in sensitizer and 0.10 M in *trans*-β-methylstyrene; ethylbenzene (0.04 M) was present as an internal VPC standard.

Aliquots were taken from the reacting solution at various times during 15 min and analyzed by VPC on a 2 ft × $^1/_8$ in. 5% SE-30 column, temperature 95 °C for 7 min, then rising to 120 °C.

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Registry No. 1, 17078-27-2; 2, 1226-42-2; 3, 33425-19-3; 4, 3457-48-5; 5, 22711-21-3; 6, 54945-17-4; 7, 134-81-6; 8, 22711-23-5; 9, 3457-46-3; 10, 2387-74-8; 11, 6067-45-4; 12, 19555-07-8; 13, 20633-06-1; 14, 20651-89-2; 15, 68347-39-7; 16, 81578-43-0; 17, 4388-88-9; 18, 431-03-8; β-methylstyrene, 637-50-3.

Stereochemically Specific Diels–Alder Additions to Norbornyl- and Norbornenyl-Fused Fulvene Systems[1]

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The title fulvenes **9** and **10** were prepared and shown to enter into stereocontrolled below-plane Diels–Alder cycloaddition with a range of dienophiles. The photoelectron spectra of **9** and **10** were also recorded and analyzed by semiempirical MO calculations. Although σ/π coupling in the two (three) highest canonical orbitals of **9** (**10**) is seen to be unimportant, the lowest canonical "π" linear combinations are coupled so strongly that pronounced rotation of the π lobes in these orbitals is seen. The extent to which this phenomenon and other factors may contribute to overall stereoselection is discussed.

On the assumption that electronic influences inherent in norbornyl and norbornenyl frameworks should be observable at more remote sites, we[3] and others[4–6] have examined cycloadditions to exocyclic dienes such as **1–3**.

1

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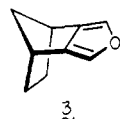

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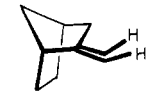
6

The expectation of pronounced π-facial stereoselectivity was founded in part upon earlier studies involving **4** and **5** where electronic effects contribute in a major way to an appreciable reactivity difference.[7] In fact, condensation of **1–3** with a variety of dienophiles proceeds from below the diene plane (as drawn) in virtually all cases.[3–6] This behavior contrasts in general with that exhibited by **6** which lacks norbornene character and consequently possesses lessened electronic directive influences.[3a,b,e]

A number of rationalizations have been applied to these observations. Our view, which has its foundations in molecular orbital theory and is supported by photoelectron spectroscopy, focuses on the evident mixing of the bicyclic σ orbital framework with the diene π_s orbital. The resulting strong interaction effects a disrotatory tilt of the π orbitals at C_1 and C_4 of the butadiene moiety such that frontier electron density is enhanced syn to the methano bridge. Antibonding interaction between the π_s orbital of the exocyclic butadiene system and the HOMO of the dienophile is consequently smaller for attack from below (Figure 1). More recently, Houk has indicated by means of calculations that π pyrmaidalization of the exocyclic double bond in **7** is such that the terminal hydrogen atoms



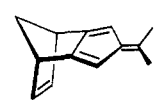
7

8

are bent in the exo direction.[8] The obvious relationship of **7** to **1** (see **8**) was cited as a possible reason for preferential approach of the dienophile from the ethano face.

Clearly, the question of whether simple geometric distortion is a factor in the π-facial stereoselective cycloadditons to **1–3** had to be resolved. Accordingly, we have proceeded to examine the Diels–Alder behavior of the norbornyl-fused dimethylfulvene systems **9** and **10**. This

9



10

pair of compounds was selected principally for two reasons. First, X-ray crystallographic[9] and electron diffraction studies[10] of 6,6-dimethylfulvene (and related molecules[11])

(1) Electronic Control of Stereoselectivity. Part 13. For part 12, see: Paquette, L. A.; Charumilind, P. *J. Am. Chem. Soc.* **1982**, *104*, 3749.

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0022-3263/83/1948-1250$01.50/0

Table I. ^{13}C NMR Chemical Shift Data ($CDCl_3$ Solution) of the Cycloadducts of 9 and 10 and Their Corresponding Epoxides[a]

	chemical shift, ppm						
cycloadduct	C_2	C_3	C_6,C_7	C_{4a},C_{8a}	C_9	C_{10}	C_{11}
11	149.91	149.91	22.57	157.68	47.72	159.14	102.24
12	149.19	149.19	25.00	64.76	38.54	148.51	110.06
Δ, ppm[b]	+0.72	+0.72	−2.43		+9.18	+10.63	−7.82
19	145.50	151.86	21.90, 21.75	50.54, 49.23	47.24	*c*	100.84
20	144.67	150.45	25.00, 24.90	66.02, 64.95	38.35	148.51	108.79
Δ, ppm[b]	+0.83	+1.41	−3.10, −3.15		+8.89	*d*	−7.95
27	*e*	*e*	139.48	160.94	69.72	~139.50	118.56
28	*e*	*e*	140.03	65.08	52.87	132.04	124.19
Δ, ppm[b]			−0.55		+16.85	+7.46	−5.63
29	*e*	*e*	139.68	160.65	69.67	139.63	117.05
30	*e*	*e*	139.82	65.54	52.72	133.07	122.49
Δ, ppm[b]			−0.14		+16.95	+6.56	−5.44

[a] See structure 11 for numbering scheme. [b] A plus sign indicates shielding and a minus sign deshielding effects of the epoxide ring. [c] This resonance can be assigned as one of three peaks, 159.97, 157.59, or 156.86 ppm. [d] The shielding effect observed in this case is 8.35–11.46 ppm. [e] Unassigned peaks.

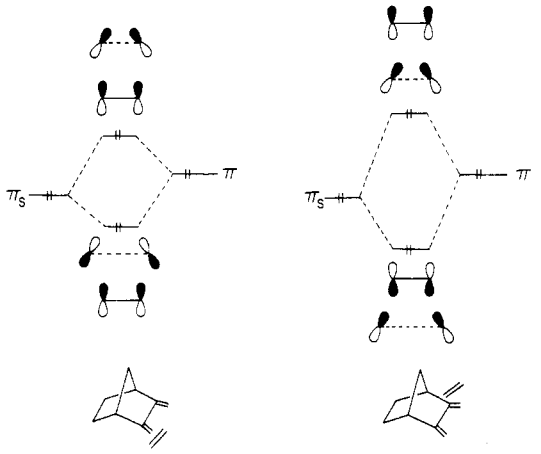


Figure 1. Interaction between the butadiene π_s and the dienophile HOMO for approach from the ethano face (left) and the methano face (right).

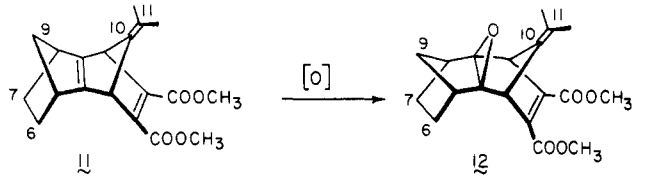
distinctly reveal the five-membered ring to be strictly planar, presumably in order to maximize π orbital overlap. Since any pyramidalization of the five-ring π bonds in **9** and **10** would result in loss of resonance energy, these compounds are also unlikely to be distorted from planarity. Second, detailed molecular orbital calculations of **9** and **10** reveal the existence not only of strong σ-π interaction in subjacent orbitals but also of π-lobe tilting reminiscent of that present in **1** and **2**. As shall be demonstrated, these structural and electronic features remain conducive to fully stereocontrolled dienophile capture from below the diene plane.

Results

Cycloadditions to 9. The preparation of **9** was accomplished via base-catalyzed condensation of **1** with acetone. Of the several bases examined, methylamine[12a] and ethanolic potassium hydroxide[12b] gave no evidence for anion formation, and *n*-butyllithium produced a mixture of condensation products which were not further characterized. However, utilization of sodium methoxide[12c] produced **9** as bright yellow needles exhibiting the expected spectral characteristics.

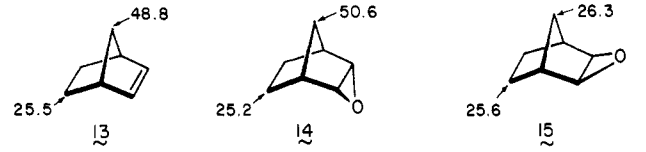
The cycloaddition reactions of **9** with several dienophiles were closely monitored by thin-layer chromatography and concurrent NMR experiments conducted in the same, though deuterated, solvent. Particular care was taken to follow the progress of these reactions closely in order to assess the timing of product appearance.

Exposure of **9** to dimethyl acetylenedicarboxylate (DMAD) in benzene solution at room temperature for 2 days under nitrogen afforded the single adduct **11** in 90% isolated yield. Upon being allowed to stand overnight in solution while exposed to the atmosphere, the air-sensitive adduct underwent partial autoxidation to **12**. The same



11 12

epoxide was formed by bubbling oxygen through a benzene solution of **11**.[13] Comparison of the ^{13}C NMR data for **11** and **12** provided the information necessary for unambiguous stereochemical assignment. Zefirov[14] has shown that the ring current and diamagnetic anisotropy effects of the epoxide ring[3c,15] in **15** act to shield the methano carbon by



13 14 15

22.5 ppm relative to that in norbornene (**13**).[16] In endo epoxide **14**, the methano carbon is slightly deshielded, whereas the ethano bridge carbons experience essentially no chemical shift alteration. Additionally, in extensive studies of compounds related in structure to **11** and **12**,[17]

(11) For selected examples, see: (a) Shimanouchi, H.; Sasada, Y.; Ashida, T.; Kakudo, M.; Murata, I.; Kitahara, Y. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1890. (b) Burzlaff, H.; Hartke, K.; Salamon, R. *Chem. Ber.* **1970**, *103*, 156. (c) Böhme, R.; Burzlaff, H. *Ibid.* **1974**, *107*, 832. (d) Ammon, H. L. *Acta Crystallogr., Sect. B* **1974**, *B30*, 1731. (e) Fallon, L.; Ammon, H. L.; West, R.; Rao, V. N. M. *Ibid.* **1974**, *B30*, 2407. (f) Ammon, H. L.; Wheeler, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 2326.

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(13) Compare: Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553.

(14) Zefirov N. S.; Kasyan, L. I.; Gnedenkov, L. Y.; Shashkov, A. S.; Cherepanova, E. G. *Tetrahedron Lett.* **1979**, *949*.

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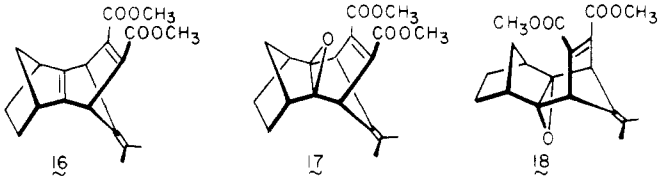
(16) Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107.

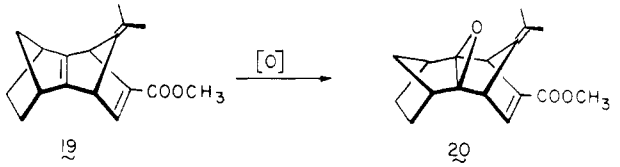
it was found that C_9 and C_{10} of the epoxidized systems are shielded to the extent of 8.7–17.0 and 6.3–14.2 ppm, respectively, relative to the precursor olefin. Moreover, very small shift changes were noted for the ethano bridge and bridgehead carbon atoms. Similar effects are seen in **12**, C_9 and C_{10} being shifted upfield (9.18 and 10.63 ppm) relative to the corresponding atoms in **11** as a consequence of their proximity to the epoxide ring. Relevantly, the epoxide also causes C_{11} in **12** to be downfield shifted (7.82 ppm) relative to its position in the spectrum of **11** (Table I). As will be seen, this more remote and opposite effect is consistently observed and constitutes an added useful diagnostic of stereochemistry.

Had DMAD addition to **9** occurred from above the plane to give **16**, epoxidation of the central double bond would have led to **17** and/or **18**. Upfield carbon shifts would be observed either for C_9 (in **17**) or C_{10} (in **18**), but not for both.



16 **17** **18**

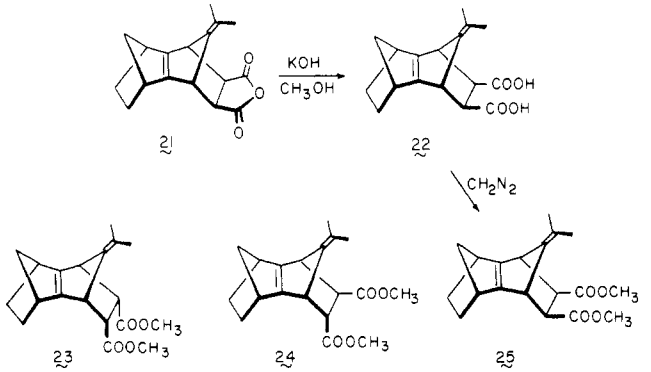
Heating a toluene solution of **9** and methyl propiolate at the reflux temperature for 3 days produced **19** as the sole cycloadduct. The relatively low yield (54%) in this instance has been traced to polymerization of the acetylenic ester under these conditions. Expectedly, the highly strained 4a,8a double bond of **19** is also prone to epoxidation when exposed to oxygen. Since C_9 and C_{10} in



19 **20**

20 are shielded relative to their counterparts in **19** (Table I), they must be situated on the same side of the molecule and proximal to the epoxide ring. Consequently, methyl propiolate also adds to **9** from the ethano face.

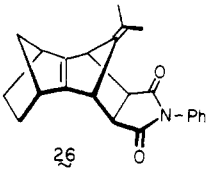
Treatment of **9** with maleic anhydride at room temperature in benzene solution for 2 days afforded only **21**. This somewhat less strained adduct is stable to air oxidation. As a result, its stereochemistry was established somewhat less directly. Thus, chromous sulfate reduction[18] of **11** produced the three possible esters **23–25** in a



21 **22** **23** **24** **25**

1.0:1.3:1.0 ratio. These isomers were separated chromatographically and their stereochemistries assigned on the basis of their NMR spectra. While both **23** and **25** exhibit symmetrical 11-line ^{13}C NMR spectra, **24** is characterized by 19 lines. The distinction between the symmetric structures rests upon the multiplicities of the protons α to the carbomethoxyl groups (singlet in the case of **25**; broadened multiplet in the case of **23**).[19] In turn, **21** was subjected to alkaline hydrolysis, and the diacid so produced (**22**) was esterified with diazomethane to give **25**. This intercorrelation establishes that maleic anhdride also attacks from below. The exo anhydride configuration is presumably adopted in violation of the Alder endo rule to avoid the obvious steric congestion that would be encountered in the endo configuration.[3]

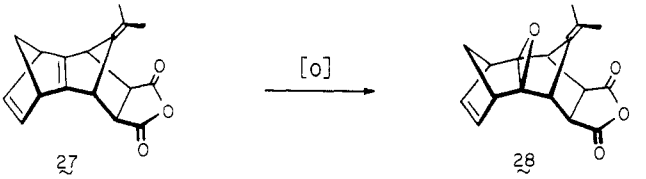
When a benzene solution of **9** was stirred with *N*-phenylmaleimide at room temperature, the single adduct **26** was obtained in 95% yield after recrystallization. Unambiguous stereochemical proof in this instance was derived by chemical intercorrelation with the *N*-phenylmaleimide adduct of **10** (see below).



26

Benzoquinone, phenyl vinyl sulfone, and methyl acrylate proved too unreactive toward **9** to be useful. When *N*-methyl- and *N*-phenyltriazolinedione were added to **9**, ene product formation was favored over the cycloaddition process.[20]

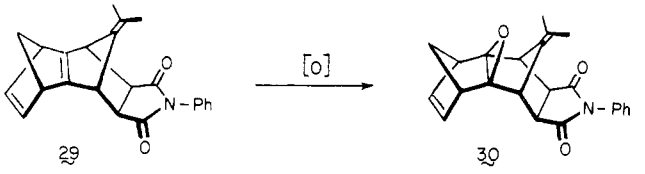
Cycloaddition to 10. When admixed with maleic anhydride, **10** gave rise to the single adduct **27**. In this example, cycloaddition does not proceed to completion due to facile dissociation. Equilibrium is attained after 7 h at room temperature. No evidence was obtained for formation of the exo adduct. Nor did the heating of **27** for prolonged periods in the absence of air produce any observable change except reversibility. Thus, the process is totally selective. On the strength of the adduct's ready conversion to **28** in air and because C_9 and C_{10} in **28** are



27 **28**

shielded relative to their positions in the ^{13}C NMR spectrum of **27** (Table I), the indicated structural formalism for **27** is considered established.

The single cycloadduct **29** was formed in the reaction of **10** with *N*-phenylmaleimide; however, due to the ease of oxidation of its 4a,8a double bond, both **29** and its epoxide **30** were isolated from the reaction mixture. As in



29 **30**

(17) Charumilind, P., unpublished observations.
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(20) (a) Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Böhm, M. C. *J. Am. Chem. Soc.* **1978**, *100*, 6510. (b) Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Böhm, M. C.; Beno, M. A.; Christoph, G. G. *Ibid.* **1981**, *103*, 7106. (c) Sasaki, T.; Manabe, T.; Hayakawa, K. *Tetrahedron Lett.* **1981**, *22*, 2579.

Table II. Comparison between the Measured Vertical Ionization Potentials of 9 and 10 ($I_{v,j}$) and Calculated Orbital Energies (ϵ_j) by Means of a Modified INDO Procedure and the MINDO/3 Method

compd	band	$I_{v,j}$	assignment[b]	ϵ_j(INDO)	ϵ_j(MINDO/3)
9	1	7.7	$(2b_1)_f$	−9.15 (20a′)	−8.57 (20a′)
	2	8.1	$(1a_2)_f$	−9.72 (14a″)	−8.58 (14a″)
10	1	7.8	$(2b_1)_f$	−9.06 (20a′)	−8.52 (20a′)
	2	8.1	$(1a_2)_f$	−9.80 (13a″)	−8.54 (13a″)
	3	8.9	π_{br}	−10.27 (19a′)	−8.98 (19a′)

[a] All values in electron volts. [b] f = fulvene moiety; br = π bridge.

the case of **27**, sharp singlets were observed for the C_1/C_4 and C_2/C_3 protons in both cases, indicating that the imide ring is exo oriented with respect to the norbornyl frame. In the ^{13}C NMR spectra, C_9 and C_{10} of **30** are shielded by 16.95 and 6.56 ppm, respectively, relative to the corresponding carbons of **29**. In addition, C_{11} in **30** is deshielded by 5.44 ppm. Catalytic hydrogenation of **29** produced a dihydro compound that exhibited spectral properties identical with those of **26**.

Photoelectron Spectra and Theoretical Assessment of 9 and 10. To analyze the σ/π interactions prevailing in **9** and **10**, semiempirical MO calculations have been evaluated in conjunction with low-energy photoelectron (PE) spectroscopy as before.[3,20a,21] In addition to the MINDO/3 method,[22] the present theoretical analysis also takes advantage of a recently developed improved INDO model[23] already successfully applied to topologically related hydrocarbons. The He(I) PE spectrum of **9** consists of two maxima at 7.7 and 8.1 eV, well separated from a series of strongly overlapping bands starting at 10 eV. For **10**, the first two maxima appear at very similar potentials (7.8 and 8.1 eV). Additionally, a third maximum is seen at 8.9 eV. Assignment of the latter to the ionization process emanating from the molecular orbital localized predominantly at the π bridge can be made in straightforward fashion (compare **2**, **6**, **31**, and **32**).[3,24] The first two ionization

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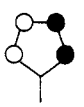
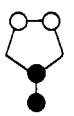
32

potentials of **9** and **10** must therefore be assigned to electron promotion from π orbitals $1a_2$ and $2b_1$ of the fulvene fragment.[25]



$1a_2$



$2b_1$

In Table II, the vertical ionization energies of **9** and **10** are compared with INDO and MINDO/3 values that have been derived by using Koopmans' approximation.[26] In contrast to the usual fulvene sequence ($1a_2$ above $2b_1$),

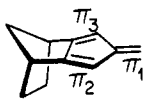
Table III. Decomposition of the Canonical "π" Linear Combinations 20a′, 14a″, and 18a′ of 9 into Localized π Orbitals (π_1, π_2/π_3) and the Most Important Delocalized σ-Ribbon Orbitals σ_i According to the INDO Method

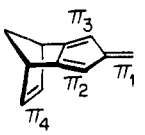
CMO	fragment	contribution, %
20a′	π_1	62.3
	π_2	14.0
	π_3	14.0
	σ_{17}	6.9
	σ_{28}	1.0
14a″	π_2	47.1
	π_3	47.1
	σ_{25}	2.8
18a′	π_1	16.8
	π_2	11.8
	π_3	11.8
	σ_{28}	49.7
	σ_{16}	3.6
	σ_{24}	2.7
	σ_{17}	2.0

Table IV. Decomposition of the Canonical "π" Linear Combinations 20a′, 13a″, 19a′, and 17a′ of 10 into Localized π Orbitals (π_1, π_2/π_3, π_4) and the Most Important Delocalized σ-Ribbon Orbitals σ_i According to the INDO Method

CMO	fragment	contribution, %
20a′	π_1	55.6
	π_2	14.4
	π_3	14.4
	$\pi_4 = \pi_{br}$	8.3
	σ_{16}	5.1
13a″	π_2	46.9
	π_3	46.9
	σ_{25}	2.7
	σ_{27}	1.8
19a′	$\pi_4 = \pi_{br}$	67.9
	π_1	7.3
	π_2	<0.1
	π_3	<0.1
	σ_{24}	12.8
	σ_{22}	6.2
	σ_{26}	1.3
17a′	π_1	23.3
	π_2	19.4
	π_3	19.4
	π_4	0.8
	σ_{26}	11.2
	σ_{24}	10.7
	σ_{22}	6.6
	σ_{16}	5.2

INDO predicts a switch in this splitting pattern for **9** and **10**, and MINDO/3 arrives at near degeneracy for these ionization events. However, the sequencing of these two MO's has no ultimate bearing on stereoselection. Upon transformtion of these canonical MO's having predominant π amplitudes into an orbital representation where the SCF orbitals are expressed as linear combinations of localized π fragments and delocalized precanonical σ-ribbon orbitals





(Tables III and IV),[27] the relevant precanonical σ-ribbon orbitals emerge (Figures 2 and 3). Relevantly, π/σ coupling in the two (three) highest canonical orbitals of **9** (**10**) is only of minor importance because their AO amplitudes arise predominantly from localized π fragments. Conse-

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(27) (a) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936. (b) Gleiter, R.; Böhm, M. C.; de Meijere, A.; submitted for publication.

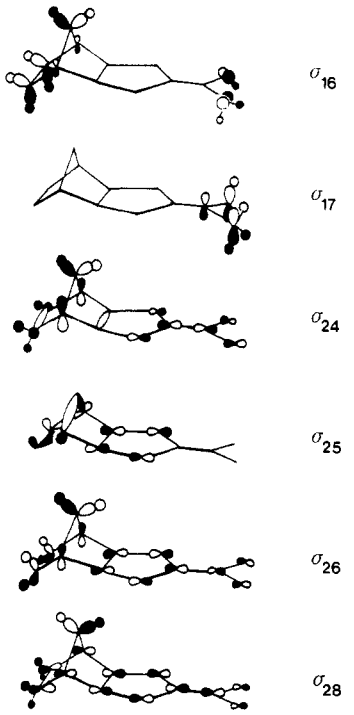


Figure 2. Schematic representation of the precanonical σ combinations contributing to the canonical "π" orbitals of **9** according to an INDO calculation.

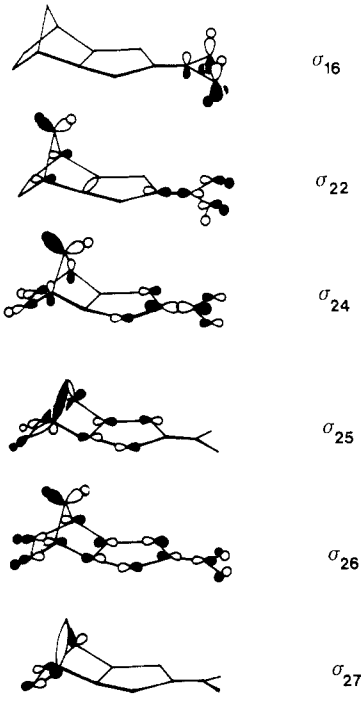


Figure 3. Schematic representation of the precanonical σ combinations contributing to the canonical "π" orbitals of **10** according to an INDO calculation.

quently, it goes unquestioned that these valence orbitals cannot contribute to factors that influence the stereoselectivity of **9** and **10** in cycloaddition reactions.

On the other hand, the lowest canonical "π" linear combinations in **9** and **10** contain significant contributions from precanonical σ-ribbon orbitals. In **9**, for example, 18a′ consists of a single precanonical MO (σ_{28}) which is strongly coupled with the π functions. Figure 2 clearly reveals that this is a typical σ-ribbon combination with large AO amplitudes in the direction of the longitudinal axis. The orbital wave function of σ_{28} contains large contributions

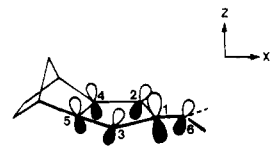


Figure 4. Schematic representation of the deformation of the π lobes in 18a′/17a′ of **9**/**10** according to the INDO model.

from both the fulvene moiety and methylene bridge. The amplitudes of the remaining σ_i functions (σ_{16}, σ_{24}, and σ_{17}) in the five-membered component are less pronounced. As a result of this strong π/σ coupling in the canonical MO's 18a′ and 17a′ of **9** and **10**, respectively, a pronounced rotation occurs in the π lobes of both orbitals. This deformation is shown schematically in Figure 4. Because of predominant x contributions, the deformation of the π lobes is restricted to the longitudinal axis. Thus, the π lobes at the terminal carbon atoms of the diene fragment are rotated in the direction of the ethano (etheno) bridge, while the opposite deformation is predicted for C_1 and C_4/C_5.

Discussion

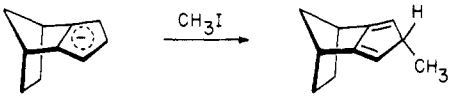
The obvious kinetic preference of dienophiles for bonding to **9** and **10** from below cannot reasonably be attributed to steric influences. The two surfaces of either fulvene ring system differ only by virtue of methano/ethano (etheno) bridges, and these carbon atoms are considered to be too remote from the bonding sites to be responsible for the observed π-facial stereoselectivity. Although the crystals obtained for **9** and **10** proved unsuitable for X-ray analysis, literature precedent[9-11] lends strong support to our assumption that their fulvene moieties are effectively planar. Since pyramidalization as in **8** is very likely absent, there exists no reason to invoke double bond distortions of this type as a possible source of stereochemical control.

On the other hand, the stereoselective behavior of **9** and **10** can be rationalized in terms of perturbational arguments similar to those which we have earlier utilized (see Figure 1).[3] Recall that the INDO results summarized in Tables II and III clearly reveal that π/σ coupling in both diene components is very strong. Consequently, in the event of topside attack (syn to the CH_2 bridge), an intense antibonding interaction develops between the occupied π orbitals of the attacking dienophile and the lowest diene function because the π lobes at C_2/C_3 are pointed inward toward the dienophile 2π component. This antibonding four-electron four-center interaction is substantially reduced during endo attack where the terminal π lobes of the diene fragment are now rotated away from the dienophile. These long-range electronic effects in **9** and **10** are calculated to be highly pronounced. Experimental support of this conclusion is found in the consistent stereochemical behavior of **9**, even when diene reactivity is allowed to fall off significantly. According to perturbation theory, these electronic features peculiar to a given diene should be most clearly apparent during cycloadditions which occur by way of early transition states.[28]

If, as we conclude, π-facial stereoselectivity in norbornyl- and norbornenyl-fused diene systems is controlled by disrotatory π-lobe tilting in filled subjacent orbitals, the phenomenon should be observable in other contexts and be subject to modulation. In subsequent papers on this

(28) (a) Sustmann, R.; Trill, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 838. (b) Sustmann, R.; Schubert, R. *Ibid.* **1972**, *11*, 840. (c) Sustmann, R. *Pure Appl. Chem.* **1974**, *40*, 569.

series, reaction of the cyclopentadienide anion **33** with methyl iodide is shown to lead exclusively to **34**.[29] Also,



33 34

35 36 37

dienophile capture by the gem-dialkylated derivatives **35** and **36** generally occurs *above* the cyclopentadiene plane[30] because of electronic interaction between the π_s butadienyl orbital and the C-alkyl σ electrons which are not present in **1**, **3**, or **9**.[1] When this admixing of electrons is further perturbed as in **37**, a return to overwhelmingly preferred *below-plane* dienophile capture is noted.[30a] Although additional study of this phenomenon is warranted, the deductions arrived at here should serve as a useful guide for predicting the possible influence on stereoselection which variations in the bridge segments of bicyclic moieties fused to exocyclic 1,3-dienes might induce.

Experimental Section

Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. Proton magnetic resonance spectra were recorded on Varian EM-390 and Bruker HX-90 spectrometers, and apparent splittings are given in all cases. Carbon-13 magnetic resonance spectra were recorded on Bruker WP-80 and WM-300 spectrometers. Mass spectra were measured on an AEI MS9 spectrometer at an ionizing energy of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. All reactions were performed under a nitrogen atmosphere unless otherwise indicated.

4,5,6,7-Tetrahydro-2-isopropylidene-4,7-methano-2*H*-indene (9). A solution of 1 (15.0 g, 0.114 mol) in acetone (26.1 g, 0.45 mol) was added dropwise to a freshly prepared methanol solution of sodium methoxide [5.3 g (0.23 mol) of sodium metal in 63 mL of anhydrous methanol]. This mixture was stirred at 55 °C for 3 h, diluted ith distilled water (50 mL), and extracted with methylene chloride (5 × 25 mL). The combined organic phases were washed with water, dried, filtered, and evaporated. The resulting oily residue was vacuum distilled and the fraction with a boiling point of 55–60 °C (0.05 torr) was collected to afford 6.5 g (33%) of **9** as yellow needles: mp 52.5–53.5 °C (from methanol); IR (KBr) 3080, 2980, 2935, 2860, 1640, 1440, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.85 (s, 2 H), 3.04 (m, 2 H), 2.05 (s, 6 H), 1.94–1.22 (m, 6 H); ^{13}C NMR ($CDCl_3$) 155.89 (s), 146.45 (s), 142.63 (s), 105.05 (d), 45.73 (t), 38.88 (d), 29.03 (m), 22.76 (q) ppm; MS, m/e (M^+) calcd 172.1252, obsd 172.1258. Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.45; H, 9.39.

4,7-Dihydro-2-isopropylidene-4,7-methano-2*H*-indene (10). A solution of **2** (2.0 g, 0.015 mol) in acetone (3.6 g, 0.062 mol) was added dropwise to a freshly prepared methanol solution of sodium methoxide [0.71 g (0.31 mol) of sodium metal in 8.8 mL of anhydrous methanol]. The mixture was stirred at 55 °C for 18 h, diluted with distilled water (10 mL), and extracted with methylene chloride (5 × 15 mL). The combined organic phases were washed with water, dried, filtered, and evaporated. Bulb to bulb distillation of the residue afforded 1.17 g of unreacted **2** [bp < 50 °C (0.05 torr)] and 0.52 g (48% based on recovered starting material) of **10** [bp < 100 °C (0.05 torr)] as a yellow oil. Recrystallization from methanol at −78 °C gave yellow needles: mp 47–48 °C; IR (KBr) 3045, 2980, 2900, 2840, 1637, 1435, 810, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.30 (m, 2 H), 5.93 (s, 2 H), 3.50 (m, 2 H), 2.31 (d, J = 8 Hz, 1 H), 2.02 (s, 6 H), 2.00 (d, J = 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 154.19, 147.97, 141.81, 136.60, 107.05,58.55, 43.93, 22.63 ppm; MS, m/e (M^+) calcd 170.1095, obsd 170.1102. Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.40; H, 8.29.

Dimethyl 1,4,5,6,7,8-Hexahydro-10-isopropylidene-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylate (11). A solution of dimethyl acetylenedicarboxylate (0.92 g, 0.0064 mol) in benzene (15 mL) was added in one portion to a solution of **9** (0.75 g, 0.0044 mol) in benzene (10 mL), and the reaction mixture was stirred at room temperature for 2 days. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) to yield 1.2 g (90%) of **11** as a viscous oil that crystallized as colorless needles upon standing: mp 91–92 °C (from hexanes); IR (KBr) 3020, 2970, 2940, 2835, 1740, 1725, 1625, 1275, 1187, 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.23 (s, 2 H), 3.74 (s, 6 H), 3.10 (m, 2 H), 1.67–1.40 (m with sharp s at δ 1.55, 8 H), 1.21–1.01 (m, 2 H), 0.68–0.35 (m, 2 H); ^{13}C NMR ($CDCl_3$) 165.69 (s), 159.14 (s), 157.68 (s), 149.91 (s), 102.24 (s), 52.62 (d), 52.04 (q), 47.72 (t), 43.16 (d), 22.57 (m), 19.03 (q) ppm; MS, m/e (M^+) calcd 314.1518, obsd 314.1526.

Upon being allowed to stand in solution, **11** underwent partial autoxidation to give **12**. The epoxide was isolated by medium-pressure liquid chromatography on silica gel (elution with 12% ethyl acetate in petroleum ether) and recrystallized to give colorless platelets: mp 120–122 °C (from diethyl ether); IR (KBr) 3005, 2975, 2950, 1720, 1608, 1323, 1260, 1178; ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 2 H), 3.77 (s, 6 H), 2.63 (m, 2 H), 1.91–0.77 (m with sharp s at δ 1.48, 12 H); ^{13}C NMR ($CDCl_3$) 164.72, 149.19, 148.51, 110.06, 64.76, 52.33, 50.44, 39.61, 38.54, 25.00, 19.03 ppm; MS, m/e (M^+) calcd 330.1467, obsd 330.1475. Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.12; H, 6.71.

Dimethyl 4a,8a-Epoxy-1,4,4a,5,6,7,8,8a-octahydro-10-isopropylidene-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylate (12). Oxygen was bubbled through a stirred solution of **11** (0.65 g, 0.0021 mol) in benzene (50 mL) for 18 h at room temperature. Solvent was removed in vacuo, and 0.18 g (26%) of **12** was isolated from the residue by medium pressure liquid chromatography on silica gel (elution with 12% ethyl acetate in petroleum ether) as a colorless crystalline solid, mp 120–122 °C (from diethyl ether). Its spectra proved identical with those described above for **12**.

Methyl 1,4,5,6,7,8-Hexahydro-10-isopropylidene-1,4:5,8-dimethanonaphthalene-2-carboxylate (19). A solution of **9** (500 mg, 2.9 mmol) in toluene (2 mL) was treated with a solution of methyl propiolate (370 mg, 4.4 mmol) in the same solvent (3 mL), and the mixture was heated at the reflux temperature for 2 days. A second aliquot of methyl propiolate (370 mg, 4.4 mmol) was added, and heating was resumed for an additional day. Solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (gradient elution with 5–20% ethyl acetate in petroleum ether) to give 400 mg (54%) of **19** as a colorless solid: mp 108–110 °C (from ether/hexanes); IR ($CDCl_3$) 3000, 2960, 2860, 1700, 1590, 1560, 1270, 1188 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.44 (d, J = 3 Hz, 1 H), 4.19 (s, 1 H), 4.04–3.90 (m, 1 H), 3.68 (s, 3 H), 2.98 (d, J = 7 Hz, 2 H), 1.84–0.95 (m, with sharp s at δ 1.55 and 1.52, 12 H); ^{13}C NMR ($CDCl_3$) 165.65 (s), 159.97 (s), 157.59 (s), 156.86 (s), 151.86 (d), 145.50 (s), 100.84 (s), 51.46 (q), 50.54 (d), 49.23 (d), 47.24 (t), 42.82 (d), 21.90 (m), 21.75 (m), 19.18 (q), 18.98 (q) ppm; MS, m/e ($^+$) calcd 256.1463, obsd 256.1470.

Upon being allowed to stand **19** partially underwent oxidation to **20**. The epoxide was isolated by medium-pressure liquid chromatography on silica gel (elution with 5% ethyl acetate in petroleum ether) and recrystallized from ether/hexanes to afford a colorless solid: mp 123–124.5 °C; IR (KBr) 3005, 2960, 2920, 2865, 1700, 1580, 1317, 1225, 1193 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.34 (d, J = 3 Hz, 1 H), 3.92 (s, 1 H), 3.73 (s and shoulder, 4 H), 2.59 (m, 2 H), 1.90–0.73 (m with sharp s at δ 1.50 and 1.47, 12 H); ^{13}C NMR ($CDCl_3$) 164.92 (s), 150.45 (d), 148.51 (s), 144.67 (s), 108.79

(29) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. in press.

(30) (a) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J., in press. (b) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F., in press.

(s), 66.02 (s), 64.95 (s), 51.75 (q), 48.45 (d), 46.94 (d), 39.37 (t), 38.35 (t), 25.00 (m), 24.90 (m), 19.22 (q), 19.03 (q) ppm; MS, m/e (M^+) calcd 272.1412, obsd 272.1417. Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.98; H, 7.40. Found: C, 75.12; H, 7.69.

Methyl 4a,8a-Epoxy-1,4,4a,5,6,7,8,8a-octahydro-10-isopropylidene-1,4:5,8-dimethanonaphthalene-2-carboxylate (20). Oxygen was bubbled through a solution of **19** (200 mg, 0.78 mmol) in benzene (25 mL) for 24 h at room temperature. Solvent was removed in vacuo, and 70 mg (33%) of **20** was isolated from the residue by medium-pressure liquid chromatography on silica gel (elution with 5% ethyl acetate in petroleum ether) as a colorless solid, mp 123–124.5 °C (from ether/hexanes). Its spectra proved identical with those described above for **20**.

1,2,3,4,5,6,7,8-Octahydro-10-isopropylidene-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylic Anhydride (21). A solution of **9** (2.00 g, 0.0116 mol) in benzene (25 mL) was treated with a solution of maleic anhydride (1.15 g, 0.0117 mol) in benzene (50 mL), and the mixture was stirred at room temperature for 2 days. Solvent was removed in vacuo, and the resulting semicrystalline solid was recrystallized several times from ether to afford 1.5 g (50%) of **21** as colorless plates: mp 114–116 °C (from ether); IR (KBr) 3000, 2980, 2960, 2875, 1835, 1770, 1225 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.95 (s, 2 H), 3.12 (m, 2 H), 2.84 (s, 2 H), 1.86–1.01 (m with sharp s at δ 1.61, 12 H); ^{13}C NMR ($CDCl_3$) 171.13, 153.26, 136.51, 116.80, 49.42, 49.13, 48.35, 43.11, 25.05, 19.90 ppm; MS, m/e (M^+) calcd 270.1256, obsd 270.1261. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.53; H, 6.75.

Dimethyl 1,2,3,4,5,6,7,8-Octahydro-10-isopropylidene-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylate (23–25). A solution of **7** (400 mg, 1.3 mmol) in dimethylformamide (15 mL) was added dropwise to an aqueous solution containing a twofold molar excess of chromous sulfate.[30] After 15 min, the reaction mixture was diluted with distilled water (50 mL) and extracted with ether (2 × 25 mL). The combined organic layers were washed with water (4 × 10 mL) and brine (2 × 10 mL), dried, filtered, and evaporated to afford 0.36 g (90%) of a pale yellow oil. Separation by medium-pressure liquid chromatography on silica gel (elution with 7% ethyl acetate in hexanes) gave 80 mg of **25** as a colorless oil and 80 mg (20%) of **23** and 100 mg (25%) of **24** as colorless solids.

For **25**: IR (neat) 3000, 2960, 2920, 1740, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.68 (s, 2 H), 3.59 (s, 6 H), 3.04 (m, 2 H), 2.40 (s, 2 H), 1.80–0.73 (m with sharp s at δ 1.63, 12 H); ^{13}C NMR ($CDCl_3$) 173.03 (s), 152.83 (s), 144.29 (s), 113.17 (s), 51.61 (q), 49.81 (t), 47.53 (dd), 47.00 (d), 43.16 (d), 25.63 (m), 20.29 (q) ppm; MS, m/e (M^+) calcd 316.1674, obsd 316.1681.

For **23**: mp 88–89 °C (from petroleum ether); IR (KBr) 3000, 2980, 2955, 2915, 1748, 1200, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.73 (m, 2 H), 3.59 (s, 6 H), 3.21 (m, 2 H), 3.00 (m, 2 H), 1.70–0.76 (m with sharp s at δ 1.51, 12 H); ^{13}C NMR ($CDCl_3$) 172.59 (s), 153.90 (s), 149.17 (s), 105.29 (s), 55.71 (t), 51.46 (q), 48.12 (d), 48.00 (d), 43.82 (d), 25.43 (m), 19.36 (q) ppm; MS, m/e (M^+) calcd 316.1674, obsd 316.1681.

For **24**: mp 112–113 °C (from diethyl ether); IR (KBr) 3000, 2970, 2920, 1863, 1727, 1263, 1188 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (d, J = 3 Hz, 1 H), 3.68 (s, 3 H), 3.65 (s, 3 H), 3.36–3.21 (m, 2 H), 3.12–2.93 (m, 2 H), 2.57 (d, 4 H), 1.93–0.50 (m with sharp s at δ 1.58 and 1.47, 12 H); ^{13}C NMR ($CDCl_3$) 174.00, 173.47, 154.58, 151.81, 146.71, 109.19, 51.95, 51.85, 51.75, 48.79, 48.06, 47.82, 47.24, 43.11, 42.97, 25.63, 24.81, 19.66, 19.52 ppm; MS m/e (M^+) calcd 316.1674, obsd 316.1681.

1,2,3,4,5,6,7,8-Octahydro-10-isopropylidene-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylic Acid (22). A solution of **21** (100 mg, 0.37 mmol) in methanol (1.15 mL) was treated with 0.61 mL of 6 M aqueous potassium hydroxide, and the mixture was stirred overnight. Methanol was removed in vacuo, and the residue was diluted with distilled water (10 mL) and acidified with 30% sulfuric acid. The suspension was filtered, and the filtrate was washed with distilled water then air-dried to afford 88 mg (83%) of **22** as a colorless solid: IR (KBr) 3000 (br), 2985, 2920, 2875, 1727, 1700, 1280, 1245, 1213 cm^{-1}; MS, m/e (M^+ – 18) 270. The product was esterified without further purification.

Esterification of 22. An ethereal solution of diazomethane was added dropwise in excess to a cooled (0 °C) solution of **22** (88 mg, 0.30 mmol) in benzene–ether (1:1, 10 mL). After 15 min, glacial acetic acid was added to consume excess diazomethane. The resulting solution was washed with saturated aqueous sodium bicarbonate solution (2 × 10 mL), distilled water (2 × 10 mL), and brine (10 mL). The organic phase was dried, filtered, and evaporated to yield 75 mg (85%) of **25** as a colorless oil whose spectral properties were identical with those of **25** reported above.

1,2,3,4,5,6,7,8-Octahydro-10-isopropylidene-*N*-phenyl-1,4:5,8-dimethanonaphthalene-2,3-dicarboximide (26). A solution of **9** (250 mg, 1.5 mmol) in benzene (2 mL) was treated with a solution of *N*-phenylmaleimide (280 mg, 1.6 mmol) in the same solvent (3 mL), and the mixture was stirred at room temperature for 1 day. Solvent was removed in vacuo to give 530 mg of **26** plus excess *N*-phenylmaleimide. Fractional recrystallization of this mixture from ether afforded 490 mg (95%) of pure **26** as colorless platelets: mp 158.5–160 °C; IR (KBr) 3020, 2970, 2940, 1772, 1700, 1640, 1400, 1383, 1200, 740, 683 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45–7.22 (m, 3 H), 7.12–6.95 (m, 2 H), 3.90 (s, 2 H), 3.10 (m, 2 H), 2.67 (s, 2 H), 1.80–0.99 (m with sharp s at δ 1.60, 12 H); ^{13}C NMR ($CDCl_3$) 176.38, 153.03, 141.42, 132.15, 129.14, 128.51, 126.37, 115.06, 49.47, 48.21, 47.63, 43.16, 25.59, 20.05 ppm; MS, m/e (M^+) calcd 345.1729, obsd 345.1737. Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71. Found: C, 79.76; H 6.73.

1,2,3,4,5,8-Hexahydro-10-isopropylidene-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylic Anhydride (27). A solution of **10** (115 mg, 0.67 mmol) and maleic anhydride (65 mg, 0.67 mmol) in deoxygenated deuterated chloroform was kept at room temperature for 7 h. NMR spectra were recorded for the resulting equilibrium mixture (resonances of the starting materials were subtracted from those of the mixture); ^1H NMR ($CDCl_3$) δ 6.60–6.43 (m), 3.98 (s), 3.60–3.40 (m), 2.49 (s), 2.40–1.90 (m), 1.63 (s); ^{13}C NMR ($CDCl_3$) 171.86 (s), 160.94 (s), 139.48 (d), 118.56 (s), 69.72 (t), 49.18 (d), 48.55 (d), 46.51 (d), 20.05 (q) ppm.

Oxygen was bubbled through this mixture for 12 h. The solvent was removed in vacuo, and the resulting oil was purified by medium-pressure liquid chromatography on silica gel (elution with 20% ethyl acetate in petroleum ether) to afford 30 mg (20%) of **28** as a colorless solid: mp 192–193 °C (from ethyl acetate/petroleum ether); IR (KBr) 2990, 2940, 2825, 1837, 1775, 1440, 1380, 1303, 1220, 1087, 1070, 920, 830, 737 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.50–6.40 (m, 2 H), 3.64 (s, 2 H), 3.22–3.10 (m, 2 H), 3.00 (s, 2 H), 2.04 (d, J = 8 Hz, 1 H), 1.57 (s, 6 H), 1.56 (d, J = 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 170.83, 140.03, 132.04, 124.19, 65.08, 52.87, 47.37, 45.44, 44.99, 20.16 ppm; MS, m/e (M^+) calcd 284.1048, obsd 284.1056. Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.59; H, 5.72.

1,2,3,4,5,8-Hexahydro-10-isopropylidene-*N*-phenyl-1,4:5,8-dimethanonaphthalene-2,3-dicarboximide (29). A solution of **10** (100 mg, 0.59 mmol) in benzene (2 mL) was treated with a solution of *N*-phenylmaleimide (200 mg, 1.2 mmol) in the same solvent (2 mL). After being stirred at room temperature for 2 days, the reaction mixture was freed of solvent in vacuo. The adduct was separated from excess *N*-phenylmaleimide by medium-pressure liquid chromatography on silica gel (elution with 20% ethyl acetate in petroleum ether) to yield 90 mg (53%) of **29** as a colorless solid: mp 134–135 °C (from ether at –78 °C); IR (KBr) 3000, 2985, 2930, 1775, 1685, 1195, 740, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.55–7.38 (m, 3 H), 7.17–7.01 (m, 2 H), 6.56 (t, J = 1.5 Hz, 2 H), 3.98 (s, 2 H), 3.52 (m, 2 H), 2.38 (s, 2 H), 2.29 (d, J = 8 Hz, 1 H), 2.16 (d, J = 8 Hz, 1 H), 1.67 (s, 6 H); ^{13}C NMR ($CDCl_3$) 177.06 (s), 160.65 (s), 149.68 (d), 139.68 (d), 139.63 (s), 134.24 (s), 129.24 (d), 128.56 (d), 126.47 (d), 117.05 (s), 69.67 (t), 49.28 (d), 47.92 (d), 45.44 (d), 20.29 (q) ppm; MS, m/e 343.1572, obsd 343.1579.

The epoxidized adduct **30** (50 mg, 27%) was also isolated as a colorless solid, mp 241–242 °C (from hexanes); IR (KBr) 2980, 2950, 2920, 1775, 1700, 1195, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.47–7.28 (m, 3 H), 7.13–6.93 (m, 2 H), 6.44 (t, J = 1.5 Hz, 2 H), 3.62 (s, 2 H), 3.14 (m, 2 H), 2.88 (s, 2 H), 2.04 (d, J = 8 Hz, 1 H), 1.59 (s and shoulder, 7 H); ^{13}C NMR ($CDCl_3$) 176.33, 139.82, 133.07, 132.00, 129.29, 128.75, 126.37, 122.49, 65.54, 52.72, 46.36, 45.39, 45.15, 20.34 ppm, MS, m/e (M^+) calcd 359.1521, obsd 359.1513.

Catalytic Hydrogenation of 29. A solution of **29** (60 mg, 0.18 mmol) in ethyl acetate containing a catalytic amount of platinum oxide was hydrogenated at atmospheric pressure. Upon completion of hydrogen uptake, the catalyst was removed by filtration

through a Celite pad, and the filtrate was evaporated. The residue was purified by preparative thin-layer chromatography on silica gel (elution with 15% ethyl acetate in petroleum ether) to afford 10 mg (20%) of a colorless solid, mp 153–155 °C (from ether). The ^1H and ^{13}C NMR spectra of this product were identical with those of adduct **26**.

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Registry No. **1**, 6675-72-5; **2**, 6675-71-4; **9**, 84988-39-6; **10**, 84988-40-9; **11**, 84988-41-0; **12**, 84988-42-1; **19**, 84988-43-2; **20**, 84988-44-3; **21**, 84988-45-4; **22**, 84988-46-5; **23**, 84988-47-6; **24**, 85027-44-7; **25**, 85027-45-8; **26**, 84988-48-7; **27**, 84988-49-8; **28**, 84988-50-1; **29**, 84988-52-3; **30**, 84988-51-2; acetone, 67-64-1; dimethyl acetylenedicarboxylate, 762-42-5; methyl propiolate, 922-67-8; *N*-phenylmaleimide, 941-69-5; maleic anhydride, 108-31-6.

[4 + 2] Cycloadditions to Norbornyl- and Norbornenyl-Fused Anthracene Systems[1]

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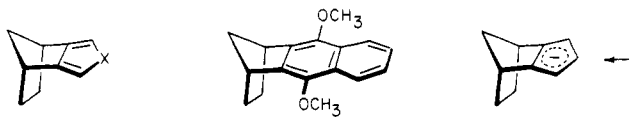
The preparation and Diels–Alder cycloadditions of 2,3-norbornadienoanthracene (**4**) and 2,3-norbornenoanthracene (**5**) are described. The purpose of this study was to determine if the fused bicyclic frameworks could exert long-range effects on π-facial stereoselectivity. In the several examples which were examined, approximate 1:1 ratios of top- and bottom-face bonding were observed, indicating that remote stereoelectronic effects were inoperative. In most cases, the stereochemical outcome of the particular cycloaddition was ascertained subsequent to chemical degration to the isomer pairs **13**/**14** or **21**/**22**.

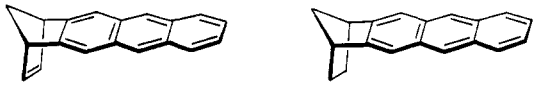
The last several years have witnessed an upsurge of interest in π-facial stereoselectivity.[1,3-8] The factors which cause the two faces of a π bond to be nonequivalent such as to favor preferential attack from one side have commanded particular attention.[3-5,9-12] Of especial interest to us have been the discoveries that norbornyl-fused dienes such as **1** (X = CH_2, O, C=C$(CH_3)_2$, etc.) enter into highly



1 **2** **3**

stereoselective Diels–Alder cycloadditions. Similarly striking stereoelectronic control is exhibited by **2** and its congeners during their capture of singlet oxygen, despite the aromatic character of the π network in these substrates.[13] The impressive ability of norbornyl frameworks to control the stereochemical outcome of chemical reactions at rather long range persists in carbanion **3** where methylation occurs regiospecifically (see arrow) and with exceptional endo stereoselectivity.[14]

Presently, we have sought to delineate the approximate limits of this phenomenon by subjecting the previously



4 **5**

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