2 H), 3.61 (m, 2 H), 2.80 (s, 2 H), 1.68 (d, J = 7.0 Hz, 2 H), 1.60 (s, 6 H), 1.57 (s, 6 H), 0.91 (dd, J = 11.5 and 4.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.39, 152.36, 146.84, 140.40, 131.88, 129.20, 128.58, 126.30, 115.79, 109.12, 48.44, 47.80, 43.37, 25.42, 20.19, 19.92; MS, m/z (M^+) calcd 385.2041, obsd 385.2043.

For **17c**: 29 mg (40%) of colorless needles, mp 139-140 °C (from hexanes); IR (KBr, cm^{-1}) 3000, 2985, 2985, 2930, 2860, 1717, 1500, 1445, 1370, 1190; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.36 (m, 3 H), 7.11-7.09 (m, 2 H), 3.91 (s, 2 H), 3.44 (m, 2 H), 2.94 (s, 2 H), 1.74 (d, J = 7.3 Hz, 2 H), 1.54 (s, 6 H), 1.49 (s, 6 H), 1.16 (dd, J = 10.5 and 4.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.61, 155.40, 150.79, 142.86, 132.02, 129.16, 128.55, 126.39, 112.92, 108.70, 49.13, 49.74, 42.19, 25.84, 19.70, 19.40; MS, m/z (M^+) calcd 385.2042, obsd 385.2050.

4a,8a-Epoxy-1,2,3,4,4a,5,6,7,8,8a-decahydro-9-(diphenylmethylene)-*N*-phenyl-*syn*-(1,4:5,8-dimethano)naphthalene-6,7-dicarboximide (18a). *m*-Chloroperbenzoic acid (11 mg, 0.064 mmol) was added to a solution of **16a** (30 mg, 0.064 mmol) in methylene chloride (5 mL) at 0 °C, and the mixture was stirred at the same temperature for 3 h and then at -10 °C for 15 h. After warming to 20 °C, the mixture was washed with 5% aqueous sodium bisulfite solution (2 × 5 mL), 10% aqueous sodium bicarbonate solution (1 × 5 mL), and water (until neutral) and then dried, filtered, and evaporated to give a colorless solid. Purification using medium-pressure silica gel chromatography (elution with 20% ethyl acetate in petroleum ether) provided 23 mg (74%) of **18a** as a colorless solid, mp 294-295 °C (from ethyl acetate); IR (KBr, cm^{-1}) 3000, 1720, 1500, 1390, 1190, 700, 690; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.07 (series of m, 15 H), 3.94 (s, 2 H), 3.66 (s, 2 H), 2.95 (m, 2 H), 1.92 (d, J = 9.7 Hz, 1 H), 1.76 (m, 4 H), 0.85 (d, J = 9.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.17 (s), 140.47 (s), 136.60 (s), 133.66 (s), 131.64 (s), 129.39 (d), 129.00 (d), 128.89 (d), 128.18 (d), 127.13 (d), 126.48 (d), 57.14 (s), 47.93 (d), 46.88 (d), 40.92 (d), 37.51 (t), 26.60 (m); MS, m/z (M^+) calcd 485.1991, obsd 485.2015.

Acknowledgment. We thank the National Institutes of Health for support of this research program through Grant CA-12115.

Registry No. 1, 6675-72-5; **10**, 93255-09-5; **12**, 98509-34-3; **13**, 84988-39-6; **14**, 98509-32-1; **15**, 98509-33-2; **16a**, 98509-35-4; **16b**, 98509-36-5; **16c**, 98509-37-6; **17c**, 98575-31-6; **18a**, 98509-38-7; **19**, 98575-30-5; benzophenone, 119-61-9; acetone, 67-64-1; *N*-phenylmaleimide, 941-69-5.

Supplementary Material Available: Crystallographic details, tables of positional and thermal parameters, as well as unit cell drawings for **13**, **14**, and **15** (Tables VI-VIII, Figures 5-7) (10 pages). Ordering information is given on any current masthead page.

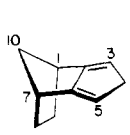
Electronic Control of Stereoselectivity 31. π-Facial Course of Diels-Alder Cycloadditions to 10-Isopropylideneisodicyclopentadiene[1]

Leo A. Paquette,* Tina M. Kravetz, and Leh-Yeh Hsu[2]

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received April 1, 1985*

Abstract: 10-Isopropylideneisodicyclopentadiene (**3**) has been synthesized and its stereoselective behavior during Diels-Alder cycloaddition to *N*-methyltriazolinedione, dimethyl acetylenedicarboxylate, *N*-phenylmaleimide, *p*-benzoquinone, and phenyl vinyl sulfone examined in detail. Structural assignments to the adducts were made on the basis of spectral data, X-ray crystal structure determination, and chemical reactivity, especially sensitivity to triplet oxygen leading to epoxide formation. Less control of π-face selectivity was seen relative to the control exhibited by the parent isodicyclopentadiene. In the case of benzoquinone, the Alder above-plane adduct was observed to be capable of retrograde fragmentation and conversion to two isomeric compounds. A second observation of interest was the isolation of **23**, only the second known example of Alder below-plane bonding in this series. The data are shown to conform plausibly to the Gleiter-Paquette electronic model for these reactions and not to fit satisfactorily the Brown-Houk torsional strain hypothesis.

Although Diels-Alder cycloadditions to isodicyclopentadiene (**1**) have been scrutinized by several groups,[3-6] no general agreement has been reached concerning the origin of the remarkable π-facial stereoselectivities that are encountered.[7-10]



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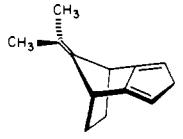

3

From among the various hypotheses offered to date, two remain as viable proposals worthy of more detailed scrutiny. The first, suggested by Gleiter and Paquette,[5b,8] is founded on the evident strong admixing of the norbornyl σ-orbital framework with the diene π_s orbital. The result is a notable disrotatory tilting within the terminal pπ orbitals toward the methano bridge. The working model invokes direct involvement of these subjacent orbital effects in the control of anti-Alder [4 + 2] cycloaddition, with preferred below-plane capture of the dienophile in order to minimize antibonding interactions. The contrasting Alder arrangement of the reactants seemingly favored by the more reactive dienophiles comes under ordinary steric control and leads to above-plane bonding.[5e]

(1) Part 30. Gallucci, J. C.; Kravetz, T. M.; Green, K. E.; Paquette, L. A. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Author to whom queries concerning the X-ray analyses should be directed.

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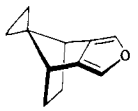
Table I. Correlation of p_y Coefficients at C(3)–C(5) of Various Isodicyclopentadiene Systems with Experimental Diels–Alder Ratios

compd	p_y coeff	product ratios (above-plane below-plane)[a]				
		PM	BQ	benzyne	DMAD	MTAD
1	−0.014	0:100	0:100	0:100	0:100	100:0
2	−0.007	54:46	61:39		32:68	50:50
3	+0.01	50:50	54:46[b]		0:100	0:100
	+0.018	100:0		100:0	100:0	
28						

[a] PM = *N*-phenylmaleimide; BQ = *p*-benzoquinone; DMAD = dimethyl acetylenedicarboxylate; MTAD = *N*-methyltriazolinedione. [b] This ratio pertains to the relative amounts of **15** and **16**; the Alder adduct **17** is not included because of inherent stereochemical differences. However, its inclusion would favorably enhance the extent of above-plane attack to 68%.

Brown and Houk attribute the observed stereoselectivities instead exclusively to torsional and steric control.[6] In their view, the downward (endo) flexing of the incipient norbornene double bond[11] substantially relieves torsional strain between cyclopentadiene ring carbons and bridgehead C–H bonds. Therefore, as long as overriding steric effects are not present in either reactant, the more staggered arrangement will be energetically more accessible and bottom attack will prevail.

The latter explanation does not allow for possible long-range electronic modulation of stereoselectivity in these systems. Rather, the focus is entirely on structural geometry, particularly the spatial arrangement of bonds in the central segment of the isodicyclopentadiene. On the other hand, the disrotation concept advanced by us is based on a superpositioning of electronic contributions from the σ frame and diene π network. Consequently, the extent of disrotation and, in fact, its precise direction should be capable of modification by through-bond (not through-space[12]) electronic changes of proper magnitude.

We have shown by X-ray analysis of isodicyclopentafulvenes that positioning of a spirocyclopropyl substituent at C-10 as in **2** does not induce measurable dihedral angle changes relative to **1**.[1] However, an appreciable alteration in the p_y contribution (σ component) to the wave function does materialize (Table I). This fact translates into a decrease in, but not reversal of, π-orbital tilting within the subjacent MO of **2**. A lessening of its predilection for below-plane [4 + 2] cycloaddition should, on this basis, be encountered. This result has been confirmed experimentally.[13a]

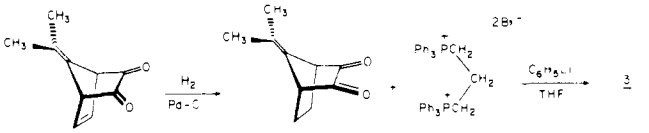
A somewhat greater alteration in the magnitude of the p_y coefficient in π_s has been calculated for **3** by MNDO methods (Table I).[14] In the preceding paper, we have already established that the structural features in a fulvene related to **3** compare closely to those of isodicyclopentafulvene.[1] The dichotomy is therefore clear. According to Brown and Houk, all three dienes should exhibit entirely comparable stereoselectivity in their Diels–Alder reactions because of the interplay of closely similar torsional effects. In contrast, the Gleiter–Paquette model requires that the ability of **2** and **3** to control the preferred approach to dienophile be measurably diminished. The behavior of **3** will be shown to correspond to the latter guidelines.

In this connection, note should be taken of the fact that substitution of the isodicyclopentadiene framework at C-10 as in **2** and **3** can exert no direct steric effect on bottom approach. Furthermore, the two substitution plans essentially bracket the original methylene group in size, the cyclopropane ring being somewhat more space-filling and the isopropylidene group less. Notwithstanding, all three arrangements appear too remote to have any direct kinetic consequence on anti-Alder above-plane cycloaddition as well.

Results

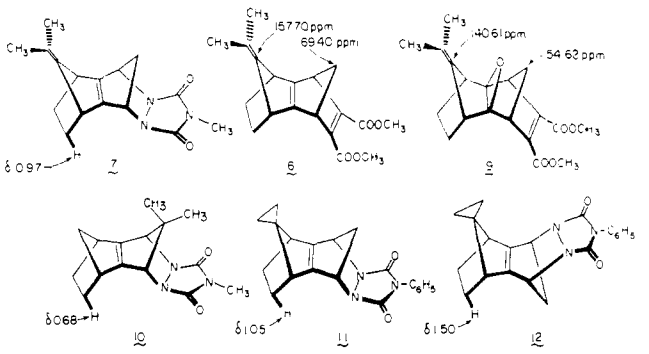
To arrive at **3**, the known α-diketone **4**[15] was hydrogenated catalytically, and **5** was subjected to twofold Wittig condensation with bis phosphonium salt **6**.[16]

In the presence of the highly reactive dienophiles *N*-methyltriazolinedione and dimethyl acetylenedicarboxylate, **3** entered exclusively into below-plane cycloaddition to give adducts **7** and **8**, respectively. The stereochemistry assigned to **7** was arrived



4 **5** **6** **3**

at principally on the basis of a comparative ^{1}H NMR analysis involving **10**–**12**. In particular, the highly shielded nature of the endo protons on the ethano bridge in **7** compares very favorably with known operation of the phenomenon in diaza-*syn*-sesquinorbornenes **10** and **11**.[5e,13] In the alternative structural as-



signment present in **12**, the urazole ring is no longer proximate to these hydrogens and a downfield shift of approximately 0.40 ppm becomes evident ($CDCl_3$ solutions).

The formulation for **8** was similarly suggested by the shielding experienced by its endo ethano protons (δ 0.57). Unequivocal chemical confirmation was gained by its facile air oxidation to deliver epoxide **9**, a reaction uniquely characteristic of *syn*-sesquinorbornadienes.[17] In addition, the consequences of oxirane magnetic anisotropy[18] are to shield *both* apical carbons in **9** relative to **8** (see formulas).

(11) *syn*-Sesquinorbornenes feature significant π-tilting in the endo direction at their central double bond. The experimental facts and a theoretical analysis may be found in: Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980.

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Table II. Crystallographic Data for **13**, **15**, and **17**.[a]

	13	15	17
formula wt, amu	345.445	280.370	280.370
space group	$C_{2/c}[C_{2h}^{8}$ no 15]	$P2_{1/c}$	$P2_{1/m}$
a, Å	28.470 (3)	15.210 (2)	8.1369 (8)
b, Å	11.473 (1)	6.260 (2)	11.386 (4)
c, Å	11.597 (5)	15.159 (2)	8.835 (2)
β, Å	99.95 (2)	95.06 (1)	113.85 (1)
vol, Å^3	3732.46	1437.57	748.61
Z	8	4	2
density (calcd), g/cm^3	1.229	1.297	1.244
radiation Mo Kα (λ = 0.7107)	Mo Kα (λ = 0.7107)	Mo Kα (λ = 0.7690)	Mo Kα (λ = 0.7660)
2θ limits	4–50°	4–50°	4–50°
scan speed, deg m^{-1}	0.65–5° (in ω)	0.65–5° (in ω)	0.65–5° (in ω)
scan type	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
scan angle, ω	0.75 + 0.35* tan θ	0.75 + 0.35* tan θ	0.75 + 0.35* tan θ
data collected	4229	2529	1119
unique data with $I > 3.0\sigma(I)$	2008	1634	699
reflections measd	$+h,+k,+l$	$+h,+k,+l$	$+h,+k,+l$
$R(F)$	0.045	0.059	0.044
$R_w(F)$	0.066	0.057	0.054

[a] All structures were solved on a Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation.

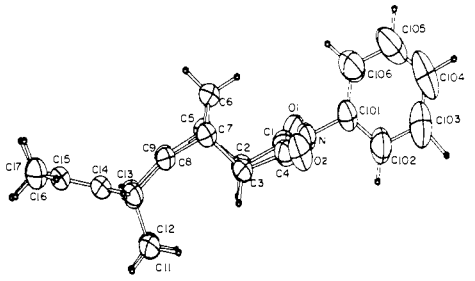
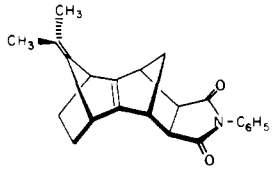


Figure 1. ORTEP drawing of **13** showing the numbering system used. Non-hydrogen atoms are drawn with 50% probability ellipsoids, while hydrogen atoms are drawn with an artificial radius.

Cycloadditions involving **3** and dienophiles of moderate reactivity resulted in capture from both faces of the diene. In the case of *N*-phenylmaleimide, adducts **13** and **14** were isolated in the approximate ratio of 1:1. These molecules differ appreciably



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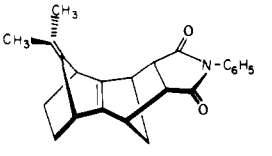

14

in their NMR spectra. For example, the endo ethano bridge protons of **13** (δ 0.89, $CDCl_3$) appear to higher field of those in **14** (δ 1.30) as expected for *syn*- and *anti*-sesquinorbornene networks, respectively.[13] In addition, the apical carbon atoms of **13** at 153.52 and 43.26 ppm are shifted to higher field than the corresponding carbons in **14** (156.89 and 44.27 ppm), again as observed in related molecules.[13] Since this pair of imides lack spin–spin coupling between the α-carbonyl and neighboring bridgehead protons, both must be of anti-Alder configuration.[19] When attempts to achieve regioselective epoxidation of the central double bond in **13** proved unsuccessful, recourse was made to X-ray crystallography. The data summarized in Tables II and

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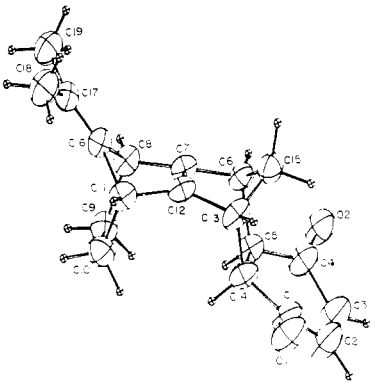


Figure 2. ORTEP drawing of **15** showing the numbering system used. Also see the caption to Figure 1.

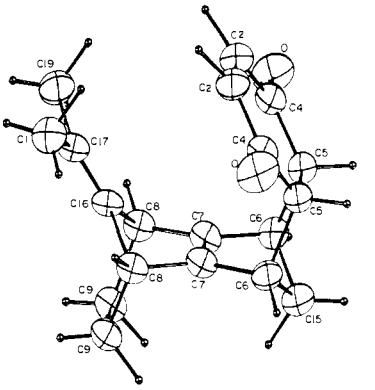
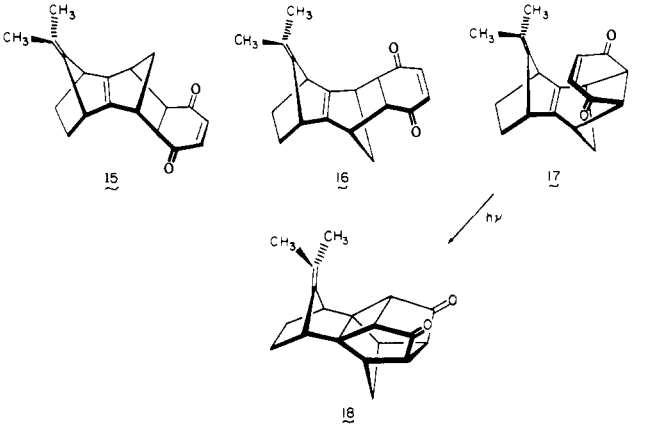


Figure 3. ORTEP drawing of **17** showing the numbering system used. Also see the capture to Figure 1.

IV–VIII and the ORTEP diagram of Figure 1 provide definitive confirmation of the preceding spectral correlations.

Admixture of equimolar amounts of **3** and benzoquinone in benzene at 20 °C, with the usual monitoring of the progress of the reaction by ^{1}H NMR at regular intervals, resulted in the formation of adducts **15**–**17** in a 1:1.17:1 ratio after 3 days. The

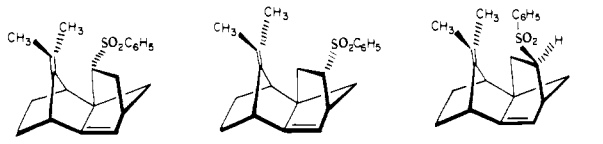


anti-Alder character of **15** and **16** was immediately apparent from the lack of coupling described above. This was not the situation with **17**, which furthermore was the only member of the triad to undergo intramolecular [2 + 2] photocyclization (with the formation of **18**). Unequivocal structural assignment to **15** was realized by X-ray crystal analysis (Tables II and IX–XIV, Figure 2). The second anti-Alder product must consequently be **16**. Through X-ray crystallography (Tables II and XV–XX, Figure 3), diketone **17** was established to be the end result of the above-plane dienophile capture.

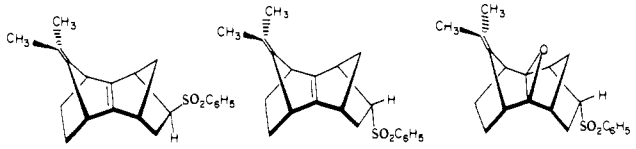
In an important ancillary development, **17** was observed slowly to undergo retrograde Diels–Alder reaction in solution at room temperature to produce a mixture of **15** and **16**. To our knowledge,

there has been reported no previous example in isodicyclopentadiene chemistry where reversibility has resulted either in structural isomerization or crossover in π-face stereoselectivity.[20] The rate at which **17** isomerizes is significantly slower than the rate of its formation. Thus, after standing for 9 days in $CDCl_3$, pure **17** was transformed to the extent of 61% into a mixture of **15** (30%) and **16** (31%). Following an elapsed time of 28 days, 19% of **17** remained and the levels of **15** (37%) and **16** (44%) were seen to closely approximate their relative proportion under kinetically controlled conditions. In fact, during the actual cycloaddition, the distribution of **15–17** gives no sign of deviating from 1:1.17:1 until days after **3** has been totally consumed.

Cycloaddition of **3** with the still less-reactive dienophile phenyl vinyl sulfone was performed in refluxing benzene for 18 h after no reaction was observed following several days at 20 °C. Five adducts were produced, individually separated by silica gel chromatography, and characterized spectroscopically and by chemical means as **19–23**. Three of these compounds (**19–21**)

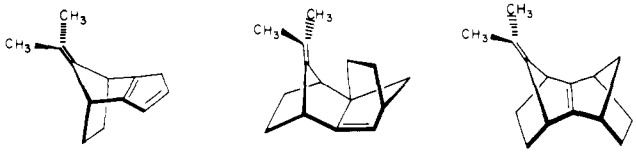


19 **20** **21**



22 **23** **24**

were determined to be so-called angular adducts derived from diene tautomer **25**, which must be in rapid equilibrium with **3** at these temperatures. The tendency of weakly reactive dienophiles to capture [1,5]-sigmatropic shift isomers such as **25** from the exo surface has previously been documented.[21] These sulfones



25 **26** **27**

were readily identified by the characteristic vinyl proton absorption of unit area in their ^1H NMR spectra. The specific assignment to **19** rests on the appreciable separation of its isopropylidene methyl singlets ($\Delta\delta$ = 0.16) relative to those in **20** (0.04) and **21** (0.02). The stereochemical disposition of the phenylsulfonly group in **20** and **21** is made with less certainty. However, their epimeric relationship is clearly defined by the observation that buffered sodium amalgam reduction of either adduct led identically to hydrocarbon **26**.

The common structural framework of **22** and **23** was also determined by independent reductive desulfonylation to **27**. The exo disposition of the phenylsulfonyl substituent in **22** follows from the high-field chemical shift (δ 0.74) of the endo-oriented protons of its ethano bridge, in line with preceding discussion. Sulfone **23** represents only the second below-plane Alder adduct to arise in the isodicyclopentadiene area.[23] The substance apparently suffers from high levels of nonbonded steric strain on its concave surface, as it was observed to undergo oxidation and formation of **24** upon exposure to the atmosphere for several days. Sulfone **22** is inert to air. As expected from precedent, the apical methylene carbon in **24** is shielded relative to its chemical shift in **23**. As with epoxide **9**, the trigonal isopropylidene carbon in **24** is deshielded (by 7.5 ppm) relative to its precursor since this atom is positioned beyond the boundary of the anisotropy cone generated by the oxirane ring.[17b]

Discussion

This investigation has led to two observations unprecedented for isodicyclopentadiene Diels–Alder chemistry. The formation of **17** and its isomerization to **15** and **16** become the prototype example of a kinetically controlled product that is not only sensitive to retrograde fragmentation but can also serve as progenitor to adducts other than itself. The isolation of **23** in 17% yield constitutes the second instance in which an Alder below-plane [4 + 2] addition has occurred. Although phenyl vinyl sulfone has given no prior indication of this particular stereoselectivity, the example is perhaps one of the more allowed possibilities because of the increased length of C–S bonds.

Notwithstanding these interesting facets, it is the π-face stereoselectivity exhibited by **3** that is most relevant. According to MNDO calculations, the orbital sequence in this isodicyclopentadiene is as follows: −9.06 (π_-), −9.66 (π_{ext}), and −10.47 eV (π_+).[14] The p_y coefficient in π_+ is 0.01. Comparison of this value with closely related congeners (Table I) suggests that the terminal diene orbitals in **3** should be tilted to an extent and in a direction comparable to that in **2**, but less than that in **1**. Although these guidelines indicate that dienophile capture from the bottom face should still be preferred, this preference should be less than that for **1**. Our experimental observations disclose that a reasonable similarity in stereoselectivity is manifested in **2** and **3**. Certain differences are, of course, in evidence. An adduct comparable to **17** is not formed in the case of **2** because of increased steric bulk in the vicinity of the apical carbon that discourages Alder capture from the top surface of the diene. With **3**, both *N*-methyltriazolinedione and dimethyl acetylenedicarboxylate add exclusively from below-plane. Reduced stereoselectivity is displayed by **2** toward these more reactive dienophiles, in agreement with a greater alteration in the through-bond contributions arising from within the norbornyl orbital framework. Therefore, when specific attention is given to the internal consistency between product distribution and the Gleiter–Paquette orbital-tilting hypothesis, the correlation is seen to be quite good despite its time-independent static focus on ground-state electronic effects.

Correspondence with the Brown–Houk torsional control argument is much less satisfactory. Their analysis requires that any modulation of stereoselectivity be intimately linked to changes in the dihedral angle relationship between the norbornyl bridgehead C–H bonds and those central to the cyclopentadiene ring. However, X-ray analyses of crystalline fulvenes derived from **1–3** reveal conclusively that little or no dihedral angle modification occurs across this series.[1] This analysis can plausibly be extended to include the furan analogue of **28** (Table I).[13a] Despite this homogeneous structural element, stereoselectivity varies considerably. The fit is therefore rather imperfect.

Finally, the X-ray analyses of **13**, **15**, and **17** (Table II) have provided additional insight into the inherent potential for deviation from planarity about the central double bond in *syn*-sesquinorbornenes. In **13** and **15**, there are found interplanar deformations

(20) In point of fact, only two examples of reversibility have been uncovered to date. (2-Norborneno)[*c*]furan adds maleic anhydride only in anti-alder fashion from the bottom face.[7b] This substance quickly reached equilibrium with its educts at 77 °C, but subsequent readdition leads to no other isomeric compound. Entirely comparable behavior was independently observed for 4,7-dihydro-2-isopropylidene-4,7-methano-2*H*-indene with the same end result.[17b]

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of 15.4° and 16.3°, respectively, with the folding occurring in a typical downward fashion. These values conform in magnitude to the extent of equilibrium nonplanar character encountered in related molecules.[1,5a,b,6a,7b,21a,22] The dihedral angle in **17** at 1.4° is significantly different from that in **15**. Essentially flat π bonds are present in most, though not all *anti*-sesquinorbornenes. Adduct **17** conforms to the more general trend despite the endo orientation of its cyclohexenedione moiety.

Experimental Section

7-(1-Methylethylidene)bicyclo[2.2.1]heptane-2,3-dione (5). A solution of **4** (3.07 g, 0.019 mol) in ethyl acetate (150 mL) containing 10% palladium on carbon was hydrogenated at atmospheric pressure. Upon consumption of 1 M equivalent of hydrogen, the catalyst was removed by filtration through a Celite pad, and the filtrate was evaporated to afford 2.95 g (98%) of **5** as bright-orange crystals, mp 125–127 °C (from hexanes); IR ($CDCl_3$, cm^{-1}) 3010, 2980, 1755, 1445, 1198; ^1H NMR (300 MHz, $CDCl_3$) δ 3.53 (m, 2 H), 2.06–2.00 (m, 2 H), 1.81–1.76 (m, 2 H), 1.75 (s, 6 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 198.09, 131.72, 127.19, 52.38, 23.96, 21.14; MS m/z (M^+) calcd 164.0837, obsd 164.0832.

10-(1-Methylethylidene)tricyclo[5.2.1.0^{2,6}]deca-2,5-diene (3). A freshly titrated ether solution of phenyllithium (6.0 mmol) was added to a mixture of bisphosphonium salt **6** (2.18 g, 3.0 mmol) in anhydrous tetrahydrofuran (20 mL) and stirred at 20 °C for 10 h. A solution of **5** (0.50 g, 3.0 mmol) in anhydrous tetrahydrofuran (5 mL) was added dropwise, and stirring was continued at 20 °C for 2 h and at 45 °C for 48 h. After being cooled to 20 °C, the mixture was diluted with water (20 mL) and extracted with pentane (3 × 10 mL). The combined organic extracts were washed with water (2 × 5 mL), dried, filtered, and freed of solvent to give a deep brown oily solid. Preparative thin-layer silica gel chromatography (elution with petroleum ether) provided 115 mg (22%) of **3** as a colorless solid, mp 48–49 °C (sublimation); IR (neat, cm^{-1}) 3075, 3000, 2935, 1453, 1370, 1107; ^1H NMR (300 MHz, $CDCl_3$) δ 5.68 (m, 2 H), 3.53 (m, 2 H), 3.08 (m, 2 H), 1.86–1.83 (m, 2 H), 1.65 (s, 6 H), 1.44–1.39 (m, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 153.70, 145.21, 113.89, 113.58, 44.20, 39.71, 28.45, 20.38; MS, m/z (M^+) calcd 172.1252, obsd 172.1207.

***N*-Methyltriazolinedione Addition to 3.** A solution of **3** (72 mg, 0.42 mmol) in deoxygenated ethyl acetate (1.5 mL) was cooled to −78 °C and was treated dropwise with a solution of 4-methyl-1,2,4-triazoline-3,5-dione (47 mg, 0.42 mmol) in the same solvent (2 mL). The reaction mixture was allowed to warm to 20 °C whereupon the solvent was evaporated to yield 110 mg (92%) of **7** as a colorless solid, mp 145 °C d (from ethyl acetate); IR (KBr, cm^{-1}) 3010, 2940, 1720, 1450, 1182, 1020; ^1H NMR (300 MHz, C_6D_6) δ 4.72 (t, J = 1.5 Hz, 2 H), 3.22 (m, 2 H), 2.41 (s, 3 H), 1.74 (dt, J = 8.7 and 1.9 Hz, 1 H), 1.60–1.56 (m, 2 H), 1.37 (s, 6 H), 0.97 (m, 2 H), 0.90 (t, J = 8.7 and 1.4 Hz, 1 H), ^{13}C NMR (20 MHz, $CDCl_3$) δ 160.65 (s), 153.12 (s), 150.50 (s), 106.79 (s), 65.60 (d), 51.10 (t), 40.95 (d), 25.81 (m), 25.17 (q), 19.42 (q); MS, m/z (M^+) calcd 285.1477, obsd 285.1488.

Anal. Calcd for $C_{16}H_{19}N_3O_2$: C, 67.35; H, 6.71. Found: C, 67.18; H, 6.72.

Dimethyl Acetylenedicarboxylate Addition to 3. A solution of **3** (100 mg, 0.58 mmol) in deoxygenated chloroform (3 mL) was treated with a solution of dimethyl acetylenedicarboxylate (91 mg, 0.64 mmol) in the same solvent (2 mL) and was stirred at 20 °C for 2 h. Solvent and excess dienophile were removed in vacuo, and the residue was purified by medium-pressure liquid chromatography on silica gel (elution with 12% ethyl acetate in petroleum ether) to give 69 mg (38%) of **8** as a colorless oil; IR ($CDCl_3$, cm^{-1}) 3000, 2960, 2935, 1730, 1715, 1440, 1263; ^1H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 2 H), 3.76 (s, 6 H), 3.57 (s, 2 H), 2.47 (dt J = 7.0 and 1.8 Hz, 1 H), 2.18 (dt, J = 7.0 and 1.3 Hz, 1 H), 1.58 (s, 6 H), 1.46 (d, J = 7.0 Hz, 2 H), 0.57 (dd, J = 11.3 and 3.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.91 (s), 157.70 (s), 150.43 (s), 147.22 (s), 109.35 (s), 69.46 (t), 52.48 (d), 52.04 (q), 43.53 (d), 22.38 (m), 19.96 (q); MS, m/z (M^+) calcd 314.1518, obsd 314.1531.

Air Oxidation of 8. A solution of **8** (40 mg, 0.13 mmol) in $CDCl_3$ (0.5 mL) was exposed to atmospheric oxygen for 22 h, and the solvent was removed in vacuo. Preparative thin-layer silica gel chromatography (elution with 20% ethyl acetate in petroleum ether) of the residue gave, in addition to recovered starting material, 15 mg (34%) of **9** as colorless needles; mp 92–93 °C (from hexanes); IR ($CDCl_3$, cm^{-1}) 3000, 2965, 1715, 1440, 1263; ^1H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 6 H), 3.46 (s, 2 H), 3.21 (s, 2 H), 2.12 (dt, J = 8.2 and 1.5 Hz, 1 H), 1.80 (dt, J = 8.2 and 1.4 Hz, 1 H), 1.57 (s, 6 H), 1.48 (d, J = 10.0 Hz, 2 H), 1.20 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 165.00 (s), 149.61 (s), 140.41 (s), 114.79 (s), 64.33 (s), 54.62 (t), 52.32 (q), 48.55 (d), 41.59 (d), 24.40 (m), 19.99 (q); MS, m/z (M^+) calcd 330.1467, obsd 330.1431.

Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.08; H, 6.71. Found: C, 68.92; H, 6.74.

Cycloaddition of 3 with *N*-Phenylmaleimide. A solution of **3** (75 mg, 0.44 mmol) in benzene (3 mL) was treated with *N*-phenylmaleimide (75 mg, 0.44 mmol) at 20 °C. After 15 h, solvent was removed in vacuo, and the resulting oil was separated into its pure components by preparative thin-layer silica gel chromatography (elution with 10% ethyl acetate in petroleum ether). Two cycloadducts were isolated in a combined yield of 63%.

For **14**: 48 mg (32%); colorless solid, mp 149–150 °C (from hexanes); IR ($CHCl_3$, cm^{-1}) 3000, 2940, 1710, 1500, 1380, 1187; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49–7.38 (m, 3 H), 7.26–7.24 (m, 2 H), 3.52 (s, 2 H), 3.36 (s, 2 H), 2.85 (s, 2 H), 1.81 (m, 2 H), 1.62 (d, J = 9.7 Hz, 1 H), 1.49 (d, J = 9.7 Hz, 1 H), 1.46 (s, 6 H), 1.30 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.06, 156.89, 153.66, 131.94, 129.13, 128.59, 126.39, 104.41, 49.30, 46.76, 44.28, 41.36, 26.25, 19.12; MS, m/z (M^+) calcd 345.1729, obsd 345.1743.

Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71. Found: C, 79.73; H, 6.69.

For **13**: 46 mg (31%); colorless solid, mp 207–208 °C (from hexanes); IR ($CHCl_3$, cm^{-1}) 3000, 2930, 1710, 1500, 1378, 1185; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49–7.36 (m, 3 H), 7.26–7.23 (m, 2 H), 3.57 (m, 2 H), 3.55 (s, 2 H), 2.79 (s, 2 H), 1.70–1.66 (m, 3 H), 1.57 (s, 6 H), 1.50 (d, J = 8.6 Hz, 1 H), 0.89 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.80, 153.52, 147.74, 131.88, 129.17, 128.62, 126.33, 108.48, 48.46, 47.08, 43.26, 43.18, 25.27, 19.81; MS m/z (M^+) calcd 345.1728, obsd 345.1715.

Diels–Alder Reaction of 3 with Benzoquinone. A solution of **3** (40 mg, 0.233 mmol) and benzoquinone (25 mg, 0.233 mmol) in benzene (2 mL) was stirred at 20 °C for 3 days. Solvent was removed in vacuo, and the resulting oil was separated into its components by medium-pressure liquid chromatography on silica gel (elution with 11% ethyl acetate in petroleum ether) to afford three adducts in 92% combined yield.

For **16**: 22 mg (34%); pale-yellow oil; IR ($CDCl_3$, cm^{-1}) 3000, 2940, 2870, 1670, 1445, 1020; ^1H NMR (300 MHz, $CDCl_3$) δ 6.72 (s, 2 H), 3.39 (s, 2 H), 3.35 (m, 2 H), 2.44 (m, 2 H), 1.80–1.75 (m, 2 H), 1.41 (s, 6 H), 1.41–1.37 (m, 1 H), 1.30–1.21 (m, 3 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 199.63, 156.12, 153.82, 141.75, 113.64, 50.27, 49.63, 45.67, 41.27, 26.38, 19.10; MS, m/z (M^+) calcd 280.1463, obsd 280.1480.

For **15**: 19 mg (29%); pale-yellow crystals, mp 166–168 °C (from hexanes); IR (KBr, cm^{-1}) 3025, 2988, 2920, 1665, 1445, 1368, 1270, 1088; ^1H NMR (300 MHz, C_6D_6) δ 6.12 (s, 2 H), 3.34 (br s, 2 H), 3.32 (br s, 2 H), 1.90 (br s, 2 H), 1.45 (s, 6 H), 1.42 (m, 2 H), 1.33 (d, J = 10 Hz, 1 H), 0.95 (d, J = 10 Hz, 1 H), 0.55 (m, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 198.99, 153.06, 148.39, 141.94, 108.21, 50.53, 49.25, 45.29, 43.31, 25.42, 19.80; MS m/z (M^+) calcd 280.1464, obsd 280.1476.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.27; H, 7.19.

For **17**: 19 mg (29%); pale-yellow crystals, mp 139–140 °C (from hexanes); IR (KBr, cm^{-1}) 3010, 2920, 2865, 1670, 1440, 1275, 1118; ^1H NMR (300 MHz, $CDCl_3$) δ 6.37 (s, 2 H), 3.66 (m, 2 H), 3.27 (m, 2 H), 3.09 (m, 2 H), 1.70–1.66 (m, 2 H), 1.55 (d, J = 8.4 Hz, 1 H), 1.42 (d, J = 8.5 Hz, 1 H), 1.25 (s, 6 H), 1.14 (m, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 199.31, 153.63, 152.74, 140.73, 104.64, 52.00, 50.08, 48.80, 41.46, 26.45, 19.04; MS, m/z (M^+) calcd 280.1463, obsd 280.1446.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.22; H, 7.23.

Photocyclization of 17. A solution of **17** (13 mg mg, 0.046 mmol) in acetonitrile-d_3 (0.4 mL) in a Pyrex tube was irradiated with a bank of 3500-A lamps in a Rayonet reactor for 8 h. Evaporation of solvent gave 13 mg (100%) of **18** as a colorless solid; mp 204–205 °C (from ether); IR ($CDCl_3$, cm^{-1}) 2975, 2940, 2890, 1763, 1749, 1450, 1377, 1240, 1150, 1067; ^1H NMR (300 MHz, $CDCl_3$) δ 2.95 (m, 2 H), 2.77 (m, 2 H), 2.75 (m, 2 H), 2.28 (d, J = 12.0 Hz, 1 H), 2.19 (m, 2 H), 1.85 (d, J = 12.0 Hz, 1 H), 1.72 (s, 6 H), 1.58 (m, 2 H), 1.25 (m, 2 H); MS m/z (M^+) calcd 280.1463, obsd 280.1476.

Cycloaddition of 3 with Phenyl Vinyl Sulfone. A solution of **3** (152 mg, 0.88 mmol) and phenyl vinyl sulfone (223 mg, 1.33 mmol) in anhydrous benzene (4 mL) was heated to reflux for 18 h. Removal of solvent followed by medium-ressure liquid chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) gave five cycloadducts in a combined yield of 92% based on recovered phenyl vinyl sulfone.

For **19**: 8 mg (3%); colorless crystals, mp 126–127 °C (from hexanes); IR ($CDCl_3$, cm^{-1}) 2975, 2885, 1450, 1298, 1155, 1070; ^1H NMR (300 MHz, $CDCl_3$) δ 7.83–7.80 (m, 2 H), 7.58–7.48 (m, 3 H), 5.55 (m, 1 H), 3.76 (d, J = 4.0 Hz, 1 H), 3.20 (m, 1 H), 2.91 (m, 1 H), 2.87 (m, 1 H), 2.03 (d, J = 8.6 Hz, 1 H), 1.95–1.89 (m, 2 H), 1.87 (s, 3 H), 1.68 (s, 3 H), 1.51–1.50 (m, 1 H), 1.48–1.30 (m, 3 H); MS, m/z (M^+) calcd 340.1497, obsd 340.1504.

For **23**: 46 mg (17%); colorless needles, mp 74–75 °C (from hexanes); IR ($CDCl_3$, cm^{-1}) 2985, 2940, 1448, 1305, 1290, 1145, 1085; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92–7.83 (m, 2 H), 7.67–7.53 (m, 3 H), 3.35 (m, 1 H), 3.26 (m, 1 H), 3.24 (m, 1 H), 3.07 (m, 1 H), 2.90 (m, 1 H), 2.17–2.09 (m, 1 H), 2.03 (m, 1 H), 1.72–1.62 (m, 2 H), 1.51 (m, 1 H), 1.41 (s, 3 H), 1.39 (s, 3 H), 1.33 (m, 1 H), 1.16 (m, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 159.10 (s), 153.47 (s), 152.97 (s), 140.29 (s), 133.35 (d), 129.25 (d), 128.26 (d), 104.15 (s), 65.33 (d), 48.99 (t), 45.05 (d), 42.10 (d), 41.55 (d), 41.11 (d), 30.02 (t), 26.35 (m), 26.19 (m), 19.14 (q); MS, m/z (M^+) calcd 340.1497, obsd 340.1507.

For **21**: 78 mg (29%); colorless crystals, mp 113–114 °C (from hexanes); IR ($CDCl_3$, cm^{-1}) 2980, 2870, 1450, 1305, 1143, 1085; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90–7.87 (m, 2 H), 7.65–7.52 (m, 3 H), 5.39 (m, 1 H), 3.24 (m, 1 H), 3.19 (d, J = 3.9 Hz, 1 H), 3.09 (m, 1 H), 2.78 (d, J = 4.1 (Hz, 1 H), 1.99 (dd, J = 12.2 and 5.2 Hz, 1 H), 1.91, (dt, J = 8.4 and 1.2 Hz, 1 H), 1 H), 1.65–1.60 (m, 2 H), 1.61 (s, 3 H), 1.56 (s, 3 H), 1.38–1.21 (m, 4 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 164.56, 144.06, 140.07, 133.29, 129.19, 128.32, 116.34, 66.15, 61.18, 47.35, 45.16, 40.24, 39.75, 30.84, 29.69, 24.00, 20.45; MS, m/z (M^+) calcd 340.1497, obsd 340.1488.

For **22**: 63 mg (24%); colorless crystals, mp 182–183 °C (from hexanes); IR ($CDCl_3$, cm^{-1}) 2995, 2880, 1450, 1305, 1295, 1147, 1087; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91–7.88 (m, 2 H), 7.68–7.54 (m, 3 H), 3.47 (m, 1 H), 3.44 (m, 1 H), 3.41 (s, 1 H), 3.14 (m, 1 H), 2.71 (m, 1 H), 2.10 (m, 1 H), 1.91 (dt, J = 8.9 and 1.6 Hz, 1 H), 1.60–1.54 (m, 2 H), 1.52 (s, 3 H), 1.51 (s, 3 H), 1.46–1.30 (m, 2 H), 0.74 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.61 (s), 149.77 (s), 148.07 (s), 140.10 (s), 133.35 (d), 129.18 (d), 128.20 (d), 107.77 (s), 64.61 (d), 46.51 (t), 45.64 (d), 43.16 (d), 42.90 (d), 42.62 (d), 29.65 (t), 25.89 (t), 25.09 (t), 19.72 (q); MS, m/z (M^+) calcd 340.1497, obsd 340.1501.

Anal. Calcd for $C_{21}H_{24}O_2S$: C, 74.08; H, 7.10. Found: C, 74.32; H, 7.35.

For **20**: 52 mg (19%); colorless solid, mp 105–106 °C (from hexanes); IR ($CDCl_3$, cm^{-1}) 2990, 2950, 2885, 1450, 1310, 1287, 1153, 1085; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84–7.82 (m, 2 H), 7.64–7.50 (m, 3 H), 5.29 (m, 1 H), 3.68 (m, 1 H), 3.23 (d, J = 3.6 Hz, 1 H), 3.01 (m, 1 H), 2.70 (d, J = 4.2 Hz, 1 H), 1.89 (m, 1 H), 1.64 (s, 3 H), 1.62 (s, 3 H), 1.58–1.22 (series of m, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.36 (s), 143.81 (s), 140.17 (s), 133.07 (d), 128.88 (d), 128.38 (d), 116.20 (s), 111.45 (d), 66.64 (d), 61.73 (s), 49.24 (t), 48.07 (d), 40.39 (d), 39.37 (d), 30.58 (m), 30.03 (t), 23.68 (m), 20.48 (q), 20.44 (q); MS, m/z (M^+) calcd 340.1497, obsd 340.1481.

Air Oxidation of 23. A neat sample of **23** (35 mg, 0.10 mmol) was exposed to atmospheric oxygen for 3 days. Preparative thin-layer chromatography of the resulting mixture on silica gel (elution with 20% ethyl acetate in petroleum ether) afforded unreacted **23** and 11 mg (30%) of **24** as a colorless solid: mp 114–115 °C (from hexanes); IR ($CDCl_3$, cm^{-1}) 2990, 2935, 2860, 1448, 1308, 1300, 1260, 1048, 1000; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87–7.84 (m, 2 H), 7.67–7.55 (m, 3 H), 3.23–3.18 (m, 1 H), 3.10 (s, 1 H), 2.84 (m, 1 H), 2.76 (m, 2 H), 2.04–1.96 (m, 1 H), 1.68–1.48 (series of m, 4 H), 1.51 (s, 3 H), 1.46 (s, 3 H), 1.40–1.23 (series of m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.48, 139.46, 133.57, 129.21, 128.19, 111.65, 63.47, 62.92, 61.47, 43.71, 40.81, 37.82, 37.73, 30.28, 29.12, 26.09, 26.07, 20.02, 19.97; MS, m/z (M^+) calcd 356.1446, obsd 356.1453.

Reductive Desulfonylation of 23. General Procedure. A solution of **23** (63 mg, 0.18 mmol) in anhydrous tetrahydrofuran (4 mL) was added to a well-stirred mixture of 6% sodium amalgam (361 mg) and disodium hydrogen phosphate (133 mg, 0.95 mmol) in anhydrous methanol (2 mL) at 20 °C. After 24 h, a second portion of 6% sodium amalgam (361 mg) and disodium hydrogen phosphate (133 mg, 0.95 mmol) was added, and stirring was continued for 8 h. The reaction mixture was diluted with pentane and filtered through a Celite pad. The filtrate was washed with water, dried, and evaporated. Purification of the resulting oil by medium-pressure liquid chromatography on silica gel (elution with petroleum ether) gave 11 mg (39% based on recovered starting material) of **27** as a colorless solid: mp 73–74 °C (sublimation); IR (neat, cm^{-1}) 2970, 2925, 2865, 1450, 1375, 1283, 1108, 783; ^1H NMR (300 MHz, $CDCl_3$) δ 3.46 (br s, 2 H), 3.02 (brs, 2 H), 1.55 (s, 6 H), 1.54–1.52 (m, 4 H), 1.39 (m, 1 H), 1.02 (d, J = 8.1 Hz, 1 H), 0.90–0.86 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.82, 149.28, 106.53, 49.47, 43.24, 43.20, 25.59, 25.23, 19.82; MS, m/z (M^+) calcd 200.1563, obsd 200.1544.

Comparable reduction of **22** (64 mg, 0.19 mmol) afforded 14 mg (50% based on recovered sulfone) of **27** as a colorless solid, mp 73–74 °C (sublimation). Its spectral parameters were identical with those reported above.

Analogous reduction of **20** (35 mg, 0.10 mmol) furnished 8 mg (99% based on recovered sulfone) of **26** as a colorless oil: IR (neat, cm^{-1}) 2970, 2920, 2870, 1445, 1375, 1307, 1287; ^1H NMR (300 MHz, $CDCl_3$) δ 5.25 (m, 1 H), 3.19 (m, 1 H), 3.85 (m, 1 H), 2.70 (m, 1 H), 1.65 (s, 3 H), 1.62 (s, 3 H), 1.60–0.85 (series of m, 10 H); MS, m/z (M^+) calcd 200.1565, obsd 200.1543.

When **21** (39 mg, 0.12 mmol) was subjected to reduction in the predescribed manner, there was isolated 9 mg (64% based on recovered sulfone) of **26** as a colorless oil. Its spectral data were identical with those reported above.

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Registry No. 3, 98509-34-3; **4**, 68347-25-1; **5**, 98509-79-6; **6**, 7333-67-7; **7**, 98509-80-9; **8**, 98509-81-0; **9**, 98509-82-1; **13**, 98575-36-1; **14**, 98509-83-2; **15**, 98509-84-3; **16**, 98575-38-3; **17**, 98575-37-2; **18**, 98509-85-4; **19**, 98509-86-5; **20**, 98575-40-7; **21**, 98509-88-7; **22**, 98575-39-4; **23**, 98509-87-6; **24**, 98509-89-8; **26**, 98509-91-2; **27**, 98509-90-1; $MeOC(O)C{\equiv}CC(O)OMe$, 762-42-5; $CH_2{=}CHSO_2Ph$, 5535-48-8; 4-methyl-Δ^1-1,2,4-triazoline-3,5-dione, 13274-43-6; *N*-phenylmaleimide, 941-69-5; *p*-benzoquinone, 106-51-4.

Supplementary Material Available: Details of the X-ray analyses of **13**, **15**, and **17**, including tables of bond distances, bond angles, least-squares plane, positional parameters, and refined temperature factor expressions (Tables III–XVII), as well as unit cell diagrams (Figures 4–6) (30 pages). Ordering information is given on any current masthead page.