Stereoselective Epoxidation of Cyclohexa-Anellated Triquinacenes with Iodine/Silver(I) Oxide As Compared to *m*-Chloroperbenzoic Acid[1]

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Iodine/silver(I) oxide (I_2/Ag_2O) reacts highly stereoselectively in the single, double, and triple *anti* epoxidation of the spherical 1,4,7-triene, 10-methyl-2,3:5,6:8,9-tris(cyclohexano)triquinacene **1**. All of the three epoxides **3**, **4**, and **5** obtained with this reagent contain the epoxy groups at the convex side of the triquinacene framework. The stereochemical course of the epoxidation with I_2/Ag_2O is clearly distinct from that observed with *m*-chloroperbenzoic acid (MCPBA), which gives the same monoepoxide (**3**) but exclusively *anti,syn* di- and triepoxides (**6**−**8**) bearing at least one epoxy group at the concave side of the triquinacene framework. Epoxidation of the related three-fold 1,4-cyclohexa*diene*, tris(cyclohexeno)triquinacene **2**, with MCPBA occurs similarly to the conversion of **1**, whereas I_2/Ag_2O reacts with high regioselectivity at the less electron-rich peripheral double bonds of **2** giving triepoxides **12** and **13**. The molecular structure of triepoxide **8** has been elucidated in detail by X-ray crystal structure analysis.

Introduction

Epoxidation of olefins has found broad application for the oxyfunctionalization of acyclic and alicyclic organic compounds.[2] In general, well-established reagents such as hydrogen peroxide, peracids, *tert*-butyl hydroperoxide, and bromine/silver carboxylates have been used preferentially in all of these studies.[3] More recently, epoxidation with dioxiranes has gained increasing interest.[4] In this paper, we demonstrate the utility of a rarely used epoxidation reagent, silver(I) oxide/iodine (Ag_2O/I_2),[5,6] and contrast it to a widely used reagent, *m*-chloroperbenzoic acid (MCPBA), with special attention to the stereochemical course of the epoxidation of polycyclic alkenes.

In an investigation aimed at the functionalization of the benzo nuclei of centropolyindans,[7−9] we studied the multiple dissolving-metal reductions of various congeners.[10] Triquinacenes **1** and **2**, which are readily obtained by Benkeser reduction and by Birch reduction, respectively, of 10-methyltribenzotriquinacene,[11] were considered particularly interesting since three-fold epoxidation at the convex side of these bowl-shaped cyclic 1,4,7-trienes should enhance the convexity of the polycyclic framework and possibly open a synthetic access to novel cage structures.[12] In contrast to cyclonona-1,4,7-triene, which undergoes stereoselective epoxidation with *m*-chloroperbenzoic acid,[13,14] epoxidation of triquinacenes constituting completely rigid *all-cis*-1,4,7-nonatriene derivatives has not been reported previously.[15]

Results

Treatment of **1** with 1.33 equiv of iodine and Ag_2O in aqueous tetrahydrofuran at ambient temperature furnished a monoepoxide, **3** (Scheme 2), as the major product, which was isolated by chromatography in 41% yield. With 2.67 equiv of the I_2/Ag_2O reagent, both **3** and a diepoxide, **4**, were formed and isolated in 40% and 21% yield, respectively. A third product, triepoxide **5**, was isolated in low yield, too. Use of 4.5 equiv of the reagent led to predominant formation of triepoxide **5**, which was isolated by chromatography in 41% yield, along with diepoxide **4** (14%) and monoepoxide **3** (9%). As shown below in detail, both **4** and **5** are the diastereomers with the highest possible molecular symmetry, i.e. C_s (**4**) and C_{3v} (**5**), bearing all of the epoxy groups at the convex side of the triquinacene framework.

Epoxidation of triquinacene **1** with MCPBA in methylene chloride at ambient temperature gave strikingly different results (Scheme 3). With again varied stoichiometry of the reagent, four epoxides were obtained after

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(1) This work was presented in part at the Chemiedozententagung 1993 in Dresden, Germany, Feb 28 to Mar 2, 1993; see Book of Abstracts: Kuck, D.; Eckrich, R. (*Arbeitsgem. Professoreu C4 Chem.*) **1993**, B-19.

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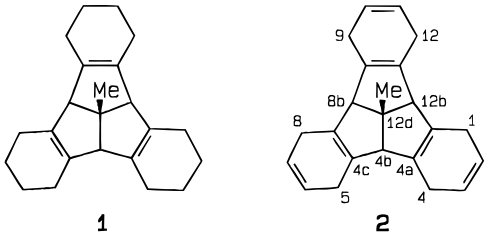
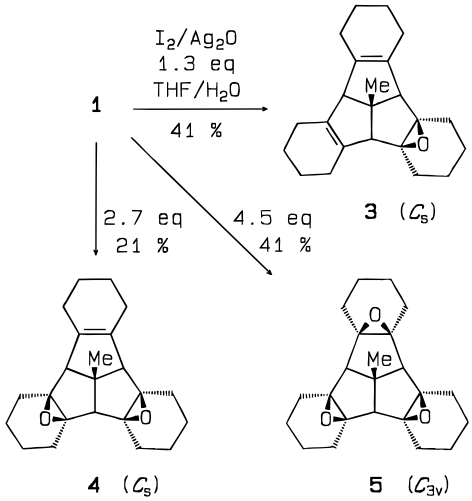
Scheme 1



1 2

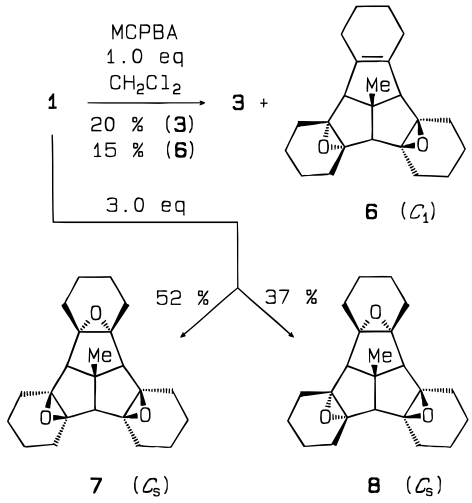
Scheme 2



3 (C_s)

4 (C_s) 5 (C_{3v})

Scheme 3



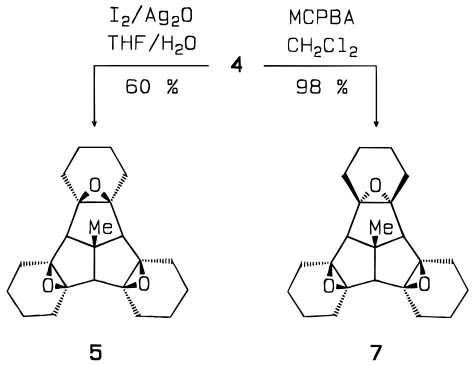
6 (C_1)

7 (C_s) 8 (C_s)

chromatographic separation, among which only the monoepoxide, **3**, is identical to that obtained with I_2/Ag_2O. Using equimolar amounts of the reagent, the unsymmetrical diepoxide **6** was isolated in low yield (15%) along with **3** (20%) and the starting material (14%). With 3.0 equiv of MCPBA, two C_s-symmetrical triepoxides, **7** and **8**, were isolated in 52% and 37% yield, respectively (Scheme 3). Neither diepoxide **4** nor triepoxide **5** obtained with I_2/Ag_2O were found in the conversions with MCPBA.

The stereochemistry of these epoxides follows from X-ray crystal structure analysis, ^{13}C NMR spectrometry, and stepwise epoxidation experiments. The X-ray structure analysis of monoepoxide **3** revealed the *anti* position[16] of the epoxy group and suggests that the first epoxidation takes place from the sterically less hindered, convex side of the triquinacene framework. Unfortunately, the measurements did not allow us to determine the structural parameters of **3** in detail due to irregular molecular packing in the crystal; nevertheless, the stereochemistry of this epoxide has been determined unequivocally and is in line with results obtained independently (see below). Similarly to **3**, single crystals of diepoxide **4** did not give sufficiently refinable X-ray data for detailed structure analysis, but do show that both of the epoxy oxygen atoms have been attached to the convex side of the triquinacene moiety. The C_s molecular symmetry of **4** is corroborated by its NMR spectra (see Experimental Section); for example, two equivalent allylic methine protons (8b-H and 12b-H) are indicated by the singlet at $\delta = 2.45$ along with the remaining methine proton (4b-H) at $\delta = 2.42$ adjacent to two oxirane rings. Similar degeneracy is found in the ^{13}C NMR spectrum of **4**; for example, a single line appears for the equivalent carbon atoms of the remaining double bond.

Scheme 4



5 7

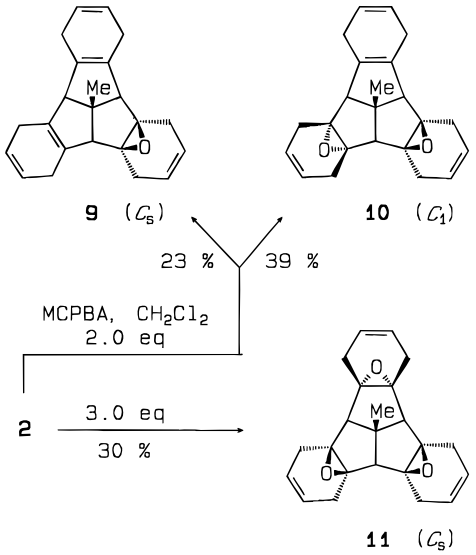
The NMR spectra of triepoxide **5** are particularly simple. The ^1H NMR spectrum of **5** displays a singlet for the three equivalent bridgehead protons. The formal C_{3v} symmetry of this C_{22} polycycle is also reflected by the presence of only five (of six possible) lines[17] in the ^{13}C NMR spectrum. Again, we did not succeed in growing suitable crystals for X-ray structural analysis of **5**. Nevertheless, the *anti,anti,anti* orientation of the three epoxy groups attached to the triquinacene core follows unequivocally from stepwise oxidation of diepoxide **4** with I_2/Ag_2O: reaction of **4** with 1.67 equiv of the reagent followed by chromatography gave **5** in 60% yield along with 8% of recovered starting material (Scheme 4).

With the exception of the monoepoxide **3**, treatment of **1** with MCPBA leads to epoxides bearing at least one epoxy group at the *concave* side of the triquinacene framework. The stereochemistry of the nonsymmetrical diepoxide **6** follows directly from the ^{13}C NMR spectrum showing, for example, two carbon resonances for the double bond and four distinct lines for the carbon nuclei of the oxirane rings. Correspondingly, the ^1H and ^{13}C NMR spectra of the triepoxides **7** and **8**, being stereoisomers of **5**, reflect their molecular C_s symmetry. In both cases, the three bridgehead methine protons appear as two singlets in a 2:1 integral ratio; three different lines are observed for the carbon nuclei of the oxirane rings together with six lines corresponding to the methylene carbon nuclei of the cyclohexane rings. Overall, the ^{13}C NMR spectra of **7** and **8** show pronounced chemical shift

(16) Prefixes *anti* and *syn* denote here the orientation of the oxirane ring with respect to the triquinacene skeleton.

(17) The resonances of the *centro*-C nucleus C(16d) and the three methine bridgehead nuclei C(4b), C(8b), and C(12b) of **5** are isochronous, as shown by using the DEPT technique.

Scheme 5



differences, including that of the central carbon atoms (C-10); however, unequivocal stereochemical assignment of these isomers on the basis of the NMR data was not possible. Fortunately, one of the triepoxides, viz. **8**, gave single crystals which were well suited for X-ray structural analysis, allowing us to evaluate the structural parameters in detail.[18] Hence, the second-eluting isomer **8** was identified as the *anti,syn,syn* triepoxide bearing two epoxy groups at the concave side of the triquinacene framework and, as a consequence, the first-eluting isomer **7** was recognized as the *anti,anti,syn* triepoxide.

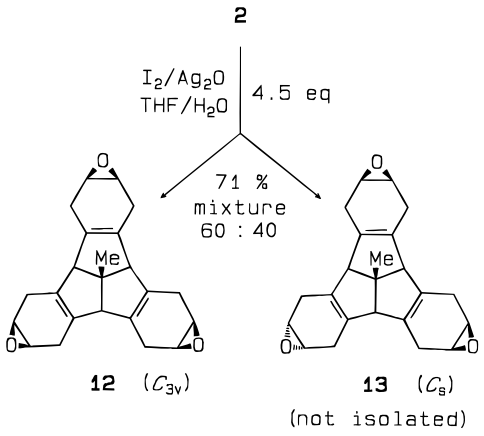
As a further proof of the consistency of the stereoassignment of the three triepoxides **5**, **7**, and **8**, reaction of the C_s-symmetrical *anti,anti* diepoxide **4**, obtained with I_2/Ag_2O as described above, with MCPBA generates the *anti,anti,syn* triepoxide **7** in almost quantitative yield (Scheme 4). This result completely contrasts with the reversed stereoselectivity of **4** by epoxidation with I_2/Ag_2O giving **5**. As a curiosity, the melting points of the triepoxides **7** and **8** were found to be almost identical (153 and 152 °C), but they are considerably lower than that of the C_3-symmetrical isomer **5** (214 °C), as expected.

The results reported above clearly show that epoxidation of triquinacene **1** with I_2/Ag_2O occurs *exclusively* at the sterically less hindered, convex side of the substrate molecule, whereas epoxidation of **1** with MCPBA acid furnishes quite distinct results, in that all of the higher epoxides (**6**−**8**) generated with the latter reagent contain at least one epoxy group at the *concave* side of the triquinane framework.

Finally, epoxidation of tris(cyclohexeno)triquinacene **2** was studied. With MCPBA this olefin revealed the same characteristics as those found for **1** (Scheme 5). Using 2.0 equiv of the reagent, only one monoepoxide, **9**, was isolated in low yield after chromatography together with the unsymmetrical diepoxide **10** (39% yield). With 3.0 equiv of MCPBA, one of the two possible C_s-symmetrical triepoxides, **11**, was obtained, but again no C_{3v} symmetrical isomer. The ^{13}C NMR spectrum of **11** exhibits close similarity to that of the saturated triepoxide **7** and clearly different chemical shifts as compared to **8**; thus triepoxide **11** was identified as the *anti,anti,syn* diastereomer.

(18) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Scheme 6



On the basis of analogy between **1** and **2** and the perfect *anti* stereoselectivity found with I_2/Ag_2O epoxidation of **1**, it was hoped that this reagent would convert **2** into the corresponding triquinacene *anti,anti,anti*-triepoxide. Surprisingly, however, I_2/Ag_2O exhibited a clear preference for the less electron-rich, peripheral double bonds in **2** (Scheme 6). Thus, treatment of **2** with 4.5 equiv of I_2/Ag_2O produced a mixture of two isomeric triepoxides, **12** and **13**, in combined 71% yield after chromatography. Fractional crystallization furnished pure **12** in low yield, i.e. a triquinacene bearing three peripheral 4,5-epoxycyclohexano rings in a C_{3v}-symmetrical manner. The regiochemistry and molecular symmetry of **12** was revealed unequivocally by NMR spectrometry (see Experimental Section). On the basis of the *anti* stereoselectivity of the primary epoxidation of **1** in general and with I_2/Ag_2O in particular, **12** has been tentatively ascribed the *anti,anti,anti* stereochemistry. Consequently, stereoisomer **13**, which has not been isolated, should bear the three epoxy groups in the *anti,anti,syn* orientation.

Discussion

From a mechanistic point of view, the perfect *anti* stereoselectivity of the iodine/silver(I) oxide reagent with triquinacene **1** is puzzling and in fact hard to understand on the basis of the present data. Assuming the preferred *anti* attack of iodine at the convex side of the three-fold olefin, the iodonium ion intermediates should react by nucleophilic substitution from the concave (*syn*) side of the bent substrate molecule and hence eventually form the *syn* epoxides, in contradiction to experiment. The exclusive formation of *anti* epoxides **3**−**5** from **1** suggests that the iodonium intermediates bear an iodine at the concave side of the polycyclic framework. In fact, iodonium ion formation is believed to be reversible in related epoxidation reactions (which, however, do not make use of Ag^I ion assistance).[19] Thus, the results presented here point to the rate-determining *syn* attack of the hydroxyl ions at the less hindered, convex side of the triquinacene framework.

On the other hand, precomplexation of silver ions at the double bonds of **1** and **2** may play an important role during epoxidation with the I_2/Ag_2O reagent. Our finding that triquinacene **2** undergoes epoxidation at the less electron-rich peripheral double bonds (cf. **12** and **13**) is

(19) Parrilli, M.; Barone, G.; Adinolfi, M.; Mangoni, L. *Gaz. Chim. Ital.* **1974**, *104*, 835.

in line with the fact that complexation of Ag^+ ions to olefins is strengthened with *decreasing* degree of alkyl substitution.[20] Hence the Ag^+ ions may accelerate the attack of iodine at the peripheral double bonds of **2**. In the case of triquinacene **1**, complexation of Ag^+ ions at the *syn* side of the double bonds would be required to induce the observed *anti* epoxidation. To the best of our knowledge, complexation of triquinacenes with Ag^I has not been studied yet; however, the complex [$(AgNO_3)_3$·*all-cis*-1,4,7-cyclononatriene] has been shown to bear all of the Ag^+ ions at the outer (i.e. *anti*) positions of the carbocycle.[21] Nevertheless, Ag^+ complexation could well be distinct under the basic conditions used in the I_2/Ag_2O epoxidation. MCPBA epoxidation has been found to be highly stereoselective, too. Obviously, here again, the first epoxidation occurs at the convex side of the substrate. It is striking, however, that with this reagent the second attack (on **3**), and even the third attack (on **4**, cf. Scheme 4) takes place, with clear preference, at the concave side of the substrates. It appears that this is due to a balance between the unfavorable steric repulsion of the adjacent epoxycyclohexane rings (as in **4** and **5**) and the kinetic control of the attack of the MCPBA reagent. Similar stereoselectivity has been found for the MCPBA epoxidation of related partially hydrogenated centropolyindans.[22]

In summary, iodine/silver(I) oxide in aqueous tetrahydrofuran has been found to be a highly stereoselective reagent for epoxidation of the triquinacenes **1** and **2**. Single, double and even triple epoxidation takes place exclusively at the convex side of the spherical framework. In contrast to previous findings,[5,6] I_2/Ag_2O and *m*-chloroperbenzoic acid were found to generate the same monoepoxide; with respect to double and triple epoxidation, however, the stereoselectivity of these reagents is strikingly different. Moreover, I_2/Ag_2O was found to differ from MCPBA in that it gives rise to epoxidation of the less electron-rich double bonds of **2**. Detailed structural and mechanistic studies appear to be necessary to understand the factors governing the stereochemical course of epoxidation with I_2/Ag_2O.

Experimental Section

General Methods. Triquinacenes **1** and **2** were prepared as described previously.[10] Melting points are uncorrected. ^{1}H NMR spectra were obtained at nominal measuring frequencies of 250 and 300 MHz with $CDCl_3$ solutions and TMS as internal standard. ^{13}C NMR spectra were measured using broad-band decoupling and the DEPT technique (at 62.8 MHz) or broad-band decoupling and the *J*-modulated spin-echo experiment (75.4 MHz). Mass spectra were recorded using double focussing instruments under electron impact ionization conditions (EI, 70 eV). Microanalyses were performed by the Mikroanalytic Laboratories of the Fakultät für Chemie, Universität Bielefeld and, alternatively, of the Institut für Organische Chemie of the Technische Hochschule Darmstadt. Chromatographic purifications were performed using silica gel (0.063−0.200 mm; Merck or Macherey-Nagel); for thin-layer chromatography, Al plates covered with silica gel (Kieselgel 60, F_{254}, Merck) were used.

X-ray Structural Analysis. The single crystal X-ray diffraction analysis of triepoxide **8** was performed using the SHELXTL PLUS (VMS) program package. Empirical formula: $C_{20}H_{30}O_3$; crystal size [mm]: 0.3 × 0.6 × 1.0; formula weight: 354.5; crystal system: monoclinic; space group $P2_1$; lattice parameters: $a = 9.711(1)$ Å, $b = 9.351(1)$ Å, $c = 11.115(1)$ Å, $\beta = 104.98(1)°$, $V = 975.0(2)$ Å^3; $Z = 2$; $d_{calc} = 1.207$ g/cm^3; $F(000) = 384$, μ(Mo K$_\alpha$) = 0.073 mm^{-1}; temp: 293 K; $2\Theta_{max} = 60°$; 1911 data collected, of which 1464 observed [$F > 3\sigma(F)$]; 234 parameters refined; residuals RF and wR_F for observed data: 0.056, 0.047; largest peak in final difference map: 0.24 e/Å^{-3}; no absorption correction. For atomic parameters, complete collection of bond lengths and angles, C atom anisotropic displacement coefficients, and H atom coordinates and isotropic displacement coefficients, see ref 18.

Epoxidation of Triquinacenes 1 and 2 Using Iodine/Silver(I) Oxide. General Procedure. To a stirred solution of triquinacene **1** or **2** in THF/water (9:1) are added the appropriate amounts of iodine and silver(I) oxide (see below for details), and stirring is continued till the mixture has completely decolorized (1−2 h). Precipitated silver iodide is removed by filtration, and the filtrate is diluted with dichloromethane to a 2- to 2.5-fold volume and dried with sodium sulfate. Evaporation of the solvents gives a solid residue, which is subjected to chromatography (see below for details).

(4aα,12cα)-4a,12c-Epoxy-1,2,3,4,4b,5,6,7,8,8b,9,10,11,12,-12b,12d-hexadecahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*a,b*]indene (3) was prepared from 460 mg (1.50 mmol) of **1** in THF/H_2O (25 mL), I_2 (508 mg, 2.0 mmol), and Ag_2O (463 mg, 2.0 mmol). Chromatography (CH_2Cl_2 or $CHCl_3$) of the product mixture (475 mg) yields pure **3** (200 mg, 41%) as colorless crystals: mp 147.5 °C; IR (KBr) ν 2933, 2858, 1438, 956 cm^{-1}; ^{1}H NMR δ 2.58 (s, 1 H), 2.47 (s, 2 H), 2.16 (m$_c$, 4 H), 1.93 (m$_c$, 7 H), 1.65 (m$_c$, 6 H), 1.47 (m$_c$, 4 H), 1.24 (m$_c$, 3 H), 1.14 (s, 3 H); ^{13}C NMR δ 140.77 (q), 131.59 (q), 74.30 (q), 70.91 (t), 65.71 (t), 58.46 (q), 29.24 (p), 26.91, 26.30, 25.86, 23.01, 22.85, 20.10 (all s); MS (EI, 70 eV) *m*/*z* (%) 322 (M$^{\bullet+}$, 85), 307 (10), 304 (19), 279 (16), 237 (16), 225 (33), 189 (100), 105 (14), 91 (18). Anal. Calcd for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.43; H, 9.26.

(4aα,4cα,8aα,12cα)-4a,12c:4c,8a-Diepoxy-1,2,3,4,-4b,5,6,7,8,8b,9,10,11,12,12b,12d-hexadecahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*a,b*]indene (4) was prepared from 920 mg (3.00 mmol) of **1** in THF/H_2O (55 mL), I_2 (2.03 g, 8.0 mmol), and Ag_2O (1.85 g, 8.0 mmol). Chromatography of the product mixture (1.15 g) with CH_2Cl_2/EtOAc (19:1) yields pure **3** (386 mg, 40%) and then **4** (208 mg, 21%) as colorless crystals: mp 122 °C; IR (KBr) ν 2938, 2858, 1442, 1361, 959 cm^{-1}; ^{1}H NMR δ 2.45 (s, 2 H), 2.42 (s, 1 H), 2.05 (m$_c$, 12 H), 1.60 (m$_c$, 8 H), 1.28 (m$_c$, 4 H), 1.11 (s, 3 H); ^{13}C NMR δ 135.70 (q), 73.71 (q), 70.40 (q), 66.82 (t), 61.56 (t), 59.80 (q), 31.46 (p), 27.35, 27.13, 25.43, 22.93, 20.28, 20.12 (all s); MS (EI, 70 eV) *m*/*z* (%) 338 (M$^{\bullet+}$, 100), 320 (35), 241 (44), 205 (69), 201 (46), 189 (70), 177 (22), 161 (66), 132 (58), 117 (41), 105 (55), 91 (62), 79 (39), 67 (35), 55 (22), 41 (53). Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.94. Found: C, 81.52; H, 9.01.

(4aα,4cα,8aα,8cα,12aα,12cα)-4a,12c:4c,8a:8c,12a-Triepoxy-1,2,3,4,4b,5,6,7,8,8b,9,10,11,12,12b,12d-hexadecahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*a,b*]indene (5) was prepared from 1.53 g (5.00 mmol) of **1** in THF/H_2O (125 mL), I_2 (5.70 g, 22.5 mmol), and Ag_2O (5.22 g, 22.5 mmol). Chromatography of the product mixture (1.70 g) with CH_2Cl_2/EtOAc (19:1) yields pure **3** (141 mg, 9%), pure **4** (241 mg, 14%), and finally, pure **5** (728 mg, 41%) as colorless crystals: mp 214 °C; IR (KBr) ν 2970, 2930, 2885, 1445, 1243, 955, 756 cm^{-1}; ^{1}H NMR δ 2.41 (s, 3 H), 2.06 (m$_c$, 12 H), 1.42 (m$_c$, 12 H), 1.12 (s, 3 H); ^{13}C NMR δ 70.51 (q), 62.32 (t and q, isochronous resonances), 33.62 (p), 26.76 (all s), 20.06 (all s); MS (EI, 70 eV) *m*/*z* (%) 354 (M$^{\bullet+}$, 19), 313 (24), 189 (27), 149 (100), 105 (38), 91 (66), 71 (10), 67 (41), 55 (44), 41 (58), (41 (48). Anal. Calcd for $C_{23}H_{30}O_3$: C, 77.93; H, 8.53. Found: C, 77.99; H, 8.53.

(2α,3α,6α,7α,10α,11α)-2,3:6,7:10,11-Triepoxy-1,2,3,4,-4b,5,6,7,8,8b,9,10,11,12,12b,12d-hexadecahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (12) was prepared from 901 mg (3.0 mmol) of **2** in THF/H_2O (100 mL), I_2 (3.43 g, 13.5 mol), and Ag_2O (3.13 g, 13.5 mol). Chromatography of the product mixture (1.70 g) with CH_2Cl_2/EtOAc (1:1) yields a mixture of **12** and **13** (746 mg, 71%, [**12**]:[**13**] ≈ 60:40 by ^{13}C NMR), from which pure **12** was obtained by recrystallization from CH_2Cl_2/MeOH as colorless crystals: mp

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342 °C; IR (KBr) ν 2988, 2942, 2898, 2811, 1421, 1412, 1257, 1229, 1013, 982, 851, 811 cm^{-1}; ^1H NMR δ 3.21 (d, $^3J = 2$ Hz, 6 H), 2.66 (s, 3 H), 2.60 (br s, 6 H), 2.37 (m_c, 6 H), 1.19 (s, 3 H); ^{13}C NMR δ 131.19 (q), 68.09 (t), 57.72 (q), 50.84 (t), 27.30 (p), 26.84 (s); MS (EI, 70 eV) *m/z* (%) 348 ($M^{\bullet+}$, 85), 330 (26), 315 (31), 273 (65), 245 (57), 217 (40), 203 (65), 179 (66), 165 (86), 115 (24), 91 (100), 77 (52), 65 (29). Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 79.11; H, 7.06.

The ^{13}C NMR spectrum of triepoxide **13** [(2α,3α,6α,7α,10*β*,-11*β*)-2,3:6,7:10,11-triepoxy-1,2,3,4,4b,5,6,7,8,8b,9,10,11,12,-12b,12d-hexadecahydro-12d-methyldibenzo[2,3:4,5]pentaleno-[1,6-*ab*]indene] was obtained by subtracting that of **12**: δ 131.44 (q), 130.96 (q), 130.76 (q), 68.46 (t), 68.24 (t), 57.43 (q), 51.61 (t), 51.09 (t), 26.75, 26.60 (s).

Conversion of 4 to 5 with Ag_2O/I_2. Reaction of diepoxide **4** (102 mg, 300 μmole) in THF/H_2O (10 mL, 9:1), I_2 (127 mg, 500 μmole) and Ag_2O (116 mg, 500 μmole) gave 100 mg of crude product from which the starting material (8 mg, 8%) and pure tripoxide **5** (64 mg, 60%) were separated.

Epoxidation of Triquinacenes 1 and 2 Using MCPBA. General Procedure. A solution of triquinacene **1** or **2** in dichloromethane is stirred at room temperature while a solution of *m*-chloroperbenzoic acid (MCPBA, 70%) in the same solvent is added dropwise within a period of 20−30 min. Stirring is continued for 2 h. The mixture is washed thrice with aqueous sodium bicarbonate (10%) and then with water and dried with sodium sulfate. The solvent is removed, and the solid residue is subjected to chromatography (see below for details).

Monoepoxide 3 and (4aα,4c*β*,8a*β*,12cα)-4a,12c:4c,8a-Diepoxy-1,2,3,4,4b,5,6,7,8,8b,9,10,11,12,12b,12d-hexadecahydro-12d-methyldibenzo[2,3:4,5]-pentaleno[1,6-*ab*]-indene (6) were obtained from 460 mg (1.50 mmol) of **1** in CH_2Cl_2 (30 mL) and 368 mg (1.5 mmol) of MCPBA (70%) in the same solvent (10 mL). Chromatography ($CHCl_3$) of the product mixture (465 mg) gave the starting material (63 mg, 14%), followed by pure **3** (98 mg, 20%) and by diepoxide **6** (76 mg, 15%) which was characterized only by its ^{13}C NMR spectrum: δ = 134.45 (q), 133.45 (q), 73.67, 72.00, 70.62, 69.95 (all q), 67.12, 66.03 (t), 63.02 (q), 61.33 (t), 29.82 (p), 28.94, 28.12, 26.52, 25.97, 25.66, 22.97, 20.28, 19.91, 19.65 (all s).

(4aα,4cα,8aα,8c*β*,12a*β*,12cα)-4a,12c:4c,8a:8c,12a-Triepoxy-1,2,3,4,4b,5,6,7,8,8b,9,10,11,12,12b,12d-hexadecahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (7) and (4aα,4c*β*,8a*β*,8c*β*,12a*β*,12cα)-4a,12c:4c,8a:8c,12a-Triepoxy-1,2,3,4,4b,5,6,7,8,8b,9,10,11,12,12b,12d-hexadecahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (8) were obtained from 920 mg (3.00 mmol) of **1** in CH_2Cl_2 (40 mL) and 2.22 g (9.0 mmol) of MCPBA (70%) in the same solvent (50 mL). Chromatography (CH_2Cl_2/EtOAc, 19:1) of the product mixture (1.02 g) yielded pure **7** (554 mg, 52%) followed by pure **8** (388 mg, 37%).

7: Colorless crystals, mp 153 °C; IR (KBr) ν 2947, 1442, 1363, 965, 955, 748 cm^{-1}; ^1H NMR δ 2.28 (s, 1 H), 2.13 (s, 2 H), 2.00 (m_c, 12 H), 1.39 (m_c, 12 H), 1.09 (s, 3 H); ^{13}C NMR δ 71.34, 70.13, 69.86 (all q), 63.61 (q), 62.69 (t), 61.93 (t), 32.03 (p), 28.57, 27.03, 25.30, 20.17, 19.95, 19.73 (all s); MS (EI, 70 eV) *m/z* (%) 354 ($M^{\bullet+}$, 39), 336 (67), 326 (79), 318 (26), 241 (88), 224 (70), 205 (48), 189 (28), 132 (100), 91 (57), 41 (48). Anal. Calcd for $C_{23}H_{30}O_3$: C, 77.93; H, 8.53. Found: C, 78.02; H, 8.64.

8: Colorless crystals, mp 152 °C; IR (KBr) ν 2948, 2859, 1450, 1260, 973, 947, 731, 717 cm^{-1}; ^1H NMR δ 1.94 (m_c, 12 H), 1.87 (s, 2 H), 1.85 (s, 1 H), 1.39 (m_c, 8 H), 1.23 (m_c, 4 H), 1.15 (s, 3 H); ^{13}C NMR δ 72.76 (q), 71.21 (q), 69.59, 68.43 (q), 62.40 (t), 60.93 (t), 31.35 (p), 28.54, 28.24, 25.53 (all s), 20.03, 19.78, 19.66 (all s); MS (EI, 70 eV) *m/z* (%) 354 ($M^{\bullet+}$, 40), 336 (4), 326 (68), 241 (97), 189 (73), 132 (100), 105 (46), 91 (65), 79 (49), 55 (43), 41 (69). Anal. Calcd for $C_{23}H_{30}O_3$: C, 77.93; H, 8.53. Found: C, 77.98; H, 8.48.

(4aα,12cα)-4a,12c-Epoxy-1,4,4b,5,8,8b,9,12,12b,12d-decahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*ab*]-indene (9) and (4a,4c*β*,8a*β*,12cα)-4a,12c:4c,8a-Diepoxy-1,4,4b,5,8,8b,9,12,12b,12d-decahydro-12d-methyl-dibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (10) were obtained from 300 mg (1.00 mmol) of **2** in CH_2Cl_2 (20 mL) and 493 mg (2.00 mmol) of MCPBA (70%) in the same solvent (10 mL). Chromatography (CH_2Cl_2/EtOAc, 19:1) of the product mixture (310 mg) gave pure **9** (72 mg, 23%) and pure **10** (130 mg, 39%).

9: Colorless crystals, mp 210 °C; IR (KBr) ν 3024, 2948, 2887, 2871, 1434, 964, 669 cm^{-1}; ^1H NMR δ 5.73 (m_c, 4 H), 5.44 (m_c, 2 H), 2.78 (m_c, 9 H), 2.65 (s, 2 H), 2.54 (m_c, 4 H), 1.25 (s, 3 H); ^{13}C NMR δ 138.30 (q), 129.26 (q), 124.37 (t), 123.99 (t), 122.08 (t), 73.00 (q), 70.74 (t), 64.78 (t), 58.90 (q), 30.00 (p), 28.26 (s), 28.04 (s), 27.83 (s); MS (EI, 70 eV) *m/z* (%) 316 ($M^{\bullet+}$, 100), 298 (17), 205 (32), 185 (48), 129 (44), 115 (35), 91 (74), 77 (25). Anal. Calcd for $C_{23}H_{24}O$: C, 87.30; H, 7.64. Found: C, 87.69; H, 7.67.

10: Colorless crystals, mp 185.5 °C; IR (KBr) ν 3023, 2900, 2872, 1427, 1356, 865, 729, 655 cm^{-1}; ^1H NMR δ 5.74 (m_c, 2 H), 5.47 (m_c, 2 H), 5.44 (m_c, 2 H), 2.61 (m_c, 12 H), 2.25 (s, 1 H), 2.18 (s, 2 H), 1.21 (s, 3 H); ^{13}C NMR δ 132.58 (q), 130.94 (q), 124.48 (t), 123.80 (t), 122.02, 121.85, 121.75, 121.64 (all t), 72.26, 71.03, 68.97, 68.67 (all q), 66.63 (t), 65.27 (t), 63.33 (q), 59.80 (t), 29.98 (p), 29.56, 29.22, 29.14, 27.57, 27.34, (all s); MS (EI, 70 eV) *m/z* (%) 332 ($M^{\bullet+}$, 16), 314 (15), 273 (15), 219 (31), 185 (40), 130 (100), 107 (48), 91 (71), 77 (22). Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 83.22; H, 7.44.

(4aα,4cα,8aα,8c*β*,12a*β*,12cα)-4a,12c:4c,8a:8c,12a-Triepoxy-1,4,4b,5,8,8b,9,12,12b,12d-decahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (11) was prepared from 751 mg (2.50 mmol) of **2** in CH_2Cl_2 (40 mL) and 1.85 g (7.5 mmol) of MCPBA (70%) in the same solvent (20 mL). Chromatography (CH_2Cl_2/EtOAc, 19:1) of the product mixture (814 mg) yielded **10** (14 mg, 1.7%), followed by pure **11** (265 mg, 30%) as colorless crystals, mp 276 °C; IR (KBr) ν 3026, 2909, 1657, 1425, 1411, 1352, 870, 851, 660 cm^{-1}; ^1H NMR δ 5.50 (m_c, 2 H), 5.47 (m_c, 4 H), 2.71 (m_c, 12 H), 2.52 (s, 1 H), 2.29 (s, 2 H), 1.21 (s, 3 H); ^{13}C NMR δ 121.96 (t), 121.41 (t), 70.60 (q), 68.60 (q), 68.32 (q), 63.87 (q), 61.67 (t), 61.31 (t), 31.82 (p), 29.16, 27.89, 27.39 (all s); MS (EI, 70 eV) *m/z* (%) 348 ($M^{\bullet+}$, 9), 312 (2), 159 (24), 147 (50), 129 (76), 107 (90), 91 (100), 77 (72), 53 (33), 41 (48). Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 79.37; H, 6.84.

Conversion of 4 to 7 with MCPBA. Reaction of diepoxide **4** (237 mg, 700 μmole) in CH_2Cl_2 (15 mL) and 173 mg (700 μmole) of MCPBA (70%) in the same solvent (4 mL) yielded pure **7** (244 mg, 98%).

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Supporting Information Available: Two views of the molecular structure of triepoxide **8**, as determined by X-ray structural analysis, with selected bond angles (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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