J. Org. Chem. 1989, 54, 3329–3333 3329

Protocol for Multiple Functionalization of the [4]Peristylane Perimeter. Density Relationships between the 2,4,6-Trione, 2,4,6,8-Tetrone, and Related Isopropylidene Congeners

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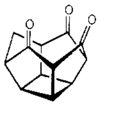
Received February 9, 1989

Details are provided for the synthesis of the tri- and tetraketones in the [4]peristylane series. Access to the latter of these compounds represents arrival at that derivative in which all four available methylene carbons are oxidized. Two approaches to 1 have been developed, the one beginning from fulvene 7 being the more efficient overall. The route from 12 to 2 is similarly efficient. The C_s symmetry of the triketone and the higher C_{4v} symmetry of the tetraketone are clearly reflected in their spectral properties. For example, the ^{1}H and proton-decoupled ^{13}C NMR spectra of 2 are characterized by two doublets and three singlets, respectively. The conformations of 1 and its isopropylidene precursor have been determined by X-ray crystallographic analysis and compared to those of two closely related molecules. Finally, the densities of several of these molecules have been determined, and commentary is made about the apparent relationship of density to the type and level of functional group present within the [4]peristylane core.

Pursuant to our goal of developing synthetic approaches to highly substituted [4]peristylanes,[2-5] we wished to prepare triketone 1 and tetraketone 2. These architecturally attractive molecules, representing the upper limit to rim functionalization of this hemispherical framework,[6] are being considered as potential precursors to spherical hydrocarbons of reduced size relative to dodecahedrane[7] and to polynitro compounds possibly having exceptionally heightened density characteristics.[5]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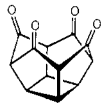
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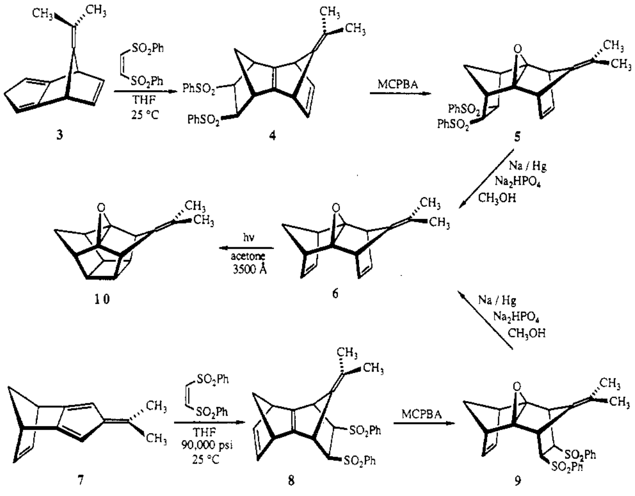
The controlled introduction of multiple carbonyl centers into any complex, conformationally rigid structural unit is an interesting synthetic challenge. In the present instance, the pronounced sensitivity of [4]peristylanes to transannular ring closure[2-5] did not encourage consideration of a route involving direct chemical oxidation of the relevant methylene groups. However, the capacity for introducing at least some of the necessary carbonyl groups via ozonolytic cleavage of appropriately positioned double bonds was considered to have merit and indeed has proven workable.

In addition to describing relatively short routes to the target compounds, we also report herein on the conformations of two repesentative molecules as determined crystallographically. Finally, the density properties of 1, 2, and several isopropylidene precursors are detailed in the context of an appreciation of the relative abilities of [4]-peristylanes to crystallize in tightly packed lattices.

Scheme I



Synthesis

In the first of two approaches to 1 (Scheme I), 10-(1-methylethylidene)tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene (3)[8] was subjected to Diels–Alder reaction with (*Z*)-1,2-bis(phenylsulfonyl)ethylene[9] in tetrahydrofuran solution at room temperature. After 3 days, the formation of 4 had proceeded to the 90+% level. The exclusive below-plane stereoselectivity[10] of this cycloaddition was evident from the ^{1}H NMR properties of the molecule (see Experimental Section) and ultimately confirmed by the chemical transformations that follow. An early indicator was the sensitivity of 4 to oxidation when its solutions in various media were exposed to air.[11] As expected for a *syn*-sesquinorbornadiene,[12] epoxidation of 4 took place regiospecifically at its central double bond. The availability of 5 made possible subsequent reductive elimination of the

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(1) Author to whom queries concerning the X-ray crystallographic analyses should be addressed at the Universität Bern.

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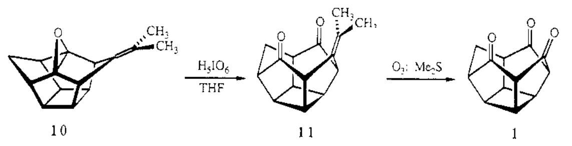
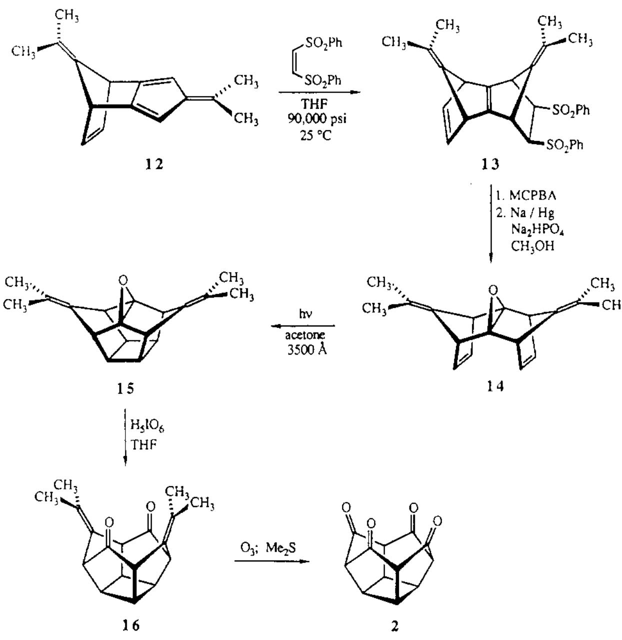
Scheme II



Scheme III



vicinal sulfone groups[13] to produce **6**. This substance was not purified due to its sensitivity to chromatographic adsorbents, but directly photolyzed in acetone solution with 3500-Å light. These conditions effected intramolecular [2 + 2] cycloaddition and concurrent formation of the caged structure **10** in 14% overall yield.

A more efficient pathway to this pivotal intermediate originated with fulvene **7**, available from the parent triene by condensation with acetone in the presence of alcoholic potassium hydroxide. Where **7** is concerned, cycloaddition to give **8** proceeded at a reasonable rate only when high-pressure conditions were used. Maintaining tetrahydrofuran solutions of these reagents at 90 000 psi and 25 °C for 9 days resulted in highly efficient (98%) conversion to **8**. Desulfonylation of the derived epoxide **9** in the predescribed manner then provided **6** in 52% overall yield.

When **10** was exposed to periodic acid in methanol, a multicomponent product mixture resulted (TLC analysis). However, substitution of the less polar tetrahydrofuran as solvent made possible the acquisition of **11** in reasonable yield (57%, Scheme II). The C_s symmetry of **11** was clearly revealed by its nine-line ^{13}C NMR and simplified ^{1}H NMR spectra. Subsequent ozonolysis of this intermediate led to the target triketone **1**, a molecule characterized by only seven carbon signals. The colorless crystals of **1** were not observed to melt below 300 °C.

The success of this pathway led us to apply an entirely similar reaction sequence to superfulvene **12**,[14] a molecule endowed with the maximum number of trigonal carbon atoms allowable to the tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene framework. As in the case of **7**, high-pressure conditions were required to engage **12** in Diels–Alder condensation with the same disulfone (Scheme III). Since **13** (71%) was as susceptible to air oxidation as **8**, the adduct was directly epoxidized. Reductive desulfonylation then furnished epoxy tetraene **14**, the inherent C_{2v} symmetry of which was strikingly apparent from its simple ^{1}H NMR (three signals) and six-line ^{13}C NMR spectra.

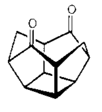
Table I. Crystal Structure Data for 1 and 11

	1	11
molecular formula	$C_{12}H_{10}O_3$	$C_{15}H_{16}O_2$
molecular mass	202.2	228.3
space group	monoclinic $P2_1/n$	orthorhombic $Pnma$
lattice parameters	a = 7.593 (5) Å b = 11.313 (8) Å c = 10.777 (6) Å β = 93.91 (5)°	a = 10.805 (6) Å b = 11.398 (8) Å c = 9.161 (6) Å
cell volume	923.6 Å^3	1128.3 Å^3
density	1.45 g cm^{-3}	1.34 g cm^{-3}
no. of molecules per unit cell	4	4 (special position 4c)
no. of obsd reflections	1464	1129
final agreement factor R	0.07	0.06
	crystal structure is disordered	

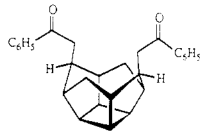
Triplet-sensitized irradiation of **14** resulted in ring closure to the caged epoxide **15** with full preservation of the high-level symmetry characteristics. Following oxidative cleavage of the epoxide unit in **15**, diketo diene **16** was isolated. Its ^{1}H NMR spectrum (in CDCl$_3$) consists of only two absorptions, a narrow multiplet of area 8 at δ 3.46 and a 12-proton singlet at δ 1.85. Ozonolysis of the isopropylidene groups in **16** delivered **2** as a very insoluble colorless solid, mp >300 °C. As a direct consequence of the symmetric positioning of the four carbonyl groups in **2**, the molecule displays only two mutually coupled doublets (J = 4.6 Hz) in its ^{1}H NMR spectrum (DMSO-d_6 solution, δ 4.15 and 3.20) and a total of only three lines in its proton-decoupled ^{13}C NMR spectrum (205.01, 66.40, and 40.23 ppm).

X-ray Crystallographic Studies

Recent work has resulted in establishing the molecular structures of [4]peristylane-2,6-dione (**17**)[15] and *endo*,*endo*-2,6-diphenacyl[4]peristylane (**18**).[16] With access to the more highly functionalized derivatives just described, the decision was made to examine, if possible, the extent to which topological changes might materialize along the outer [4]peristylane periphery as the number of trigonal centers increases. Originally, the intention was to study **1**, **2**, **11**, and **16** from the X-ray crystallographic vantage point. Eventually, it became clear that it would not be possible to obtain **2** from **16** in crystalline form suitable for X-ray analysis (Table I).



17



18

Diketone **17** is recognized to possess almost perfect C_{2v} symmetry in the crystal. The four-membered ring and both five-membered rings bearing the ketone groups are almost planar, while the remaining two five-membered

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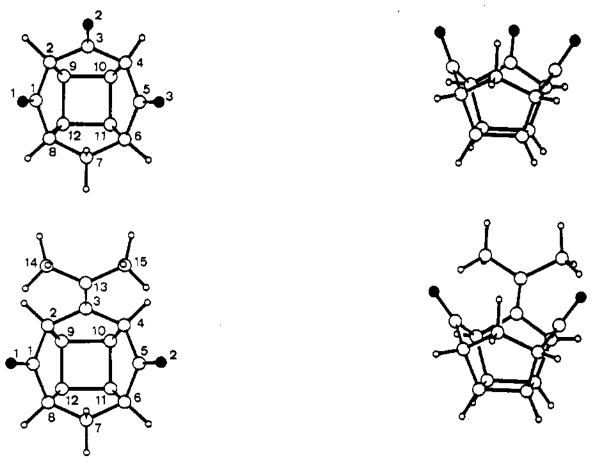


Figure 1. Two different views each of the [4]peristylane-2,4,6-trione molecule (1, top) and its 4-isopropylidene derivative 11 (bottom) as well as the numbering schemes used.

rings show half-chair conformations. The four-membered ring is notable in having two long opposed C–C bonds [1.563 (2) and 1.564 (2) Å]. In contrast, the solid-state topography of **18** deviates considerably from C_2 symmetry and, in fact, has only a single long cyclobutane C–C bond [1.58 (2) Å]. The two cyclopentane rings carrying the side chains adopt half-chair conformations, while the other five-membered rings are almost planar and the cyclobutane ring is perfectly planar. The pair of phenacyl substituents are decidedly pointing outward from the molecule.

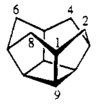
Trione **1** exhibits approximate C_s symmetry. In contrast to **17** and **18**, all five-membered rings in **1** show half-chair conformations, the phenomenon being somewhat less pronounced for the ketone-bearing rings. The respective torsion angles are C(12)–C(8)–C(1)–C(2) = 14.0°, C(9)–C(2)–C(3)–C(4) = 18.5°, C(10)–C(4)–C(5)–C(6) = 13.9°, and C(11)–C(6)–C(7)–C(8) = 24.2° (see Figure 1). The four-membered ring is perfectly planar. All C–C bonds in the cyclobutane ring are within 1.555 (2) Å, and most remarkably, there is no lengthening of any C–C bond in this sector of the molecule as observed in **11**, **17**, and **18**.

Dione **11** has perfect C_s symmetry in the crystal, with the molecule residing on a crystallographic mirror plane. Similar to **1**, its five-membered rings show more or less pronounced half-chair conformations. The corresponding torsion angles are C(12)–C(8)–C(1)–C(2) = 17.5° and C(10)–C(4)–C(5)–C(6) = 17.1° for the ketone-bearing rings and C(9)–C(2)–C(3)–C(4) = 17.4° for the ring with the attached side chain. The corresponding torsion angle for the fourth cyclopentane subunit is C(11)–C(6)–C(7)–C(8) = 22.5°. In this instance, the four-membered ring is perfectly planar, forming a trapezoid with base lines C(9)–C(10) = 1.561 (3) Å and C(11)–C(12) = 1.571 (3) Å and side C(9)–C(12) = 1.566 (3) Å.

Crystal Density Measurements

Prior to the present work, the densities of seven [4]peristylanes had been determined (Table II), and certain trends have become apparent. Thus, the presence of long, pendant groups (e.g., phenacyl) oriented transannularly and endo along the upper rim is not beneficial to the enhancement of density. When a pair of carbonyl groups are analogously positioned, as is the case in the 2,6-dione, the consequences are quite beneficial. Strikingly, further replacement of these carbonyls by geminal nitrogen groups as in the 6,6-dinitro 2-ketone and especially the 2,2,6,6-tetranitro derivative serves to improve crystal lattice packing dramatically to the 1.7 g/cm^3 level. Rather curiously, a 9-nitro group does not in general exert an effect that increases crystal density still further; nor is its presence found to be deleterious.

Table II. Summary of Known Density Values for Functionalized [4]Peristylanes



literature data	ρ, g/cm^3	new data	ρ, g/cm^3
endo,*endo*-2,6-diphenacyl[16]	1.28	4-isopropylidene 2,6-dione (**11**)	1.34
2,6-dione[15]	1.42	2,4,6-trione (**1**)	1.45
9-nitro 2,6-dione[5b]	1.52	4,8-bis(isopropylidene) 2,6-dione (**16**)	1.30
6,6-dinitro 2-one[5a]	1.67	2,4,6,8-tetrone (**2**)	1.54
6,6,9-trinitro 2-one[5b]	1.68		
2,2,6,6-tetranitro[5a]	1.70		
2,2,6,6,9-pentanitro[5b]	1.72		

Our present objective was to determine what alterations, if any, in density properties would accompany rehybridization of the third and fourth [4]peristylane rim methylene groups into trigonal centers. Accordingly, such measurements have been made on **1**, **2**, **11**, and **16**. The long-range goal was to set the stage for proper evaluation of the density characteristics of the 2,2,4,4,6,6-hexanitro- and 2,2,4,4,6,6,8,8-octanitro[4]peristylanes once these highly nitrated species become available.

At the experimental level, it proved possible to derive the density values for **1**, **11**, and **16** from unit cell determinations. The accuracy of these data is consequently quite high. Since **2** is a very insoluble compound that does not crystallize at all well, recourse had to be made instead to the flotation method, and this value is therefore somewhat less reliable. Aqueous cesium chloride solutions were utilized[17] for this purpose.[18]

The ρ value for **1** (1.45 g/cm^3) reveals the triketone to be only slightly more dense than the 2,6-dione (Table II). However, the presence of a large isopropylidene group at C-4 alongside the 2,6-dicarbonyl network lowers ρ appreciably. This is taken again to be a reflection of the fact that large substituents along the ring (excluding of course nitro) do not accommodate crystal packing well.

Of perhaps greater interest is the more highly functionalized pair **2** and **16**. The ρ value of 1.54 g/cm^3 for the tetraketone sets it apart as the most dense member of the pure carbonyl series. In actuality, the density gap between **1** and **2** (0.9 g/cm^3) represents an incremental contribution to ρ significantly greater than that between **1** and the 2,6-dione ($\Delta\rho$ = 0.03 g/cm^3, see Table II). The situation in the isopropylidene derivatives is precisely the reverse, with **16** (ρ = 1.30 g/cm^3) being somewhat less dense than both its lower congener **11** (ρ = 1.34 g/cm^3) and **2**. These findings are consistent with the steric bulk argument advanced above.

Experimental Section

10-(1-Methylethylidene)tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene (3). To a suspension of 1,3-trimethylenebis(triphenylphosphonium bromide) (4.50 g, 6.19 mmol) in 30 mL of dry tetrahydrofuran was added 8.3 mL of 1.5 M *n*-butyllithium under nitrogen at room temperature. The red suspension was stirred overnight, at which point a solution of 7-(1-methylethylidene)bicyclo[2.2.1]hept-5-

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[17] Paquette, L. A.; Nakamura, K.; Engel, P. *Chem. Ber.* **1986**, *119*, 3782.

[18] Compare also: Eaton, P. E.; Ravi Shankar, B. K.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185.

ene-2,3-dione (1.00 g, 6.17 mmol) in 20 mL of tetrahydrofuran was introduced dropwise. The dark brown mixture was stirred at room temperature for 2 h and at 45 °C for 3 days. After cooling, the reaction mixture was diluted with water and extracted with pentane. The combined organic extracts were washed with water and brine, dried, and concentrated. Silica gel chromatography (elution with petroleum ether) furnished 275 mg (26%) of **3**, sublimation of which gave rise to a white powder, mp 61–62 °C: ^{1}H NMR (80 MHz, CDCl$_3$) δ (dd, J = 2.1, 1.8 Hz, 2 H), 5.69 (td, J = 1.5, 0.6 Hz, 2 H), 4.00 (td, J = 2.0, 0.5 Hz, 2 H), 3.25 (t, J = 1.5 Hz, 2 H), 1.60 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$) (ppm) 152.47, 152.25, 138.86, 113.92, 108.96, 46.01, 44.96, 19.61; MS *m/z* (M$^+$) calcd 170.1096, obsd 170.1082.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.38; H, 8.23.

(*Z*)-1,2-Bis(phenylsulfonyl)ethylene Addition to 3. A solution of **3** (0.429 g, 2.52 mmol) and (*Z*)-1,2-bis(phenylsulfonyl)ethylene (0.778 g, 2.52 mmol) in 10 mL of tetrahydrofuran was magnetically stirred at room temperature under an atmosphere of argon. After 3 days, 0.786 g of white precipitate was collected by filtration and washed with hexanes. The second crop of **4** was obtained by adding hexanes to the mother liquor. The total yield was 1.08 g (90%): colorless solid, mp 226.5 °C dec; ^{1}H NMR (80 MHz, CDCl$_3$) δ 8.01–7.42 (m, 10 H), 6.62 (dd, J = 2.0, 1.8 Hz, 2 H), 3.75 (m, 2 H), 3.39 (s, 2 H), 2.76 (d, J = 2.0 Hz, 2 H), 2.7–2.5 (m, 1 H), 1.7–1.5 (m, 1 H), 1.41 (s, 6 H); ^{13}C NMR (20 MHz, CDCl$_3$) (ppm) 159.93, 141.12, 139.22, 133.49, 128.95, 128.42, 99.71, 64.36, 48.89, 47.24, 43.26, 18.81 (1 C not observed); MS *m/z* (M$^+$ − $SO_2C_6H_5$) calcd 337.1263, obsd 337.1292.

Epoxidation of 4. To a magnetically stirred solution of **4** (100 mg, 0.20 mmol) in cold (0 °C) dichloromethane (20 mL) was added dropwise a solution of *m*-chloroperbenzoic acid (40 mg) in the same solvent (5 mL). The reaction mixture was stirred at 0 °C for 4 h, then washed with 5% sodium bisulfite solution, saturated sodium bicarbonate solution, water, and brine, dried, and concentrated. Purification by silica gel chromatography (elution with 1:1 petroleum ether–ethyl acetate) furnished 62 mg (65%) of **5** as colorless crystals, mp 207–209 °C (from dichloromethane–hexanes): ^{1}H NMR (80 MHz, CDCl$_3$) δ 8.1–7.5 (m, 10 H), 6.54 (t, J = 2.0 Hz, 2 H), 3.72 (d, J = 2.5 Hz, 2 H), 3.42 (m, 2 H), 3.03 (d, J = 0.9 Hz, 2 H), 2.26 (dt, J = 11, 1.4 Hz, 1 H), 1.91 (m, 1 H), 1.38 (s, 6 H); ^{13}C NMR (20 MHz, CDCl$_3$) (ppm) 147.92, 140.74, 140.21, 133.69, 129.09, 128.48, 107.76, 67.00, 64.49, 46.46, 44.01, 35.07, 18.93; MS *m/z* (M$^+$ − 2$SO_2C_6H_5$) calcd 228.0973, obsd 228.0920.

Anal. Calcd for $C_{27}H_{26}O_5S_2{\cdot}0.5CH_2Cl_2$: C, 61.50; H, 5.07. Found: C, 61.43; H, 5.13.

Reductive Desulfonylation of 5. To a magnetically stirred mixture of **5** (254 mg, 0.514 mmol), disodium hydrogen phosphate (500 mg), and 7.5 mL of methanol was gradually added 10 g of 1.5% sodium amalgam under nitrogen over 7 h. After an additional 11 h of stirring at 20 °C under nitrogen, water was added and the mixture was extracted with dichloromethane. The combined organic layers were washed with water and brine, dried, and concentrated to give crude **6**, which was used immediately without further purification: ^{1}H NMR (80 MHz, CDCl$_3$) δ 6.27 (t, J = 1.9 Hz, 2 H), 6.09 (t, J = 1.6 Hz, 2 H), 3.62 (m, 2 H), 3.06 (m, 2 H), 2.3–1.1 (series of m, 2 H), 1.50 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$) (ppm) 148.19, 143.59, 143.13, 105.99, 75.63, 50.57, 47.87, 45.57, 19.25; MS *m/z* (M$^+$) calcd 212.1201, obsd 212.1207.

Sensitized Photocyclization of 6. The above sample of **6** was dissolved in 10 mL of acetone, placed in a Pyrex tube, and irradiated in a Rayonet reactor with a full bank of 3500-Å lamps for 17 h. After the evaporation of solvent, the residue was chromatographed on silica gel (elution with 5:1 petroleum ether–dichloromethane) to give 15.7 mg (14% overall from **5**) of **10** as a white solid, mp 88 °C: ^{1}H NMR (80 MHz, CDCl$_3$) δ 2.85 (m, 2 H), 2.61 (m, 4 H), 2.29 (m, 2 H), 1.62 (s, 6 H), 1.50 (dt, J = 10.8, 1.4 Hz, 1 H), 1.26 (dt, J = 10.8, 1.4 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$) (ppm) 138.24, 122.49, 62.63, 40.74, 38.92, 38.70, 32.51, 20.85 (1 C not observed); MS *m/z* (M$^+$) calcd 212.1201, obsd 212.1218.

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.71; H, 7.63.

4-(1-Methylethylidene)tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene (7). To a magnetically stirred solution of tricyclo[5.2.1.0^{2,6}]-deca-2,5,8-triene (7.32 g, 56.2 mmol) in acetone (30.1 g, 517 mmol) was added dropwise 120 mL of 25% ethanolic potassium hydroxide at 0 °C. The resulting brown solution was stirred at room temperature for 2 days, treated with water, neutralized with 10% hydrochloric acid, and extracted with dichloromethane. The combined organic extracts were washed with water and brine, dried, and concentrated. Purification of the residue by silica gel chromatography (elution with petroleum ether) gave 7.57 g (79%) of **7** as a yellow oil, which solidified in the freezer and could be sublimed: yellow solid, mp 47–48 °C; ^{1}H NMR (80 MHz, CDCl$_3$) δ 6.35 (m, 2 H), 6.01 (d, J = 0.4 Hz, 2 H), 3.55 (m, 2 H), 2.04 (s, 6 H), 2.4–1.9 (m, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) (ppm) 154.04, 147.86, 141.56, 138.45, 106.94, 58.47, 43.87, 22.54; MS *m/z* (M$^+$) calcd 170.1095, obsd 170.1098.

Sequential Diels–Alder Addition of (*Z*)-1,2-Bis(phenylsulfonyl)ethylene to 7 and Epoxidation of 8. A solution of **7** (2.83 g, 16.6 mmol) and (*Z*)-1,2-bis(phenylsulfonyl)ethylene (5.14 g, 16.7 mmol) in 9 mL of tetrahydrofuran was placed under 90 000 psi in a high-pressure reactor. After 9 days at room temperature, the yellowish adduct was collected by filtration and air-dried: 7.74 g (98%) of **8** as a light yellow powder, mp 125 °C dec. This material was directly epoxidized: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.07–7.42 (m, 10 H), 6.49 (t, J = 1.8 Hz, 2 H), 3.88 (d, J = 0.6 Hz, 2 H), 3.26 (br s, 2 H), 2.75 (s, 2 H), 2.11 (dt, J = 6.7, 1.7 Hz, 1 H), 1.90 (dt, J = 6.7, 1.2 Hz, 1 H), 1.80 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$) (ppm) 159.67, 141.44, 139.27, 138.74, 133.32, 128.89, 128.24, 119.30, 69.80, 63.11, 48.76, 47.55, 21.02; MS molecular ion too fleeting to be accurately mass-measured.

To a magnetically stirred solution of **8** (8.24 g, 17.2 mmol) in 200 mL of cold (0 °C) dichloromethane was added dropwise a solution of *m*-chloroperbenzoic acid (3.71 g) in 100 mL of the same solvent. The reaction mixture was stirred at 0 °C for 4 h and then washed with 5% sodium bisulfite solution, saturated sodium bicarbonate solution, water, and brine. Following drying and solvent evaporation, the residue was recrystallized from dichloromethane–hexanes to give 6.16 g (62%) of **9** as colorless, solvated crystals, mp 227–228 °C: ^{1}H NMR (80 MHz, CDCl$_3$) δ 8.1–7.4 (m, 10 H), 6.60 (t, J = 2 Hz, 2 H), 3.66 (s, 2 H), 3.63 (d, J = 0.9 Hz, 2 H), 2.89 (m, 2 H), 1.89 (dt, J = 8.0, 1.6 Hz, 1 H), 1.78 (s, 6 H), 1.39 (dt, J = 8.0, 1.4 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$) (ppm) 141.22, 139.92, 133.49, 131.89, 129.04, 128.19, 125.73, 65.81, 63.69, 53.36, 45.59, 44.65, 21.16; MS *m/z* (M$^+$) calcd 494.1222, obsd 494.1175.

Anal. Calcd for $C_{27}H_{26}O_5S_2{\cdot}CH_2Cl_2$: C, 58.03; H, 4.87. Found: C, 58.06; H, 4.90.

Reductive Desulfonylation of 9. To a mechanically stirred mixture of **9** (5.00 g, 10.1 mmol), disodium hydrogen phosphate (10.0 g), and methanol (150 mL) was added 175 g of 1.5% sodium amalgam portionwise under argon at 20 °C over 7 h. After a further 3 h, water was introduced and the mixture was extracted with dichloromethane. The combined organic layers were washed with water and brine, dried, and concentrated to give crude **6** (1.83 g, 85%), spectroscopically identical with the material prepared above.

4-(1-Methylethylidene)[4]peristylane-2,6-dione (11). A solution of **10** (55.4 mg, 0.261 mmol) and periodic acid (60.4 mg, 0.265 mmol) in tetrahydrofuran (10 mL) was stirred at room temperature for 5.5 h. The reaction mixture was added to water and extracted with dichloromethane. The organic extracts were washed with 10% sodium bisulfite solution and brine, dried, and concentrated. After silica gel chromatography (elution with 3:1 petroleum ether–ethyl acetate), there was isolated 34.3 mg (57%) of **11** as colorless crystals, mp 183–184 °C (from dichloromethane–hexanes): IR (KBr, cm^{-1}) 3020, 3010, 2980, 2935, 1720, 1450, 1375, 1180, 1165, 1015, 725; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.50 (m, 6 H), 2.72 (m, 2 H), 2.34 (dt, J = 14, 10 Hz, 1 H), 2.24 (dt, J = 14, 1.4 Hz, 1 H), 1.89 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$) (ppm) 222.54, 134.91, 131.49, 56.56, 53.34, 43.21, 41.61, 41.12, 22.44; MS *m/z* (M$^+$) calcd 228.1151, obsd 228.1148.

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.71; H, 7.17.

[4]Peristylane-2,4,6-trione (1). Ozone was passed into a solution of **11** (48.2 mg, 0.211 mmol) in 35 mL of cold (−78 °C) dichloromethane until the solution turned blue. The reaction mixture was purged with argon and treated with a solution of dimethyl sulfide (45.9 mg, 0.739 mmol) in 5 mL of dichloromethane at −78 °C. After the temperature rose to 25 °C, the solution was washed with water and brine, dried, and concentrated. Chromatographic purification of the residue (silica gel, elution with ethyl acetate) furnished 33.7 mg (79%) of **1** as colorless crystals, mp >300 °C (from ethyl acetate–dichloromethane–hexanes): IR (KBr, cm^{-1}) 3015, 2980, 2940, 1760, 1725, 1700, 1445, 1160, 1145, 1015, 995; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (m, 2 H), 3.72 (m, 2 H), 3.27 (m, 2 H), 2.96 (m, 2 H), 2.22 (dt, J = 14, 10 Hz, 1 H), 1.94 (d, J = 14 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) 214.06, 199.25, 66.06, 53.39, 44.96, 37.50, 35.70; MS m/z (M$^+$) calcd 202.0630, obsd 202.0623.

Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.11; H, 5.11.

4,10-Bis(1-Methylethylidene)tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene (12). To a magnetically stirred solution of **3** (500 mg, 2.94 mmol) in acetone (20 mL) was added a solution containing 12 g of potassium hydroxide in 36 mL of ethanol. The resulting dark brown reaction mixture was stirred at room temperature for 3 days, neutralized with 10% hydrochloric acid while being cooled in an ice bath, and extracted with pentane. The combined organic phases were washed with water and brine, dried, and concentrated. Purification of the residue by chromatography on silica gel (elution with 10:1 petroleum ether–dichloromethane) furnished 558 mg (90%) of **12** as a yellow solid, mp 116–117 °C: ^{1}H NMR (80 MHz, $CDCl_3$) δ 6.51 (dd, J = 2.1, 1.8 Hz, 2 H), 6.00 (d, J = 0.5 Hz, 2 H), 4.05 (td, J = 2.0, 0.6 Hz, 2 H), 2.06 (s, 6 H), 1.59 (s, 6 H); ^{13}C NMR (75 MHz, C_6D_6) (ppm) 151.83, 151.30, 148.71, 140.01, 138.76, 108.53, 106.42, 45.46, 22.14, 19.45; MS m/z (M$^+$) calcd 210.1409, obsd 210.1399.

(*Z*)-1,2-Bis(phenylsulfonyl)ethylene Addition to 12. A solution of **12** (1.10 g, 5.23 mmol) and (*Z*)-1,2-bis(phenylsulfonyl)ethylene (1.61 g, 5.22 mmol) in 20 mL of tetrahydrofuran was placed under 90 000 psi in a high-pressure reactor. After 3 days at room temperature, the precipitated white solid was collected by filtration and air-dried to give 1.93 g (71%) of **13** as a colorless solid, mp 141–143 °C dec: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95–7.53 (m, 10 H), 6.63 (t, J = 1.9 Hz, 2 H), 3.92 (d, J = 0.6 Hz, 2 H), 3.80 (m, 2 H), 2.76 (s, 2 H), 1.81 (s, 6 H), 1.40 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) 158.99, 158.36, 141.34, 139.32, 137.90, 133.32, 128.89, 128.15, 119.84, 100.00, 63.48, 49.10, 47.53, 21.07, 18.88; MS (FAB) m/z (M + H)$^+$ calcd 519, obsd 519.

This material was directly epoxidized without further purification.

Epoxidation of 13. A magnetically stirred solution of **13** (2.30 g, 4.43 mmol) in 70 mL of cold (−10 °C) dichloromethane was treated dropwise with a solution of *m*-chloroperbenzoic acid (970 mg of 80–85% purity) in 30 mL of the same solvent. The reaction mixture was stirred at 0 °C for 5 h, washed with 5% sodium bisulfite solution, saturated sodium bicarbonate solution, water, and brine, dried, and evaporated. The residue was recrystallized from dichloromethane–hexanes to give 1.84 g (78%) of the epoxy disulfone as colorless crystals, mp 192 °C dec: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04–7.56 (m, 10 H), 6.55 (t, J = 2.0 Hz, 2 H), 3.64 (s, 2 H), 3.62 (d, J = 0.85 Hz, 2 H), 3.45 (m, 2 H), 1.77 (s, 6 H), 1.38 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) 146.48, 141.09, 139.90, 133.57, 130.52, 129.10, 128.24, 126.16, 108.16, 65.78, 62.73, 46.39, 45.39, 21.19, 19.03; MS m/z (M$^+$) calcd 534.1534, obsd 534.1534.

Anal. Calcd for $C_{30}H_{30}O_5S_2$: C, 67.39; H, 5.66. Found: C, 67.00; H, 5.89.

Reductive Desulfonylation to 14. A mechanically stirred mixture of the above epoxide (1.56 g, 2.92 mmol), disodium hydrogen phosphate (3.0 g), and methanol (50 mL) was treated during 6 h under argon with 50 g of 1.5% sodium amalgam. The reaction mixture was stirred overnight at room temperature under argon, treated with water, and extracted with dichloromethane. The combined organic extracts were washed with water and brine, dried, and concentrated. There was isolated 580 mg (79%) of yellowish-colored **14**, which was utilized directly in the next step: mp 125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.29 (dd, J = 1.9, 1.5 Hz, 4 H), 3.65 (t, J = 1.5 Hz, 4 H), 1.49 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) 146.41, 143.11, 106.74, 74.52, 47.60, 19.31; MS m/z (M$^+$) calcd 252.1514, obsd 252.1529.

Photocycloaddition of 14. Unpurified **14** (560 mg, 2.2 mmol) was dissolved in acetone (155 mL) and irradiated for 17.5 h in Pyrex tubes mounted within a Rayonet reactor equipped with a full bank of 3500-Å lamps. After evaporation of the solvent, the residue was chromatographed on silica gel (elution with 3:1 petroleum ether–dichloromethane). There was obtained 180 mg (32%) of **15** as a colorless solid, mp 150–150.5 °C: ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.88 (m, 4 H), 2.64 (m, 4 H), 1.63 (s, 12 H); ^{13}C NMR (75 Hz, $CDCl_3$) (ppm) 136.65, 122.74, 61.41, 40.72, 40.01, 20.99; MS m/z (M$^+$) calcd 252.1515, obsd 252.1522.

Oxidative Cleavage of 15. A solution of **15** (164 mg, 0.650 mmol) and periodic acid (153 mg, 0.671 mmol) in 20 mL of tetrahydrofuran was stirred at room temperature for 5 h. The precipitated solid was filtered off, and the filtrate was evaporated to dryness. The residue was dissolved in dichloromethane and washed with 10% sodium bisulfute solution and brine. After drying and solvent evaporation, there was obtained 82 mg (47%) of **16** as a white solid, mp 228.5–229 °C (from methylene chloride–hexanes), following silica gel chromatography (elution with 10:1 petroleum ether–ethyl acetate): IR (CH_2Cl_2, cm^{-1}) 2990, 2920, 2860, 1730, 1715, 1375, 1180, 1145, 1010; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.46 (m, 8 H), 1.85 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) 215.32, 134.52, 132.99, 56.44, 41.77, 22.59; MS m/z (M$^+$) calcd 268.1463, obsd 268.1439.

[4]Peristylane-2,4,6,8-tetrone (2). A solution of **16** (50 mg, 0.19 mmol) in 30 mL of cold (−78 °C) dichloromethane was ozonolyzed until the solution turned blue. Following the addition of a solution of dimethyl sulfide (76 mg) in 5 mL of dichloromethane, the reaction mixture was allowed to warm to room temperature and evaporated to dryness. The residue was washed with water and air-dried to give 20 mg (49%) of **2** as an off-white powder, mp >300 °C: IR (KBr, cm^{-1}) 3035, 2980, 1780, 1740, 1125, 1010, 785, 705; ^{1}H NMR (300 MHz, DMSO-d_6) δ 4.15 (d, J = 4.6 Hz, 4 H), 3.20 (d, J = 4.6 Hz, 4 H); ^{13}C NMR (75 MHz, DMSO-d_6) (ppm) 205.01, 66.40, 40.23; MS m/z (M$^+$) calcd 216.0422, obsd 216.0447.

X-ray Crystallographic Analyses of 1 and 11. Both crystals are colorless. The space groups were determined by preliminary Weissenberg photographs with Cu Kα radiation. Determination of the lattice parameters and intensity measurements were made with a Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71065 Å). The cell parameters were calculated by a least-squares procedure from reflections determined by the Nonius peak hunting procedure in the range $5° < 2\theta < 17°$. Independent reflections in the range $2° \le 2\theta \le 56°$ were measured at T = 18 (2) °C by the ω–2θ scan technique. After every 200 reflections, the orientation of the crystals was controlled, and after every 3.3 h, the intensity was checked. No significant deviation (less than 3σ) could be observed. Reflections with $I < 3.5\sigma(I)$ were indicated as unobserved. The intensities were corrected for Lorentz and polarization effects, but no absorption correction was applied.

Acknowledgment. We thank the National Institutes of Health (through Grant CA-12115) and the U.S. Army Research and Development Command for their financial support of this study. Compounds **3** and **12** were initially prepared in these laboratories by T. M. Kravetz and L. M. Waykole.

Supplementary Material Available: Tables of fractional coordinates and anisotropic/isotropic temperature factors, and torsion angles, as well as bond distances and angles for **1** and **11** (8 pages). Ordering information is given on any current masthead page.