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Syntheses of Systems Containing Strained Double Bonds: Cycloaddition Reactions of *trans*-3,8-Dicarbomethoxydihydroheptelene

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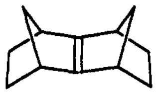
The two strained systems **5** and **6** are the objectives of synthetic and structural studies because of their relationship to *syn*- and *anti*-sesquinorbornenes. The Diels–Alder cycloaddition of maleic anhydride, *p*-benzoquinone, dimethylacetylene dicarboxylate, singlet oxygen, and benzyne to *trans*-3,8-dicarboxydihyroheptalene **7** have been investigated. It is shown that the second addition to this system goes only with dienophiles such as singlet oxygen and benzyne. Compound **15**, a derivative of the anti compound **6**, was synthesized and the structure investigated by X-ray diffraction. Although the molecule is strained, the central double bond exhibits a planar environment. The structure of compound **9**, a precursor to a derivative of the syn compound **5**, is reported. The double-bond environment at the ring juncture differs significantly from planarity, and the folding angle is 7.3°.

Introduction

Pyramidalized alkenes are molecules containing C–C double bonds in which one or both of the sp^2 carbon atoms do not lie in the same plane as the attached atoms. Evidence for pyramidalization first came from NMR studies on norbornadiene[1] and has been substantiated by X-ray studies of crystalline norbornenes and sesquinorbornenes.[2] More recently, Ermer et al.[3] reported the geometry about the double bond in a norbornene derivative studied by neutron diffraction. In 1980, *syn*-**1** and *anti*-sesquinorbornene **2** were synthesized independently by Bartlett[4] and Paquette.[5] X-ray studies performed on the anhydride and phenylsulfone derivatives of **1**[2a,b] showed that the π-bonded carbons are significantly pyramidalized with folding angles ranging from 16 to 18°. In contrast, the anhydride derivative of *anti*-sesquinorbornene **2** was found to exhibit a planar double-bond geometry. A number of theories have been proposed to rationalize these distortions.[6] Recently, Paquette[7] reported the synthesis of the *syn*- and *anti*-sesquinorbornatrienes **3** and **4**; however, structural data were not reported. More recently, Paquette et al.[8] synthesized the derivative **3a** in which structural analysis indicates a pyramidalization angle or folding angle of 32.4°. Much of the literature on the pyramidalization of alkenes through 1988 is covered in a review of Borden.[9]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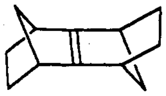
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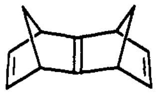
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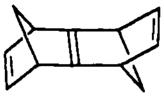
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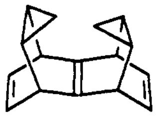
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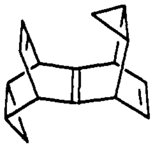
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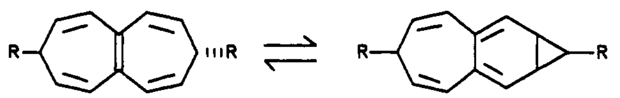

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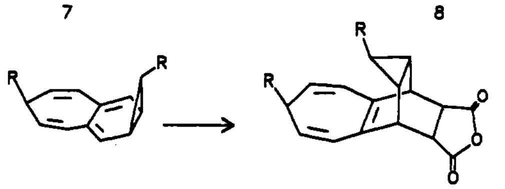

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In this paper, we describe attempts to synthesize derivatives of the new systems **5** and **6** which are related to *syn*- and *anti*-sesquinornatriene.

Results and Discussion

Compounds **5** and **6** are bisnorcaranes. To obtain these structural units, one can take advantage of the cycloheptatriene–norcaradiene equilibrium. It is well-known

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that cycloheptatriene is in equilibrium with its valence isomer, norcaradiene,[10] and π-electron-withdrawing substituents at C-7 shift the CHT-NOR equilibrium in favor of norcaradiene.[11] Therefore, Diels–Alder additions of dienophiles to these cycloheptatriene derivatives lead primarily to the formation of norcaradiene-type addition products. For this reason we selected the biscycloheptatriene derivative **7**[12] (R = CO_2CH_3) to prepare derivatives of compounds **5** and **6**. To investigate the reactivity of **7** the Diels–Alder reaction with several dienophiles was studied.

The dihydroheptalene derivative **7** was subjected to Diels–Alder cycloaddition with maleic anhydride in chloroform solution at room temperature. After 3 h the reaction was complete, and only isomer **9** was isolated (98% yield). Careful examination of the ^1H NMR spectrum did not reveal the presence of other isomers (exo/endo). The 360-MHz spectrum showed absorptions at δ 6.05–5.25 (AB-system) and 2.2 (tt) with relative intensities of 4:1, indicating only one cycloheptatriene moiety had undergone cycloaddition. The resonances of the other protons are in accord with the proposed structure. The mirror plane symmetry of **9** is evident from the 13-line ^{13}C-NMR spectrum; however, on the basis of the ^1H and ^{13}C NMR spectrum it is not easy to establish the exact configuration of the anhydride ring. To determine unequivocally the relative configuration and to investigate the geometry about the double bond at the ring junction, the X-ray structure was determined. Maleic anhydride added to the *exo*-norcaradiene isomer from the side opposite to the cyclopropane ring, as expected. The double bond exhibits a fold angle of 7.3 (2)°. This distortion might be attributed to orbital interactions between the π-system and the cyclopropaneethano bridge system; however, no theoretical calculations have been made. This double bond is lengthened to 1.360 (3) Å, while the shared cyclopropane bond of 1.478 (3) Å is significantly shorter than the other two bonds in the cyclopropane ring (1.516 (3) and 1.514 (3) Å). The formation of only one isomer may indicate a strong secondary orbital effect[13] of the unreacted cycloheptatriene ring directing the endo approach of the maleic anhydride.

With *p*-benzoquinone as dienophile, the single adduct **10** was isolated in an 85% yield. Although the stereochemistry of the cycloaddition product (exo/endo) was not established by ^1H NMR spectroscopy, comparison with the data from **9** indicates the compound should have the endo configuration. The monoaddition was clearly evident from the NMR spectrum. The signals belonging to the unreacted cycloheptatriene ring form an AX system at 6.07–5.19 ppm. A singlet at 6.60 ppm arises from the olefinic protons of the *p*-benzoquinone ring. The ^{13}C spectrum is in complete agreement with the proposed structure and expected symmetry of the molecule.

Attempted cyclization of the molecule to the corresponding cage compound **14** failed due to the unfavorable endo configuration of the carbomethoxy group on the cyclohextatriene ring. It is known that C-7 substituted cycloheptatriene derivatives give exclusively (except for cyano derivatives) exo addition products.[14]

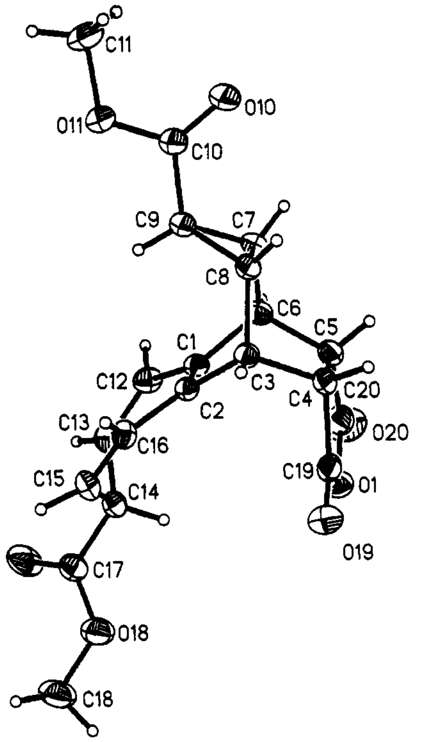
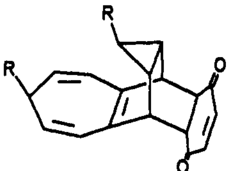


Figure 1. Thermal ellipsoid drawing of compound **9**.

When **7** was reacted with dimethyl acetylenedicarboxylate in chloroform solution at 65 °C, cycloaddition proceeded to completion within 10 days, and the lone adduct **11** (R = CO_2CH_3) was obtained (88% yield). Structural assignment followed from the ^1H and ^{13}C NMR spectra.



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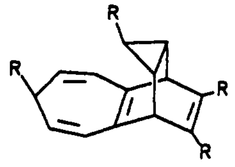

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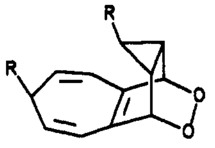

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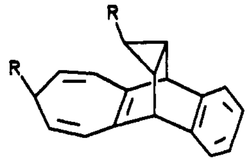

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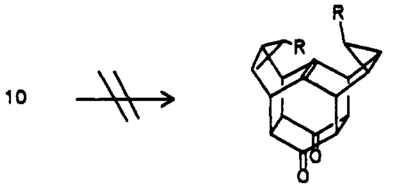

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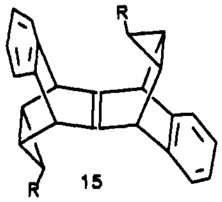

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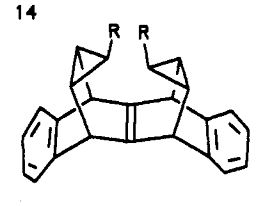

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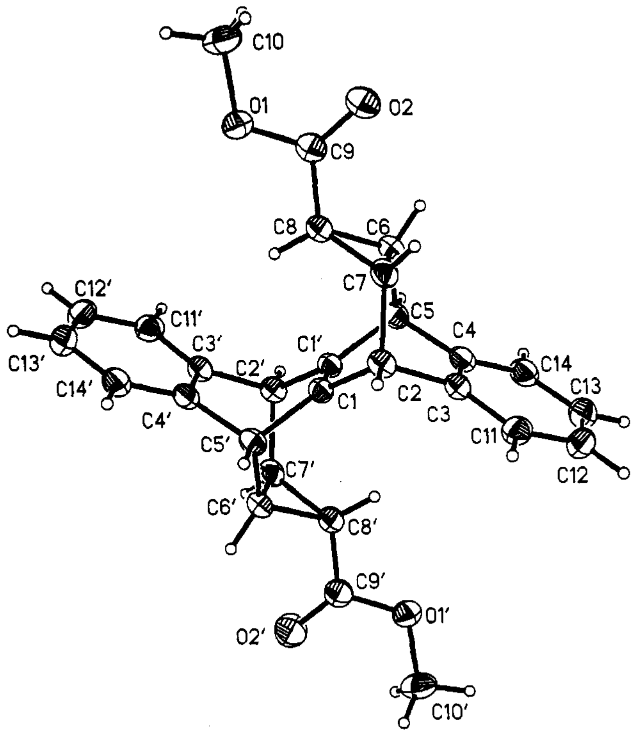
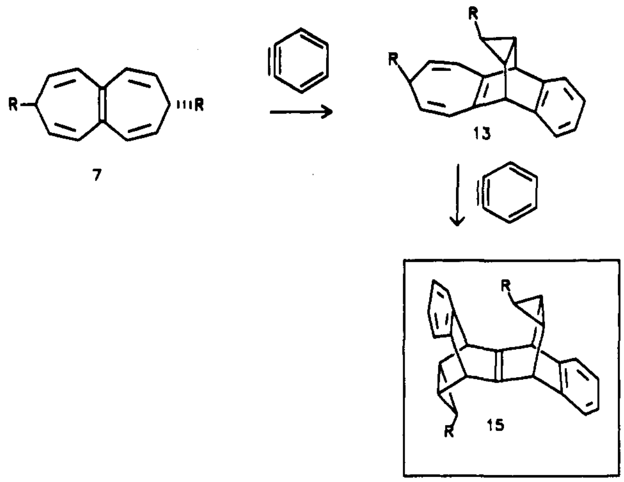
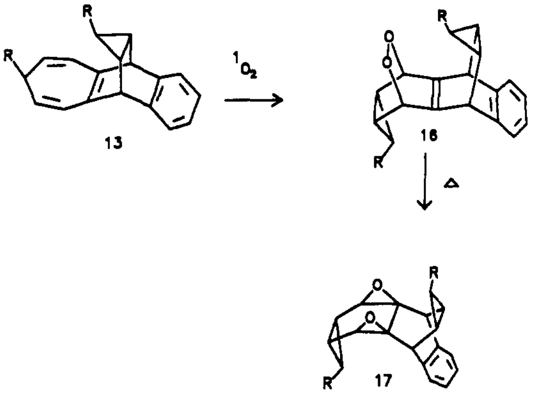


Figure 2. Thermal ellipsoid drawing of compound **15**.

The endoperoxidation of cisoid-1,3-dienes with singlet oxygen has progressed to the point where it is an important and reliable synthetic procedure.[15] Because of similarities with the familiar Diels–Alder reaction, a direct mechanistic parallel was drawn between the two processes. The cycloaddition reactions of singlet oxygen with cycloheptatriene derivatives have been well studied.[16] Tetraphenylporphine-sensitized photooxygenation of dihydroheptalene derivative **7** in chloroform solution at 0 °C afforded the norcaradiene-type endoperoxide **12**. Due to the stability of this endoperoxide, further transformations, e.g., bis-epoxide formation and isomerization to the hydroxy ketone, were unsuccessful.

Benzyne, as traditionally generated from anthranilic acid,[17] reacted with **7** to give a complex mixture of products. However, when benzyne was generated from benzenediazonium 2-carboxylate hydrochloride[8,18] and propylene oxide in refluxing ethylene chloride, the two products **13** and **15** were isolated. The structural assignments were made from the NMR data. In compound **15** the ^1H spectrum of the benzyne protons exhibits an AA′BB′ pattern as expected from molecular symmetry. Bridgehead protons appear at 4.05 ppm as a quasi-triplet while the cyclopropane protons are located at 1.80 and 0.28 ppm. A nine-line ^{13}C spectrum is consistent with the C_{2h} symmetry of **15**. The resonance of greatest interest is that associated with the central double bond which appears at 140.55 ppm. The resonances for the central carbon atoms in compounds **1**–**4** are shifted to lower fields;[4,5] however, the pyramidalization in **1** and **3** does not have much effect on the chemical shift. The crystal structure of **15** was determined, and the molecule has C_{2h} symmetry with the central double bond of normal length (1.329 (3) Å) and the π-system rigorously planar.





Bartlett et al.[18] have reviewed some of the chemistry of **1** and **2**. Reaction of the pyramidalized double bond in the syn isomer with a variety of reagents results in addition to the exo face of the double bond. Competition experiments[19] between **1** and **2** showed the syn isomer reacted faster than the anti isomer in concerted cycloaddition, but was considerably less reactive toward ionic addition. Analogous to this work epoxidation, bromination and hydrogenation of compound **15** were attempted. In all cases, only unreacted starting material was isolated. This can be rationalized in terms of steric effects associated with the adjacent cyclopropane and benzene rings.

To synthesize additional bis-cycloaddition products, the mono adduct **9** was exposed to a variety of dienophiles under different reaction conditions. No addition products were isolated. Raising the reaction temperature led to shifts in the proton spectrum of the seven-membered ring. The reaction of singlet oxygen with the benzyne adduct **13** was investigated. The photooxygenation of **13** was carried out in the presence of tetraphenylporphine as described earlier. The ^1H spectrum indicated the complete consumption of the starting material and was consistent with the formation of the symmetrical endoperoxide **16**. The compound is not as stable as the norcaradiene endoperoxide, and it was converted quantitatively to the bis-epoxide **17** by heating at 50 °C. The disappearance of the olefinic resonances in the ^{13}C spectrum indicated the formation of the expected bis-epoxide **17** by addition of the oxygen diradicals formed, initially, to the adjacent double bond. The bis-epoxide has been characterized fully.

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In this work only the isomer **15** corresponding to the new system **6** has been synthesized. Work continues on the preparation of **18** or related compounds which will be the first compounds corresponding to the *syn*-sesquinorbornene analogue **5**.

Experimental Section

General. Infrared spectra were obtained from films on NaCl plates for liquids or from solution in 0.1-mm cells or KBr pellets for solids. The ^{1}H NMR and ^{13}C NMR spectra were recorded on 250-, 360-, or 400-MHz spectrometers. All column chromatography was performed on silica gel (60-mesh), while all TLC separations were carried out on 0.2-mm silica gel on aluminum plates. All X-ray data were collected by standard techniques and the structures solved by direct methods.[20]

5,16-Dicarbomethoxy-12-oxopentacyclo[7.5.3.0^{2,8}.0^{10,14}.0^{15,17}]heptadeca-2(8),3,6-triene-11,13-dione (9). To a solution of 272 mg (1 mmol) of **7** (R = CO_2CH_3) in 30 mL of $CHCl_3$ was added 147 mg (1 mmol) of maleic anhydride at rt. After the solution was stirred at rt for 3 h, the reaction was complete, solvent was evaporated, and excess maleic anhydride was removed by sublimation. Crystallization of the residue from $CHCl_3$/ether afforded the endo adduct **9** (362 mg, 98%) as colorless crystals, mp 205–206 °C: ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.05 (dd, A of AX-System, J = 8.8, 1.0 Hz, 2 H, olefinic), 5.25 (dd, X of AX-system, J = 8.8, 5.2 Hz, 2 H, olefinic), 3.66 (m, bridghead, 2 H), 3.37 (m, H-10, H-14, 2 H), 2.20 (tt, J = 5.2, 1.0 Hz, H-5, 1 H), 1.88 (m, H-15, H-17, 2 H), 1.07 (t, J = 2.8 Hz, cyclopropane, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 172.71, 171.79, 170.71, 135.70, 125.35, 114.52, 52.33, 52.03, 45.53, 42.85, 38.31, 20.80, 20.54; mass spectrum m/z (rel. intensity) 370 (M^+), 178 (100).

5,17-Dicarbomethoxypentacyclo[7.4.3.0^{2,8}.0^{10,15}.0^{16,18}]octadeca-2(8),3,6,12-tetraene-11,14-dione (10). *p*-Benzoquinone (135 mg, 1.15 mmol) and **7** (272 mg, 1 mmol) were dissolved in 15 mL of $CHCl_3$. The solution was stirred at rt for 2 d, and the color of the reaction mixture turned from green to red. The solvent was evaporated and the residue purified by crystallization from $CHCL_3$/ether giving 323 mg (85%) of the monoaddition product **10**: colorless needles, mp 204–206 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.60 (s, olefinic, 2 H), 6.07 (dd, A of AX-system, J = 8.7, 1.07 Hz, 2 H), 5.19 (dd, X of AX-system, J = 8.7, 5.64 Hz, 2 H), 3.6 (m, bridgehead, 2 H), 3.29 (m, 2 H), 1.98 (m, 2 H), 1.96 (tt, J = 5.64, 1.07 Hz, H-5, 1 H), 0.64 (t, J = 2.83 Hz, cyclopropane, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.98, 172.24, 141.14, 137.21, 125.78, 114.51, 52.06, 51.50, 47.56, 42.84, 40.75, 20.56, 17.54; mass spectrum m/z 370 (M^+), 321 (77), 44 (100). Anal. Calcd for $C_{22}H_{20}O_6$: C, 69.46; H, 5.30. Found: C, 69.27; H, 5.34.

5,11,13,14-Tetracarbomethoxytetracyclo[7.3.2.0^{2,8}.0^{10,11}]tetradeca-2(8),3,6,13-tetraene (11). A solution of 272 mg (1 mmol) of **7** and 213 mg (1.5 mmol) dimethylacetylene dicarboxylate in 15 mL of $CHCl_3$ was stirred at 65 °C for 10 d. The solvent was evaporated and the adduct purified by crystallization from $CHCl_3$/petroleum ether: colorless needles (240 mg, 88%), mp 114–116 °C; ^{1}H NMR (400 MHz, DMSO) δ 6.35 (dd, A of AX-system, J = 8.39, 0.8 Hz, 2 H), 4.98 (dd, X of AX-system, J = 8.39, 5.49 Hz, 2 H), 4.39 (m, bridgehead, 2 H), 2.11 (m, cyclopropane, 2 H), 1.86 (tt, J = 5.49, 0.8 Hz, H-5, 1 H), 1.08 (t, J = 2.75 Hz, cyclopropane, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.49, 170.27, 165.26, 145.95, 138.99, 124.43, 105.06, 52.19, 52.03, 51.54, 44.11, 41.31, 29.04, 27.58; mass spectrum m/z 414 (M^+, 2), 355 (100). Anal. Calcd for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 64.01; H, 5.28.

4,11-Dicarbomethoxy-13,14-dioxatetracyclo[7.3.2.0^{2,8}.0^{10,12}]dodeca-1(7),2-triene (12). In 30 mL of $CHCl_3$ were dissolved 15 mg of TPP and 272 mg (1 mmol) of **7**. The solution was irradiated with a projection lamp (150 W) while a stream of O_2 was bubbled vigorously through the system at 0 °C. After a total irradiation time of 1 h the solvent was evaporated and the residue analyzed spectroscopically. The product decomposed upon standing at room temperature: ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.27 (d, A of AB-system, J = 8.6, 2 H), 5.27 (dd, B of AB-system), J = 8.6, 7.2 Hz, 2 H), 5.07 (m, bridgehead, 2 H), 2.83 (t, J = 7.2 Hz, H-5, 1 H), 2.33 (m, cyclopropane, 2 H), 0.95 (t, J = 2.8, cyclopropane, 1 H).

Reaction of 7 with Benzyne. To a refluxing solution of **7** (136 mg, 0.5 mmol) in 10 mL of ethylene dichloride were added, under N_2, 232 mg (1.25 mmol) of benzenediazonium 2-carboxylate hydrochloride and 1 mL of propylene oxide. After 1 h, an additional 232 mg (1.25 mmol) diazonium salt and 1 mL of propylene oxide were added. The colorless solution became dark. The reaction mixture was refluxed 2 h longer and the solvent evaporated. Crystallization of the residue from $CHCl_3$/ether furnished the biscycloaddition product **15** (20% yield).

4,10-Dicarbomethoxy-*trans*,*trans*-2,6,8,12-dibenzohexacyclo[5.5.0.0^{3,5}.0^{9,11}]dodec-1(7)-ene (15): colorless needles, mp > 275 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.04–7.25 (AA′BB′-system, aromatic, 8 H), 4.1 (quasi t, bridgehead, 4 H), 1.80 (m, cyclopropane, 4 H), 0.28 (t, cyclopropane, 2 H); ^{13}C (62.5 MHz, $CDCl_3$) δ 172.11, 145.15, 140.55, 125.13, 123.46, 51.49, 44.11, 29.11, 27.16. Anal. Calcd for $C_{28}H_{24}O_4$: C, 79.22; H, 5.70. Found: C, 78.95; H, 5.66. The residue was chromatographed on a silica gel column, and the monobenzyne adduct **13** was eluted (ethylacetate/hexane (1:3)) to give an isolated yield of 15%. The purity was about 95% as estimated by NMR: ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.22 (AA′BB′, aromatics, 4 H), 6.24 (d, A of AB-system, J = 8.0 Hz, olefinic, 2 H), 4.82 (dd, B of AB-system, J = 8.0, 5.2 Hz, olefinic, 2 H), 4.27 (m, bridgehead, 2 H), 2.08 (m, cyclopropane, 2 H), 1.78 (t, J = 5.2 Hz, 1 H), 1.53 (t, J = 1.3 cyclopropane, 1 H). When the reaction was carried out with a 7-fold excess of *benzenediazonium 2-carboxylate hydrochloride*, **15** was the only characterizable product (40%). The monobenzene addition product **13** was not detected.

Synthesis of 17. In 20 mL of $CHCl_3$ were dissolved 15 mg of TPP and 110 mg (1 mmol) of **13**. The solution was irradiated with a projection lamp (150 W) while a stream of oxygen was vigorously bubbled through the system at 0 °C. After a total irradiation time of 1 h the solvent was evaporated and the residue analyzed spectroscopically. The endoperoxide was formed quantitatively but was unstable. **16**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.43–7.00 (AA′BB′-system, aromatic, 4 H), 5.12 (m, bridgehead, 2 H), 4.23 (m, 2 H), 2.27–1.57 (m, cyclopropane, 5 H), 0.0 (t, cyclopropane, 1 H). The endoperoxide **16** was unstable at room temperture and rearranged over 4 d to the corresponding bis-epoxide **17**. Heating in $CHCl_3$ at 50 °C for 1 h was enough to convert **16** completely to **17**. The bis-epoxide **17** was recrystallized from $CHCl_3$/ether. Colorless solid: mp 223–224 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.2–7.3 (AA′BB′-system, aromatic, 4 H), 3.11 (br s, epoxide, 2 H), 3.05 (t, cyclopropane, 1 H), 2.02 (m, cyclopropane, 2 H), 1.90 (m, cyclopropane, 2 H), 0.51 (t, cyclopropane, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 172.60, 171.14, 140.33, 127.72, 125.02, 59.03, 53.48, 52.12, 51.87, 43.07, 27.81, 23.23, 21.44. Anal. Calcd for $C_{22}H_{20}O_6$: C, 69.46; H, 5.30. Found: C, 69.12; H, 5.21.

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Registry No. **6**, 136823-99-9; **7**, 136824-00-5; **9**, 136838-33-0; **10**, 136838-34-1; **11**, 136838-35-2; **12**, 136838-36-3; **13**, 136838-37-4; **15**, 136824-01-6; **16**, 136824-02-7; **17**, 136824-03-8; maleic anhydride, 108-31-6; *p*-benzoquinone, 106-51-4; dimethyl acetylenedicarboxylate, 762-42-5; benzenediazonium-2-carboxylate hydrochloride, 4661-46-5; propylene oxide, 75-56-9.

Supplementary Material Available: IR peaks, complete mass spectra peaks, methyl group resonances, and X-ray data for **9** and **15** (11 pages). Ordering information is given on any current masthead page.

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[20] Watson, W. H.; Kashyap, R. P.; Plummer, B. F. *Acta Crystallogr.* **1991**, *C47*, 584. Crystal data. Compound **9**: triclinic, $P\bar{1}$, a = 7.722 (2) Å, b = 10.395 (3) Å, c = 12.301 (3) Å, α = 111.64 (2)°, β = 97.03 (2)°, γ = 100.38 (2)°, R = 0.057, wR = 0.0471 for 3037 reflections. Compound **15**: $P2_1/c$, a = 8.490 (2) Å, b = 16.567 (4) Å, c = 7.739 (1) Å, β = 96.93 (2)°, R = 0.0576, wR = 0.0479 for 1807 reflections.