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# Dissolving-Metal Reduction of a Hemispherical Dichloro Diester. Tests of Relative Enolate Nucleophilicity within a Mixed Dianion and Oxidative Behavior of a Trisecododecahedryl Alcohol

Leo A. Paquette,* Douglas W. Balogh,[1a] Robert J. Ternansky,[1b] William J. Begley,[1c] and Martin G. Banwell[1d]

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

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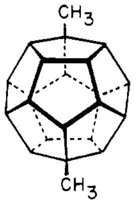
Reduction of dichloro diester **3** with lithium in liquid ammonia generates a dianion (**6**), condensation of which with 1,2-dibromoethane results predominantly in alkylation $\alpha$ to the carbomethoxy group. The resulting monoanion is not subject to transannular cyclization. Its protonation therefore delivers products such as **12**. The less favored route which involves electrophilic attack $\alpha$ to the ketone carbonyl leads irreversibly to transannular hydroxy esters of general formula **10**. Such products do not appear serviceable in the pursuit of dodecahedranes. Although the reactions of **6** with heteroatomic electrophiles did not proceed favorably, the dianion responded very nicely to regioselective monoprotonation–overreduction. With the isolation of **19a** in 50% yield, chemical "stitching" of framework bonds could next be accomplished with relative ease. Unfortunately, however, the trisecododecahedrane alcohol so produced (**23**) could not be oxidized to its aldehyde. The failures of this process are discussed. The findings have an important bearing on those guidelines which must be implemented in order to adapt this chemistry to a successful synthesis of the unsubstituted dodecahedrane molecule.

Our consideration of different synthetic strategies for the construction of 1,16-dimethyldodecahedrane (**1**) led us to become very much attracted to that approach which involves the tandem dissolving-metal reduction–methylation of dichloro diester **3** as its key step.[2,3] In fact, all of the other routes investigated proved to be synthetic dead ends and were eventually discarded. For this and other reasons, the decision was made to concentrate on this chemistry to gain access not only specifically to **1** but also to monosubstiuted derivatives of this aesthetically delightful carbocyclic framework as well. Of course, the prospect that the same scheme would ultimately make available the parent hydrocarbon (**2**) held additional fascination and challenge.



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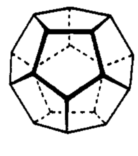

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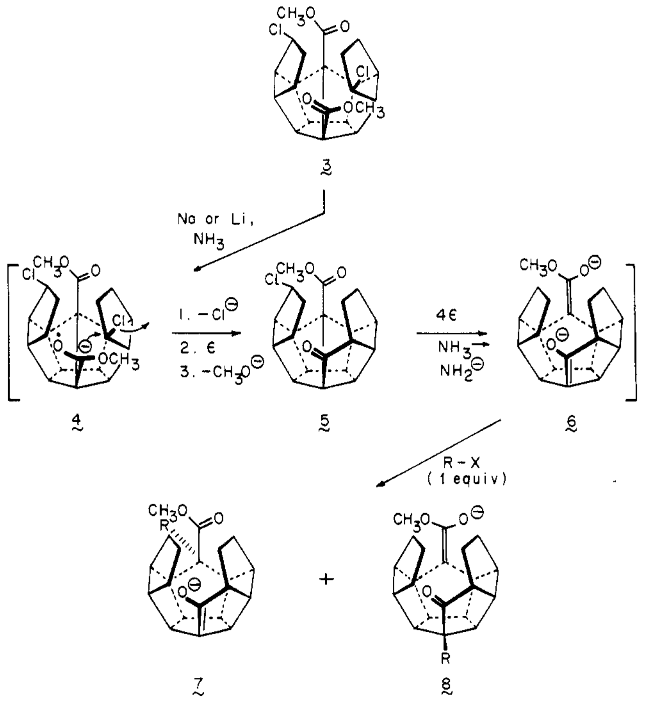
Scheme I



The immediate tasks before us were to assess in detail the relative nucleophilicites of the two anionic centers in **6** as generated from **3** (Scheme I) and, more importantly, to achieve control of regioselectivity in a manner which would enhance the extent of formation of **7** (desired) relative to **8** (unwanted). A desirable side issue was attenuation, if possible, of the customarily high propensity of carbanions such as **8** for transannular bond formation.[4] So little information was available in the literature about the above points that recourse could not be made by analogy to simpler model systems. This contribution is, therefore, confined to a systematic exploration of these chemical phenomena.[5]

**Mechanistic Course of the Dichloro Diester Reduction.** Those familiar with the area of electroorganic chemistry will recognize that the reduction of **3** should follow a well-defined course having its basis in the half-wave potentials of the component functional groups. One relevant facet which has generated considerable interest for more than 2 decades is that dealing with electrore-

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[1] (a) Presidential Fellow, The Ohio State University, 1979–1980. (b) The Ohio State University Fellow, 1977–1978. (c) Postdoctoral Fellow of the Science Research Council (London), 1975–1977. (d) Graduate School Postdoctoral Fellow, The Ohio State University, 1979–1980.

[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. Pacquette, L. A. *Ibid.* **1982**, *104*, 784. (d) Paquette, L. A.; Balogh, D. W. *Ibid.* **1981**, *103*, 228.

[3] Paquette, L. A. "Organic Synthesis Today and Tomorrow"; Trost, B. M.; Hutchinson, C. R., Eds.; Pergamon Press: London, 1981, p 335.

[4] Balogh, D. W.; Paquette, L. A. *J. Org. Chem.* **1980**, *45*, 3038 and references cited therein.

[5] Application of these findings to dodecahedrane syntheses are detailed elsewhere: (a) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Taylor, W. J. *J. Am. Chem. Soc.*, in press. (b) Paquette, L. A.; Ternansky, R. J.; Balogh, W. J. *Ibid.*, in press. (c) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *Ibid.* **1982**, *104*, 4502. (d) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *Ibid.* **1982**, *104*, 4503.

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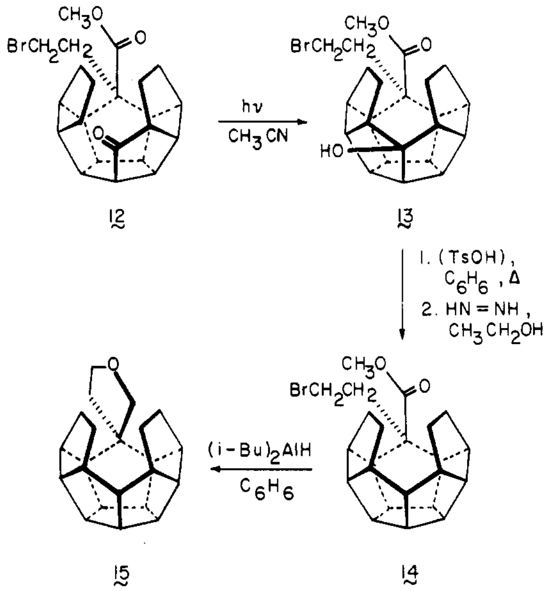
duction of carbon–halogen bonds.[6] For those haloalkanes which offer no special mode of electronic stabilization, acquisition of an electron and scission of the C–X bond is so rapid that the two steps are frequently assumed to be concerted.[6c,7] For the present purposes, the important factor to consider is the relative ease of reduction of covalent carbon–chlorine bonds. It is in fact well-known that ease of reduction follows the order RI > RBr > RCl > RF.[6] Furthermore, chloroalkanes have received minimal attention because their reduction potentials are generally so negative that the polarographic waves are deformed by background decomposition.[8]

While the carbonyl groups of esters are less readily reduced than those of ketones and aldehydes, the first waves leading to radical anions (or the protonated forms thereof) appear almost always at more positive potentials that those of alkyl chlorides.[9] It follows, therefore that electron transfer to **3** should occur more rapidly to the more electropositive carbomethoxy group, generating radical anion **4**. In fact, such chemoselectivity materializes *cleanly* when reduction is effected with an alkali metal in liquid ammonia at reduced temperatures.

Once **4** is generated, two chemical transformations are, in principle, accessible to the radical anion. The first is based upon recognition of the fact that **3** is a 1,4-dicarbonyl system and consequently subject to cleavage of its highly strained central bond.[10] However, the structural precondition for this reaction is proper stereoelectronic alignment of the carbonyl $p\pi$ orbitals with the $\sigma$ bond.[10e,11] In **4**, this requires that *both* oxygenated carbons be oriented in that manner which projects their pendant groups into space already occupied by the endo protons of the proximal transannular methylene groups. For this reason, suitable stereoelectronic overlap of the negatively charged carbon with the ester carbonyl group is expected to be sufficiently sterically disfavored to allow the second option to become kinetically dominant. More favorably, the intramolecular $S_N2$ displacement of the chloride ion which is illustrated requires only that one of the congested centers be properly oriented. Furthermore, molecular models of **4** reveal that the alignment required of the nucleophilic carbon for backside attack at C–Cl is relatively low in steric demand.[12]

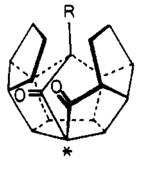
Scheme II



Following construction of a new framework bond in this manner, addition of a second electron and loss of methoxide ion is anticipated with formation of **5**. Continued reduction of this intermediate should, again from known typical half-wave reduction potentials, involve electron transfer to the ketone carbonyl. At this stage, central bond cleavage is inevitable. Since the resulting ester enolate is geometrically unable to displace the second halogen, this chlorine becomes subject to independent reductive cleavage. In overall terms, therefore, a single cyclization results, and solutions of dianion **6** are thereby made available.

**Monoalkylation of Dianion 6.** In our earliest experiments involving the trapping of **6** which are described elsewhere,[2] liquid ammonia solutions of the dianion were treated with large excessess of methyl iodide. Our rationale was based simply on the concern that first-formed intermediate **8** (R = $CH_3$) would be especially prone to transannular aldol cyclization. The presence of a high concentration of electrophilic reagent was, therefore, an attempt to shunt the system away from this impending intramolecular process toward the desired bimolecular one. Our efforts were rewarded with a 65% yield of product.[2]

The situation changes abruptly if monofunctionalization of **6** is made the target objective. For synthetic reasons which will be made clear subsequently, it became imperative that alkylation be achieved selectively $\alpha$ to the carbomethoxy group as in **6**. To our advantage, this anion was viewed by us to be an intermediate whose propensity for subsequent Claisen cyclization would be extensively reduced because of the severe contortion demanded of the asterisked carbon in **9**. In contrast, anion **8** was considered



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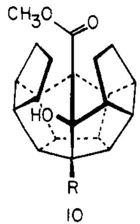

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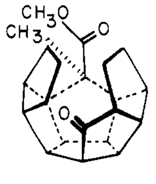

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to be a substance precariously balanced on the precipice, from which it could fall into an energetically beneficial but synthetically useless valley represented by hydroxy ester **10**. Clearly then, preferential electrophile capture at the

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(6) (a) Elving, P. J. *Rec. Chem. Progr.* **1953**, *14*, 99. (b) Rifi, M. R. "Organic Electrochemistry"; Baizer, M. M. Ed.; Marcel Dekker: New York, 1973; Chapter 6. (c) Fry, A. J. "Synthetic Organic Electrochemistry"; Harper and Row: New York, 1972. (d) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970; p 201. (e) Fry, A. J. *Top. Curr. Chem.* **1973**, *34*, 1. (f) Rifi, M. R. "Technique of Electroorganic Synthesis"; Weinberg, N. L. Ed.; Wiley: New York, 1975; Part II, p 170. (g) Rifi, M. R.; Covitz, F. H. "Introduction to Organic Electrochemistry"; Marcel Dekker: New York, 1974, Chapter 4. (h) Elving, P. J.; Pullman, B. *Adv. Chem. Phys.* **1961**, *3*, 1.

(7) Bard, A. J.; Merz, A. *J. Am. Chem. Soc.* **1979**, *101*, 2959.

(8) Abeywickrema, R. S.; Della, E. W. *J. Org. Chem.* **1981**, *46*, 2352 and relevant references cited therein.

(9) (a) Allen, M. J. "Organic Electrode Processes"; Reinhold: New York, 1958; p 58. (b) Perrin, C. L. "Progress in Physical Organic Chemistry"; Wiley: New York, 1965; Vol. 3, p 195. (c) Popp, F. D.; Schultz, H. P. *Chem. Rev.* **1962**, *62*, 29.

(10) (a) Paquette, L. A.; Wyvratt, M. J.; Schallner, O.; Schneider, D. F.; Begley, W. J.; Blankenship, R. M. *J. Am. Chem. Soc.* **1976**, *98*, 6744. (b) Paquette, L. A.; Wyvratt, M. J.; Berk, H. C.; Moerck, R. E. *Ibid.* **1978**, *100*, 5845. (c) Balogh, D.; Begley, W. J.; Bremner, D.; Wyvratt, M. J.; Paquette, L. A. *Ibid.* **1979**, *101*, 749. (d) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *Ibid.* **1979**, *101*, 6991. (e) Paquette, L. A.; Wyvratt, M. J.; Schallner, O.; Muthard, J. L.; Begley, W. J.; Blankenship, R. M.; Balogh, D. *J. Org. Chem.* **1979**, *44*, 3616.

(11) Grinshaw, J.; Haslett, R. J. *J. Chem. Soc., Chem. Commun.* **1974**, 174.

(12) The likelihood that the new framework bond is formed by radical coupling following reduction of the proximal C–Cl bond in **4** cannot, of course, be dismissed and remains a distinct possibility.

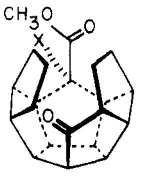
ketone enolate center in **6** would seriously frustrate our aims.

Because little information on the relative reactivities of disconnected ester and ketone enolates in a dianionic species could be uncovered,[13] we delved directly into experimentation. The observation was promptly made that addition of **3** to a solution of 6 equiv of *lithium metal* in liquid ammonia at −78 °C results in the onset of fading of the deep blue color. Remarkably, addition of 1 equiv of methyl iodide at this instant, followed by neutralization with solid ammonium chloride, ultimately provided **11** in 46% yield. The major accompanying product turned out to be **10** ($R = CH_3$).[5a]

Despite the success of these initial experiments, there exist certain features of this reaction which remain somewhat mystifying. As an example, it may be mentioned that 1,2-dibromoethane, when placed under the above circumstances, does not function in its traditional role as a brominating agent toward carbanions.[14] Instead, $S_N2$ attack occurs on carbon to give **12** in 46% yield. Irradiation of this beautifully crystalline solid in acetonitrile resulted again in conversion via a homo-Norrish reaction to the tertiary alcohol **13** (Scheme II) which was dehydrated and reduced with diimide. This three-step sequence, which proceeds free of any difficulty, brings about fabrication of the functionalized trisecododecahedrane **14**. Upon reduction with diisobutylaluminum hydride, **14** was converted into the novel spirocyclic tetrahydrofuran **15**. This last chemical event confirms the geminal placement of the two functional groups in **14** and its precursors.

Isolated alongside **12** was the transannular hydroxy ester **10** (R = H) in 35% yield. Two points are deserving of mention at this time. First, we did not succeed in inhibiting the intramolecular aldol condensation of intermediate **8** (R = H) over a wide range of conditions. Second, and more significantly, the product distributions experimentally observed for **11**/**10** ($R = CH_3$) and **12**/**10** (R = H) show that C-alkylation of **6** at the site α to the ester enolate (leading to **7**) is kinetically favored by a factor approaching 2 relative to attack at the ketone enolate center (leading to **8**). These favorable product distributions were further embellished by the ease of separation of the isomeric products as a direct consequence of the pronounced difference in their polarities.

**Condensation of 6 with Heteroatomic Electrophiles.** Quite clearly, the regioselective attachment of **7** to an R group which would tolerate a number of synthetic transformations, and yet be ultimately removable, was still an important prerequisite for further progress toward dodecahedrane (**2**). We therefore undertook a detailed study of the behavior of **6** toward various sulfenylating agents, mainly in the hope that a workable method of introducing heteroatoms α to the ester functionality might be achieved in good yield. The first insight into the inherent difficulties with this scheme materialized when the reductive cyclization of **3** was followed by addition of 1 equiv of dimethyl disulfide. In various experiments of this type, desired keto ester **16a** was indeed produced, but in 11% yield at a maximum. Somewhat surprisingly, the level of **10** ($R = SCH_3$) was relatively enhanced (36%). Attempts to heighten the quantity of **16a** by addition of 2 equiv of dimethyl disulfide gave only trace quantities of the compound of interest. Instead, low yields of the bis- (**18a**) and tris-thiomethylated (**17a**) derivatives were produced. In anticipation that the more reactive methyl thiobenzenesulfonate reagent would lend itself more ideally to our purposes, **6** was treated with 1 equiv of this reagent. Controlled thiomethylation was not observed, a mixture of **10** (R = H, 16%), **10** ($R = SCH_3$, 36%), and **18a** (8%) being isolated. Needless to say, innumerable efforts to induce introduction of the methylthio group were made, but only with discouraging results. Phenyl thiobenzenesulfonate proved equally unpromising as an electrophile.



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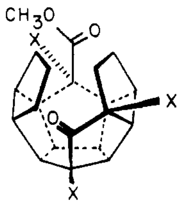

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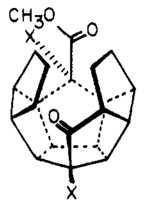

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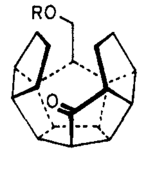
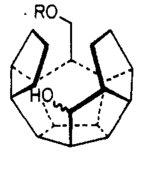
a, $X = SCH_3$ ; b, R = Br

Related attempts to effect the regioselective bromination of **6** with 2,3-dibromo-2,3-dimethylbutane[15] were equally unsuccessful. The variability of our experiences with the reductive substitution of **3** has served only to accentuate our belief that many underlying features of this chemistry remain to be understood.

**Reduction–Protonation of 3.** Because of the refusal of dianion **6** to cooperate in the formation of α-heterosubstituted derivatives of **7**, we sought to achieve the overreduction of **6** to keto alcohol **19a**. For this reaction to be successful, it is mandatory that **6** be protonated with good regioselectivity to give **7** (R = H) under conditions where ensuing reduction of the carbomethoxy group occurs more rapidly than transannular closure to **10** (R = H). In essence, therefore, a sterically facilitated *intramolecular* cyclization has to be intercepted. Gratifingly, this potentially serious problem was circumvented by maintaining a sufficient concentration of lithium metal in the reaction mixture such that ester reduction occurs immediately following monoprotonation of the bis enolate anion. Approximately 12 equiv of lithium metal gave the best results. Under these conditions, a mixture of **19a** (53%) and **20a** was obtained. Some overreduction of the ketone carbonyl proved inevitable; the yield of diol **20a** was nevertheless somewhat variable (5–20%). With the ester group reduced as in **19a**, transannular cyclization is, of course, no longer possible. Fortunately, **20a** could be efficiently recycled to the desired **19a** by selective acetylation of its primary hydroxyl group, oxidation with pyridinium chlorochromate, and alkaline saponification. The endo nature of the hydroxymethyl group in **19a** was established by infrared dilution studies. In more concentrated $CDCl_3$ solution,



19a, R = H
b, $R = COCH_3$



20a, R = H
b, $R = COCH_3$

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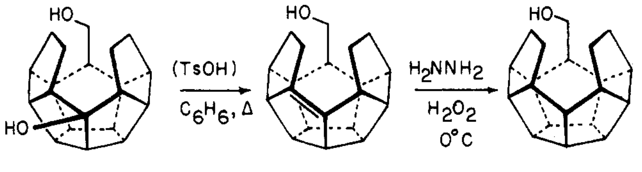
[13] We are aware of two examples where this issue has been raised. In their attempts to effect the chemospecific sulfenylation of methyl 9-oxodecanoate with dimethyl disulfide, Trost, Salzmann, and Hiroi [*J. Am. Chem. Soc.* **1976**, *98*, 4887] were never able to attain >30% of the desired α-carbomethoxy sulfenylated product. The extent of reaction which occurred α to the ketone carbonyl was not stated. In contrast, treatment of the dienolate of 17β-carbomethoxy-5β-androstan-3-one with 2 equiv of dimethyl disulfide gave rise exclusively and quantitatively to α-carbomethoxy sulfenylated product.

[14] See, for example: (a) Greene, A. E.; Muller, J.-C.; Ourisson, G. *J. Org. Chem.* **1974**, *39*, 186. (b) Bond, F. T.; DiPietro, R. A. *Ibid.* **1981**, *46*, 1315.

[15] Kofron, W. G.; Hauser, C. R. *J. Am. Chem. Soc.* **1968**, *90*, 4126.

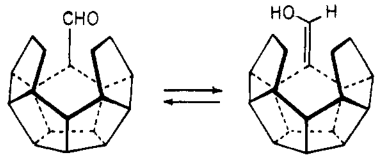
absorptions attributable to both inter- and intramolecularly hydrogen bonded hydroxyl groups were clearly apparent at 3440 and 3600 cm$^{-1}$, respectively. At high dilution, the substantive reduction in intensity of the 3440-cm$^{-1}$ band was not shared by its counterpart at 3600 cm$^{-1}$. The successful interconversion of **20a** with **19a** in turn confirms our stereochemical assignment to the diol.

Hydroxy ketone **19a** was converted to trisecododecahedrane diol **21** through the now familar photoinduced homo-Norrish cyclization. Diol **21** underwent regiospecific acid-catalyzed dehydration to unsaturated primary alcohol **22**, which was reduced with diimide to give **23**. This beautifully crystalline alcohol sports a simple 12-line $^{13}$C NMR spectrum consistent with its $C_s$-symmetric nature.



21 22 23

**Oxidation of Trisecododecahedrane Alcohol 23.** The installation of additional framework bonds with **23** requires that the oxygenated carbon be chemically modified to make it responsive to photochemical activation. Consequently, aldehyde **24** immediately became the next target objective. At the outset, this appeared to be a modest aim. However, a great deal of experimentation has subsequently shown that we had grossly misjudged the actual state of affairs in this most sterically congested molecule. The first hint of difficulty appeared when treatment of **23** with pyridinium chlorochromate (PCC)[16] provided no **24**. Instead, a mixture of $\alpha,\beta$-unsaturated aldehyde **26** and olefin **27** was obtained. The same unsaturated hydrocarbon materialized upon dehydration of **23** with Burgess' reagent.[17] The situation was not at all improved when recourse was made to PCC under buffered (NaOAc) conditions (24% of **26**; 42% of **27**), pyridinium dichromate,[18] activated manganese dioxide,[19] or MnO$_2$ on carbon.[20] The latter group of reagents delivered either **26** alone or a mixture of **26** and **27**. In an effort to frustrate both overoxidation and dehydration, we examined the suitability of the highly touted RuCl$_2$(PPh$_3$)$_3$[21] and KH-PtCl$_2$(PEt$_3$)$_2$[22] reagent systems for our purposes. Whereas the first transition-metal complex gave only **26**, the latter generated a plethora of products. As anticipated, those oxidants which act at the mechanistic level by activating the hydroxyl group via conversion to a good leaving group, e.g., the Pfitzner–Moffatt[23] and Doering–Parikh reagents,[24] transformed **23** uniquely into **27**. An exception to this behavior was observed with the Corey–Kim reagent[25] which afforded only the $\alpha,\beta$-unsaturated aldehyde. The latter course of events was also followed when **23** was exposed to the action of *N*-phenyltriazolinedione[26] or the Swern reagent.[27] In a mechanistically relevant discovery, **23** was found to be smoothly converted to norketone **28** under the conditions of Jones oxidation.



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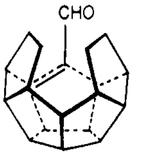

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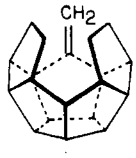

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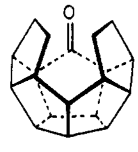

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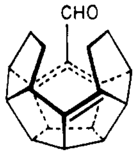
Taken as a whole, our preceding experiences suggest that the first-formed product in those reactions which lead to **26** and **28** is indeed the desired saturated aldehyde **24**. However, the enormous steric crowding around the periphery of the central cavity within **24** serves to promote enolization of the aldehyde carbonyl. Thus, enol **25** becomes the key intermediate in these transformations.[28] Since the susceptibility of **25** to oxidation can be intuitively assumed to be greater than, or at least comparable to, that of its saturated precursor, the steady-state concentration of the enol likely never increases to the point where its spectroscopic observation becomes possible. The heightened oxidizing power of the Jones reagent is believed to allow for continued oxidation of **25** with ultimate extrusion of the original carbinol carbon.

Examination of molecular models of alcohols **22** and **23** revealed that the double bond in **22** caused distortion of the carboxylic framework adequate to release an appreciable level of the steric congestion about the CH$_2$OH group found in **23**. Consequently, the effect of various oxidants on **22** was next studied. With PCC, conversion to mixtures of **29** (two isomers) and the dehydration product (diene) was observed in all too reminiscent fashion. Only **24** was formed when silver carbonate on Celite was utilized. Jones oxidation produced the norketone, in agreement with earlier precedent. Strikingly, however, manganese dioxide in dichloromethane solution furnished chromatographically separable mixtures of **29** (42%) and **30** (45%). In contrast to the appreciable lability of $\alpha,\beta$-unsaturated aldehydes **26** and **29**, **30** proved entirely stable and, in fact, surprisingly resistant to air oxidation. These findings served to solidify our position that the abnormal response of **23** to oxidation was due chiefly, if not totally,



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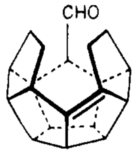

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(16) Corey, E. J.; Suggs, J. W. *Tetraheron Lett.* **1975**, 2647.

(17) Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A. *J. Am. Chem. Soc.* **1970**, *92*, 5224; *J. Org. Chem.* **1973**, *38*, 26.

(18) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.

(19) Reviews: Fatiadi. *Synthesis* **1976**, 65, 133.

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to its especially congested environment.

In further pursuit of our objective to prepare **24**, the possibility that oxidation of **23** to the aldehyde level might be achieved indirectly was also considered. If the alcohol were first functionalized and the derivative subsequently degraded in the absence of an oxidizing agent, it is conceivable that **24** would survive and prove capable of isolation. Very few schemes fall into this category. In the Barton procedure,[29] reaction of an alcohol with phosgene in quinoline is followed by treatment with dry dimethyl sulfoxide and triethylamine. Dimethyl sulfoxide displaces the chlorine atom of the chloroformate intermediate and serves as the indirect oxidant (provided that elimination is not competitive). In the case of **23**, conversion to the chloroformate proceeded in quantitative yield. However, following exposure of this product to $Me_2SO/Et_3N$, there was isolated only $\alpha,\beta$-unsaturated aldehyde **26** and starting alcohol.

The persistency of these problems led us to consider a scheme which, in priciple would generate **24** photochemically under conditions where its homo-Norrish cyclization would be equally favorable. This tandem excited-state oxidation–cyclization, if successful, would obviate the necessity of isolating and handling **24**. Binkley has described a photochemical method for the conversion of alcohols to ketones and aldehydes which involves the irradiation of pyruvate esters.[30,31] This precedent was followed, and **23** was uneventfully condensed with pyruvyl chloride. Upon direct irradiation of this pyruvate ester in benzene through Pyrex as prescribed,[30,31] mixtures of numerous components (separable on preparative TLC) were formed. Aldehyde **24** was clearly not present. In companion experiments, direct oxidation of such mixtures and chromatographic separation gave no indication that the desired trisecododecahedryl ketone had been produced.

In a final attemp to generate the desired aldehyde **24**, the reduction of $\alpha,\beta$-unsaturated aldehyde **26** was examined. It was found that **26** could be reduced under dissolving-metal conditions ($Li/NH_3$/*tert*-butyl alcohol) to yield, upon workup, the saturated aldehyde in its enol form (**25**). Unfortunately, **25** proved to be extremely susceptible to air oxidation (in contrast to **30**), being completely converted to **26**. Furthermore, photolysis of **25** in deoxygenated toluene–ethanol (9:1) solution at −78 °C did not provide unequivocal evidence for the formation of the desired homo-Norrish product.

A number of attempts to photocyclize **26** and **30** were similarly to no avail. On the basis of these results, it became evident that a modified approach was required in order to arrive successfully at target compound **2**.

## Experimental Section

Proton magnetic resonance spectra were obtained with Varian T-60 and EM-390 spectrometers except where indicated; apparent splittings are given in all cases. $^{13}C$ NMR spectra were recorded on Bruker Wp-80, HX-90, and WM-300 spectrometers. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

**Methyl Octadecahydro-7-(2-bromoethyl)-3-oxo-3*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalene-7-carboxylate (12).** Lithium wire (10 mg, 1.43 mg at) which had been stripped of oxide was added to 40 mL of liquid ammonia (freshly distilled from sodium metal) at −78 °C under nitrogen. After 15 min, 7 mL of dry tetrahydrofuran was added followed by a solution of **3** (100 mg, 0.24 mmol) in 5 mL of the same solvent until approximately 95% of the dichloro diester had been introduced. The reaction mixture was stirred at −78 °C for 30 min. (If the blue color dissipated during this time, an additional 2 mg of lithium was added.) The remaining solution of **3** was added to quench the blue color, and 1,2-dibromoethane (48 mg, 0.24 mmol) was introduced in rapid dropwise fashion. Following 15 min of stirring at −78 °C, solid ammonium chloride (200 mg, 3.8 mmol) was added in one portion and the ammonia evaporated. The residue was taken up in ether (80 mL) and washed twice with water and once with brine prior to drying. Solvent evaporation left a clear oil which was subjected to preparative TLC purification on silica gel (elution with 10% ether–45% hexane–45% dichloromethane). At $R_f$ 0.5, the transannular hydroxy ester **10** (R = H) was isolated (25 mg, 35%), identical with material characterized below.

The band at $R_f$ 0.4 proved to **12**: 45 mg (46%); mp 166–168 °C (from ethyl acetate); IR (KBr) 2925, 1725, 1250, 1148 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 4.0–0.95 (series of m, 26 H), 3.64 (s, 3 H); $^{13}C$ NMR ($CDCl_3$) 226.46, 174.11, 64.60, 61.16, 59.26, 59.19, 57.44, 57.32, 55.12, 54.68, 54.04, 53.23, 53.11, 51.68, 51.09, 50.92, 50.83, 35.05, 30.84 (2 C), 30.51, 27.95, (27.33 ppm; mass spectrum, *m/e* calcd ($M^+$) 432.1300, obsd 432.1312. Anal. Calcd for $C_{23}H_{29}BrO_3$: C, 63.74; H, 6.74. Found: C, 63.79; H, 6.84.

**Methyl Octadecahydro-3b-hydroxy-7-(2-bromoethyl)-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-carboxylate (13).** A solution of **12** (50 mg 0.12 mmol) in 20 mL of acetonitrile (some warming necessary) was deaerated with nitrogen and irrdiated with a 450-W Hanovia lamp for 16 h through a Pyrex filter at 15 °C. Concentration of the reaction mixture gave a powdery white solid which was not further purified; IR ($CDCl_3$) 3450, 2942, 1729 $cm^{-1}$; $^1H$ NMr ($CDCl_3$) $\delta$ 3.8–0.9 (series of m, 26 H) and 3.69 (s, 3 H).

**Methyl Hexadecahydro-7-(2-bromoethyl)-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]-pentalene-7-carboxylate (14).** A solution of **13** (50 mg, 0.12 mmol) and *p*-toluenesulfonic acid (2 mg) in 10 mL of benzene was heated at 70 °C for 4 h, cooled, and concentrated in vacuo.

The unpurified olefin was dissolved in 10 mL of absolute ethanol and cooled to 0 °C. Hydrazine (400 mg, 25 mmol) was introduced, followed by the dropwise addition of hydrogen peroxide (30%, 1.6 g) over a 1-h period. The reaction mixture was gradually warmed to 25 °C and stirred for 8 h. Dichloromethane was added to dissolve a fluffy white solid which had formed, and this solution was added to 80 mL of ether. The combined organic layers were washed with water (2×) and brine, dried, and evaporated. the crude product was crystallized from ethyl acetate to give pure **14**. The mother liquors were subjected to preparative TLC purification (dichloromethane–hexane, 1:1). Additional **14** was isolated from the $R_f$ 0.45 band (total yield of 40 mg, 81%, for three steps): mp 152–153.5 °C; IR (KBr) 2928, 1728, 1250, 1145 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.8–0.9 (series of m, 26 H), 3.63 (s, 3 H); $^{13}C$ NMR ($CDCl_3$) 174.53, 70.40, 66.46, 64.04, 63.21, 58.16, 57.19, 52.92, 51.36, 50.93, 49.62, 31.17, 30.39, 28.50 ppm (1C not observed) mass spectrum, *m/e* calcd ($M^+$, $Br^{79}$) 416.1351, obsd 416.1364. Anal. Calcd for $C_{23}H_{29}Br\,O_3$: C, 66.18; H, 7.00. Found: C, 66.50; H, 7.00.

**Reduction of 14.** To a stirred solution of **14** (38 mg, 0.09 mmol) in benzene (6 mL) which had been blanketed with nitrogen was added a toluene solution of diisobutylaluminum hydride (250 $\mu$1, 0.25 mmol). After 10 h, the excess reagent was quenched by addition of methanol, and the reaction mixture was poured into ether (60 mL). Water (10 mL) was added, and the aqueous phase was adjusted to pH 6. The layers were separated, and the ether layer was washed with water (2×) and brine prior to drying. The concentrated filtrate crystallized on standing. Preparative TLC on silica gel (elution with 10% dichloromethane–15% ether–75% hexane) gave 25 mg (89%) of **15** as a colorless solid: mp 151–152.5 °C (from ethyl acetate); IR (KBr) 2920, 1056, 890 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 4.12 (s, 2 H), 4.1–1.0 (series of m, 22 H), 3.67 (t, *J* = 6 Hz, 2 H), 1.76 (t, *J* = 6 Hz, 2 H); $^{13}C$ NMR ($CDCl_3$) 70.40, 70.06, 67.00, 65.25, 64.96, 59.42, 57.97, 52.19 (2 C), 51.56, 50.44, 30.83,

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30.73 ppm (14th signal not observed and may overlap); mass spectrum, *m/e* calcd ($M^+$) 308.2140, obsd 308.2147. Anal. Calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15. Found: C, 85.60; H, 9.08.

**Reduction–Methylthiolation of 3. (A) Use of Dimethyl Disulfide.** Reduction of **3** (50 mg, 0.12 mmol) with lithium wire (5 mg, 0.71 mmol) in tetrahydrofuran (5 mL–liquid ammonia (10 mL) was achieved as previously described. To this reaction mixture was added a solution of dimethyl disulfide (12 mg, 0.13 mmol) in 1 mL of dry tetrahydrofuran. After 15 min at −78 °C, solid ammonium chloride (120 mg) was added, and the ammonia was evaporated. The residue was added to ether (50 mL) and the organic solution was washed with water (2×) and brine prior to drying. The clear oil obtained on solvent evaporation was purified by preparative TLC on silica gel (elution with 10% dichloromethane–15% ether–75% hexane). Two major bands were observed.

(a) $R_f$ 0.45; 16 mg (36%) of transannular cyclization product **10** (R = $SCH_3$) as a colorless solid; mp 122–123.5 °C (from ethyl acetate); IR ($CDCl_3$) 3445, 2940, 1695, 1118 cm$^{-1}$ $^1$H NMR ($CDCl_3$) $\delta$ 5.31 (s, 1 H), 3.72 (s, 3 H), 3.6–1.1 (series of m, 21 H), 2.08 (s, 3H); $^{13}$C NMR ($CDCl_3$) 177.98, 83.75, 69.72, 60.59, 59.91, 57.58, 57.24, 56.70, 55.68, 54.42, 51.70, 50.68, 49.28, 48.35 (2 C), 48.16, 32.72, 26.80, 25.97, 25.44, 24.13, 11.80 ppm; mass spectrum, *m/e* calcd ($M^+$) 372.1759, obsd 372.1767. Anal. Calcd for $C_{22}H_{203}$,s: C, 70.93; H, 7.58. Found: C, 71.09; H, 7.60.

(b) $R_f$ 0.25; 5 mg (11%) of **16a**; IR ($CDCl_3$) 2940, 1720, 1430, 1260 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 4.1–0.9 (series of m, 22 H), 3.67 (s, 3 H), 2.06 (s, 3 H); mass spectrum, *m/e* 372 ($M^+$).

**(B) Use of Methyl Thiobenzenesulfonate.** Reduction of **3** (50 mg, 0.12 mmol) in the predescribed manner followed by the addition of methyl thiobenzenesulfonate (23 mg, 0.12 mmol) gave a reaction mixture which was purified by preparative TLC on silica gel. Four principal products were observed.

(a) $R_f$ 0.5; 6 mg (16%) of **10** (R = H) as a crystalline solid, mp 75–76 °C; IR (KBr) 3450, 1690 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 5.13 (s, 1 H), 3.68 (s, 3 H), 2.9–1.1 (series of m, 22 H); $^{13}$C NMR ($CDCl_3$) 178.37, 80.10, 60.54, 60.20, 59.96, 56.80, 56.17, 52.98, 51.80 (2 C), 51.41, 49.37, 48.55 (2 C), 48.26, 32.58, 27.82, 25.78, 25.49, 24.52 ppm (1C not observed); mass spectrum, *m/e* calcd ($M^+$) 326.1882, obsd 326.1888. Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.22; H, 7.98.

(b) $R_f$ 0.45; 16 mg (36%) of **10** (R = $SCH_3$) identical with the material isolated in section A.

(c) $R_f$ 0.3; 4 mg (8%) of **18a**; IR ($CDCl_3$) 2930, 1720, 1430, 1252 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 4.0–0.9 (series of m, 21 H), 3.67 (s, 3 H), 2.16 (s, 3 H), 2.05 (s, 3 H).

(d) $R_f$ 0.2; 9 mg of an unidentified material.

**(C) Use of Excess Methyl Thiobenzenesulfonate.** Reduction of **3** (50 mg, 0.12 mmol) in the predescribed manner followed by addition of 90 mg (0.48 mmol) of methyl thiobenzenesulfonate gave a product mixture which consisted of two major bands on silica gel TLC: (a) $R_f$ 0.45; 20 mg (45%) of **10** (R = $SCH_3$). (b) $R_f$ 0.40; 15 mg (27%) of **17a**; IR ($CDCl_3$) 2931, 1721, 1430, 1254 cm$^{-1}$ $^1$H NMR ($CDCl_3$) $\delta$ 4.30–0.8 (series of m, 20 H), 3.66 (s, 3 H), 2.26 (s, 3 H), 2.20 (s, 3 H), 2.03 (s, 3 H).

**Octadecahydro-7-(hydroxymethyl)-3*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalen-3-one (19a), Octadecahydro-3-hydroxy-1*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalene-7-methanol (20a), and Methyl Hexadecahydro-9-hydroxy-1,4,8-methanedipentaleno[1,2,3-*cd*:1′,2′,3′-*gh*]pentalene-4(1*H*)-carboxylate (10, R = H).** A solution of lithium (125 mg, 18.1 mmol) in distilled ammonia (60 mL) was cooled to −80 °C (dry ice/ether) under argon. A solution of **3** (500 mg, 1.18 mmol) in tetrahydrofuran (5 mL) was added in dropwise fashion over 2 min. After 8 min, a solution of 25% tetrahydrofuran in ethanol (6.25 mL) was added rapidly, and the resulting mixture was stirred for an additional 2 min at −80 °C. Solid ammonium chloride was added rapidly to discharge the blue color, and the ammonia was evaporated. The residue was added to water (100 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with water (50 mL), dried, and filtered. Evaporation of the solvnet in vacuo gave a clear oil which was subjected to preparative TLC on silica gel (10% ether in dichloromethane elution). At $R_f$ 0.5, hydroxy ketone **19a** was obtained; 186 mg (53%). Recrystallization from ethyl acetate gave pure **19a**: mp 165–170 °C; IR (KBr) 3480, 2940, 1710 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 4.0 (d, $J_{AB}$ = 7.5 Hz, 2 H), 3.8–1.1 (series of m, 24 H); $^{13}$C NMR ($C_5D_5N$) 225.23, 66.69, 61.38, 60.94, 59.10, 57.15, 55.56, 54.49, 53.73, 53.16, 52.59, 51.33, 51.20, 50.70, 48.17, 35.46, 31.92, 30.60, 29.96, 28.13 ppm; mass spectrum, *m/e* calcd ($M^+$) 298.1933, obsd 298.1927. Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.45; H, 8.85.

At $R_f$ 0.45, diol **20a** was obtained (amounts varied from run to run). Recrystallization from ethyl acetate gave the analytically pure material: mp 230–232 °C; IR (KBr) 3600, 3430, 3350, 2930, 1020 cm$^{-1}$; $^1$H NMr ($C_5$,$d_5N$) $\delta$ 5.6 (s, 1 H), 4.3 (m, 2 H), 3.4–1.0 (series of m, 25 H); $^{13}$C NMR ($C_5D_5N$) 79.47, 66.66, 61.75, 61.03, 59.72 (2 C), 58.94, 58.36, 53.74, 52.82, 52.48, 51.80, 51.17, 50.54, 48.06, 34.71, 31.80, 30.58, 28.84, 24.56 ppm; mass spectrum, no $M^+$ observed, *m/e* 282 ($M^+ - H_2O$). Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.77; H, 9.36.

At $R_f$ 0.8, hydroxy ester **10** (R = H) was obtained in minor amounts which varied from run to run.

**Octadecahydro-3-hydroxy-7-(acetoxymethyl)-1*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalene (20b).** To a solution of **20a** (150 mg, 0.5 mmol) in pyridine (5 mL) were added 4-(dimethylamino)pyridine (5 mg) and acetic anhydride (108 mg, 1.1 mmol). The mixture was stirred at 25 °C for 5 h, cooled to 0 °C, and acidified with 5 N hydrochloric acid. The resulting aqueous solution was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with 5 N hydrochloric acid and saturated sodium bicarbonate solution prior to drying and solvent evaporation. The residue was subjected to preparative TLC on silica gel (elution with 50% ether in hexane) to give 90 mg (53%) of **20b** as a colorless solid: mp 152–153 °C (from ethyl acetate–hexane); IR ($CDCl_3$) 3600, 1725 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 4.42 (m, 2 H), 4.13 (t, $J_{AXX'}$ = 7.5 Hz, 1 H), 3.70–1.20 (series of m, 24 H), 2.04 (s, 3 H); mass spectrum, *m/e* 342.

**Octadecahydro-7-(acetoxymethyl)-3*H*-cyclopenta[3,4]pentaleno[2,1,6-*gha*]pentaleno[1,2,3-*cd*]pentalen-3-one (19b).** To a stirred suspension of pyridinium chlorochromate (85 mg, 0.394 mmol) in dichloromethane (5 mL) was added a solution of **20b** (90 mg, 0.26 mmol) in dichloromethane (6 mL). After 2 h, ether (15 mL) was added to precipitate the inorganic salts and the resulting solution was filtered. The filtrate was concentrated and applied directly to a preparative TLC plate (silica gel). Elution with 50% ether in hexane gave keto acetate **19b**: $R_f$ 0.5: 67 mg (75%); IR ($CDCl_3$) 1725 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 4.41 (d, $J_{AB}$ = 7.5 Hz, 2 H), 3.8–0.1 (series of m, 23 H), 2.05 (s, 3 H); mass spectrum, *m/e* calcd ($M^+$) 340.2038, obsd 340.2033.

**Alkaline Hydrolysis of 19b.** Keto acetate **19b** (67 mg, 0.20 mmol) was dissolved in 20% aqueous methanol (5 mL), and potassium hydroxide (33 mg, 0.60 mmol) was added. After being stirred for 1.5 h, the mixture was concentrated to dryness, and water (10 mL) was added. The aqueous solution was extracted with dichloromethane (3 × 10 mL), and the combined organic extracts were washed with water (10 mL), dried, concentrated in vacuo, and applied to a preparative TLC plate (silica gel). Elution with 50% ether in hexane gave 50 mg (85%) of **19a** ($R_f$ 0.5) which was identical in all respects with the authentic sample.

**Octadecahydro-3b-hydroxy-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-methanol (21).** Hydroxy ketone **19a** (49 mg, 0.16 mmol) was dissolved in a solution of 20% *tert*-butyl alcohol in benzene (5 mL). Three drops of triethylamine were added, and the mixture was irradiated for 16 h through Pyrex with a 450-W Hanovia lamp. The crystalline material which had formed was filtered and dried to yield 37 mg (76%) of pure **21**; mp 240 °C dec; IR (KBr) 3400, 3260, 2930, 1010 cm$^{-1}$; mass spectrum, *m/e* calcd ($M^+$) 298.1933, obsd 298.1940. Anal. Calcd for $C_{23}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.21; H, 8.80.

**1,1a,1b,2,3,3a,4,5,5a,6,6a,6b,6c,6d,6e,6f-Hexadecahydro-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-methanol (22).** To a suspension of diol **21** (80 mg, 0.27 mmol) in benzene (30 mL) was added a single crystal of *p*-toluenesulfonic acid. This mixture was heated to 60 °C for about 1 h until complete dissolution occurred, cooled, concentrated in vacuo, and applied directly to a preparative TLC plate (silica gel). Elution with 50% ether in hexane gave the desired product: 73 mg (95%) at $R_f$ 0.6 Recrystallization from ethyl acetate–hexane gave pure **22**: mp 300 °C dec; IR (KBr) 3370, 2940, 1005 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 4.1 (d, $J_{AB}$ = 7.5 Hz, 2 H), 3.73 (m, 2 H), 3.6–1.3 (series of m, 20 H); $^{13}$C NMR (CDCl$_3$) 139.72, 137.34, 74.96, 72.24, 70.35, 64.42 (2 C), 61.56, 54.23, 53.70, 53.45, 51.70, 50.25, 49.08, 48.84, 46.75, 30.25, 28.74, 27.53, 24.03 ppm; mass spectrum, *m/e* calcd (M$^+$) 280.1827, obsd 280.1835. Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.44; H, 8.79.

**Octadecahydro-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene-7-methanol (23).** Hydroxy olefin **22** (57 mg, 0.20 mmol) was dissolved in 4 mL of an ethanol–tetrahydrofuran solution (5:1). The solution was cooled to 0 °C and anhydrous hydrazine (352 $\mu$L, 10.4 mmol) was added, followed by the dropwise addition of cold 30% aqueous hydrogen peroxide (1.1 mL of 30%, 10 mmol) over a period of 1.5 h. The temperature was increased gradually to 25 °C and stirring was continued for 8 h. The mixture was added to water (10 mL) and extraced with dichloromethane (3 × 10 mL). The combined organic extracts were washed with water (2 × 10 mL), dried, and evaporated to give 57 mg (100%) of crude **23**. Preparative TLC on silica gel (50% ether in hexane elution) gave the pure alcohol at $R_f$ 0.3: mp > 250 °C; $^1$H NMR (CDCl$_3$) $\delta$ 4.28 (d, $J_{AB}$ = 7.5 Hz, 2 H), 3.7–1.4 (series of m, 24 H); $^{13}$C NMR (CDCl$_3$) 80.69, 70.25, 67.09, 65.49, 61.51, 58.45, 55.39, 51.70, 51.56, 51.46, 31.56, 31.02 ppm; mass spectrum, *m/e* calcd (M$^+$) 282.1984, obsd 282.1988. Anal. Calcd for $C_{20}H_{26}O$: C, 85.06; H, 9.28. Found: C, 84.66; H, 9.54.

**Oxidation of 23 with Pyridinium Chlorochromate. Octadecahydro-7-methylene-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalene (27) and $\alpha,\beta$-Unsaturated Aldehyde 26.** To a suspension of pyridinium chlorochromate (14 mg, 0.064 mmol) in dry dichloromethane (1 mL) was added a solution of alcohol **23** (12 mg, 0.042 mmol) in dichloromethane (2 mL). After 30 min, ether (5 mL) was added, and the organic solution was decanted from the salts, concentrated, applied directly to a preparative TLC plate (silica gel), and eluted with 50% ether in hexane. The band at $R_f$ 0.8 consisted of olefin: 6 mg (55%); $^1$H NMR (CDCl$_3$) $\delta$ 4.90 (br s, 2 H), 3.6-1.5 (series of m 22 H); mass spectrum *m/e* calcd (M$^+$) 264.1878, obsd 264.1885.

A second band ($R_r$ 0.6) consisted of $\alpha,\beta$-unsaturated aldehyde **26**, as a white crystalline solid: IR (KBr) 2940, 1665, 1615, 1385 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 10.2 (s, 1 H), 4.0–1.4 (series of m, 21 H); $^{13}$C NMR (CDCl$_3$) 186.97, 172.96, 137.80, 69.97, 68.70, 67.42, 63.11, 57.96, 57.41, 54.92, 53.95, 51.83, 51.10, 49.64, 48.97 (2 C), 33.68, 30.95, 29.98, 28.28 ppm; mass spectrum, *m/e* calcd (M$^+$) 278.1671, obsd 278.1680.

**Independent Synthesis of 27.** A solution of **23** (30 mg, 0.11 mmol) in benzene (10 mL) was treated with 30 mg (0.12 mmol) of the Burgess reagent,[17] and the mixture was stirred at 25 °C under nitrogen for 1 h. Following a reflux period of 1 h, the solution was cooled, added to hexane (20 mL), and washed with water (2×) and brine. The dried organic phase was evaporated to leave a crystalline residue. This material was eluted through a short silica gel column to give 24 mg (86% of **27**, whose spectral properties were identical with those of the hydrocarbon isolated above.

**Jones Oxidation of 23. Octadecahydro-1,6-methanocyclopenta[3,4]pentaleno[2,1,6-*cde*]pentaleno[2,1,6-*gha*]pentalen-7-one (28).** To a cold (0 °C) solution of **23** (90 mg, 0.32 mmol) in 6 mL of acetone and 2 mL of tetrahydrofuran was added 15 drops of stock Jones reagent solution (from 200 g of sodium dichromate dihydrate, 272 g of concentrated sulfuric acid, and 600 mL of water) during a 10-min period. After 30 min, excess oxidant was quenched by addition of isopropyl alcohol. The resulting mixture was added to water and extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with saturated sodium bicarbonate solution (10 mL), water, and brine prior to drying and solvent evaporation. There was obtained 43 mg (51%) of crystalline **28**. Preparative TLC purification on silica gel (elution with dichloromethane–ether, 9:1) gave colorless crystals: mp 218–222 °C (from ethyl acetate); IR (KBr) 2920, 1710, 1445 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 4.0–0.8 (series of m, 22 H); $^{13}$,c NMR (CDCl$_3$) 227.45, 68.93, 65.60, 60.50, 58.86, 57.59, 53.52, 51.52, 49.88, 30.03, 29.25 ppm; mass spectrum, *m/e* calcd (M$^+$) 266.1671, obsd 266.1679.

**Manganese Dioxide Oxidation of 22.** A solution of **22** (48 mg, 0.17 mmol) in degassed dichloromethane (12 mL) was treated while stirred with 600 mg of commercial manganese dioxide (Alfa Ventron, 94% purity). Stirring was continued at room temperature for 18 h, at which time the reaction mixture was filtered through a Celite pad. The retained solids were washed with copious amounts of ethyl acetate–dichloromethane (1:1). Concentration of the combined filtrates afforded an oily solid which was directly subjected to preparative TLC on silica gel (elution with ether–petroleum ether, 1:1). Two major bands were observed.

(a) $R_f$ 0.55; 20.2 mg (42%) of the aldehyde dienes **29** as a crystalline mixture of isomers; mp > 250 °C; IR (CDCl$_3$) 2940, 1640, 1600 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 9.94 (s, 1 H), 4.0–1.5 (series of m, 19 H); $^{13}$C NMR (CDCl$_3$) 191.71, 187.95, 185.70, 180.24, 175.02, 142.92, 142.43, 141.28, 139.52, 71.67, 71.49, 71.12, 69.61, 69.18, 63.78, 61.41, 57.35, 56.07, 54.19, 53.77, 53.16, 52.49, 48.00, 46.97, 46.49, 46.00, 31.74, 31.19, 30.71, 28.70, 28.34, 25.67, 22.64, 20.57 ppm; mass spectrum, *m/e* calcd (M$^+$) 276.1514, obsd 276.1524.

(b) $R_f$ 0.60; 21.5 mg (45%) of **30** as a colorless crystalline solid; mp 181–183 °C; IR (CDCl$_3$) 2940, 1710 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 9.42 (s, 1 H), 4.0–1.5 (series of m, 21 H); $^{13}$C NMR (CDCl$_3$) 204.69, 141.64, 140.25, 72.70, 69.43, 64.08, 62.81, 62.57, 59.29, 55.41, 54.98, 52.07, 51.40, 51.04, 48.00, 46.18, 29.74, 29.43, 25.85 23.24 ppm; mass spectrum, *m/e* calcd (M$^+$) 278.1671, obsd 278.1680.

**Dissolving-Metal Reduction of 26.** To 5 mL of liquid ammonia (freshly distilled from sodium) was added 5 mg (0.7 mmol) of lithium wire. The mixture was stirred at the reflux temperature under argon until the lithium had dissolved. A solution of **26** (30 mg, 0.11 mmol) and *tert*-butyl alcohol (8.2 mg, 0.11 mmol) in tetrahydrofuran (2 mL) was added dropwise over 10 min. After an additional 30 min of stirring, solid ammonium chloride was added to discharge the blue color, and the ammonia was evaporated. The residue was taken up in dichloromethane (50 mL), washed with water, dried, and filtered. Evaporation of the solvent in vacuo gave 30 mg (100%) of **25** as an air-sensitive white solid: IR (CDCl$_3$) 3600, 2930, 1240, 840 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 6.15 (s, 1 H), 3.6–1.1 (series of m, 23 H).

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**Registry No.** **3**, 71342-50-2; **10** (R = H), 86785-60-6; **10** (R = $SCH_3$), 86785-64-0; **12**, 86785-59-3; **13**, 86785-61-7; **14**, 86785-62-8; **15**, 86785-63-9; **16a**, 86785-65-1; **17a**, 86785-67-3; **18a**, 86785-66-2; **19a**, 86785-69-5; **19b**, 86785-71-9; **20a**, 86785-68-4; **20b**, 86785-70-8; **21**, 86785-72-0; **22**, 86785-73-1; **23**, 86785-74-2; **25**, 86785-80-0; **26**, 86785-76-4; **27**, 86785-75-3; **28**, 86785-77-5; **29** (isomer 1), 86785-78-6; **29** (isomer 2), 86785-81-1; **30**, 86785-79-7; dimethyl disulfide, 624-92-0; methyl thiobenzenesulfonate, 1125-25-3.