

**4-Methyl-3-phenethyl-2-cyclohexen-1-one (11).** To 80.3 mg (3.34 mmol) of magnesium in 7.0 mL of dry ether was added dropwise 620.6 mg (3.28 mmol) of  $\beta$ -phenethyl bromide in 2.0 mL of dry ether. The reaction was initiated with a warm water bath and then stirred at room temperature until the magnesium shavings had reacted (1.5 h). The dark solution was cooled to 9–5 °C, and 499.7 mg (3.25 mmol) of 3-ethoxy-6-methyl-2-cyclohexen-1-one<sup>13</sup> was added dropwise in 5 mL of dry ether. The solution became clear and was stirred for 10 h at room temperature whereupon 5.0 mL of 10% aqueous hydrochloric acid and 5.0 mL of ether were added to the solution, and the mixture was stirred for 1 h at room temperature, poured into water, and extracted three times with 50 mL of ether. The ether extracts were washed with 10% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, water, and brine and dried. Removal of solvent in vacuo gave 581.0 mg (83%) of crude material. Kugelrohr distillation [bp 160–190 °C (1.0 mmHg)] afforded 499.1 mg (71%) of volatile material. Preliminary TLC purification on silica (hexane–ether, 1:1 v/v) gave, after final VPC purification on column D, a product identical with **11** by comparison of IR and NMR (220 and 60 MHz) spectra,  $R_f$ , and VPC retention time.

**Decomposition of 1-Diazo-5-methyl-trans-5-decen-9-yn-2-one (5).** To a solution of 488.1 mg (2.4 mmol) of diazo ketone **5** in 300 mL of dry dichloromethane cooled to 0–5 °C under nitrogen was added in one addition 3.07 mL (3.550 g, 25 mmol) of boron trifluoride etherate. The solution immediately turned dark, and after a few seconds a vigorous evolution of nitrogen was observed. The solution was allowed to slowly warm to 10 °C over a period of 30 min and poured into saturated aqueous sodium bicarbonate. The organic phase was washed with saturated aqueous sodium bicarbonate, water, and brine and dried. Removal of solvent in vacuo gave 474.9 mg of crude material. VPC (column B) and gas chromatographic (column F)—mass spectral analyses indicated a very complex reaction mixture. Two principal fractions (**16a,b**) were, however, isolated by VPC on column B.

Fraction I [**16a**: 13% yield; mass spectrum,  $m/e$  196 ( $M^+$ ), for a fluorine compound; IR 1715 (vs)  $\text{cm}^{-1}$ ; NMR (220 MHz)  $\delta$  1.32 (s, 3 H),  $\delta$  1.85 (d,  $J = 18$  Hz, 3H)] was oxidized in the following manner. To a solution of 17.2 mg (0.129 mmol) of ruthenium dioxide, 266.4 mg (1.25 mmol) of sodium periodate in 5 mL of water, and 11 mL of acetone was added 20.2 mg of fraction I. The bright yellow solution immediately turned dark and was stirred at room temperature for 4 h. Isopropyl alcohol (4 mL) was added, and the solution was stirred for 30 min at room temperature, filtered, poured into water, and extracted with ether. The ether extracts were washed with saturated aqueous sodium bi-

carbonate, water, and brine and dried. Removal of solvent in vacuo and VPC purification on column B gave a product identical with *cis*-7a-methyl-2,3,3a,6,7,7a-hexahydro-1*H*-indene-1,5-dione (**17**)<sup>18</sup> by comparison of IR and NMR (220 MHz) spectra and VPC retention time.

Fraction II [**16b**: 22% yield; mass spectrum,  $m/e$  196 ( $M^+$ ), for a fluorine compound; NMR (220 MHz)  $\delta$  1.32 (s, 3H), 1.93 (d,  $J = 19$  Hz, 3H)] was oxidized as described above. To a solution of 16.5 mg (0.124 mmol) of ruthenium dioxide, 215.0 mg (1.0 mmol) of sodium periodate in 5 mL of water, and 11 mL of acetone was added 14.7 mg of fraction II. Again, VPC purification on column B gave a product identical with *cis*-7a-methyl-2,3,3a,6,7,7a-hexahydro-1*H*-indene-1,5-dione (**17**) by comparison of IR and NMR (220 MHz) spectra and VPC retention time.

Oxidation of 150.5 mg of the crude reaction mixture with 106.7 mg (0.78 mmol) of ruthenium dioxide and 1.5379 g (7.2 mmol) of sodium periodate in 20 mL of water and 45 mL of acetone, as described above, gave 110.3 mg of product. VPC purification on column B gave two fractions, A and B, in a ratio of 5.6:1, respectively. Fraction A was identical with *cis*-7a-methyl-2,3,3a,6,7,7a-hexahydro-1*H*-indene-1,5-dione (**17**) by comparison of IR and NMR (220 MHz) spectra and VPC retention time. Fraction B was identical with *trans*-7a-methyl-2,3,3a,6,7,7a-hexahydro-1*H*-indene-1,5-dione (**18**)<sup>18</sup> by comparison of IR and NMR (220 MHz) spectra and VPC retention time.

Decomposition of diazo ketone **5** in dichloromethane under the optimal conditions (1 mg/mL, >5.0 equiv boron trifluoride etherate, 5–10 °C) led to a 41% yield of bicyclic products. Under a variety of other conditions 4-methyl-3-(3'-pentynyl)-2-cyclohexen-1-one (**15**) was isolated as a moderate to major product: IR 2960 (m), 2930 (s), 2860 (m), 1675 (vs), 1622 (m), 1445 (m), 1250 (m), 1200 (m)  $\text{cm}^{-1}$ ; NMR (220 MHz)  $\delta$  1.21 (d,  $J = 7$  Hz, 3 H), 1.75 (s, 3 H), 1.67–1.85 (m, 1 H), 1.85–2.53 (m, 8H), 5.68 (s, 1 H).

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## Double-Bond Deformation in Two Crystalline Derivatives of *syn*-Sesquinorbornene ( $\Delta^{4a,8a}$ -Octahydro-1,4,5,8-dimethanonaphthalene)

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**Abstract:** The cycloaddition of maleic anhydride to isodicyclopentadiene (**1**) leads under a variety of conditions to similar amounts of the *anti*-sesquinorbornene *endo*-anhydride **2** and the *syn*-sesquinorbornene *exo*-anhydride **3**, the structures being established by X-ray crystallography. Whereas the double-bond system of **2** is planar, that of the *syn*-sesquinorbornene derivatives **3** and **6** has a dihedral angle of 162–164° between the planes of the two rings sharing the double bond, the bending being such as to spread the methylene bridges apart. Phenyl azide reacts with **3** but not with **2**. An X-ray study confirms the structure **7** of the adduct obtained by Paquette and co-workers from phenyl azide and *syn*-sesquinorbornene. The results of X-ray crystallographic studies of **2**, **3**, **6**, and **7** are presented.

Although *syn*-<sup>2</sup> and *anti*-sesquinorbornenes<sup>3</sup> have only recently been prepared and characterized, the ring system has been of interest ever since Alder and co-workers<sup>4</sup> in 1956 added maleic anhydride to "isodicyclopentadiene" (**1**) in ether and reported that

the single product added phenyl azide to yield an *N*-phenyl-triazoline. Of the four possibilities (**2**–**5**) the structure **2**, an *anti*-sesquinorbornene *endo*-anhydride, was assigned to the product of the Diels–Alder reaction. Reservations about this assignment<sup>5</sup> were strengthened by the observation of Sugimoto et al.<sup>6</sup> that methyl acrylate and methyl propiolate added to **1** on the *endo* side to give products with the *syn*-sesquinorbornene ring system.

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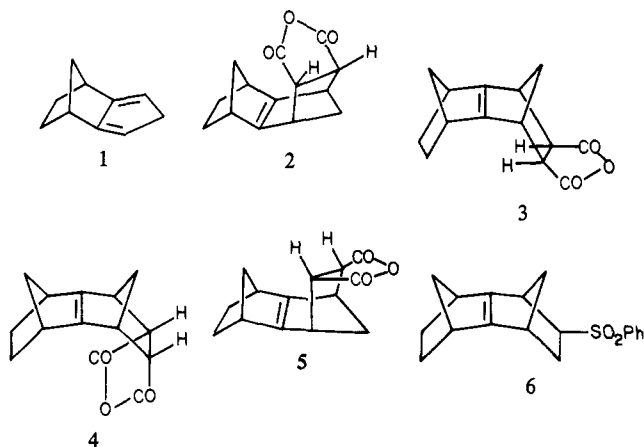
(2) (a) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (b) *Ibid.*, **1980**, *102*, 7218.

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Recently Paquette et al.<sup>2b,7</sup> reported that maleic anhydride with **1** in benzene at 25 °C yielded a 2:1 mixture of the syn-*exo* and syn-*endo* anhydrides **3** and **4**.

In connection with our synthetic approach to sesquinorbornene, which initially yielded only the anti hydrocarbon,<sup>3</sup> we also carried out some additions to the diene **1**, including the addition of maleic anhydride under conditions like those of Alder and co-workers. Like the Paquette group, we obtained a mixture of two products, but X-ray crystallographic studies showed these to be **2** and **3**, not **3** and **4**. Variation of the solvent (ether, benzene, deuteriochloroform, acetonitrile) and of the temperature (from 6 to 80 °C.) varied the ratio only from 55:45 to 35:65. After the appearance of Paquette's work<sup>2,7,8</sup> we suspended direct synthetic work on the syn-sesquinorbornene system but are continuing the exploitation of the sesquinorbornene ring system as an adjunct to mechanism studies. In this paper we present the X-ray structural analyses of **2** and **3**, which have revealed an unexpected dependence of the sesquinorbornene double-bond conformation on the syn or anti configuration.

### Results and Discussion

The structures of the anti-*endo* (**2**) and syn-*exo* (**3**) anhydrides are shown in Figures 1 and 2. Bond lengths and valence angles are given in Tables I and II while intramolecular contacts and interplanar angles are given in Tables III and IV. The C(4a)–C(8a) distance in compound **2** of 1.326 (3) Å is normal for an isolated double bond and the interplanar angle of 177.9° between C(1)C(8a)C(4a)C(4) and C(8)C(8a)C(4a)C(5) is consistent with the planarity expected for such a bond. Intramolecular contact distances H(6en)–H(10en) = 3.35 (4), H(9en)–O(13) = 2.96 (3), H(9ex)–H(6ex) = 2.66 (5), and H(2ex)–H(10ex) = 2.58(5) Å indicate no significant steric interactions; however, angles of less than 110° between the double and single bonds and C(sp<sup>3</sup>) angles of less than 100° correspond to the ring strain inherent in the norbornene system.

Bond lengths and valence angles in the syn-*exo* compound (**3**) are similar to those observed in **2**; however, the *interplanar angle* of 163.6° between C(1)C(8a)C(4a)C(4) and C(8)C(8a)C(4a)C(5) indicates a significant departure of the double bond from planarity. The 1.332 (3) Å C(4a)–C(8a) distance in **3** is statistically equivalent to that found in **2**. Normal-length *twisted* double bonds with torsion angles of 155° or less are well documented;<sup>10</sup> however, this type of *bent* double bond has not to our knowledge been reported previously. The 16.4° deviation from planarity is statistically significant and must be explicable in terms of some structural feature.

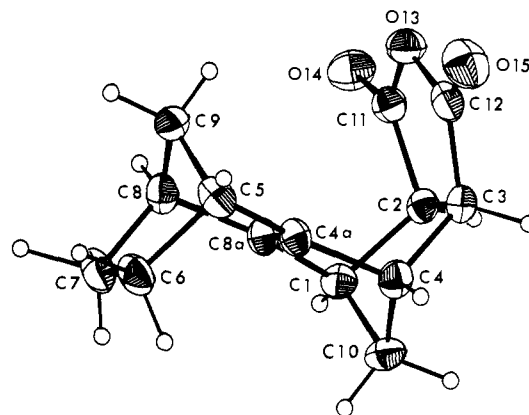


Figure 1. ORTEP drawing of anti-*endo*-sesquinorbornene anhydride (**2**). Thermal ellipsoids are drawn at the 35% probability level.

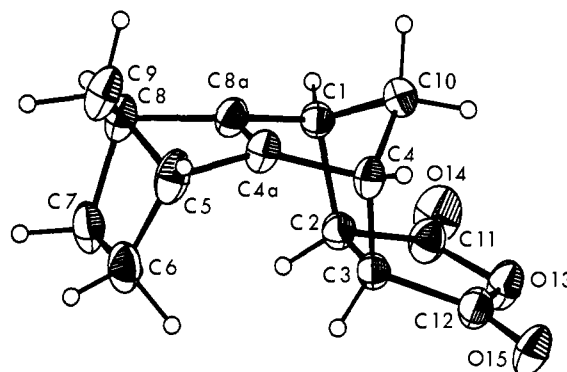


Figure 2. ORTEP drawing of syn-*exo*-sesquinorbornene anhydride (**3**). Thermal ellipsoids are drawn at the 35% probability level.

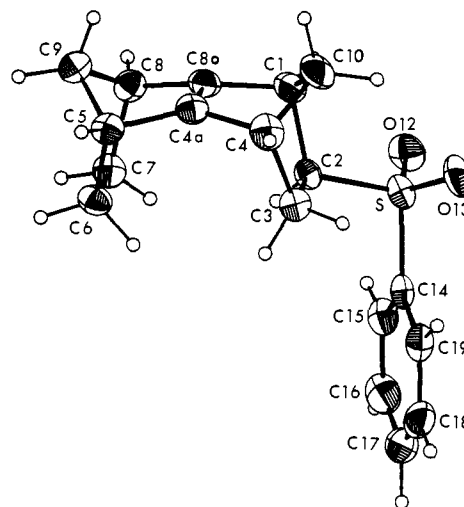


Figure 3. ORTEP drawing of 2-*exo*-(phenylsulfonyl)-syn-sesquinorbornene (**6**). The ellipsoids are drawn at the 35% probability level.

The deviation of the C(4a)–C(8a) double bond from planarity might be attributed to (i) intramolecular steric interactions, (ii) relief of ring strain, and (iii) intermolecular interactions. Intramolecular contacts of importance in compound **3** are H(9en)–H(10en) = 4.07 (3) Å, H(7en)–H(2en) = 2.35 (4) Å, H(10ex)–O(13) = 2.70 (3) Å, and H(9ex)–H(6ex) = 2.63 (4) Å. The short H(7en)–H(2en) distance arises because of the bending of the double bond and would be relieved by a return to planarity. A return to planarity would not result in any significant intramo-

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(8) We thank Professor Paquette for sending preprints of his papers on sesquinorbornene and related chemistry.

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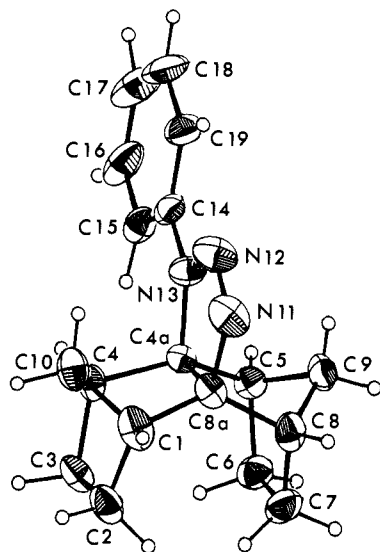


Figure 4. ORTEP drawing of *syn*-sesquinorbornene-phenyl azide adduct (7). Thermal ellipsoids are drawn at the 35% probability level.

lecular contacts between any of the other atom pairs, and the bent double bond cannot be related to intramolecular steric interactions between atoms.

Since the bicyclo [2.2.1] ring system is more compatible with  $sp^3$  than with  $sp^2$  internal bond angles, the kind of rehybridization associated with the bending might be expected to diminish ring strain, and this provides a second possible cause for the double-bond distortion. However, ring strain should be of the same magnitude in the anti-endo (2) and the syn-exo (3) compounds. The groups about the double bond in 2 constitute a planar system, and the thermal parameters indicate no disorder or unusual motion which might be indicative of a bent double bond.

Table V lists all intermolecular contact distances less than 3.0 Å and packing diagrams for 2, 3, and 6 are shown in Figures 5-7. The H(10en)-H(9en) ( $x, y, z; 1-x, 1/2+y, 3/2-z$ ) distance of 2.36 (5) Å in 3 is slightly less than the sum of the van der Waals

radii, but it is equivalent to the H(7en)-H(2en) intramolecular contact of 2.35 Å. The hydrogen atoms on C(9) and C(10) are shifted from their calculated positions by the intermolecular contact which would be further accentuated if the molecule were planar. However, it is difficult to rationalize the double-bond distortion and hydrogen atom shifts in terms of a gain in the van der Waals packing energy.

In order to assess the importance of intermolecular contacts and of the anhydride ring atoms, we determined the structure of the syn-exo 2-phenyl sulfonyl compound (6)<sup>2</sup>. The structure is shown in Figure 3. The bond lengths and valence angles are similar to those of 2 and 3 (see Tables I and II). The C(4a)-C(8a) distance of 1.330 (5) Å and the interplanar angle of 162.0° (Table IV) are statistically equivalent to those observed for 3. The anhydride ring is thus eliminated as a factor contributing to the nonplanarity of the double bond. Again intramolecular contacts and ring strain can be eliminated as causative factors; however, as seen from the list of intermolecular contacts in Table V, the packing interactions differ considerably from those of 3. Most significantly, the short H(10en)-H(9en) interaction is missing. Although a number of short contact distances are found, they either favor the planar structure or have little influence upon the geometry around the double bond. The carbon skeletons in 3 and 6 are the same, but the removal of the strong H(9)⋯H(10) intermolecular interaction observed in 3 permits the hydrogen atoms to approach their calculated equilibrium positions resulting in an H(9en)⋯H(10en) distance of 3.75 (6) Å. (Table III) A return to planarity would reduce this distance further, but it still would exceed the normal van der Waals contact distance. We are forced to conclude that the intermolecular contacts are not responsible for the distortion from planarity. The observed geometry must be inherent in the molecular framework and not a result of external forces.

An examination of the molecular framework of 3 and 6 raises the interesting question of the distribution of  $\pi$ -electron density. Although the room-temperature structural data are not accurate enough to locate quantitatively the  $\pi$ -electron density, difference Fourier calculations in the plane containing C(4a), C(8a), and the  $\pi$  bond indicate significantly more density above the plane, i.e., on the C(9), C(10) side. These data may indicate a trend

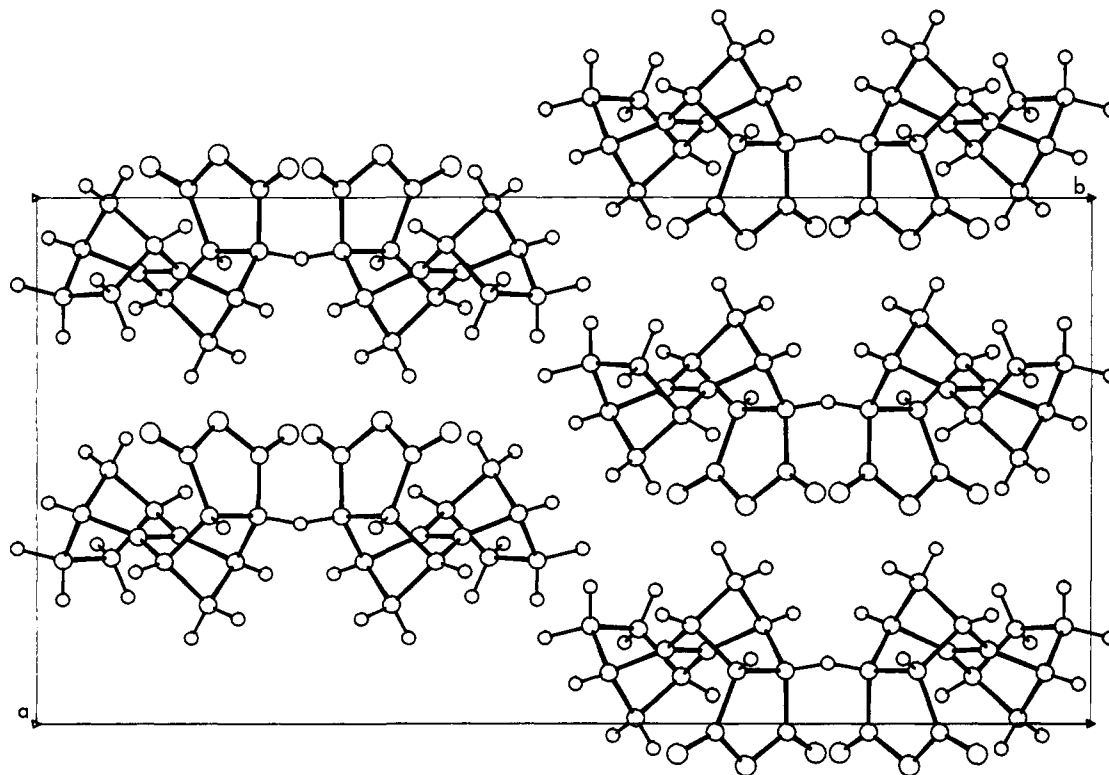


Figure 5. Packing diagram for *anti-endo*-sesquinorbornene anhydride (2).

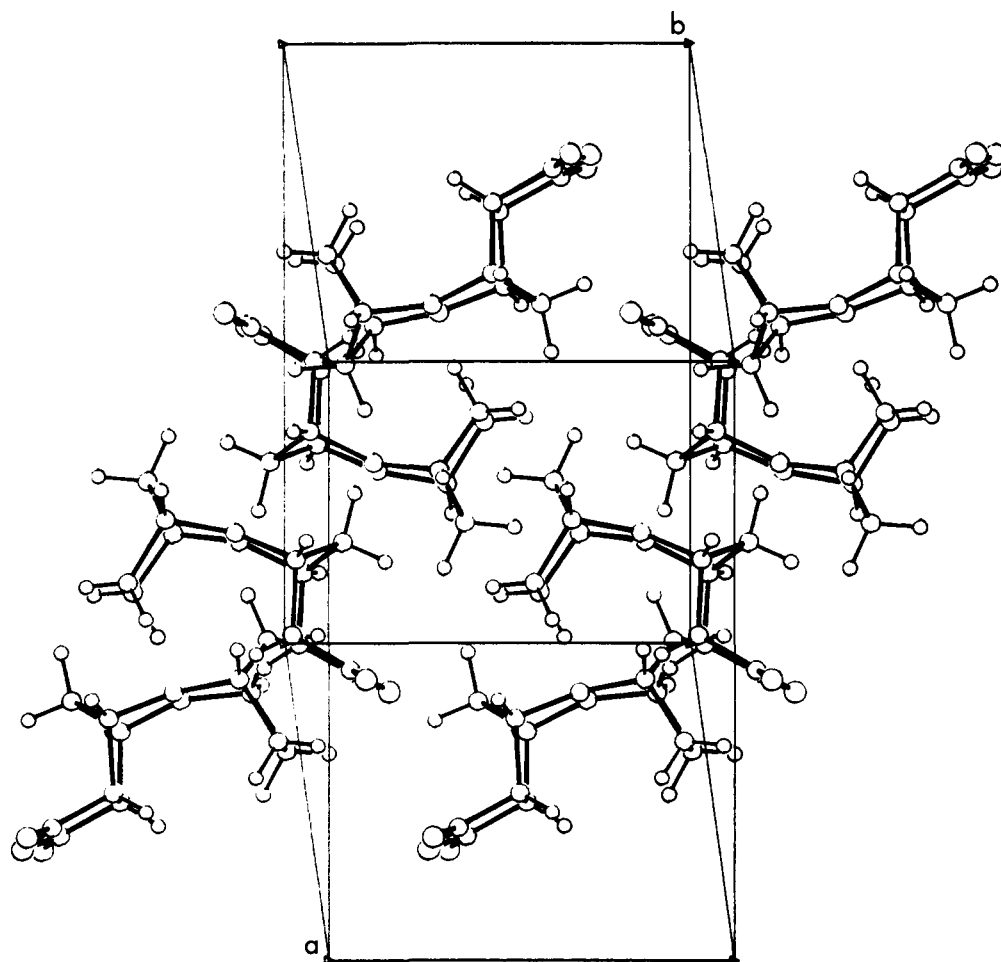


Figure 6. Packing diagram for *syn-exo*-sesquinorbornene anhydride (3).

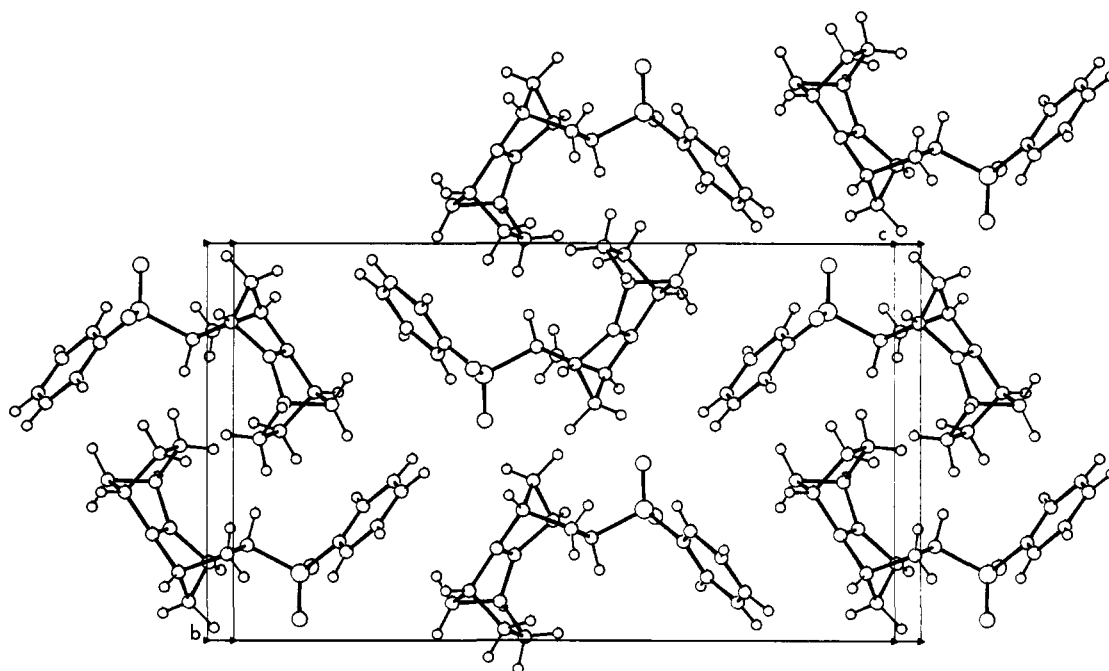


Figure 7. Packing diagram for 2-*exo*-(phenylsulfonyl)-*syn*-sesquinorbornene (6).

toward pyramidal ( $sp^3$ ) hybridization although the length of the C(4a)–C(8a) bond remains normal. A low-temperature X-ray and neutron diffraction study would afford more quantitative information on  $\pi$ -electron distribution.

Paquette and co-workers have shown that phenyl azide adds to *syn*-sesquinorbornene yielding a single *N*-phenyltriazoline

product.<sup>8</sup> We confirm this as the phenyl azide adduct (7); the molecular structure is shown in Figure 4. The crystal contains two equivalent independent molecules in the asymmetric unit. The phenyl azide has added exclusively from the C(9), C(10) side. This is consistent with the picture of a bent double bond in which the H(9en)···H(10en) separation has been expanded. The tria-

Table I. Bond Distances (Å)

	2	3	6	7	
	anti-endo	syn-exo	sulfone	phenyl azide adduct	
C(1)-C(2)	1.561 (3)	1.563 (3)	1.565 (4)	1.528 (5)	1.524 (5)
C(1)-C(8a)	1.515 (3)	1.509 (3)	1.523 (5)	1.536 (4)	1.551 (3)
C(1)-C(10)	1.540 (3)	1.541 (4)	1.546 (5)	1.521 (5)	1.541 (5)
C(2)-C(3)	1.537 (3)	1.540 (3)	1.554 (4)	1.530 (4)	1.530 (4)
C(3)-C(4)	1.567 (3)	1.567 (4)	1.555 (5)	1.534 (4)	1.523 (4)
C(4)-C(4a)	1.505 (3)	1.509 (3)	1.507 (4)	1.550 (4)	1.541 (3)
C(4)-C(10)	1.539 (4)	1.541 (3)	1.524 (6)	1.540 (4)	1.544 (3)
C(4a)-C(5)	1.510 (3)	1.508 (3)	1.523 (4)	1.549 (4)	1.558 (3)
C(4a)-C(8a)	1.326 (3)	1.332 (3)	1.330 (5)	1.545 (3)	1.555 (3)
C(5)-C(6)	1.550 (4)	1.531 (5)	1.544 (5)	1.520 (4)	1.527 (4)
C(5)-C(9)	1.537 (4)	1.562 (3)	1.539 (5)	1.533 (4)	1.542 (4)
C(6)-C(7)	1.531 (4)	1.549 (4)	1.535 (5)	1.552 (4)	1.542 (4)
C(7)-C(8)	1.554 (4)	1.545 (4)	1.554 (4)	1.530 (5)	1.540 (5)
C(8)-C(8a)	1.515 (3)	1.503 (3)	1.512 (5)	1.536 (4)	1.544 (5)
C(8)-C(9)	1.528 (4)	1.543 (5)	1.546 (5)	1.534 (4)	1.526 (4)
C(2)-C(11)	1.491 (3)	1.495 (4)			
C(3)-C(12)	1.488 (4)	1.500 (3)			
C(11)-O(13)	1.372 (3)	1.378 (3)			
C(12)-O(13)	1.394 (3)	1.389 (3)			
C(11)-O(14)	1.195 (3)	1.189 (4)			
C(12)-O(15)	1.189 (3)	1.197 (3)			
C(2)-S(11)			1.787 (3)		
S(11)-O(12)			1.437 (3)		
S(11)-O(13)			1.439 (2)		
S(11)-C(14)			1.771 (3)		
C(14)-C(15)			1.385 (5)	1.377 (4)	1.392 (4)
C(14)-C(19)			1.377 (4)	1.409 (5)	1.397 (5)
C(15)-C(16)			1.373 (5)	1.389 (4)	1.384 (5)
C(16)-C(17)			1.374 (8)	1.349 (8)	1.363 (7)
C(17)-C(18)			1.371 (7)	1.375 (8)	1.347 (9)
C(18)-C(19)			1.378 (6)	1.409 (5)	1.399 (7)
C(8a)-N(11)				1.505 (4)	1.497 (4)
C(4a)-N(13)				1.482 (3)	1.487 (4)
N(11)-N(12)				1.244 (3)	1.247 (5)
N(12)-N(13)				1.357 (3)	1.367 (3)
N(13)-C(14)				1.401 (3)	1.395 (4)
C(1)-H(1) <sup>a</sup>	0.95 (3)	0.96 (3)	1.01 (4)	0.94 (3)	0.99 (3)
C(2)-H(2) <sup>a</sup>	0.99 (3)	0.97 (3)	0.99 (4)	0.96 (4)	1.01 (4)
C(3)-H(3 <sub>exo</sub> ) <sup>a</sup>	...	...	1.00 (4)	0.94 (4)	0.95 (4)
C(5)-H(5) <sup>a</sup>	0.98 (3)	0.98 (3)	0.93 (4)	0.95 (3)	0.98 (3)
C(6)-H(6 <sub>en</sub> ) <sup>a</sup>	1.00 (4)	1.04 (3)	1.01 (4)	1.01 (4)	0.99 (4)
C(6)-H(6 <sub>exo</sub> ) <sup>a</sup>	1.12 (3)	0.92 (3)	1.00 (4)	0.96 (3)	0.94 (4)
C(9)-H(9 <sub>en</sub> )	0.88 (4)	1.04 (3)	0.98 (4)	0.92 (3)	0.90 (3)
C(9)-H(9 <sub>exo</sub> )	0.94 (3)	1.05 (2)	1.03 (4)	1.00 (4)	0.98 (3)
C(10)-H(10 <sub>en</sub> )	0.98 (3)	1.04 (3)	0.98 (4)	0.96 (3)	0.99 (3)
C(10)-H(10 <sub>ex</sub> )	1.01 (3)	0.99 (3)	1.06 (4)	0.99 (4)	0.97 (3)
C(15)-H(15)	...	...	0.94 (4)	1.02 (3)	0.91 (4)
C(16)-H(16)	...	...	1.00 (4)	1.00 (3)	1.07 (3)
C(17)-H(17)	...	...	1.01 (4)	1.02 (3)	0.94 (4)
C(18)-H(18)	...	...	0.91 (4)	0.91 (3)	0.99 (4)
C(19)-H(19)	...	...	0.92 (5)	0.96 (3)	0.85 (3)

<sup>a</sup> Equivalent distances averaged.

zoline ring is planar and the average H(2)···H(7) and H(3)···H(6) distances are 1.76 and 1.81 Å for molecules 1 and 2. These strong steric interactions between backside hydrogens were not of sufficient magnitude to prevent the addition of the phenylazide. It may be said that in *syn*-sesquiorbornene the rehybridization attending addition to the double bond has already begun in the ground-state hydrocarbon.

It is of interest that the *N*-phenyl bond in 7 lies in the plane of the triazoline ring, indicating sp<sup>2</sup> hybridization of that nitrogen atom as well as of the two in the N=N double bond.

What structural features of *syn*-sesquiorbornene lead to the deviation of the double bond from planarity? It is suggested that the C(4a)-C(8a) π cloud exerts a space demand as does a substituent group and that the resulting repulsive force is greater with the bonds involving C(9) and C(10) than with those involving C(2), C(3), C(6), and C(7). This difference between bonding-electrons-π-cloud repulsion on the two faces of the double bond leads to a deviation from planarity. The deviation from planarity is attended by partial rehybridization at the C(4a) and C(8a) centers, with an increase in π-electron density above the plane.

The structure represents a compromise between optimum π-bond strength, σ-π repulsion, and ring strain. The σ-π repulsions are symmetrical in the anti-endo compound (2) and the double bond remains planar.

From the observation<sup>3</sup> that *anti*-sesquiorbornene fails to add singlet oxygen in normal concerted fashion, it seemed likely that this alkene would afford clear distinctions between concerted and stepwise mechanisms of cycloaddition. In the simplest view of a concerted cycloaddition between two symmetrical molecules, both new bonds are formed simultaneously, and in such a case the hindrance in *anti*-sesquiorbornene would be complete, while the H(9)-H(10) spacing in *syn*-sesquiorbornene, as now observed, leaves the possibility of concerted approach of certain reagents on the exo face of the double bond. The differing behavior of 2 and 3 toward phenyl azide appeared at first sight to be an example of this simple distinction; however, further exploration reminds us that reaction mechanisms do not generally conform to the most simplified picture. It turns out that, in contrast to the anti-anhydride 2, *anti*-sesquiorbornene itself reacts with phenylazide more than half as fast as its *syn* isomer.<sup>13</sup> If this is a concerted

Table II. Valence Angles (Deg)

	2 anti-endo	3 syn-exo	6 sulfone	7 phenyl azide adduct	
C(8a)C(1)C(2)	105.3 (2)	106.7 (2)	104.7 (2)	114.1 (3)	114.4 (2)
C(8a)C(1)C(10)	100.3 (2)	98.3 (2)	98.6 (3)	99.6 (2)	100.2 (2)
C(2)C(1)C(10)	98.6 (2)	99.5 (1)	100.1 (2)	99.7 (3)	99.1 (2)
C(1)C(2)C(3)	103.5 (2)	103.7 (2)	103.3 (2)	103.0 (2)	103.0 (2)
C(1)C(2)C(11)	114.1 (2)	110.7 (2)			
C(3)C(2)C(11)	104.4 (2)	104.2 (2)			
C(2)C(3)C(4)	103.4 (2)	103.5 (1)	103.0 (2)	104.3 (2)	104.4 (2)
C(2)C(3)C(12)	104.3 (2)	103.9 (2)			
C(4)C(3)C(12)	114.8 (2)	113.3 (2)			
C(3)C(4)C(4a)	106.3 (2)	105.9 (2)	107.5 (3)	114.5 (2)	113.9 (2)
C(3)C(4)C(10)	98.6 (2)	100.0 (2)	99.8 (3)	98.3 (2)	99.2 (2)
C(4a)C(4)C(10)	100.0 (2)	98.1 (1)	99.1 (3)	99.5 (2)	100.1 (2)
C(4)C(4a)C(8a)	108.2 (2)	108.4 (2)	108.4 (3)	102.1 (2)	102.8 (2)
C(4)C(4a)C(5)	144.1 (2)	140.3 (2)	139.3 (3)	139.3 (3)	129.6 (2)
C(5)C(4a)C(8a)	107.7 (2)	107.8 (2)	108.2 (3)	102.9 (2)	102.8 (2)
C(4a)C(5)C(6)	105.0 (2)	107.5 (3)	106.2 (2)	113.6 (2)	114.4 (2)
C(4a)C(5)C(9)	99.3 (2)	98.1 (2)	98.5 (3)	100.4 (2)	99.6 (2)
C(6)C(5)C(9)	99.4 (2)	100.3 (2)	99.7 (3)	99.7 (2)	98.5 (2)
C(5)C(6)C(7)	104.1 (2)	103.2 (2)	104.0 (2)	102.9 (2)	104.1 (2)
C(6)C(7)C(8)	103.4 (2)	104.0 (3)	103.5 (3)	103.4 (2)	103.0 (3)
C(7)C(8)C(8a)	104.9 (2)	106.8 (2)	107.3 (2)	114.9 (3)	114.1 (2)
C(7)C(8)C(9)	99.2 (2)	99.7 (2)	99.2 (3)	98.7 (2)	99.8 (2)
C(8a)C(8)C(9)	99.3 (2)	98.4 (2)	98.7 (3)	99.9 (2)	99.5 (3)
C(8)C(8a)C(4a)	108.6 (2)	108.6 (2)	108.0 (3)	103.4 (2)	103.4 (2)
C(8)C(8a)C(1)	143.4 (2)	139.9 (2)	140.3 (3)	128.7 (2)	129.1 (3)
C(1)C(8a)C(4a)	108.0 (2)	108.1 (2)	107.6 (3)	104.3 (2)	103.2 (2)
C(5)C(9)C(8)	95.4 (2)	94.0 (3)	94.8 (2)	94.2 (2)	94.9 (2)
C(1)C(10)C(4)	94.7 (2)	95.3 (2)	95.2 (3)	94.6 (2)	93.7 (2)
C(2)C(11)O(13)	110.6 (2)	110.9 (2)			
C(2)C(11)O(14)	129.5 (2)	128.8 (2)			
O(13)C(11)O(14)	119.9 (2)	120.3 (2)			
C(3)C(12)O(13)	110.2 (2)	110.5 (2)			
C(3)C(12)O(15)	129.7 (2)	130.2 (2)			
O(13)C(12)O(15)	120.1 (3)	119.3 (2)			
C(11)O(13)C(12)	110.5 (2)	110.2 (2)			
C(1)C(2)S(11)			112.1 (2)		
C(3)C(2)S(11)			114.2 (2)		
C(2)S(11)O(12)			107.3 (1)		
C(2)S(11)O(13)			110.5 (1)		
C(2)S(11)C(14)			103.7 (1)		
O(12)S(11)O(13)			118.2 (2)		
O(12)S(11)C(14)			108.1 (1)		
O(13)S(11)C(14)			108.1 (1)		
S(11)C(14)C(15)			118.4 (2)		
S(11)C(14)C(19)			120.6 (2)		
C(15)C(14)C(19)			121.0 (3)	119.4 (2)	119.2 (3)
C(14)C(15)C(16)			119.8 (4)	120.9 (3)	120.7 (3)
C(15)C(16)C(17)			119.5 (4)	121.0 (4)	120.2 (4)
C(16)C(17)C(18)			120.3 (4)	119.0 (4)	119.5 (5)
C(17)C(18)C(19)			121.2 (4)	122.3 (5)	123.0 (5)
C(14)C(19)C(18)			118.2 (3)	117.3 (3)	117.5 (4)
C(4a)C(8a)N(11)				103.8 (2)	104.9 (2)
C(1)C(8a)N(11)				106.4 (2)	106.7 (2)
C(8)C(8a)N(11)				107.7 (3)	107.2 (1)
C(8a)N(11)N(12)				111.9 (2)	110.8 (2)
N(11)N(12)N(13)				111.9 (2)	113.0 (3)
N(12)N(13)C(4a)				112.6 (2)	111.9 (2)
N(13)C(4a)C(8a)				99.8 (2)	99.3 (2)
C(4)C(4a)N(13)				108.2 (2)	109.3 (2)
C(5)C(4a)N(13)				108.3 (2)	108.3 (2)
C(4a)N(13)C(14)				127.3 (2)	127.8 (2)
N(12)N(13)C(14)				120.0 (2)	120.2 (3)
N(13)C(14)C(15)				121.1 (2)	120.6 (3)
N(13)C(14)C(19)				119.5 (2)	120.2 (3)

reaction (and the evidence for preferred concerted reaction by phenyl azide is persuasive<sup>14</sup>), then the process must begin with enough bond formation at one carbon of the double bond to initiate rehybridization, a necessary condition for the spreading of the bridges that allows the reagent access to the second carbon of the double bond. The transition state of a concerted reaction need

not be symmetrical and cannot be so with an unsymmetrical reagent; the requirement of concert is only that the reaction path does not pass through any energy minimum when only one of the two new bonds has been formed. If the phenyl azide reactions are an example of this principle, then the difference between the anhydride **2** and *anti*-sesquinorbornene itself lies in the closeness (2.96 Å) between H(9en) and O(13) in the anhydride **2**. This is a more hindered side of the double bond than the anti hydrocarbon has; at the same time initial attack on the opposite face

(13) Winter, W. J., unpublished work.

(14) Huisgen, R.; Grashey, R.; Sauer, J. *Chem. Alkenes* 1964, 835-844.

Table III. Nonbonding Intramolecular Distances (Å)

	2 anti-endo	3 syn-exo	6 sulfone	7 phenyl azide adduct	
O(13)-H(9en)	2.96 (3)				
H(6en)-H(10en) <sup>a</sup>	3.35 (4)				
H(9ex)-H(6ex) <sup>a</sup>	2.66 (5)	2.63 (4)			
H(2ex)-H(10ex) <sup>a</sup>	2.58 (5)				
H(2en)-H(7en) <sup>a</sup>		2.35 (4)	2.32 (5)	1.76 (5)	1.81 (4)
H(9en)-H(10en)		4.07 (3)	3.75 (6)		
H(10ex)-O(13)		2.70 (3)	2.54 (4)		
N(11)-H(9en)				2.44 (4)	2.60 (3)
N(11)-H(10en)				2.55 (4)	2.57 (3)
N(12)-H(9en)				2.50 (3)	2.56 (3)
N(12)-H(10en)				2.51 (4)	2.48 (3)
N(13)-H(9en)				2.53 (3)	2.48 (3)
N(13)-H(10en)				2.47 (3)	2.44 (2)

<sup>a</sup> Equivalent values averaged: 6-10 with 7-10, 9-6 with 9-7, 2-10 with 3-10, 2-7 with 3-6.

Table IV. Dihedral Angles (Deg) between Planes<sup>a</sup>

	2 anti-endo	3 syn-exo	6 sulfone	7 phenyl azide adduct	
AB	177.9	163.6	162.0	136.8	136.2
AC	129.0	125.8	126.5	120.5	120.7
AD	111.9	112.6	112.1	119.5	119.3
CD	119.1	121.6	121.4	120.0	120.0
BE	127.9	125.1	125.9	121.2	120.4
BF	111.1	113.5	113.0	119.2	119.3
EF	121.0	121.4	121.0	119.6	120.3
DG	119.8	116.8			
AH				111.3	111.8
BH				111.8	111.9

<sup>a</sup> Definition of planes: A = C(1)C(8a)C(4a)C(4); B = C(5)C(4a)C(8a)C(8); C = C(1)C(10)C(4); D = C(1)C(2)C(3)C(4); E = C(5)C(8)C(9); F = C(5)C(6)C(7)C(8); G = anhydride ring; H = C(4a)C(8a)N(11)N(12)N(13).

cannot bring about the required reshaping of the molecule without early collision of H(9en) and O(13).

Even with singlet oxygen, a deviation from the least motion reaction path has been detected in cycloaddition to a methylidihydropyran.<sup>15</sup> The most subtle problem of mechanism presented by cycloadditions in general is to distinguish between an allowed concerted reaction which follows an unsymmetrical reaction path and an actual (equally allowed) stepwise addition via biradical or dipolar ionic intermediates. This distinction is not afforded by the sesquinorbornene stereochemical criterion, but only where an intermediate can be captured or epimerized.

It has long been suspected that there is something about the electronic structure of the norbornene ring system that predisposes toward rapid reaction on the exo face of the double bond. Huisgen et al.<sup>16</sup> have recently shown that reactivity of the double bond in some bicyclo[2.n.n]alkenes, varying over 3-4 orders of magnitude, is correlated in part with ring strain but that the effects on reactivity of the lowering of bridge size from bicyclo[2.2.2]octene to norbornene cannot be repeated by extension to bicyclo[2.1.1]hexenes. They suggest that the facts might be accommodated by a contribution from the nonequivalent orbital extension proposed on theoretical grounds by Fukui.<sup>17</sup> Whereas the effect in a single norbornene ring has eluded unequivocal physical detection, it now appears that two cooperating norbornene systems can produce both an unmistakable bending and some very characteristic chemical behavior.<sup>18</sup>

(15) Frimer, A. A.; Bartlett, P. D.; Boschung, A. F.; Jewett, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 7977.

(16) Huisgen, R.; Ooms, P. H. J.; Mingin, M.; Allinger, N. L. *J. Am. Chem. Soc.* **1980**, *102*, 3952.

(17) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054.

(18) Recent ab initio calculations predict a double bond deformation of 4.9° in norbornene: Wipff, G.; Morokuma, K. *Tetrahedron Lett.* **1980**, *21*, 4446.

Table V. Intermolecular Contacts of 3.00 Å or Less

Anti-Endo Anhydride (2)			
	(x, y, z)(x, y, 1 + z)		
H(4)-H(7en)	2.42 (4)	H(3)-H(8)	2.61 (4)
	(x, y, z)(1 - x, -y, 1 - z)		
H(6en)-O(15)	2.71 (3)	H(5)-H(5)	2.70 (5)
	(x, y, z)(1 - x, -y, -z)		
H(6ex)-H(9ex)	2.76 (5)		
	(x, y, z)(x + 1/2, 1/2 - y, 1 - z)		
H(10ex)-O(14)	2.57 (3)		
	(x, y, z)(x, 1/2 - y, 1/2 + z)		
H(3)-H(1)	2.74 (4)	H(2)-H(1)	2.40 (4)
H(2)-H(8)	2.71 (4)		
	(x, y, z)(3/2 - x, -y, 1/2 + z)		
H(4)-H(6ex)	2.36 (4)	H(6en)-H(7en)	2.62 (4)
	(x, y, z)(1/2 + x, y, 1/2 - z)		
H(10en)-H(9en)	2.46 (5)	H(10en)-H(8)	2.63 (5)
H(6en)-H(9en)	2.69 (5)		
Syn-Exo Anhydride (3)			
	(x, y, z)(x, 1 + y, z)		
H(10ex)-H(6ex)	2.64 (3)	H(10ex)-H(7ex)	2.65 (4)
	(x, y, z)(-x, 1 - y, 1 - z)		
O(15)-H(6en)	2.76 (3)	O(15)-H(3)	2.69 (3)
	(x, y, z)(1 - x, 1/2 + y, 3/2 - z)		
H(10en)-H(9en)	2.36 (5)	H(10en)-H(5)	2.96 (4)
	(x, y, z)(-x, 1/2 + y, 3/2 - z)		
O(13)-H(2)	2.85 (2)	O(13)-H(3)	2.70 (3)
O(13)-H(6en)	2.97 (3)	O(13)-H(7en)	2.99 (2)
O(15)-H(2)	2.79 (3)	O(15)-H(7en)	2.79 (4)
	(x, y, z)(x, 3/2 - y, 1/2 + z)		
O(14)-H(4)	2.62 (3)		
	(x, y, z)(x, 1/2 - y, 1/2 + z)		
H(7en)-H(5)	2.91 (4)	H(1)-H(5)	2.76 (5)
H(2)-H(5)	2.64 (3)		
Syn-Exo Sulfone (6)			
	(x, y, z)(1 + x, y, z)		
H(1)-H(4)	2.75 (5)	H(15)-H(18)	2.65 (6)
O(12)-H(19)	2.73 (5)		
	(x, y, z)(1 - x, 1 - y, 1 - z)		
H(10ex)-H(3ex)	2.69 (6)	O(13)-H(4)	2.59 (4)
	(x, y, z)(1 - x, -y, 1 - z)		
H(7ex)-H(3en)	2.76 (5)	H(6en)-H(6en)	2.31 (5)
H(6en)-H(7en)	2.55 (5)	H(6ex)-H(3en)	2.81 (5)
	(x, y, z)(1 - x, 1/2 + y, 1/2 - z)		
O(13)-H(17)	2.42 (4)	H(19)-H(16)	2.71 (6)
	(x, y, z)(1 + x, 1/2 - y, 1/2 + z)		
H(9en)-H(18)	2.38 (6)		
	(x, y, z)(x, 1/2 - y, 1/2 + z)		
H(4)-H(17)	2.66 (6)		

Interaction between the  $\pi$  and  $\sigma$  systems in isodicyclopentadiene has also been considered theoretically by Paquette, Gleiter, and

Table VI. Atomic Coordinates of *anti*-Sesquinorbornene *endo*-Anhydride (2)

	x	y	z
C(1)	6885 (2)	1890 (1)	3611 (3)
C(2)	6008 (2)	2104 (1)	4927 (3)
C(3)	6004 (2)	1644 (1)	6303 (3)
C(4)	6886 (2)	1212 (1)	5638 (3)
C(4a)	6411 (2)	963 (1)	4031 (3)
C(5)	5970 (2)	430 (1)	3234 (3)
C(6)	6867 (2)	253 (1)	1920 (4)
C(7)	6809 (3)	710 (1)	549 (3)
C(8)	5900 (2)	1116 (1)	1232 (3)
C(8a)	6385 (2)	1362 (1)	2851 (3)
C(9)	5108 (2)	686 (1)	2013 (4)
C(10)	7723 (2)	1630 (1)	4867 (3)
C(11)	4845 (2)	2111 (1)	4269 (3)
C(12)	4839 (2)	1435 (1)	6316 (3)
O(13)	4204 (1)	1723 (1)	5113 (2)
O(14)	4448 (2)	2386 (1)	3150 (3)
O(15)	4425 (2)	1076 (1)	7160 (3)
H(1)	712 (3)	218 (1)	287 (4)
H(2)	615 (3)	249 (1)	538 (3)
H(3)	623 (3)	178 (1)	743 (3)
H(4)	709 (3)	94 (1)	649 (3)
H(5)	575 (3)	11 (1)	377 (4)
H(6en)	762 (3)	25 (1)	244 (4)
H(6ex)	664 (3)	-18 (1)	147 (4)
H(7en)	756 (3)	87 (1)	45 (4)
H(7ex)	654 (3)	57 (1)	-75 (4)
H(8)	554 (3)	141 (1)	39 (4)
H(9en)	453 (3)	85 (1)	249 (4)
H(9ex)	478 (3)	46 (1)	116 (4)
H(10en)	837 (3)	147 (1)	427 (4)
H(10ex)	800 (3)	192 (1)	571 (4)

Table VII. Atomic Coordinates of *syn*-Sesquinorbornene *exo*-Anhydride (3)

	x	y	z
C(1)	3315 (2)	5016 (2)	9047 (2)
C(2)	1862 (2)	4967 (2)	8526 (2)
C(3)	1246 (2)	4977 (2)	7079 (2)
C(4)	2407 (2)	5075 (2)	6908 (2)
C(4a)	3107 (2)	3535 (3)	7398 (2)
C(5)	3093 (3)	1875 (3)	6959 (2)
C(6)	2137 (3)	933 (3)	7121 (3)
C(7)	2749 (3)	897 (3)	8575 (3)
C(8)	3998 (2)	1826 (3)	9092 (2)
C(8a)	3635 (2)	3497 (2)	8647 (2)
C(9)	4363 (3)	1295 (3)	8140 (3)
C(10)	3305 (2)	6113 (3)	8055 (2)
C(11)	1436 (2)	6479 (3)	8801 (2)
C(12)	447 (2)	6439 (3)	6661 (2)
O(13)	633 (2)	7287 (2)	7700 (2)
O(14)	1729 (2)	7030 (3)	9798 (2)
O(15)	-265 (2)	6941 (2)	5619 (2)
H(1)	381 (2)	532 (3)	996 (2)
H(2)	162 (2)	407 (3)	883 (2)
H(3)	68 (2)	412 (3)	661 (2)
H(4)	233 (2)	541 (3)	617 (2)
H(5)	318 (2)	184 (3)	620 (2)
H(6en)	126 (2)	143 (3)	663 (2)
H(6ex)	196 (2)	-7 (3)	692 (2)
H(7en)	213 (2)	149 (3)	880 (2)
H(7ex)	291 (2)	-11 (3)	898 (2)
H(8)	459 (2)	165 (3)	997 (2)
H(9en)	450 (2)	7 (3)	824 (3)
H(9ex)	520 (2)	179 (3)	829 (3)
H(10en)	419 (2)	638 (3)	819 (2)
H(10ex)	292 (2)	717 (3)	795 (2)

co-workers<sup>2b</sup> as the controlling factor in approach of dienophiles in the Diels-Alder reaction. Their treatment does not predict the kind of bond deformation here observed; but it seems likely that as the variegated pattern of Diels-Alder geometry becomes better understood, the interactions in question will find their place among the forces determining both ground-state geometry and reactivity.

Table VIII. Atomic Coordinates of *syn*-Sesquinorbornene-2-yl Phenyl Sulfone (6)

	x	y	z
C(1)	9122 (5)	1974 (3)	10320 (2)
C(2)	7617 (4)	2407 (2)	9703 (1)
C(3)	5390 (5)	2188 (3)	9908 (2)
C(4)	5871 (6)	1727 (3)	10632 (2)
C(4a)	6941 (5)	2675 (3)	11051 (1)
C(5)	6368 (5)	3735 (3)	11431 (2)
C(6)	6030 (5)	4712 (3)	10914 (2)
C(7)	8223 (5)	4909 (3)	10702 (2)
C(8)	9612 (5)	4005 (3)	11112 (2)
C(8a)	8846 (5)	2835 (3)	10869 (2)
C(9)	8584 (6)	4047 (3)	11764 (2)
C(10)	7784 (7)	985 (3)	10555 (2)
S(11)	8100 (1)	1701 (1)	8953 (0)
O(12)	10283 (4)	1864 (2)	8880 (1)
O(13)	7297 (5)	548 (2)	8939 (1)
C(14)	6585 (5)	2495 (2)	8320 (1)
C(15)	7548 (6)	3382 (3)	8018 (2)
C(16)	6412 (9)	4016 (4)	7527 (2)
C(17)	4331 (9)	3760 (5)	7340 (2)
C(18)	3386 (6)	2887 (5)	7647 (2)
C(19)	4495 (5)	2239 (3)	8140 (2)
H(1)	1050 (6)	178 (3)	1020 (2)
H(2)	785 (6)	321 (3)	959 (2)
H(3en)	433 (6)	283 (3)	982 (2)
H(3ex)	456 (6)	160 (3)	963 (2)
H(4)	452 (6)	135 (3)	1078 (2)
H(5)	533 (6)	374 (3)	1173 (2)
H(6en)	502 (6)	450 (3)	1050 (2)
H(6ex)	558 (6)	543 (3)	1113 (2)
H(7en)	831 (6)	482 (4)	1022 (2)
H(7ex)	867 (6)	572 (3)	1082 (2)
H(8)	1101 (6)	412 (3)	1113 (2)
H(9en)	914 (6)	337 (4)	1201 (2)
H(9ex)	859 (6)	484 (4)	1199 (2)
H(10en)	855 (6)	70 (4)	1097 (2)
H(10ex)	762 (6)	33 (4)	1019 (2)
H(15)	894 (7)	361 (4)	816 (2)
H(16)	723 (6)	458 (4)	729 (2)
H(17)	351 (6)	423 (4)	698 (2)
H(18)	201 (6)	270 (4)	756 (2)
H(19)	390 (7)	161 (4)	831 (2)

### Experimental Section

Isodicyclopentadiene (1) was prepared as described by Alder, Flock, and Janssen.<sup>4</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>): 5.68 (s, 2 H), 3.04 (br s, 4 H), 1.0-1.88 (series of multiplets, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 155.7, 113.9, 46.1, 45.2, 38.4, 28.6 ppm. Maleic anhydride, 99% pure, was purchased from the Aldrich Chemical Co. Phenyl vinyl sulfone was obtained by H<sub>2</sub>O<sub>2</sub> oxidation of phenyl vinyl sulfoxide (Aldrich Chemical Co., Inc.) as reported.<sup>9</sup> The adduct 6 was prepared as in ref 2. <sup>13</sup>C NMR (CDCl<sub>3</sub>): 157.4, 150.5, 140.1, 133.4, 129.2, 128.1, 64.3, 50.4, 47.2, 45.5, 42.8, 42.6, 42.2, 29.4, 25.9, 24.9 ppm.

IR spectra were obtained with Perkin-Elmer 197 and Beckman IR 4250 spectrophotometers. <sup>1</sup>H NMR spectra were obtained on JEOL JNM-MH 100 and Varian 390 90-MHz spectrometers. <sup>13</sup>C NMR spectra were obtained on a JEOL FX 60 spectrometer. In all cases tetramethylsilane was used as an internal standard.

Vapor chromatography was performed on a Perkin-Elmer Sigma 3 machine equipped with a 6-ft. nickel column packed with 5% SE-30 on Chromosorb W-AW 60-80 mesh. Mass spectral analysis was performed on a Finnigan OWA 1020 GC-MS-DS equipped with a 6-ft column of

(19) **Note Added in Proof:** Although no specific mention of double bond deformation was found in the crystal structure literature, an analysis of literature data indicates that such deformations may be a common but overlooked phenomenon. Norbornene derivatives containing diacid, dihydrogen, and dihalogen substituents on the double bond, as well as compounds in which the double bond is part of a phenyl ring, show deformations of 3° to 9°. When a halogen is present on the methano bridge above the  $\pi$ -system, the deformation appears to be reduced. Declercq, J. P.; Germain, G.; Henke, H. *Cryst. Struct. Commun.* 1973, 3, 405. DeLacey, T. P.; Kennard, C. H. L. *J. Chem. Soc., Perkin Trans. 3* 1972, 2153. Koyama, H.; Okada, K. *J. Chem. Soc.* 1969, 940. Sato, T.; Shiro, M.; Koyama, H. *Ibid.* 1968, 935. Pfluger, C. E.; Harlow, R. L.; Simonson, S. H. *J. Cryst. Mol. Struct.* 1973, 3, 277. Golic, L.; Leban, I. *Cryst. Struct. Commun.* 1980, 9, 739. Ealick, S. E.; Van der Helm, D. *Ibid.* 1975, 4, 369. Kennard, C. H. L.; Smith, G.; Holmoller, S. *Acta Crystallogr., Sect. B* 1979, B35, 493.



Table IX. Atomic Coordinates of Phenyl Azide Adduct (7) from *syn*-Sesquinorbornene

Molecule 1			Molecule 2		
x	y	z	x	y	z
C(1)	2387 (2)	2088 (3)	C(1)	171 (2)	6610 (2)
C(2)	2391 (2)	888 (3)	C(2)	-177 (2)	5600 (3)
C(3)	3121 (2)	450 (2)	C(3)	535 (2)	4804 (2)
C(4)	3461 (1)	1442 (2)	C(4)	1203 (1)	5418 (2)
C(4a)	2905 (1)	1888 (2)	C(4a)	1574 (1)	6352 (2)
C(5)	2503 (2)	1311 (2)	C(5)	1929 (1)	6347 (2)
C(6)	2070 (2)	267 (3)	C(6)	1377 (2)	5826 (2)
C(7)	1329 (2)	674 (3)	C(7)	641 (2)	6595 (2)
C(8)	1436 (2)	1904 (3)	C(8)	872 (2)	7508 (2)
C(8a)	2169 (2)	2314 (2)	C(8a)	858 (2)	7169 (2)
C(9)	1767 (2)	2048 (3)	C(9)	1788 (2)	7543 (2)
C(10)	3297 (2)	2296 (3)	C(10)	673 (2)	6067 (3)
N(11)	2214 (2)	3522 (2)	N(11)	1122 (2)	8130 (2)
N(12)	2809 (2)	3795 (2)	N(12)	1805 (2)	7975 (2)
N(13)	3251 (1)	2927 (2)	N(13)	2129 (1)	6991 (2)
C(14)	3934 (2)	3075 (2)	C(14)	2871 (2)	6667 (2)
C(15)	4399 (2)	2209 (3)	C(15)	3208 (2)	5670 (2)
C(16)	5073 (2)	2358 (4)	C(16)	3939 (2)	5341 (3)
C(17)	5283 (3)	3352 (6)	C(17)	4337 (3)	5993 (5)
C(18)	4835 (3)	4230 (5)	C(18)	4012 (3)	6955 (5)
C(19)	4144 (2)	4125 (3)	C(19)	3279 (2)	7336 (3)
H(1)	207 (2)	244 (2)	H(1)	-26 (2)	713 (2)
H(2en)	189 (2)	47 (2)	H(2en)	-37 (2)	577 (2)
H(2ex)	255 (2)	87 (2)	H(2ex)	-63 (2)	531 (2)
H(3en)	299 (2)	-10 (2)	H(3en)	72 (2)	446 (2)
H(3ex)	353 (2)	20 (2)	H(3ex)	39 (2)	421 (2)
H(4)	403 (2)	140 (2)	H(4)	162 (2)	494 (2)
H(5)	284 (2)	125 (2)	H(5)	250 (2)	604 (2)
H(6en)	244 (2)	-18 (2)	H(6en)	125 (2)	508 (2)
H(6ex)	187 (2)	-7 (2)	H(6ex)	170 (2)	581 (2)
H(7en)	133 (2)	37 (2)	H(7en)	10 (2)	625 (2)
H(7ex)	83 (2)	53 (2)	H(7ex)	60 (2)	688 (2)
H(8)	90 (2)	228 (2)	H(8)	58 (2)	816 (2)
H(9en)	187 (2)	277 (2)	H(9en)	212 (2)	795 (2)
H(9ex)	138 (2)	180 (2)	H(9ex)	192 (2)	770 (2)
H(10en)	347 (2)	301 (2)	H(10en)	101 (2)	656 (2)
H(10ex)	360 (2)	213 (2)	H(10ex)	34 (2)	558 (2)
H(15)	429 (2)	144 (3)	H(15)	294 (2)	523 (3)
H(16)	543 (2)	173 (3)	H(16)	418 (2)	456 (3)
H(17)	575 (2)	359 (3)	H(17)	483 (2)	574 (3)
H(18)	498 (2)	491 (3)	H(18)	431 (2)	742 (3)
H(19)	379 (2)	467 (3)	H(19)	305 (2)	792 (3)

5% Carbowax 20M on Chromosorb W-AW (60–80 mesh).

Melting points are uncorrected and were taken on a Thomas Hoover capillary melting point apparatus for mp <200 °C and a Meltemp (Laboratory Devices) apparatus for mp >200 °C.

**Cycloaddition of Maleic Anhydride to 1.** The reaction was carried out as described in ref 4. The reaction mixture was worked up after 19 h of standing at room temperature, although it appeared in a later experiment that the reaction was already complete after about 0.5-h. There was no difference in product composition between the 0.5-h and the 19-h reactions.

A 1-g sample of the mixture so formed was used on a chromatography column (length 10 in.; id 0.5 in.), using silica gel 100–200 mesh from Davison Chemical. The first fraction (eluant petroleum ether/ether, 1:1 v/v) contained 150 mg of a mixture of **2** and **3** (1:2 w/w), the second fraction (eluant ethyl ether) contained 560 mg of **2** and **3** (1:1 w/w), and the third fraction (eluant ethyl ether) consisted of a mixture of **2**, **3**, and the diacid of **3** (7:2:1 w/w/w) and weighed 240 mg.

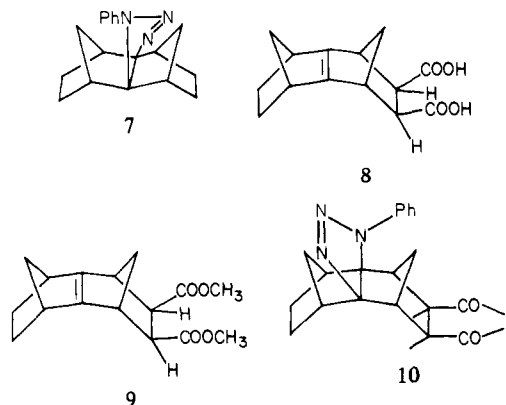
**2:** mp 96 °C (lit.<sup>1</sup> 96 °C); IR (KBr) 1870, 1785 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.60 (m, 2 H), 3.40 (m, 2 H), 2.96 (m, 2 H), 1.5–1.8 (m, 4 H), 0.9–1.5 (m, 4 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 171.92, 153.60, 60.36, 52.82, 48.73, 45.68, 42.04, 26.18.

**3:** mp 112–116 °C; IR (KBr) 1870, 1785 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.40 (m, 2 H), 3.02 (m, 2 H), 2.78 (m, 2 H), 1.0–1.8 (series of m, 6 H), 0.64–0.84 (m, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 171.66, 154.12, 50.22, 48.86, 47.89, 45.03, 42.69, 24.88. The Diacid **8:** mp 155–160 °C; IR (CHCl<sub>3</sub>) 2400–3400, 2960, 2870, 1700, 1400, 1320, 1250, 1110, 905 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 10.20 (br s, 2 H), 3.20 (br s, 2 H), 3.02 (br s, 2 H), 2.42 (br s, 2 H), 2.12 (double m, 1 H), 0.7–1.8 (series of m, 7 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 180.23, 154.12, 50.61, 48.15, 46.98, 46.52, 42.75, 25.47.

**Addition of Phenyl Azide to 3.** To a solution of 230 mg (1 mmol) of **3** in ethyl acetate was added 108 mg (1 mmol) of phenyl azide, and the

mixture was stirred for 18 h. The precipitate formed was filtered off: mp 230–233 °C (lit.<sup>4</sup> 233–236 °C); IR (KBr) 2950, 2890, 1830, 1750, 1580, 1450, 1210, 1040, 900 cm<sup>-1</sup>; <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>) δ 7.30 (m, 4 H), 6.97 (m, 1 H), 4.17 (br s, 1 H), 3.80 (br s, 1 H), 2.50–3.20 (series of m, 4 H), 1.96–2.35 (m, 2 H), 1.0–1.85 (series of m, 6 H); <sup>13</sup>C NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>) δ 175.29, 175.10, 139.89, 130.99, 123.51, 115.91, 100.25, 76.28, 48.73, 46.33, 45.29, 26.70, 25.59.

When a mixture of **2** and **3**, as obtained from the reaction of **1** with maleic anhydride, was made to react with phenyl azide, the triazolone adduct **10** precipitated out of the reaction mixture, whereas almost pure



**2** could be recovered from the filtrate. In a separate experiment it was shown that no reaction had taken place between **2** and phenyl azide.

**Addition of Phenyl Azide to the Dibasic Acid 8.** To a solution of 50 mg (0.22 mmol) of **8** in chloroform was added 100 mg of phenyl azide (0.84 mmol). The mixture was stirred for 24 h at room temperature. The solvent was removed to leave a yellowish liquid, from which the excess of phenyl azide was removed by column chromatography using petroleum ether as eluant. The residue after eluting with ether/chloroform (1:1 v/v) showed the following: IR (CHCl<sub>3</sub>) 2400–3400, 2970, 2890, 1710, 1600, 1470, 1340, 1125, 1050, 920 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.08 (br s, 2 H), 6.8–7.4 (m, 5 H), 3.96 (m, 2 H), 3.20 (br s, 2 H), 2.96 (br s, 2 H), 2.0–2.6 (series of m, 2 H), 0.8–1.8 (series of m, 6 H).

*syn*-Sesquiorbornene and its phenyl azide adduct **7** were prepared by the methods of Paquette and co-workers.<sup>8</sup> The sample of the triazoline adduct **7** used for the structure determination showed the following: mp 127–130 °C; IR (KBr) 3050, 2960, 2940, 1600, 1495, 1475, 1450, 1345, 1280, 1040 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.16 (m, 3 H), 6.6–7.1 (m, 2 H), 2.88 (m, 2 H), 2.60 (m, 2 H), 1.0–2.40 (series of m, 12 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 139.50, 129.23, 121.50, 114.68, 99.41, 45.16, 45.03, 43.47, 25.53, 24.50. <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>) showed also the absorption at δ 75.63, which was hidden under the CDCl<sub>3</sub> triplet when CDCl<sub>3</sub> was the solvent.

**Derivatization of 8 Using Diazomethane.** To a solution of **8** in chloroform was added dropwise a solution of diazomethane in tetrahydrofuran until the color of the reaction mixture remained that of diazomethane. There was an instantaneous, vigorous reaction upon the addition of the first drops of diazomethane. The solvents and the excess of diazomethane were evaporated under reduced pressure, and the diester **9** was obtained in quantitative yield: IR (neat) 2960, 2880, 1730, 1430, 1350, 1320, 1270, 1250, 1190, 1110, 1045, 910, 730 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.64 (s, 6 H), 3.20 (br s, 2 H), 3.03 (br s, 2 H), 2.44 (br s, 2 H), 2.0–2.25 (m, 1 H), 0.7–1.90 (series of m, 7 H); mass spectrum, *m/e* 276, 248, 217, 185, 132, 104, 91, 77. Diazomethane, added to a solution of **3** in chloroform, did not react; unchanged **3** was recovered after about 20 min.

**Reactions of 2 and 3 with MCPBA.** To 230 mg (1 mmol) of separate solutions of **2** and **3** in 15 mL of dichloromethane was added 200 mg (1.14 mmol) of *m*-chloroperbenzoic acid in 15 mL of dichloromethane. After 20 min of reaction at room temperature, more than 95% of **2** was still present and about 40% of **3** had reacted. After about 8 h of reaction, no **3** was left, whereas after 33 h of reaction, still 60% of **2** was present. These observations indicate that the *syn*-*exo* anhydride **3** is about a hundred times as reactive toward MCPBA as the *anti*-*endo* anhydride **2**. The product from **3** showed the following: mp 164–168 °C; IR (CHCl<sub>3</sub>) 2980, 2900, 1865, 1785, 1260, 1090, 1030, 920, 800 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.68 (br s, 2 H), 3.25 (br s, 2 H), 2.88 (br s, 2 H), 1.0–2.2 (series of m, 6 H), 0.6–0.85 (m, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 171.71, 57.44, 47.95, 44.90, 40.74, 38.98, 33.40, 26.90.

**X-ray Analysis.** All data were collected on a Syntex P2<sub>1</sub> diffractometer system by the  $\theta$ - $2\theta$  scanning technique using a variable-scan speed and graphite-monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). Room-temperature lattice parameters were refined by a least-squares procedure using 15 reflections whose angles were measured by a centering routine associated with the diffractometer. Space groups were determined by systematic absences and statistics. Periodically monitored reference reflections showed no significant changes in intensity. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The direct-methods program MULTAN<sup>11</sup> was used to calculate phases

for the larger  $|E|$  values. The phase set with the largest combined figure of merit revealed the molecular framework in all cases. Difference Fourier calculations yielded the coordinates of all hydrogen atoms after anisotropic refinement of the heavy atoms. Full-matrix least-squares refinements were terminated when the *R* value became stationary. *R* is defined as  $\sum ||F_o| - |F_c|| / \sum |F_o|$ . The function minimized in the refinement was  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1/\sigma(I)$  was determined from counting statistics. H atom thermal parameters were not refined.

Final difference maps were checked for any residual electron density, and the shift/error for all parameters was examined. Atomic scattering factors were calculated by the X-RAY program.<sup>12</sup> Bond distances and valence angles are presented in Tables I and II. Nonbonding intramolecular distances and interplanar angles are presented in Tables III and IV while intermolecular distances are listed in Table V.

***anti*-Sesquiorbornene *endo*-Anhydride (2).** C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>; *M<sub>r</sub>* = 230.27; crystal dimension 0.90 × 0.66 × 0.13 mm; space group *Pbca*; *a* = 12.024 (2), *b* = 23.799 (5), *c* = 7.845 (2) Å; *V* = 2244.9 (8) Å<sup>3</sup>; *Z* = 8; *d*<sub>calcd</sub> = 1.36 g cm<sup>-3</sup>;  $\mu = 7.88$  cm<sup>-1</sup>. Of the 1830 independent reflections measured 1446 had intensities greater than 3 $\sigma(I)$ . Final *R* = 0.057, 0.35 e Å<sup>-3</sup> largest peak in the difference Fourier and 0.1 average shift/error for all parameters. Atomic positional parameters are presented in Table VI.

***syn*-Sesquiorbornene *exo*-Anhydride (3).** C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>; *M<sub>r</sub>* = 230.27; crystal dimension 0.83 × 0.50 × 0.45 mm; space group *P2<sub>1</sub>/c*; *a* = 12.421 (3), *b* = 8.488 (2), *c* = 12.445 (2) Å;  $\beta = 121.89$  (1)°; *V* = 1114.1 (4) Å<sup>3</sup>; *Z* = 4; *d*<sub>calcd</sub> = 1.37 g cm<sup>-3</sup>;  $\mu = 7.94$  cm<sup>-1</sup>. Of the 1832 independent reflections measured 1638 had intensities greater than 3 $\sigma(I)$ . Five reflections were omitted because of extinction. Final *R* = 0.074, 0.2 e Å<sup>-3</sup> largest peak in the difference Fourier and 0.09 average shift/error for all parameters. Atomic positional parameters are presented in Table VII.

***syn*-Sesquiorbornene-2-yl Phenyl Sulfone (6).** C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>S; *M<sub>r</sub>* = 300.42; crystal dimension 0.25 × 0.16 × 0.16 mm; space group *P2<sub>1</sub>/c*; *a* = 6.405 (1), *b* = 11.662 (2), *c* = 20.241 (2) Å;  $\beta = 96.98$  (1)°; *V* = 1500.7 (5) Å<sup>3</sup>; *Z* = 4; *d*<sub>calcd</sub> = 1.33 g cm<sup>-3</sup>;  $\mu = 18.71$  cm<sup>-1</sup>. Of the 2513 independent reflections measured, 1798 had intensities greater than 3 $\sigma(I)$ . Final *R* = 0.048, 0.17 e Å<sup>-3</sup> largest peak in the difference Fourier and 0.09 average shift/error for all parameters. Atomic positional parameters are presented in Table VIII.

***syn*-Sesquiorbornene-Phenyl Azide Adduct (7).** C<sub>18</sub>H<sub>21</sub>N<sub>3</sub>; *M<sub>r</sub>* = 279.39; crystal dimension 0.5 × 0.4 × 0.4 mm; space group *P2<sub>1</sub>/c*; *a* = 17.882 (3), *b* = 12.355 (2), *c* = 14.434 (3) Å;  $\beta = 113.02$  (1)°; *V* = 2935.0 (9) Å<sup>3</sup>; *Z* = 8; *d*<sub>calcd</sub> = 1.26 g cm<sup>-3</sup>;  $\mu = 5.97$  cm<sup>-1</sup>. Two independent molecules in the asymmetric unit. Of the 4002 independent reflections measured, 3015 had intensities greater than 3 $\sigma(I)$ . Final *R* = 0.057, 0.2 e Å<sup>-3</sup> largest peak in the difference Fourier and 0.1 average shift/error for all parameters. Atomic positional parameters are listed in Table IX.

In Tables VII–IX the usual practice is followed whereby *X* = *x/a*, *Y* = *y/b*, and *Z* = *z/c*, the dimensions of the unit cell being *a*, *b*, and *c*.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters and structure factors (70 pages). Ordering information is given on any current masthead page.