Role of Pendant Methyl Groups in Controlling the Rate and Stereochemical Outcome of Diels-Alder Additions to Tricyclo[5.2.1.$0^{2,6}$]decadienes and -trienes

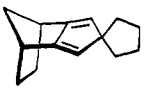
Leo A. Paquette,*[2a] Peter C. Hayes,[2a,3] Pana Charumilind,[2a] Michael C. Böhm,[2b] Rolf Gleiter,*[2b] and John F. Blount[2c]

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210, Institut für Organische Chemie der Universität Heidelberg, D-6900 Heidelberg, West Germany, and Research Department, Hoffmann-LaRoche, Inc., Nutley, New Jersey 07110. *Received July 15, 1982*

Abstract: The stereoselectivities of the Diels-Alder reactions of six methyl-substituted norbornyl- and norbornenyl-fused cyclopentadiene systems (**3-5**) with various dienophiles have been examined. Whereas **3a** enters into cycloaddition from the above-plane direction for steric reasons, the responses of **3b**, **4c**, and **5** are attributed to electronic influences. Molecular orbital calculations have also been carried out in support of this conclusion. The rates of dimethyl acetylenedicarboxylate cycloaddition to **3a**, **3b**, **5**, and six related compounds provide further indication that steric factors are not the primary determinant of π-facial stereoselectivity. The use of ^{13}C NMR spectroscopy as a diagnostic for the elucidation of *syn*- and *anti*-sesquinorbornene stereochemistry is also detailed, as are the intimate intimate structural features of four adducts which have been subjected to X-ray crystal structure analysis. Particular attention is given to the extent of deformation about the central double bond.

The effect of substituents on the stereoselectivity of Diels-Alder additions to norbornyl- and norbornenyl-fused diene systems has recently received detailed attention in these laboratories.[1,4,5] The remarkable contrast in the behavior of **1** (below-plane attack) and

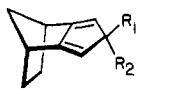
1



2

2 (above-plane attack) served to raise a number of questions pertaining to the possible perturbing role of steric influences. Thus, the presence of alkyl groups in certain dienes and not others could exert a rate-retarding effect to an extent sufficient to permit a stereochemically different pathway to become dominant. The 2-fold purpose of the present study was to extend the range of substituents to include methyl groups both directly on the cyclopentadiene ring and the apical norbornyl carbon atom, and to perform kinetic studies which would reveal in quantitative terms the impact made by these appendages on cycloaddition rate.

The monomethyl-substituted hydrocarbons **3a**, **4a**, and **4b** were



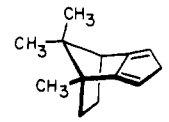
3a, $R_1 = H, R_2 = CH_3$

3b, $R_1 = R_2 = CH_3$

4a, $R_1 = H, R_2 = CH_3$

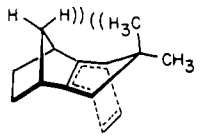
4b, $R_1 = CH_3, R_2 = H$

4c, $R_1 = R_2 = CH_3$

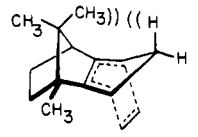


5

available from an earlier study,[6] as was the camphor-derived substrate **5**.[7] Synthetic approaches to **3b** and **4c** are described below. These systems provide various types of steric encumbrance which must be superimposed upon those existing factors which normally contribute to stereoselective [4 + 2] cycloaddition. Thus, the lone methyl group which is projected below the π surface of the cyclopentadiene ring in **3a** and **4a** can be expected to alter dienophile accessibility to the usually preferred endo face. At issue is whether this steric imbalance is adequate to modulate π-facial stereoselectivity and, if so, at what kinetic expense, if any. As concerns **3b** and **4c**, the geminal methyl pair restores more equitable steric balance to approach from above and below the cyclopentadiene unit, but with added steric restrictions to both bonding schemes. Also to be considered if below-plane attack occurs is the extent to which nonbonded steric interactions between apical bridges (see **6**) might become an issue of some consequence.



6



7

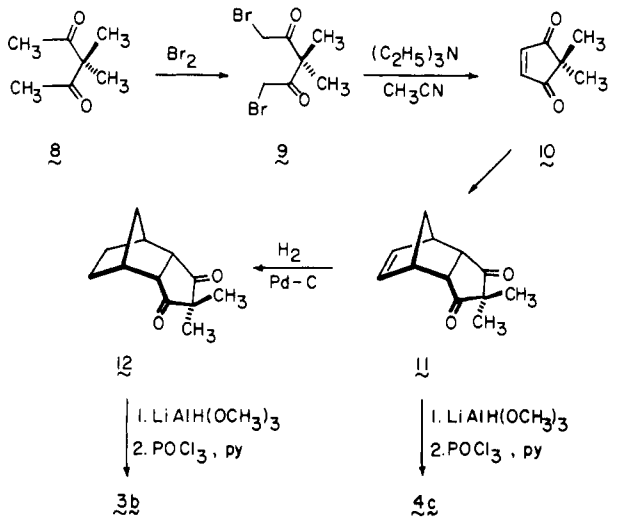
Diene **5** was studied in order to examine the complementary state of affairs depicted in transition state **7**.

Results

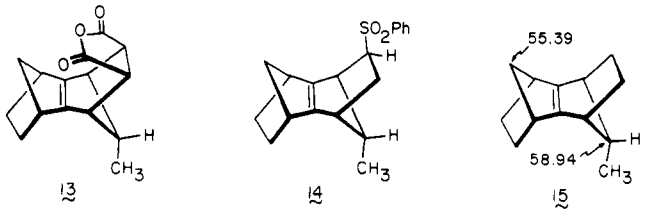
Synthesis. The starting material for the preparation of **3b** and **4c** was 2,2-dimethyl-4-cyclopentene-1,3-dione (**10**). Although Agosta and Smith have reported a preparation of **10** from its dihydro derivative by *N*-bromosuccinimide oxidation,[8] this procedure proved problematic in our hands. However, the alternative route later devised by Jefferson, McDonald, and Smith[9] which involves the bromination of open-chain diketone **8** followed by cyclizative 2-fold dehydrobromination of **9** delivered **10** reproducibly. Following Diels-Alder addition of **10** to cyclopentadiene and catalytic hydrogenation,[8] endo/exo mixtures of **11** and **12** (slightly richer in the depicted endo isomers) were obtained. This stereochemical inhomogeneity presented no difficulty, and the unpurified mixtures were directly reduced with lithium trimethoxyaluminum hydride and dehydrated with phosphorus oxychloride in pyridine.[10] Both resulting hydrocarbons displayed eight-line ^{13}C NMR spectra in accord with their symmetry.

(1) Electronic Control of Stereoselectivity. 16. For part 15, see: Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105* (second paper of this series in this issue).
(2) (a) Columbus. (b) Heidelberg. (c) Nutley.
(3) Graduate School Postdoctoral Fellow, 1981-1982.
(4) (a) Paquette, L. A.; Schaefer, A. G.; Blount, J. F.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.*, in press. (b) Paquette, L. A.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Org. Chem.*, in press. (c) Paquette, L. A.; Charumilind, P. *J. Am. Chem. Soc.* **1982**, *104*, 3749.
(5) Paquette, L. A.; Bellamy, F.; Böhm, M. C.; Gleiter, R. *J. Org. Chem.* **1980**, *45*, 4913.
(6) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1983**, *105* (first paper of this series in this issue).
(7) Burgstahler, A. W.; Boger, D. L.; Naik, N. C. *Tetrahedron* **1976**, *32*, 309.
(8) Agosta, W. C.; Smith, A. B. *J. Org. Chem.* **1970**, *35*, 3856.
(9) Jefferson, P.; McDonald, E.; Smith, P. *Tetrahedron Lett.* **1978**, 585.
(10) Paquette, L. A.; Klinger, F. *J. Org. Chem.* **1982**, *47*, 272.

0002-7863/83/1505-3148$01.50/0



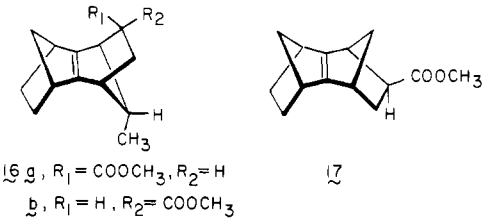
Cycloadditions to 3a. Maleic anhydride added to diene **3a** at room temperature in benzene solution and gave adduct **13** as the



sole observable product (≥97%). The endo configuration of the anhydride moiety was immediately apparent from its ^{1}H NMR spectrum which shows the vicinal coupling constant between the tertiary α-carbonyl and neighboring bridgehead protons to be ~1.5 Hz.[11] Its characterization as an *anti*-sesquinorbornene derivative rests upon ample ^{13}C analogy with adducts of established structure (Table I). The striking similarity of the chemical shifts among the four anti-endo anhydrides requires no additional comment. Although the number of known syn-endo isomers is more limited it is clear that the data for **13** are incompatible with this particular stereochemical assignment. Finally, as has been pointed out elsewhere,[1] the apical carbon atoms of syn-exo adducts generally experience rather marked shielding relative to their stereoisomers and are usually distinguishable on this basis.

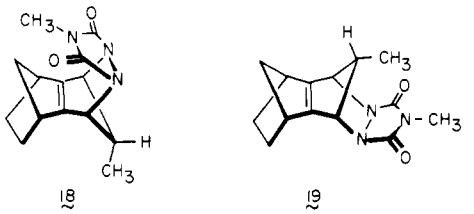
Stirring **3a** with the less reactive phenyl vinyl sulfone reagent in dichloromethane for 18 days at room temperature furnished **14** as the only symmetrical adduct.[12] Although the configuration of the phenylsulfonyl group was deduced to be endo from ^{1}H NMR data (vicinal bridgehead proton appears as a doublet with J = 3 Hz), the molecule's topology was convincingly established only after sodium amalgam reduction[13] to **15**. In this hydrocarbon, the chemical shift of the apical carbons (see formula) are downfield of those in *syn*-sesquinorbornene (50.26 ppm),[14] but compare closely with those of the anti isomer (54.51 ppm).[15]

Methyl acrylate reacted inefficiently with **3a** to give **16a** and **16b** in equal amounts, along with a lesser quantity of an unsym-



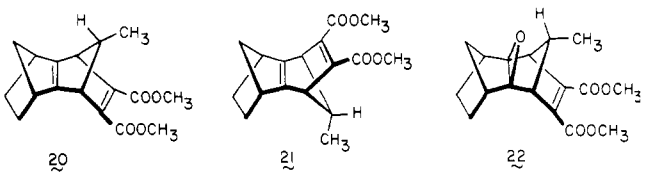
metrical adduct.[16] The stereodisposition of the carbomethoxy groups was assigned on the basis of the relative polarity of the epimers on silica gel. The *anti*-sesquinorbornene character of the esters was ascertained by their mutual unreactivity toward diimide (97% recovery in both instances). In contrast, **17** has been shown to be readily reduced by this reagent.[14,17] Consequently, dienophile capture has again proceeded stereoselectively from above the diene π system.

N-Methyltriazolinedione added rapidly to **3a** at −78 °C to produce a 93:7 mixture of urazoles **18** and **19**. Although only



18 was isolated in analytically pure form, the ^{13}C NMR spectra of both isomers were recorded. As can be seen from the compilation in Table II, there exists a dichotomy in apical carbon shifts between syn and anti stereoisomers which parallels that made evident in Table I. Nonetheless, to place our assignments beyond reproach, a confirmatory X-ray crystal structure analysis was carried out on **18** (Figure 1). Of interest in connection with this highly reactive dienophile is the finding that a small percentage of below-plane attack is able to operate despite the sterically disadvantaged status of that π surface.

Dimethyl acetylenedicarboxylate (DMAD) added to **3a** at 20 °C with still higher below-plane stereoselectivity to give a 70:30 mixture of **20** and **21**. From the compilation provided in Table



III, it is clear that syn/anti stereodifferentiation can be accomplished with reasonable confidence from ^{13}C data alone. Nonetheless, further confirmation was achieved by subjecting both substances to peracid epoxidation. As expected for **20**, conversion to **22** was complete in less than 30 min at room temperature. For **21**, only 11% conversion to epoxide was achieved after 3 days in refluxing dichloromethane. Thus, DMAD once again has exerted somewhat of a maverick role by engaging in preferential [4 + 2] π-facial stereoselection opposite that observed with olefinic (as opposed to acetylenic) dienophiles.[1]

4a/4b–Maleic Anhydride Reaction Profile. Because of the availability of **4a** and **4b** only as an inseparable isomeric mixture,[6] studies involving these dienes were confined to maleic anhydride. Were indiscriminate stereoselection to prevail, a total of eight cycloadducts would be formed. As matters turned out, only four

(11) Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 3724.

(12) Under these reaction conditions, **14** was isolated in 38% yield, accompanied by an unsymmetrical product (28%) which has been tentatively formulated as i (see Experimental Section). Earlier work in this laboratory [Paquette, L. A.; Williams, R. V.; Carr, R. V. C.; Charumilind, P.; Blount, J. *J. Org. Chem.* **1982**, *47*, 4566] has shown that dienophiles of low reactivity are prone to add in similar fashion to the 1,5-hydrogen-shifted isomer in the parent isodicyclopentadiene example. When **3a** and phenyl vinyl sulfone were heated in dichloromethane at the reflux temperature for 36 h, the majority of the cycloaddition product was i (18%); 68% of unreacted **3a** was also recovered. Under still more forcing conditions (toluene, reflux, 15 h), 50% consumption of diene occurred and i was formed to the extent of 21%.

(13) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

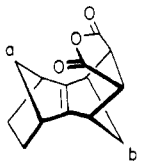
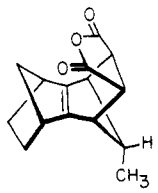
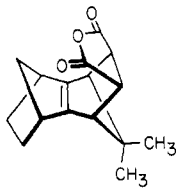
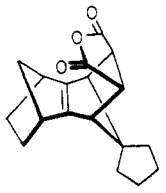
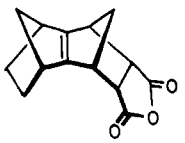
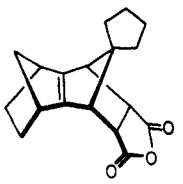
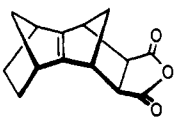
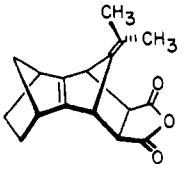
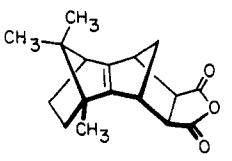
(14) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186, 7218.

(15) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022.

(16) When the cycloaddition was conducted in carbon tetrachloride solution at 42 °C for 4 days, there was isolated after chromatography the epimeric esters **16a** (10%) and **16b** (10%), and a third colorless oil (3.7%) tentatively formulated as ii (see Experimental Section and footnote 12).

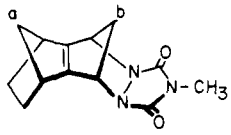
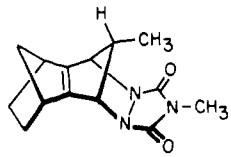
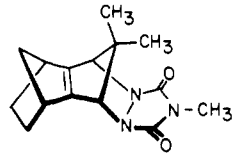
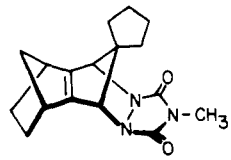
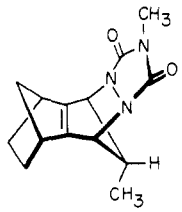
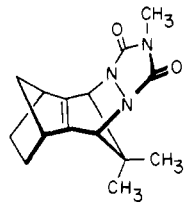
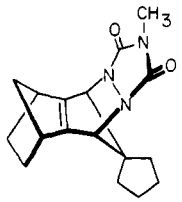
(17) Sugimoto, T.; Kobuke, Y.; Furukawa, J. *J. Org. Chem.* **1976**, *41*, 1457.

Table I. Selected ^{13}C Chemical Shifts in Maleic Anhydride Adducts of Several Isodicyclopentadiene Derivatives (ppm, $CDCl_3$ Solution)

compd	apical carbon a	apical carbon b	ethano bridge	α-carbonyl	ref
		A. Anti-Endo Series			
	52.91	60.40	26.22	48.83	*c, d*
	53.79	64.96	25.29	51.12	this work
	53.52	69.24	24.82	54.56	this work
	53.69[a]	81.27	25.05	53.65[a]	*e*
		B. Syn-Endo Series			
	47.00[b] or 46.58	50.66[b]	25.46	48.11	*c, d*
	55.98	82.63	25.05	55.34	*e*
		C. Syn-Exo Series			
	44.96	50.20	24.76	48.84	*c, d*
	49.42	140.35	25.05	49.13	*f*
	59.47	52.53	24.86, 31.65	49.71, 49.71	this work

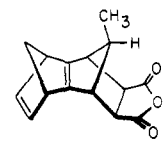
[a] Overlapping peaks. [b] These signals could not be readily distinguished and may be interchanged. [c] Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186, 7218. [d] Watson, W. H., Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *Ibid.* **1981**, *103*, 2022. [e] Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *Ibid.* **1983**, *105* (second paper of this series in this issue. [f] Paquette, L. A.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Org. Chem.*, in press.

Table II. Selected ^{13}C Chemical Shifts in *N*-Methyltriazolinedione Adducts of Several Isodicyclopentadiene Derivatives (ppm, $CDCl_3$ Solution)

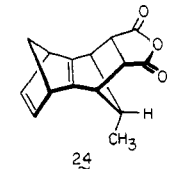
compd	apical carbon a	apical carbon b	ethano bridge	ref
A. Syn Series				
	54.86	55.41	25.73	*a*
	54.52	63.16	25.68	this work
	53.06	64.23	24.95	this work
	52.72	75.01	24.86	*b*
B. Anti Series				
	55.54	58.74	25.05	this work
	53.22	69.00	24.88	this work
	55.30	75.64	24.90	*b*

[a] Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186, 7218. [b] Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R., Bass, L. S.; Clardy, J. *Ibid.* **1983**, *105* (second paper of this series in this issue).

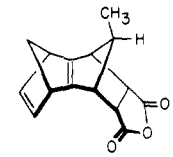
products could be detected by various chromatographic techniques. It proved possible to separate these isomers by medium-pressure liquid chromatography. Their order of elution from silica gel (isolated yields given in parenthesis) was **23** (27%), **24** (9%), **25** (5%), and **26** (25%). The pure anhydrides were subsequently subjected to catalytic hydrogenation under controlled conditions. The dihydro compounds proved useful in facilitating structural assignments. By use of ^1H NMR criteria analogous to those described earlier, it was clear that the succinic anhydride moieties in **25** and **26** were oriented endo, while **23** and **24** were exo isomers. The remaining important distinctions, those concerned with the



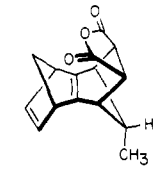
23



24



25



26

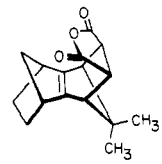
syn or anti disposition of the methano bridges, were deduced primarily from ^{13}C NMR data. In Table IV, we have compiled the chemical shifts of the key carbon signals in **23–26** and their hydrogenation products.

Since **26** was transformed into **13** on reduction, its identification as the endo-anti isomer is considered secure. The downfield position of apical carbon b, a phenomenon particularly characteristic of endo anhydrides (Table I), finds added parallel in **25** and **29** in agreement with the proton-based assignments. In accordance with those trends noted previously, the chemical shifts of the apical carbons in syn isomers **25** and **29** are appropriately upfield on their counterparts in the *anti*-sesquinorbornenes. This correlation applies as well to **23**/**27** and **24**/**28** (Table IV). In added substantiation of these structural formalisms, we note the effect of anhydride geometry on methyl proton shielding. With adoption of an exo orientation as in **23** (δ 0.98), **24** (0.82) and their respective dihydro derivatives **27** (0.93) and **28** (0.82), the chemical shifts appear relatively normal. However, an endo anhydride configuration induces a nontrivial shielding effect which displaces the methyl signals to higher field. The data for **25** (0.68), **26** (0.60), **29** (0.68), and **13** (0.67) are exemplary.

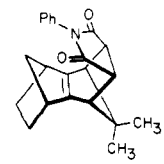
The findings just described indicate that **4a** and **4b** enter into Diels–Alder addition with maleic anhydride stereospecifically from the π surface opposite that occupied by the methyl substituent for obvious steric reasons. It is of some interest that above-plane approach to **4a** is partitioned 64% exo and 36% endo while bonding from below in **4b** favors the exo orientation to the extent of 85%. These ratios are thought simply to reflect the relative steric bulks of the etheno and methano bridges which are made apparent to the approaching maleic anhydride in the endo transition states.

Consequences of Geminal Dimethyl Substitution as in 3b and 4c. With the placement of geminal methyl substituents on the cyclopentadiene ring as in **3b** and **4c**, a return to a more closely balanced steric situation is achieved. What then will be the effect of a methyl substituent? Will below-plane stereospecificity be observed as in the parent hydrocarbon,[14,17] or will these alkyl groups perturb the diene π orbital shapes and energies adequately to promote preferential capture from the above-plane direction? The pivotal role played in particular by **3b** is perhaps best gauged by the diametrically opposite stereoselectivity response given by **1** and **2**.[1]

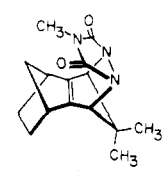
To resolve these questions, diene **3b** was allowed to react with maleic anhydride, *N*-phenylmaleimide, and *N*-methyltriazolinedione. In each instance, cycloaddition proceeded smoothly and efficiently to provide a single adduct (each ≥97% purity within our detectability limits). The structure of anhydride **30** was suggested by its spectral data and confirmed by three-dimensional X-ray crystal structure analysis (Figure 2). The parallelisms between the spectra of **30** and **31** are particularly



30

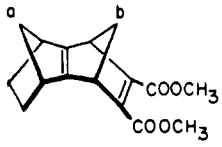
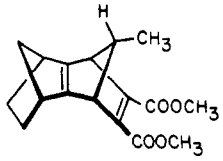
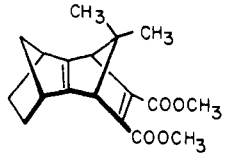
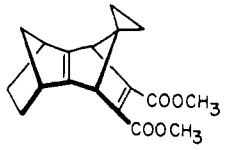
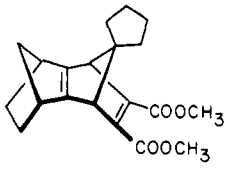
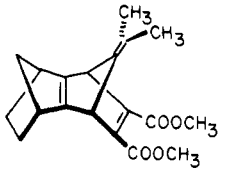
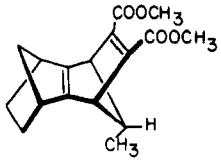
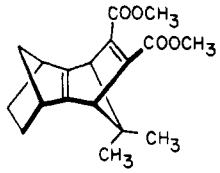
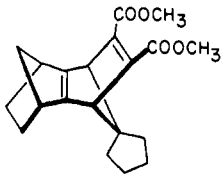


31



32

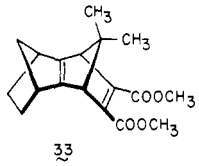
Table III. Selected ^{13}C Chemical Shifts in Dimethyl Acetylenedicarboxylate Adducts of Several Isodicyclopentadiene Derivatives (ppm, $CDCl_3$ Solution)

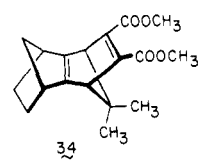
compd	apical carbon a	apical carbon b	ethano bridge	etheno bridge	ref
		A. Syn Series			
	48.30	70.05	22.08	150.16	*a*
	48.11	77.05	22.62	147.54	this work
	48.16	82.63	22.72	149.34	this work
	48.01	66.22	22.57	150.06	*b*
	48.11	93.94	22.67	149.92	*b*
	47.72	159.14	22.57	149.91	*c*
		B. Anti Series			
	55.34	83.70	25.68	155.16	this work
	55.59	88.02	25.15	159.97	this work
	55.15	100.30	25.29	153.85	*b*

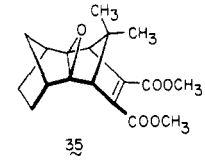
[a] Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186, 7218. [b] Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *Ibid.* **1983**, *105* (second paper of this series in this issue).

striking. Thus, the apical carbon atoms of the anhydride (53.79 and 64.96 ppm) compare closely to those of the imide (53.65 and 69.00 ppm). Additionally, the methyl signals of **31** (δ 1.0 and 0.72) almost overlap those of **30** (1.0 and 0.82). On this basis, the endo-anti configuration of **31** can be assigned with reasonable confidence. In the case of **32**, recourse was again made to X-ray analysis (Figure 3) for the substantiation of structure.

In contrast to the above, DMAD reacted with **3b** to give a mixture of two adducts in a 70:30 ratio. Identification of the major adduct as **33** was realized by means of ^{13}C NMR correlations (Table III) and peracid oxidation to give **35**. Similarly, **34** clearly belongs to the *anti*-sesquinorbornadiene class on the basis of its

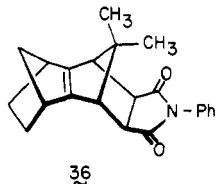

33

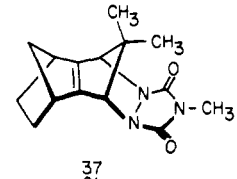

34


35

^{13}C NMR spectrum (Table III) and resistance to epoxidation. Once again, therefore, the acetylenic diester has distinguished itself by engaging in kinetically controlled stereoselection predominately opposite that followed by the trio of olefinic dienophiles.

Much like the triene corresponding to **2**,[1] **4c** entered only with reluctance into Diels–Alder reactions. When heated with *N*-phenylmaleimide in refluxing benzene for 6 days, a two-component cycloadduct mixture was produced in low yield. The majority of **4c** was left unchanged. During the chromatographic process required to separate the unreacted **4c**, the major adduct was destroyed almost totally. Following catalytic hydrogenation, it proved possible to isolate **36** whose spectral features, especially

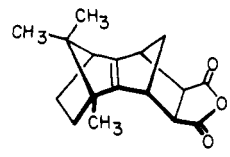

36

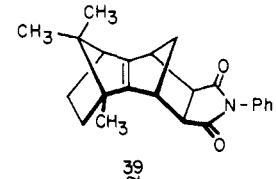

37

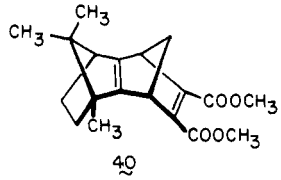
its unsubstituted apical carbon absorption at 50.73 ppm and closely spaced methyl proton signals at δ 1.16 and 1.14, identify it as the previously unknown exo-syn isomer.

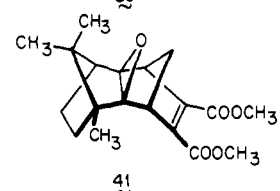
In a somewhat parallel situation, *N*-methyltriazolinedione added to **4c** at room temperature to give a 56:44 mixture of adducts. Medium-pressure liquid chromatographjy on silica gel served to decompose the major component. Because the remaining isomer was slowly transformed in air to a red oil, its characterization was deferred until after partial hydrogenation. The resulting stable colorless solid was shown to be **37** by a combination of ^{13}C (Table II) and ^{1}H NMR data (δ_{CH_3} = 1.30 and 1.08). Therefore, the presence of a third double bond in **4c** serves to promote reasonable levels of competitive below-plane attack. Partial loss of stereoselectivity of comparable magnitude has been observed previously.[1,4a]

π-Facial Stereoselective Behavior of 5. Maleic anhydride reacted smoothly with **5** in benzene solution at room temperature to deliver the dissymmetric adduct **38** (98%). The exo orientation


38

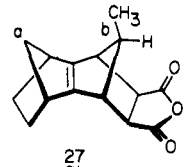
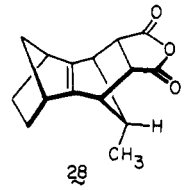
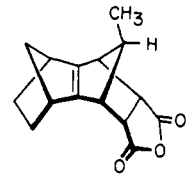
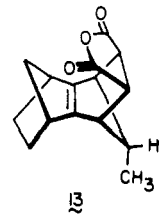

39


40

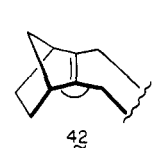

41

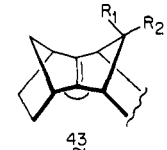
of the anhydride moiety as well as the syn disposition of the methano bridges were confirmed by X-ray analysis (Figure 4). The ^{13}C NMR data for **38** proved to be important adjuncts to our correlation chart (Table I). Under identical conditions, *N*-phenylmaleimide and DMAD added efficiently to **5** to give **39** and **40** as the only isolable adducts. In typical fashion, **40** underwent oxidation to **41**. This demonstration of the proclivity of dienophiles of varying reactivity to add to **5** from below the π plane conforms to the pattern originally established by isodicyclopentadiene and, more recently, the spirocyclopropane **1**. On the other hand, this preferred direction of attack is opposite that exhibited by **2** and **3b**.

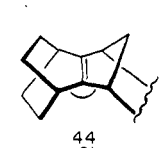
Table IV. Selected ^{13}C Chemical Shifts in the Maleic Anhydride Adducts of **4a**/**4b** and Their Dihydro Derivatives (ppm, $CDCl_3$ Solution)

compd	apical carbon a	apical carbon b	ethano (etheno) bridge	α-carbonyl
23	52.25	52.68	139.48	47.34
 27	50.59	52.14	25.39	42.53
24	53.02	54.18	143.46	48.99
 28	55.54	54.81	25.29	41.22
25	51.12	63.84	143.70	45.83
 29	52.04	66.56	25.34	43.26
26	52.09	66.37	143.66	48.89
 13	53.79	64.96	25.29	51.12

Intramolecular π-Bond Distortions in the Adducts. It is now well established that *syn*-sesquinorbornenes and closely allied molecules are structurally deformed in that manner which spreads the methylene bridges apart.[1,4,15,18–21] The dihedral angles between the planes which flank the central double bond in the various frameworks have been determined to be 4.5–10° in **42**, 11.8–18.0°


42


43


44

in **43**, and 11.8° in the one example of **44**. Indeed, there appears to be a direct correlation between the number of syn-oriented norbornene rings and the level of distortion. In this connection, anhydride **38** is no exception (Table V). As its final atomic parameters, bond lengths, and bond angles denote (Tables VI–IX), the two planes of interest intersect at a 15.5° angle in a downward (endo) direction (Figure 4).

(18) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1980**, *45*, 4922.
(19) Pinkerton, A. A.; Schwarzenbach, D.; Stibbard, J. H. A.; Carrupt, P.-A.; Vogel, P. *J. Am. Chem. Soc.* **1981**, *103*, 2095.
(20) Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1818.
(21) Gleiter, F.; Spanget-Larsen, J. *Tetrahedron Lett.* **1982**, 927.

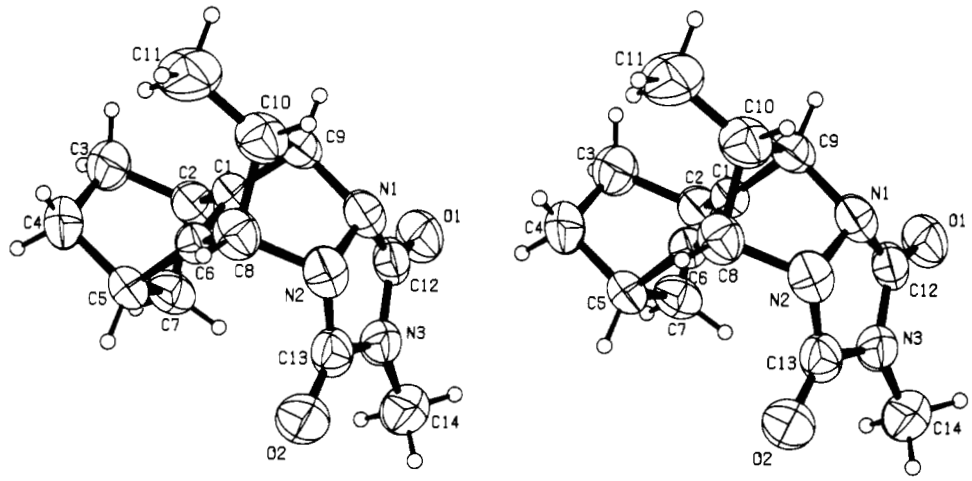


Figure 1. X-ray stereoview of **18** showing within molecular conformation in the crystal.

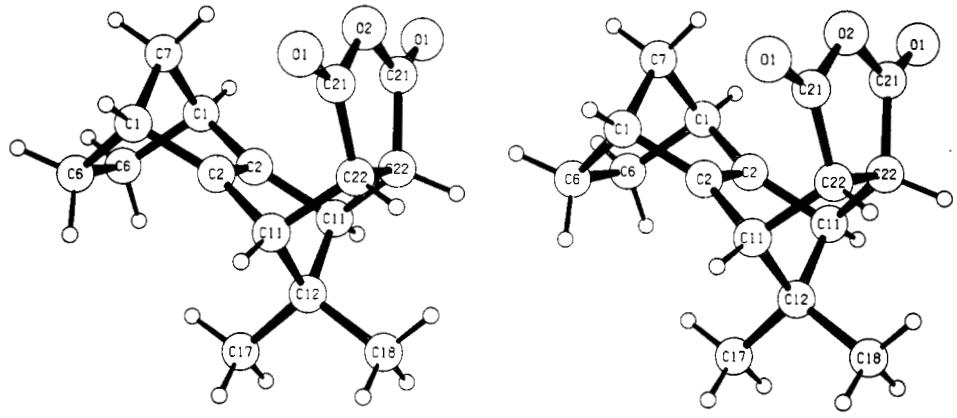


Figure 2. X-ray stereoview of **30** showing the molecular conformation in the crystal.

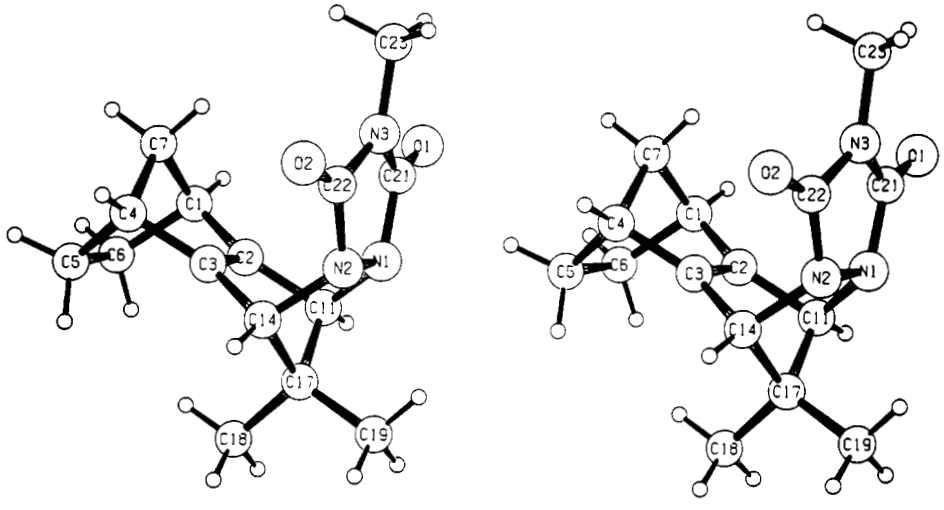


Figure 3. X-ray stereoview of **32** showing the molecular conformation in the crystal.

By way of comparison, *anti*-sesquinorbornenes show only low-level distortion, if any, the maximum dihedral angle deviation observed to date being 2.0°.[1,15] This is also true for **18** (Tables X–XIII, Figure 1), **30** (Tables XIV–XVIII, Figure 2), and **32** (Tables XIX–XXII, Figure 3). However, this triad of molecules provides insight into a phenomenon not previously given attention. Since their methano bridges are dissimilarly substituted, the resulting tilt will either be toward the substituted bridge or away from it in the direction of the methano bridge. In all three examples, our findings are that the respective angular distortions of 0.44°, 0.48°, and 1.8°, small as they may be, are discretely away from the geminal methyl groups. We assign no significance to this fact at the moment except to point out that the large intramolecular contacts suggest that nonbonded steric factors are quite likely unimportant.

Comparative Analysis of the Diels–Alder Reactivity of Tricyclo[5.2.1.0^{2,6}]decadienes toward DMAD. The π-facial stereoselectivity shown by tricyclo[5.2.1.0^{2,6}]decadienes in Diels–Alder reactions can clearly be modified by substitution of the tetrahedral carbon of the cyclopentadiene ring. These striking chemical phenomena may have their origin in (a) steric hindrance changes which selectively restrict dienophile approach from above or below the diene π plane, (b) modifications in the energies and shapes of frontier and subjacent MO's as a consequence of through-bond and through-space orbital interactions, (c) variations in the timing of the respective transition states with a corresponding crossover

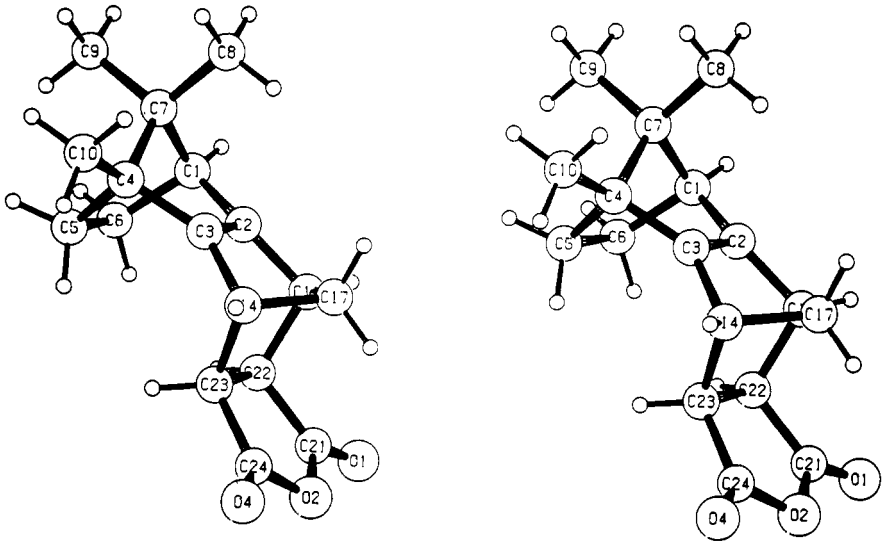


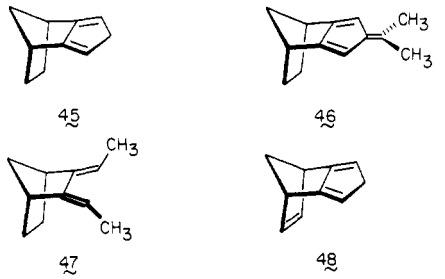
Figure 4. X-ray stereoview of **38** showing the molecular conformation in the crystal.

Table V. Crystallographic Data for Selected Cycloadducts[a]

	38	18	30	32
formula	$C_{17}H_{20}O_3$	$C_{14}H_{17}N_3O_2$	$C_{16}H_{18}O_3$	$C_{15}H_{19}N_3O_2$
space group	$P2_1$	$P2_1/a$	$P2_1/m$	$P2_1/n$
a, Å	11.442 (5)	11.475 (2)	8.559 (1)	8.535 (5)
b, Å	7.090 (4)	14.469 (2)	9.798 (2)	21.69 (2)
c, Å	9.152 (4)	7.900 (2)	8.451 (1)	8.109 (6)
β, deg	107.61 (3)	95.24 (1)	112.24 (1)	109.25 (5)
Z	2	4	2	4
D_{calcd}, g cm^{-3}	1.278	1.318	1.308	1.281
reflctns measd	1050	1770	940	1911
reflctns obsd[b]	939	1741	812	1478
R (R_w)	0.043 (0.049)	0.063 (0.079)	0.047 (0.056)	0.061 (0.067)
cryst size, mm	0.05 × 0.10 × 0.55	0.25 × 0.5 × 0.6	0.15 × 0.30 × 0.30	0.20 × 0.20 × 0.6
max θ, deg	57	57	57	57
least-squares refinement	full matrix	full matrix	full matrix	full matrix
Hilger–Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination				

[a] All structures were solved by a multiple-solution procedure (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*). [b] Reflections were regarded as significant if $I > 2.5\ \sigma(I)$.

from reactant-like (when early) to product-like characteristics (when late), and (d) a combination of these influences. In an effort to acquire background kinetic information, we have also measured the rates of addition of DMAD to **1–3** and **5**, as well as to the four structurally related systems **45–48**. The selection of DMAD



45 46 47 48

followed from the consideration of several practical matters including its heightened reactivity which enabled measurements to be made at reasonable temperatures under pseudo-first-order conditions, its lack of olefinic protons which enabled quantitative analysis of diene (or triene) disappearance in that region of the ^{1}H NMR spectrum, and its formation with certain substrates of *syn*- and *anti*-sesquinorbornadiene adduct pairs, thus enabling comparison of attack from two directions.

The reactions were conducted in $CDCl_3$ solution with toluene as internal standard in the probe of a Bruker HX-90 FT NMR spectrometer. Close attention was paid to standardization of the experimental conditions, care being taken to set such variables as spinning rate, solution volume, tube length, etc. as rigorously identical as possible in all runs. The cycloadditions, which were found to adhere nicely to first-order kinetics when 15-fold excess of DMAD was used, were followed for more than 3 half-lives in all cases. For each kinetic determination, at least 25 concentration measurements of the reacting diene were taken. The pseudo-first-order rate constants (k_1), which were measured at different temperatures and extrapolated to 25 °C by standard least-squares procedures using the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values obtained from slopes of Arrhenius plots, are collected in Table XXIII. The errors reported for E_a and $\Delta H^{\ddagger}$ were calculated on the basis of the standard deviations of these slopes and the maximum uncertainty in the temperature during measurement (±0.5 °C). The errors in $\Delta S^{\ddagger}$ were calculated from the standard deviations of the y intercept values in the Arrhenius plots and may be a bit low (although systematically so). When two stereoisomers were produced, the k_1 (25 °C) was factored by the product composition to give the respective rate for above- and below-plane attack.

When the rate constants for below-plane attack on **45**, **3a**, and **3b** are compared. a reactivity order of 950:300:1 is seen at 25 °C. Thus, the presence of an endo-methyl substituent on the cyclopentadiene ring causes an approximate 3-fold dropoff in cycloaddition rate. On the other hand, placement of a pair of methyl groups at this position causes an additional 300-fold dropoff in reactivity. Whereas the rate retardation observed for **3a** is attributable to the added primary steric encumbrance, this argument must be inordinately stretched for **3b** unless methyl–methyl buttressing effects on secondary nonbonded steric interactions such as pictured in **6** gain importance in the transition state. However, our measurements indicate the kinetic behavior of **5**, whose reactivity might be attenuated to a comparable extent as indicated

Table XXIII. Summary of Rate Data[a] for DMAD Cycloadditions to Tricyclo[5.2.1.0^{2,6}]decadienes and Related Molecules in Deuteriochloroform Solution

compd	k_1(measd), 10^4 s^{-1} (temp, °C)				$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	A	corr coeff	below-plane attack: $k_{25\,°C}$, 10^4 s^{-1}	below-plane attack: k_{rel}	above-plane attack: $k_{25\,°C}$, 10^4 s^{-1}	above-plane attack: k_{rel}
5	2.18 (−21.7)	3.26 (−17.5)	3.33 (−17.2)	6.24 (−12.0)	20.0 ± 0.3	12.4 ± 0.3	−25.8 ± 1.3	3.93×10^7	0.9978	126	1		
	9.59 (−6.7)	9.28 (−6.0)	15.5 (−1.5)	16.2 (−0.3)									
45	2.27 (−28.5)	3.33 (−22.0)	4.63 (−18.0)	5.82 (−15.5)	20.1 ± 0.8	10.5 ± 0.8	−32.1 ± 3.3	1.68×10^6	0.9857	120	0.95		
	7.79 (−12.0)	11.8 (−9.3)	12.3 (−8.5)										
47	2.34 (−11.0)	3.00 (−8.0)	5.39 (−2.0)	7.99 (2.5)	20.5 ± 0.2	13.2 ± 0.2	−24.5 ± 0.9	7.44×10^7	0.9991	55.8	0.44		
	11.0 (5.5)	11.9 (6.0)	15.6 (9.6)										
3a	1.81 (−18.3)	1.77 (−18.0)	3.87 (−8.0)	4.50 (−7.5)	20.5 ± 0.7	11.4 ± 0.7	−30.5 ± 2.6	3.63×10^6	0.9936	37.9	0.30	16.3	1
	9.15 (2.0)	11.8 (2.5)											
2	2.13 (−9.0)	2.17 (−8.9)	4.61 (1.75)	4.80 (2.0)	21.0 ± 0.5	10.8 ± 0.5	−34.1 ± 1.7	6.01×10^5	0.9967	18.8	0.15	6.26	0.38
	10.0 (12.0)	11.4 (12.0)											
1	2.57 (−3.0)	2.21 (−3.0)	5.83 (6.4)	5.64 (7.2)	21.0 ± 0.6	12.8 ± 0.6	−27.5 ± 2.2	1.62×10^7	0.9946	24.8	0.20		
	8.56 (12.0)	14.8 (17.0)	12.3 (17.0)										
48	1.10 (−7.6)	3.51 (4.2)	3.20 (4.5)	6.88 (10.8)	21.0 ± 0.8	14.6 ± 0.8	−21.6 ± 2.7	3.15×10^8	0.9913	24.2	0.19		
	5.73 (11.0)	8.59 (11.2)	13.2 (18.0)	13.6 (18.0)									
	12.9 (18.2)												
46	1.93 (23.0)	2.04 (23.2)	4.07 (31.8)	4.00 (31.8)	22.4 ± 0.2	14.0 ± 0.2	−28.1 ± 0.6	1.20×10^7	0.9996	2.31	0.018		
	8.11 (41.6)	8.44 (42.0)	17.5 (51.0)										
3b	1.35 (24.2)	3.05 (31.3)	3.18 (31.3)	3.01 (31.3)	22.6 ± 0.7	15.8 ± 0.7	−22.7 ± 2.4	1.83×10^8	0.9941	1.20	0.001	0.47	0.03
	7.42 (41.3)	8.08 (41.3)	14.1 (51.0)	14.6 (51.0)									

[a] Only the rate of disappearance of the starting materials could be conveniently followed. Therefore, the activation parameters necessarily apply to combined above- and below-plane attack where this is operative.

in transition state **7**, to be slightly faster than that of unsubstituted **45**! As a consequence, we do not view the secondary influences delineated in **6** and **7** to be the *primary factor* behind the low reactivity of **3b**. This conclusion is supported by the X-ray data on **38** which show the "inside" apical methyl group to be well beyond the van der Waals range of the opposed apical hydrogen. Can an electronic effect lie behind the kinetic phenomenon? The photoelectron spectroscopy studies and theoretical calculations to be described in the next section address this question.

It is of interest in this connection that **1** and **2** are 200 and 150 times, respectively, more reactive than **3b**. We see, therefore, that spiroannulation does not have as deleterious a kinetic effect as simpler geminal dimethyl substitution. Perhaps relevantly, the dimethylfulvene **46**, which is known to experience appreciable electronic perturbation,[4b] also exhibits low-order reactivity (only 18 times faster than **3b**). In fact, its reaction rate happens to be identical with that of triene **48** where through-space and through-bond interactions with the isolated π orbital perturb the diene orbitals in a disadvantageous way. The **45**/**48** reactivity difference of 5 is significantly less than that reported for the **49**/**50** pair (k_{rel} = 56:1).[22]

49

50

As an added point, the relative rate constant for 2,3-diethylidenenorbornane **47** is interesting. This open-chain analogue is only 2.2 times less reactive than **45**, despite the strong likelihood that its double bonds do not enjoy a 1,4-distance as conducive to [4 + 2] bonding as does a cyclopentadiene ring.[4a,23] However, added methyl groups are positioned at the reaction centers, a feature which frequently results in modest rate acceleration.[24] The influence of these opposed effects on rate appear to be rather closely balanced.

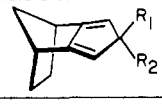
Although the systems that exhibit a propensity for above-plane attack are less numerous, certain intriguing features are already apparent. For example, while the reactivity order **3a** > **2** > **3b** persists for both bonding schemes, the spread for above-plane stereoselectivity is appreciably smaller (33.3:12.7:1) than that for below-plane dienophile capture (300:150:1). This pattern is hardly what one would expect on the basis of steric factors alone, viz.,

(22) (a) Hardy, M.; Carrupt, P.-A.; Vogel, P. *Helv. Chim. Acta* **1976**, *59*, 1685. See also: (b) Chollet, A.; Mahaim, C.; Foetisch, C.; Hardy, M.; Vogel, P. *Ibid.* **1977**, *60*, 59. (c) Pilet, O.; Chollet, A.; Vogel, P. *Ibid.* **1979**, *62*, 2341. (d) Gabioud, R.; Vogel, P. *Tetrahedron* **1980**, *36*, 149. (e) Schwager, L.; Vogel, P. *Helv. Chim. Acta* **1980**, *63*, 1176.

(23) (a) Sustmann, R.; Böhm, M. Sauer, J. *Chem. Ber.* **1979**, *112*, 833. (b) Scharf, H.-D.; Plum, H.; Fleischhauer, J.; Schleker, W. *Ibid.* **1979**, *112*, 862. (c) Rücker, C.; Lang, D.; Sauer, J.; Friege, H.; Sustmann, R. *Ibid.* **1980**, *113*, 1663 and relevant references cited in these papers.

(24) For example, tetracyanoethylene adds twice as rapidly to *trans,trans*-2,4-hexadiene as compared to butadiene (Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779).

Table XXIV. Summary of Diels–Alder Stereoselectivities for Alkyl-Substituted Tricyclo[5.2.1.$0^{2,6}$]decadienes

	above-plane/below-plane stereoselection							
	maleic anhydride	*N*-phenyl-maleimide	methyl acrylate	phenyl vinyl sulfone	benzo-quinone	*N*-methyl-triazolinedione	DMAD	methyl propiolate
$R_1 = R_2 = H$	25/75[a]		<3/>97	<3/>97	<3/>97	<3/>97	<3/>97	<3/>97
$R_1 = H, R_2 = CH_3$	>97/<3		>97/<3	>97/<3		93/7	30/70	
$R_1 = R_2 = CH_3$	>97/<3	>97/<3				>97/<3	30/70	
$R_1,R_2 = (CH_2)_2$		<3/>97		<3/>97	<3/>97		<3/>97	
$R_1,R_2 = (CH_2)_4$	>97/<3	>97/<3		>97/<3	>97/<3	>97/<3	25/75	
$R_1,R_2 = =C(CH_3)_2$	<3/>97	<3/>97	*b*	*b*	*b*	*c*	<3/>97	<3/>97

[a] Ratio variable and somewhat dependent on solvent. [b] Dienophile proved insufficiently reactive for this dione. [c] Ene product formation was kinetically favored.

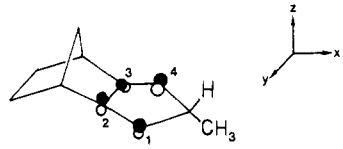


Figure 5. Schematic representation of the deformation of the π lobes in the lowest symmetric canonical π orbital of **3a**.

a steric effect nonlinear in the number of methyl groups is required. The most reactive diene (**3a**) projects a hydrogen in the exo direction while both **2** and **3b** have alkyl appendages protruding above the surface. Yet the reactivity differences are small in absolute terms. On the other hand, all three dienes project alkyl groups in the endo direction, a steric phenomenon which should cause kinetic leveling if steric accessibility were the principal issue and buttressing contributions were insignificant. The reactivity differences from the below-plane direction are more highly magnified by a factor of 10. The collective results appear most cohesively interpreted in terms of the molecular orbital analysis which follows.

We interject a cautionary note here. Because DMAD is not a sterically demanding reagent, one should not extend the kinetic profile just discussed to other dienophiles. It may well be that 2π components having greater transition-state steric requirements will generate reactivity scales differing somewhat in the diene sequence.

Theoretical Assessment of 3a, 3b, and 4c. On the basis of earlier calculations dealing with **1** and **2**, it was anticipated that **3b** and **4b** would exhibit entirely comparable interactions between their π and σ networks. As before, the relevant orbital energies and wave functions were derived through use of an improved INDO model.[25] By means of this technique, the predicted orbital sequences for **3a**, **3b**, and **4b** (π on top of σ orbitals) were determined to be in agreement with the assignment of the photoelectron spectra of these hydrocarbons,[26] given the usual assumption that Koopmans' theorem[27] is valid for such systems. Once again, the MO calculations predict a deformation of the lowest occupied π orbital or the diene unit, the phenomenon resulting from allowed coupling of the pure π orbitals with delocalized σ orbitals in the corresponding canonical MO's. The magnitude of this π/σ interaction can be quantitatively estimated by means of those theoretical procedures suggested by Heilbronner and Schmelzer.[28] Herein, we present an exemplary analysis of the nature of π/σ interaction in **3a**; the results for the other isodicyclopentadienes dealt with in this paper are entirely similar.

The lowest symmetric canonical π orbital within **3a** shows a strong rotation of its π lobes with respect to the plane of symmetry (x,z plane in Figure 5) in that sense wherein the p lobes at centers 1 and 4 of the diene are bent away from the methano bridge. At the same time, the p lobes at positions 2 and 3 are tilted toward this CH_2 group. The relevant one-electron functions that are coupled within this linear combination are summarized in Table XXV and Figure 6. Of particular note is the finding that the symmetrical canonical π MO contains only 62.4% pure π contribution. The remaining contributions are given in terms of so-called precanonical orbitals,[28] the largest σ admixtures arising from the MO's ψ_{20} and ψ_{29}. The precanonical MO ψ_{20} is localized predominantly at the methano bridge of the norbornyl fragment and the $CHCH_3$ unit of the pentadienyl ring. On the other hand, orbital ψ_{29} is a typical σ-ribbon orbital with significant coefficients at the four carbon centers from the π system. It is precisely this combination that leads to the strong deformation of the π lobes in the corresponding canonical MO. Precanonical MO's ψ_{15} and ψ_{22} contain large contributions at the CH_2 bridge while ψ_{18} is localized at the $CHCH_3$ unit of the pentadiene ring. This analysis reveals the deformation of the lowest occupied π orbital of **3a** (Figure 5) to be influenced by the norbornyl moiety as well as by those other substituents bonded to the cyclopentadiene ring.

The above-plane stereoselectivity (anti to the CH_3 group) observed in cycloaddition reactions to **3a** is thus due not only to steric effects (CH_3 group) but also to electronic factors. The antibonding four-center four-electron interaction between the symmetrical π MO of **3a** and the π orbital of the dienophile is smaller if the dienophile approaches from the side anti to the methyl group. Perturbational calculations have shown that the energy difference

Table XXV. Fragmentation of the Lowest Canonical "π-orbital" of 3a into Pure π Functions and Precanonical σ Linear Combinations

MO	%
π_1	31.2
π_2	31.2
ψ_{20}	11.3
ψ_{29}	10.0
ψ_{15}	6.8
ψ_{22}	2.8
ψ_{18}	2.8

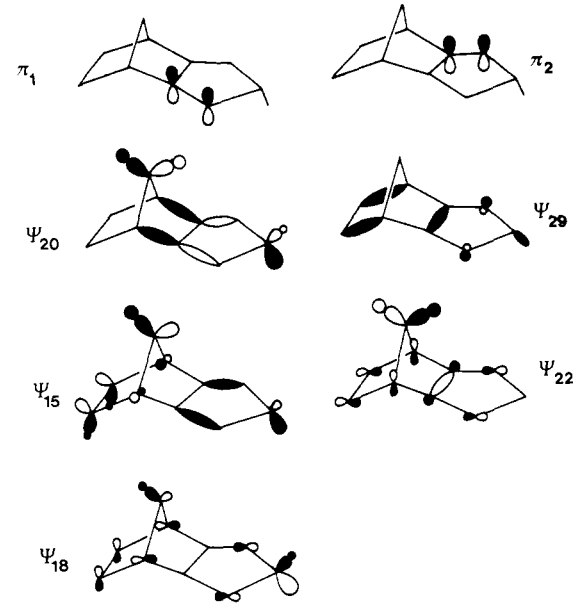


Figure 6. One-electron functions that are coupled wtihin the linear combination that generates the orbital shown in Figure 5.

(25) Böhm, M. C.; Gleiter, R. *Theor. Chim. Acta* **1981**, *59*, 127, 153.
(26) Gleiter, R.; Flatow, A., unpublished results.
(27) Koopmans, T. *Physica* (*The Hague*) **1934**, *1*, 104.
(28) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936.

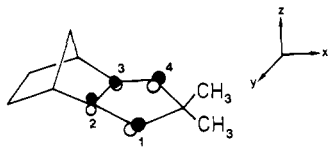


Figure 7. Lowest occupied π orbital in **3b** as determined by the INDO procedure.

for the approach from above and below the pentadienyl plane amounts to 5–20 kJ/mol.[14]

The deformation of the lowest occupied π orbital in **3b** within the INDO framework is shown schematically in Figure 7. A rotation identical with that in **3a** is predicted with respect to the x,z plane. That is, the π lobes at the terminal carbon atoms of the diene are again rotated away from the methylene group. Interestingly, there is seen to be superimposed on this rotation a second one in which the terminal p lobes are further bent toward the CH_3 groups, while those at centers 2 and 3 of the diene unit are turned toward the CH_2 bridge (Figure 7).

Rotation of the lowest occupied π orbital of **3b** in this manner favors attack of a dienophile from above as in **3a**. The observed preference of the endo configuration of maleic anhydride or *N*-phenylmaleimide can be interpreted in terms of a secondary orbital interaction between the HOMO of the diene unit and the LUMO of the anhydride group. The situation is more complex if the dienophile has a second occupied MO with a π system perpendicular to the first one as in DMAD or the triazolinedione. With dienophiles of this type, possible coupling between additional occupied MO's and the symmetrical π combination of a diene unit must be taken into account. This could well give rise to a dynamically induced π/σ coupling that modifies the orientation of the π lobes. In these cases, a detailed investigation of those interactions prevailing in the transition state is necessary since the simple static model fails.

The deformation of the π functions in **4c** parallels the results obtained for **3b**. The additional double bond does not lead to a topologically different rotation of the π orbitals. The π/σ interactions in **5** are too weak to rationalize the stereochemistry of the cycloadditions observed, at least in terms of our time-dependent static model.

Discussion

Stepwise analysis of those factors which control the stereochemical outcome of Diels–Alder additions to tricyclo[5.2.1.$0^{2,6}$]decadienes and -trienes requires two assumptions. The advocacy of kinetic control takes its justification largely from the internal consistency of a large number of observations. While reversibility is not discounted, it is required that product stereochemistry not be affected by the existence of an equilibrium. At least two examples of this phenomenon have been clearly delneated.[4b,20] The second salient point deals with transient π complex formation which, if involved, is amalgamated for simplicity into the overall product-controlling reaction profile (Curtin–Hammett principle).

If the preceding considerations are as firm as they appear to be, the observed above-plane/below-plane ratios must be dictated by electronic or steric factors, or a combination of these effects. At first glance, the cycloaddition stereoselectivities for alkyl-substituted tricyclo[5.2.1.$0^{2,6}$]decadienes summarized in Table XXIV appear somewhat indiscriminate, although almost always heavily biased in one direction or the other. Mere comparison of the cycloaddition stereoselectivities of **3a** and **45** reveals that the presence of an endo-methyl substituent is adequate to favor above-plane bonding except when DMAD is involved. However, a purely steric analysis does not account for the variability in stereoselection which is observed as one proceeds from **45** and **1** (below-plane) to **3b** and **2** (above-plane). All four dienes are equivalently substituted on both faces of the cyclopentadiene ring and share in common the proximity of a fused norbornane ring. Without doubt, dienophiles should engage in bonding to the less sterically encumbered parent diene **45** (and to **5** as well) more readily than to the three alkylated congeners and this is borne out by the kinetic data (Table XXIII).

Vogel has argued that cycloaddition stereoselectivity in these systems may be governed by the relative stabilities of the isomeric adducts.[20] In these terms, the closely similar structures of **1**, **2**, and **3b** should lead to entirely comparable product profiles. Our findings demonstrate that the behavior of **1** is distinctively different (although comparable to that of **45**) and lends no credence to this proposal.

Rather, electronic influences which are modifiable by the *type* of alkyl substitution provide the most satisfying rationalization of the stereochemical crossovers which are seen. The first key to a solution is found in **45** where the σ orbitals of the norbornane framework have been shown through calculations to mix appreciably with the subjacent diene π_s orbital. This interaction induces disrotatory tilting toward the methano bridge in the diene orbitals which in turn minimizes the level of antibonding interaction with the approaching dienophile on the endo face.[14,29] In **1**, a superimposition of interactions from the Walsh orbitals of the spiroannulated cyclopropane ring takes place. Importantly, the resulting linear combinations do not deform the orbital tilting originally present in **45** and, in fact, act to reinforce this effect.[1] The net result is favored below-plane dienophile capture in both systems. In fulvene **48**, pronounced rotation of the π lobes is again seen, but restricted only to the longitudinal axis.[4b] Below-plane stereoselectivity continues to be overwhelmingly preferred.

When the special effects of a three-membered ring or external double bond are removed and replaced by more usual alkyl substitution as in **2**–**4**, terminal diene π orbital deformation materializes as before. In these situations, however, the lobes are rotated outwardly from the apical CH_2 group, a phenomenon which is spectroscopically observable.[4c] The level of antibonding interaction between π_s of the diene moiety and the dienophile HOMO now becomes considerably smaller for above-plane attack and leads to *anti*-sesquinorbornene products.

It is quite possible that the orbital distortions to which we refer have kinetic consequences as well. The weight of evidence in Table XXIII is, however, inadequate to serve as the sole basis for distinguishing these subtle effects. This equivocation arises because our kinetic investigations have so far been restricted to DMAD, an acetylenic dienophile; certainly, a broader range of electron-deficient olefins (particularly those that behave with "cleaner" stereoselectivity) must be examined in order to define with confidence any possible interrelationship between eelctronic topology and rate.

Experimental Section

Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. The ^{1}H NMR spectra were determined with Varian EM-390 and Bruker HX-90 instruments, and apparent splittings are given in all cases. The ^{13}C spectra were obtained with a Bruker WP-80 spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***endo,anti*-1,2,3,4,5,6,7,8-Octahydro-10-methyl-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylic Anhydride (13).** A solution of **3a** (330 mg, 2.26 mmol) and maleic anhydride (221 mg, 2.26 mmol) in benzene (40 mL) was stirred at room temperature for 15 h. The solvent was evaporated and the oily residue was purified by MPLC on silica gel (elution with 20% ethyl acetate in hexanes). There was isolated a single adduct (390 mg, 71%), mp 108–109 °C (from hexanes), identified as **13**: ^{1}H NMR ($CDCl_3$) δ 3.80–3.58 (m, 2 H), 3.23–3.06 (m, 2 H), 3.00–2.80 (m, 2 H), 2.60–2.30 (q, J = 6 Hz, 1 H), 2.00–1.67 (m, 2 H), 1.60–1.03 (m, 4 H), 0.67 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 171.81, 150.45, 64.96, 53.79, 51.12, 48.89, 41.66, 25.29, 11.75; mass spectrum, m/e (M^+) calcd, 244.1099; obsd, 244.1105.

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.99; H, 6.73.

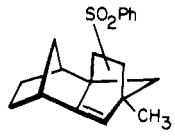
***endo,anti*-1,2,3,4,5,6,7,8-Octahydro-10-methyl-2-(phenylsulfonyl)-1,4:5,8-dimethanonaphthalene (14).** A solution of **3a** (500 mg, 3.42 mmol) and phenyl vinyl sulfone (550 mg, 3.30 mmol) in dichloromethane (2 mL) was stirred at room temperature for 18 days. The solvent was

(29) Paquette, L. A.; Carr, R. V. C.; Arnold, E.; Clardy, J. *J. Org. Chem.* **1980**, *45*, 4907.

evaporated and the residue was subjected to preparative TLC on silica gel (elution with 10% ethyl acetate in hexane). The more rapidly eluted adduct (410 mg, 38%), white needles, mp 128–129.5 °C (from ether) was identified as **14**: ^{1}H NMR ($CDCl_3$) δ 8.0–7.8 (m, 2 H), 7.67–7.40 (m, 3 H), 3.1–2.6 (m, 6 H), 2.4–2.1 (m, 1 H), 1.9–1.03 (m, 7 H), 0.63 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 155.65, 150.36, 140.45, 133.32, 129.24, 128.22, 66.85, 56.46, 55.35, 49.33, 46.75, 41.27, 40.93, 31.61, 25.49, 25.25, 11.75; mass spectrum, m/e (M^+) calcd, 314.1340; obsd, 314.1349.

Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05. Found: C, 72.46; H, 7.08.

Also isolated was a more polar adduct which has been tentatively assigned structure i solely on the basis of its spectra: 300 mg (28%);



i

colorless crystals, mp 107–108 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 7.86–7.43 (m, 5 H), 5.16 (s, 1 H), 3.56–3.40 (m, 1 H), 2.76 (br s, 1 H), 2.20 (br s, 1 H), 1.40 (s, 3 H), 1.96–1.26 (m, 10 H); ^{13}C NMR (ppm, $CDCl_3$) 163.12, 141.37, 133.12, 128.99, 128.41, 116.95, 70.10, 60.93, 58.79, 57.63, 41.95, 39.47, 38.74, 34.13, 31.51, 24.61, 19.32; mass spectrum, m/e (M^+) calcd, 314.1340; obsd, 314.1346.

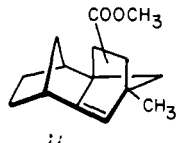
Reduction Desulfonylation of 14. Into a stirred mixture of 6% sodium amalgam (2.0 g) and disodium hydrogen phosphate (400 mg, 0.80 mmol) in 20 mL of anhydrous methanol was syringed a solution of **14** (250 mg, 0.80 mmol). After 4 days, pentane (50 mL) and water (50 mL) were added, and the organic phase was separated after shaking. Following drying and solvent evaporation, the residue was taken up in pentane and eluted through a column of basic alumina. The eluate was evaporated to give 93 mg of a mixture of two hydrocarbons. VPC purification (12 ft × 0.25 in. 5% SE 30, 150 °C) gave pure **15** (31 mg, 23%): ^{1}H NMR ($CDCl_3$) δ 2.77 (m, 2 H), 2.47 (m, 2 H), 2.05–1.63 (series of m, 5 H), 1.40–0.90 (series of m, 6 H), 0.63 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 150.16, 58.94, 55.39, 47.38, 40.93, 27.62, 25.88, 12.72.

The minor unsymmetrical component (16.3 mg, 6%) was not identified: ^{1}H NMR ($CDCl_3$) δ 2.93 (m, 2 H), 2.80 (m, 2 H), 2.20–1.05 (series of m, 10 H), 0.80 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 157.01, 150.26, 54.76, 53.60, 50.30, 43.40, 43.06, 42.53, 35.10, 34.28, 25.73, 20.24.

***anti*-Methyl 1,2,3,4,5,6,7,8-Octahydro-10-methyl-1,4:5,8-dimethanonaphthalene-2-carboxylates (16).** A solution of **3a** (1.60 g, 10.9 mmol) and methyl acrylate (1.76 g, 20.5 mmol) in carbon tetrachloride (2 mL) was placed in a stoppered flask and stirred magnetically at 42 °C for 4 days. TLC and VPC analysis showed that ca. 40% of **3a** remained after this time. The solvent was evaporated and the residue was subjected to preparative TLC on silica gel (triple elution with 2% ethyl acetate in hexane). There was isolated 147 mg (10%) of **16a** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 3.67 (s, 3 H), 3.0–2.7 (m, 3 H), 2.6–1.2 (series of m, 11 H), 0.63 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 176.91, 153.17, 150.74, 56.85, 55.44, 51.70, 51.56, 47.09, 46.02, 41.17, 41.02 33.45, 25.73, 25.59, 12.14; mass spectrum, m/e (M^+) calcd, 232.1463; obsd, 232.1466.

The next less polar component proved to be **16b**: a colorless oil; 141 mg (10%); ^{1}H NMR ($CDCl_3$) δ 3.63 (s, 3 H), 3.20–2.50 (m, 5 H), 2.27–1.13 (series of m, 9 H), 0.63 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 175.31, 152.40, 147.59, 60.10, 54.67, 51.36, 51.27, 47.68, 45.59, 41.46, 41.02, 32.04, 25.83, 25.68, 12.28; mass spectrum, m/e (M^+) calcd, 232.1463; obsd, 232.1458.

A third colorless oil (52 mg, 4%) tentatively formulated as ii was also



ii

isolated: ^{1}H NMR ($CDCl_3$) δ 5.06 (s, 1 H), 3.67 (s, 3 H), 2.83 (br s, 1 H), 2.80–2.63 (m, 1 H), 2.27 (br s, 1 H), 1.43 (s, 3 H), 2.20–1.13 (series of m, 10 H); ^{13}C NMR (ppm, $CDCl_3$) 175.36, 164.10, 117.20, 61.61, 57.92, 56.56, 51.17, 49.37, 41.95, 39.76, 38.84, 34.23, 31.80, 25.78, 24.86, 19.23; mass spectrum, m/e (M^+) calcd, 232.1463; obsd, 232.1469.

***anti*-1,4,5,6,7,8-Hexahydro-*N*,10-dimethyl-1,4:5,8-dimethanophthalazine-2,3-dicarboximides (18 and 19). A. NMR Tube Experiment.** *N*-Methyltriazolinedione (147 mg, 1.30 mmol) dissolved in $CDCl_3$ (2 mL) was added to a cold (−78 °C) solution of **3a** (190 mg, 1.30 mmol) in 1 mL of the same solvent. After 15 min, the ^{1}H and ^{13}C NMR spectra of this reaction mixture were recorded. The presence of a minor adduct (≤7%) was detected by ^{13}C NMR spectroscopy, and its spectrum (and percentage) was determined by peak subtraction

For **19**: ^{13}C NMR (ppm, $CDCl_3$) 161.23, 151.72, 68.02, 63.16, 54.52, 41.61, 25.68, 25.34, 14.03.

B. Preparative-Scale Experiment. A cold (−40 °C), magnetically stirred solution of **3a** (500 mg, 3.42 mmol) in ethyl acetate was treated dropwise with a solution of *N*-methyltriazolinedione (390 mg, 3.42 mmol) in the same solvent (5 mL). The disappearance of the pink color occurred rapidly and a colorless precipitate formed slowly. After 1 h at this temperature, the reaction mixture was concentrated to a volume of 2 mL, cooled to −78 °C, and filtered to give 400 mg of **18**. The filtrate was evaporated and the residue was recrystallized from ethyl acetate–hexanes to furnish an additional 115 mg (total yield 58%) of **18**, mp 151–153 °C dec (from ether). The minor adduct was not isolated in pure form.

For **18**: ^{1}H NMR ($CDCl_3$) δ 4.73 (m, 2 H), 2.98 (m, 3 H), 2.90 (s, 3 H), 1.97–1.78 (m, 2 H), 1.48–1.00 (m, 4 H), 0.71 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 161.28, 148.36, 69.08, 58.74, 55.54, 40.97, 25.34, 25.05, 10.49; mass spectrum, m/e (M^+) calcd, 259.1321; obsd, 259.1314.

Anal. Calcd for $C_{14}H_{17}N_3O_2$: C, 74.97; H, 7.55. Found: C, 74.86; H, 74.9.

Dimethyl *anti*-1,4,5,6,7,8-Hexahydro-10-methyl-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylates (20 and 21). A solution of **3a** (460 mg, 3.17 mmol) in chloroform (30 mL) was treated with dimethyl acetylenedicarboxylate (450 mg, 3.17 mmol), stirred at 20 °C for 3 h, and freed of solvent in vacuo. The residue was purified by MPLC on silica gel (elution with 15% ethyl acetate in hexane). Two adducts were formed in a 65:35 ratio (recorder integration).

For **20**: colorless oil (53 mg, 58%); ^{1}H NMR ($CDCl_3$) δ 3.70 (s, 6 H), 3.36 (s, 2 H), 2.98 (br s, 2 H), 1.53–1.26 (m, 5 H), 1.06 (d, J = 6 Hz, 3 H), 0.60–0.43 (m, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 166.52, 159.63, 147.54, 77.05, 57.43, 51.95, 48.11, 43.01, 22.62, 13.30; mass spectrum, m/e (M^+) calcd, 288.1361; obsd, 288.1369.

For **21**: colorless oil (240 mg, 26%); ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 6 H), 3.53 (s, 2 H), 3.10 (br s, 2 H), 2.00–1.73 (m, 2 H), 1.50–1.10 (m, 5 H), 0.70 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 165.84, 158.71, 155.16, 83.70, 57.43, 55.35, 51.85, 42.53, 25.68, 13.93; mass spectrum, m/e (M^+) calcd, 288.1361; obsd, 288.1366.

Epoxidation of 20. A solution of *m*-chloroperbenzoic acid (290 mg, 1.67 mmol) in dichloromethane (10 mL) was added dropwise to a stirred solution of **20** (400 mg, 1.39 mmol) in the same solvent (40 mL) at 0 °C. The reaction mixture was stirred at room temperature for 30 min and washed with 10% sodium thiosulfate and saturated sodium bicarbonate solutions and water prior to drying. Following solvent evaporation, the residual oil was purified by MPLC on silica gel (elution with 15% ethyl acetate in hexanes). There was isolated 400 mg (95%) of **22**: ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 6 H), 3.07 (s, 2 H), 2.60 (br s, 2 H), 2.00–1.70 (m, 2 H), 1.53–1.13 (m, 5 H), 0.90 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 165.65, 146.86, 65.98, 60.10, 53.79, 52.24, 40.15, 38.94, 25.05, 11.07; mass spectrum, m/e ($M^+ - CH_3$) calcd, 289.1076; obsd, 289.1084.

Epoxidation of 21. A solution of *m*-chloroperbenzoic acid (130 mg, 0.75 mmol) and **21** (180 mg, 0.62 mmol) in dichloromethane (50 mL) was heated at the reflux temperature for 3 days. Workup in the predescribed manner and MPLC purification as before afforded 20 mg (11%) of epoxide as a colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 6 H), 3.33 (s, 2 H), 2.76 (br s, 2 H), 2.10–1.95 (m, 2 H), 1.77–1.60 (m, 5 H), 1.30 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 164.63, 146.71, 73.02, 60.06, 52.14, 52.00, 39.81 (3 C), 26.46;, 15.34; mass spectrum, m/e (M^+) calcd, 304.1311; obsd, 304.1319.

Maleic Anhydride Addition to 4a/4b. A magnetically stirred solution of a 1:1 mixture of **4a** and **4b** (200 mg, 1.39 mmol) and maleic anhydride (136 mg, 1.39 mmol) in benzene (25 mL) was heated at the reflux temperature overnight. Following the evaporation of solvent, the residue was subjected to MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether). Four products were isolated (the first two were partially overlapped and required rechromatography to achieve separation).

Fraction 1, **23** (90 mg, 27%): mp 156–158 °C (from hexanes); ^{1}H NMR ($CDCl_3$) β 6.53 (t, J = 1.5 Hz, 2 H), 3.43 (br s, 2 H), 3.28 (s, 2 H), 2.43 (s, 2 H), 2.4–2.0 (m, 3 H), 0.98 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 172.35, 159.48, 139.48, 70.83, 52.68, 50.25, 48.65, 47.34, 11.07; mass spectrum, m/e (M^+) calcd, 242.0943; obsd, 242.0950.

Fraction 2, **24** (31 mg, 9%): mp 149–150 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 6.84 (t, J = 1.5 Hz, 2 H), 3.52 (br s, 2 H), 3.27 (s, 2 H), 3.07 (s, 2 H), 2.40 (d, J = 5 Hz, 2 H), 2.28 (q, J = 6 Hz, 1 H), 1.98 (d, J = 5 Hz, 2 H), 0.68 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 171.67, 163.08, 143.46, 79.86, 54.18, 53.02, 51.27, 48.99, 11.26; mass spectrum, m/e (M^+) calcd, 242.0943; obsd, 242.0950.

Fraction 3, **25** (16 mg, 5%): mp undertermined; ^{1}H NMR ($CDCl_3$) δ 6.55 (t, J = 1.5 Hz, 2 H), 3.58 (br s, 2 H), 3.48 (br s, 2 H), 3.36 (br s, 2 H), 2.28 (q, J = 6 Hz, 1 H), 2.20–2.00 (m, 2 H), 0.82 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 172.06, 163.12, 143.70, 77.63, 63.84, 51.12, 50.01, 45.83, 14.42; mass spectrum, m/e (M^+) calcd, 242.0943; obsd, 242.0950.

Fraction 4, **26** (83 mg, 25%): mp 98–99 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 6.82 (t, J = 1.5 Hz, 2 H), 3.73 (m, 2 H), 3.53 (m, 2 H), 3.25 (m, 2 H), 2.80 (q, J = 6 Hz, 1 H), 2.30 (d, J = 6 Hz, 1 H), 2.03 (d, J = 6 Hz, 1 H), 0.60 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 171.72, 161.08, 143.66, 77.73, 66.37, 52.09, 49.91, 48.89, 11.89; mass spectrum, m/e (M^+) calcd, 242.0943; obsd, 242.0950.

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.37; H, 5.82. Found: C, 73.95; H, 6.00.

Hydrogenation of the Maleic Anhydride Adducts. The reductions were carried out in ethyl acetate solutions containing 5% palladium on carbon at atmospheric pressure for 20 min. The individual products, obtained in quantitative yield, were recrystallized from hexane.

23 → 27: mp 167–168 °C; ^{1}H NMR ($CDCl_3$) δ 3.27 (s, 2 H), 3.03 (br s, 2 H), 2.80 (s, 2 H), 2.23–1.97 (q, J = 6 Hz, 1 H), 1.83–1.48 (m, 3 H), 1.30–1.12 (m, 1 H), 0.93 (d, J = 6 Hz, 3 H), 0.85–0.63 (m, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 171.72, 151.72, 52.72, 52.14, 50.59, 49.91, 42.53, 25.39, 11.60; mass spectrum, m/e (M^+) calcd, 244.1099; obsd, 244.1105.

24 → 28: mp 126–127 °C; ^{1}H NMR ($CDCl_3$) δ 3.10 (s, 4 H), 2.93 (br s, 2 H), 2.30 (q, J = 6 Hz, 1 H), 1.83 (d, J = 8 Hz, 2 H), 1.40 (br s, 2 H), 1.18 (d, J = 8 Hz, 2 H), 0.68 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 171.77, 153.46, 55.54, 54.81, 51.75, 41.22, 25.29, 11.31; mass spectrum, m/e (M^+) calcd, 244.1099; obsd, 244.1105.

25 → 29: mp 140–141 °C; ^{1}H NMR ($CDCl_3$) δ 3.53 (m, 2 H), 3.30 (m, 2 H), 3.00 (m, 2 H), 2.30 (q, J = 6 Hz, 1 H), 1.80–0.90 (series of m, 6 H), 0.82 (d, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 173.13, 156.33, 66.56, 56.41, 52.04, 46.51, 43.26, 25.34, 14.95; mass spectrum, m/e (M^+) calcd, 244.1099; obsd, 244.1105.

26 → 13: mp 108–109 °C; spectral properties identical with those reported earlier.

4,5,6,7-Tetrahydro-2,2-dimethyl-4,7-methano-2*H*-indene (3b). A cold (0 °C), stirred suspension of lithium aluminum hydride (6.15 g, 0.162 mmol) in dry tetrahydrofuran (350 mL) was treated dropwsie under nitrogen with dry methanol (19.8 mL, 0.487 mol). Following 30 min at 0 °C, a solution of **12** (5.8 g, 0.030 mol) in dry tetrahydrofuran (60 mL) was added dropwise over 15 min at 0 °C. The reaction mixture was stirred at 25 °C for 5 h, treated dropwise with water (250 mL) with external cooling, and filtered. The separated solids were leached with dichloromethane (2 × 250 mL), and the combined filtrates were washed with 10% hydrochloric acid (200 mL) and water (200 mL) prior to drying. Solvent evaporation left 5.1 g (86%) of diol isomers obtained as a colorless solid, mp 140–141 °C (from hexanes). For the major component: ^{1}H NMR ($CDCl_3$) δ 3.64 (m, 2 H), 2.65 (m, 6 H), 2.5 (m, 2 H, OH), 2.0–0.93 (m, 4 H), 1.10 (s, 3 H), 0.93 (s, 3 H); mass spectrum, m/e (M^+ − 2) calcd, 194.1307; obsd, 194.1311.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.31; H, 10.28.

A solution of the diol (2.55 g, 13 mmol) in dry pyridine (43 mL) was stirred at room temperature under nitrogen while freshly distilled phosphorus oxychloride (2.6 mL, 28 mmol) was added dropwise over 2 min. The reaction mixture was stirred at room temperature for 15 min, boiled for 15 min, cooled, and poured onto ice containing a little hydrochloric acid. The product was extracted into ether (2 × 75 mL) and washed with 10% hydrochloric acid (3 × 100 mL), saturated sodium bicarbonate solution, water, and brine prior to drying. Solvent evaporation left a yellow oil, distillation of which afforded diene **3b** as a colorless liquid (0.70 g, 34%); bp 60–62 °C (3 mm); ^{1}H NMR ($CDCl_3$) δ 5.40 (s, 2 H), 2.90 (m, 2 H), 2.0–1.6 (m, 4 H), 1.6–1.3 (m, 2 H), 1.20 (s, 3 H), 1.17 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 150.55, 128.02, 57.77, 45.15, 38.16, 28.79, 23.55, 22.91; mass spectrum, m/e (M^+) calcd, 160.1252; obsd, 160.1257.

4,7-Dihydro-2,2-dimethyl-4,7-methano-2*H*-indene (4c). A 3.0 g (15.8 mmol) sample of **11** was reduced with lithium aluminum hydride (3.21 g, 85 mmol) and methanol (10.34 mL, 0.255 mol) in dry tetrahydrofuran (180 mL) as described above. After the same workup, there was isolated 2.8 g (91%) of a pale yellow solid, recrystallization of which from hexanes gave the diol isomers as a colorless crystalline solid, mp 149–150 °C. For the major component: ^{1}H NMR (CD_3COCD_3) δ 6.03 (t, J = 2 Hz, 2 H), 3.55 (m, 2 H), 3.2–2.6 (m, 6 H), 1.5 (m, 2 H), 1.00 (s, 3 H), 0.95 (s, 3 H).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.03; H, 9.35.

Treatment of the diol mixture (2.8 g, 14.4 mmol) in dry pyridine (45 mL) with phosphorus oxychloride (2.88 mL, 31 mmol) in the predescribed manner gave a yellow oil (1.70 g). Distillation gave **4c** (370 mg, 16%) as a faintly yellow oil, bp 48–53 °C (1.75 mm). The product was collected at −78 °C and stored in a freezer under nitrogen. The hydrocarbon was distilled an additional two times prior to PE analysis: ^{1}H NMR ($CDCl_3$) δ 6.20 (t, J = 2 Hz, 2 H), 5.38 (s, 2 H), 3.28 (m, 2 H), 2.14 (br d, J = 8 Hz, 1 H), 1.88 (br d, J = 8 Hz, 1 H), 1.18 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 148.61, 137.49, 128.22, 59.96, 57.77, 43.21, 24.13, 22.58; mass spectrum, m/e (M^+) calcd, 158.1095; obsd, 158.1100.

***endo*,*anti*-1,2,3,4,5,6,7,8-Octahydro-10,10-dimethyl-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylic Anhydride (30).** A solution of **3b** (200 mg, 1.25 mmol) and maleic anhydride (120 mg, 1.25 mmol) in benzene (4 mL) was heated at the reflux temperature under a nitrogen atmosphere for 86 h. Solvent evaporation left 320 mg (100%) of a single adduct: colorless crystalline solid, mp 114–115 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 3.77 (m, 2 H), 2.92 (m, 4 H), 1.85 (br d, 2 H), 1.65–1.10 (m, 4 H), 1.0 (s, 3 H), 0.82 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 172.23, 151.47, 69.24, 54.56, 53.52, 48.49, 42.12, 24.82, 22.88, 21.00; mass spectrum, m/e (M^+) calcd, 258.1256; obsd, 258.1265.

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.40; H, 7.08.

1,2,3,4,5,6,7,8-Octahydro-10,10-dimethyl-*N*-phenyl-1,4:5,8-dimethanonaphthalene-2,3-dicarboximide (31). A solution of **3b** (200 mg, 1.25 mmol) and *N*-phenylmaleimide (220 mg, 1.25 mmol) in chloroform (4 mL) was heated at the reflux temperature under nitrogen for 5 days. Evaporation of solvent gave a yellowish solid, the ^{1}H NMR spectrum of which indicated it to be homogeneous. MPLC purification on silica gel (elution with 10% ethyl acetate in hexanes) gave 350 mg (83%) of **31** as a colorless solid: mp 168.5–169 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 7.45–7.10 (m, 5 H), 3.53 (m, 2 H), 2.82 (m, 4 H), 1.9–1.55 (m, 2 H), 1.32–1.05 (m, 4 H), 1.0 (s, 3 H), 0.72 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 177.14, 150.62, 132.17, 128.78, 127.80, 125.74, 69.00, 53.65, 53.22, 47.46, 42.06, 24.88, 23.12, 21.42; mass spectrum, m/e (M^+) calcd, 333.1729; obsd, 333.1736.

Anal. Calcd for $C_{2i}H_{23}NO_2$: C, 79.25; H, 6.95. Found: C, 79.19; H, 7.00.

***anti*-1,4,5,6,7,8-Hexahydro-*N*,10,10-trimethyl-1,4:5,8-dimethanophthalazine-2,3-dicarboximide (32).** A solution of **3b** (200 mg, 1.25 mmol) in ethyl acetate (5 mL) was treated dropwise with a solution of *N*-methyltriazolinedione (140 mg, 1.25 mmol) in the same solvent (5 mL) at −78 °C under a dry nitrogen atmosphere. The reaction mixture was stirred at −78 °C for 30 min, allowed to warm to room temperature, and evaporated. Chromatography of the residue on silica gel (elution with 20% ethyl acetate in hexanes) gave 340 mg (100%) of **32**: colorless crystals, mp 128–130 °C dec (from hexanes); ^{1}H NMR ($CDCl_3$) δ 4.47 (s, 2 H), 3.00 (m, 2 H), 2.90 (s, 3 H), 1.85 (m, 2 H), 1.4–0.9 (m, 4 H), 1.3 (s, 3 H), 0.8 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 161.52, 148.95, 72.29, 64.23, 55.25, 41.36, 25.34, 24.66, 21.89, 19.71; mass spectrum, m/e (M^+) calcd, 273.1477; obsd, 273.1485.

Anal. Calcd for $C_{15}H_{19}N_3O_2$: C, 65.91; H, 6.99. Found: C, 65.92; H, 7.01.

***syn*- and *anti*-Dimethyl 1,4,5,8-Tetrahydro-10,10-dimethyl-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylates (33 and 34).** A solution of **3b** (100 mg, 0.625 mmol) and dimethyl acetylenedicarboxylate (160 mg, 1.13 mmol) in chloroform (2 mL) was stirred under nitrogen at room temperature for 7 h. Solvent evaporation, followed by removal of starting materials at 0.3 mm, gave 180 mg of an oil. MPLC purification on silica gel (elution with 10% ethyl acetate in hexanes) gave major adduct **33** (140 mg) and minor component **34** (40 mg) (total yield 90%).

For **33**: oil; ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 6 H), 3.30 (s, 2 H), 2.95 (br s, 2 H), 1.7–1.1 (m, 4 H), 1.28 (br s, 6 H), 0.55 (br d, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 166.57, 157.30, 149.34, 82.63, 61.95, 51.90, 48.16, 42.87, 24.03, 22.72, 22.43; mass spectrum, m/e (M^+) calcd, 302.1518; obsd, 302.1525.

For **34**: oil; ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 6 H), 3.32 (s, 2 H), 3.05 (m, 2 H), 1.9–1.0 (m, 6 H), 1.20 (s, 3 H), 0.87 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 166.28, 159.97, 153.46, 88.02, 62.38, 55.59, 51.85, 43.01, 25.15, 23.98, 22.72; mass spectrum, m/e (M^+) calcd, 302.1518; obsd, 302.1525.

Peracid Epoxidation of 33. A solution of **33** (270 mg, 0.894 mmol) and *m*-chloroperbenzoic acid (172 mg of 85% purity, 0.994 mmol) in dichloromethane (15 mL) was heated at the reflux temperature for 20 h. The cooled solution was washed with 5% sodium thiosulfate (2 × 50 mL) and saturated sodium bicarbonate solutions (50 mL) and water (50 mL) prior to drying. Solvent evaporation left 220 mg of a viscous oil. MPLC purification on silica gel (elution with 5% ethyl acetate in hexanes) gave 150 mg (54%) of epoxide **35** as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 6 H), 3.00 (s, 2 H), 2.60 (br s, 2 H), 1.38 (s, 3 H), 1.08 (s, 3 H), 1.9–0.7 (series of m, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 165.61, 148.98, 70.82, 66.39, 57.59, 52.25, 40.48, 38.50, 27.91, 26.63, 25.24; mass spectrum, m/e (M^+) calcd, 318.1467; obsd 318.1475.

***N*-Phenylmaleimide Addition to 4c.** A solution of **4c** (200 mg, 1.27 mmol) and *N*-phenylmaleimide (1.10 g, 6.35 mmol) in benzene (5 mL) was heated at reflux under a nitrogen atmosphere for 6 days. Direct MPLC purification of the reaction mixture on silica gel (elution with 10% ethyl acetate in petroleum ether) gave 50 mg (12%) of an adduct (A) and 1 g of recovered dienophile. For A: ^{1}H NMR ($CDCl_3$) δ 7.5–7.2 (m, 5 H), 6.52 (m, 2 H), 3.45 (m, 2 H), 3.18 (s, 2 H), 2.3–2.1 (m, 4 H), 1.22 (s, 3 H), 1.18 (s, 3 H); mass spectrum, *m/e* (M^+) 331. This material was directly hydrogenated.

Catalytic Hydrogenation of A. A solution of A (45 mg, 0.136 mmol) in ethyl acetate (3 mL) was hydrogenated over 5% palladium on charcoal (5 mg) at atmospheric pressure for 20 min. Filtration and evaporation gave 40 mg (89%) of a dihydro adduct. MPLC purification on silica gel (elution with 10% ethyl acetate in hexanes) afforded **36** (35 mg) as a colorless solid: mp 193–193 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 7.58–7.15 (m, 5 H), 3.18 (s, 2 H), 3.05 (m, 2 H), 2.79 (s, 2 H), 1.85–0.85 (m, 6 H), 1.16 (s, 3 H), 1.141 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 177.30, 154.14, 132.39, 129.19, 128.46, 125.84, 55.69, 50.73, 49.62, 42.96, 25.83, 21.31 (2 C) (quaternary apical carbon not seen); mass spectrum, *m/e* (M^+) calcd, 333.1729; obsd, 333.1736.

***N*-Methyltriazolinedione Addition to 4c.** A solution of **4c** (200 mg, 1.27 mmol) in ethyl acetate (5 mL) was treated at −20 °C under nitrogen with a solution of *N*-methyltriazolinedione (140 mg, 1.27 mmol) in 5 mL of the same solvent. The reaction mixture was stirred at room temperature for 30 min and evaporated to give a 56:44 mixture (^{1}H NMR analysis) of adducts (340 mg, 100%). MPLC purification on silica gel (elution with 30% ethyl acetate in petroleum ether) destroyed one isomer and furnished the other (160 mg, 47%) as a substance (B) which slowly decomposes in air to a red oil: ^{1}H NMR ($CDCl_3$) δ 6.52 (t, J = 1.5 Hz, 2 H), 4.61 (s, 2 H), 3.60 (m, 2 H), 2.76 (s, 3 H), 2.31 (m, 2 H), 1.28 (s, 3 H), 1.10 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 159.58, 159.39, 142.88, 74.86, 71.08, 61.85, 48.60, 25.15, 21.36, 21.2; mass spectrum, *m/e* (M^+) calcd, 271.1321; obsd, 271.1330.

Catalytic Hydrogenation of B. A solution of B (140 mg, 0.517 mmol) in ethyl acetate (15 mL) containing 5% Pd/C (50 mg) was hydrogenated as predescribed. There was obtained 130 mg (93%) of **37** as a colorless solid: mp 168–170 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 4.5 (s, 2 H), 3.07 (m, 2 H), 2.87 (s, 3 H), 1.68–1.28 (m, 4 H), 1.30 (s, 3 H), 1.08 (s, 3 H), 0.68 (d of t, J = 7.5 and 1.5 Hz, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 159.34, 152.50, 71.71, 64.23, 53.06, 42.14, 24.95 (2 C), 21.89, 21.55; mass spectrum, *m/e* (M^+) calcd, 273.1477; obsd, 273.1485.

Anal. Calcd for $C_{15}H_{19}N_3O_2$: C, 65.91; H, 7.01. Found: C, 65.86; H, 7.10.

***syn*-1,2,3,4,5,6,7,8-Octahydro-5,9,9-trimethyl-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylic Anhydride (38).** A solution of **5** (200 mg, 1.15 mmol) and maleic anhydride (113 mg, 1.15 mmol) in benzene (2 mL) was stirred under nitrogen at room temperature overnight. Evaporation of solvent left 306 mg (98%) of a single adduct as a colorless solid: mp 188.0–188.5 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 3.48 (br s, 1 H), 3.42 (br s, 1 H), 2.89 (br s, 2 H), 2.59 (d, J = 3 Hz, 1 H), 2.0–1.3 (series of m, 6 H), 1.15 (s, 3 H), 0.82 (s, 3 H), 0.78 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 171.81, 171.72, 155.45, 152.01, 59.47, 54.52, 52.53, 49.47 (2 C), 48.21, 46.51, 45.39, 31.65, 24.86, 19.66, 18.30, 12.09; mass spectrum, *m/e* (M^+) calcd, 272.1412; obsd, 272.1419.

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.11; H, 7.39.

***syn*-1,2,3,4,5,6,7,8-Octahydro-5,9,9-trimethyl-*N*-phenyl-1,4:5,8-dimethanonaphthalene-2,3-dicarboximide (39).** A solution of **5** (200 mg, 1.15 mmol) and *N*-phenylmaleimide (200 mg, 1.15 mmol) in benzene was stirred under nitrogen at room temperature overnight. Solvent evaporation left a single adduct (395 mg, 99%) which was purified by MPLC on silica gel (elution with 10% ethyl acetate in hexanes). There was obtained 340 mg (85%) of **39** as colorless plates: mp 184.5–185.0 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 7.6–7.15 (m, 5 H), 3.45 (br s, 1 H), 3.40 (br s, 1 H), 2.73 (br s, 2 H), 2.58 (d, J = 3 Hz, 1 H), 2.1–1.5 (series of m, 6 H), 1.18 (s, 3 H), 0.82 (s, 3 H), 0.76 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 178.00 (2 C), 155.55 (2 C), 152.20, 132.00, 129.14, 128.56, 127.78, 126.42, 59.42, 54.52, 52.67, 48.84 (2 C), 47.09, 45.34, 44.28, 31.94, 25.20, 19.81, 18.45, 12.23; mass spectrum, *m/e* (M^+) calcd, 347.1885; obsd, 347.1892.

Anal. Calcd for $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25. Found: C, 79.51; H, 7.29.

***syn*-Dimethyl 1,4,5,6,7,8-Hexahydro-5,9,9-trimethyl-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylate (40).** A solution of **5** (200 mg, 1.15 mmol) and freshly distilled dimethyl acetylenedicarboxylate (163 mg, 1.15 mmol) in chloroform (2 mL) was stirred at room temperature under nitrogen for 2 h. Evaporation of solvent gave 360 mg of a yellow oil whose ^{1}H NMR spectrum showed one adduct to be present. MPLC purification afforded 220 mg (61%) of **40** as a yellowish oil: ^{1}H NMR (200 MHz) ($CDCl_3$) δ 3.757 (s, 3 H), 3.752 (s, 3 H), 2.56 (br d, J = 3.7 Hz, 1 H), 2.50 (d of t, J = 6.8 and 1.9 Hz, 1 H), 2.22 (d of t, J = 6.8 and 1.25 Hz, 1 H), 1.66–1.33 (m, 4 H), 1.11 (s, 3 H), 0.87 (s, 3 H), 0.76 (s, 3 H), 0.55–0.41 (m, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 166.18, 165.94, 160.02, 155.89, 150.84, 150.60, 70.10, 58.16, 54.67, 53.01, 52.63, 51.95 (2 C), 50.83, 29.32, 22.33, 19.42, 18.01, 12.14; mass spectrum, *m/e* (M^+) calcd, 316.1674; obsd, 316.1681.

Peracid Oxidation of 40. A solution of **40** (310 mg, 0.981 mmol) and *m*-chloroperbenzoic acid (220 mg of 85%, 1.28 mmol) in dichloromethane (10 mL) was heated at the reflux temperature for 22 h and worked up as previously described. The resulting colorless oil (400 mg) was purified by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether) to give 160 mg (48%) of **41**; ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 6 H), 3.37 (m, 2 H), 2.17 (m, 2 H), 1.9–1.0 (series of m, 5 H), 1.18 (s, 3 H), 1.10 (s, 3 H), 0.85 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 165.26, 165.11, 149.72, 149.53, 68.70, 65.40, 55.93, 53.35, 52.24, 50.25, 49.47 (2 C), 48.31, 47.87, 32.33, 25.63, 24.52, 22.72, 12.14; mass spectrum, *m/e* (M^+) 332.

Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.65; H, 7.28. Found: C, 68.60; H, 7.31.

Acknowledgment. Financial support for the research conudcted at the Ohio State University was provided by the National Cancer Institute (Grant CA-12115). The work in Heidelberg was supported by the Fonds der Chemischen Industrie and BASF Aktiengesellschaft, Ludwigshafen.

Registry No. 1, 81897-89-4; **2**, 81897-93-0; **3a**, 83134-57-0; **3b**, 85268-28-6; **4a**, 85221-93-8; **4b**, 85234-90-8; **4c**, 85268-29-7; **5**, 85317-09-5; **8**, 3142-58-3; **9**, 63518-01-4; **10**, 26154-22-3; **11**, 26157-43-7; **11** 1,3-diol, 85268-30-0; **12**, 26157-44-8; **12** 1,3-diol, 85268-31-1; **13**, 85268-32-2; **14**, 85317-10-8; **15**, 85268-33-3; **16a**, 85268-34-4; **16b**, 85317-11-9; **18**, 85268-35-5; **19**, 85317-12-0; **20**, 85268-36-6; **21**, 85317-13-1; **21** epoxide, 85268-37-7; **22**, 85317-14-2; **23**, 85268-38-8; **24**, 85317-15-3; **25**, 85317-16-4; **26**, 85317-17-5; **27**, 85317-18-6; **28**, 85317-19-7; **29**, 85317-20-0; **30**, 85268-39-9; **31**, 85268-40-2; **32**, 85268-41-3; **33**, 85268-42-4; **34**, 85317-21-1; **35**, 85268-43-5; **36**, 85317-22-2; **37**, 85317-23-3; **38**, 85268-44-6; **39**, 85317-24-4; **40**, 85268-45-7; **41**, 85268-46-8; **45**, 6675-72-5; **46**, 84988-39-6; **47**, 85268-47-9; **48**, 6675-71-4; A, 85268-48-0; B, 85268-49-1; i, 83151-98-8; ii, 85268-27-5; DMAD, 762-42-5; maleic anhydride, 108-31-6; *N*-phenylmaleimide, 941-69-5; methyl acrylate, 96-33-3; phenyl vinyl sulfone, 5535-48-8; benzoquinone, 106-51-4; *N*-methyltriazolinedione, 13274-43-6; methyl propiolate, 922-67-8; cyclopentadiene, 542-92-7.

Supplementary Material Available: Tables (Tables VI–XXII) of final atomic parameters, bond lengths, and bond angles for **38**, **18**, **30** (including torsion angles), and **32** (16 pages). Ordering information is given on any current masthead page.