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# Synthesis and Structure of Cyclopropano-Annelated Homosesquinorbornene Derivatives Containing Pyramidalized Double Bonds: Evidence for the Sterical Effect of a Cyclopropyl Group on the Degree of C=C Double-Bond Pyramidalization

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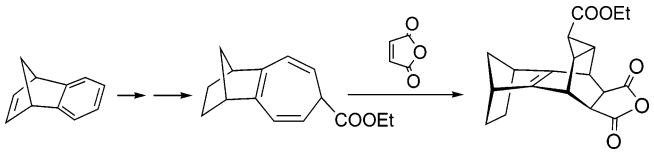


*endo*- and *exo*-2,3,4,7-tetrahydro-1*H*-1,4-methanobenzocycloheptene-7-carboxylic acid ethyl esters have been synthesized, and their Diels−Alder cycloaddition reactions with maleic anhydride, dimethyl acetylenedicarboxylate and singlet oxygen have been investigated. The X-ray analysis of four adducts indicated the pyramidalization of the central double bond. Density functional theory calculations on the isolated products and model compounds showed excellent agreement between the experimental and theoretical determined butterfly angles. Furthermore, it has been shown that a cyclopropyl group fused to [2.2.2] system decreases significantly the degree of the pyramidalization which is attributed to the steric interactions between the cyclopropyl group and ethano bridge of the norbornene systems. Due to the instability of the bicyclic endoperoxides, their X-ray analysis could not be carried out. DFT calculations on model compounds showed increased bending in the case of the product obtained by the addition of singlet oxygen to *endo*-2,3,4,7-tetrahydro-*1H*-1,4-methanobenzocycloheptene-7-carboxylic acid ethyl ester.

## Introduction

The pyramidalized alkenes contain carbon−carbon double bonds in which one or both of the $sp^2$ carbon atoms do not lie in the plane of the attached atoms.[1] For example, the double bonds in norbornene (**1**) and norbornadiene (**2**) are pyramidalized in the *endo*-direction about 7° and 2.4°, respectively.[2] The observed *exo*-selectivity[3] in norbornene and related compounds is certainly not surprising, since both electronic and steric factors would be expected to favor attack on the convex face of the pyramidalized double bond. *syn*-Sesquinorbornene (**3**), which consists of two norbornene units sharing a single bond, is known to have a strong pyramidalized double bond ranging from 16 to 18°.[4] The double bonds in bicyclo[2.2.2]octadienes are similarly pyramidal, in contrast to the double bond in norbornenes

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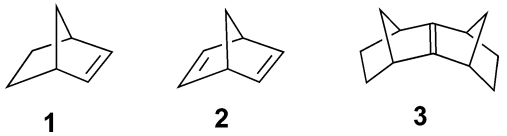
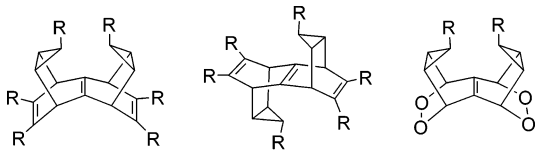
in the *exo* direction and the pyramidalization degree is somewhat less.[5]



**1** **2** **3**

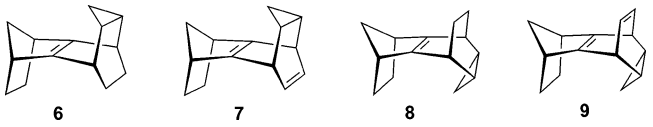
Various explanations for the double-bond pyramidalization have been put forward in the literature, based on either torsional or hyperconjugative effects.[1b,6] The usefulness of ab initio methods with the inclusion of electron correlation methods to determine the pyramidalization degree has been demonstrated.[7] Holthausen and Koch[2c] demonstrated from their calculations on various norbornene derivatives that hyperconjugation as well as torsional effects play important roles in determining the extent of the nonplanarity of the double bonds. As an alternative, density functional theory (DFT) has been used in studying the geometries of pyramidalized alkenes.[7−9]



*syn*-**4** *anti*-**4** *syn*-**5**

R= $CO_2CH_3$

In recent years, we reported the detailed investigations on synthesis, structure analysis and chemical properties of pyramidalized alkenes.[10] We synthesized a series of compounds with *syn*-**4** and *anti*-**4** geometries and determined the pyramidalization angles which ranged from 16.4 to 19.9° for the *syn*-isomers, while the *anti* isomers have a planar structure.



**6** **7** **8** **9**

Herein, we report the selective synthesis of the newly conceptualized compounds having the skeletons **6**−**9** with *syn*- and *anti*-configurations. Furthermore, we discuss their X-ray structures as well as theoretical investigations on these molecules.

## Results and Discussion

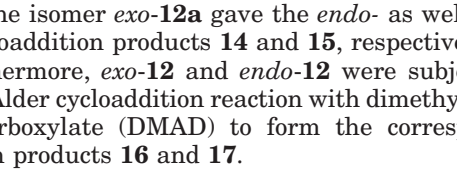
Compounds such as **6**−**9** have fused norbornene and norcarane moieties. It was visualized that a norcarane pattern fused to norbornene moiety could be generated through Diels−Alder cycloaddition reactions to the corresponding cycloheptatriene derivatives.[11]

Benzonorbornadiene (**10**) served as the starting point for the synthesis.[12] The cycloaddition of carbenes to aromatic compounds is an important method for the construction of seven-membered rings.[13] To avoid the addition of the carbene to C=C double bond in benzonorbornadiene unit, the double bond was first hydrogenated to give **11** almost in quantitative yield.[12] The $Rh_2(CF_3COO)_4$-catalyzed addition of ethyl diazoacetate to benzonorbornene (**11**) afforded the isomeric cycloheptatriene (CHT) derivatives *endo*-**12** and *exo*-**12** in a ratio of 31:69 (in a total yield of 18% based on carbene) (Scheme 1). The exact configuration of ester groups attached to cycloheptatriene unit was determined after cycloaddition reactions.

A mixture of CHT derivatives *endo*-**12** and *exo*-**12** was reacted with maleic anhydride to give three isolable products **13**−**15**. Careful examination of the $^1H$ and $^{13}C$ NMR spectra of the products, isolated after fractional crystallization showed exclusive formation of norcaradiene-type adducts **13**−**15** (Scheme 2).

Cycloheptatriene derivatives (*endo*-**12** and *exo*-**12**) are in equilibrium with their valence isomers *endo*-**12a** and *exo*-**12a**. Maleic anhydride can approach the diene unit in cycloheptatriene from the less-crowded side. The *exo*-cycloadduct **13** was formed as a single isomer by the addition of maleic anhydride to *endo*-**12a**. On the other hand, the isomer *exo*-**12a** gave the *endo*- as well as the *exo*-cycloaddition products **14** and **15**, respectively.

Furthermore, *exo*-**12** and *endo*-**12** were subjected to Diels−Alder cycloaddition reaction with dimethyl acetylenedicarboxylate (DMAD) to form the corresponding addition products **16** and **17**.



**16** **17**

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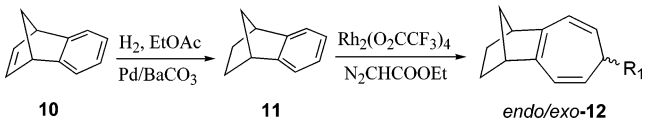
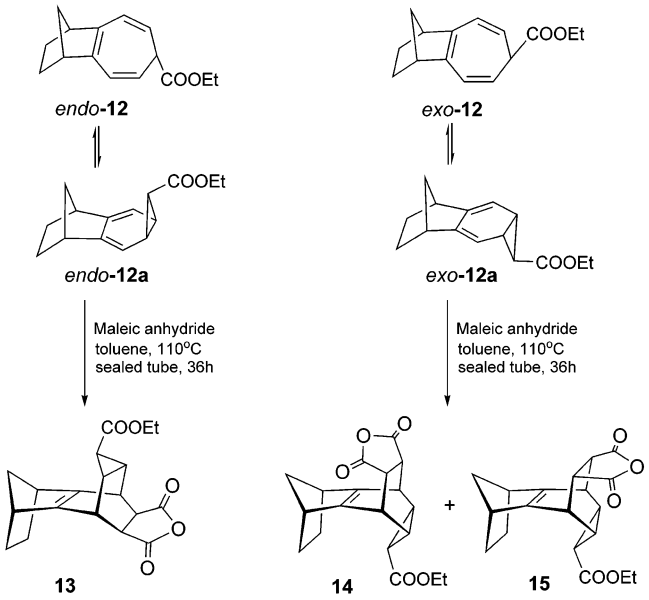
**SCHEME 1**



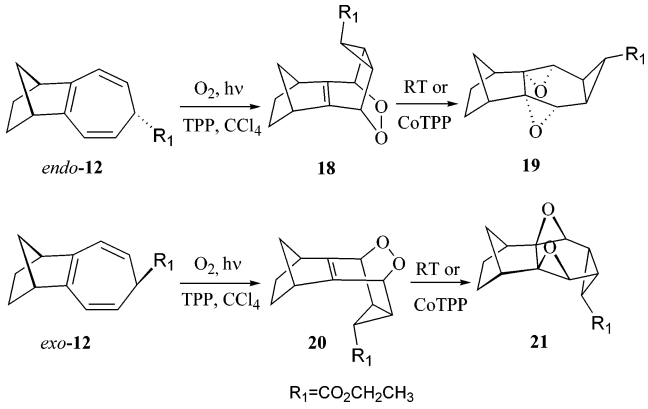

**SCHEME 2**




To determine the exact configurations of the adducts **13**−**15** and **17** and the starting cycloheptatriene derivatives **12** and the degree of the bending at the central C=C double bond, X-ray structure analyses of **13**−**15** and **17** were carried out.

The compounds resulting from these cycloaddition reactios are stable. To test the stability and reactivity of compounds having pyramidalized double bonds where the C−C linkages are replaced by −O−O− functional group, we studied the cycloaddition of *exo*- and *endo*-**12** with singlet oxygen. The photooxygenation of *endo*-**12** was carried out in $CCl_4$ in the presence of tetraphenylporphyrin (TPP) as sensitizer. The norcaradiene endoperoxide **18** was isolated in 32% yield after recrystallization from ether/hexane at low temperatures. All efforts to obtain suitable crystals of **18** for an X-ray analysis failed. Norcaradiene endoperoxides are quite stable at room temperature.[15] However, the endoperoxide **18** rearranged quantitatively to the corresponding bisepoxide **19** upon standing at room temperature (Scheme 3). This rearrangement of **18** was also effected at lower temperatures by cobalt(II)tetraphenylporphyrin (CoTPP).[16] The endoperoxide **20** formed from the reaction of *exo*-**12** with singlet oxygen could not be isolated. The bicyclic endoperoxide **20** rearranged to the corresponding bisepoxide **21** during crystallization at low temperatures. The facile

**SCHEME 3**




conversion of the endoperoxides **18** and **20** into the corresponding bisepoxides **19** and **21** can be rationalized in terms of pyramidalized double bonds and other steric effects. This increases the strain in the endoperoxide moiety and as a consequence results in the increased reactivity.

**X-ray Diffraction Structures.** The molecular structures of **13**−**15** and **17** were established by X-ray diffraction analysis (Figure 1). The frames were integrated with the SAINT software package using a narrow-frame algorithm,[17] and the structures were solved and refined using the SHELXTL program package.[18] The data were checked using PLATON.[19] The X-ray data collection and processing are given in supporting material containing bond distances and angles. Some of the selected bond lengths and dihedral angles are given in Table 1.

## Computational Methods

To obtain more detailed information on the degree of the double-bond pyramidalization, we performed a series of DFT calculations for the unsubstituted compounds **6**−**9**, **22**, and **23**. The GAUSSIAN 98W[20] program suite was used for density functional theory calculations, employing Becke's three-hybrid method[21] and the exchange functional of Lee, Yang, Parr[22] (B3LYP). The geometry optimizations of molecules **6**−**9**, **22**, and **23** were achieved at the B3LYP/6-31G(d) level, which is very successful in modeling fused polycyclic systems and in predicting the degree of pyramidalization of fused double bond (Table 2).[7] Vibrational frequencies were computed for all structures to verify the identity of each stationary point as a minimum (no imaginary frequencies).

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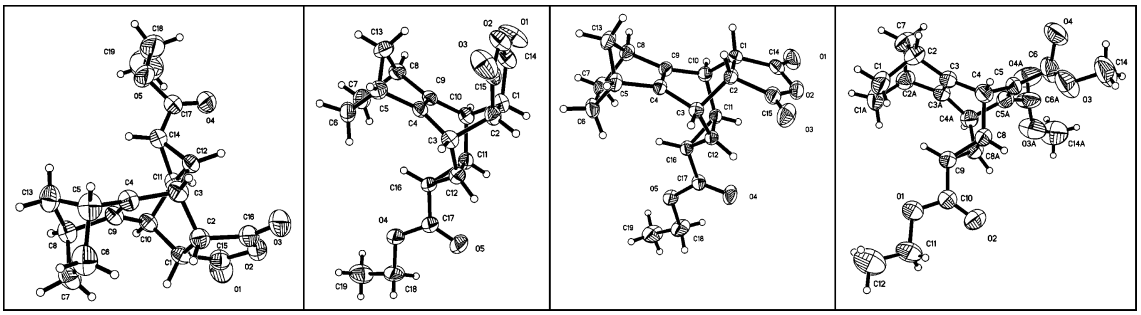
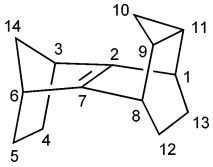


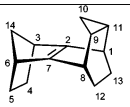
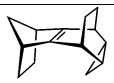
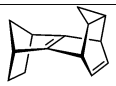
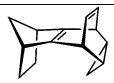
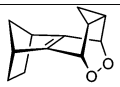
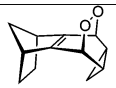
**FIGURE 1.** Thermal ellipsoid drawings of compounds **13**−**15** and **17**.

**TABLE 1. Selected Physical Data of Compounds 13−15 and 17**



| | bond lengths (Å) | bond angles (deg) | | | | | butterfly angles (deg) | | |
|---|---|---|---|---|---|---|---|---|---|
| | $C_2$=$C_7$ | $C_6C_7C_2$ | $C_7C_2C_3$ | $C_8C_7C_2$ | $C_1C_2C_7$ | $C_6C_7C_8$ | $C_3C_2C_7C_8$ | $C_1C_2C_7C_6$ | avg |
| **13** | 1.327 | 107.4 | 108.4 | 115.2 | 115.0 | 135.6 | 167.3 | −165.1 | 13.6 |
| **14** | 1.330 | 107.9 | 108.2 | 115.4 | 115.2 | 136.7 | 177.0 | −175.9 | 3.5 |
| **15** | 1.309 | 108.2 | 107.8 | 115.4 | 115.4 | 136.0 | 174.9 | −174.2 | 5.4 |
| **17** | 1.328 | 108.0 | 108.0 | 114.6 | 114.6 | 137.0 | 174.8 | −174.8 | 5.2 |

**TABLE 2. Selected B3LYP/6-31G(d) Geometrical Properties of Molecules 6, 7, 8, 9, 22 and 23**

| |  **6** |  **8** |  **7** |  **9** |  **22** |  **23** |
|---|---|---|---|---|---|---|
| **Bond / Å** | | | | | | |
| $C_1C_2$ | 1.50189 | 1.50290 | 1.50987 | 1.51279 | 1.49500 | 1.49680 |
| $C_2C_3$ | 1.51878 | 1.52086 | 1.51665 | 1.52055 | 1.51541 | 1.51861 |
| $C_2C_7$ | 1.34513 | 1.34432 | 1.34233 | 1.34139 | 1.34802 | 1.34179 |
| **Angle / °** | | | | | | |
| $C_1C_2C_3$ | 135.893 | 136.868 | 135.716 | 137.452 | 134.593 | 138.914 |
| $C_1C_2C_7$ | 115.188 | 115.215 | 114.500 | 114.505 | 112.880 | 113.079 |
| $C_3C_2C_7$ | 107.807 | 107.802 | 107.910 | 107.891 | 107.840 | 107.990 |
| **Dihedral Angle / °** | | | | | | |
| $C_1C_2C_7C_6$ | -169.893 | -176.777 | -166.926 | 176.302 | -159.444 | 178.786 |
| $C_3C_2C_7C_8$ | 169.893 | 176.777 | 166.926 | -176.302 | 159.444 | -178.786 |
| $C_8C_{12}C_{13}H_{13}$ | - | - | 176.744 | 178.111 | - | - |
| $\psi$ | 10.107 | 3.223 | 13.074 | 3.698 | 20.556 | 1.214 |
| $\psi 2$ | - | - | 3.256 | 1.889 | - | - |

[a] $\psi$ = butterfly bending angle ($C_2$=$C_7$ double bond) and $\psi 2$ = butterfly bending angle ($C_{12}$=$C_{13}$ double bond).

One of the parameters which is used to describe the out-of-plane deformation is the pyramidalization angle defined by Borden ($\cos\phi$ =-cos(RCC)/(cos0.5(RCR)).[1a] Recently, Margetic et al.[7b] reported pyramidalization in terms of the butterfly bending angle ($\psi$) which is defined as $\psi = 180° - D_1$. $D_1$ is the dihedral angle $C_1-C_2-C_3-C_4$ ($C_5-C_3-C_2-C_6$) as shown in Figure 2. In this paper, we will report all pyramidalization angles in terms of butterfly angle $\psi$.

The selected structural parameters and energies of **6**−**9**, **22**, and **23** are summarized in Table 2. Recently, Margetic et al.[7b] calculated a bending angle of 10.5° for the compound **24** (Chart 1). Annelation of a cyclopropane ring in the ethano bridge of [2.2.2] system in **24** (forming **6**) does not have any remarkable effect on the degree of the pyramidalization. The bending angle is slightly changed from 10.5° to 10.1°. On the other hand, insertion of a double bond in **6** into the [2.2.2] part to give **7**

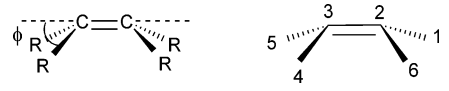
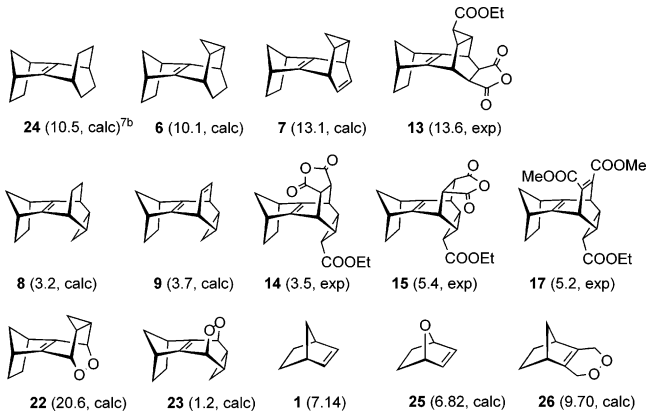


**FIGURE 2.** Definition of pyramidalization parameters.

**CHART 1. Calculated and Experimentally Determined Butterfly Bending Angles of Some Selected Compounds**




increases the butterfly angle from 10.1° to 13.1°. This increase in the pyramidalization is consistent with the increase in strain going from the saturated system **24** to the corresponding unsaturated system. Similar trends have been reported by Margetic et al.[7b] The compound **13** which has the same skeleton as **6** shows a bending angle of 13.6° determined experimentally by X-ray single-crystal analysis. This value is in good agreement with those calculated for **7**. We assume that the anhydride ring fused to homonorbornane skeleton in **13** increases the strain in the molecule which ends up with the further pyramidalization of the central double bond.

Of particular interest is the situation in the *exo*-isomers **8**, **9**, **14**, **15**, and **17**. Annelation of a cyclopropane ring in the ethano bridge in **24** in the *endo*-position (by going from **24** to **8**) has a dramatic influence on the degree of the pyramidalization. The corresponding butterfly angles are changed from 10.5° to 3.2°. The comparison of **24** with **6** has shown that the cyclopropanation does not have an important effect on the degree of pyramidalization although the cyclopropane ring causes an additional strain in the [2.2.2] system in **6**. The significantly decrease of the pyramidalization of the central C=C bond in **8** can be attributed only to the steric repulsion between the cyclopropyl group and the ethano-bridge of [2.2.1] system. Introduction of an additional double bond in the molecule **8** to give **9** slightly increases the double-bond bending from 3.2° to 3.7° as expected. Our experimental finding for **14**, **15**, and **17** show bending angles of 3.5, 5.4, and 5.2°, respectively. These angles are in good agreement with those calculated for **8** and **9**.

Unfortunately, the bicyclic endoperoxide **20** was not stable. All efforts to obtain suitable crystals of **18** for an X-ray analysis failed. We therefore carried out DFT calculations on model compounds **22** and **23** in order to investigate the butterfly angles. Since the agreement between theory and experiments for the corresponding carbon compounds is good, we were confident that the calculated geometries for **22** and **23** are reliable. Most notable is the increased pyramidality (20.1°) of the central double bond in **22**. Recently, we have studied the effects of an oxygen atom on the degree of pyramidalization. The degree of the out-of-plane bending in **25** (6.82°) did not differ significantly from that of **1** (7.14). However, the fusion of the peroxide bridge as in **26** increased the degree of the pyramidalization from 7.14° up to 9.70° (Chart 1).[8c] Increased pyramidalization caused by the peroxide linkage was also observed in the case of *syn*-**5**.[8b] Orbital interactions between the peroxide system and central double bond plays a role.[8b,8c] Electron transfer from the central double bond (C=C) into the $\sigma$C−O antibonding orbitals weakens the double bond. A weaker double bond is more susceptible to bending. In the case of **23** the steric interaction between the cyclpropyl group and *syn*-ethano bridge decreases significantly the degree of pyramidalization.

## Experimental Section

**Reaction of 1,2,3,4-Tetrahydro-1,4-methano-naphthalene (11) with Ethyl Diazoacetate.** To a magnetically stirred solution of 1,2,3,4-tetrahydro-1,4-methanonaphthalene (**11**)[12] (40 g, 0.27 mol) and rhodium(II)triflouroacetate dimer $[Rh_2(O_2CCF_3)_4]$ (100 mg, 0.15 mmol) was added ethyl diazoacetate (5.5 g, 0.054 mol) dropwise during 2.5 h at room temperature. The resulting mixture was stirred for 12 h at room temperature, and then distilled under vacuum (10 Torr) to remove the unreacted benzonorbornane and ethyl diazoacetate and to minimize the isomerization of the formed products. The first fraction was the ethyl diazoacetate (1.7 g) which was collected at 40 °C. As the second fraction, benzonorbornane (**11**) (34.7 g) was distilled between 42 and 50 °C. Oily residue (5.5 g) was chromatographed on silica gel (110 g) eluting with ethyl acetate:hexane (1:99). The first fraction consisted of *exo*/*endo*-**12** (2.0 g) in a ratio of 9:1. Last fractions gave a colorless oil mixture of *exo*/*endo*-**12** (1.0 g) in a ratio of 1:4. Repeated chromatography gave analytical pure samples.

**Ethyl *endo*-tricyclo[7.2.1.0$^{2,8}$]dodeca-2(8),3,6-triene-5-carboxylate (*endo*-12):** pale yellow liquid (2.0 g, 15.8%, based on ethyl diazoacetate); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 6.30 (d, $J$ = 7.9 Hz, 2H), 4.65 (dd, $J$ = 7.9, 6.1 Hz, 2H), 4.17 (q, $J$ = 7.2 Hz, 2H), 3.00 (m, 2H), 2.29 (t, $J$ = 6.1 Hz, 1H), 1.82−1.74 (m, 2H), 1.62 (dt, $J$ = 8.4, 1.8 Hz, 1H), 1.34 (bd, $J$ = 8.4 Hz, 1H), 1.26 (t, $J$ = 7.2 Hz, 3H), 1.21−0.9 (m, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 175.5, 148.7, 123.5, 99.6, 62.6, 50.5, 47.8, 42.9, 28.7, 16.1; IR ($CH_2Cl_2$, cm$^{-1}$) 2968, 2871, 1739, 1612, 1458, 1381, 1297, 1189, 1112, 1042, 946, 758. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.19; H, 7.78.

**Ethyl *exo*-tricyclo[7.2.1.0$^{2,8}$]dodeca-2(8),3,6-triene-5-carboxylate (*exo*-12):** pale yellow liquid (1.0 g, 7.9% based on ethyl diazoacetate); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 6.35 (bd, $J$ = 8.8 Hz, 5.28 (dd, $J$ = 8.8, 5.5 Hz, 2H), 4.25 (q, $J$ = 7.1 Hz, 2H), 3.13 (m, 2H), 2.38 (t, $J$ = 5.5 Hz, 1H), 1.87−1.71 (m, 2H), 1.68−1.08 (m, 4H), 1.31 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 175.3, 149.4, 125.7, 115.8, 62.8, 48.1, 47.2, 28.6 (2C), 16.2; IR ($CH_2Cl_2$, cm$^{-1}$) 2968, 2871, 1739, 1605, 1451, 1370, 1304, 1189, 1104, 1042. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.45; H, 7.71.

**Reaction of *endo*/*exo*-12 Mixture with Maleic Anhydride.** A mixture of *endo*/*exo*-**12** (400 mg, 1.52 mmol) and freshly sublimed maleic anhydride (1.2 g, 12.24 mmol) in 10 mL of toluene was placed into a glass tube, and the tube was sealed and heated at 110−115 °C for 36 h. After cooling to room temperature the solvent was removed under vacuum. The residue was dissolved in 50 mL of $CHCl_3$ and washed with HCl solution (10%, 3 × 50 mL), $NaHCO_3$ solution (1 × 50 mL) and dried over $CaCl_2$. The formed products (500 mg) were separated after repeated fractional crystallization from $CH_2Cl_2$/ether. The first fraction was the isomer **14**.

**Ethyl 1*R*(*S*),3*R*(*S*),6*S*(*R*),8*S*(*R*),9*S*(*R*),13*R*(*S*),14*R*(*S*),16*S*(*R*)-11-oxahexacyclo[6.5.3.1$^{3,6}$.0$^{2,7}$.0$^{9,13}$.0$^{14,16}$]heptadec-2(7)-ene-10,12-dione-15-carboxylate (14):** colorless crystals (50 mg, 8.8%, mp 178−179 °C); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.05 (q, $J$ = 7.1 Hz, 2H), 3.77 (br s, 2H), 3.31 (br s, 2H), 2.83 (br s, 2H), 1.82−1.78 (m, 2H), 1.67 (br s, 2H), 1.28−1.13 (m, 2H), 1.20 (t, $J$ = 7.1 Hz, 3H), 1.10−1.06 (m, 2H), 0.50 (t, $J$ = 3.0 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 173.8, 173.6, 144.9, 62.8, 53.8, 48.4, 46.2, 36.8, 27.1, 23.3, 23.2, 16.2; IR (KBr, cm$^{-1}$) 2960, 2883, 1851, 1778, 1716, 1470, 1420, 1279, 1239, 1162, 1073, 931, 842. Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.61; H, 6.34.

Further crystallization of the residual mixture from $CH_2Cl_2$/ether yielded a mixture (80.0 mg) of **15:14** in a ratio of 6:4 in refrigerator. This mixture (40.0 mg) was recrystallized from ether at room temperature. The obtained crystals were identified as **15**.

**Ethyl 1*R*(*S*),3*R*(*S*),6*S*(*R*),8*S*(*R*),9*R*(*S*),13*S*(*R*),14*R*(*S*),1*S*(*R*)-11-oxahexacyclo[6.5.3.1$^{3,6}$.0$^{2,7}$.0$^{9,13}$.0$^{14,16}$]heptadec-2(7)-ene-10,12-dione-15-carboxylate (15):** colorless crystals (20 mg, 3.5%, colorless crystals, mp 188−189 °C); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.05 (q, $J$ = 7.1 Hz, 2H), 3.71 (br. s, 2H), 3.10

(m, 2H), 2.93 (m, 2H), 1.86−1.82 (m, 2H), 1.70 (m, 2H), 1.34−1.10 (m, 4H), 1.20 (t, $J$ = 7.1 Hz, 3H), 0.40 (t, $J$ = 3.0 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 173.6, 173.2, 146.2, 62.7, 54.7, 49.9, 46.1, 35.9, 27.2, 20.4, 18.3, 16.1; IR (KBr, cm$^{-1}$) 2968, 2871, 1863, 1786, 1720, 1451, 1420, 1304, 1235, 1162, 1073, 927, 768. Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.47; H, 6.15.

The residue was crystallized from $CH_2Cl_2$/ether at 0 °C to give a mixture of **13** and **14** (200 mg) in a ratio of 7.5:2.5. This mixture (200 mg) was recrystallized from $CH_2Cl_2$/ether at room temperature. The obtained crystals were identified as **13**.

**Ethyl 1*S*(*R*),3*R*(*S*),6*S*(*R*),8*R*(*S*),9*R*(*S*),13*S*(*R*),14*R*(*S*),16*S*(*R*)-11-Oxahexacyclo[6.5.3.1$^{3,6}$.0$^{2,7}$.0$^{9,13}$.0$^{14,16}$]heptadec-2(7)-ene-10,12-dione-15-carboxylate (13):** white crystals (50 mg, 8.8%, white crystals, mp 179−180 °C); $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 4.08 (q, $J$ = 7.2 Hz, 2H), 3.69 (br. s, 2H), 2.93 (br. s, 2H), 2.84 (m, 2H), 1.79−1.71 (m, 4H), 1.49 (bd, $J$ = 7.8 Hz, 1H), 1.29 (d, $J$ = 3.0 Hz, 1H), 1.22 (t, $J$ = 7.2 Hz, 3H), 1.18 (m, 1H), 0.88−0.81 (m, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 173.7, 172.7, 144.6, 62.7, 51.0, 50.2, 46.1, 35.6, 27.5, 20.2, 18.9, 16.1; IR (KBr, cm$^{-1}$) 2971, 2883, 1855, 1778, 1716, 1420, 1304, 1235, 1177, 1066, 919, 815, 758. Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.50; H, 6.11.

**Ethyl 10,13-dimethyl-1*S*(*R*),3*S*(*R*),6*R*(*S*),8*R*(*S*),9*S*(*R*),11*R*(*S*)-pentacyclo[6.3.2.1$^{3,6}$.0$^{2,7}$.0$^{9,11}$]tetradeca-2(7),12-diene-10,12,13-tricarboxylate (16).** A solution of 100 mg (0.44 mmol) of *endo*-**12** and 85 mg (0.60 mmol) of dimethyl acetylenedicarboxylate in 5 mL of toluene was placed into a glass tube, and the tube was sealed and heated at 110 ± 5 °C for 12 h. The mixture was cooled to room temperature, and the solvent mixture was removed under vacuum. Chromatography on silica gel (30 g) eluting with ethyl acetate/hexane (95%) gave DMAD (18 mg) as the first fraction. The second fraction afforded the cycloadduct **16** (140 mg, 87%). Crystallization from $CH_2Cl_2$/ether gave analytical pure sample of **16**: mp 94−95 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.12 (br. s, 2H), 4.05 (q, $J$ = 7.3 Hz, 2H), 3.74 (s, 6H), 2.85 (br. s, 2H), 2.09 (m, 3H), 1.52−1.45 (m, 3H), 1.21 (t, $J$ = 7.3 Hz, 3H), 1.20 (bd, $J$ = 8.4 Hz, 1H), 0.65−0.60 (m, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 172.9, 168.7, 150.4, 147.2, 62.3, 53.9, 49.6, 45.8, 43.0, 33.2, 30.8, 26.0, 16.1; IR (KBr, cm$^{-1}$) 2971, 2883, 1728, 1439, 1304, 1216, 1143, 1035. Anal. Calcd for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50. Found: C, 67.49; H, 6.69.

**Ethyl 10,13-Dimethyl 1*R*(*S*),3*S*(*R*),6*R*(*S*),8*S*(*R*),9*R*(*S*),11*S*(*R*)-pentacyclo[6.3.2.1$^{3,6}$.0$^{2,7}$.0$^{9,11}$]tetradeca-2(7),12-diene-10,12,13-tricarboxylate (17).** A solution of 110 mg (0.48 mmol) of *exo*-**12** and 90 mg (0.63 mmol) dimethyl acetylenedicarboxylate in 7 mL of toluene was placed into a glass tube. The tube was sealed and heated at 110 ± 5 °C. After 12 h, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. Chromatography on silica gel (30 g) eluting with ethyl acetate/hexane (95%) gave as the first fraction DMAD (25 mg). Second fraction afforded the cycloadduct **17** (142 mg, 80%). The analytically pure sample was obtained by crystallization from $CH_2Cl_2$/ether: white crystals; mp 143−144 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.32 (m, bridgehead, 2H), 4.03 (q, $J$ = 7.2 Hz, 2H), 3.79 (s, 6H), 2.96 (m, 2H), 1.98 (m, 2H), 1.87−1.84 (m, 2H), 1.34 (bd, $J$ = 7.3 Hz, 1H), 1.22−1.15 (m, 3H), 1.19 (t, $J$ = 7.2 Hz, 3H), 1.01 (t, $J$ = 3.0 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 172.7, 168.5, 151.2, 149.4, 62.4, 55.7, 54.0, 46.4, 43.9, 33.6, 30.6, 27.8, 16.1; IR (KBr, cm$^{-1}$) 3463, 3417, 2973, 2872, 1754, 1650, 1619, 1446, 1407, 1311, 1253, 1214, 1141, 1041. Anal. Calcd for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50. Found: C, 68.03; H, 6.52.

**Photooxygenation of *endo*-12.** Tetraphenylporphyrin (10 mg) and *endo*-**12** (150 mg, 0.65 mmol) were dissolved in 50 mL of $CCl_4$. The solution was irradiated with a projection lamp (500 W) while a slow stream of dry oxygen was passed through it continuously at 10 °C. After a total irradiation time of 30 min, the solvent was evaporated at low temperature (0−10 °C). The residue was purified by crystallization from ether/hexane giving **ethyl 1*S*(*R*),3*S*(*R*),6*R*(*S*),8*R*(*S*),9*S*(*R*),11*R*(*S*),11*S*(*R*)-12,13-dioxapentacyclo[6.3.2.1$^{3,6}$.0$^{2,7}$.0$^{9,11}$]tetradec-2(7)-ene-10-carboxylate (18):** 55 mg, (32%) as pale yellow crystals (crystals melt at room temperature); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.13 (dd, $J$ = 3.6 Hz, 2.2 Hz, 2H), 4.11 (q, $J$ = 7.1 Hz, 2H), 3.03 (m, 2H), 2.20 (m, 2H), 1.67−1.61 (m, 3H), 1.37 (bd, $J$ = 8.7 Hz, 1H), 1.24 (t, $J$ = 7.1 Hz, 3H), 1.36−1.07 (m, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 173.5, 144.0, 77.9, 62.8, 48.2, 45.9, 27.1, 24.6, 18.1, 16.2. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.80; H, 6.92.

**Conversion of Endoperoxide 18 into Bisepoxide 19.** (a) **18** (150 mg, 0.57 mmol) was dissolved in 10 mL of $CHCl_3$. Endoperoxide **18** was rearranged at room temperature to the corresponding bisepoxide **19** in quantitative yield upon stirring at room temperature for 24 h. Crystallization from $CH_2Cl_2$/ether yielded **ethyl 3,9-dioxahexacyclo[9.2.1.0$^{2,4}$.0$^{2,10}$.0$^{5,7}$.0$^{8,10}$]-tetradecane-6-carboxylate (19)** (55 mg, 37%) as a white powder (mp 149−150 °C).

(b) To solution of endoperoxide **18** in $CDCl_3$ in a NMR tube (0.1 mmol) was added CoTPP (5 mg) at 0 °C. Monitoring of the reaction by $^1$H NMR indicated that the rearrangement to the corresponding bisepoxide **19** was complete in a few minutes: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.17 (q, $J$ = 7.2 Hz, 2H), 3.36 (m, 2H), 2.10−1.91 (m, 6H), 1.72−1.59 (m, 4H), 1.58 (t, $J$ = 4.6 Hz, 1H), 1.29 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 173.1, 66.0, 63.1, 55.8, 42.4, 36.6, 25.6, 25.3, 24.4, 16.1; IR (KBr, cm$^{-1}$) 2979, 2875, 1728, 1458, 1362, 1312, 1181, 1008, 927; mass spectrum *m/z* 263 ($M^+$, 5), 262 (34), 234 (18), 218 (23), 217 (100), 189 (53), 188 (44), 187 (39), 171 (35), 143 (87), 115 (98), 91 (49), 77 (42). Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.42; H, 6.95.

**Photooxygenation of *exo*-12 and Conversion of Endoperoxide 20 into Bisepoxide 21.** Tetraphenylporphyrin (10 mg) and *exo*-**12** (180 mg, 0.78 mmol) were dissolved in 50 mL of $CCl_4$. The solution was irradiated with a projection lamp (500 W) while a slow stream of dry oxygen was passed through it continuously at 10 °C. After a total irradiation time of 30 min, the solvent was evaporated at low temperature (0−10 °C). $^1$H NMR analysis of residue indicated the formation of the expected endoperoxide **20** in quantitative yield, which was unstable at room temperature. **20** slowly rearranged to the corresponding bisepoxide **21** at 0 °C. Crystallization from $CH_2Cl_2$/ether yielded **21** (isolated yield 30%) as a white powder (mp 109−110 °C). Furthermore, the rearrangement into bisepoxide **21** was catalyzed by CoTPP (5 mg) at 0 °C as described above: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.17 (q, $J$ = 7.1 Hz, 2H), 3.39 (m, 2H), 2.17−2.06 (m, 4H), 1.79−1.71 (m, 3H), 1.50−1.33 (m, 4H), 1.29 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 173.1, 68.0, 63.1, 53.3, 43.1, 37.8, 27.4, 26.1, 25.0, 16.1; IR (KBr, cm$^{-1}$) 2999, 2972, 2883, 1726, 1483, 1456, 1368, 1290, 1182, 1105, 1059, 1020, 928. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.58; H, 6.83.

**Crystallographic data** (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary with publication numbers CCDC-241944, CCDC-241943, CCDC-241942, and CCDC-241941 for the compounds **13**, **14**, **15**, and **17**, respectively. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223336033 or e-mail: deposit@ccdc.cam.ac.uk

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**Supporting Information Available:** Cartesian coordinates and energy values for the optimized structures **6**−**9**, **22**, and **23** at the B3LYP/6-31G(d) level and the X-ray data for **13**−**15** and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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