g (40.5 mmol) of *N*-bromosuccinimide and 0.03 g of dibenzoyl peroxide. This solution was stirred and refluxed under a nitrogen atmosphere for 3 h. The solution was then cooled to room temperature and the succinimide was removed by suction filtration. The succinimide was washed with two 5-mL portions of CCl_4, and the filtrates were combined. The CCl_4 was removed under reduced pressure to give 4.2 g (64% yield) after distillation: bp 65 °C (24 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3 H), 1.77 (s, 6 H), 4.08 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.2 (q, J = 127 Hz), 20.2 (q, J = 127 Hz), 21.3 (q, J = 125 Hz), 37.0 (t, J = 162 Hz), 124.8 (s), 133.1 (s).

2,3-Dimethyl-2-butenyl *p*-Methylphenyl Sulfide (8). A solution of 0.55 g (4.2 mmol) of sodium 4-methylthiophenoxide and 0.68 g (4.2 mmol) of 1-bromo-2,3-dimethyl-2-butene in 10 mL of absolute ethanol was stirred for 30 min. The well-mixed solution was then poured into 20 mL of saturated NaCl and extracted with several portions of petroleum ether. The organic layer was dried with $MgSO_4$ and removed under reduced pressure to give 0.62 g (80% yield) of **8**. The sulfide product was purified by preparative gas chromatography (retention time 18 min) and by distillation: bp 82 °C (0.03 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 3 H), 1.64 (s, 3 H), 1.77 (s, 3 H), 2.31 (s, 3 H), 3.53 (s, 2 H), 7.07 (d, J = 8 Hz, 2 H), 7.26 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.1 (q, J = 125 Hz), 20.2 (q, J = 125 Hz), 20.8 (q, J = 125 Hz), 21.0 (q, J = 125 Hz), 39.9 (t, J = 140 Hz), 123.0 (s), 129.4 (d, J = 162 Hz), 129.5 (s), 131.2 (d, J = 160 Hz), 133.5 (s), 136.3 (s).

1-[(4-Methylphenyl)sulfinyl]-2,3-dimethyl-2-butene (6). A 5-mL CH_2Cl_2 solution of 254 mg of MCPBA (85%) was added to 10 mL of methylene chloride containing 260 mg of **8** at 0 °C. This mixture was warmed to room temperature and stirred for 1 h. It was then poured into 10 mL of 10% aqueous $NaHCO_3$. The organic layer was separated, washed with saturated NaCl, and dried with $MgSO_4$. The solvent was removed under reduced pressure and the sulfoxide was purified by passing it down a 20-cm long, 3-cm diameter flash column containing 8 g of silica gel (60–200 mesh) column with hexane/ethyl acetate (9/1) elution: 83% yield; ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 3 H), 1.64 (s, 3 H), 1.67 (s, 3 H), 2.42 (s, 3 H), 3.43 (d, J = 12 Hz, 1 H), 3.77 (d, J = 12 Hz, 1 H), 7.29 (d, J = 8 Hz, 2 H), 7.49 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.7 (q, J = 126 Hz), 20.7 (q, J = 126 Hz), 21.0 (q, J = 126 Hz), 21.4 (q, J = 125 Hz), 64.5 (t, J = 140 Hz), 117.4 (s), 124.3 (d, J = 163 Hz), 129.6 (d, J = 165 Hz), 134.2 (s), 140.9 (s), 141.4 (s).

1-[(4-Methylphenyl)sulfonyl]-2,3-dimethyl-2-butene (7). Two equivalents of MCPBA was added to a 10 mL CH_2Cl_2 solution of 85 mg of **8** at 0 °C. This solution was stirred for 1 h, warmed to room temperature, and washed with saturated aqueous $NaHCO_3$ and water. The organic layer was separated and dried over $MgSO_4$, the solvent was removed at low pressure, and the sulfone was purified by chromatography: 67% yield; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 3 H), 1.62 (s, 3 H), 1.77 (s, 3 H), 2.46 (s, 3 H), 3.92 (s, 2 H), 7.44 (d, J = 8.2 Hz, 2 H), 7.74 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.45 (q, J = 125 Hz), 20.6 (q, J = 125 Hz), 21.0 (q, J = 125 Hz), 21.6 (q, J = 125 Hz), 61.8 (t, J = 140 Hz), 116.0 (s), 128.4 (d, J = 160 Hz), 129.5 (d, J = 160 Hz), 135.8 (s), 136.3 (s), 144.4 (s).

General Photolysis Conditions. The singlet-oxygen reactions were performed in 5-mm NMR tubes containing 0.5 mL of acetone-d_6. The temperature was maintained by submersion in a methanol bath held at −78 °C by the use of a refrigerator probe (FTS Systems Inc. Flexicool). Prior to photolysis, the samples were saturated with oxygen for 20 min. The concentrations of the starting materials and dye were approximately 5×10^{-2} M and 2×10^{-5} M, respectively. The irradiation was conducted under continuous oxygen bubbling by using a 750-W, 120-V tungsten halogen lamp and by filtering out the high-energy light with a 1-cm 0.5% $K_2Cr_2O_7$ filter solution. The samples were deoxygenated prior to monitoring by NMR by bubbling argon through the NMR tube for 15 min. Removal of the oxygen results in an improved NMR spectrum.

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Stereochemical Course of Diels–Alder Cycloadditions to Hydroxymethyl-Substituted Plane-Nonsymmetric Cyclopentadienes[1]

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Abstract: Steric, electronic, and potential hydrogen-bonding factors governing π-facial stereoselectivity in hydroxymethyl-substituted cyclopentadienes **4** and **6** have been investigated. The stereochemical response of **4** is no different than that of hydrocarbon **5**. In both examples, only below-plane dienophilic capture operates. The predominance of *anti*-7-hydroxymethyl isomers in these cycloadditions involving **6** has been ascribed predominantly to differential steric factors. Kinetically preferred endo stereoalignment in all of the adducts derived from **6** signals additionally that hydrogen bonding has no evident kinetic consequence. Accordingly, a properly positioned CH_2OH substituent does not find it possible to contravene approach to **4** and **6** from their less sterically hindered surfaces.

In the 50 years that have elapsed since its discovery,[4] the Diels–Alder reaction has been heavily exploited to take advantage of its superb regio- and stereochemistry.[5] The end result often involves the elaboration of as many as four contiguous stereogenic centers in a single laboratory step. However, [4 + 2] cycloadditions have the latent capacity for still greater stereochemical latitude in those situations where plane-nonsymmetric 1,3-dienes are involved. Because the reactive faces of such 4π reagents are

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(1) Part 41 in the series dealing with isodicyclopentadienes and related molecules. (a) For part 40, see: Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Crocq, V. *Organometallics* **1988**, *7*, 1873. (b) For part 39, consult: Paquette, L. A.; Gugelchuk, M. *J. Org. Chem.* **1988**, *53*, 1835.

(2) Recipient of a "Bourse Lavoisier" postdoctoral fellowship awarded by the Ministère des Affaires Étrangères, Paris, France.

(3) Author to whom inquiries regarding the X-ray crystallographic analyses should be directed.

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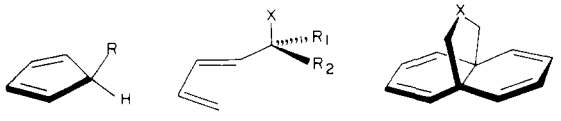
different, adequate control of π-facial selectivity would result in setting five or more centers of symmetry in one maneuver.

Recently, some attention has been brought to bear on elucidating the degree of diastereoselectivity capable of being exerted by a proximal substituent. The major thrusts to date have involved 5-substituted 1,3-cyclopentadienes (**1**)[6-14] and the allylic substituted



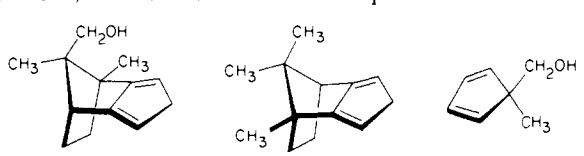
1 **2** **3a**, X = O; **b**, X = S

acyclic 1,3-dienes (**2**).[15] In the first category, the directions and magnitudes of the diastereofacial preferences have been such as to generate serious problems in mechanistic analysis.[16-19] When the R group in **1** is a simple alkyl residue such as methyl, condensation with *N*-phenylmaleimide gives rise to equal amounts of syn and anti adducts.[7] Thus, it is curious that steric effects are not capable of greater stereochemical discrimination. Similar product distributions have been seen with 9,10-dihydrofulvene (**1**, R = 5-cyclopentadienyl) in its reactions with dimethyl acetylenedicarboxylate[20] and *N*-phenyltriazolinedione.[21] Where 1,2,3,4,5-pentamethylcyclopentadiene is concerned, the level of anti capture by *N*-phenylmaleimide rises to 80% of the total.[13] The condensation of 5-(methoxymethyl)cyclopentadiene with α-chloroacrylonitrile proceeds with 100% anti stereoselectivity.[22]

When the R group in **1** is a halogen, cycloaddition often (R = I, Br)[10] though not always (R = Cl)[8,10] occurs from the less sterically hindered anti surface. On the other hand, the consequences of positioning R = OAc, OH, OCH_3, NHAc, and NH_2 at that site are to enhance markedly the preponderance of contrasteric dienophile capture.[13] Most often, the adduct resulting from bonding to the sterically more hindered syn face is produced exclusively. This strong diastereofacial preference is, however, almost completely reversed when R is a sulfur residue such as SCH_3, $SOCH_3$, and SO_2CH_3.[13] The SH substituent seemingly has low control of π-facial selectivity.[13] Interestingly, these effects are the reverse of those seen in propellanes **3a** and **3b**, where cycloaddition occurs anti to oxygen and syn to sulfur.[23]

Attempts to arrive at the origin of these divergent results have culminated in several interesting rationalizations. In early work, Fukui proposed that the direct bonding of a heteroatom to a cyclopentadiene ring causes the HOMO to be biased toward the syn surface, thereby inducing kinetically conrolled dienophile capture from that direction.[16] Anh favored taking into account van der Waals–London interactions in addition to the usual orbital factors.[17] Gleiter and Paquette have concluded that the observed π-facial stereoselectivities are due to σ/π interaction, which results in disrotation of the pπ lobes at the reaction centers.[18] Finally, Kahn and Hehre have emphasized electrostatic interactions such that electrophilic dienophiles are expected to add preferentially to the more nucleophilic diene face that presumably resides syn to the heteroatom.[19] This simple electrostatic model cannot be straightforwardly extended to the sulfur systems and has, in fact, failed to correlate a number of additional pieces of data.[14,25j] Rather, the data for those derivatives of **1** where a heteroatom is directly bonded to the cyclopentadienyl ring correlate well with the notion that differential spiroconjugative effects[24] are at play.

In an attempt to develop an improved understanding of substituent effects in these reactions, so as to allow for the appropriate design of facially selective Diels–Alder cycloadditions in organic synthesis, we chose to examine the responses of dienes **4** and **6**



4 **5** **6**

to a representative set of dienophiles. These systems were selected for the following reasons: (1) their hydroxyl group is not bonded directly to the cyclopentadiene ring, thereby removing from consideration the need for extrapolation of the interplay of σ/π interactions and the like; (2) the retention of van der Waals–London attractive forces and electrostatic effects, with the added bonus of possible hydrogen bonding between the pendant hydroxyl and at least one segment of the dienophile; (3) the possibility of including the known diene **5**[25-27] as a close prototype of **4**, but lacking completely of heteroatomic substitution. Given the penchant of **5** for below-plane dienophile capture,[26a] the issue in this instance was whether the influence of the hydroxyl group in **4** would prove adequate to induce dienophile capture syn to itself; and (4) a more equitable steric balance in **6** relative to the situation prevailing in **1**.

Results

Preparation of 4 and 6. The key intermediate for arrival at **4**, viz. L-(+)-8-hydroxyisoborneol (**8**), was obtained in eight steps from D-(+)-bromocamphor (**7**) by methods earlier described.[28-33]

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Scheme I

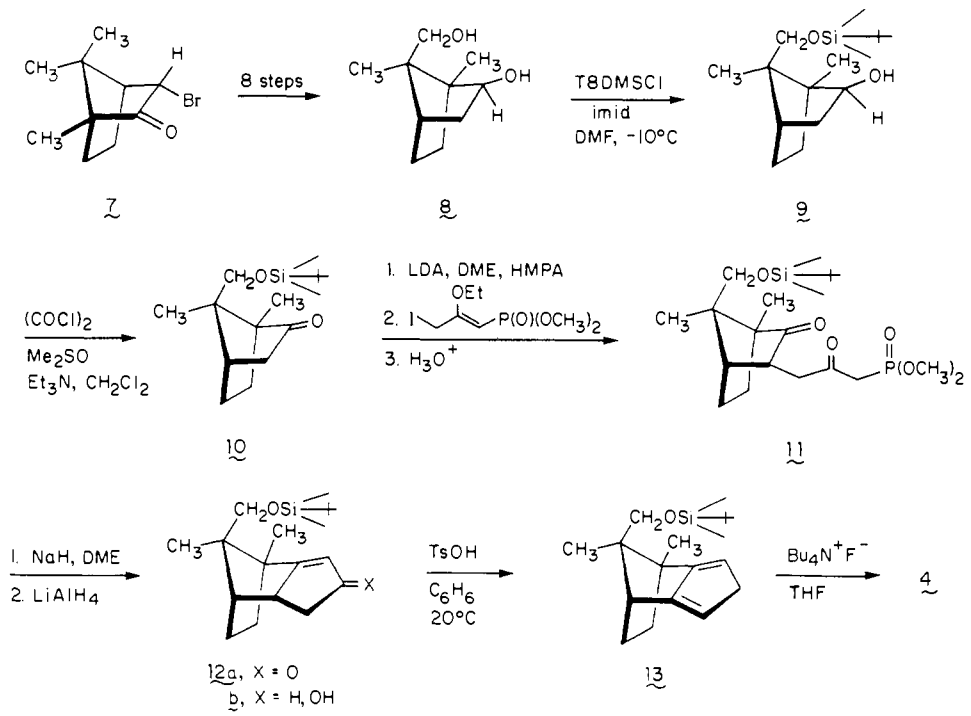


Table I. Chemical Shifts of the Endo Ethano Bridge Protons in Selected *syn*-Sesquinobornene Adducts

dienophile	diene 5	diene 4
	14b	**17**
N-phenylmaleimide	0.80–0.75 ($CDCl_3$)	0.87–0.82 ($CDCl_3$)
	0.54–0.35 (C_6D_6)	0.51–0.36 (C_6D_6)
	15	**18**
benzoquinone	0.83–0.72 ($CDCl_3$)	0.90–0.82 ($CDCl_3$)
	0.58–0.40 (C_6D_6)	0.56–0.40 (C_6D_6)
	16	**19**
4-cyclopentene-1,3-dione	0.90–0.83 (DMSO-d_6)	0.89–0.80 (DMSO-d_6)

The reaction sequence initially made available D-(+)-isoketopinic acid, which was in turn reduced with sodium borohydride and rearranged under acid-catalyzed (CF_3COOH) conditions according to Corey[30] in order to make available L-(−)-8-apoisoborneol-7-carboxylic acid lactone with complete retention of configuration.[31,34] Reduction of this tricyclic compound with lithium aluminum hydride gave rise in turn to diol **8** (Scheme I).

The monoprotection of **8** as silyl ether **9** was accomplished selectively in 85% yield by reaction with *tert*-butyldimethylsilyl chloride and imidazole in cold (−10 °C) dimethylformamide. In order to initiate the annulation process, **9** was subjected to Swern oxidation and the lithium enolate of **10** was alkylated with dimethyl 3-iodo-2-ethoxy-1-propenylphosphonate[35] in 1,2-dimethoxyethane (DME) solution containing HMPA. Direct mild aqueous acidic hydrolysis furnished diketo phosphonate **11** in 50% overall yield.

Horner–Emmons cyclization was accomplished efficiently (89%) by heating **11** with sodium hydride in DME. Hydride reduction of **12a** gave alcohol **12b**, which underwent smooth dehydration by stirring with 10 mol % *p*-toluenesulfonic acid in benzene at room temperature. These conditions allowed as well for double-bond migration into the thermodynamically favored arrangement reflected in **13**. Finally, deprotection of the hydroxyl group was accomplished conventionally in 90% yield. The structural formulas in Scheme I reflect the proper absolute configurational assignments to this enantiomeric series.

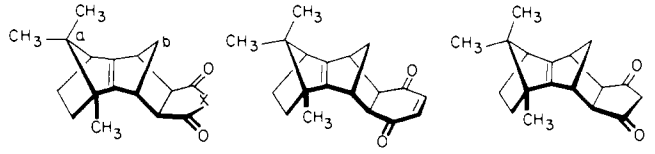
Table II. Chemical Shifts of the Apical Carbons in **14–16**[a]

compd	apical carbon a	apical carbon b
14a	59.47	52.53
14b	59.42	52.67
15	59.56	52.73
16	58.58	51.96

[a] In $CDCl_3$ solution (except for **16**-DMSO-d_6) at 75 MHz.

The preparation of **6** began with diethyl adipate and was accomplished in six steps (Scheme II) by protocols reported earlier by Müller and Herberich,[36] and by Dubois and Fort.[37]

π-Facial Selectivity Studies Involving 5. Initially, consideration was given to the stereochemical outcome of Diels–Alder additions to **5**. Hayes had already shown that maleic anhydride, *N*-phenylmaleimide, and dimethyl acetylenedicarboxylate are captured by **5** exclusively from the below-plane direction, as in **14**.[26a]



Expectedly, the situation with benzoquinone and 4-cyclopentene-1,3-dione is no different. Stirring with 1 equiv of these dienophiles in benzene solution at room temperature for 2 and 7 days, respectively, gave rise to **15** and **16** as exclusive adducts.

The exo orientation of the carbonyl centers in **15** and **16** (the latter compound actually exists as a mixture of enol forms) was readily discerned by virtue of the lack of spin–spin coupling between the neighboring α-CO and bridgehead protons.[38] Two

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Scheme II

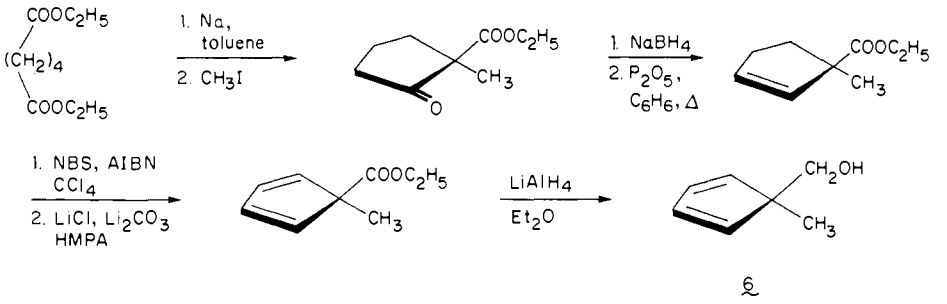

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Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	17	22
compd	$C_{23}H_{25}NO_3$	$C_{13}H_{14}O_3$
color/shape	colorless/ parallelepiped	yellow/fragment
formula wt	363.46	218.25
space group	$P2_12_12_1$	$P\bar{1}$
temp, °C	−150	20
cell constants[a]		
a, Å	9.668 (1)	7.124 (7)
b, Å	10.360 (1)	7.511 (6)
c, Å	18.600 (2)	10.886 (9)
α, deg		97.71 (8)
β, deg		101.79 (9)
γ, deg		98.64 (9)
cell vol, Å^3	1863	555.5
formula units/unit cell	4	2
D_{calcd}, g cm^{-3}	1.30	1.30
μ_{calcd}, cm^{-1}	0.48	0.54
diffractometer/scan	Enraf-Nonius CAD-4/θ − 2θ	Enraf-Nonius CAD-4/θ − 2θ
radiation, graphite monochromator	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
max crystal dimens, mm	0.10 × 0.33 × 0.35	0.15 × 0.20 × 0.30
scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
std reflctns	600; 080; 0, 0, 14	300; 030; 006
decay of stds	±3%	−6% (not corrected)
no. of measd reflctns	1911	1919
2θ range, deg	2 ≤ 2θ ≤ 50	2 ≤ 2θ ≤ 50
range of *hkl*	+11,+12,+22	+8,±8,±12
no. of obsd reflctns [$F_o \geq 5\sigma(F_o)$][b]	1535	1143
computer programs[c]	SHELX[45]	SHELX[45]
structure solution	MULTAN[47]	MULTAN[47]
no. of params varied	244	145
weights	$[\sigma(F_o)^2 + 0.00002F_o^2]^{-1}$	$[\sigma(F_o)^2]^{-1}$
GOF	3.25	2.6
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.047	0.068
R_w	0.048	0.058
largest feature final diff map	0.6 e$^-$ Å^{-3}	0.3 e$^-$ Å^{-3}

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 20 reflections $\theta > 19°$. [b] Corrections: Lorentz-polarization. [c] Neutral scattering factors and anomalous dispersion corrections from reference 46.

additional important stereochemical parameters could be gleaned from their NMR spectra. It has long been recognized that the endo protons on the ethano bridge of *syn*-sesquinorbornene derivatives are notably shielded (upfield of δ 1.0), whereas those of their anti counterparts are not.[26,39] The compilation in Table I shows that the relevant protons of **15** and **16** are indeed displaying the chemical shift pattern characteristic of the syn series. Also apparent in these adducts is the striking similarity of the ^{13}C chemical shifts of their apical carbons (for the a/b designation, see **14**) to those of adducts of established structure (Table II).

Consequently, where **5** is concerned, there clearly exists a strong predilection for kinetically controlled below-plane [4 + 2] cycloaddition.

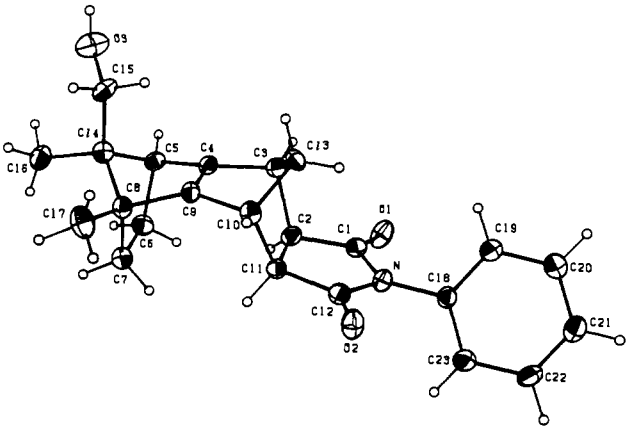
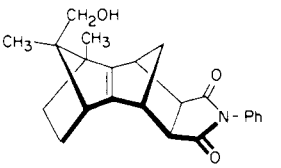


Figure 1. Computer-generated perspective drawing of **17** as determined by X-ray crystallography. The atom numbering is arbitrary.

Stereochemical Course of Diels–Alder Cycloadditions to 4. While four isomeric adducts can in principle be formed in the Diels–Alder cycloaddition of *N*-phenylmaleimide to **4**, only one results when reaction is conducted in benzene solution at 20 °C for 1 week. In line with the preceding spectral considerations (e.g., Table I), the product was identified as **17**. This conclusion was



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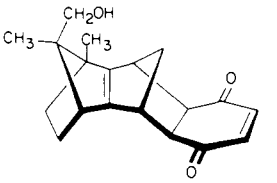

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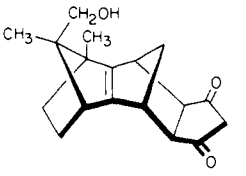

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confirmed by X-ray crystallographic analysis of the hydrogen-bonded polymer of **17** (Figure 1, Table III). The endo deformation of the central double bond in **17** amounts to 15.95°, this level of folding comparing well with data culled from structurally related systems.[40]

Benzoquinone and 4-cyclopentene-1,3-dione were also examined because, like *N*-phenylmaleimide, these dienophiles possess electron-rich sites capable of engaging in hydrogen bonding to

(38) (a) Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, 90, 3724. (b) Marchand, A. P. *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*; Verlag Chemie International: Deerfield Beach, FL, 1982.

(39) (a) Paquette, L. A.; Kravetz, T. M.; Hsu, L.-Y. *J. Am. Chem. Soc.* **1985**, *107*, 6598. (b) Paquette, L. A.; Green, K. E.; Gleiter, R.; Schäfer, W.; Gallucci, J. C. *Ibid.* **1984**, *106*, 8232. (c) Paquette, L. A.; Gugelchuk, M.; Shu, L.-Y. *J. Org. Chem.* **1986**, *51*, 3864.

(40) Paquette, L. A.; Doherty, A. M. *Polyquinane Chemistry. Syntheses and Reactions*; Springer-Verlag: New York, 1987; pp 72–73.

Table IV. Product Distributions for [4 + 2] Cycloadditions to **6**

dienophile	solvent	conditions[a]	product distribution: *syn*-CH_3 (%)	product distribution: *syn*-CH_2OH (%)
N-phenylmaleimide	C_6H_6	rt, 5 days	**20** (87)	**21** (13)
benzoquinone	C_6H_6	rt, 5 days	**22** (84)	**23** (16)
4-cyclopentene-1,3-dione	C_6H_6	65 °C, 5 days	**24** (85)	**25** (15)
tetracyanoethylene	C_6H_6	rt, 20 h	**26** (87)	**27** (13)
(*Z*)-1,2-bi(phenylsulfonyl)ethylene	CH_2Cl_2	rt, 90000 psi	**28** (82)	**29** (18)

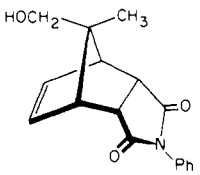
[a] rt, room temperature.

the hydroxyl group in **4**. Nonetheless, when these reagent pairs were allowed to stand in benzene for extended time periods, the only adducts produced proved to be **18** and **19**, respectively. As before, two groups of ^1H NMR signals were particularly diagnostic of stereochemical detail. The exo orientation of the cyclohexenedione and cyclopentanedione rings was apparent from the singlet nature of the pair of bridgehead protons. Also, the shielded nature of the endo ethano protons (Table I) is consistent only with the existence of *syn*-sesquinorbornene structures.

The primary point of interest in this phase of our work is the realization that the presence of a primary hydroxyl group syn to the diene network has no observable consequence on π-face selectivity despite the latent potential for hydrogen bonding between **4** and the dienophile in the above-plane activated complex.

Stereoselective Behavior of 6 in [4 + 2] Cycloadditions. In order to obtain a more direct calibration of the magnitude of the "hydroxyl steering effect" and to gain further insight into its advantageous or disadvantageous role, **6** was engaged in reaction with five different dienophiles. The stereochemical consequences of these cycloadditions are summarized in Table IV and establish the convincing negative preference for addition syn to the hydroxymethyl substituent.

Condensation with *N*-phenylmaleimide at room temperature gave rise to an 87:13 mixture of adducts **20** and **21**. As for each experiment described herein, the product composition was assayed



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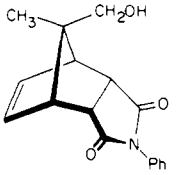

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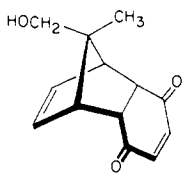

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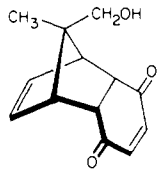

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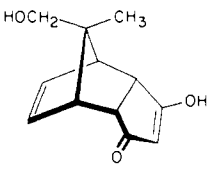

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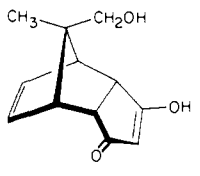

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by 300-MHz ^1H NMR analysis of the unpurified reaction mixtures directly after solvent removal in vacuo. Repeated recrystallization of the **20**/**21** mixture from ethyl acetate provided for the isolation of pure **20**. The spectral properties of the minor constituent were deduced from an enriched mixture by difference. In both cases, the two protons positioned α to the carbonyl are seen to be spin-coupled to the bridgehead hydrogens due to the exo orientation of the former. Here the similarities end. Major adduct **20** differs from **21** in displaying its methyl singlet to lower field (δ 1.17 vs 1.13). Also, the syn relationship of the hydroxymethyl substituent to the vinylic protons in **20** has shielding consequences not observed in **21** (Table V).

Where benzoquinone is concerned, formation of the isomer pair **22** and **23** was noted to arise with a partitioning of 84:16. In

Table V. Selected Stereochemically Distinctive Proton Chemical Shifts for **20**–**29**[a]

adduct	methyl signal	norbornenyl olefinic protons
20	1.17	6.20
21	1.13	6.22
22	1.13	6.00
23	1.04	6.00
24	1.02	5.77
25	0.97	5.82
26[b]	1.58	6.65
27[b]	1.29	6.79
28[c]	0.86	6.33
29[c]	0.80	6.39

[a] Recorded at 300 MHz in $CDCl_3$ solution except where noted. All values are in δ. [b] Recorded in CD_3COCD_3 and CD_3CN solution. [c] Recorded in CD_3SOCD_3 solution.

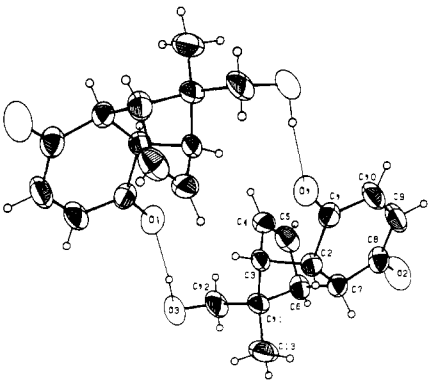
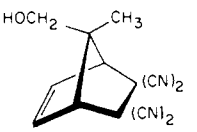


Figure 2. ORTEP drawing of **22** showing the manner in which crystallization occurs to give a hydrogen-bonded dimer.

common with **20**, major product **22** exhibits a lower field methyl absorption than **23**, and its vinylic protons are more shielded than those seen for **23**. Unequivocal confirmation of the structural assignment to **22** was confirmed by X-ray crystallography (Figure 2, Table III). Interestingly, this adduct crystallizes as a hydrogen-bonded dimer.

With 4-cyclopentene-1,3-dione and tetracyanoethylene, essentially comparable product distributions of 85:15 and 87:13 were realized. The *syn*-methyl character of **24** and **26**, respectively,



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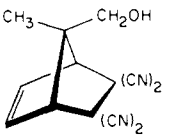

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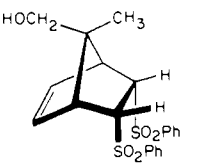

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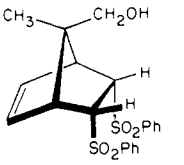

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was established in the same manner as before (Table V). The noteworthy point here is the unwavering percentage of *syn*-methyl cycloaddition (84–87%) that is demonstrated as one progresses from imide through conjugated enone to nitrile functionality in the dienophile.

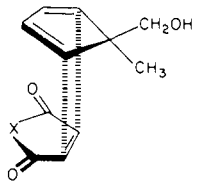
As further test of this indifference to functionality type, **6** was also reacted with (*Z*)-1,2-bis(phenylsulfonyl)ethylene.[41] To achieve a reasonable reaction rate in this case, the cycloaddition was performed at 90000 psi in dichloromethane solution for 2

(41) DeLucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596.

days.[42] As in the earlier examples, **28** (**82**%) was found to predominate substantially over **29** (18%).

Discussion

In striking contrast to what has been reported for cycloadditions to 5-oxygenated 1,3-cyclopentadienes,[9,13] we find no evidence for a syn directing effect of a primary hydroxyl group in cycloadditions involving either **4** or **6**. The inability of the oxygenated center in **6** to control π-facial selectivity is notable from at least two perspectives. The distribution of adducts **20–29** shows clearly that transition states related to **30** are of lower energy than those



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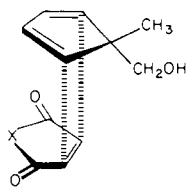

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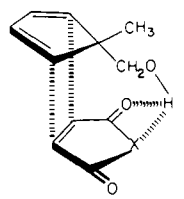

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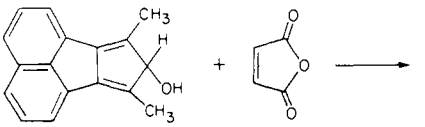
represented by **31**. The preference for **30** can be attributed predominantly to steric factors since the hydroxymethyl group is somewhat more bulky than methyl.[43] The fact that both models are Alder-like in their orientational arrangement suggests that hydrogen bonding has no evident kinetic consequence. Were this the case, such interactions would result in anti-Alder alignment of the reaction partners as in **32**.

The inability of this simple model to operate effectively may stem from the fact that hydrogen bonding per se does not provide simultaneously for proper spatial alignment of the frontier oribtals of the reactants. This would certainly be true for **4** and would involve a minimum ring size of eight where **6** is concerned. However, any future assessment of this question must account as well for the Alder stereochemistry followed by alcohols **33** and **35** in their reaction with maleic anhydride. Despite the syn-facial outcome common to this pair of cycloadditions, bonding occurs exclusively distal from the substituent having the potential for intramolecular coordination.

In this connection, the results of X-ray analysis of **22** hold interest. Crystallization of this adduct from ethyl acetate–petroleum ether mixtures provided for the isolation of yellow prisms where the hydroxyl group from each constituent molecule is coordinated in a dimeric relationship to one of the carbonyl groups of the other (Figure 2). At least in this context, a significant proton-induced interaction is detectable.

The facial outcome of those cycloadditions to **4** and **6** studied here is such that juxtapositioning of the addend planes so as to offer the least nonbonded steric repulsion is seen to be clearly favored.[44] Consequently, the presence of a hydroxymethyl group does not contravene approach from the less hindered surface either electronically or by means of potential hydrogen bonding. Such latent intermolecular interaction does not appear to materialize even in benzene solution, thereby signaling that low external



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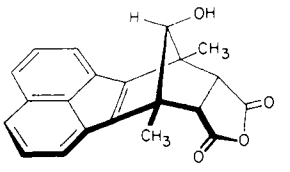

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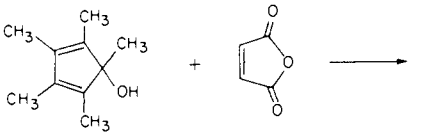

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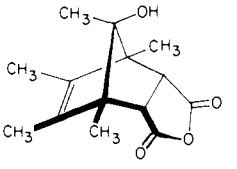

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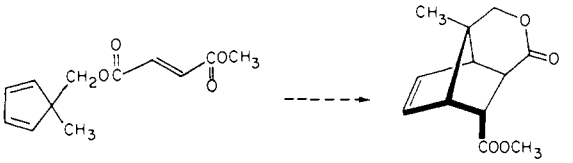
solvation of the diene hydroxyl and the carbonyl and cyano groups in the dienophile does not lend itself to contrasteric behavior.

Since heteroatom-directed control of π-facial selectivity is not a necessary regulatory phenomenon, distal oxygen adducts predominate. There exists in principle a covalent option that is capable of extending the synthetic utility and regioselectivity of these cycloadditions in complementary fashion. Thus, through the mere expediency of preliminarily linking the reaction partners as in **37**, for example, subsequent heating should trigger bond formation exclusively syn to the oxygen atom. These alternatives remain to be tested.



37 **38**

Experimental Section

L-8-[(*tert*-Butyldimethylsilyl)oxy]isoverbanol (9). To a cold (−10 °C), magnetically stirred solution of **8** (7.0 g, 41.1 mmol) and imidazole (6.15 g, 40.3 mmol) in anhydrous dimethylformamide (70 mL) was added dropwise a solution of *tert*-butyldimethylsilyl chloride (6.81 g, 45.2 mmol) in 20 mL of the same solvent. The reaction mixture was stirred at −10 °C for 1 h, allowed to warm to 0 °C during 30 min, diluted with 400 mL of ether, and washed with water (100 mL). The aqueous layer was extracted with ether, and the combined organic phases were dried and evaporated. Silica gel chromatography (elution with petroleum ether) of the residue gave 1.17 g (7%) of the disilylated compound and 9.87 g (84%) of **9**.

For **9**: colorless solid, mp 50–52 °C; IR (film, cm^{-1}) 3350, 2950, 2930, 2880, 2850, 1475, 1465, 1255, 1180, 1165, 1005, 845, 780; ^1H NMR (300 MHz, $CDCl_3$) δ 3.87 (d, J = 10.3 Hz, 1 H), 3.53 (d, J = 10.3 Hz, 1 H), 3.58 (dd, J = 7.7, 3.6 Hz, 1 H), 2.41 (br s, 1 H), 1.88 (dd, J = 4.1 Hz, 1 H), 1.81–1.46 (m, 4 H), 1.03–0.97 (m, 2 H), 0.94 (s, 3 H), 0.89 (s, 9 H), 0.87 (s, 3 H), 0.04 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 79.39, 66.42, 51.64, 49.35, 41.96, 40.28, 34.54, 27.63, 25.96, 18.29, 15.54, 12.13, −5.45; MS m/z (M^+ − t-Bu) calcd 227.1467, obsd 227.1460.

For the disilylated compound: colorless oil; IR (film, cm^{-1}) 2950, 2930, 2850, 1470, 1260, 1120, 1090, 1065, 840, 780; ^1H NMR (300 MHz, $CDCl_3$) δ 4.15 (d, J = 10.3 Hz, 1 H), 3.29 (d, J = 10.3 Hz, 1 H),

(42) Paquette, L. A.; Gugelchuk, M. *J. Org. Chem.* **1988**, *53*, 1835.

(43) The A value for CH_2OH has been determined both in the cyclohexane system (Buchanan, G. W.; Stothers, J. B. *Chem. Commun.* **1967**, 1250) and in 1,3-dioxane (Eliel, E. L.; Kaloustian, M. K. *Chem. Commun.* **1970**, 290). In the latter case, no intramolecular hydrogen bonding is seen for the axial conformer and it is quite clear that polar interactions are involved. From both values, CH_2OH appears to be "smaller" than CH_3, but of course this is because the oxygen substituent tends to stabilize the axial form.

(44) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537.

(45) Sheldrick, G. M. SHELX 76, a system of computer programs for X-ray structure determination as locally modified, University of Cambridge, England, 1976.

(46) *International Tables for X-ray Crystallography*; Kynoch Press, Birmingham, England, 1974; Vol. IV, pp 72, 99, 149. (Present distributor: D. Reidel, Dordrecht, The Netherlands).

(47) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Universities of York, England, and Louvain, Belgium.

3.52 (t, J = 5.5 Hz, 1 H), 1.97 (m, 1 H), 1.68–1.53 (m, 4 H), 1.00–0.91 (m, 2 H), 0.90–0.89 (2 s, 21 H), 0.83 (s, 3 H), 0.02 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 79.61, 65.74, 52.29, 49.46, 41.78, 41.46, 34.24, 26.45, 26.03, 25.88, 18.34, 17.99, 14.99, 12.39, −4.51, −5.02, −5.35; MS m/z (M^+ − t-Bu) calcd 341.2332, obsd 341.2316.

L-(−)-**8-Hydroxycamphor *tert*-Butyldimethylsilyl Ether (10).** To a cold (−55 °C), magnetically stirred solution of oxalyl chloride (0.73 mL, 8.35 mmol) in anhydrous dichloromethane (20 mL) was slowly added dropwise a solution of dimethyl sulfoxide (1.18 mL, 16.6 mmol) in the same solvent (4 mL). The reaction mixture was stirred for 5 min before a solution of **9** (2.15 g, 7.56 mmol) in 8 mL of dry dichloromethane was introduced dropwise. The agitation was continued at −55 °C for 20 min, at which point triethylamine (5.3 mL, 38 mmol) was slowly added. The mixture was allowed to warm gradually to room temperature during 50 min and water (30 mL) was added in one portion. The aqueous phase was extracted with dichloromethane, and the combined organic layers were washed with 1% hydrochloric acid (20 mL) and brine (50 mL), dried, and carefully evaporated. The resulting light yellow solid was purified by silica gel chromatography (elution with 10% ether in petroleum ether) to give 1.73 g (81%) of **10** as long, colorless needles: mp 63–64 °C (from petroleum ether); IR (KBr, cm^{-1}) 2950, 2930, 2850, 1735, 1675, 1465, 1420, 1400, 1380, 1365, 1320, 1285, 1260, 1165, 1100, 1070, 1060, 1025, 1010, 880, 845, 780; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.32 (d, J = 10.5 Hz, 1 H), 3.28 (d, J = 10.5 Hz, 1 H), 2.41–2.28 (m, 2 H), 0.99 (s, 3 H), 0.89 (s, 3 H), 0.85 (s, 9 H), 0.0 (s, 3 H), −0.02 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 218.72, 66.08, 56.54, 52.08, 42.91, 39.88, 30.65, 27.17, 25.77, 18.13, 14.67, 9.72, −5.67; MS m/z (M^+ − CH_3) calcd 267.1780, obsd 267.1771; $[\alpha]^{24}_D$ −18.5° (c 1.11, $CHCl_3$). Anal. Calcd for $C_{16}H_{30}O_2Si$: C, 68.03; H, 10.70. Found: C, 68.19; H, 10.71.

L-(−)-**3-[(Dimethylphosphinoxy)-2-ketopropyl]-8-[(*tert*-butyldimethylsilyl)oxy]camphor (11).** Diisopropylamine (14.9 mL, 106 mmol) was dissolved in anhydrous DME (220 mL) under nitrogen, cooled to −78 °C, and treated dropwise with n-butyllithium in hexane (68.5 mL of 1.55 M, 106 mmol). After 1 h of stirring at −78 °C, **10** (30.0 g, 106 mmol) dissolved in DME (160 mL) was introduced dropwise and the reaction mixture was allowed to warm to −20 °C during 1 h, recooled to −78 °C, treated with HMPA (18.5 mL, 106 mmol), and stirred for 20 min. At this point, a mixture of dimethyl 3-bromo-2-ethoxypropenylphosphonate (29.0 g, 106 mmol) and dried sodium iodide (1.6 g, 10.6 mmol) in DME (140 mL) was introduced during 10 min, the solution was allowed to warm to room temperature, and stirring was maintained for 18 h. The reaction mixture was poured into water (250 mL) and extracted with ether (3 × 25 mL). The combined organic layers were washed with brine (250 mL), dried, and concentrated.

The residual oil was dissolved in acetone (560 mL), treated with 1 N hydrochloric acid (20 mL), and stirred at room temperature for 4 h. Following neutralization with anhydrous potassium carbonate, the solvent was removed under reduced pressure. The residue was taken up in dichloromethane and washed with saturated sodium bicarbonate and water. The dried concentrate was resilylated by treatment with *tert*-butyldimethylchlorosilane (12.0 g, 79.6 mmol) and imidazole (10.9 g, 160 mmol) in dimethylformamide (300 mL). After overnight stirring, the solution was diluted with ether (300 mL) and washed with water (200 mL). The aqueous phase was extracted with ether (3 × 300 mL), and the combined organic layers were dried and evaporated. Finally, silica gel chromatography (elution with 20% ethyl acetate in petroleum ether) returned 7.57 g (25%) of unreacted **10**. An increase in solvent polarity to pure ethyl acetate afforded 23.7 g (50%) of **11** as a clear colorless oil: IR (film, cm^{-1}) 2950, 2920, 2845, 1730, 1710, 1460, 1255, 1105, 1030, 835, 805, 780; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (d, J = 11.2 Hz, 3 H), 3.66 (d, J = 11.2 Hz, 3 H), 3.32 (s, 2 H), 3.17–2.79 (series of m, 4 H), 2.57 (dd, J = 13.7, 3.9 Hz, 1 H), 2.28–2.26 (m, 1 H), 1.62–1.52 (m, 2 H), 1.39–1.35 (m, 1 H), 1.16–1.13 (m, 1 H), 0.92 (s, 3 H), 0.80 (s, 3 H), 0.77 (s, 9 H), −0.076 (s, 3 H), −0.080 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 219.15, 199.52 (d, J = 6.0 Hz), 65.61, 56.82, 52.84 (d, J = 6.6 Hz), 52.68 (d, J = 6.3 Hz), 51.22, 44.94, 43.81, 41.29 (d, J = 127.6 Hz), 41.07, 31.65, 25.55, 20.15, 17.90, 9.76, −5.90, −5.93; MS m/z (M^+ − CH_3) calcd 431.2019, obsd 431.2024; $[\alpha]^{24}_D$ −5.9° (c 1.38, $CHCl_3$).

(−)-**(1*R*,7*S*,10*R*)-1,10-Dimethyl-11-[(*tert*-butyldimethylsilyl)oxy]tricyclo[5.2.1.0^{2,6}]dec-2-en-4-one (12a).** To a suspension of sodium hydride (520 mg, 21.7 mmol) in dry 1,2-dimethoxyethane (150 mL) was added under nitrogen a solution of **11** (9.68 g, 21.7 mmol) in 75 mL of the same solvent. The reaction mixture was refluxed for 21 h, cooled, and poured into brine. The aqueous layer was extracted with dichloromethane, and the combined organic layers were dried and concentrated. Silica gel chromatography of the resultant brown oil (elution with 10% ethyl acetate in petroleum etther) gave 6.22 g (89%) of **12a** as a colorless crystalline solid: mp 92–92.5 °C (from petroleum ether); IR (KBr, cm^{-1}) 2940, 2920, 2845, 1685, 1605, 1075, 830, 770; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (d, J = 2.65 Hz, 1 H), 3.58 (d, J = 10.5 Hz, 1 H), 3.37 (d, J = 10.4 Hz, 1 H), 3.34 (br s, 1 H), 2.48 (dd, J = 16.7, 6.1 Hz, 1 H), 2.28–2.21 (m, 2 H), 1.92–1.84 (m, 1 H), 1.70–1.60 (m, 1 H), 1.27–1.18 (m, 2 H), 1.14 (s, 3 H), 1.05 (s, 3 H), 0.88 (s, 9 H), 0.04 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 210.04, 202.59, 121.44, 66.35, 56.74, 53.30, 48.67, 45.07, 42.81, 40.96, 25.81, 19.75, 18.20, 14.96, 11.57, −5.56; MS m/z (M^+) calcd 320.2172, obsd 320.2133; $[\alpha]^{23}_D$ −64° (c 1.06, $CHCl_3$). Anal. Calcd for $C_{19}H_{32}O_2Si$: C, 71.19; H, 10.06. Found: C, 70.80; H, 10.05.

(1*R*,7*S*,10*R*)-1,10-Dimethyl-11-[(*tert*-butyldimethylsilyl)oxy]tricyclo[5.2.1.0^{2,6}]dec-2-en-4-ol (12b). To a stirred suspension of lithium aluminum hydride (190 mg, 5.0 mmol) in anhydrous ether (100 mL) was added dropwise under nitrogen a solution of **12a** (1.6 g, 5.0 mmol) in 50 mL of the same solvent. The reaction mixture was stirred at room temperature for 30 min and hydrolyzed with saturated sodium sulfate solution. The white precipitate was removed by filtration and thoroughly washed with ether. The combined filtrates were dried and evaporated to leave **12b** as a yellowish oil, which was used directly in the next step: IR (film, cm^{-1}) 3300, 2940, 2920, 2850, 1460, 1250, 1110, 1085, 1060, 1030, 1005, 985, 835, 770; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.25 (d, J = 2.8 Hz, 1 H), 5.08 (m, 1 H), 3.54 (d, J = 10.1 Hz, 1 H), 3.25 (d, J = 10.1 Hz, 1 H), 2.93 (br s, 1 H), 2.29 (quint, J = 5.6 Hz, 1 H), 1.98 (t, J = 4 Hz, 1 H), 1.81–1.70 (m, 2 H), 1.61–1.54 (m, 1 H), 1.49–1.40 (m, 1 H), 1.36–1.15 (m, 2 H), 0.97 (s, 3 H), 0.96 (s, 3 H), 0.88 (s, 9 H), 0.015 (s, 3 H), 0.005 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 166.32, 119.72, 82.15, 66.52, 58.15, 49.77, 49.34, 44.29, 41.57, 40.79, 25.87, 19.64, 18.22, 15.23, 12.24, −5.50; MS m/z (M^+) calcd 322.2328, obsd 322.2318.

(−)-**(1*R*,7*S*,10*R*)-1,10-Dimethyl-11-[(*tert*-butyldimethylsilyl)oxy]tricyclo[5.2.1.0^{2,6}]deca-2,5-diene (13).** The oily **12a** obtained above was dissolved in benzene (150 mL), treated with p-toluenesulfonic acid (95 mg, 0.5 mmol), and stirred for 12 h at room temperature under nitrogen. The reaction mixture was neutralized with anhydrous potassium carbonate, dried, and evaporated. Chromatography of the residue on neutral alumina (pentane elution) gave 663 mg (45% overall) of **13** as a colorless oil: IR (film, cm^{-1}) 2940, 2850, 1470, 1390, 1300, 1260, 1150, 1080, 1010, 905, 840, 780, 770; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57 (s, 1 H), 5.51 (s, 1 H), 3.11–2.90 (m, 4 H), 2.58 (d, J = 4.3 Hz, 1 H), 1.93–1.84 (m, 1 H), 1.77–1.69 (m, 1 H), 1.30–1.15 (m, 2 H), 1.04 (s, 3 H), 0.93 (s, 3 H), 0.76 (s, 9 H), −0.16 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 159.37, 154.09, 115.55, 113.57, 66.99, 59.74, 48.57, 45.01, 44.51, 35.58, 27.03, 25.96, 18.29, 13.37, 12.91, −5.48, −5.56; MS m/e (M^+ − t-Bu) calcd 247.1518, obsd 247.1497; $[\alpha]^{25}_D$ −0.6° (c 1.28, $CHCl_3$).

(−)-**(1*R*,7*S*,10*R*)-1,10-Dimethyltricyclo[5.2.1.0^{2,6}]deca-2,5-dien-11-ol (4).** To a solution of **13** (660 mg, 2.17 mmol) in anhydrous tetrahydrofuran (40 mL) was added 30 mL of 1 M tetra-n-butylammonium fluoride solution in tetrahydrofuran (30 mmol). The reaction mixture was stirred under nitrogen at room temperature for 7 h, poured into brine (50 mL), and extraced with ether. The combined organic layers were dried and evaporated, and the resultant oil was purified by silica gel chromatography (elution with 3:1 pentane–ether). There was isolated 370 mg (90%) of **4** as a colorless solid: mp 52.5–53.5 °C (from pentane); IR (film, cm^{-1}) 3240, 2940, 2860, 1460, 1445, 1385, 1030, 1020, 895, 760; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (d, J = 1.4 Hz, 1 H), 5.62 (s, 1 H), 3.23 (s, 2 H), 3.10 (AB, $\Delta\nu$ = 35.6 Hz, J = 23.0 Hz, 2 H), 2.72 (d, J = 4.3 Hz, 1 H), 2.01–1.95 (m, 1 H), 1.87–1.80 (m, 1 H), 1.41–1.22 (m, 3 H), 1.14 (s, 3 H), 1.06 (s, 3 H); MS m/z (M^+) calcd 190.1357, obsd 190.1384; $[\alpha]^{26}_D$ 2.2° (c 0.91, $CHCl_3$). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.59; H, 9.54.

Cycloaddition of Benzoquinone to 5. A solution of **5** (86 mg, 0.5 mmol) and p-benzoquinone (54 mg, 0.5 mmol) in dry deoxygenated benzene (1.5 mL) was stirred under nitrogen at room temperature for 2 days. The solvent was removed in vacuo and the residue was subjected to MPLC (silica gel, elution with 10% ethyl acetate in petroleum ether). There was isolated 45 mg (32%) of **15** as the only observable adduct: bright yellow solid, mp 125.5–126 °C (from hexane); IR (KBr, cm^{-1}) 2945, 2915, 1665, 1275, 1125, 1105, 1025, 885; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (s, 2 H), 3.33 (s, 4 H), 3.27 (s, 1 H), 2.56 (d, J = 3.5 Hz, 1 H), 2.41 (s, 2 H), 1.84–1.76 (m, 1 H), 1.59–1.48 (m, 2 H), 1.38–1.34 (m, 1 H), 1.13 (s, 3 H) 0.78 (s, 3 H), 0.74 (s, 3 H), 0.78–0.74 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 199.12, 199.01, 155.03, 151.71, 141.82, 141.71, 59.56, 54.49, 52.73, 50.54, 49.56 (2 C), 48.74, 46.24, 32.02, 25.27, 19.82, 18.38, 12.20; MS m/z (M^+) calcd 282.1619, obsd 282.1611. Anal. Calcd $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.75; H, 7.77.

Cycloaddition of 4-Cyclopentene-1,3-dione to 5. A solution of **5** (43 mg, 0.2 mmol) and 4-cyclopentene-1,3-dione (24 mg, 0.2 mmol) in 1.5 mL of dry benzene was stirred under nitrogen at room temperature for 1 week. Evaporation of the solvent left a white, poorly soluble solid,

which was triturated with benzene and dried. Adduct **16** was obtained as a white powder (35 mg, 52%): mp 203–205 °C; IR (KBr, cm^{-1}) 2985, 2950, 2865, 1610–1350 (br), 1315, 1260, 1225, 1175; ^1H NMR (300 MHz, DMSO-d_6) δ 12.02 (br s, 1 H), 5.05 (s, 1 H), 2.90 (s, 1 H), 2.84 (s, 1 H), 2.49 (d, J = 2.9 Hz, 1 H), 2.38 (br s, 2 H), 1.76–1.72 (m, 1 H), 1.52–1.43 (m, 3 H), 1.07 (s, 3 H), 0.90–0.83 (m, 2 H), 0.77 (s, 3 H), 0.72 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d_6) ppm 154.71, 151.05, 107.79, 58.58, 53.59, 51.96, 42.97, 42.41, 31.74, 24.98, 19.80, 18.31, 12.24; MS m/z (M^+) calcd 270.1620, obsd 270.1601.

Diels–Alder Reaction of 4 with *N*-Phenylmaleimide. A solution of **4** (199 mg, 1.04 mmol) and *N*-phenylmaleimide (181 mg, 1.04 mmol) in 3 mL of dry benzene was stirred under nitrogen at room temperature for 7 days. Solvent evaporation left a white residue containing a single adduct, which was purified by MPLC on silica gel (elution with 50% ethyl acetate in petroleum ether) to give 304 mg (80%) of **17** as a colorless solid: mp 171.5–172 °C (from ethyl acetate–petroleum ether); IR (KBr, cm^{-1}) 3460, 2950, 2870, 1770, 1700, 1495, 1385, 1185, 1025, 1010, 875, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49–7.35 (m, 3 H), 7.26–7.22 (m, 2 H), 3.70 (d, J = 10.5 Hz, 1 H), 3.49 (s, 1 H), 3.44 (s, 1 H), 3.30 (d, J = 10.5 Hz, 1 H), 2.80 (br s, 3 H), 1.86–1.82 (m, 1 H), 1.76–1.57 (m, 3 H), 1.23 (br s, 1 H), 1.16 (s, 3 H), 0.90 (s, 3 H), 0.87–0.82 (m, 2 H); ^1H NMR (300 MHz, C_6D_6) δ 7.44–7.02 (m, 5 H), 3.44 (dd, J = 10.3 Hz, 1 H), 3.24 (s, 1 H), 3.22 (s, 1 H), 3.06 (dd, J = 10.3 Hz, 1 H), 2.59 (d, J = 3.4 Hz, 1 H), 2.09 (m, 2 H), 1.58–1.52 (m, 1 H), 1.36–1.30 (m, 3 H), 0.90 (s, 3 H), 0.77 (s, 3 H), 0.71 (br s, 1 H), 0.51–0.36 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 176.77 (2 C), 155.84, 151.08, 131.79, 129.13, 128.61, 126.31, 66.14, 64.32, 53.87, 48.80, 48.75, 48.47, 46.95, 45.25, 44.42, 32.28, 25.17, 13.60, 12.80; MS m/z (M^+) calcd 363.1834, obsd 363.1815. Anal. Calcd for $C_{23}H_{25}NO_3$: C, 76.00; H, 6.93. Found: C, 75.82; H, 7.08.

X-ray Crystallographic Analysis of 17. A transparent single crystal of **17** was mouned on a pin and transferred to the goniometer. The crystal was cooled to −150 °C during data collection by a stream of cold nitrogen gas. The space group was determined to be the acentric $P2_12_12_2$ from the systematic absences. A summary of data collection parameters is given in Table III.

Least-squares refinement with isotropic thermal parameters led to R = 0.087. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 $Å^2$. The methyl hydrogen atoms were located from a difference Fourier map and included with fixed contributions (B = 5.5 $Å^2$). Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.047 and R_w = 0.048.

Benzoquinone Addition to 4. A solution of **4** (202 mg, 1.06 mmol) and benzoquinone (115 mg, 1.06 mmol) in dry, deoxygenated benzene (3 mL) was stirred under nitrogen at room temperature for 15 days. Solvent evaporation and MPLC of the residue (silica gel, elution with 50% ethyl acetate in petroleum ether) afforded **18** as the sole adduct (221 mg, 70%): bright yellow solid, mp 155–156 °C (from ethyl acetate–petroleum ether); IR (KBr, cm^{-1}) 3480, 2985, 2955, 2925, 2880, 2865, 1660, 1385, 1275, 1020, 925, 910, 890, 705; ^1H NMR (300 MHz, $CDCl_3$) δ 6.73 (s, 2 H), 3.69 (d, J = 10.6 Hz, 1 H), 3.37 (s, 1 H), 3.32 (s, 1 H), 3.29 (d, J = 10.6 Hz, 1 H), 2.80 (d, J = 3.4 Hz, 1 H), 2.43 (m, 2 H), 1.86–1.79 (m, 1 H), 1.63–1.58 (m, 1 H), 1.54 (d, J = 9.3 Hz, 1 H), 1.38 (d, J = 9.3 Hz, 1 H), 1.16 (s, 3 H), 0.88 (s, 3 H), 0.90–0.82 (m, 2 H); ^1H NMR (300 MHz, C_6D_6) δ 6.14 (s, 2 H), 3.946 (d, J = 10.4 Hz, 1 H), 3.27 (s, 1 H), 3.22 (s, 1 H), 3.07 (d, J = 10.4 Hz, 1 H), 2.58 (d, J = 2.6 Hz, 1 H), 1.92 (d, J = 1.9 Hz, 2 H), 1.57–1.48 (m, 1 H), 1.35–1.28 (m, 1 H), 1.09 (d, J = 9.1 Hz, 1 H), 1.06 (d, J = 9.1 Hz, 1 H), 0.96 (s, 3 H), 0.75 (s, 3 H), 0.63 (br s, 1 H), 0.56–0.40 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 197.77 (2 C), 155.29, 150.68, 141.31, 141.21, 65.81, 64.75, 53.81, 49.63, 49.59, 48.89, 48.60, 46.53, 32.58, 25.44, 13.61, 12.30; MS m/z (M^+) calcd 298.1569, obsd 298.1571. Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.49; H, 7.43. Found: C, 76.09; H, 7.52.

Cycloaddition of 4 with 4-Cyclopentene-1,3-dione. A solution of **4** (205 mg, 1.08 mmol) and 4-cyclopentene-1,3-dione (104 mg, 1.08 mg) in dry benzene (3 mL) was stirred at room temperature under nitrogen for 7 days. A white precipitate gradually deposited from solution. Solvent evaporation left a poorly soluble white solid, which was triturated several times with benzene and dried. There was obtained 162 mg (52%) of **19** as a white powder: mp 171–173 °C; IR (KBr, cm^{-1}) 3485, 2945, 2865, 1700–1300 (br), 1175, 1080, 835; ^1H NMR (300 MHz, DMSO-d_6) δ 5.05 (s, 1 H), 4.06 (br s, 1 H), 3.44 (d, J = 10.2 Hz, 1 H), 3.01 (d, J = 10.2 Hz, 1 H), 2.87 (s, 1 H), 2.83 (s, 1 H), 2.63 (d, J = 3.2 Hz, 1 H), 2.38 (br s, 2 H), 1.73–1.66 (m, 1 H), 1.52–1.43 (m, 3 H), 1.04 (s, 3 H), 1.1–0.95 (m, 1 H), 0.89–0.80 (m, 2 H), 0.76 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d_6) ppm 154.60, 150.25, 107.80, 63.83, 63.62, 52.78, 48.15, 42.97, 42.45, 41.20, 32.37, 24.93, 13.56, 12.85; MS m/z (M^+) calcd 286.1569, obsd 286.1562.

Cycloaddition of *N*-Phenylmaleimide to 6. A solution of **6** (509 mg, 4.62 mmol) and *N*-phenylmaleimide (800 mg, 4.62 mmol) in dry benzene (10 mL) was stirred under nitrogen at room temperature for 5 days. Precipitation of a white solid occurred during this time. Evaporation of the solvent in vacuo left a colorless solid containing the adducts **20** and **21** in a 6.7:1 ratio (300 MHz, ^1H NMR analysis). The yield was 87%. Repeated recrystallization from ethyl acetate allowed the isolation of pure **20** as colorless plates, mp 213–214 °C. The spectral properties of **21** were obtained from an enriched mixture with **13**.

For **20**: IR (KBr, cm^{-1}) 3540, 3060, 2980, 2880, 1760, 1690, 1595, 1500, 1460, 1380, 1275, 1245, 1235, 1200, 1160, 1120, 1040, 1020, 920, 880, 750, 730, 700, 670, 625; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.35 (m, 3 H), 7.15–7.12 (m, 2 H), 6.20 (t, J = 1.9 Hz, 2 H), 3.61 (s, 2 H), 3.59 (dd, J = 2.6, 1.4 Hz, 2 H), 3.14 (m, 2 H), 1.50 (br s, 1 H), 1.17 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 176.79, 133.64, 129.05, 128.57, 126.55, 67.91, 65.40, 50.32, 44.96, 17.09; MS m/z (M^+) calcd 283.1208, obsd 283.1206. Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05. Found: C, 72.05; H, 6.11.

For **21**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.35 (m, 3 H), 7.15–7.12 (m, 2 H), 6.22 (t, J = 2.1 Hz, 2 H), 3.57 (s, 2 H), 2.54 (m, 2 H), 3.17 (m, 2 H), 1.58 (br s, 1 H), 1.13 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 176.86, 133.80, 131.83, 129.01, 128.56, 126.52, 67.11, 65.27, 50.53, 44.82, 16.39.

Diels–Alder Reaction of 6 with Benzoquinone. A solution of **6** (510 mg, 4.63 mmol) of benzoquinone (500 mg, 4.63 mmol) in dry benzene (8 mL) was stirred at room temperature for 5 days, evaporated, and analyzed by 300-MHz ^1H NMR. The ratio of **22** to **23** was thereby shown to be 5.25:1 (yield 81%). The major adduct was isolated as pure yellow prisms, mp 130–131 °C, by repeated recrystallization from ethyl acetate–petroleum ether. The spectra of **23** were obtained by difference from an enriched mixture.

For **22**: IR (KBr, cm^{-1}) 3510, 3030, 2980, 2950, 1655, 1600, 1390, 1380, 1300, 1280, 1135, 1020, 980, 955, 885, 840, 740, 655; ^1H NMR (300 MHz, $CDCl_3$) δ 6.59 (s, 2 H), 6.00 (t, J = 1.9 Hz, 2 H), 3.56 (s, 2 H), 3.41 (m, 2 H), 3.18 (m, 2 H), 1.57 (br s, 1 H), 1.13 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 199.50, 142.32, 134.58, 65.05, 62.15, 53.40, 47.32, 17.24; MS m/z (M^+) calcd 218.0943, obsd 218.0951.

For **23**: ^1H NMR (300 MHz, $CDCl_3$) δ 6.56 (s, 2 H), 6.00 (t, J = 2.0 Hz, 2 H), 3.53 (s, 2 H), 3.38 (m, 2 H), 3.21 (m, 2 H), 1.95 (br s, 1 H), 1.04 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 199.46, 142.21, 134.82, 65.68, 61.19, 53.73, 47.28, 15.48.

X-ray Crystallographic Analysis of 22. A yellow single-crystal fragment of **22** was mounted on a pin and transferred to the goniometer. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. Statistical tests indicated that the space group was centric and the subsequent solution and successful refinement of the structure in the space group $P\bar{1}$ confirmed this. A summary of data collection parameters is given in Table III.

The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 $Å^2$. Least-squares refinement with isotropic thermal parameters led to R = 0.148. The methyl and hydroxyl hydrogen atoms were located from a difference Fourier map and included with fixed contributions (B = 5.5 $Å^2$). Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.068 and R_w = 0.058.

Diels–Alder Reaction of 6 with 4-Cyclopentene-1,3-dione. A solution of **6** (515 mg, 4.68 mmol) and 4-cyclopentene-1,3-dione (450 mg, 4.68 mmol) in 8 mL of dry benzene was stirred under nitrogen at 65 °C for 5 days. The solvent was removed in vacuo and the solid residue was analyzed by ^1H NMR at 300 MHz (DMSO-d_6 solution). The ratio of **24** to **25** was 5.66:1 (yield 71%). The two isomers could not be separated by repeated recrystallization.

For the mixture: IR (KBr, cm^{-1}) 3350, 2980, 2680, 1570, 1570, 1400, 1320, 1300, 1285, 1260, 1240, 1190, 1175, 1020, 995, 790, 745, 695; MS m/z (M^+) calcd 206.0943, obsd 206.0946.

For **24**: ^1H NMR (300 MHz, DMSO-d_6) δ 5.77 (t, J = 1.7 Hz, 2 H), 4.83 (s, 1 H), 3.30 (s, 2 H), 3.10 (m, 2 H), 2.59 (m, 2 H), 1.02 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d_6) ppm 196.99, 131.37, 108.19, 67.64, 64.65, 48.08, 16.86.

For **25**: ^1H NMR (300 MHz, DMSO-d_6) δ 5.82 (t, J = 1.9 Hz, 2 H), 4.82 (s, 1 H), 3.37 (s, 2 H), 3.10 (m, 2 H), 2.64 (m, 2 H), 0.97 (s, 3 H).

Cycloaddition of Tetracyanoethylene to 6. A magnetically stirred solution of **6** (503o mg, 4.57 mmol) in 8 mL of dry benzene at room temperature was blanketed with nitrogen and treated with TCNE (586 mg, 4.57 mmol). A bright orange color developed immediately. After 20 h, the solvent was removed in vacuo and the colorless solid was analyzed by 300-MHz ^1H NMR analysis. The **26**:**27** ratio was thereby shown to be 6.7:1 (87% yield). Repeated recrystallization from acetone–petroleum ether provided pure **26** as colorless crystals: mp 192–194

°C; IR (KBr, cm^{-1}) 3545, 3470, 3300, 1475, 1460, 1370, 1300, 1220, 1175, 1050, 1040, 935, 830, 750, 650; ^1H NMR (300 MHz, CD_3CN) δ 6.65 (t, J = 2.1 Hz, 2 H), 3.83 (t, J = 2.1 Hz, 2 H), 3.42 (br s, 2 H), 3.03 (m, 1 H), 1.58 (s, 3 H); ^{13}C NMR (75 MHz, CD_3CN) ppm 139.18, 113.31, 113.22, 66.61, 66.47, 60.73, 46.93, 19.21. Anal. Calcd for $C_{13}H_{10}N_4O$: C, 65.54; H, 4.23. Found: C, 65.40; H, 4.36.

For **27**: ^1H NMR (300 MHz, acetone-d_6) δ 6.79 (t, J = 2.1 Hz, 2 H), 4.14 (t, J = 2.1 Hz, 2 H), 3.61 (s, 2 H), 2.86 (br s, 1 H), 1.29 (s, 3 H).

Cycloaddition of (*Z*)-1,2-Bis(phenylsulfonyl)ethylene to 6. A solution of **6** (100 mg, 9.09×10^{-4} mol) and the disulfone (841 mg, 2.73 mmol) in 1.5 mL of dichloromethane was maintained at 90 000 psi and room temperature for 2 days. Solvent removal left a white solid (86%), ^1H NMR analysis of which (300 MHz) showed **28** and **29** to be present in a 4.55:1 ratio. Repeated recrystallization of this material from dichloromethane–methanol provided pure **28** as colorless crystals: mp 299–300 °C; IR (KBr, cm^{-1}) 3505, 1445, 1365, 1335, 1295, 1270, 1185, 1160, 1145, 1085, 1040, 765, 735, 720, 695, 610; ^1H NMR (300 MHz, DMSO-d_6) δ 7.99–7.96 (m, 4 H), 7.76–7.73 (m, 6 H), 6.33 (t, J = 1.6 Hz, 2 H), 4.55 (s, 2 H), 4.33 (t, J = 5.5 Hz, 1 H), 3.15 (d, J = 5.5 Hz, 2 H), 2.49 (m, 2 H), 0.86 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d_6) ppm 141.28, 133.51, 133.22, 129.12, 128.14, 69.61, 62.55, 61.77, 53.48, 16.66; MS m/z ($M^+ - SO_2C_6H_5$) calcd 277.0898, obsd 277.0968. Anal. Calcd for $C_{21}H_{22}O_5S_2$: C, 60.27; H, 5.30. Found: C, 59.87; H, 5.42.

For **29**: ^1H NMR (300 MHz, DMSO-d_6) δ 7.98–7.80 (m, 4 H), 7.76–7.63 (m, 6 H), 6.39 (m, 2 H), 4.55 (m, 2 H), 4.33 (t, J = 5.2 Hz, 1 H), 3.15 (d, J = 5.2 Hz, 2 H), 2.58 (m, 2 H), 0.80 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d_6) ppm 141.34, 134.54, 133.77, 129.51, 127.82, 69.35, 62.69, 61.28, 52.76, 16.09.

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Supplementary Material Available: Tables of bond distances and angles, least-squares planes, final fractional coordinates, and thermal parameters for **17** and **22** (11 pages); observed and calculated structure factors for **17** and **22** (6 pages). Ordering information can be found on any current masthead page.

Binuclear Electron Reservoir Complexes:[1] Syntheses, Reactivity, and Electronic Structure of the 37- and 38-Electron Fulvalene Complexes $(Fe_2(\mu_2,\eta^{10}\text{-}C_{10}H_8)(arene)_2)^{n+}$, n = 0, 1

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Abstract: One-electron reduction of the dications $(Fe_2Fv(Ar)_2)^{2+}$ **2–8** in THF with Na/Hg gives high yields of the 37e⁻ Fe^IFe^{II} mixed-valence complexes **9–15**. The C_6Me_6 complex $(Fe_2Fv(HMB)_2)^+PF_6^-$, **9**, is thermally stable at 20 °C, whereas analogues with other arene ligands are not and need be isolated at lower temperatures. The symmetrical, purple complexes **9–15** show three g values around 2 by ESR spectroscopy at 77 or 4.2 K as Fe^I monomers. Mössbauer spectra of **9** and of $(Fe_2Fv(C_6H_6)_2)^+PF_6^-$, **10**, show only one quadrupole doublet at 293, 77, and 4.2 K, the parameters of which are not temperature dependent, unlike those of the Jahn–Teller active Fe^I monomers and of the localized Fe^IFe^{II} mixed-valence complexes. In addition, Mössbauer spectra, under external applied magnetic field, show the presence of only one electron for the "Fe_2" unit. Thus, the mixed-valence complexes $(Fe_2Fv(arene)_2)^+$ are delocalized on the Mössbauer time scale (10^7 s^{-1}). EHT and SCC-Xα calculations were performed and compared for both the monomeric Fe^I and the dimeric Fe^IFe^{II} and Fe^IFe^I complexes. A good agreement was found with Mössbauer parameters. The MO diagram of the 37e⁻ species shows a large HOMO–LUMO gap as expected from the non-variation of the quadrupole splitting values with the temperature. Two-electron reductions of **2**, **3**, and **8** in THF also using Na/Hg give the green organometallic 38e⁻ biradicals $Fe_2Fv(C_6R_6)_2$ (R = Me, **16**; R = H, **17**; R = Et, **22**). Jahn–Teller active Fe^I units are observed by Mössbauer spectroscopy in high-temperature phase. An antiferromagnetic transition occurs at 37 K, for **16**, as indicated by the Mössbauer and magnetic susceptibility data. The magnetic coupling of **16** at low temperature may be facilitated by the steric effect of the methyl substituents on the rotation around the C–C bond.

Among the various organometallic and inorganic families disclosing several stable oxidation states,[2] mononuclear organoiron "electron reservoir" complexes[3] have proved useful because of the simplicity of their large scale preparation,[4] the possibilities of functionalization,[5] and their efficient stoichiometric[6] as well as catalytic electron-transfer processes.[7,8] However, the number of available oxidation states is limited in mononuclear frameworks. The redox series is richer in binuclear species, specially if mixed-valence states are accessible. For instance, nature uses binuclear ferredoxins[9] (Fe_2S_2) as redox catalysts in the respiratory chain. To what extent the fulvalene bridge brings about satisfactory delocalization can be understood from the interaction and mutual

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(1) (a) Preliminary synthetic studies were effected in the Laboratoire de Chimie des Organométalliques, University of Rennes I. (b) *Organometallic Electron Reservoirs*; part 36. For part 35 see: Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F. *Organometallics*, in press. Part 34 reports the syntheses and electrochemistry of the 36e⁻ precursors: *Organometallics*, in press. (c) This paper overlaps with parts of the third cycle theses of M.-H.D. and J.G. Desbois, M.-H.; Astruc, D.

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