Pyramidalized Double Bonds Containing Endoperoxide Linkages: Photooxygenation of Dimethyl *cis*-3,8-Dihydroheptalene-3,8-dicarboxylate

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Diels−Alder cycloaddition utilizing singlet oxygen as the dienophile with dimethyl *cis*-3,8-dihydroheptalene-3,8-dicarboxylate (**5**) has been investigated, and monoaddition product **7** has been isolated. The addition of a second singlet oxygen to the cycloheptatriene unit in **7** gave *syn*-bis(norcaradiene) bis(endoperoxide) **4**. ^{1}H NMR spectral studies and theoretical calculations indicate the increased pyramidalization in ***syn*-4** compared with carbon analogue. The increased pyramidalization results from hyperconjugation between the central π-bond and the four adjacent C−O bonds and by rehybridization at C3, C4, C5, and C6. Furthermore, the increased reactivity for ***syn*-4**, which is probably arising from further folding of the central double bond, is also in agreement with theoretical calculations.

Introduction

Chemists continue to be fascinated by the imposition of stress and strain upon organic molecules. The strained ring systems are unusually reactive and often unstable.[1] Theoretical work has shown that a trigonal center of a double bond pyramidalizes when located in an unsymmetrical environment.[2] When there is an unsymmetrical arrangement of allylic bonds with respect to an alkene, there is a driving force for pyramidalization[3] in order to achieve partial staggering of the alkene with respect to the allylic bonds. Furthermore, Houk has postulated that the electron density of the alkenyl π-bond influences the degree of the pyramidalization. In 1980, syn- and antisesquinorbornene were synthesized independently by Bartlett[4] and Paquette.[5] X-ray studies[6] showed that the π-bonded carbons in the syn isomer are significantly pyramidalized, with folding angles ranging from 16 to 18°.

Reaction of the pyramidalized double bonds with a variety of reagents results in addition to the exo face of the double bond.[7] The observed stereochemistry 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.

In recent years, we have been concerned with the synthesis, structure analysis, and chemical properties of pyramidalized alkenes and have reported the synthesis of ***syn*-** and ***anti*-1−3**[8] (Chart 1). It has been found that, in asymmetric environments, double bonds tend to pyramidalize slightly in order to minimize eclipsing interactions. The results of X-ray analysis showed that compounds in syn structures are pyramidalized and that the relevant pyramidalization angle varies between 16.4 and 19.9°, while anti isomers have a planar structure.

The syn and anti structures **1**−**3**, resulting from the addition of such dienophiles as benzyne or dimethyl acetylenedicarboxylate to dimethyl *cis*- and *trans*-3,8-dihydroheptalene-3,8-dicarboxylate (**5**), are stable. The strong carbon−carbon bond linkages in **1**−**3** can tolerate the strain energies inherent in these molecules. To test the stability and reactivity of a compound where the C−C linkages in **1**−**3** are replaced by −O−O− functional groups, we have undertaken the synthesis of ***syn*-4.** In this regard, we studied the cycloaddition reactions of *cis*-heptalene **5** with singlet oxygen.

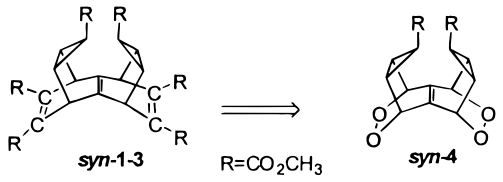

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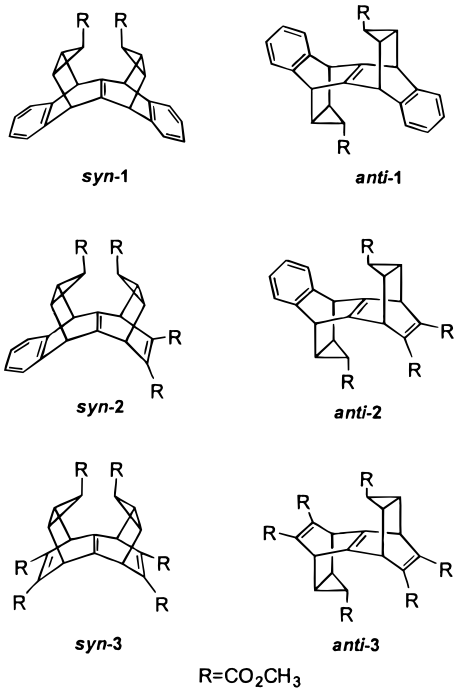
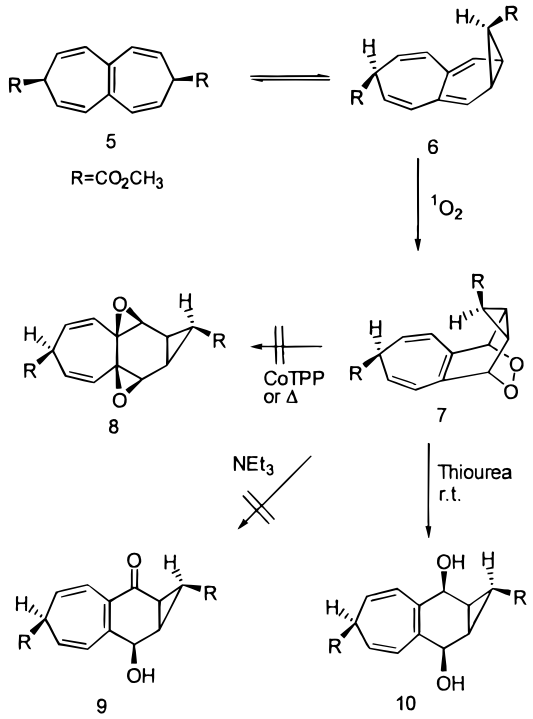
Chart 1



Scheme 1



Results and Discussion

Dimethyl *cis*-3,8-dihydroheptalene-3,8-dicarboxylate (**5**) was synthesized previously as reported by us.[8c] It has been shown that singlet oxygen adds to 7-substituted cycloheptatriene derivatives to form bicyclic endoperoxides, whose structures (cycloheptatriene or norcaradiene) vary with the nature of the substituents.[9] The equilibrium for the symmetry-allowed valence isomerization of cycloheptatriene and norcaradiene has been demonstrated.[10] Electron-accepting substituents, such as −CHO, −COOR, and −CN at C-7, tend to shift the equilibrium to the norcaradiene side, while electron-donating substituents favor the cycloheptatriene structure.

The photooxygenation of **5** was carried out in CCl_4 in the presence of tetraphenylporphyrine (TPP) as sensitizer. To isolate the monoaddition product, the reaction was stopped after 2 h. The norcaradiene endoperoxide **7** was isolated in 27% yield after crystallization from $CHCl_3$/ether following flash chromatography over florisil (Scheme 1). The 200 MHz ^{1}H and 50 MHz ^{13}C NMR spectra of endoperoxide **7** completely support the proposed structure, with 11 signals in the ^{13}C NMR spectrum being in perfect agreement with the symmetry of the molecule.

Next, we turned our attention to the chemical reactions of **7** and studied CoTPP-catalyzed rearrangement of this endoperoxide **7**. We have previously applied this reaction to unsaturated bicyclic endoperoxides with strained and perturbed diene moieties and found that the CoTPP-catalyzed reaction suppresses certain side reactions such as the formation of epoxy ketones.[11] To our surprise, thermolysis and CoTPP-catalyzed reaction of endoperoxide **7** resulted in the formation of polymeric materials instead of the expected diepoxide **8**. Furthermore, base-catalyzed rearrangement[12] with NEt_3 also gave polymeric materials and did not produce the desired hydroxy ketone **9**.

However, one isolable product derived from **7** was formed upon reduction of the peroxide linkage by thiourea. It is well established[12] that thiourea reduces only the oxygen−oxygen bond where other functionalities in the molecule remain unchanged. The reaction of **7** with thiourea in methanol gave diol **10** (Scheme 1). The ^{1}H and ^{13}C NMR spectra of **10** confirmed the expected symmetrical structure. IR analysis also indicated the presence of hydroxyl groups. We then investigated the oxidation of diol **10** with MnO_2. Diketone **12** was the expected product in this reaction, which can be formed by oxidation of allylic diol **10**. However, the elemental analysis of the isolated product confirmed a molecular formula of $C_{15}H_{12}O_6$, which corresponds to the ring-contracted product **11**. The ^{1}H and ^{13}C NMR spectra both support the proposed structure.

For this unusual conversion of **10** to **11**, we propose the mechanism depicted in Scheme 2. First, an allylic oxidation takes place to form **12**. Then an intramolecular hydrogen shift in the cycloheptatriene unit of **12** followed by oxidation of the double allylic methylene protons in the seven-membered ring will furnish the tropone derivative **14**. In the final step, the decarbonylation of tropone will afford homonaphthoquinone derivative **11** (Scheme 2). It is well-known from the literature[13] that cycloheptatriene can easily form benzene derivatives by losing the methylene group upon undergoing oxidation reactions.

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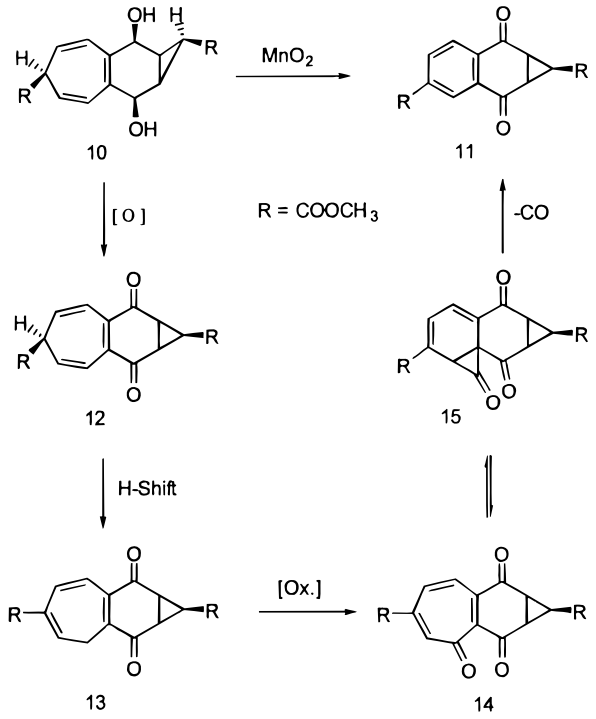
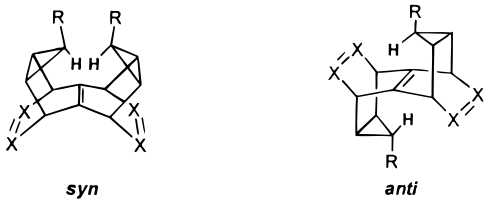
Scheme 2



Construction of the ***syn*-4** framework was achieved upon successful addition of 2 mol of singlet oxygen to **5** during prolonged photooxygenation under the previously given reaction conditions. Bis(endoperoxide) ***syn*-4** was isolated in 20% yield (after crystallization). The ^{1}H and ^{13}C NMR spectra of ***syn*-4** confirmed a symmetrical molecule (Figure 1). All efforts to obtain suitable crystals of ***syn*-4** for an X-ray analysis were failed.

The ^{1}H NMR spectrum of ***syn*-4** consists of four groups of signals, which are assigned to bridgehead (endoperoxide), methoxyl, cyclopropane, and cyclopropyl (adjacent to the ester group). The ^{13}C NMR spectrum of ***syn*-4** exhibits 6 lines in accordance with the proposed structure. The ^{1}H NMR spectrum of ***syn*-4** is very similar to that of ***syn*-3**. The position of the cyclopropyl proton where the carbomethoxyl group is attached is very informative in view of the steric effects.



Comparison of the ^{1}H NMR spectra of ***syn*-1** with ***anti*-1** indicates that the cyclopropane proton resonance in ***syn*-1** is shifted remarkably downfield (2.68 ppm) (Figure 1). In contrast, the cyclopropyl proton in ***anti*-1** resonates at 0.3 ppm. The high-field resonance of this proton (0.3 ppm) can be accounted by the location of the cyclopropyl proton in the shielding cone of the central double bond.[14] However, we attribute the extraordinary shift of cyclopropyl proton (which is also located over the double bond) in ***syn*-1** to steric compression between these internal cyclopropyl protons. It is well-known that interactions related to the van der Waals effect cause a paramagnetic contribution to the shielding constants which results in a shift to lower field.[15] In the compounds ***syn*-1−3**, the cyclopropyl protons resonate in the region of 2.5−2.68 ppm (Table 1). On the other hand, the measured pyramidalization angle in ***syn*-1−3** was found to vary between 16.4 and 19.9°. Therefore, we see a correlation between the chemical shift and the degree of the pyramidalization angle in these compounds. However, the internal cyclopropyl protons in ***syn*-4** resonate at 1.44 ppm. This is a remarkable upfield shift compared to those of ***syn*-1−3**. This upfield shift can be ascribed to partial relief of the proton−proton repulsion in ***syn*-4**. Inductive effect of the oxygen atoms in the peroxide linkages cannot be responsible for this shift, since oxygen atoms can cause a change in the chemical shift to lower field and not to higher field. We assume, then, on the basis of the chemical shift of the internal cyclopropyl protons in ***syn*-4** that the central double bond in ***syn*-4** should be more pyramidalized than in ***syn*-1−3.**

Increased reactivity of the bis(endoperoxide) ***syn*-4** could be observed by its facile rearrangement to the corresponding bis(epoxide) **16** in nearly quantitative yield upon standing at room temperature (Scheme 3). Norcaradiene endoperoxides are usually quite stable at room temperature. One of the common reactions of unsaturated [*n*.2.2] bicyclic endoperoxides is cleavage of the weak oxygen−oxygen bond followed by addition of the oxygen radicals to the adjacent double bond to give the corresponding bis(epoxides) with the syn-configuration. This increased reactivity also supports the higher degree of pyramidalization.

To compare the effect of the two different bridging systems (oxygen−oxygen and carbon−carbon), we have synthesized the compound **18**.

We recently reported[8c] the synthesis of **17** by addition of *p*-benzoquinone to *cis*-heptalene derivative **5**. The reaction of **17** with singlet oxygen gave *syn*-endoperoxide **18** as the sole product. The structural assignment was made from the NMR data. Cyclopropyl protons (C*H*CO-OR) are resonating at 1.31−1.78 ppm, respectively. These values are between those of **4** and ***syn*-1−3**. On the basis of these values, we propose that the folding of the central double bond in **17** is higher than in ***syn*-1−3** but less than found in ***syn*-4.** This compound also rearranged at room temperature (Scheme 4). The disappearance of the olefinic resonances in the ^{13}C spectrum indicated the formation of the expected bis(epoxide) **18** in quantitative yield.

Theoretical Calculations

Models for ***syn*-3** and ***syn*-4** (Figure 2) were obtained by replacing the ester groups with hydrogens (R = H). Geometries of ***syn*-3** and ***syn*-4** were optimized in C_{2v} symmetry by employing Becke's three parameter hybrid functional[16] and the 6-31G*[17] basis set. The calculations were carried out with Gaussian 94.[18] Electronic struc-

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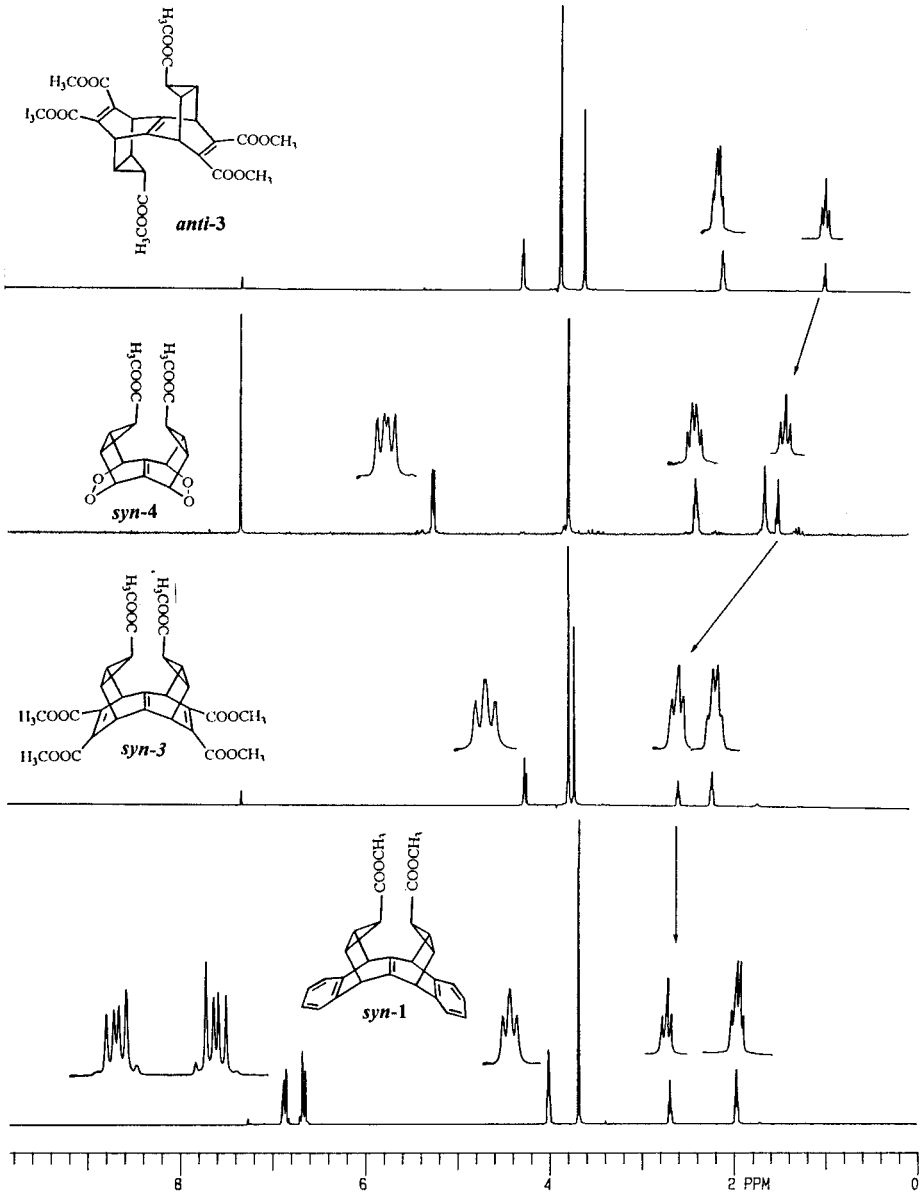

Figure 1. 200 MHz ^{1}H NMR spectra of the compounds ***syn*-1**, ***syn*-3**, ***anti*-3**, and ***syn*-4**.

Table 1. Cyclopropyl (C*H*COOR) Resonances of the Compounds 1−4 and 18 in ppm

compd	syn-isomer	anti-isomer
1	2.68	0.28
2	2.60	0.08−1.06
3	2.53	0.94
4	1.44	
18	1.78−1.31	

tures were analyzed with the natural bond orbital (NBO) method[19−21] which is available in Gaussian 94.

In Figure 2 experimental[8] and theoretical bond lengths are compared for ***syn*-3**. Bond angles are compiled in Table 2. Theoretical bond lengths are between 0.005 and 0.017 Å larger than experimental ones. Only the C7═C9 bond is calculated to be shorter compared to the experimental bond distance. This is most likely due to the absence of the ester groups, whose π-systems can interact with the C7═C9 bond. Bond angles are reproduced by theory with deviations of less than 1°. The bending angle at the central pyramidalized double bond is 3° smaller in theory than in the X-ray structure. Considering that all ester groups were removed for the calculations, the agreement between theory and experiment is very good.

Peroxide ***syn*-4** could not be crystallized. Only the theoretical geometry (Figure 1 and Table 2) and the NMR spectrum are available for structural analysis. Since the agreement between theory and experiment for the carbon compound is good, we are confident that the calculated geometry of ***syn*-4** is reliable. Most notable are the increased pyramidality (19.9° vs 16.9°), the increased length of the C1═C2 bond (1.345 Å vs 1.339 Å), and the

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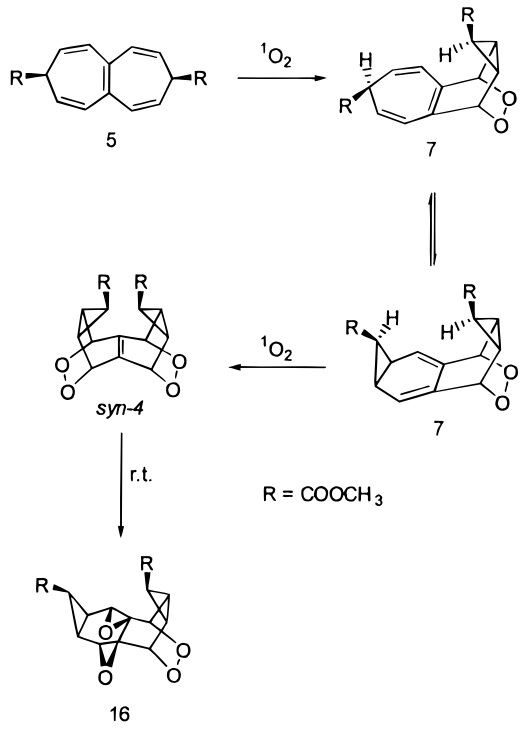
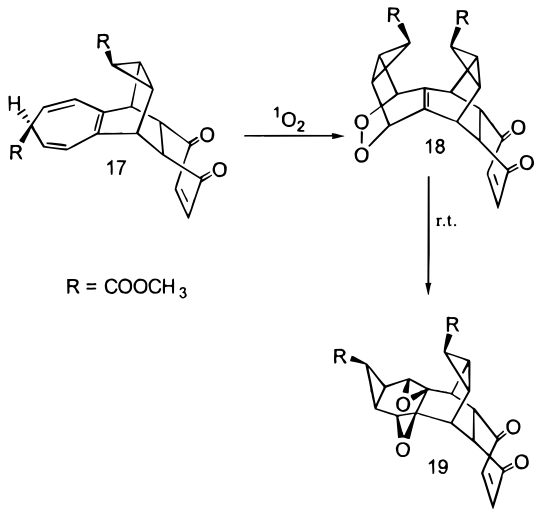
Scheme 3



Scheme 4



larger distance between the nonbonded cyclopropane hydrogens (2.062 Å vs 1.813 Å) in ***syn*-4** as compared to ***syn*-3**. Thus, theoretical calculations fully confirm conclusions based on the different chemical shifts of the cyclopropane protons in the NMR-spectra of ***syn*-3** and ***syn*-4**. Further differences between ***syn*-3** and ***syn*-4** arise for the C1−C3, C3−C11, and C11−C13 bond distances. In ***syn*-4** the former two are shortened by 0.017 and 0.039 Å; the latter is lengthened by 0.017 Å. Changes in bond angles are rather subtle with maximum differences of 3.3° between ***syn*-3** and ***syn*-4**.

In principle, three factors could be responsible for the observed geometrical differences between ***syn*-3** and ***syn*-4**. First, the longer O7−O9 bond as compared to C7═C9 allows for some relieve of steric strain and could account for the increased distance between the cyclopropane hydrogens. This, however, would reduce the strain on the double bond and decrease rather than increase bending

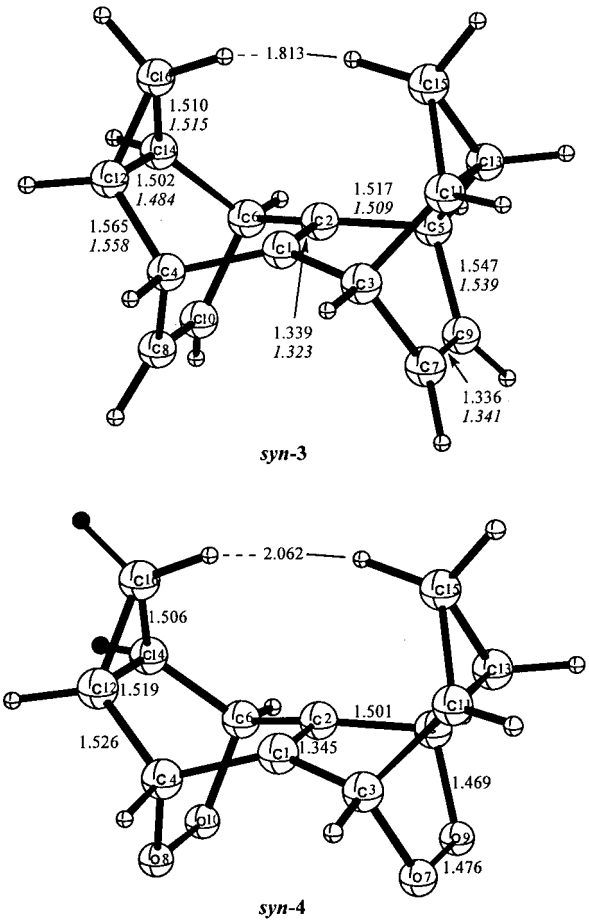


Figure 2. Calculated structures of the compounds ***syn*-3** and ***syn*-4**.

Table 2. Theoretical and Experimental Bond Angles for *syn*-3 and Theoretical Bond Angles for *syn*-4

	***syn*-3**		***syn*-4**
	expt[7]	theory	theory
1−3−7	105.7	106.0	106.2
1−3−11	110.5	110.1	113.0
2−1−3	114.7	114.1	112.7
3−7−9	112.7	113.7	110.4
3−11−15	123.5	124.2	123.4
7−3−11	101.5	102.2	105.5
11−13−15	60.8	60.2	59.7
11−15−13	58.9	59.7	60.5
3−1−2−6	19.9	16.9	19.7

of the central double bond. Thus, the increased bending of ***syn*-4** is most likely not due to steric effects.

Second, orbital interactions between the peroxide system and the central double bond might play a role. NBO analysis shows that there are very few significant orbital interactions in these systems. In the carbon compound all of the larger interactions are found within the cyclopropane ring and are due to steric strain of the small ring system. In the peroxide there are four additional orbital interactions involving $\pi_{C1=C2}$ as a donor and the four σ_{C-O} antibonds as acceptors. These orbital interactions weaken the C1═C2 bond by charge withdrawal and cause the C1═C2 bond to lengthen. Since a weaker double bond is more susceptible to bending, these orbital interactions might be responsible for the increased bending of ***syn*-4**.

The third factor is the rehybridization of carbon 3 and the symmetrically equivalent carbons 4−6 as stated by

Bent's rule.[22] According to Bent's rule, electronegative substituents prefer to be bound to hybrids with increased p-character. The underlying reason is that p-electrons are more weakly bound than s-electrons and can therefore be withdrawn more easily. Charge withdrawal of preferentially p-electrons causes the remaining bonds to be higher in s-character. This rehybridization is confirmed by NBO analysis. In ***syn*-3** C3 employs an $sp^{3.13}$ hybrid for bonding with C7, and in ***syn*-4** C3 uses an $sp^{4.66}$ hybrid for the corresponding bond with O7. The C3−C1 bond is formed with $sp^{2.78}$ and $sp^{2.53}$ hybrids, and the C3−C11 bond involves $sp^{3.18}$ and $sp^{2.58}$ hybrids in ***syn*-3** and ***syn*-4**, respectively. The higher s-character employed by C3 for these bonds is consistent with the decreased distances between C3 and C1 and between C3 and C11 and with the increase of the C1−C3−C11 angle of 2.9°.

Conclusion

In summary, theoretical and experimental results are in excellent agreement and predict the peroxide compound ***syn*-4** to be more pyramidalized than ***syn*-3**. Electronic structure analysis suggests that the increased pyramidalization in ***syn*-4** results from two factors. Hyperconjugation between the central π-bond and the four adjacent C−O bonds weakens the C1═C2 bond and causes the C1═C2 bond to lengthen. The weaker double bond is more susceptible to bending. Furthermore, the increased pyramidalization can be attributed to rehybridization at C3, C4, C5, and C6. The increased distance between cyclopropane hydrogens can be rationalized by the increased pyramidalization of the central double bond. The increased reactivity for these norcaradiene-type endoperoxides which is probably arising from further folding of the central double bond is also in agreement with the theoretical calculations.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus. IR spectra were obtained from films on NaCl plates for liquids or KBr pellets for solids on a Perkin-Elmer 377 infrared recording spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a 200 (50) MHz spectrometer and are reported in δ units with $SiMe_4$ as internal standard. All column chromatography was performed on silica gel (60 mesh, Merck) and florisil (60−100 mesh).

Photooxygenation of dimethyl *trans*-3,8-Dihydroheptalene-3,8-dicarboxylate (5). Dimethyl 13,14-Dioxatetracyclo[7.3.2.0.^{2,8}0^{10,12}]tetradeca-2(8)3,6-triene-5,11-dicarboxylate (7). Tetraphenylporphyrin (10 mg) and diester **5** (100 mg, 0.37 mmol) were dissolved in 80 mL of CCl_4. The solution was irradiated with a projection lamp (50 W) while a slow stream of dry oxygen was passed through it continuously at 10 °C. After a total irradiation time of 2 h, the solvent was evaporated at low temperature (0−10 °C). The residue was filtered through florisil (5 g) eluting with $CHCl_3$ (100 mL) to give endoperoxide **7** as colorless solid (30 mg, 27%,): mp 133−134 °C from $CHCl_3$/ether; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.30 (d, A part of AX system, J = 9.2 Hz, 2H), 5.42 (dd, X part of AX system, J = 9.2 and 5.5 Hz, 2H), 5.10 (m, 2H), 3.85 (s, 3H), 3.65 (s, 3H), 2.36−2.29 (m, 3H), 0.96 (t, J = 3.1 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.07, 171.80, 135.68, 124.61, 116.13, 77.70, 53.06, 52.61, 44.62, 22.36, 16.38; IR (KBr, cm^{-1}) 2950, 1730, 1720, 1440, 1410, 1330, 1295, 1250, 1165, 1020 and 940. Anal. Calcd for $C_{16}H_{16}O_6$: C, 63.2; H, 5.3. Found: C, 63.4.; H, 5.1.

(22) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

Dimethyl (la*R*,2*R*,8*S*,8a*S*)-2,8-dihydroxy-l,la,2,5,8,8a-hexahydrocyclopropa[4,5]benzo[*a*]cycloheptene-1,5-dicarboxylate (10). The endoperoxide **7** (35 mg, 0.11 mmol) was dissolved in 5 mL of $CHCl_3$. A solution of thiourea (20 mg, 0.26 mmol) in 5 mL of methanol was added dropwise in 2−3 min. After the solution was stirred at room temperature for 2 h, the solvent was evaporated. The residue was dissolved in 100 mL of $CHCl_3$, washed with water (3 × 25 mL), and dried over $MgS0_4$. The reduction product **10** was obtained as a colorless liquid (30 mg, 85%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.26 (d, A part of AX system, J = 8.3 Hz, 2H), 5.11 (dd, X part of AX system, J = 8.3 and 5.7 Hz, 2H), 4.56 (m, 2H), 3.75 (s, 3H), 3.65 (s, 3H), 2.35 (t, J = 5.7 Hz, 1H), 2.17 (m, 2H), 1.24 (t, J = 3.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.83, 172.89, 136.38, 128.47 (2C), 68.26, 52.96, 52.54, 40.69, 25.31, 23.11; IR (NaCl, cm^{-1}) 3400, 3020, 2950, 1720, 1720, 1435, 1285, and 975. Anal. Calcd for $C_{16}H_{18}O_6$: C, 62.7; H, 5.9. Found: C, 62.2.; H, 6.1.

Oxidation of Diol 10. *exo*-Dimethyl 2,7-Dioxo-1a,2,7,-7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene-1,4-dicarboxylate (11). Freshly prepared active MnO_2 (l g, 72 mmol) was added to a solution of **10** (100 mg, 0.32 mmol) in 20 mL of $CHCl_3$ at room temperature. The reaction mixture was stirred at room temperature for 7 days. The precipitate was filtered out and washed with $CHCl_3$. The combined organic layers were evaporated to give colorless crystals (30 mg, 32%, mp 85−86 °C) from ether: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.65 (d, J = 1.5 Hz, 1H), 8.39 (dd, A part of AX system, J = 8.0 and 1.5 Hz, 1H), 8.08 (d, X part of AX system, J = 8.0, 1H), 3.90 (s, 3H), 3.70 (s, 3H), 3.19 (d, J = 4.4, 2H), 2.65 (t, J = 4.4, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 189.82, 189.57, 168.81, 165.54, 136.22, 135.40, 135.22, 132.72, 129.09, 128.05, 53.44, 53.24, 34.35 (2C), 31.42; IR (KBr, cm^{-1}) 3050, 2940, 1725, 1680,1600, 1440, 1310, 1280, 1200, and 960. Anal. Calcd for $C_{15}H_{12}O_6$: C, 62.5; H, 4.4. Found: C, 62.1; H, 4.4.

Photooxygenation of 5 with 2 mol of $^1O_2$. *exo,exo*-Dimethyl 13,14,15,16-Tetraoxahexacyclo[7.3.2.2^{3,7}.0^{2,8}-.0^{4,6}0^{10,12}]hexadec-2(8)-ene-5,11-dicarboxylate (*syn*-4). Tetraphenylporphyrin (10 mg) and diester **5** (100 mg, 0.37 mmol) were dissolved in 75 mL of CCl_4. The solution was irradiated with a projection lamp (50 W) while a slow stream of dry oxygen was passed through it continuously at 0 °C. After a total irradiation time of 24 h, the solvent was evaporated at low temperature (0−10 °C). Crystallization of the residue from CH_2Cl_2/ether yielded bis(norcaradiene) bis(endoperoxide) ***syn*-4** as a colorless powder (15 mg, 20%), dec 117−119 °C: ^{1}H NMR (200 MHz $CDCl_3$) δ 5.18 (m, 4H), 3.71 (s, 3H), 2.33 (m, 4H), 1.44 (t, J = 3.2 Hz, 2H); ^{13}C NMR (50 MHz $CDCl_3$) δ 171.23, 135.48, 75.18, 52.88, 22.16, 16.43; IR (KBr, cm^{-1}) 3040, 3000, 2950, 1715, 1435, 1330, 1250, 1160, 940, and 925.

Rearrangement of 4 at Room Temperature. *exo,exo*-Dimethyl (1*R*,2*R*,4*S*,5*S*,7*R*, 8*R*,l0*S*,11*S*,12*S*,14*R*)-3,9,15,16-Tetraoxaheptacyclo[9.3.2.0^{2,4}.0^{2,10}.0^{5,7}0^{8,10}0^{12,14}]hexadecane-6,13-dicarboxylate (16). A solution of bis(norcaradiene) bis(endoperoxide) ***syn*-4** (25 mg, 0.07 mmol) in $CHCl_3$ (10 mL) was stirred at room temperature for 5 days. The rearrangement of the bis(endoperoxide) **syn-4** to **16** was monitored by ^{1}H NMR spectroscopy. ^{1}H NMR analysis indicated that bis-(epoxy) endoperoxide **16** was formed quantitatively. Crystallization from $CHCl_3$/ether gave **16** (isolated yield 63%), dec 170 °C: ^{1}H NMR (200 MHz $CDCl_3$) δ 4.21 (m, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.39 (br s, 2H), 2.42 (m, 2H), 2.13 (br d, A part of A_2B system, J = 4.3 Hz, 2H), 2.05 (t, B part of A_2B system, J = 4.3, 1H), 1.64 (t, J = 2.2 Hz, 1H); ^{13}C NMR (50 MHz $CDCl_3$) δ 171.31, 170.73, 57.43, 53.03, 52.94, 50.77 (2C), 21.64, 21.46, 20.28 (2C); IR (KBr, cm^{-1}) 3000, 2940, 1720, 1715, 1445, 1310, 1170, and 1020. Anal. Calcd for $C_{16}H_{18}O_8$: C, 57.1; H, 4.8. Found: 57.5; H, 4.6.

Photooxgenation of 17[8e] and Conversion of Endoperoxide 18 into Bis(epoxide) 19. Tetraphenylporphyrin (10 mg) and compound **17** (280 mg, 0.74 mmol) were dissolved in 30 mL of $CHCl_3$. The solution was irradiated with a projection lamp (50 W) while a slow stream of dry oxygen was passed through it continuously at 10 °C. After a total irradiation time of 3.5 h, the solvent was evaporated at low temperature (0−

10 °C). ^{1}H NMR analysis of the residue indicated the formation of the expected endoperoxide **18** in quantitative yield which was unstable at room temperature.

Dimethyl (1*R*,3*R*,4*R*,6*S*,7*S*,9*S*,10*S*,15*R*,16*R*,18*S*)-11,14-Dioxo-19,20-dioxahexacyclo[7.6.3.2^{3,7}0^{2,8}0^{10,15}0^{16,18}]icosa-2(8),12-diene-5,17-dicarboxylate (18). Data: ^{1}H NMR (200 MHz $CDCl_3$) δ 6.51 (s, 2H), 4.66 (m, 2H), 3.83 (m, 2H), 3.63 (s, 3H), 3.62 (s, 3H), 3.06 (m, 2H), 2.06 (m, 4H), 1.91 (m, 2H), 1.78 (br. t, 1H), 1.31 (t, J = 2.9 Hz, 1H); ^{13}C NMR (50 MHz $CDCl_3$) δ 197.30, 172.93, 171.53, I41.28, 136.58, 75.73, 52.69, 52.60, 50.27, 37.58, 22.13, 21.93,18.89. The endoperoxide **18** was unstable and rearranged at room temperature to the corresponding bis(epoxide) **19** in 8 days in quantitative yield. Crystallization from $CHCl_3$/ether yielded **19 (**isolated yield **72%)** as a colorless solid, mp 229−231 °C.

Dimethyl (1*R*,2*R*,4*S*,5*S*,7*R*,8*R*,10*S*,11*S*,12*S*,17*R*,18*R*,-20*S*)-3,9-Dioxa-13,16-dioxoheptacyclo[9.6.3.0^{2,4}.0^{2,10}.0^{5,7}.0^{8,10}.0^{12,17}.0^{18,20}]icos-14-ene-6,19-dicarboxylate (19). Data: ^{1}H NMR (200 MHz $CDCl_3$) δ 6.88 (s, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 3.25 (br s, 2H), 3.20 (m, 2H), 2.59 (m, 2H), 2.08−1.98 (m, 3H), 1.94 (m, 2H), 1.61 (t, J = 3.1 Hz, 1H); ^{13}C NMR (50 MHz $CDCl_3$) δ 197.36, 171.99, 171.45, 141.38, 58.47, 52.86, 52.82, 50.27, 46.08, 40.41, 22.43, 21.99, 21.74, 19.27; IR (KBr, cm^{-1}) 3030, 3000, 2950,1730,1665,1505,1490, 1310, 1285, 1165, 970, and 950. Anal. Calcd for $C_{22}H_{20}O_8$: C, 64.1; H, 4.9. Found: C, 63.8.; H, 4.7.

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