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Topologically Spherical Molecules. An Efficient Synthesis of C_{16}-Hexaquinacene and Its Lack of Neutral Homoaromatic Character

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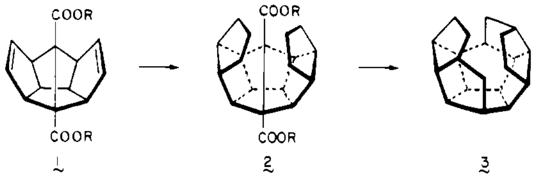
Abstract: The feasibility of gaining access to C_{16}-hexaquinacene in eight steps from the domino Diels–Alder adduct **5** was explored. With lithium hydride and methyllithium, this diacid was transformed to the diacetyl derivative **6** whose methyl groups were σ bonded by formation of the dienolate at low temperature and oxidative coupling with Cu(II). Selenium dioxide oxidation of the resulting 1,4-cyclohexanedione ring in **9** gave the pivotal trienedione **10.** When irradiated, **10** underwent efficient $\pi^2s + \pi^2s$ closure to the caged diketone **12**, a molecule ideally constructed stereoelectronically for ready cleavage of both of its 1,4-dicarbonyl systems. This transformation, which was achieved with zinc in hot acetic acid, produced **14** which was in turn converted to the title compound in three conventional steps. The electronic and structural properties of **4** are summarized, and a brief outline of preliminary reactions is given.

An efficient synthesis of the pentagonal dodecahedrane molecule requires development of a workable combination of regiocontrolled cyclopentane annulation, stereocontrolled incorporation of *all* 20 carbon atoms, and minimization of steric congestion during construction of the last of the requisite carbon–carbon bonds (total of 30). In two preceding papers,[2,3] we have described an attack on this problem beginning with **1**[4,5] and proceeding via appropriate annulation at its olefinic centers (→ **2**), more advanced ring closure, and cleavage of the central σ bond to produce an octaquinane system of type **3.** Although many of the intermediates generated in that program hold considerable promise for continued progress toward the target polyhedron, our ability to elaborate additional useful carbon frameworks would have the virtue of expanding the number of synthetic prerogatives at the critical late stages of sphere construction. Herein we detail alternative synthetic strategy which again utilizes **1** as starting material, but otherwise differs intrinsically from the earlier approach. As before, heavy reliance has been placed upon maintenance of at least C_s or C_2 symmetry throughout, partly for aesthetic reasons and partly for brevity in synthetic manipulation. By such means, the triene **4,** known as C_{16}-hexaquinacene, has been prepared in eight steps. The hydrocarbon is characterized by three mirror planes intersecting a threefold rotation axis. Additionally, its highly convex topology orients the double bonds in a most unique geometry and spatial relationship. The physical and chemical consequences of this arrangement, as known to the present time, also are discussed.



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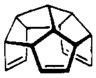

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Synthesis

As alluded to above, the starting point was the readily available diacid **5** which, although already hexacyclic, does not have its five-membered rings properly arrayed relative to those in **4**, Therefore, some degree of structural reorganization was required. Furthermore, since **5** contains only 14 carbon atoms, it was imperative to incorporate two additional methine groups, or precursors to such functionality. This was achieved directly at the outset by sequential treatment of **5** with 2 equiv of lithium hydride and a comparable quantity of methyllithium, followed by dropwise addition to cold dilute hydrochloric acid. Diketone **6** was isolated in 94% yield. Alternative methodology exists for the conversion of hindered carboxylic acids to methyl ketones; the condensation of acid chlorides with lithium di-

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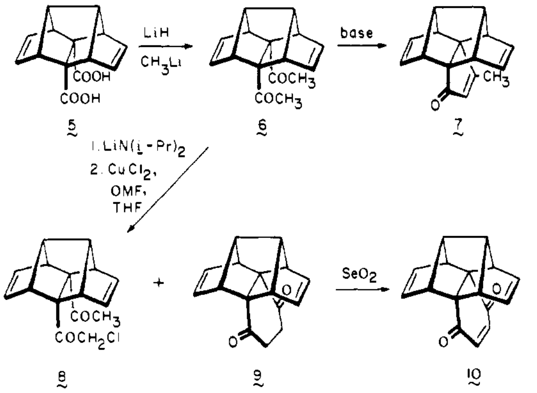
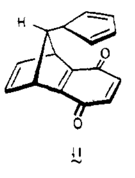
methylcuprate has been shown to be particularly effective.[6] However, in the present instance, such experimental conditions afforded **6** in lower yield (63%).



Consideration was now given to linking of these newly introduced carbon atoms by a double bond. The skeleton of **6** is highly rigid; the two acetyl groups are consequently projected into close proximity. As a result, the situation is ideal for efficient aldolization with formation of **7**. In actual fact, **7** was readily obtained under a variety of alkaline conditions. For our purposes, this reaction was undesirable for it not only links a methyl carbon to a carbonyl group, but also destroys C_{2v} symmetry. To construct the 1,4-cyclohexanedione part structure found in **9**, this complication had to be circumvented. In due course, it was determined that the dienolate of **6** could be generated on treatment with *2 equiv* of lithium diisopropylamide in tetrahydrofuran-hexane solution at −78 °C. The significance of this finding was immediately apparent; were it feasible to oxidize this intermediate to the corresponding diradical, carbon-centered bond formation should ensue. In an adaptation of Saegusa's coupling procedure,[7] the cold dienolate solution was added *inversely* under carefully controlled conditions to anhydrous cupric chloride dissolved in dimethylformamide-tetrahydrofuran (7:1). Condensation proceeded smoothly to give **9** in 58% isolated yield. Variable amounts of **7**, **8**, and an incompletely identified product were also recovered. In our opinion, **7** results when monoenolate happens to be present at the outset of the coupling procedure. An ancillary study established that addition of 1 equiv of lithium diisopropylamide to **6** at −78 °C in the predescribed manner produced substantial amounts of **7**. The isolation of **8** was not particularly surprising in view of literature precedent[8,9] concerning the action of cupric and lithium chlorides on ketones and their enolates in dimethylformamide solution.

The infrared spectrum of **9** shows a single carbonyl absorption at 1693 cm^{-1}. Its ^{1}H NMR is characterized by three rather symmetrical multiplets at δ 6.05, 3.59, and 2.60 and an upfield singlet at 2.33 for the olefinic, allylic bridgehead, saturated methine, and α-carbonyl protons, respectively. The structural assignment was fully confirmed by the ^{13}C NMR spectrum which comprises only six lines.

Subsequently, **9** was heated with selenium dioxide and potassium dihydrogen phosphate in dioxane solution to introduce a third double bond as in **10** (75%). We found it necessary to restrict the duration of the oxidation to 1.5 h. When the reaction time was prolonged, the yield of **10** was appreciably reduced. This is perhaps attributable to complications arising from thermal retrograde Diels-Alder fragmentation of **10** to give **11**. Since this point was not directly investigated in this instance and rests only on analogy,[10] it must be regarded purely as an assumption. Notwithstanding, such a side reaction has not proven to be a serious problem.



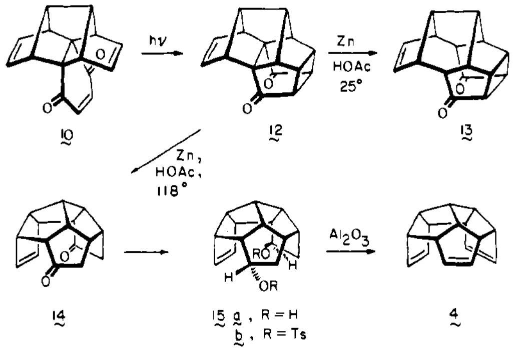
11

Our synthetic approach now called for [2+2] cycloaddition of the enedione moiety in **10** to one of the norbornene double bonds. Although generation of a cyclobutane ring in this fashion is a well-known, excited-state transformation,[11] **10** enjoys a special advantage because of its C_{2v} symmetry. Because of the identity of its pair of isolated π systems, incorporation of one or the other into the four-membered ring becomes immaterial since the same product (**12**) is elaborated. Regiospecificity is therefore not an issue and **10** was efficiently (87%) photocyclized to its highly strained cage isomer when irradiated in benzene solution through Pyrex with 3500-Å light.

With the successful completion of this step, it is seen that the level of symmetrization has been temporarily reduced to C_2. However, this feature, which is attested to by the nine-line ^{13}C NMR spectrum of **12**, is more than offset by most favorable stereoelectronic considerations. Since our ultimate intention was to cleave the central bond present in these molecules, it becomes very important for the carbonyl groups of the 1,4-diketone system to be properly disposed as to geometry. As we have discussed in some detail elsewhere,[2,12] structural factors must not lock the carbonyl pπ orbitals and the C_2-C_3 bond in an orthogonal relationship. This situation prevails in **10** and, in accord with theory, this substance proved stable to the most forcing reducing agents. In **12**, the highly folded nature of the molecule changes the situation entirely; now, the 1,4-dicarbonyl substituents are ideally aligned for maximum through-bond interaction.[13]

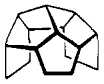
At the experimental level, simple treatment of **12** with zinc and acetic acid at room temperature resulted exclusively in fission of the central norbornyl-like bond to give **13**, The chemoselectivity of this reduction was established by off-resonance ^{13}C NMR techniques. In agreement with the indicated assignment, all eight noncarbonyl carbon signals appear as doublets. If cleavage of the cyclobutane ring had occurred, a combination of six doublets, one triplet, and one singlet would have been seen. The high level of strain present in the inner confines of **12** are made clearly apparent by the preferred formation of **13**.

Once the central bond is cleaved, the structure adopts a more spherical contour and the geometric relationship of the carbonyl groups in the remaining 1,4-diketone part structure becomes less ideal than present originally in **12**. Nonetheless, the second-stage reduction can be accomplished without difficulty by merely raising the reaction temperature to the reflux point of acetic acid (118 °C). These conditions transform either **12** or **13** to the highly valued enedione **14**. This beautifully crystalline substance is characterized by relatively simple spectra which conform to the presence of a molecular plane of symmetry.



Three steps were required to convert this tetrahydrohexaquinacenedione to **4**: (a) lithium aluminum hydride reduction;

(b) conversion to the endo,endo ditosylate **15b**; and (c) activated neutral alumina promoted elimination of 2 equiv of the sulfonic acid.[14,15] The fascinating hydrocarbon so obtained melts at a rather elevated temperature, 231.5-235 °C. The structure follows from analytical and spectroscopic data to be discussed and from a three-dimensional X-ray crystal analysis.[16] The fully saturated $C_{16}H_{22}$ hexacyclic system **16** was obtained in 88% yield by catalytic hydrogenation of **4** over 10% palladium on charcoal.



16

Assessment of Neutral Homoaromatic Character. In his original formulation of the theory,[17] Winstein viewed a homoaromatic molecule to be a cyclic (4*n* + 2) "aromatic" polyolefin in which the conjugation had been interrupted at one or more sites by methano or ethano bridges. The π-electronic structure of the parent polyene was envisioned to be only slightly perturbed and to maintain a major portion of its original stability. Experimental support for homoaromaticity has relied chiefly on ^{1}H NMR data obtained for charged systems,[18,19] although recent years have witnessed several theoretical assessments of the question.[20-23] The picture that has emerged is that the requisite orbital overlap, which is intermediate between pp-π and pp-σ,[24] can be attained with certain structural modifications; but the often dominant role of steric and ring size effects is most restricting and makes sweeping predictions difficult.[18,19,25]

Because of the driving force for charge dispersal embodied in ionic systems, homoaromaticity should be, and is, more important in cations and anions than in neutral compounds, if present at all.[26,27] When charge is lacking, it becomes possible to apply additional criteria to gain quantitative assessment of the extent of through-space orbital interaction, if present. Of these, X-ray crystal structure analysis and photoelectron spectroscopy prove to be most informative. Such added refinement would be equally attractive for ions, but the experimental task in the latter instances is, of course, more complicated.

C_{16}-Hexaquinacene (**4**) may be viewed as a more extensively puckered form of triquinacene (**17**) and *cis*^{3}-1,4,7-cyclononatriene (**18**). Together, the three molecules comprise a unique group of trienes whose constituent double bonds adopt progressively different degrees of possible pp-σ π-orbital overlap. Of decided interest is the question of whether one or more members of this series may partake of homoaromatic stabilization.

17

18

To this end, we have recently demonstrated the reliability of rather simple calculations to arrive at an estimate of the extent of interpenetration of the p_z orbitals on those atoms which must interact through space.[24,28] This index of "bond order" is given by an overlap integral and is based upon experimental knowledge of the internuclear distance separating the two trigonal carbon atoms and the orientation of the two p orbitals relative to an internuclear vector and each other. Such information can be gained by X-ray techniques.

Photoelectron data are somewhat more difficult to interpret because hyperconjugative through-bond effects operate simultaneously and only the net result, namely, the magnitude of the splitting of otherwise degenerate molecular energy levels, can be measured spectroscopically. In tandem with precise three-dimensional structural information and appropriate calculations, however, a rather accurate estimate can be made of prevailing through-space effects.

Crystal structure analysis of **17**[26] has shown the key nonbonded carbon atoms to be 2.533 Å apart and canted by 59.18°. The resultant orbital overlap proved to be quite low (S = 0.054).[24] For **18**, the distance and angle are both reduced in magnitude to 2.46 Å[29] and 54.18°. Accordingly, the extent of orbital interpenetration is somewhat improved (S = 0.066).[24] Photoelectron spectroscopic studies of **17**[30] and **18**[31] have provided parallel results. Thus, in the case of **17**, the energy difference between the bands corresponding to ionization from the e(π) and $a_1(\pi)$ orbitals was found to be only 0.35-0.4 eV; for **18**, the observed splitting was 0.9 eV, corresponding to a resonance integral (β) of −0.3 eV. This difference has justifiably been attributed not to varying degrees of homoaromatic character but to hyperconjugative effects.[30,32] While the interaction of $a_1(\pi)$ with the σ frame in **17** is stronger than that involving e(π), those involving e(π) and $a_1(\pi)$ in **18** are of similar magnitude. The answer to the critical question of whether stabilization is made possible by those π-orbitals arrangements found in **17** and **18** is decidedly negative.

Molecular models of C_{16}-hexaquinacene (**4**) suggested that the enhanced spherical topology of this triene should lead to a much improved in-plane alignment of the pπ orbital triad. The precise geometry of **4** was determined by X-ray analysis[16] and the three double bonds were thereby shown to occupy fixed positions having their lobes projected toward the molecular cavity at an angle of 33.99°. However, at this angle π-π repulsions appear *not* to be comfortably avoided, for the three cyclopentene rings are puckered *outward* so as to make a 5.4° dihedral angle with the C_{3v} symmetric vertical plane! As a consequence, the important intramolecular distance across each gap is increased enormously to 2.848 Å. Therefore, despite the highly favorable angle of cant (which would be reduced well below 30° without such outward distortion), closed shell repulsion effects reduce the magnitude of orbital interpenetration in **4** to only 0.054, a value identical with that previously determined for **17**.

Photoelectron studies of **4** again implicate a strong overriding of any possible homoconjugation by effective hyperconjugative interaction with the σ framework.[16]

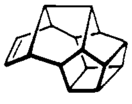
We are, therefore, forced to conclude that σ overlap of the pπ orbitals in **4** is completely ineffective. Although the pπ orbital canting in C_{16}-hexaquinacene is by far the most favorable of any system yet synthesized, π-π repulsion sets in rather than homoconjugative interaction. Do these findings ring the death knell on the possibility of uncovering homoaromatic character in neutral systems? Our answer is decidedly in the affirmative.

Preliminary Studies of the Chemical Behavior of C_{16}-Hexaquinacene. The nonexistence of homoconjugative overlap in **4** has certain chemical ramifications. For example, the triene proved to be inert to attempted reduction with potassium in liquid ammonia or oxidation with $Co(Az)_3$ in a flow-through system.[33]

We also have not yet found it possible to complex **4** to certain transition metals such as Mo(III) and Rh(I). In this connection, a close parallelism exists with the behavior of triquinacene (**17**) under similar circumstances[34] and is probably due to the inaccessibility of approach to the midpoint or interior of the concave surface.

Vacuum pyrolysis of **4** at 800 °C and 0.1 mm afforded a complex mixture of aromatic products. At lower temperatures, C_{16}-hexaquinacene was recovered unchanged. Although secondary reactions were minimized by subliming **4** through a hot tube directly onto a cold finger, the composition of the product mixture proved very sensitive to small variations in the temperature and pressure. Characterization was therefore not pursued.

Irradiation of **4** in pentane solution through Vycor with a medium pressure 450-W Hanovia lamp for 33.5 h afforded 32% of unchanged **4** and a major photoproduct in 22% yield. The photolysis mixture was separated by preparative thin-layer chromatography on silica gel with hexane. The mass spectrum of the photoproduct showed it to be isomeric with **4** and its ^{1}H NMR spectrum integrated for only two olefinic protons. These data, together with the presence of only nine lines in the ^{13}C spectrum, led to the assignment of structure **19**. Whereas **4** does exhibit a propensity for [2+2] intramolecular cycloaddition, we have uncovered no evidence for [2+2+2] photoisomerization to give **20** under a wide variety of sensitized and unsensitized conditions.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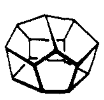
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Experimental Section

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 a Perkin-Elmer Model 467 instrument. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

7,8-Diacetyl-3a,3b,4,6a,7,7a-hexahydro-3,4,7-metheno-3*H*-cyclopenta[*a*]pentalene (6). A. Direct Methylation of 5. Lithium hydride was suspended in 100 mL of dry tetrahydrofuran in a flame-dried, 500-mL, three-necked flash equipped with a magnetic stirring bar, nitrogen inlet, rubber septum, and additional funnel. A solution of diacid **5** (4.38 g, 17.9 mmol) in 75 mL of dry tetrahydrofuran was added dropwise via cannula to the stirred reaction mixture. Stirring at room temperature was continued for 45 min; the mixture was cooled to 0 °C and methyllithium (1.84 M in ether, 60 mL, 100 mmol) was added dropwise rapidly. After completion of the addition, the cooling bath was removed and the reaction mixture was stirred at room temperature overnight prior to transfer via cannula to a cold (0 °C), stirred solution consisting of 1 L of water, 300 mL of 10% hydrochloric acid, and 300 mL of saturated ammonium chloride solution. This mixture was extracted with ether (1 × 200 mL, 3 × 100 mL), and the combined organic layers were washed with water (200 mL), saturated aqueous sodium bicarbonate solution (50 mL), and water (2 × 100 mL). After drying, concentration afforded 4.04 g (94%) of almost pure **6** which was further purified by column chromatography on silica gel (elution with 20% ethyl acetate in hexane). The diketone was obtained as long white needles (from hexane): mp 113 °C; $\nu_{\max}{}^{\mathrm{KBr}}$ 1682, 1353, and 1273 cm^{-1}; ^{1}H NMR (ppm, CDCl$_3$) 6.10 (m, 4 H), 3.31 (m, 4 H), 2.58 (m, 2 H), and 2.02 (s, 6 H); ^{13}C NMR (ppm, CDCl$_3$) 207.24, 132.96, 77.19, 65.12, 59.47, and 28.95; *m/e* calcd 240.1150, obsd 240.1155.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.91; H, 6.82.

B. Cuprate Addition to the Diacid Chloride. Diacid **5** (0.98 g, 4.0 mmol) was dissolved in benzene (40 mL) and pyridine (5 mL). Thionyl chloride (1.7 mL) was added and the mixture was stirred at room temperature for 3 h and heated at reflux for 30 min. The solvent was evaporated, the residue was again dissolved in benzene (20 mL), and solvent removed one more time.

In a separate flask, lithium dimethylcuprate was prepared by addition of ethereal methyllithium (30.44 mL of 1.86 M, 56 mmol) to cuprous iodide (5.12 g, 28 mmol) in anhydrous ether (40 mL) at −5 °C with stirring. This mixture was cooled to −78 °C and the diacid chloride in ether (30 mL) and tetrahydrofuran (10 mL) was introduced dropwise. After 2 h at −78 °C, absolute methanol (4 mL) was slowly added. The reaction mixture was allowed to warm to room temperature and poured into saturated ammonium chloride solution (300 mL). The ether layer was separated and the aqueous phase extracted with ether (3 × 75 mL). The combined ethereal extracts were washed with water (100 mL), dried, and evaporated to leave a yellow oil. Crystallization from ether–hexane afforded 0.60 g (63%) of **6.**

3,3a,3b,4,6a,7a-Hexahydro-1,3,4,7-[1]pentanyl[5]ylidyne-7*H*-cyclopenta[*a*]pentalene-9,12-dione (**9**). In a flame-dried, 500-mL, three-necked flask equipped with a nitrogen inlet, magnetic stirring bar, rubber septum, and addition funnel were placed diisopropylamine (5.50 g, 54.3 mmol) and 90 mL of dry tetrahydrofuran (distilled from lithium aluminum hydride). This solution was treated dropwise at 0 °C with *n*-butyllithium (1.6 M in hexane, 26 mL, 43 mmol) and stirred at 0 °C for an additional 30 min. The base was cooled in a dry ice–isopropyl alcohol bath and a solution of **6** (4.81 g, 20.0 mmol) in 60 mL of dry tetrahydrofuran was added dropwise over 1 h. After being stirred at −78 °C for an additional 3 h, the reaction mixture was transferred via cannula to a flame-dried, 1-L, three-necked flask containing anhydrous cupric chloride (6.15 g, 45.7 mmol, dried at 100 °C/house vacuum then 80 °C/1 mm) in 400 mL of dry dimethylformamide (distilled from calcium hydride) and 50 mL of dry tetrahydrofuran at −78 °C The initially light green solution quickly became dark brown as the bisenolate was added. After completion of the addition, the cooling bath was removed and the reaction mixture was stirred for 1 h before being transferred via cannula to an ice-cold, stirred, solution of water (1 L), 10% aqueous hydrochloric acid (50 mL), and saturated aqueous ammonium chloride solution (300 mL). This mixture was extracted with methylene chloride (1 × 300 mL, 3 × 150 mL) and the combined organic extracts were washed with water (3 × 1 L) prior to drying. Concentration followed by chromatography on silica gel (elution with 10% ethyl acetate in hexane) afforded 2.76 g (57.5% yield) of diketone **9.** Further purification could be affected by recrystallization from hexane and sublimation (110 °C/0.3 mm): mp 214–215 °C; $\nu_{\max}{}^{\mathrm{KBr}}$ 1693 and 1301 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) δ 6.05 (m, 4 H), 3.59 (m, 4 H), 2.60 (m, 2 H), and 2.33 (s, 4 H); ^{13}C NMR (CDCl$_3$) 210.22, 133.21, 69.30, 67.12, 61.29, 39.02 ppm; *m/e* calcd 238.0994, obsd 238.1000.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.63; H, 5.97.

From run to run, differing amounts of **7, 8,** and a yet unidentified substance were isolated. Aldol product **7** was purified by preparative TLC on silica gel (elution with 50% ether in hexane), recrystallization from hexane, and sublimation at 60 °C and 0.2 mm, mp 163-164 °C; $\nu_{\max}{}^{\mathrm{KBr}}$ 2980, 1675, 1589, 1433, and 1331 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.88 (m, 4 H), 3.22 (m, 2 H), 3.12 (m, 2 H), 2.95 (m, 2 H), and 1.92 (d, J = 1.5 Hz, 3 H); ^{13}C NMR (CDCl$_3$) 205.36, 172.11, 137.42, 131.96, 130.60, 73.13, 70.40, 64.24, 61.38, 60.17, and 16.54 ppm; *m/e* calcd 222.1045, obsd 222.1048.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.36; H, 6.45.

In the case of **8**, purification was effected by chromatography on silica gel (elution with ether/dichloromethane/hexane (1:1:6)), recrystallization from carbon tetrachloride and sublimation at 100 °C and 0.2 mm: mp 118.5–119.5 °C; $\nu_{\max}{}^{\mathrm{CHCl_3}}$ 2970, 1693, 1357, and 1285 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.30 (m, 2 H), 6.01 (m, 2 H), 3.99 (s, 2 H), 3.47 (m, 2 H), 3.30 (m, 2 H), 2.65 (m, 2 H), and 2.12 (s, 3 H); ^{13}C NMR (CDCl$_3$) most intense peaks at 207.49, 200.63, 135.18, 131.05, 81.12, 73.13, 66.15, 64.24, 59.96, 47.09, and 27.55 ppm; *m/e* calcd 274.0769, obsd 274.0767.

Anal. Calcd for $C_{16}H_{15}ClO_2$: C, 69.94; H, 5.50. Found: C, 69.78; H, 5.48.

3,3a3b,4,6a,7a-Hexahydro-1,3,4,7-[2]penten[1]yl[5]ylidyne-7*H*-cyclopenta[*a*]pentalene-9,12-dione (**10**). Diene dione **9** (1.24 g, 5.20 mmol) was dissolved in 40 mL of dry dioxane (distilled from sodium benzophenone ketyl), and selenium dioxide (1.72 g, 15.5 mmol) plus potassium dihydrogen phosphate (2.56 g, 18.8 mmol) were added under a nitrogen atmosphere. The mixture was heated at the reflux temperature with stirring for 1.5 h and allowed to come to room temperature prior to filtration and concentration. The residue was taken up in 100 mL of dry ether, and an insoluble yellow solid was separated by filtration. The filtrate was again concentrated, and the residue was taken up in a minimal amount of dichloromethane. Red selenium was removed by filtration, and the filtrate was extracted with saturated aqueous sodium bicarbonate solution (40 mL). The aqueous phase was extracted with additional dichloromethane (25 mL), and the combined organic layers were washed with water (40 mL) and dried. Concentration afforded 0.92 g (75%) of **10.** An analytical sample was obtained by repeated recrystallization from hexane and sublimation at 100 °C and 0.2 mm: mp 222-223.5 °C; $\nu_{\max}{}^{\mathrm{KBr}}$ 2990, 2965, 1663, 1585, 1340, 1300, and 1286 cm^{-1}; ^{1}H NMR (CDCl$_3$)

δ 6.61 (s, 2 H), 5.94 (m, 4 H), 3.66 (m, 4 H), and 2.67 (m, 2 H); ^{13}C NMR ($CDCl_3$) 200.14, 143.58, 132.72, 66.75, 66.21, and 60.81 ppm; *m/e* calcd 236.0837, obsd 236.0842.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.24; H, 5.10.

1a,2,2a,2b,3,5a,6b,6c-Octahydro-1*H*-1,2,3,5b-ethanylylidynecyclobuta[1,2,3-*cd*]pentaleno[1,2,3-*gh*]pentalene-6,8(6a*H*)-dione (12). A solution of **10** (390 mg, 1.65 mmol) in 450 mL of dry benzene was irradiated through Pyrex under a nitrogen atmosphere for 1.5 h with a bank of 3500-Å lamps in a Rayonette reactor. Two runs were combined and the solvent was evaporated under reduced pressure to give 679 mg (87%) of **12** as a light golden oil which was used without further purification: ^{1}H NMR ($CDCl_3$) δ 5.88 (m, 2 H), and 3.62-2.35 (br m, 10 H); ^{13}C NMR ($CDCl_3$) 209.00, 128.47, 76.56, 70.15, 63.27, 52.46, 48.73, 48.52, and 38.20 ppm; *m/e* calcd 236.0837, obsd 236.0842.

1a,2,2a,2b,3,5a,5b,6a,6b,6c-Decahydro-1,2,3-ethanylylidenecyclobuta[*cd*]pentaleno[1,2,3-*gh*]pentalene-6,8(1*H*)-dione (13). To a magnetically stirred solution of **12** obtained from 180 mg (0.762 mmol) of **10** in a glacial acetic acid (10 mL) was added 750 mg of zinc dust. The reaction mixture was stirred at ambient temperature for 6 h, poured into ice water (75 mL) and dichloromethane (10 mL). The mixture was filtered and the precipitate washed well with dichloromethane. The layers were separated and the aqueous phase was extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with water (2 × 50 mL), saturated sodium bicarbonate solution (50 mL), and water (50 mL) prior to drying. Evaporation left 140 mg of crude product which was purified by preparative TLC on silica gel (elution with 20% ether in dichloromethane). There was isolated 67 mg (37% from **10**) of **13**, colorless crystals: mp > 360 °C (from 95% ethanol); ν_{max}^{KBr} 1719 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.83 (s, 2 H), 4.00-3.20 (br m, 8 H), and 3.20-2.74 (m, 4 H); ^{13}C NMR ($CDCl_3$) 219.71, 131.08, 61.38, 60.35, 60.17, 59.14, 58.111, 44.79, and 44.57 ppm; *m/e* calcd 238.0994, obsd 238.1000.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.49; H, 5.97.

2,2a,3,4,4a,4b,5,7a,7b,7c-Decahydro-3,4,5-[1]propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]pentalene-1,9-dione (14). Unpurified photoproduct **12** obtained from 4.16 g (17.6 mmol) of **10** was divided into three portions consisting of 1.56, 1.57, and 1.03 g. Each of these samples was dissolved in 30 mL of glacial acetic acid and 5 g of activated zinc dust was added. The reaction mixtures were stirred magnetically at the reflux temperature for 14 h, allowed to cool to room temperature, and poured into 300 mL of ic-water prior to filtration. The precipitate was washed with dichloromethane and the filtrate was extracted with methylene chloride (3 × 100 mL). The combined organic layers were washed with water (100 mL), saturated aqueous sodium bicarbonate solution (100 mL), and water (100 mL) before drying. Concentration gave a gold-colored solid which was purified by chromatography on silica gel. Elution with 10% ethyl acetate in hexane returned 0.28 g of **10**, while 2.35 g (60% based on unrecovered material) of **14** was obtained upon elution with 30-50% ethyl acetate in hexane. The analytical sample was obtained by sublimation at 160 °C and 0.4 mm, followed by recrystallization from hexane and another sublimation (130 °C, 0.2 mm): mp 216-128 °C; ν_{max}^{KBr} 1718 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.70 (s, 2 H), 3.61 (m, 6 H), 3.01 (m, 4 H), and 2.19 (m, 4 H); ^{13}C NMR ($CDCl_3$) 219.93, 131.57, 60.38, 59.17, 58.71, 57.65, 56.07, 43.82, and 42.54 ppm; *m/e* calcd 240.1150, obsd 240.1153.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.97; H, 6.69.

2,2a,3,4,4a,4b,5,7a,7b,7c-Decahydro-3,4,5-[1]propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]pentalene-*endo*,*endo*-1,9-diol (15a). Lithium aluminum hydride (4.01 g, 106 mmol) was suspended in 25 mL of dry tetrahydrofuran contained in a 300-mL, three-necked flask equipped with a nitrogen inlet, magnetic stirring bar, condenser, and addition funnel. A solution of **14** (1.08 g, 4.50 mmol) in 40 mL of dry tetrahydrofuran was introduced dropwise over 1 h and the reaction mixture was heated at the reflux temperature for 13 h. Excess hydride was quenched by dropwise addition of a saturated aqueous sodium sulfate solution (40 mL) at 0 °C. The mixture was filtered and the white salts were washed extensively with dichloromethane. The filtrate was washed with water (2 × 50 mL) and saturated aqueous sodium bicarbonate solution (50 mL) before drying. Concentration under reduced pressure afforded 0.81 g of **15a**. Dissolution of the lithium salts in 200 mL of 10% hydrochloric acid and extraction with methylene chloride gave an additional 0.21 g of **15a** (total yield 93%). Recrystallization from ethyl acetate produced a white crystalline solid, mp 240-243 °C (corr); ν_{max}^{KBr} 3310, 2929, 2918, 2908, 1068, and 1050 cm^{-1}; *m/e* calcd 244.1463, obsd 244.1468.

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.31; H, 8.35.

2,2a,3,4,4a,4b,5,7a,7b,7c-Decahydro-3,4,5-[1]propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]pentalene-*endo*,*endo*-1,9-diol Di-*p*-toluenesulfonate (15b). Diol **15a** (780 mg, 3.19 mmol) was dissolved in 25 mL of dry pyridine under nitrogen, *p*-toluenesulfonyl chloride (2.43 g, 12.76 mmol) was added in one portion, and the reaction mixture was stirred at room temperature for 48 h before being poured into 250 mL of ice-water and extracted with dichloromethane (3 × 100 mL). The combined organic layers were washed with water (100 mL), cold 2 N hydrochloric acid (1 × 100 mL, 1 × 150 mL), water (100 mL), saturated aqueous sodium bicarbonate solution (100 mL), and water (100 mL). Drying and concentration gave 2.15 g of solid which was recrystallized from ethyl acetate to afford 1.28 g (73%) of **15b**, mp 169.5-170.5 °C; ν_{max}^{KBr} 2936, 1600, 1356, 1189, 1175, 1096, 1001, 976, 957, 946, 927, 903, 896, 862, 840, 829, 810, 666, 573, and 557 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 4 H), 7.23 (d, J = 8.5 Hz, 4 H), 5.80 (s, 2 H), 5.08-4.50 (m, 2 H), 3.53-1.33 (br m, 14 H), and 2.35 (s, 6 H); *m/e* observed base peak at 208.

Anal. Calcd for $C_{30}H_{32}O_6S_2$: C, 65.19; H, 5.84. Found: C, 65.23; H, 5.84.

2a,4,4a,4b,5,7a,7b,7c-Octahydro-3,4,5-[1]propen[1]yl[3]ylidene-3*H*-dicyclopenta[*a*,*cd*]pentalene. C_{16}-Hexaquinacene (4). Ditosylate **15b** (583 mg, 1.06 mmol) was dissolved in 20 mL of dry dichloromethane under a nitrogen atmosphere, and 5 g of activated neutral alumina (heated at 400 °C for 24 h and allowed to cool under vacuum) was added. The mixture was stirred for 1 h prior to removal of the dichloromethane on a rotary evaporator. The coated alumina was further dried under vacuum and then suspended under nitrogen in 20 mL of dry toluene. The mixture was heated at the reflux temperature with magnetic stirring for 2 days. After being cooled to room temperature, the alumina was separated by gravity filtration and leached with methylene chloride/ether (1:1). Concentration of the filtrate afforded 215 mg of white solid which was chromatographed on neutral alumina. Elution with hexane gave C_{16}-hexaquinacene (**4**) which was recrystallized from ethyl acetate to yield 90.8 mg (41%) of white needles: mp 231.5-234 °C (bath preheated to 226 °C); ν_{max}^{KBr} 3030, 2936, 2900, 1353, 743, and 720 cm^{-1}; $\lambda_{max}^{cyclohexane}$ 192 nm (ϵ 19 979); ^{1}H NMR ($CDCl_3$) δ 5.36 (s, 6 H) and 3.76-3.20 (m, 10 H); ^{13}C NMR ($CDCl_3$) 131.57, 60.15, 54.91, and 53.06 ppm; *m/e* calcd 208.1251, obsd 208.1254.

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.72.

Dodecahydro-3,4,5-[1]propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]-pentalene. C_{16}-Hexaquinane (16). A 59.4-mg (0.285 mmol) sample of **4** dissolved in ethyl acetate (10 mL) was treated with 10% palladium on charcoal (21 mg) and hydrogenated in a Parr apparatus for 15 h at 50 psig. The catalyst was separated by filtration and the filtrate concentrated under reduced pressure to give 54 mg (88%) of **16**: mp 177-180 °C (from acetone); ν_{max}^{KBr} 2988, 2985, 2936, and 2858 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.77-2.17 (br m, 10 H) and 2.07-1.13 (br m, 12 H); ^{13}C NMR ($CDCl_3$) 65.978 (d), 54.471 (d), 49.083 (d), 30.246 ppm (t); *m/e* calcd 214.1721, obsd 214.1725.

Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.32; H, 10.35.

Photolysis of C_{16}-Hexaquinacene (4). Synthesis of 19. A magnetically stirred, degassed solution of **4** (104 mg, 0.50 mmol) in 450 mL of purified pentane was irradiated through Vycor with a medium-pressure 450-W Hanovia lamp for 33.5 h under nitrogen. Concentration in vacuo afforded an oily solid which was purified by preparative thin-layer chromatography on silica gel (elution with hexane) to afford 15.3 mg of an unidentified compound plus solvent residue (R_f 0.62), 15.6 mg of **19** (R_f 0.53, 22% based on **4** consumed), and 33.6 mg of recovered **4** (R_f 0.35). Photoproduct **19** was further purified by column chromatography on 10% silver nitrate-silica gel. Hexane elution removed solvent residue and elution with 20% ether in hexane gave **19** as a waxy solid. Sublimation at 40 °C and 1.2 mm onto a finger cooled by methanol at −78 °C circulated by a varistaltic pump furnished pure **19**, mp 153-156 °C; $\nu_{max}^{CHCl_3}$ 2950 cm^{-1}; ^{1}H NMR (CCl_4) δ 5.63 (s, 2 H) and 3.57-2.13 (br m, 14 H); ^{13}C NMR ($CDCl_3$) 133.32, 63.31, 62.38, 59.33, 56.70, 56.07, 49.37, 43.45, and

42.87 ppm; *m/e* calcd 208.1252, obsd 208.1256.

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.27; H, 7.81

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Diels–Alder Reactions of *trans*-1-Methoxy-3-trimethylsilyloxy-1,3-butadiene

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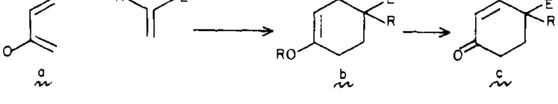
Abstract: Enol silylation of *trans*-4-methoxybut-3-en-2-one affords *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (**1**). This compound has been demonstrated to be a valuable diene in Diels–Alder reactions. These processes provide new and effective routes to aromatic and cyclohexenone systems. The pathways by which the intermediate 3-methoxy-1-silyloxycyclohexenes are transformed to cyclohexenones are considered.

The Diels–Alder cycloaddition has proven to be one of the more reliable reactions in preparative organic chemistry.[1] Its virtually[1,2] perfect cis stereospecificity, its relatively predictable endo selectivity,[1,3] and its excellent regioselectivity,[1,4] particularly with dienes and dienophiles of complementary polarity, have all been used to advantage.[5] Considerable improvements have been realized via recourse to Lewis acid catalysis[6,7] and high pressures.[8]

In embarking on our study in 1974,[9a-d] we noted the relatively modest functionalities which had been incorporated into the dienic components of the cycloaddition. Of particular interest was the scenario implicit in eq 1 wherein utilization of

Eq. 1



diene a would eventually afford the 4-substituted cyclohexenone c via adduct b.

A Russian group[10] had, in fact, reported the preparation of 1,3-diethoxybutadiene, through the cracking of the bis acetal of formylacetone. We had experienced some difficulties in carrying out this pyrolysis in a manner consistent with survival of the highly acid-labile product.

This suggested to us what was probably the main reason for the underutilization of functionalized alkoxydienes in Diels–Alder reactions. The primary route to enol ethers involves the cracking of acetals—a relatively troublesome process.[11a-c]

Fortunately, an alternative which is simple and, above all, more amenable to adaptation by nonspecialized laboratories presented itself. Largely as a result of the pioneering studies of Stork[12a] and House,[12b,c] the value of trimethylsilyl (Me_3Si) enol ethers as enolate equivalents had become apparent.[13,14] Both 1-trimethylsilyloxy- and 2-trimethylsilyloxy-1,3-butadiene had been prepared by enol silylation of their α,β-unsaturated carbonyl precursors (crotonaldehyde and methyl vinyl ketone, respectively).[15a,b] Moreover, Frainnet[15a] had described in each case an example of a Diels–Alder reaction of each of these TMSO butadienes.[16a-f]

It was found that the readily (and commercially) available vinylogous ester *trans*-4-methoxybut-3-en-2-one could be

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