Electronic Control of Stereoselectivity. 26. On the Inability of Fused Cyclopropane Rings To Direct the Stereochemical Course of Dienophile Capture by Tetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodeca-2,5,11-triene and Its Dihydro Derivative[1]

Pana Charumilind and Leo A. Paquette*

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received May 24, 1984*

Abstract: The π-facial stereoselectivities exhibited by tricyclo[5.2.2.$0^{2,6}$]undeca-2,5,8-triene (**2**), tetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]-dodeca-2,5-diene (**10**), and tetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodeca-2,5,11-triene (**11**) have been determined for dienophiles of wide-ranging reactivity. Structural assignments have been made through combined use of ^{1}H and ^{13}C NMR spectroscopy, select chemical transformations, especially regiospecific epoxidation and photocyclization, and chemical intercorrelation via hydrogenation of the adducts. [4 + 2] bonding to **2** occurs preferentially syn to the etheno bridge with maleic anhydride, *N*-phenylmaleimide, and *N*-methyltriazolinedione. In contrast, dimethyl acetylenedicarboxylate exhibits reversed stereoselectivity. An entirely similar stereochemical profile is observed for **11**, thereby denoting that stereoselectivity is likewise dominated by the double bond. Compound **10** shows modest stereoselectivity with *N*-methyltriazolinedione—an 85:15 preference for reaction on the π-face remote from the cyclopropane moiety—but negligible selectivity with the other three dienophiles. Accordingly, a cyclopropane ring interacts less strongly with the cyclopentadiene unit than an etheno bridge. Finally, the frequently dichotomous course of dimethyl acetylenedicarboxylate and *N*-methyltriazolinedione cycloadditions is addressed.

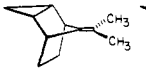
While isodicyclopentadiene (**1**) reacts with dienophiles predominantly, though not exclusively, from below plane,[2] preliminary studies of [4 + 2] cycloadditions to **2** have signaled a drop-off in stereoselection,[3] These results are considered to be a manifestation of lessening in **2** of important long-range electronic interactions that guide product development in **1** and relatively remote steric differences.

1

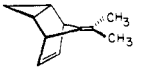
2

Some time ago, Heilbronner and co-workers demonstrated by means of photoelectron spectroscopy (PE) that homoconjugation between the pπ double bond and symmetric e_s cyclopropane Walsh orbital in tricyclo[3.2.1.$0^{2,4}$]oct-6-ene is strongly dependent upon configuration.[4] Thus, while the exo isomer experiences substantial interaction of this type, endo isomer **3** is essentially devoid of the phenomenon.

3



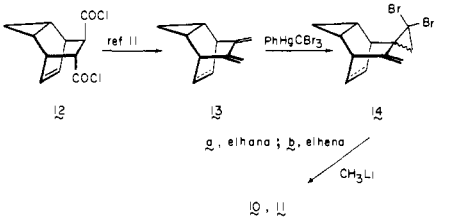
4



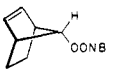
5

In contrast, the stereoelectronic conditions in **4** are strongly conducive to effective homoconjugation between the exocyclic double bond and cyclopropane ring.[5] For **5**, where a direct comparison of the competitive interaction between endocyclic and exocyclic double bonds with e_s is possible, only the latter condition

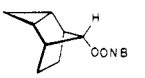
Scheme I



is considered operative.[5] These results conform to data derived from solvolysis experiments which indicate neighboring group participation by a double bond as in **6** (10^{11}-fold rate enhancement)[6] to be exceeded by that from an endo cyclopropane ring as in **7** (factor of 10^{14}).[7]



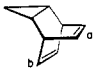
6



7

Along similar lines, the response of **8** and **9** to PE analysis has shown that homoconjugation involving the fused cyclopropane ring operates in both systems, but it is confined only to π_a in **9**.[8,9]

8



9

With these interesting considerations in mind, we have undertaken to expand our earlier examination of the Diels–Alder behavior of **2** and subsequently to determine the level of stereocontrol, if any, offered by the anti-oriented cyclopropane ring in **10** and **11**. The present experimental tests were designed to determine if the greater through-space homoconjugative capability

(1) Part 25: Paquette, L. A.; Hathaway, S. J.; Gallucci, J. C. *Tetrahedron Lett.* **1984**, 2659.

(2) (a) Paquette, L. A. In "Stereochemistry and Reactivity of Pi Systems"; Watson, W. H., Ed.; Verlag Chemie: Weinheim/Bergstr., Germany, 1983, in press. (b) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328. (c) See also: Ginsburg, D. *Tetrahedron* **1983**, *39*, 2095. (d) For a notable exception, consult: Paquette, L. A.; Green, K. E.; Hsu, L.-Y. *J. Org. Chem.* **1984**, *49*, 3650.

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

(4) Bischof, P.; Heilbronner, E.; Prinzbach, H.; Martin, H. D. *Helv. Chim. Acta* **1971**, *54*, 1072.

(5) Heilbronner, E.; Martin, H. D. *Helv. Chim. Acta* **1972**, *55*, 1490.

(6) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183.

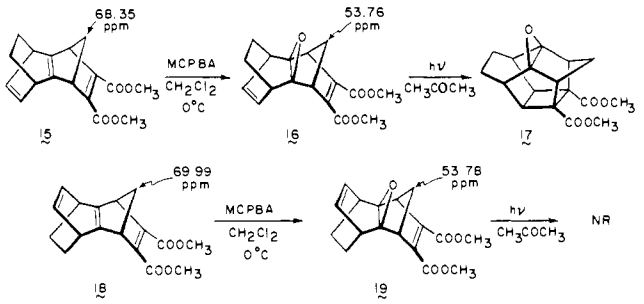
(7) (a) Tanida, H.; Tsuji, T.; Irie, T. *J. Am. Chem. Soc.* **1967**, *89*, 1953. (b) Battiste, M. A.; Deyrup, C. L.; Pincock, R. E.; Haywood-Farmer, J. *Ibid.* **1967**, *89*, 1954.

(8) Bruckmann, P.; Klessinger, M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 524.

(9) Gleiter, R.; Böhm, M. C.; de Meijere, A.; Preuss, T. *J. Org. Chem.* **1983**, *48*, 796.

0002-7863/84/1506-8225$01.50/0

Scheme II



of a fused three-membered ring would be reflected in enhanced stereoselection during dienophile capture.

Results

Substrate Synthesis. The starting material for the synthesis of **10** and **11** was the fumaryl chloride adduct (**12**) of cycloheptatriene,[10] which was transformed into **13a** and **13b** by the method of Butler and Snow (Scheme I).[11] To achieve suitable annulation, recourse was made to the Skattebøl rearrangement.[12-14] Treatment of either hydrocarbon with 1 equiv of phenyl(tribromomethyl)mercury in refluxing benzene[16] resulted in regiospecific addition (for **13b**) to one of the exocyclic double bonds and formation of a mixture of dibromocyclopropane isomers. Subsequent exposure of **14a** and **14b** to ethereal methyllithium afforded **10** and **11** in 79 and 85% yield, respectively.

Response of 2 to Cycloaddition. The π-face stereoselectivity exhibited by **2** in Diels–Alder reactions was originally assessed with dimethyl acetylenedicarboxylate (DMAD),[3] methyl propiolate,[3] benzyne,[3] and *N*-methyltriazolinedione.[17] In the intervening years, it has become apparent that ground-state σ/π interaction within a fused cyclopentadiene ring can be modified under the influence of the frontier orbitals of the attacking dienophile as reaction proceeds.[2b] This time-dependent phenomenon appears to be most influential when the dienophile possesses an additional orthogonal π obtial (i.e., is triply unsaturated) or nonbonded pair of electrons (as in triazolinediones) which do not enter directly into bonding.[18] Coincidentally, all four reagents initially examined fall into this category. For this reason and because it has remained unclear whether the added electronic perturbation always acts in direct opposition to the ground-state interaction pattern, we have proceeded to scrutinize nonacetylenic dienophiles as well.

X-ray structure analysis has previously established that *N*-methyltriazolinedione cycloadds to **2** exclusively from the direction of its etheno bridge.[17] Conversely, the trio of acetylenic dienophiles are thought to capture **2** predominantly (~80%) from the opposite face.[3] In these latter studies, stereochemical assignments were based upon a detailed analysis of ^{1}H NMR spectra. To confirm this impressive crossover in stereoselection, we have set out first to reinvestigate the DMAD reaction and to achieve unequivocal confirmation of the original structural conclusions by chemical means.

Table I. Product Distributions in Diels–Alder Additions to **2**, **10**, and **11**

substrate	dienophile[a]	reaction temp, °C	stereoselectivity[b] syn to ethano	syn to etheno	syn to cyclopropano
2	MTAD	−35	0	100	
	DMAD	20	77	23	
	MA	20	20	80	
	PM	20	15	85	
10	PVS	40	40		60
	PM	20	40		60
	DMAD	20	57		43
	MTAD	−78	85		15
11	PVS	40		80	20
	PM	20		80	20
	DMAD	20		16	84
	MTAD	−78		100	0

[a] MTAD = *N*-methyltriazolinedione; DMAD = dimethyl acetylenedicarboxylate; MA = vmaleic anhydride; PM = *N*-phenylmaleimide; PVS = phenyl vinyl sulfone. [b] All values have been normalized to 100%.

To this end, **2** was treated as before with DMAD and the pair of adducts was separated chromatographically. When the minor stereoisomer (**15**) was next submitted to controlled peracid oxidation, regiospecific formation of epoxide **16** could be realized (Scheme II). As anticipated, the oxirane ring was introduced into the central portion of the molecule from the exo surface, as revealed by the appreciable shielding ($\Delta\delta$ = 14.6 ppm) of the methano bridge carbon atom in **16** relative to that in **15** (see formulas).[19] The same regiochemical and spectral consequences were observed upon identical conversion of major adduct **18** to **19** ($\Delta\delta$ = 16.2 ppm).

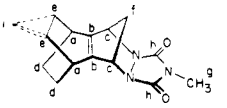
Whereas the double bonds remaining in **16** are positioned in close spatial proximity, those in **19** are not. Consequently, only **16** should be subject to intramolecular photocycloaddition, as was found to be the case. Isomer **19** proved unreactive to identical conditions of irradiation. The formation of **17** with retention of the molecular plane of symmetry was clearly indicated by its ^{1}H and ^{13}C NMR spectra. Accordingly, the original stereochemical assignments must be considered established beyond doubt and the original ^{1}H NMR correlations viewed as reliable (Table I).

Triene **2** reacts with maleic anhydride in chloroform solution at room temperature to give a mixture of **20a** and **21a** in a ratio of 80:20 (determined by integration of the ^{1}H NMR spectrum of the mixture). By means of spinning plate chromatography, the major isomer could be obtained in pure condition. Although the minor component remained somewhat contaminated with **20**,

its ^{1}H and ^{13}C NMR spectra could easily be obtained by subtractive methods. The exo configuration of the anhydride ring in both products was revealed by the absence of spin coupling between the norbornene bridgehead protons and those α to the carbonyl group.[20] In **20a**, the proximity of the outer bicyclo-

(10) Alder, K.; Jacobs, G. *Chem. Ber.* **1953**, *86*, 1528.
(11) Butler, D. N.; Snow, R. A. *Can. J. Chem.* **1972**, *50*, 795.
(12) Skattebøl, L. *Tetrahedron* **1967**, *23*, 1107.
(13) Reinarz, R. B.; Fonken, G. L. *Tetrahedron Lett.* **1973**, 4591. Brinker, U.; Fleischhauer, I. *J. Am. Chem. Soc.* **1981**, *103*, 2116; *Tetrahedron* **1981**, *37*, 4495.
(14) The success of the carbene (carbenoid) rearrangement which eventually leads to the cyclopentadiene ring[15] appears highly dependent upon the existing level of ring strain. In [2.2.2] bicyclic systems such as **14a** and **14b**, the requisite isomerization is efficient [see also: Butler, D. N.; Gupta, I. *Can. J. Chem.* **1978**, *56*, 80]. When smaller [2.2.1] bicyclic substrates are involved, allene formation may dominate heavily [Mebane, R. C.; Schuster, G. B. *J. Org. Chem.* **1983**, *48*, 810 reference 31], but need not [Charumilind, P.; Kravetz, T. unpublished results].
(15) The particular arrangement of the cyclopentadiene double bonds depicted in **10** and **11** is the thermodynamically more stable: (a) Paquette, L. A.; Williams, R. V.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 4566. (b) Subramanyam, R.; Bartlett, P. D.; Watson, W. H.; Galloy, J. *Ibid.* **1982**, *47*, 4491.
(16) Seyferth, D.; Burlitch, J. M. *J. Organomet. Chem.* **1965**, *4*, 127. Seyferth, D.; Lambert, R. L., Jr. *Ibid.* **1969**, *16*, 21.
(17) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1980**, *45*, 4922.
(18) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105*, 3136.
(19) Paquette, L. A.; Charumilind, P.; Gallucci, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 7364 and relevant references cited therein.
(20) (a) Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 3724. (b) Marchand, A. P. "Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems"; Verlag Chemie International: Deerfield Beach, FL, 1982.

Table II. ^{13}C NMR Data for *N*-Methyltriazolinedione Adducts ($CHCl_3$ Solution)



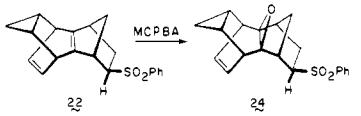
compd	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
38	30.01	145.13	67.37	25.98	26.27	51.39	25.03	160.72	
48	30.56	149.39	66.95	23.35	23.35	50.88	24.81	160.94	18.35
49	30.83	150.40	67.37	24.81	22.43	51.51	25.05	160.21	15.92
36	37.97	152.49	65.88	131.03	17.09	49.18	25.20	160.60	15.58
37	36.55	146.69	66.14	134.79	25.18	49.40	25.36	161.10	

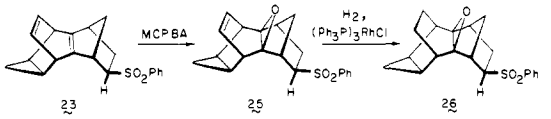
[2.2.2]octadiene double bond to the α-carbonyl protons induces an appreciable shielding effect on their chemical shift relative to those in **21a** (δ 2.60 vs. δ 2.80). This differential is considered to be adequate grounds for unambiguous stereochemical definition.

Comparable treatment of **2** with *N*-phenylmaleimide gave rise to a very similar distribution of **20b** and **21b**. These isomers were readily separated and structural assignments again deduced on the basis of the sizable chemical shift differences between the sets of α-carbonyl protons (δ 2.52 vs. δ 2.80).

These experiments define a preferred π-face stereoselectivity for two prototypical olefinic dienophiles which is comparable to that followed by *N*-methyltriazolinedione, although not with the same exclusivity.

Cycloaddition Reactions Involving 11. This phase of the study began with phenyl vinyl sulfone, a dienophile of moderately low reactivity.[21] When equimolar amounts of the sulfone and **11** were heated in dichloromethane for 2 weeks, the chromatographically separable adducts **22** and **23** were formed in a ratio of 80:20.

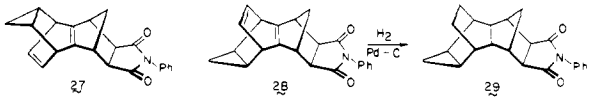




Major product **22** was identified as the result of below-plane capture on the basis of the more shielded nature of its α-sulfonyl proton (δ 2.32) relative to that in **23** (δ 2.89). As before, the chemical shift difference of 0.57 ppm is attributed to anisotropy effects emanating from the spatially proximate etheno bridge in **22**. The exo configuration of the phenylsulfonyl group in both adducts was apparent from the small coupling constant between the bridgehead and α-sulfonyl protons ($\sim$1.1 Hz).[20]

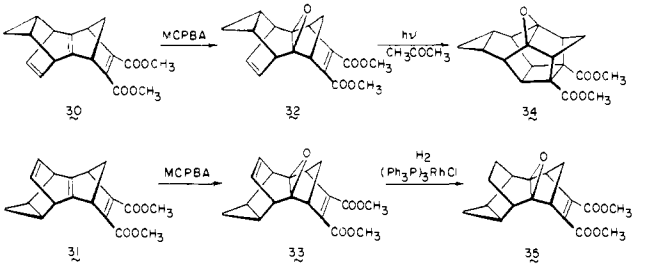
Conversion of **22** and **23** to epoxides **24** and **25** was achieved conventionally. When these substances were individually subjected to catalytic hydrogenation in the presence of Wilkinson's catalyst, only the reduction of **25** to **26** was observed. The double bond in **24** is evidently too sterically crowded on both of its faces to permit facile saturation.

Exposure of **11** to the somewhat more reactive *N*-phenylmaleimide reagent in chloroform solution at room temperature for 3 days afforded an 80:20 mixture of **27** and **28** which could be separated by chromatography. Comparison of the ^1H NMR spectra of these substances denoted once again a wide discrepancy in the chemical shift of the α-carbonyl protons. Since the

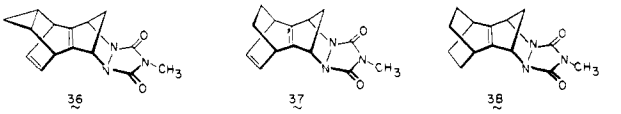


>C*H*CO– hydrogens in **27** appear at δ 2.43, 0.49 ppm upfield of those in **28**, it follows that the indicated structural formalism is established. In agreement with earlier findings, only **28** could be successfully hydrogenated exhaustively (Pd/C) in good yield.

When **11** was next allowed to stand with the substantially more reactive dimethyl acetylenedicarboxylate ($CHCl_3$, room temperature, 4 h), the pair of adducts **30** and **31** was produced. However, because of the intrinsic lability of these compounds,[22] in situ epoxidation was effected prior to isolation. Following chromatographic separation, oxiranes **32** and **33** were obtained in a ratio of 16:84. The ready photocyclization of **32** to **34** in acetone solution and uneventful catalytic hydrogenation of **33** to **35** convincingly support the structural assignments.



Following admixture of **11** with *N*-methyltriazolinedione in cold (−78 °C) ethyl acetate solution, a single adduct was formed in essentially quantitative yield within 5 min. Although crystals of this substance could not be obtained in a form suitable for X-ray analysis, its assignment as **36** could be arrived at with reasonable confidence by direct comparison of its ^{13}C NMR spectrum with those of **37** and **38**.[17] As seen in Table II, the chemical shift of the apical methano carbon in **36** (49.18 ppm) compares closely to that of **37** (49.40 ppm) for which X-ray data are available.[17] On the other hand, the same carbon in **38** at 51.39 ppm appears somewhat downfield of the other two. As will be described subsequently, the region of this absorption is seemingly typical for those systems in which the lower flanking bridge of the [2.2.2]bicyclooctenyl moiety lacks unsaturation.



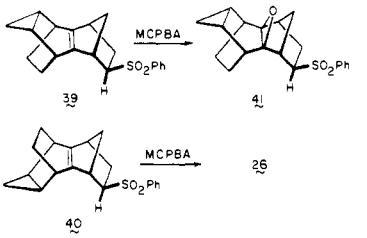
Thus, we see that **11** exhibits a predilection for below-plane dienophile capture toward phenyl vinyl sulfone, *N*-phenylmaleimide, and *N*-methyltriazolinedione in a manner reminiscent of **2**. Once again, however, DMAD plays a maverick role and prefers to enter into Diels–Alder cycloaddition with above-plane stereoselectivity.

Cycloadditive Behavior of 10. Condensation of **10** with phenyl vinyl sulfone resulted in the formation of **39** and **40**, with the latter adduct predominating (ratio of 40:60 by ^1H NMR analysis). Since this pair of isomers was not separable by chromatography, the mixture was directly oxidized with 1 equv of *m*-chloroperbenzoic acid. A new epoxy sulfone (**41**) and the previously characterized **26** were efficiently produced; the latter oxirane was obtained in

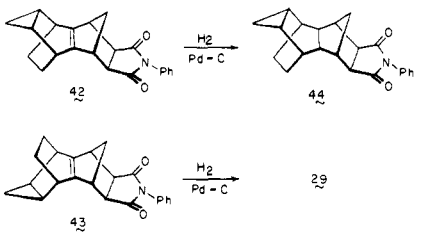
(21) (a) Carr, R. V. C.; Paquette, L. A. *L. Am. Chem. Soc.* **1980**, *102*, 853. (b) Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4976. (c) Kinney, W. A.; Crouse, G. D.; Paquette, L. A. *Ibid.* **1983**, *48*, 4986.

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

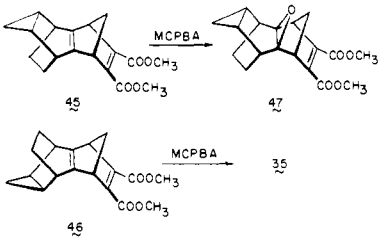
60% yield. The obvious conclusion that the principal adduct leads to **26** of established configuration serves as the basis of our structural assignment.



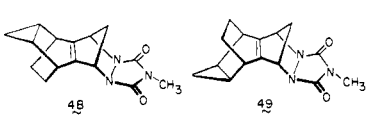
When a solution of **10** and *N*-phenylmaleimide was allowed to react at room temperature for 4 days, conversion to a 40:60 mixture (^{1}H NMR analysis) of **42** and **43** was observed. When all attempts to achieve chromatographic separation of the two isomers failed, hydrogenation over palladium on charcoal was effected. In this fashion, conversion to **44** and **29** was realized, at which point it proved possible to deduce simply the relevant stereochemistry of the products,



In our examination of the reaction between **10** and DMAD, a 98% yield of a 57:43 mixture of **45** and **46** (^{1}H NMR analysis) was achieved. Again in this instance, correlation of these adducts with those of the triene series was achieved through epoxidation. In this connection, the conversion of **46** to **35** proved especially significant.



An instantaneous reaction occurred between **10** and *N*-methyltriazolinedione at −78 °C, Although the ^{1}H NMR spectrum of the solid product gave no indication that two isomers had been formed, ^{13}C NMR analysis revealed that as much as 15% of a second adduct was present. The relevant carbon shifts for **48** and **49**, which are given in Table I, indicate expectedly that both molecules are very closely related to **38**. In particular, note should be taken of the appearance of the apical methano carbon at approximately 51 ppm in all three molecules. Although

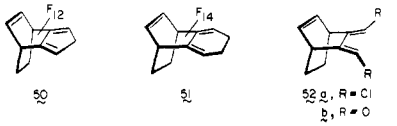


structural assignment is decidedly less rigorous in this instance, the major product is considered to be **48**, the product of below-plane stereoselectivity, on the strength of the shielding effect experienced by its apical methano carbon relative to that in **49** (Δ ppm = 0.63). This phenomenon is in the same direction and of comparable magnitude to the distinctive features which characterize **36** and **37** (Δ ppm = 0.22, Table I). Attempts to saturate the peripheral double bond in **36** as a means of arriving at **48** in an independent fashion were without success, rupture of the cyclopropane ring occurring when conditions were forced.

Discussion

Where triene **2** is concerned, the collective results show that Diels–Alder cycloaddition involving olefinic dienophiles proceeds with a moderate kinetic preference for bonding to that cyclopentadiene face which is syn to the etheno bridge. Relevantly, the same stereochemical course is followed exclusively by *N*-methyltriazolinedione.[17] Comparable stereoselectivity is not encountered with DMAD and other highly reactive acetylenes which demonstrate a tendency to attack from the direction of the ethano bridge.[3]

The exo face of **2** (as illustrated herein) is not likely projecting to the approaching dienophile less sterically crowded conditions relative to the endo surface. If this were so, one would have expected the sterically demanding rod-shaped acetylenic dienophiles[15b,19] to exhibit strong exo face stereoselectivity as well. This behavior is not seen. The analogues **50**,[23] **51**,[24] **52a**,[25] and **52b**[26] similarly indicate that differential steric factors do not play a dominant role in their cycloaddition chemistry.



Extensive comment has previously been made concerning the ground-state electronic character of **1**.[2] In this system, substantial electronic interaction between high-lying σ orbitals within the norbornyl unit and the neighboring *s-cis*-butadiene moiety is believed to cause pronounced disrotatory tilting of the terminal pπ orbitals in ψ_1 toward the methano bridge, with resultant facilitation of below-plane attack. The advantage to endo face stereoselectivity materializes as the direct result of a reduction in the level of antibonding interaction between filled orbitals in the diene and dienophile. *Stated differently, approach to the surface having the lesser electron density results in a lowering of $\Delta H^{\ddagger}$ for cycloaddition.*

The lessened steric strain in a bicyclo[2.2.2]octenyl nucleus leads to a reduction in the energy of its σ orbitals and a concurrent drop-off in the intensity of long-range interaction.[17] Calculations of the INDO and SPINDO type reveal that some disrotatory tilting of the terminal diene π orbitals toward the ethano bridge does persist in **2**, although noticeably less so than in **1**.[27] Above-plane attack (syn to the etheno bridge) should consequently be moderately favored. Indeed, the stereoselectivity adopted by maleic anhydride, *N*-phenylmaleimide, and *N*-methyltriazolinedione conforms to this theoretical model.

The face selectivity observed for **11** is remarkably similar to that seen for **2**. Thus, with dienophiles of widely varied reactivity (phenyl vinyl sulfone, *N*-phenylmaleimide, and *N*-methyltriazolinedione) an obvious kinetic preference for capture syn to the etheno bridge is again observed (80, 80, and 100%, respectively), The parallel extends further to DMAD which, as before, shows the interesting trait of favoring cycloaddition from the opposite cyclopentadiene surface (84%).

These results draw one to the conclusion that those electronic effects, if any, which emanate from the laterally fused cyclopropane ring in **11** have less impact than those of the etheno bridge on π-face stereoselectivity in its Diels–Alder reactions. At first glance, this conclusion would appear to stand in direct contradiction to the impressively powerful long-range effects previously encountered in **4**, **5**, and **7–9**. However, hints that correlations between cycloaddition behavior and other (electronic, solvolytic, etc.) phenomena need not hold in these systems have quite recently

(23) Feast, W. J.; Musgrave, W. K. R.; Preston, W. E. *J. Chem. Soc., Perkin Trans 1* **1972**, 1830.
(24) Feast, W. J.; Hughes, R. R.; Musgrave, W. K. R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 152.
(25) Avenati, M.; Hagenbuch, J.-P.; Mahaim, C.; Vogel, P. *Tetrahedron Lett.* **1980**, 3167.
(26) Avenati, M.; Vogel, P. *Helv. Chim. Acta* **1983**, *66*, 1279.
(27) Böhm, M.; Gleiter, R., private communication.

Table III, Cycloaddition Reactions of Homobarrelene (**9**)[29]

X	% of **53**	% of **54**	% of **55**	ref
CH_2	39		61	*a*
CCl_2	35	14	51	*b*
0	10	15	75	*c*
NNPht	23	5	72	*c*
S		14	86	*c*
$C(O)CCl_2$	14		86	*d*
C(O)NH[e]		3	8	*f*

[a] de Meijere, A.; Weitemeyer, C.; Schallner, O. *Chem. Ber.* **1977**, *101*, 1504. [b] Proksch, E. Ph.D. Dissertation, University of Gottingen, 1977. [c] Preuss, T. Ph.D. Dissertation, University of Hamburg, 1983. [d] Erden, I.; de Meijere, A. *Tetrahedron Lett.* in press. [e] Rearrangement products predominate in this instance. [f] Volz, W. E.; Paquette, L. A. *J. Org. Chem.* **1976**, *41*, 57.

begun to surface. The most notable of these investigations involves homobarrelene (**9**), the conversion of which to **53–55** upon reaction

53 **54** **55**

with select reagents has been examined in detail chiefly by de Meijere and co-workers (Table III).[28] Although attack at the more electronically perturbed olefinic center (π_A) in **9** is generally preferred, π_B can become involved to an extent as high as 35%, despite strong steric deterrent to approach toward one of its surfaces.

As previously noted, we believe that the competing faces of the cyclopentadiene ring in **11** do not differ significantly in steric accessibility, especially since anti-Alder stereochemistry is adhered to on both surfaces. However, our theoretical model requires that the laterally fused cyclopropane ring interact with the conjugated diene through the σ framework. This is an important distinction. In the molecules examined earlier, the cyclopropane ring exercised its influence by interactions through space. While its ability to function by such mechanisms is excellent, provided that dihedral angle relationships are favorable,[29] no significant effects are evident when the constraint of operating through σ bonds is imposed. In the following paper,[30] the simple expedient of reorienting the cyclopropane ring into a spiro arrangement is shown to provide for a return to long-range interaction.

In view of the foregoing, one must anticipate that neither face of the cyclopentadiene ring in **10** should be in a position to offer a kinetic advantage to an approaching dienophile. Although certain small differences in the relevant molecular orbitals are likely to arise as reaction is initiated on either surface and coupling between all components grows stronger, feeble face selectivities should persist. Our observations are consistent with this conclusion.

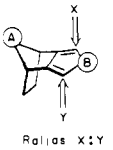
Some comment on the frequently encountered dichotomous stereochemical pathways followed by DMAD and *N*-methyltriazolinedione (MTAD) in cycloaddition reactions involving bicyclic fused dienes is in order. Both reagents are highly polarizable and possess a pair of electrons orthogonal to those involved in the [4 + 2] bonding process. However, the similarity generally stops here (Tables I and IV). Example 1, where the stereochemical course followed by DMAD and MTAD is precisely the same as that charted by common olefinic dienophiles, may be unique. Unfortunately, the formation of ill-defined products with MTAD in cases of 2 and 3 precludes extension of this generalization to these examples. Nevertheless, it is relevant that DMAD does follow the stereochemical trend set by *N*-phenylmaleimide in both of these instances.

(28) We are deeply thankful to Professor de Meijere for making available to us some of his results in advance of publication. See also: Erden, I.; de Meijere, A. *Tetrahedron Lett.* **1983**, 3811.

(29) Gleiter, R. *Top. Curr. Chem.* **1979**, *86*, 197.

(30) Paquette, L. A.; Green, K. E.; Gleiter, R., Schäfer, W.; Gallucci, J. C. *J. Am. Chem. Soc.*, following paper in this issue.

Table IV, Comparative Analysis of π-Face Stereoselectivity



Ratios X:Y

example		*N*-phenylmaleimide	DMAD	MTAD	ref
1	A = CH_2 B = CH_2	<10:>90[a]	0:100	0:100	*c*
2	A = CH_2 B = $C{=}C(CH_3)_2$	0:100	0:100	*b*	*d*
3	A = CH_2 B = C–CH_2–CH_2	23:77	0:100	*b*	*e*
4	A = CH_2 B = C–$(CH_2)_3$–CH_2	100:0	27:75	100:0	*e*
5	A = CH_2 B = $C(CH_3)_2$	100:0	30:70	100:0	*f*
6	A = CH=CH B = CH_2	80:20	14:86	100:0	*g*
7	A = CH_2 B = *exo,exo*-diethylidene	0:100	0:100	100:0	*h*

[a] Values extrapolated from studies involving maleic anhydrdide and other olefinic dienophiles. [b] Ill-defined products result. [c] References 3 and 17. [d] Paquette, L. A.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Org. Chem.* **1983**, *48*, 1250. [e] Reference 18. [f] Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3148. [g] Reference 17 and present work. [h] Reference 1.

Examples 4–6 are particularly revealing. Whereas *N*-phenylmaleimide and MTAD share a common reaction channel, DMAD bonds preferentially to these dienes from the opposite face. Accordingly, as reaction proceeds, the interplay between polarizability and eventual π-face stereoselectivity seemingly induces DMAD to develop electronic influences which act in direct opposition to existing ground-state interaction patterns. *N*-Methyltriazolinedione gives evidence of being less influenced by these dynamic forces, although their effects have been observed in one acyclic example (case 7).

In conclusion, lateral fusion of a cyclopropane ring necessitates the involvement of a bicyclo[2.2.2]octane core. The resultant release of ring strain relative to norbornyl leads to lowering of the framework σ orbital energies to levels which cause mixing with the subjacent diene π_s orbital to be weak and incapable of dramatically influencing π-face stereoselectivity. A laterally fused cyclopropane ring is not capable of product determinative electronic transmission through the σ network.

Experimental Section[31]

Tetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodeca-2,5-diene (10). To a solution of **13a**[11] (1.82 g, 12.7 mmol) in dry benzene (10 mL) was added phenyl(tribromomethyl)mercury (6.7 g, 12.67 mmol), and the mixture was heated at the reflux temperature for 6 h. The precipitated phenylmercuric bromide was separated by filtration through Celite, and the filtrate was evaporated. The residue was redissolved in hexane and passed through a column of neutral alumina (1 × 10 cm, 300 mL elution). The eluate was concentrated to dryness to give **14a** which was used without further purification.

A solution of **14a** (3.5 g, 11.0 mmol) in anhydrous ether (700 mL) was treated slowly with ethereal methyllithium (29 mL of 1.5 M, 43.8 mmol),

(31) All cycloaddition reactions were conducted simultaneously on a preparative scale and on a microscale in an NMR tube. The progress of each Diels–Alder process was monitored by integrating the disappearance of starting diene and dienophile, as well as the appearance of the adduct(s) vs. time. In no instance was formation of an extraneous product noted, and complete consumption of diene was invariably achieved. The less than quantitative isolated yields are the result of mechanical losses during chromatography (scale dependent) and, in certain cases (DMAD adducts, ethylene extrusion; MA adducts, partial hydrolysis during chromatography), brought on by a chemical side reaction. In no example was reversibility noted. On this basis, the product ratios are tacitly assumed to be the end result of kinetic control.

and stirring at room temperature was maintained overnight. The reaction mixture was poured into cold water and extracted with ether (2 × 100 mL). The combined organic layers were dried and evaporated to leave **10** which was purified by elution through neutral alumina with petroleum ether. There was isolated 1.37 g (79%) of the diene as a colorless oil (prep VPC, 15% SE-30, 150 °C) which crsytallized on standing in the refrigerator: mp 30–31 °C; ^{1}H NMR ($CDCl_3$) δ 5.85 (s, 2 H), 3.07 (d, J = 23.3 Hz, 1 H), 2.95 (d, J = 23.3 Hz, 1 H), 2.92 (br s, 1 H), 1.60 (d, J = 8.0 Hz, 2 H), 1.26 (d, J = 8.0 Hz, 2 H), 1.08–1.00 (m, 3 H), 0.70–0.62 (m, 1 H); ^{13}C NMR ($CDCl_3$) 152.60, 117.28, 41.12, 30.08, 24.45, 16.68, 9.03 ppm; m/e (M^+) calcd 158.1096, obsd 158.1115.

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.64; H, 8.88.

Tetracyclo[5,3,2,0^{2,6},0^{8,10}]dodeca-2,5,11-triene (11), Paralleling the above procedure, **13b**[11] (3.0 g, 20.83 mmol) was treated with phenyl(tribromomethyl)mercury (11.0 g, 20.83 mmol) in dry benzene (50 mL) at reflux for 6 h. There was obtained 5.8 g (88%) of the dibromocyclopropane mixture **14b**.

A solution of **14b** (3.2 g, 10.13 mmol) in ether (600 mL) was treated slowly with ethereal methyllithium (27 mL of 1.5 M, 40.51 mmol). After the mixture was stirred overnight, the usual workup gave 1.50 g (95%) of **11** as colorless oil (prep VPC, 5% SE-30, 165 °C): ^{1}H NMR ($CDCl_3$) δ 5.96 (d, J = 3.3 Hz, 1 H), 5.93 (d, J = 3.3 Hz, 1 H), 5.74 (s, 2 H), 3.64–3.58 (m, 2 H), 3.09 (s, 2 H), 1.13–1.06 (m, 2 H), 0.62–0.55 (m, 1 H), 0.50–0.43 (m, 1 H); ^{13}C NMR ($CDCl_3$) 151.34, 129.11, 115.63, 42.62, 35.72, 12.59, 7.55 ppm; m/e (M^+) calcd 156.0939, obsd 156.0930.

Anal. Calcd for $C_{12}H_{12}$: C, 92.26, H, 7.74. Found: C, 91.86; H, 7.80.

Reaction of 2 with Dimethyl Acetylenedicarboxylate, A solution of **2** (190 mg, 1.32 mmol) and DMAD (187 mg, 1.32 mmol) in chloroform (20 mL) was stirred at room temperature for 2 h under a nitrogen atmosphere and evaporated. The oily residue was purified by spinning plate chromatography (silica gel, elution with 10% ethyl acetate in petroleum ether) to give 180 mg (48%) of **18** and 40 mg (14%) of **15**, the latter being contaminated with the benzonorbornadiene resulting from extrusion of ethylene from either adduct. The spectral properties of these products conformed to data previously reported.[3]

Epoxidation of 18, To a stirred solution of **18** (110 mg, 0.38 mmol) of dichloromethane (15 mL) cooled to 0 °C was added *m*-chloroperbenzoic acid (80 mg, 0.46 mmol) dissolved in 5 mL of the same solvent. The reaction mixture was stirred at room temperature for 30 min, shaken with saturated sodium carbonate solution, dried, and evaporated. Spinning plate chromatography of the residue (silica gel, elution with 10% ethyl acetate in petroleum ether) afforded 95 mg (83%) of **19** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.98–5.94 (m, 2 H), 3.77 (s, 6 H), 3.36 (s, 2 H), 3.04 (br s, 2 H), 2.02 ($^1/_2A_2B_2$, J = 8.2 Hz, 1 H), 1.72 ($^1/_2A_2B_2$, J = 8.2 Hz, 1.17 (s, 4 H); ^{13}C NMR ($CDCl_3$) 165.07, 149.38, 131.23, 61.14, 53.76, 52.33, 49.60, 33.58, 21.94 ppm; m/e (M^+ - CH_3O) calcd 271.0970, obsd 271.0980.

Epoxide 16, This substance can be prepared most conveniently by direct epoxidation of the **15**/**18** mixture as isolated directly from the cycloaddition. From 160 mg (0.56 mmol) of this mixture and 100 mg (0.58 mmol) of *m*-chloroperbenzoic acid in dichloromethane (50 mL), there could be isolated following spinning plate chromatography (silica gel, elution with 10% ethyl acetate in petroleum ether) 30 mg (18%) of **16** and 125 mg (74%) of **19**.

For **16**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 6.20–6.17 (m, 2 H), 3.79 (s, 6 H), 3.33 (s, 2 H), 3.12 (br s, 2 H), 1.86–1.73 (m, 3 H), 1.39 ($^1/_2A_2B_2$, J = 8.6 Hz, 1 H), 0.89 ($^1/_2A_2B_2$, J = 8.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 165.07, 149.38, 131.23, 61.19, 53.76, 52.28, 49.60, 33.58, 21.94 ppm; m/e (M^+ - CH_3O) calcd 271.0970, obsd 271.0980.

Photocyclization of 16, A solution of **16** (30 mg, 0.10 mmol) was dissolved in acetone-d_6 (0.5 mL), placed in an NMR tube, and irradiated with a long-wavelength TLC ultraviolet lamp for 1 h. The solvent was evaporated, and the product was filtered through a short silica gel column to give 27 mg (90%) of **17**; ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 6 H), 2.88–2.87 (m, 2 H), 2.57 (s, 2 H), 2.20 (s, 2 H), 1.68 ($^1/_2$AB, J = 11.4 Hz, 1 H), 1.53 ($^1/_2A_2B_2$, J = 9.6 Hz, 2 H), 1.44 ($^1/_2$AB, J = 11.4 Hz, 1 H), 1.34 ($^1/_2A_2B_2$, J = 9.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 172.07, 60.86, 60.10, 51.90, 44.03, 36.70, 31.01, 27.57, 14.50 ppm; m/e (M^+) calcd 302.1154, obsd 302.1119.

Comparable irradiation of **19** resulted in no reaction.

Reaction of 2 with Maleic Anhydride, A solution of **2** (100 mg, 0.69 mmol) and maleic anhydride (68 mg, 0.69 mmol) in chloroform (15 mL) was stirred at room temperature for 6 h, at which point TLC analysis indicated the reaction to be complete. The solvent was evaporated and the residue purified by spinning plate chromatography (silica gel, elution with 10% ethyl acetate in petroleum ether). In this fashion (including band shaving techniques), only **20a** (80 mg, 48%) could be obtained in a pure state. The remainder of the material was a mixture of **20a** and **21a** (^{1}H NMR analysis of reaction mixture showed their ratio to be 4:1).

For **20a**: colorless solid, mp 145–146 °C (from ether); ^{1}H NMR ($CDCl_3$) δ 6.21–6.19 (m, 2 H), 3.64 (br s, 2 H), 3.41 (s, 2 H), 2.60 (s, 2 H), 1.53–1.31 (m, 6 H); ^{13}C NMR ($CDCl_3$) 171.96, 151.18, 133.91, 49.27, 48.29, 42.44, 37.19, 25.27 ppm; m/e (M^+) calcd 242.0943, obsd 242.0968.

For **21a** (data obtained by spectral substraction): ^{1}H NMR ($CDCl_3$) δ 6.33–6.30 (m, 2 H), 3.78 (br s, 2 H), 3.53 (s, 2 H), 2.89 (s, 2 H), 1.55–1.23 (m, 4 H), 0.89–0.88 (m, 2 H); ^{13}C NMR ($CDCl_3$) 171.58, 150.25, 135.05, 49.82, 49.27, 44,52, 37.46, 25.60 ppm.

Reaction of 2 with *N*-Phenylmaleimide, A solution of **2** (100 mg, 0.69 mmol) and *N*-phenylmaleimide (120 mg, 0.69 mmol) in chloroform (15 mL) was stirred overnight at room temperature. Solvent evaporation followed by spinning plate chromatography (silica gel, elution with 10% ethyl acetate in petroleum ether) afforded 100 mg (46%) of **20b** and 20 mg (9%) of **21b**. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of these products to be 83:17.

For **20b**: colorless crystals, mp 154–155 °C (from ether); ^{1}H NMR ($CDCl_3$) δ 7.48–7.37 (m, 3 H), 7.24–7.20 (m, 2 H), 6.25–6.22 (m, 2 H), 3.67 (br s, 2 H), 3.40 (s, 2 H), 2.52 (s, 2 H), 1.56–1.33 (m, 6 H); ^{13}C NMR ($CDCl_3$) 177.21, 151.13, 134.02, 129.10, 128.49, 126.42, 48.07, 47.47, 41.46, 37.19, 25.38 ppm; m/e (M^+) calcd 317.1416, obsd 317.1410.

Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.04. Found: C, 79.36; H, 6.18.

For **21b**: colorless solid, mp 210–211 °C (from ether); ^{1}H NMR ($CDCl_3$) δ 7.52–7.15 (m, 5 H), 6.35–6.33 (m, 2 H), 3.81 (br s, 2 H), 3.52 (s, 2 H), 2.80 (s, 2 H), 1.61–1.33 (m, 4 H), 1.01–0.95 (m, 2 H); ^{13}C NMR ($CDCl_3$) 176.99, 150.36, 135.22, 129.20, 128.71, 126.47, 48.67, 48.51, 43.42, 37.63, 25.87 ppm; m/e (M^+ - C_2H_4) calcd 289.1103, obsd 289.1101.

Reaction of 11 with Phenyl Vinyl Sulfone, A solution of **11** (250 mg, 1.60 mmol) and phenyl vinyl sulfone (269 mg, 1.60 mmol) in dichloromethane (50 mL) was heated at the reflux temperature for 2 weeks. After solvent evaporation, the residue was purified by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether). There was isolated 280 mg (54%) of **22** and 70 mg (14%) of **23**. Planimetric analysis of several MPLC traces revealed the product ratio to be 80:20.

For **22**: colorless solid, mp 125–126 °C (from hexane–ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 7.89–7.82 (m, 2 H), 7.60–7.50 (m, 3 H), 5.81–5.76 (m, 2 H), 3.56–3.47 (m, 2 H), 3.34 (s, 1 H), 3.01 (br s, 1 H), 2.32 (dt, J = 4.6 and 1.2 Hz, 1 H), 1.85 ($^1/_2$AB, J = 9.1 Hz, 1 H), 1.38 ($^1/_2$AB, J = 9.1 Hz, 1 H), 1.18–1.12 (m, 2 H), 1.00–0.95 (m, 1 H); ^{13}C NMR ($CDCl_3$) 158.45, 152.22, 140.30, 133.20, 129.92, 129.15, 128.00, 63.11, 46.65, 43.86, 43.48, 38.61, 37.90, 27.13, 15.54, 15.38, 12.42 ppm; m/e (M^+) calcd 324.1183, obsd 324.1169.

For **23**: semisolid; ^{1}H NMR ($CDCl_3$) δ 7.95–7.90 (m, 2 H), 7.65–7.53 (m, 3 H), 5.95–5.91 (m, 2 H), 3.65–3.60 (m, 2 H), 3.43 (s, 1 H), 3.14 (br s, 1 H), 2.93–2.85 (m, 1 H), 2.19–2.12 (m, 1 H), 1.88 ($^1/_2$AB, J = 8.7 Hz, 1 H), 1.52–1.37 (m, 1 H), 1.30 ($^1/_2$AB, J = 8.7 Hz, 1 H), 0.97–0.84 (m, 3 H), 0.66–0.60 (m, 1 H); ^{13}C NMR ($CDCl_3$) 159.22, 153.15, 140.36, 133.41, 130.35, 129.31, 128.28, 65.13, 47.52, 46.16, 44.41, 39.38, 38.94, 29.81, 20.90, 20.13, 20.02 ppm; m/e (M^+) calcd 324.1183, obsd 324.1169.

Epoxidation of 22, Reaction of **22** (50 mg, 0.15 mmol) with 1 equiv of MCPBA in dichloromethane (20 mL) in the usual manner (room temperature, 1 h) followed by spinning plate chromatography on silica gel (elution with 12% ethyl acetate in petroleum ether) afforded 45 mg (88%) of **24** as a colorless solid: mp 169–170 °C (from ether); ^{1}H NMR ($CDCl_3$) δ 7.87–7.82 (m, 2 H), 7.65–7.51 (m, 3 H), 5.82–5.77 (m, 2 H), 3.20–3.09 (m, 2 H), 3.03–2.99 (m, 1 H), 2.83 (s, 1 H), 2.53 (br s, 1 H), 1.99–1.90 (m, 1 H), 1.66–1.55 (m, 2 H), 1.44–1.39 (m, 1 H), 0.98–0.90 (m, 2 H), 0.17 to −0.04 (m, 2 H); ^{13}C NMR ($CDCl_3$) 139.54, 133.63, 129.53, 129.37, 128.60, 128.22, 64.25, 62.94, 62.72, 42.82, 39.87, 34.46, 34.24, 31.72, 28.17, 7.61, 3.73 ppm; m/e (M^+) calcd 340.1133, obsd 340.1106.

Epoxidation of 23, Comparable treatment of **23** (70 mg, 0.22 mmol) with 1 equiv of MCPBA in dichloromethane (30 mL) led to the isolation of 65 mg (87%) of **25** as a colorless solid: mp 164–165 °C (from ether); ^{1}H NMR ($CDCl_3$) δ 7.94–7.89 (m, 2 H), 7.69–7.56 (m, 3 H), 5.43–5.39 (m, 2 H), 3.95–3.94 (m, 1 H), 3.33–3.24 (m, 2 H), 3.07 (s, 1 H), 2.82 (br s, 1 H), 2.26–2.18 (m, 2 H), 1.75 ($^1/_2$AB, J = 9.7 Hz, 1 H), 1.53 ($^1/_2$AB, J = 9.7 Hz, 1 H), 1.24–1.20 (m, 1 H), 1.05–1.01 (m, 1 H), 0.46–0.42 (m, 1 H), 0.36–0.28 (m, 1 H); ^{13}C NMR ($CDCl_3$) 139.50, 133.74, 129.53, 128.23, 123.96 (2 C), 63.93, 58.58, 57.27, 44.33, 41.24, 35.77 (2 C), 33.53, 30.63, 13.30, 11.99, 10.13 ppm; m/e (M^+) calcd 340.1133, obsd 340.1106.

Catalytic Hydrogenation of 25, A solution of **25** (65 mg, 0.19 mmol) in methanol (20 mL) containing 0.1 mol equiv of tris(triphenylphosphine)rhodium(I) chloride was hydrogenated at atmospheric pressure

for 3 h. The solvent was evaporated, and the residue was purified by spinning plate chromatography on silica gel. There was obtained 55 mg (85%) of **26**: colorless solid, mp 155–156 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 7.90–7.87 (m, 2 H), 7.69–7.55 (m, 3 H), 3.85 (dt, J = 6.8 and 1.6 Hz, 1 H), 3.00 (s, 1 H), 2.77 (br s, 1 H), 2.54 (br s, 1 H), 2.46 (br s, 1 H), 2.22–2.11 (m, 2 H), 1.57 ($^1/_2$AB, J = 9.0 Hz, 1 H), 1.43 ($^1/_2$AB, J = 9.0 Hz, 1 H), 1.38 ($^1/_2A_2B_2$, J = 7.6 Hz, 2 H), 1.23–1.19 (m, 1 H), 1.04 ($^1/_2A_2B_2$, J = 7.6 Hz, 2 H), 0.90–0.86 (m, 1 H), 0.62–0.54 (m, 1 H); ^{13}C NMR ($CDCl_3$) 139.48, 133.69, 129.48, 128.28, 63.49, 63.16, 61.52, 44.68, 41.62, 30.41, 29.75 (3C), 25.11, 24.83, 19.70, 18.77, 10.18 ppm; m/e (M^+) calcd 342.1290, obsd 342.1319.

Anal. Calcd for $C_{20}H_{22}O_3S$: C, 70.15; H, 6.48. Found: C, 70.16; H, 6.63.

Reaction of 11 with *N*-Phenylmaleimide. A solution of **11** (120 mg, 0.77 mmol) and *N*-phenylmaleimide (133 mg, 0.77 mmol) in chloroform (15 mL) was stirred at room temperature for 3 days. The solvent was evaporated, and the residue was purified by spinning plate chromatography (silica gel, elution with 10% ethyl acetate in petroleum ether) to give 130 mg (51%) of **27** and 25 mg (10%) of **28**. ^{1}H NMR analysis of the unpurified reaction mixture indicated the ratio to be 80:20.

For **27**: colorless solid, mp 199–200 °C (from ether); ^{1}H NMR ($CDCl_3$) δ 7.45–7.36 (m, 3 H), 7.25–7.21 (m, 2 H), 5.91–5.88 (m, 2 H), 3.68 (br s, 2 H), 3.45 (s, 2 H), 2.43 (s, 2 H), 1.56–1.47 (m, 2 H), 1.25–1.20 (m, 2 H), 0.50–0.45 (m, 2 H), ^{13}C NMR ($CDCl_3$) 177.21, 156.16, 131.99, 130.02, 129.15, 128.55, 126.42, 48.07, 46.98 40.74, 38.67, 15.38, 12.26 ppm; m/e (M^+) calcd 329.1416, obsd 329.1419.

Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81. Found: C, 80.07; H, 5.96.

For **28**: colorless solid, mp 199–200 °C (from ether); ^{1}H NMR ($CDCl_3$) δ 7.51–7.39 (m, 3 H), 7.28–7.24 (m, 2 H), 6.02–5.98 (m, 2 H), 3.79 (br s, 2 H), 3.57 (s, 2 H), 2.92 (s, 2 H), 1.50 (s, 2 H), 1.10–1.06 (m, 2 H), 0.99–0.95 (m, 1 H), 0.75–0.69 (m, 1 H); ^{13}C NMR ($CDCl_3$) 176.99, 156.65, 131.95, 130.30, 129.26, 128.71, 126.47, 49.05, 48.73, 42.88, 42.88, 39.43, 20.58 (2 C) ppm; m/e (M^+) 329.1416, obsd 329.1440.

Catalytic Hydrogenation of 28. A solution of **28** (25 mg, 0.08 mmol) of methanol (20 mL) containing 10% palladium on charcoal (10 mg) was hydrogenated overnight at atmospheric pressure. The reaction mixture was filtered through Celite and evaporated to give 25 mg (99%) of **29** as a colorless solid: mp 223–224 °C (from ether); ^{1}H NMR ($CDCl_3$) δ 7.47–7.37 (m, 3 H), 7.27–7.22 (m, 2 H), 3.69 (s, 2 H), 2.97 (br s, 2 H), 2.24 (br s, 2 H), 2.04 (s, 2 H), 1.51 (A_2B_2, J = 7.8 Hz, 2 H), 1.44 (s, 2 H), 1.20–1.15 (m, 4 H), 0.65–0.57 (m, 1 H), 0.35–0.16 (m, 1 H); ^{13}C NMR ($CDCl_3$) 179.28, 132.32, 129.20, 128.60, 126.47, 45.88, 45.77, 44.13, 36.53, 28.11, 27.51, 12.59, 4.33 ppm; m/e (M^+) calcd 333.1729, obsd 333.1692.

Reaction of 11 with Dimethyl Acetylenedicarboxylate. A solution of **11** (170 mg, 1.09 mmol) and DMAD (155 mg, 1.09 mmol) in chloroform (30 mL) was stirred at room temperature for 4 h, at which point TLC analysis indicated the cycloaddition to be complete. The solvent was removed, and the oily residue was purified by spinning plate chromatography (silica gel, elution with 10% ethyl acetate in petroleum ether) under a nitrogen atmosphere. Since no isomer separation could be achieved, the mixture was redissolved in dichloromethane and treated with MCPBA in the usual manner. After 10 min at room temperature, epoxidation was complete. The customary chromatographic workup furnished 40 mg (12%) of **32** and 210 mg (61%) of **33**.

For **32**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 5.74–5.72 (m, 2 H), 3.78 (s, 6 H), 3.34 (s, 2 H), 3.26–3.23 (m, 2 H), 1.93 ($^1/_2$AB, J = 8.5 Hz, 1 H), 1.43 ($^1/_2$AB, J = 8.5 Hz, 1 H), 1.03–0.98 (m, 2 H), 0.17–0.14 (m, 1 H), 0.01 to –0.23 (m, 1 H); ^{13}C NMR ($CDCl_3$) 164.78, 149.97, 131.03, 71.61, 51.99, 50.49, 46.36, 35.88, 8.16, 4.18 ppm; m/e (M^+) calcd 314.1154, obsd 314.1115.

For **33**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 5.53–5.46 (m, 2 H), 3.80 (s, 6 H), 3.46 (s, 2 H), 3.25–3.24 (m, 2 H), 2.19 ($^1/_2$AB, J = 8.1 Hz, 1 H), 1.76 ($^1/_2$AB, J = 8.1 Hz, 1 H), 0.86–0.76 (m, 2 H), 0.65–0.54 (m, 2 H); ^{13}C NMR ($CDCl_3$) 165.07, 149.05, 124.72, 65.73, 52.94, 52.17, 49.77, 35.93, 15.60, 12.70 ppm; m/e (M^+) calcd 314.1154, obsd 314.1115.

Photocyclization of 32. An acetone-d_6 solution (2 mL) of **32** (20 mg, 0.06 mmol) was irradiated with a long-wavelength TLC lamp for 3 h, at which point the ^{1}H NMR spectrum indicated reaction to be complete. Only the formation of **34** was observed: ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 6 H), 2.74–2.72 (m, 2 H), 2.57 (br s, 2 H), 2.55 (br s, 2 H), 1.75 ($^1/_2$AB, J = 11.9 Hz, 1 H), 1.57 ($^1/_2$AB, J = 11.9 Hz, 1 H), 0.89–0.83 (m, 2 H), 0.42–0.40 (m, 1 H), 0.18–0.13 (m, 1 H); ^{13}C NMR ($CDCl_3$) 171.77, 60.01 (2 C), 51.95, 43.60, 37.38, 32.14, 28.84, 5.39 (2 C) ppm; m/e (M^+) calcd 314.1154, obsd 314.1136.

Catalytic Hydrogenation of 33. A methanolic solution (20 mL) of **33** (80 mg, 0.25 mmol) and tris(triphenylphosphine)rhodium chloride (12 mg) was hydrogenated at atmospheric pressure for 15 h. The solvent was evaporated, and the residue was purified by preparative TLC on silica gel (elution with 10% ethyl acetate in petroleum ether). There was isolated 70 mg (87%) of **35** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 6 H), 3.48 (s, 2 H), 2.58 (br s, 2 H), 1.92 ($^1/_2$AB, J = 8.4 Hz, 1 H), 1.62 ($^1/_2$AB, J = 8.4 Hz, 1 H), 1.46 ($^1/_2A_2B_2$, J = 7.7 Hz, 2 H), 1.14 ($^1/_2A_2B_2$, J = 7.7 Hz, 2 H), 1.05 (br s, 1 H), 0.82 (br s, 3 H); ^{13}C NMR ($CDCl_3$) 165.07, 149.27, 69.28, 52.17, 50.86, 49.44, 30.30, 24.18, 18.60, 15.27 ppm; m/e (M^+) calcd 316.1311, obsd 316.1281.

Reaction of 11 with *N*-Methyltriazolinedione. To a cold (–78 °C) ethyl acetate solution (10 mL) of **11** (70 mg, 0.45 mmol) was added 51 mg (0.45 mmol) of *N*-methyltriazolinedione in the same solvent (5 mL). Cycloaddition was complete in 5 min, whereupon the solvent was evaporated to leave a single adduct (^{13}C NMR analysis). Recrystallization from ether gave 100 mg (83%) of **36** as a colorless solid: mp 130 °C dec; ^{1}H NMR ($CDCl_3$) δ 5.84–5.81 (m, 2 H), 5.12 (s, 2 H), 3.78–3.74 (br s, 2 H), 2.70 (s, 3 H), 2.13 ($^1/_2$AB, J = 8.6 Hz, 1 H), 1.90 ($^1/_2$AB, J = 8.6 Hz, 1 H), 1.24–1.20 (m, 2 H), 0.59–0.51 (m, 2 H); ^{13}C NMR, see Table I; m/e (M^+) calcd 271.1321, obsd 271.1303.

Reaction of 10 wtih Phenyl Vinyl Sulfone. A solution of **10** (100 mg, 0.63 mmol) and phenyl vinyl sulfone (106 mg, 0.63 mmol) in dichloromethane was stirred at the reflux temperature for 9 days. The solvent was evaporated, and the oily residue was subjected to MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether). In addition to 17 mg (17%) of recovered **10**, there was obtained 135 mg (66%) of an inseparable mixture of **39** and **40** as a light brown oil (ratio 40:60, ^{1}H NMR analysis prior to chromatogaphy); m/e (M^+) calcd 326.1340, obsd 326.1348.

Epoxidation of the 39/40 Mixture. Oxidation of the preceding mixture (200 mg, 0.01 mol) with *m*-chloroperbenzoic acid (127 mg, 0.74 mmol) in dichloromethane (40 mL) as previously described (room temperature, 1 h) led after spinning plate chromatography (silica gel, elution with 15% ethyl acetate in petroleum ether) to a mixture of **41** and **26** (ratio 40:60): 185 mg (87%); colorless solid, mp 133–136 °C (from ether). The spectra of **41** were obtained by appropriate subtraction techniques: ^{1}H NMR ($CDCl_3$) δ 3.65 (dt, J = 6.9 and 1.9 Hz, 1 H), 3.04 (s, 1 H), 2.76 (br s, 1 H), 2.51 (br s, 1 H), 2.46 (br s, 1 H), 2.19–2.06 (m, 2 H); ^{13}C NMR ($CDCl_3$) 139.48, 133.69, 129.48, 128.28, 63.49, 63.16, 61.52, 44.68, 41.62, 30.41, 29.75 (3 C), 25.11, 24.83, 19.70, 18.77, 10.18 ppm; m/e (M^+) calcd 342.1289, obsd 342.1282.

Reaction of 10 with *N*-Phenylmaleimide. A solution of **10** (100 mg, 0.63 mmol) and *N*-phenylmaleimide (109 mg, 0.63 mmol) in chloroform (15 mL) was stirred at room temperature for 4 days, at which point TLC analysis showed the cycloaddition to be complete. The solvent was evaporated, and the solid residue (one spot on TLC) was purified by recrystallization from ether to give 150 mg (72%) of colorless crystals, mp 185–186 °C, as a mixture of **42** and **43**. ^{1}H NMR analysis prior to purification indicated their ratio to be 40:60. In particular, **42** was characterized by three absorptions (in $CDCl_3$) at δ 3.48, 2.95, and 2.72, whereas the same signals for **43** appeared at δ 3.48, 2.90, and 2.85; m/e (M^+) calcd 331.1556, obsd 331.1596.

Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39. Found: C, 79.61; H, 6.47.

Hydrogenation of the 42/43 Mixture. A methanol solution (30 mL) of the preceding mixture (50 mg, 0.15 mmol) containing 10% palladium on charcoal was hydrogenated at atmospheric pressure for 4 h. After filtration through Celite, the filtrate was evaporated and the solid residue was purified by spinning plate chromatography (silica gel, elution with 10% ethyl acetate in petroleum ether). A mixture of **44** and **29** (35 mg, 70%) was obtained as a colorless solid, mp 185–207 °C (from ether). For **44** (obtained by subtraction): ^{13}C NMR ($CDCl_3$) 179.12, 132.32, 129.20, 128.60, 126.47, 44.95 (2 C), 43.31, 37.63, 27.84, 20.24, 18.99, 5.65 ppm; m/e (M^+) calcd 333.1729, obsd 333.1670.

Reaction of 10 with Dimethyl Acetylenedicarboxylate. A solution of **10** (130 mg, 0.82 mmol) and DMAD (129 mg, 0.91 mmol) in chloroform (15 mL) was stirred at room temperature for 4 h (TLC analysis indicated completion of reaction). The solvent was evaporated, and the residue was purified by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). There was isolated 240 mg (98%) of a mixture of **45** and **46** in a ratio of 57:43 (^{1}H NMR analysis); m/e (M^+) calcd 300.1361, obsd 300.1330. This mixture was directly epoxidized.

Epoxidation of the 45/46 Mixture. Epoxidation of the predescribed mixture (240 mg, 0.80 mmol) in dichloromethane (25 mL) as before followed by MPLC purification on silica gel (elution with 10% ethyl acetate in petroleum ether) gave 210 mg (83%) of a mixture of **47** and **35** (ratio 59:41). The spectral data for **47** were obtained by appropriate subtractive measures: ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 6 H), 3.41 (s, 2 H), 2.52 (br s, 2 H), 2.08 ($^1/_2$AB, J = 8.2 Hz, 1 H), 1.72 ($^1/_2$AB, J = 8.2 Hz, 1 H), 1.14–0.81 (m, 4 H), 0.64–0.61 (m, 2 H), 0.47–0.44 (m, 2 H); ^{13}C NMR ($CDCl_3$) 165.06, 149.54, 63.32, 51.95, 50.09 (2C), 28.94,

21.06, 14.61, 5.48 ppm; *m/e* (M^+) calcd 316.1311, obsd 316.1291.

Reaction of 10 with *N*-Methyltriazolinedione. To a stirred solution of **10** (100 mg, 0.63 mmol) in ethyl acetate (25 mL) cooled to -78 °C was added a solution of *N*-methyltriazolinedione (72 mg, 0.64 mmol) in the same solvent (5 mL). Decoloration occurred immediately to give a solid residue which was indicated by ^{13}C NMR to be a mixture of **48** and **49** (85:15 ratio): ^1H NMR ($CDCl_3$) δ 5.13 (s, 3 H), 2.91 (br s, 2 H), 2.76 (s, 3 H), 2.24 ($^1/_2$AB, J = 8.5 Hz, 1 H), 1.88 ($^1/_2$AB, J = 8.5 Hz), 1.50 ($^1/_2A_2B_2$, J = 7.6 Hz, 2 H), 1.20-1.13 (m, 1 H), 0.99 ($^1/_2A_2B_2$, J = 7.6 Hz, 2 H), 0.80-0.67 (m, 3 H). The ^{13}C NMR data for **48** and **49** are given in Table I; *m/e* (M^+) calcd 271.1321, obsd 271.1303.

Acknowledgment is made to the National Cancer Institute (Grant CA-12115) for the financial support of this research, FT-NMR (300 MHz) spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Grant CHE-7910019).

Registry No. **2**, 73321-24-1; **10**, 93304-29-1; **11**, 93304-30-4; **13a**, 36439-90-4; **13b**, 36439-89-1; **14a** (isomer 1), 93304-31-5; **14a** (isomer 2), 93381-81-8; **14b** (isomer 1), 93304-32-6; **14b** (isomer 2), 93381-82-9; **15**, 73321-39-8; **16**, 93304-33-7; **17**, 93304-34-8; **18**, 73347-30-5; **19**, 93381-83-0; **20a**, 93304-35-9; **20b**, 93304-36-0; **21a**, 93381-84-1; **21b**, 93381-85-2; **22**, 93304-37-1; **23**, 93381-86-3; **24**, 93304-38-2; **25**, 93381-87-4; **26**, 93304-39-3; **27**, 93304-40-6; **28**, 93381-88-5; **29**, 93304-41-7; **30**, 93304-42-8; **31**, 93381-89-6; **32**, 93304-43-9; **33**, 93381-90-9; **34**, 93349-06-5; **35**, 93304-44-0; **36**, 93304-45-1; **37**, 74987-28-3; **38**, 74998-57-5; **39**, 93304-46-2; **40**, 93381-91-0; **41**, 93381-92-1; **42**, 93304-47-3; **43**, 93381-93-2; **44**, 93304-41-7; **45**, 93304-48-4; **46**, 93381-94-3; **47**, 93381-95-4; **48**, 93304-49-5; **49**, 93381-96-5; phenyl(tribromomethyl)mercury, 3294-60-8; dimethyl acetylenedicarboxylate, 762-42-5; maleic anhydride, 108-31-6; *N*-phenylmaleimide, 941-69-5; phenyl(vinyl)sulfone, 5535-48-8.

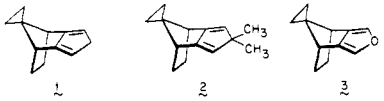
Electronic Control of Stereoselectivity. 27. The Effect of Apical Spirocyclopropane Substitution on the Stereochemical Course of Diels-Alder Cycloadditions to Norbornyl-Fused Diene Systems[1a]

Leo A. Paquette,*† Kenneth E. Green, Rolf Gleiter,*[1b] Wolfgang Schäfer,[1b] and Judith C. Gallucci[1c]

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210, and the Institut für Organische Chemie der Universität Heidelberg, D-6900 Heidelberg, West Germany. *Received May 24, 1984*

Abstract: The three new 7-spirocyclopropyl-substituted isodicyclopentadiene analogues **1-3** were prepared, and their stereoselective behavior toward various dienophiles was evaluated. Whereas the unadorned diene **1** exhibits no strong predilection for above-plane or below-plane [4 + 2] cycloaddition, the furan analogue **3** enters into Diels-Alder reaction totally by top-face bonding. This contrasting behavior is analyzed from the theoretical vantage point and attributed to the existence of strong σ/π interaction and its effect on the subjacent orbital (π_1). In the case of the parent hydrocarbon (**36**), strong disrotatory tilting of the terminal pπ orbitals of the diene unit toward the methano bridge is encountered and below-plane addition is kinetically favored in most instances. Where **1** is concerned, the spirocyclopropane function at C-7 reduces the size of the p_y coefficient at these centers. The observable effect is greatly reduced π-face stereoselectivity. The heterocyclic ring in furan **3** induces disrotatory motion in a direction opposite to that of **36** and gives rise to opposite stereochemical phenomena. The behavior of sterically congested **2** is believed to be controlled instead by intermolecular steric interactions. The X-ray crystal structure of adduct **32** indicates the molecule to be downwardly pyramidalized at its double bond by an astounding 21.8°.

In the preceding paper, it was shown that incorporation of a cyclopropane ring along one of its edge bonds into a bicyclic fused cyclopentadiene as in tetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodeca-2,5,11-triene and -2,5-diene does not lead to pronounced stereocontrol of Diels-Alder cycloadditions by the three-membered ring.[1] Presently, attention is turned to the triad of molecules **1-3** which share in common a 7-spirocyclopropylnorbornane part structure. The impetus for this study arose from two directions.



1 2 3

The first originates from photoelectron (PE) spectroscopic measurements which reveal that considerable through-space interaction operates between the e_A Walsh orbital in **4** and the antisymmetric π-linear combination of the two double bonds.[2a] Although this phenomenon is expectedly attenuated in **5**[3] and **6**,[4] the effects continue to persist at a reasonable level. Our theoretical model for π-face differentiation in isodicyclopentadiene and its analogues rests heavily, however, on the existence of long-range electronic interaction through the σ bond network.[5] On this basis, through-space options[6] were expected to have little

4 5 6

† The Ohio State University.

(1) (a) Part 26: Charumilind, P.; Paquette, L. A. *J. Am. Chem. Soc.*, preceding paper in this issue. (b) Universität Heidelberg. (c) Individual to whom queries regarding the X-ray crystal structure analysis should be directed at The Ohio State University.

(2) (a) Brogli, F.; Heilbronner, E.; Ipaktschi, J. *Helv. Chim. Acta* **1972**, *55*, 2447. (b) Heilbronner, E.; Martin, H.-D. *Ibid.* **1972**, *55*, 1490.

(3) Bischof, P.; Böhm, M.; Gleiter, R.; Snow, R. A.; Doecke, C. W.; Paquette, L. A. *J. Org. Chem.* **1978**, *43*, 2387.

(4) Dougherty, D.; Blankespoor, R. L.; McGlynn, S. P. *J. Electron Spectrosc. Relat. Phenom.* **1979**, *16*, 245.

(5) (a) Paquette, L. A. In "Stereochemistry and Reactivity of Pi Systems"; Watson, W. H., Ed., Verlag Chemie: Weinheim/Bergstr., Germany **1983**, pp 41-73. (b) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328. (c) See Also: Ginsburg, D. *Tetrahedron* **1983**, *39*, 2095.

0002-7863/84/1506-8232$01.50/0