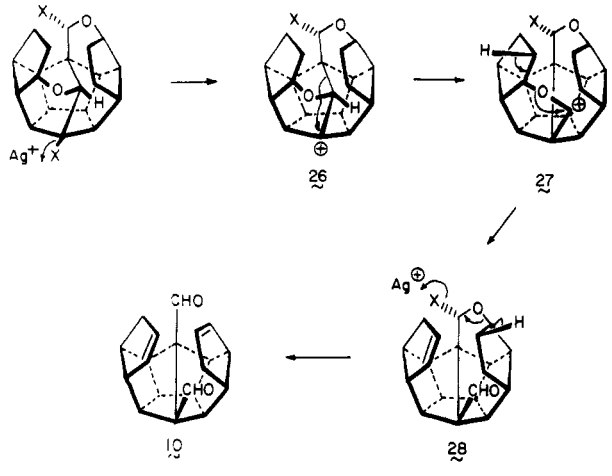
In yet another study, we have observed that reduction of "open" dilactone **2** with diisobutylaluminum hydride also leads to the formation of **17**.

Mechanistically, it appears that attack of an electrophile on **15** proceeds as expected through cation **23**, which experiences rapid capture by the transannular double bond to deliver **24**. The relief of nonbonded steric interactions now having been achieved, final product formation ensues in conventional fashion.



23 24 25

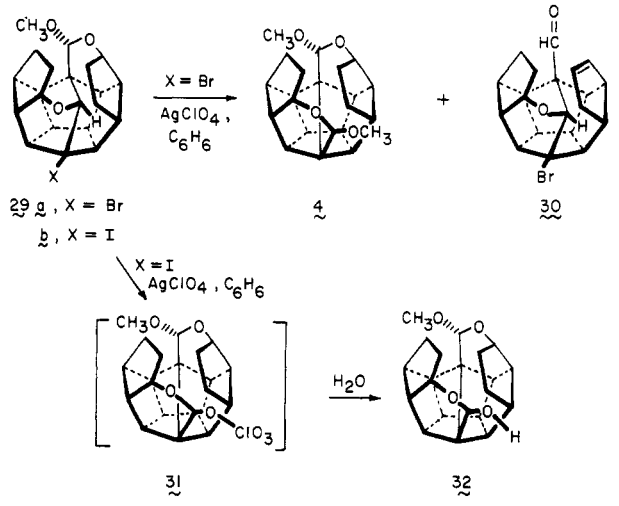
While considering useful synthetic roles for these transannular products, we were struck by the potentially attractive possibility that suitable substitution of E and X in **25** with appropriate leaving groups might allow for return to C_2-symmetric intermediates. More specifically, the utilization of groups responsive to coordination to Ag^+ ion could trigger the following sequence of events, although the illustrated timing of the steps could be reversed in practice. Thus, ionization of tertiary cation **26** might result in a 1,2 Wagner–Meerwein shift with transient formation of oxonium ion **27** whose collapse to **28** is precedented by earlier observations. Subsequent attack by silver ion at



26 27 28 10

the other reactive center could similarly induce ring opening with creation of the second olefinic aldehyde unit needed to generate **10**. It was recognized that the desired conversion of **26** to **27** was, in fact, the formal reversal of the **13** → **14** transposition observed previously. However, a factor whose weighting had not yet been directly assessed, viz., the extent to which C–C bond participation assists departure of the leaving group in the rate-determining transition state, was thought to hold considerable promise. Indeed, this phenomenon proved to be operative and of direct importance to the synthetic plan.

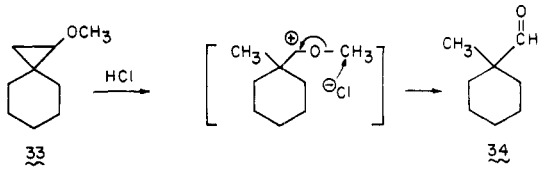
The critical choice of substituents was dictated by the well-known affinity of Ag^+ for covalently bound bromine and iodine and the more recently established ability of silver ion to promote the ionization of reactive methyl ethers.[11] In the event, reaction of **15** with *N*-bromosuccinimide and *N*-iodosuccinimide in methanol solution produced **29a** and **29b**, respectively. To test our assumptions, we treated **29a** in turn with 1 equiv of silver perchlorate dissolved in dry benzene. Two products were isolated in a 1:1 ratio. The first was identified as the known dimethyl acetal **4** and the second as the unsaturated aldehyde **30**. The formation of **4** and **30** in equal amounts is interesting and is taken to mean that **29a** was actually transformed through **26** (X = OCH_3) to **27** (X = OCH_3). Surprisingly, however, this last intermediate must be transformed into diketal **4** by abstraction of methoxide from starting **29a**. This step, which is apparently kinetically favored relative to abstraction of $-OCH_3$ by silver ion, delivers **24** (E = Br) which now experiences customary ring opening. The behavior of iodo derivative **29b** is somewhat different, for reasons which are not understood. This substrate was efficiently converted to perchlorate **31** (identified by direct ^1H NMR analysis of the mixture when the reaction was conducted in benzene-d_6). During workup, this labile product experienced hydrolytic conversion to a product believed to be **32**.



29 a, X = Br; b, X = I 4 30 31 32

Although this investigation had been rewarded with concrete proof of the feasibility of reversible Wagner–Meerwein relocation of the internal σ bond, it had not provided the desired synthetic entry to **10**. Particularly exasperating was our finding that **30** proved to be totally inert to silver salts even under forcing conditions.

Consequences of Cyclopropanation. At this point, our conceptual approach took a new twist, predicated in large part upon earlier findings by Wenkert and his coworkers.[12] More specifically, the emphasis shifted to cyclopropyl ethers of the type **33**, acid hydrolysis of which has been shown to proceed via transient oxonium ions to α-methyl carboxaldehyde products (e.g., **34**). Should the



33 34

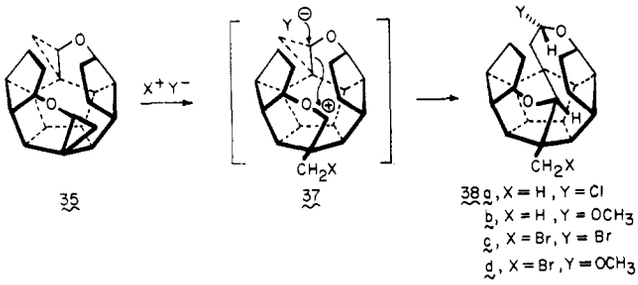
chemical reactivity of **35** be foreshadowed by these observations and the intervening oxonium ions experience ring opening to product ene aldehyde units, it was anticipated that the attractive hexaquinane **36** might be formed.

Although bis(dihydropyran) **15** was found to undergo efficient Simmons–Smith cyclopropanation, our expectations for **35** were not vindicated. The complication was not due to a loss in regiospecificity of cyclopropane ring

(11) Zon, G.; Paquette, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 5478.

(12) Wenkert, E.; Mueller, R. A.; Reardon, E. J., Jr.; Sathe, S. S.; Scharf, D. J.; Tosi, G. *J. Am. Chem. Soc.* **1970**, *92*, 7428.

opening, for the available evidence points clearly to the intervention of **37**. Rather, it so happens that this intermediate continues to share with its precursor molecules a marked proclivity for kinetically controlled transannular bonding. To illustrate, the heating of **35** in acidic methanol resulted in conversion to **38b** in good yield. The choice

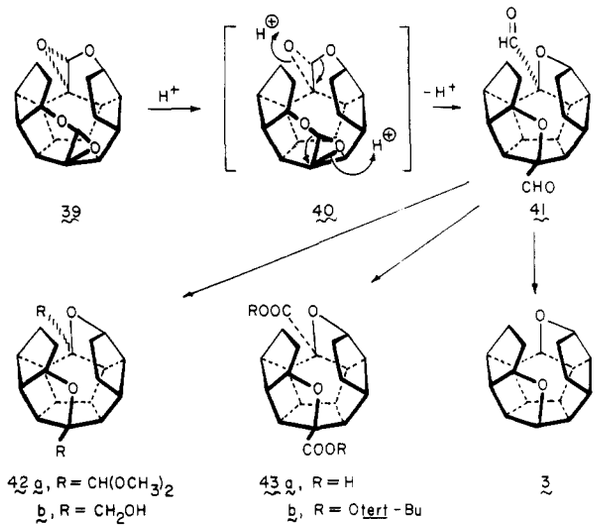


35 **37** **38** a, X = H, Y = Cl; b, X = H, Y = OCH_3; c, X = Br, Y = Br; d, X = Br, Y = OCH_3

of conditions is not important. Use of anhydrous hydrogen chloride in dichloromethane at room temperature provided **38a** in quantitative yield. The bromination of **35** proceeded analogously to give **38c**. The structural assignments follow convincingly from the close similarity of their ^1H NMR spectra to those previously recorded for **29a** and **29b**. The reactive nature of the chlorine atom in **38a** and of one bromine substituent in **38c** was established by methanolysis. The resultant isolation of cyclic acetals **38b** and **38d**, respectively, further confirmed their α-halo ether disposition.

A possible rationalization of these results is illustrated in structure **37**. The essentials of our thinking lay responsibility for the exceptionally facile transannular capture of the first-formed cation on the fact that the interior of the molecule is essentially devoid of solvation. As a result, functional groups positioned on the opposite side of the molecular framework become hyperreactive toward the reaction center, since the well-known amelioration of reactivity brought about by intervening solvent molecules is now absent. Importantly, this feature results in loss of control over the reaction pathway, since those parameters which are normally subject to variation by the experimentalist are now of little or no consequence.

Controlling Influences of Epoxidation. Concurrent with the preceding work, the chemistry of the diepoxide congener **39** was being actively assessed. Like **35**, this α,β-epoxy ether possesses two strained three-membered rings rigidly held in rather close transannular proximity; the substance is also shelf stable, in contrast to the customary lability of those members of this class of compounds which are not aryl substituted.[13] But contrary to **35**, the response of **39** to electrophilic reagents does *not* lead to transannular bonding. In the presence of a wide range of acidic reagents, **39** was rapidly isomerized to the ring-contracted dialdehyde **41**. For preparative work, it proved most convenient simply to elute **39** through a silica gel column. The simplicity of the ^1H [($CDCl_3$) δ 9.66 (s, 2 H), 4.70 (m, 2 H), 3.60–1.40 (m, 18 H)] and ^{13}C NMR spectra [($CDCl_3$) 205.51, 103.43, 92.53, 63.50 (2 C), 61.72, 57.95, 49.20, 34.15, 29.73 ppm] of **41** confirms the retention of a molecular C_2 axis in this heterocyclic octaquinane derivative. We regard the formation of **41** to be the likely



39 **40** **41** **42** a, R = $CH(OCH_3)_2$; b, R = CH_2OH **43** a, R = H; b, R = O*tert*-Bu **3**

result of epoxide opening toward the tertiary cation center with simultaneous or subsequent 1,2-oxygen migration as shown in **40**.

Conversion of the dialdehyde into diacetal **42a** and diol **42b** by standard methods was straightforward. Accordingly, the pendant carbonyl groups of **41** appear normal in their reactivity toward the usual addition reactions. However, attempts to decarbonylate **41** by either traditional[14] or more modern procedures[15] afforded no material which could be characterized as **3**. The di-*tert*-butyl perester **43b** also did not respond satisfactorily to thermal[16] and photochemical decomposition.[17] The successful preparation of the dioxatrisecododecahedrane was ultimately achieved by irradiation (275-W sunlamp) of an intimate mixture of **41**, acetophenone, benzyl mercaptan, and ethyl benzoate (solvent)[18] at 140 °C under argon for several hours. This procedure was adapted from earlier work by Cohen.[19] The ^1H NMR spectrum of the colorless crystalline solid is characterized by a narrow multiplet at δ 4.55–4.0 (4 H) and a broad series of absorptions at δ 3.3–1.5 (18 H). The more diagnostic ^{13}C NMR spectrum consists of nine signals (see Experimental Section). Occasionally, the yield of **3** fell below 90%. When this occurred, the monoaldehyde was isolated, an indication of incomplete decarbonylation.

A direct comparison of the intimate structural features of **3** with **4**, when the latter becomes available, should prove interesting because of the lesser strain energy in the first molecule.

One should not be left with the impression that **39** is not subject to transannular reaction. For now, it is perhaps sufficient to report that sodium in liquid ammonia containing no proton source quantitatively reduced the di-

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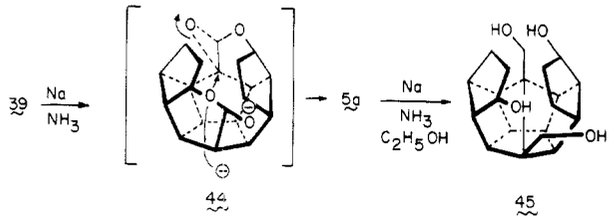
epoxide to dilactol **5a**. When a quantity of ethanol was added to the reaction mixture, more extensive reduction to tetrol **45** was observed. In both instances, the strained



44 45

internal σ bond was reintroduced. Evidently, the first-formed carbanion finds transannular opening of the second epoxide ring as in **44** kinetically feasible. In accord with the suggestion that **5a** intervenes on the pathway to **45**, independent reduction of the dilactol likewise gave the tetrol.

Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained with Varian A-60A, Varian HA-100, and Bruker HX-90 spectrometers; apparent splittings are given in all cases. Carbon spectra were recorded with the Bruker unit. Infrared spectra were determined on Perkin-Elmer Models 137 and 467 instruments. 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.

Tetradecahydro-5*H*,6*H*-1,5b,12:5a,10,11-dimethenodicyclopenta[*e*,*e*']benzo[2,1-*c*:3,4-*c*']dipyran-5α,6α-diol (5a). A. Reduction of Dilactone 1 with Lithium Aluminum Hydride. To a solution of 1 (364 mg, 1.12 mmol) in 50 mL of dry tetrahydrofuran was added lithium aluminum hydride (85 mg, 2.24 mmol) at 0 °C under nitrogen. After being stirred for 1.5 h at 0 °C, the reaction mixture was freed of excess hydride by quenching at 0 °C with aqueous 10% ammonium chloride solution (35 mL). The crude mixture was filtered through Celite, and the resulting layers were separated. After extraction of the aqueous layer with dichloromethane (3 × 25 mL), the combined organic layers were washed with water (1 × 50 mL) and dried. Upon removal of the solvent, a white solid was obtained which when recrystallized from acetone afforded 331 mg (90%) of dilactol **5a**: mp 252–255 °C; ν_{max} (KBr) 3390, 1070, 1020, 1002 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 5.96 (d, J = 3 Hz, 2 H), 4.07 (br s, 2 H), 2.68–1.48 (br m, 20 H); m/e calcd 328.1674, obsd 328.1682.

Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.14; H, 7.27. Found: C, 73.07; H, 7.31.

B. Formation of 5a Directly from Diketo Diester 6. To a solution of **6** (200 mg, 0.52 mmol) in 10 mL of dry tetrahydrofuran was added lithium aluminum hydride (158 mg, 4.16 mmol) in small portions under nitrogen. After being stirred at room temperature for 2 h, the suspension was worked up as described above to give crude dilactol which when recrystallized from acetone afforded 100 mg (59%) of pure **5a**.

C. Hydrolysis of Acetal 5b. A solution of **5b** (398 mg, 1.12 mmol) in 40 mL of dry dichloromethane was saturated at 0 °C with anhydrous hydrogen bromide gas (1 h). The saturated solution was permitted to stir at room temperature for 2.5 h. After slow addition of the reaction mixture to 100 mL of water, the layers were separated. The aqueous phase was extracted further with dichloromethane (3 × 50 mL). The combined organic extracts were washed with dilute aqueous sodium bicarbonate solution (1×), water (1×), and brine (1×) before drying and evaporation of the solvent. There was obtained a yellow solid (0.38 g) which upon recrystallization from acetone afforded 235 mg (64%) of dilactol **5a**.

Tetradecahydro-5α,6α-dimethoxy-5*H*,6*H*-1,5b,12:5a,-10,11-dimethenodicyclopenta[*e*,*e*']benzo[2,1-*c*:3,4-*c*']dipyran (5b). A. Acid-Catalyzed Methanolysis of Dilactol 5a. A solution of **5a** (175 mg, 0.533 mmol) in 30 mL of dry methanol containing a catalytic amount of sulfuric acid was stirred for 5 h under nitrogen. The heterogeneous mixture was concentrated to 10 mL of solution under reduced pressure. The concentrate was treated with 75 mL of dichloromethane and washed with dilute aqueous sodium bicarbonate solution, water, and brine prior to drying. Concentration afforded, after recrystallization from ether, 170 mg (90%) of **5b**. Recrystallization from acetone afforded the analytically pure material: mp 205.5 °C; ν_{max} (KBr) 1085, 1041, 982, 960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.40 (s, 2 H), 3.88 (br s, 2 H), 3.41 (s, 6 H), 2.75–1.47 (m, 18 H); ^{13}C NMR ($CDCl_3$) 99.98 (d), 68.71 (d), 58.24 (d), 55.25 (d), 53.50 (d), 50.44 (s), 49.66 (d), 44.46, 44.20, 38.29, 24.57 ppm; m/e calcd 356.1987, obsd 356.1991.

Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 73.97; H, 7.98.

B. Methanolysis of Chloro Ether 9. A solution of **9** (56 mg, 0.152 mmol) in 3 mL of dry methanol was stirred under nitrogen for 10 h. The heterogeneous mixture was dissolved in 10 mL of dichloromethane and extracted with water (1×) and brine (1×) before drying. Removal of the solvent afforded 62 mg (100%) of slightly impure **5b**.

Hexadecahydro-1,5-bis(formyloxy)-4,10-diiodo-4,8,9-metheno-1*H*-cyclopenta[1,2-*a*:4,3-*a*']dipentalene (7). Calcium carbonate (0.80 g, 8 mmol) and lead tetraacetate (0.896 g, 2.02 mmol) were refluxed in cyclohexane (100 mL) with stirring for 10 min. At this point dilactol **5a** (226 mg, 0.81 mmol) together with iodine (823 mg, 3.24 mmol) was added and the heating continued for 1.25 h with simultaneous irradiation of the reaction mixture by a sunlamp. After the mixture was cooled, the inorganic salts were separated by filtration and washed with a small amount of ether. The combined filtrates were washed with aqueous sodium thiosulfate solution, dried, and evaporated to leave 380 mg (81%) of white crystalline solid. Recrystallization from benzene/hexane gave pure **7** as colorless plates, mp 248–249 °C with decomposition beginning at 200 °C; ν_{max} (KBr) 1725, 1710 sh cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.13 (d, J = 1 Hz, 2 H), 5.10 (m, 2 H), 3.30–1.0 (br m, 18 H); ^{13}C NMR ($CDCl_3$) 161.16 (d), 75.86 (d), 67.98 (d), 65.77 (d), 51.80 (d), 46.94 (s), 45.32 (d), 40.95 (d), 30.38 (t), 20.07 (t) ppm; mass spectrum, m/e 580.

Anal. Calcd for $C_{20}H_{22}I_2O_4$: C, 41.40; H, 3.82. Found: C, 41.48; H, 3.88.

Hexadecahydro-1,5-dihydroxy-4,10-diiodo-4,8,9-metheno-1*H*-cyclopenta[1,2-*a*:4,3-*a*']dipentalene (8). A 170-mg (0.293-mmol) sample of **7** was suspended in 10 mL of 18% aqueous methanol and treated with potassium hydroxide (98.6 mg, 1.76 mmol). The mixture was stirred at room temperature for 2–3 h until a clear solution resulted. The solvent was evaporated, and the residue was recrystallized from methanol to give 142 mg (93%) of **8** as long colorless needles: mp 179–180 °C; ν_{max} (KBr) 3480, 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.33 (br m, 2 H), 2.90–1.25 (br m, 20 H); ^{13}C NMR ($CDCl_3$) 75.64 (d), 69.28 (d), 66.20 (d), 51.80 (d), 49.53 (s), 47.26 (d), 41.00 (d), 33.40 (t), 20.50 (t) ppm; mass spectrum, m/e 524 (M^+).

Anal. Calcd for $C_{18}H_{22}I_2O_2$: C, 41.24; H, 4.23. Found: C, 41.23; H, 4.17.

5α,6α-Dichlorotetradecahydro-5*H*,6*H*-1,5b,12:5a,10,11-dimethenodicyclopenta[*e*,*e*']benzo[2,1-*c*:3,4-*c*']dipyran (9). A. Chlorinative Substitution of Dilactol 5a. Dilactol **5a** (50 mg, 0.152 mmol) was stirred in freshly distilled thionyl chloride (2 mL) for 1 h under nitrogen. After this period, the excess thionyl chloride was removed in vacuo to give a white solid. The product was dissolved in benzene and again evaporated to dryness to remove any residual thionyl chloride: yield 55 mg (100%); ^{1}H NMR ($CDCl_3$) δ 6.63 (s, 2 H), 4.17 (m, 2 H), 2.80–1.50 (br m, 18 H); ^{13}C NMR ($CDCl_3$) 95.50 (d), 71.76 (d), 59.46 (d), 55.44 (s), 53.44 (d), 49.83 (d), 44.32, 43.76, 37.50 (t), 24.33 (t) ppm; mass spectrum, m/e 364.

B. Chlorinative Substitution of Diacetal 5b. A solution of **5b** in 3 mL of thionyl chloride was stirred at 25 °C under a nitrogen atmosphere for 30 min. The excess reagent was removed under reduced pressure, and benzene (5 mL) was added and similarly evaporated. This last step was repeated to give a quantitative yield of **9** (^{1}H NMR analysis).

2,3,3a,3b,4a,4b,7,7a,7b,7c,7d,8,8a,8b-Tetradecahydro-8-fluoro-1,4,8-(epoxymetheno)dipentaleno[1,2,3-*cd*:1',2',3'-*gh*]pentalene-4(1*H*)-carboxaldehyde (12). A. Treatment of Chloro Ether 9 with Silver Tetrafluoroborate. To a solution of **9** (111 mg, 0.305 mmol) in 6 mL of dry benzene was added dry silver tetrafluoroborate (122 mg, 0.627 mmol) under nitrogen.

Boron trifluoride was evolved, and a yellow precipitate resulted. After being stirred for 15 min, the benzene solution was passed through a short column of Florisil with dichloromethane elution. A colorless oil (50 mg, 53%) was obtained which was recrystallzied from dichloromethane/hexane to yield **12** as white crystals: mp 149–152 °C; ν_{max} (KBr) 3020, 2720, 1712, 1109, 1089, 707 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 9.96 (s, 1 H), 5.80 (m, 1 H), 5.51 (m, 1 H), 4.96 (d, J = 7 Hz, 1 H), 4.09 (br s, 1 H), 3.44–1.0 (br m, 16 H); m/e calcd 312.1525, obsd 312.1531.

B. Treatment of Acetal 5b with Trimethyloxonium Tetrafluoroborate. A heterogeneous mixture of **5b** (90 mg, 0.253 mmol) and trimethyloxonium tetrafluoroborate (80 mg, 0.54 mmol) in 8 mL of dry dichloromethane was stirred at room temperature for 15 h. The reaction mixture was diluted with aqueous sodium bicarbonate solution and extracted with dichloromethane. The combined extracts were washed with water and dried. Removal of the solvent afforded an oil which was chromatographed on silica gel (10% ether/hexane) to yield 69 mg (87%) of crystalline **12**.

2,3,3a,3b,4a,4b,7,7a,7b,7c,7d,8,8a,8b-Tetradecahydro-8-hydroxy-1,4,8-(epoxymetheno)dipentaleno[1,2,3-*cd*:1′,2′,3′-*gh*]pentalene-4(1*H*)-carboxaldehyde Perchlorate (11). To a solution of **9** (100 mg, 0.275 mmol) in 2 mL of dry benzene was added 3.3 mL (0.626 mmol) of 0.1898 M silver perchlorate in benzene under nitrogen. The initial white precipitate slowly darkened, at which point (30 min) the benzene solution was passed through a short column of Florisil with dichloromethane solution. Upon removal of the solvent, 60 mg (56%) of a colorless, crystalline product (**11**) was obtained. Recrystallization from benzene/hexane afforded white needles (40 mg): no melting point (decomposed slowly at 104 °C; rapid heating caused an explosion!); ν_{max} (KBr) 1718 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.99 (s, 1 H), 5.85 (m, 1 H), 5.55 (m, 1 H), 4.90 (d, J = 2.5 Hz, 1 H), 4.22 (m, 1 H), 3.70–1.00 (br m, 16 H); ^{13}C NMR ($CDCl_3$) 204.37 (d), 134.56 (d), 129.23 (d), 98.74 (s), 71.76 (d), 70.33 (d), 64.22 (s), 58.50 (d), 57.66 (d), 53.76 (d), 51.81 (d, 2 C), 50.12 (d), 47.91 (d), 45.70 (d), 43.75, 41.80, 37.70, 31.59 (t), 24.57 (t) ppm.

Anal. Calcd for $C_{20}H_{21}ClO_6$: C, 61.15; H, 5.36. Found: C, 61.39; H, 5.56.

1,2,2a,4b,4b,5,6,6a,8b,8c,8d,8e,8f,8h,8i-Hexadecahydro-3,7-dioxadicyclopenta[*cd*,*c*′*d*′]pentaleno[2,1,6-*hia*:5,4,3-*h*′*i*′*a*′]diindene (15) and Tetradecahydro-5*H*,6*H*-1,5b,-12:5a,10,11-dimethenodicyclopenta[*e*,*e*′]benzo[2,1-*c*:3,4-*c*′]-dipyran (16). Dilactol **5a** (816 mg, 2.48 mmol) was stirred in 19 mL of thionyl chloride for 1 h under nitrogen. After this period, excess thionyl chloride was removed in vacuo. The residue was dissolved in 25 mL of dry benzene and again evaporated to dryness. The solid **9** was dried in vacuo for 3 h.

A solution of **9** in 30 mL of dry tetrahydrofuran was added over 1 h to a solution of sodium (570 mg, 0.025 g-atom) in 150 mL of dry ammonia under nitrogen at −33 °C. Upon completion of the addition, the reaction mixture was stirred for an additional 2 h at −33 °C. After the addition of an excess of solid ammonium chloride, a solution of methanol in tetrahydrofuran was introduced at −78 °C. After the complete consumption of sodium, the ammonia was permitted to evaporate under a nitrogen flow. The concentrate was diluted with 100 mL of water and extracted with ether (5 × 40 mL). The combined organic layers were washed with water (1 × 100 mL) and brine (1 × 100 mL) before drying. Removal of solvent yielded 0.79 g of a mixture of **15** (93%) and **16** (7%) (^{1}H NMR analysis).

The crude product was chromatographed on silica gel (100 g). Elution with 10% ether/petroleum ether afforded 562 mg (77%) of pure dihydropyran **15** (R_f 0.7). Recrystallization from hexane yielded high-density, white crystals: mp 116–118 °C (sealed capillary); ν_{max} (KBr) 3078, 1674, 1118 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.22 (br s, 2 H), 4.56–4.20 (m, J = 3.5 Hz, 2 H), 3.57–2.34 (m, 10 H), 2.34–1.25 (m, 8 H); ^{13}C NMR ($CDCl_3$) 139.12 (d), 119.80 (s), 75.91 (d), 58.51 (d), 53.66 (d), 48.59 (d), 47.96 (d), 44.70 (d), 39.04 (t), 28.76 (t) ppm; m/e calcd 294.1620, obsd 294.1624.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.38; H, 7.57.

Continued elution with 10% ether/petroleum ether afforded 56 mg (7.6%) of **16** which was purified further by sublimation at 85 °C (0.2 mm): mp 88–90 °C; ν_{max} (KBr) 1164, 1068, 795 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.74 (1/2 ABq, J_{AB} = 10.5 Hz, $\Delta\nu_{AB}$ = 76.3 Hz, 2 H), 3.79 (br s, 2 H), 3.47 (1/2 ABq, J_{AB} = 10.5 Hz, $\Delta\nu_{AB}$ = 76.3 Hz, 2 H), 2.90–1.17 (m, 18 H); ^{13}C NMR ($CDCl_3$) 73.08 (d), 67.33 (t), 59.94 (d), 54.63 (d), 54.39 (d), 47.94 (s), 44.75 (d), 44.35 (d), 38.87 (t), 25.01 (t) ppm; m/e calcd 296.1776, obsd 296.1782.

Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.72; H, 8.02.

Ethyl acetate elution of the column yielded 71 mg of the acid-hydrolysis product **17**.

Synthesis of Hydroxy Aldehyde 17. A. Acid Hydrolysis of 15. To a cold (−78 °C) saturated solution of hydrogen chloride in dichloromethane (20 mL) was added dropwise a solution of **15** (150 mg, 0.510 mmol) in 3 mL of dry dichloromethane under nitrogen during 10 min. After the solution was permitted to stir at −78 °C for 30 min, the excess hydrogen chloride was removed by degassing the solution with nitrogen as the reaction mixture warmed to room temperature (45 min). The solvent was evaporated under reduced pressure to yield **25** (E = H, X = Cl) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.58 (s, 1 H), 4.67–4.10 (br m, 2 H), 3.95 (br s, 1 H), 3.20–1.18 (br m, 19 H).

This chloro ether is extremely sensitive toward moisture. Dichloromethane (100 mL) was added, and the resulting solution was washed with dilute aqueous sodium bicarbonate solution 1×), water (1×), and brine (1×). After the solution was dried, concentration afforded a white solid (165 mg) which was recrystallized from acetone to yield 132 mg (83%) of pure **17**: mp 229–234 °C; ν_{max} (KBr) 3362, 1704, 1051 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.95 (s, 1 H), 5.30 (br s, 1 H), 4.46–4.08 (m, 1 H), 4.02 (br s, 1 H), 3.12–1.04 (br m, 20 H); ^{13}C NMR ($CDCl_3$) 208.33 (d), 71.68 (d), 70.53 (d), 70.14 (d), 62.65 (d), 59.62 (s), 55.50 (d), 54.45 (d), 52.47 (d), 51.48 (d, 2C), 48.56, 46.69, 46.52, 44.65, 41.90, 38.92, 38.15, 25.60, 23.73 ppm; m/e calcd 312.1725, obsd 312.1729.

Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.77; H, 7.70.

B. Reduction of Dilactone 2 with Diisobutylaluminum Hydride. To a cold (0 °C) solution of **2** (50 mg, 0.153 mmol) in 1.5 mL of dry toluene was added 0.35 mL of a 25% solution of diisobutylaluminum hydride (0.41 mmol) in hexane under nitrogen. After the mixture was stirred for 3.5 h at room temperature, 10 mL of a 10% aqueous ammonium chloride solution was added. The precipitated salts were removed by filtration through Celite and thoroughly washed with tetrahydrofuran. After separation of the filtrate layers, the aqueous portion was extracted with dichloromethane (2 × 25 mL). The combined extracts were washed with water (1 × 50 mL) before drying. Removal of the solvent yielded a complex mixture. Purification was effected by a simple ether wash which afforded 14.5 mg (30%) of pure **17**. The ether-soluble products were not identified.

2,3,3a,3b,4a,4b,7,7a,7b,7c,7d,8,8a,8b-Tetradecahydro-1,4,8-(epoxymetheno)dipentaleno[1,2,3-*cd*:1′,2′,3′-*gh*]pentalene-4(1*H*)-carboxaldehyde (18). In certain instances, varying lots of silica gel were found to convert bis(dihydropyran) **15** to **18** when elution through the column was made with ether: ν_{max} (KBr) 2740, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.83 (s, 1 H), 5.78 (m, 1 H), 5.50 (m, 1 H), 4.79 (s with fine splitting, 1 H), 3.94 (s, 1 H), 3.40–1.00 (br m, 17 H); ^{13}C NMR ($CDCl_3$) 207.24 (d), 133.87 (d), 129.99 (d), 71.25 (d), 68.70 (d), 62.93 (s), 59.05, 57.65, 54.50 (2 C), 53.53, 53.04, 48.31, 46.67, 43.45, 42.18, 38.84, 38.11, 33.68, 24.64 ppm; mass spectrum, m/e 294 (M^+, weak), 266 (M^+ − CO, base peak).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.51; H, 7.55.

8-Bromohexadecahydro-4α-methoxy-4*H*-7,4a,8-(epoxymetheno)-1*H*-3-oxacyclopenta[*cd*]pentaleno[1′,2′,3′:3,4]pentaleno[2,1,6-*hia*]indene (29a). The bis(dihydropyran) **15** (106 mg, 0.361 mol) was dissolved in 25 mL of dry methanol (freshly distilled from magnesium methoxide) under a nitrogen atmosphere. The solution was cooled to −10 °C and *N*-bromosuccinimide (65 mg, 0.37 mmol) was added slowly in portions with stirring. After 5 min (deposition of white crystals noted), the reaction mixture was allowed to warm to 25 °C and stirred for an additional 2.5 h. The volume was reduced to ca. 8 mL, and the resulting crystals were filtered off and air-dried to give 90 mg of pure **29a**, mp 188–190 °C. The filtrate was evaporated to near dryness and filtered again to provide an additional 30 mg of product (total yield 90%); ν_{max} (KBr) 1081, 995 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.05 (s, 1 H), 4.90 (br s, 1 H), 4.48

(br s, 1 H), 4.15 (br s, 1 H), 3.42 (s, 3 H), 3.0–1.5 (m, 19 H); ^{13}C NMR ($CDCl_3$) 101.13, 71.85, 70.93, 66.51, 58.74, 56.07, 55.93, 54.08, 53.89, 52.33, 48.79, 48.31, 47.97, 46.56, 46.41, 40.10, 37.67, 23.84, 22.72 ppm (20th signal not observed and may overlap); mass spectrum, *m/e* 406, 404.

Anal. Calcd for $C_{21}H_{25}BrO_3$: C, 62.22; H, 6.17. Found: C, 62.24; H, 6.31.

8-Iodohexadecahydro-4α-methoxy-4*H*-7,4a,8-(epoxymetheno)-1*H*-3-oxacyclopenta[*cd*]pentaleno[1′,2′,3′:3,4]pentaleno[2,1,6-*hia*]indene (29b). The bis(dihydropyran) **15** (101.5 mg, 0.345 mmol) was dissolved in dry methanol (20 mL) under nitrogen and *N*-iodosuccinimide (78.8 mg, 0.35 mmol) was added in portions at 25 °C. After 1 h, the volume of solvent was reduced to ca. 7 mL, and the white crystals were separated by filtration to give 120 mg of pure **29b**, mp 153–155 °C dec. Further concentration afforded an additional 35 mg of **29b** (total yield 99%): ν_{max} (KBr) 1080, 992 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.99 (s, 1 H), 4.87 (br s, 1 H), 4.72 (br s, 1 H), 3.40 (s, 3 H), 3.2–1.5 (br m, 19 H); ^{13}C NMR ($CDCl_3$) 101.07, 76.66, 71.66, 70.64, 60.88, 57.14 (2 C), 55.93, 54.33, 54.04, 52.92, 49.03, 48.31, 48.21, 47.68, 46.56, 46.36, 40.00, 37.63, 23.69, 22.87 ppm; *m/e* calcd 452.0850, obsd 452.0858.

Anal. Calcd for $C_{21}H_{25}IO_3$: C, 55.76; H, 5.57. Found: C, 55.72; H, 5.51.

Exposure of 29a to Silver Perchlorate. 8-Bromo-2,-3,3a,3b,4a,4b,7,7a,7b,7c,7d,8,8a,8b-tetradecahydro-1,4,8-(epoxymetheno)dipentaleno[1,2,3-*cd*:1′,2′,3′-*gh*]pentalene-4(1*H*)-carboxaldehyde (30). To a solution of bromo acetal **29a** (133 mg, 0.328 mmol) in dry benzene (10 mL) was added 1.48 mL of 0.222 M silver perchlorate in benzene (0.328 mmol). The mixture was stirred for 30 min and placed directly on a Florisil column (tetrahydrofuran elution) to give 120 mg of crude product. This material was subjected to purification on preparative TLC (silica gel, 10% ether in hexane). There was isolated 58 mg (47%) of **30**: mp 138–139.5 °C; ν_{max} (KBr) 2930, 1710, 1081, 710, 674 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.93 (s, 1 H), 5.80 (m, 1 H), 5.50 (m, 1 H), 4.85 (br m, 1 H), 4.55 (br m, 1 H), 3.7–1.0 (m, 16 H); *m/e* calcd 372.0725, obsd 372.0732.

Anal. Calcd for $C_{20}H_{21}BrO_2$: C, 64.35; H, 5.67. Found: C, 64.04; H, 5.75.

Obtained as well was 25 mg (21%) of **4**, with spectral properties identical with those of the authentic sample.

Exposure of 29b to Silver Perchlorate. Tetradecahydro-5α-hydroxy-6α-methoxy-5*H*,6*H*-1,5b,12:5a,10,11-dimethenodicyclopenta[*e*,*e*′]benzo[2,1-*c*:3,4-*c*′]dipyran (32). A solution of iodo acetal **29b** (50.4 mg, 0.112 mmol) in 15 mL of dry benzene under a nitrogen atmosphere was treated with 0.51 mL of 0.222 M silver perchlorate in benzene (0.113 mmol) in one portion. A yellow precipitate formed instantly. The reaction mixture was stirred for 15 min prior to the addition of solid sodium chloride to remove unreacted silver ion. The precipitate was separated by filtration and the filtrate concentrated. Preparative TLC on silica gel (elution with 10% ether in hexane) yielded 25 mg of a substance tentatively assigned structure **32**: ^1H NMR ($CDCl_3$) δ 5.90 (m, 1 H), 5.39 (s, 1 H), 4.06 (br m, 1 H), 3.85 (br m, 1 H), 3.41 (s, 3 H), 2.6–1.5 (m, 18 H).

Eicosahydro-4,8-dioxadicyclopenta[*cd*]cyclopropa[*g*]-pentaleno[2,1,6-*hia*:5,4,3-*h*′*i*′*a*′]diindene (35). Silver acetate (44 mg) was dissolved in hot acetic acid (15 mL) under nitrogen. To this solution was added zinc dust (1.098 g, 16.8 mg-atoms), and the mixture was stirred for a few minutes. The acetic acid was decanted off and the zinc–silver couple was washed with acetic acid (15 mL) and then ether (4 × 15 mL). Ether (15 mL) and methylene iodide (3.0 g, 11.2 mmol) were added, and the suspension was refluxed for 30 min under nitrogen. At this point, 165 mg (0.560 mmol) of **15** was introduced prior to overnight heating at the reflux temperature. The cooled supernatant was decanted into a separatory funnel, and the residue was thoroughly washed with ether. The combined ether solutions were washed with 10% hydrochloric acid (2 × 20 mL), aqueous sodium thiosulfate (20 mL), and saturated sodium bicarbonate solutions (20 mL) prior to drying and concentration. There remained 180 mg (100%) of **35** judged to be pure by ^1H NMR analysis. Recrystallization from methanol gave colorless prisms: mp 181–186° dec, with prior softening at 165 °C; ν_{max} (KBr) 3120–3000 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.056, 5.014, 4.975, 4.929 (X part of ABX system, 2 H), 3.700, 3.664, 3.628 (t, 2 H), 3.3–1.3 (br m, 18 H), 0.749, 0.703, 0.681, 0.635 (B part of ABX, 2 H), 0.459, 0.387, 0.374, 0.306 (A part of ABX, 2 H); ^{13}C NMR ($CDCl_3$) 68.14, 60.54, 57.57, 52.50, 48.83, 47.37, 47.10, 38.63, 21.85, 20.93, 9.12 ppm; mass spectrum, *m/e* 322.

Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.53; H, 8.13.

Acid-Promoted Ring Opening of 35. A. 9-Methyloctadecahydro-4α-methoxy-1*H*-8,5a,9-(epoxymetheno)-3-oxacyclopenta[*cd*]pentaleno[1′,2′,3′:3,4]pentaleno[2,1,6-*ija*]azulene (38b). A suspension of **35** (88 mg, 0.273 mmol) in a 50% solution of concentrated hydrochloric acid in methanol (5 mL) was heated at reflux with stirring for 30 min. The resulting dark colored solution was cooled, diluted with water (20 mL), and extracted with dichloromethane (3 × 15 mL). The combined organic extracts were washed with saturated sodium bicarbonate solution (15 mL), dried, and evaporated. The residual dark oil (90 mg) was chromatographed on silica gel (elution with 10% ether in hexane) to give 70 mg (72%) of **38b**: colorless needles from hexane, mp 141 °C; ^1H NMR ($CDCl_3$) δ 4.789 (s, 1 H), 4.518, 4.469, 4.414, 4.365 (X part of ABX, 1 H), 4.081 (m, 1 H), 4.045 (m, 1 H), 3.335 (s, 3 H), 2.75–1.30 (br m, 20 H), 1.082 (s, 3 H); *m/e* calcd 354.2195, obsd 354.2200.

Anal. Calcd for $C_{23}H_{30}O_3$: C, 77.93; H, 8.53. Found: C, 77.58; H, 8.47.

B. Two-Step Procedure. Bis(cyclopropyl ether) **35** (30 mg, 0.093 mmol) was dissolved in dichloromethane which had been saturated with hydrogen chloride (2 mL). After being stirred at room temperature for 30 min, the solution was evaporated to dryness to provide a quantitative yield of **38a**: mp 153–155 °C dec, with prior softening at 130 °C; ^1H NMR ($CDCl_3$) δ 5.65, 5.58, 5.48, 5.40 (X part of ABX, 1 H), 4.68 (br m, 1 H), 4.29 (br m, 1 H), 4.08 (m, 1 H), 3.32–1.35 (br m, 20 H), 1.07 (s, 3 H); *m/e* calcd 258.1699, obsd 258.1706.

The above product was suspended in dry methanol (2 mL) and stirred at room temperature for 24 h during which time dissolution occurred. Removal of the solvent under reduced pressure left a white solid whose spectral characteristics were identical with those of **38b** isolated earlier.

Bromination of 35. 9-(Bromomethyl)octadecahydro-4α-methoxy-1*H*-8,5a,9-(epoxymetheno)-3-oxacyclopenta-[*cd*]pentaleno[1′,2′,3′:3,4]pentaleno[2,1,6-*ija*]azulene (38d). A solution of **35** (30 mg, 0.093 mmol) and bromine (9.84 μL, 0.191 mmol) in carbon tetrachloride (2 mL) was refluxed for 1 h. The cooled reaction mixture was evaporated to dryness under reduced pressure, and the residue was recrystallized from benzene/hexane to give pure **38c** as fine white needles, mp 225–226 °C dec with prior sintering at ~200 °C.

A sample of this material (16 mg, 0.033 mmol) was stirred in dry methanol (2 mL) for 24 h prior to removal of the solvent under reduced pressure and recrystallization of the residue from methanol. There was isolated 10 mg (72%) of **38d**: mp 188–189 °C dec; ^1H NMR ($CDCl_3$) δ 4.916 (m, 1 H), 4.535, 4.486, 4.430, 4.382 (X part of ABX, 1 H), 4.11–4.0 (br m, 2 H), 3.762 (s, 2 H), 3.341 (s, 3 H), and 2.83–1.40 (br m, 20 H); *m/e* calcd 432.1300, obsd 432.1308.

Anal. Calcd for $C_{23}H_{29}BrO_3$: C, 63.74; H, 6.74. Found: C, 63.41; H, 6.80.

Hexadecahydro-4a*H*,8a*H*-1,4,5,8-tetraoxadicyclopenta-[*cd*]oxireno[*g*]pentaleno[2,1,6-*hia*:5,4,3-*h*′*i*′*a*′]diindene (39). To a stirred solution of **15** (200 mg, 0.68 mmol) in dry ether (15 mL) was added *m*-chloroperbenzoic acid (280 mg of 85% purity, 1.38 mmol), and epoxidation was allowed to proceed for 3 h at room temperature. The reaction mixture was transferred to a separatory funnel where it was washed with 10% sodium carbonate solution (4 × 20 mL) and water (20 mL) prior to drying. Concentration gave a white solid which was triturated with a small amount of warm hexane to remove residual *m*-chloroperbenzoic acid. There was obtained 150 mg (67%) of **39**: small colorless needles from ethyl acetate/hexane, mp 197–200 °C dec; ^1H NMR ($CDCl_3$) δ 5.826 (s, 2 H), 4.046 (m, 2 H), 3.30–1.43 (br m, 18 H); ^{13}C NMR ($CDCl_3$) 81.27, 71.03, 62.18, 53.45, 48.38, 47.30, 45.79, 45.09, 38.29, 21.84 ppm; mass spectrum, *m/e* 308 ($M^+ - H_2O$), 297 ($M^+ - HCO$).

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.42; H, 6.81.

Hexadecahydro-3,6-dioxadicyclopenta[3,4]pentaleno[2,-1,6-*cde*:2′,1′,6′-*gh′a*]pentalene-3a,6a-dicarboxaldehyde (41). A 250-mg (0.766 mmol) sample of **39** was taken up in dichloromethane and adsorbed onto silica gel. The substance was allowed to remain on the column for 2 h before elution (CH_2Cl_2) was initiated. There was obtained 110 mg (44%) of dialdehyde **41**: colorless prisms from benzene/hexane, mp 190–200 °C dec; ν_{max} (KBr) 2790, 2690, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) 9.663 (s, 2 H), 4.70 (m, 2 H), 3.60–1.40 (br m, 18 H); ^{13}C NMR ($CDCl_3$) 205.51, 103.43, 92.53, 63.50, (2 C), 61.72, 57.95, 49.20, 34.15, 29.73 ppm; mass spectrum, *m/e* 297 (base peak, $M^+ - HCO$), no M^+.

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.83; H, 6.91.

Hexadecahydro-3,6-dioxadicyclopenta[3,4]pentaleno[2,-1,6-*cde*:2′,1′,6′-*gh′a*]pentalene-3a,6a-dicarboxaldehyde Bis(dimethyl acetal) (42a). A solution of **41** (30 mg, 0.092 mmol) in dry methanol (5 mL) containing 1 drop of concentrated sulfuric acid was stirred at room temperature for 2 h. The resulting precipitate was separated by filtration and recrystallized from methanol to give 30 mg (78%) of **42a**: mp 193–195 °C; ν_{max} (KBr) 2960, 1520, 1200, 1170, 1090, 900, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.80 (m, 2 H), 4.02 (s, 2 H), 3.46 (s, 6 H), 3.43 (s, 6 H), 3.40–1.60 (br m, 18 H); ^{13}C NMR ($CDCl_3$) 109.28, 102.58, 92.00, 62.77, 62.09, 61.80, 58.26, 57.72, 54.13, 50.25, 33.90, 29.00 ppm.

Anal. Calcd for $C_{24}H_{34}O_6$: C, 68.87; H, 8.19. Found: C, 68.71; H, 8.13.

3a,6a-Bis(hydroxymethyl)hexadecahydro-3,6-dioxadicyclopenta[3,4]pentaleno[2,1,6-*cde*:2′,1′,6′-*gh′a*]pentalene (42b). Dialdehyde **41** (70 mg, 0.215 mmol) was dissolved in dry methanol (8 mL) at 0 °C. Sodium borohydride (64 mg, 1.72 mmol) was added, and the reaction mixture was stirred at room temperature for 18 h. After acidification with dilute acetic acid, the product was extracted in dichloromethane (3 × 10 mL), and the combined organic layers were washed with water, saturated sodium bicarbonate solution, and brine prior to drying and evaporation of solvent. The residual white solid was chromatographed on silica gel to give 50 mg (70%) of the highly insoluble diol **42b**: mp > 260 °C; ν_{max} (KBr) 3400, 2940, 1450, 1190, 1110, 1075, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.68 (t, J = 5.5 Hz, 2 H), 3.60 (d, J = 10,8 Hz, 2 H), 3.30 (d, J = 10.8 Hz, 2 H), 3.8–1.5 (m, 20 H).

Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.54; H, 7.98.

Hexadecahydro-3,6-dioxadicyclopenta[3,4]pentaleno[2,-1,6-*cde*:2′,1′,6′-*gh′a*]pentalene-3a,6a-dicarboxylic Acid (43a). Silver oxide was freshly prepared by addition of a solution of sodium hydroxide (184 mg, 4.6 mmol) in 5 mL of water to a solution of silver nitrate (390 mg, 2.3 mmol) in 25 mL of water. The brown precipitate was stirred for 5 min under nitrogen at which time 155 mg (0.475 mmol) of **41** dissolved in tetrahydrofuran (5 mL) was introduced dropwise. The mixture was stirred for 7 h at 25 °C and filtered. The filtrate was acidified with 2 N hydrochloric acid and extracted with dichloromethane (4 × 25 mL). The combined organic layers were washed with water and brine before drying. Solvent removal left 50 mg (29%) of dicarboxylic acid **43a**: mp 240 °C dec (from methanol/ethyl acetate); ^1H NMR ($CDCl_3$) δ 6.0–5.0 (br m, 2 H), 4.62 (m, 2 H), 4.18 (m, 2 H), 3.9–1.5 (br m, 16 H); mass spectrum, *m/e* 313 ($M^+ - COOH$).

Anal. Calcd for $C_{20}H_{22}O_6$: C, 67.04; H, 6.15. Found: C, 66.68; H, 6.47.

Di-*tert*-butyl Hexadecahydro-3,6-dioxadicyclopenta-[3,4]pentaleno[2,1,6-*cde*:2′,1′,6′-*gh′a*]pentalene-3a,6a-dipercarboxylate (43b). Dicarboxylic acid **43a** (290 mg, 0.81 mmol) was heated at reflux with thionyl chloride (25 mL) for 3 h under nitrogen. The excess reagent was removed under reduced pressure, benzene (25 mL) was added, and the evaporation was repeated. The residue was finally placed under high vacuum for 30 min prior to being dissolved in dry ether (25 mL) and tetrahydrofuran (5 mL) and cooled to 0 °C. Pyridine (0.75 mL) was added followed by *tert*-butyl hydroperoxide (510 mg, 5.67 mmol). This mixture was stirred for 2 h and filtered. The filtrate was washed with cold 3% aqueous sulfuric acid solution, cold 5% sodium carbonate solution, and ice-cold water. The organic phase was dried and concentrated to give *tert*-butyl perester **43b** (50 mg, 14%) which was used without further purification.

Octadecahedro-3,6-dioxadicyclopenta[3,4]pentaleno[2,-1,6-*cde*:2′,1′,6′-*gh′a*]pentalene (3). Dialdehyde **41** (100 mg, 0.31 mmol) was placed in a 0.5-mL flat-bottomed reaction vessel along with acetophenone (7.4 mg, 0.061 mmol), benzyl mercaptan (1 mg, 0.008 mmol), and ethyl benzoate (3 drops) as solvent. The mixture was stirred magnetically, heated to 140 °C under argon, and irradiated with a 275-W sunlamp. The immediate evolution of carbon monoxide was noted. After 2 h, an additional milligram of benzyl mercaptan was added to again promote gas evolution which had subdued. Two hours later, the mixture was allowed to cool, and product purification was achieved by preparative TLC on silica gel (elution with 40% ether in hexane). There was isolated 80 mg (90%) of **3** as a fluffy white solid: mp 156–158 °C (from methanol); ν_{max} (KBr) 2940, 2842, 1085, 1026, 896 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.55–4.0 (m, 4 H), 3.3–1.5 (br m, 18 H); ^{13}C NMR ($CDCl_3$) 91.08, 90.30, 62.68, 62.29, 61.36, 56.22, 49.57, 34.08, 28.84 ppm; *m/e* calcd 270.1620, obsd 270.1613.

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.80; H, 8.13.

Reduction of 39 with Sodium in Liquid Ammonia. A. In the Absence of a Proton Source. Sodium metal (28 mg, 1.23 mg-atom) was dissolved in freshly distilled (from sodium) ammonia under an inert atmosphere. A solution of **39** (50 mg, 0.153 mmol) in anhydrous tetrahydrofuran (3 mL) was introduced dropwise at −33 °C. Upon completion of the addition, the mixture was stirred for 2 h prior to the addition of solid ammonium chloride until loss of the blue color. Evaporation of the ammonia was followed by quenching with 50 mL of 10% hydrochloric acid. The mixture was extracted with dichloromethane (3 × 10 mL), and the combined organic layers were washed with water, dried, and evaporated. There remained 50 mg (100%) of product, whose spectra were identical with those of **5a**.

B. In the Presence of Ethanol as a Proton Source. To 15 mL of anhydrous liquid ammonia cooled to −78 °C was added 150 mg (6.52 mg-atom) of sodium metal followed by 2 mL of absolute ethanol. Diepoxy ether **39** (100 mg, 0.306 mmol) in dry tetrahydrofuran (4 mL) was introduced dropwise during 15–20 min, and stirring at −33 °C was continued for 1 h prior to the addition of solid ammonium chloride and workup as described above. There was isolated 50 mg (50%) of the very insoluble tetrol **45** which could be recrystallized from pyridine/dichloromethane and obtained as small prisms: mp 268–272 °C dec; ν_{max} (KBr) 3380 cm^{-1}; ^1H NMR (pyridine-d_5) δ 7.29 (s, 2 H), 5.53, 5.48, 5.44, 5.38 (X part of ABX, 2 H), 4.73, 4.68, 4.59, 4.54, 4.44, 4.34, 4.31, 4.21 (AB part of ABX and m, 6 H), 2.69–1.48 (br m, 18 H); ^{13}C NMR (pyridine-d_5) 74.96 (d), 59.72 (2 C, t and s), 59.23 (d), 54.81 (s), 50.30 (d), 48.11 (d), 42.38 (d), 35.83 (t), 23.01 (t) ppm; mass spectrum, *m/e* (rel intensity) 332 (M^+, 3), 314 ($M^+ - H_2O$, 100), 296 ($M^+ - 2H_2O$, 60).

Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 71.96; H, 8.45.

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