to dipole–dipole interactions, primarily on the basis of the Fourier coefficients and the data shown in Tables XIII and XIV. Further computations, particularly on the esters of the title compounds, are clearly required to resolve the relative importance of dipole–dipole and hydrogen bond interactions with more certainty.

Torsional and Steric Control of Stereoselectivity in Isodicyclopentadiene Cycloadditions

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Abstract: An MM2 model to calculate the relative energies of stereoisomeric transition states of Diels–Alder reactions of isodicyclopentadiene and substituted derivatives has been developed. The model is based upon ab initio and constrained-synchronous MNDO transition-state calculations on unsubstituted systems. Trends in observed stereoselectivities as a function of diene and dienophile substituents are reproduced. The success of this model supports the hypothesis that torsional factors influence the stereoselectivities of the reactions of the parent system, while this torsional preference for attack on the bottom face of isodicyclopentadiene can be overridden by steric effects involving substituents on either the dienophile or the isodicyclopentadiene.

Isodicyclopentadiene (**1a**) undergoes Diels–Alder cycloadditions with a variety of dienophiles from the *bottom* face.[1-5] This stereoselectivity contrasts with that observed for additions and cycloadditions to norbornene, which occur from the *top* (exo) face.[6-10] What property of the norbornene skeleton causes attack on the *bottom* of an exocyclic double bond of **1a** and on the *top* of the endocyclic double bond of norbornene? In this paper, we develop a consistent hypothesis to explain these phenomena and the variations in stereoselectivity which are observed upon substitution of isodicyclopentadiene or upon alterations of the dienophile. Our explanation is based upon torsional and steric effects and permits predictions of stereoselectivities for as yet unstudied cases. A computational model is also developed to provide semi-quantitative predictions of stereoisomer ratios in reactions of substituted species.

There is general accord that the stereoselectivities of the reactions of norbornene are a result of the asymmetric arrangement of the allylic CH and CC bonds. This asymmetric arrangement is enforced by the rigid norbornene skeleton. However, the specific mechanism by which this asymmetric arrangement directs attack is controversial. Brown proposed that the exo attack by a variety of reagents is a result of steric effects,[6] since the enthano bridge is larger than the methano bridge. In partial accord with this proposal, reactions of norbornadiene are less selective than those of norbornene, but additions and cycloadditions still occur preferentially from an exo face of a double bond.[10] Schleyer proposed that torsional strain between the C_1H and C_2H bonds, and between the C_3H and C_4H bonds, is relieved upon exo attack but increases upon endo attack.[11] Tee et al. noted that less nuclear motion is involved in the formation of the exo product, so that exo attack is in accord with the principle of least nuclear motion.[12] Fukui

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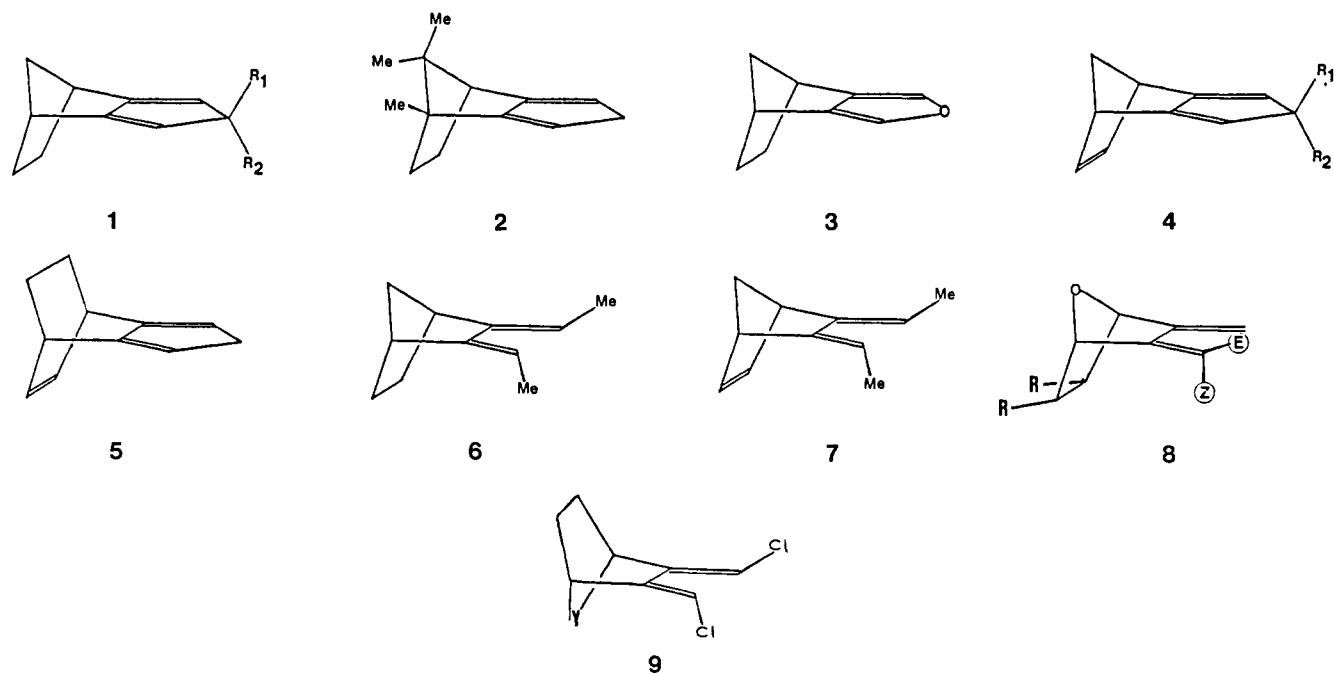
Figure 1. Isodicyclopentadiene and analogues for which Diels–Alder reactions have been reported. See Table I for substituents on **1, 4, 8** and **9**.

proposed that the π electron density on the exo face of norbornene is greater than that on the endo face, due to mixing of σ and π orbitals; exo attack by electrophiles is proposed to occur due to this nonequivalent orbital extension,[13] known elsewhere as orbital distortion.[14] We[10] and Morokuma and Wipff[15] pointed out the relationship between alkene pyramidazation and stereoselectivity, and Gleiter and Spanget-Larsen later proposed that this distortion is the sole reason for exo attack.[16] More recently, we have developed the hypothesis that torsional effects involving all the bonds to C_2 (or C_3) and those at C1 (or C4) cause both the endo pyramidization of norbornene and the exo attack of various reagents on norbornene.[10] This argument properly focusses upon the transition states of reactions, rather than the isolated reactants, to explain rate phenomena. This explanation incorporates Schleyer's previous hypothesis about the origin of exo attack but is based primarily upon the finding that torsional effects involving partially formed bonds are as large as those involving fully formed bonds.[10,17-19]

There are fewer explanations for stereoselectivity in cyclo-additions of isodicyclopentadiene and related species. Gleiter and Paquette proposed a unique explanation:[3a,k] the norbornane skeleton causes mixing of σ and π orbitals of the diene, such that the lowest energy π orbital (ψ_1) of the diene tilts its terminal π orbitals inward on top and outward on the bottom. A dienophile then approaches from the bottom to avoid closed-shell repulsion between the dienophile π_s HOMO and the tilted ψ_1 orbital of the diene. These two orbitals overlap more upon top attack. Although the effects of substituents on isodicyclopentadiene upon stereo-selectivities could be explained by these arguments, variations in stereoselectivity with different dienophiles could not be explained.[3i] We propose an alternative explanation later but note that π orbital

tilting is well-known in norbornene and *syn*-sesquinorbornene:[20] the two p orbitals making up the π bond are tilted outward on the exo face of the molecule. If this tilting controlled the ste-reoselectivity of additions to norbornene, it might cause norbornene to react on the endo face with dienes such as cyclopentadiene, in contrast to experience.

Vogel first proposed that the stereoselectivity of cycloadditions of various dienes listed in Figure 1 is determined by product stabilities. That is, the factors that cause *syn*-sesquinorbornene (the product of bottom attack of ethylene on isodicyclopentadiene) to be more stable[20] than anti (the product of top attack) should also operate in the transition states for these cycloadditions.[5a] Latter, Vogel found cases of cycloadditions to substituted 7-oxa-2,3-dimethylenenorbornanes which could not be explained by the thermodynamic stabilities of the products. Consequently, he proposed that the preference for top attack in these cases is due to polarizability.[5c] Our torsional explanation, described in more detail later, is indeed related to the greater stability of *syn*-sesquinorbornene, but it is a transition-state effect which can also explain the preference for bottom attack in reactions of dimethylenenorbornene and analogues.[31]

Some time ago, we suggested that the upward pyramidalization of the exocyclic methylene calculated for methylenenorbornene might be related to the preference for bottom attack.[10a] However, this bending is exceedingly small, and this ground-state effect may not necessarily be manifested in transition states.

Details about the diverse points of view described above are given in the recently published proceedings of a symposium on the subject.[19] We now offer a general hypothesis to explain the stereoselectivities of isodicyclopentadiene reactions, tested by calculations and found to rationalize both substituent and dien-ophile variations.

Stereoselectivities of the Diels–Alder Reactions of Isodicyclopentadiene and Analogues

In 1956, Alder et al. reported that the product of the reaction of isodicyclopentadiene with maleic anhydride was the result of top attack.[1] In 1967, Kobuke et al. reported the Diels–Alder reactions of isodicyclopentadiene with methyl acrylate and methyl propiolate. The products were the result of bottom attack.[2] More recently, many additional examples have been investigated.

In 1980, Paquette et al. reinvestigated the reaction of maleic anhydride with isodicyclopentadiene (**1a**). Only the *syn*-sesqui-

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norbornene derivative, resulting from bottom attack, was initially found.[3a] Later, Paquette reported an isomer ratio of 25:75 for the top:bottom attack.[3j] This same reaction was also investigated under a variety of reaction conditions by Bartlett et al.[4a] The stereoselectivity changes in different solvents and ratios of 45:55 to 65:35 (top:bottom) were reported. As shown in Table I, all dienophiles prefer bottom attack on **1a**, except triazolinediones and tetracyanoethylene (TCNE).

Many other related Diels–Alder reactions have been investigated. Figure 1 lists the isodicyclopentadienes and analogues for which Diels–Alder stereoselectivities have been studied, and Table I summarizes the reported stereoisomer ratios.

The cycloaddition of (2-norbornene)[*c*]furan (**3**), an oxa-analogue of isodicyclopentadiene, with maleic anhydride in $CDCl_3$ over a large range of temperatures (−60 to 150 °C) gave only one isomer resulting from bottom attack.[5a] The oxadimethylene compounds, **8a**, **8b**, and **8c**, reacted with TCNE and *N*-phenyltriazoline to give preferentially the adduct resulting from top attack.[5c]

Paquette has studied the cycloadditions of **1a** and substituted derivatives with a variety of dienophiles.[3a,b] These studies revealed alterations in the π-facial selectivities as substituents at the methylene unit of cyclopentadiene moiety were altered. The selectivity was also found to be a function of the particular dienophile. These patterns are shown in Table I. Reactions involving the unsubstituted, **1a**, or spirocyclopropane derivative, **1d**, prefer bottom attack with most of the dienophiles, while the dimethyl or spirocyclopentane derivatives, **1c** and **1e**, undergo top attack with all dienophiles except dimethyl acetylenedicarboxylate (DMAD).[3i,j] Paquette and Gleiter explained this in terms of tilting of the ψ_1 orbitals of these molecules. That is, calculations indicated that the orbital tilting changes direction according to the substituent at the methylene unit, thereby altering the face which has the minimum repulsion between ψ_1 of the diene and the HOMO of the alkene. Calculations showed that the orbital tilting for **1a** and **1d** was opposite to that of **1c** and **1e**.[3i-k] However, orbital tilting does not explain the difference in selectivity found for DMAD.

Paquette and Gleiter also argued that the selectivity could not be governed by the stability of the isomeric adducts. The reactions of **1c**, **1d**, and **1e** would be expected to have comparable product profiles, due to the fact that each is substituted by alkyl groups, suggesting that the isomeric products of these reactions should have similar relative energies.[3j] Paquette and Gleiter also suggest that steric interactions are not the major controlling factor in these reactions. They argued that if steric interactions between a methyl of **1c** and the norbornene methylene bridge caused **1c** to undergo top attack, then the reaction of 1,7,7-trimethylisodicyclopentadiene (**2**) should also give top attack. These (apparently non-operative) steric interactions between methyl hydrogens and a hydrogen on the methylene bridge are shown in Figure 2.[3j]

Isodicyclopentatriene (**4a**) and derivatives, **4b–f**, show similar stereoselectivity patterns to those found for the diene derivative but an increased propensity for bottom attack.[3a,b,d,e] As described later, this is most probably due to decreased steric hindrance to attack from the bottom face of the diene when the ethano bridge is replaced by an etheno bridge. Compound **5** gives top attack with MTAD but a bottom preference with acetylenic dienophiles.[3a,b,e] The dimethylene compounds, **6** and **7**, usually favor bottom attack.[3l] The exclusive preference for top attack to **8a**, **8b**, and **8c** arises because only TCNE has been studied.[5c] This dienophile also adds on top in **1a**.[4c] The uniqueness of TCNE may also explain the bottom selectivity in reactions of **9a–d** but the top attack in **9e,f**.[5b]

Results and Discussion

Transition Structures for Diels–Alder Reactions. Our hypothesis about the origin of stereoselectivity in isodicyclopentadiene cycloadditions began with our computational study of the parent Diels–Alder reaction of butadiene with ethylene.[20] Figure 3 shows a top view of the C_s STO-3G ab initio transition structure, which has been show to be an authentic transition structure with one

imaginary vibrational frequency. The detailed geometry, given in Table II, is discussed elsewhere.[20] Of particular note for the isodicyclopentadiene stereoselectivity issue is the 14.9° out-of-plane bending of the hydrogens at C2 and C3. As we have described earlier,[20] this out-of-plane bending of the hydrogens at C2 and C3 arises as a direct consequence of the earliness of this transition state, so that there is substantial double bond character in the C1–C2 and C3–C4 bonds. C1 and C4 pyramidalize and rotate inward to achieve overlap of the p orbitals on these carbons with the ethylene termini. To maintain the π-bonding between C1 and C2 and between C3 and C4, the p orbitals at C2 and C3 rotate inward on the side of the diene nearest the dienophile. This is necessarily accompanied by C2 and C3 hydrogen movement toward the attacking dienophile. Our hypothesis is that when norbornene is fused at C2 and C3 of butadiene, then the tendency of endo bending of norbornenes[18] will be manifested in a preference for bottom attack in Diels–Alder reactions.

The isodicyclopentadiene system is too large to study at the ab initio level. Therefore, we have investigated semiempirical alternatives. Although MNDO calculations[21] predict a stepwise mechanism for the butadiene–ethylene reaction,[22] we have found that if synchronicity is forced, the resulting MNDO energy maximum with respect to the forming bond 1–6 and 4–5 bond lengths is very similar to the transition structure obtained by ab initio STO-3G calculations. The geometrical parameters obtained for these two structures are compared in Table II. The similarities between the two C_s geometries are quite remarkable. The bond lengths of the butadiene moiety are nearly identical, and only a slight difference in the ethylene bond length is found. Both structures are more reactant-like than product-like, in accord with the exothermicity of the reaction. The only appreciable differences between the two transition structures are the forming CC distances and the calculated activation energies.

MNDO Forced-Synchronous Transition Structures for Isodicyclopentadiene Reactions. Approximate transition structures were obtained for top and bottom attack of ethylene on isodicyclopentadiene. The geometries were located by MNDO reaction coordinate calculations and were constrained to be synchronous by enforcing C_s symmetry. The top and bottom transition structures are shown in Figure 4. The side view shown illustrates the bending which takes place at the fusion of the cyclopentadiene and norbornene moieties. The bending is 4.2° upward and 2.8° downward for top and bottom attack, respectively. The terminal carbons of the diene and ethylene are significantly pyramidalized. This pyramidalization and the nonparallel planes approach of the ethylene to the diene are similar to those found for the ab initio and MNDO butadiene–ethylene transition structures.

The isomeric transition structures differ in energy by 0.3 kcal/mol, with MNDO favoring the top attack. We believe that this failure of MNDO to predict the observed preference for bottom attack is related to the MNDO underestimation of torsional effects. This may also be the reason for the greater bending in the transition state for top attack in the MNDO calculations, whereas the hypothesis developed here would lead to the prediction that downward bending upon bottom attack should be larger than upward bending upon top attack (see later). As a consequence, MNDO predicts that the double bond of *syn*-sesquinorbornene is flat and that the difference in energy between *anti*- and *syn*-sesequinorbornene is 0.3 kcal/mol in favor of *anti*-sesquinorbornene. Experimentally, derivatives of *syn*-sesquinorbornene are bent by 16–18°,[8a] and calculations indicate that this isomer is several kcal/mol more stable than *anti*-sesquinorbornene,[18] which has a planar alkene moiety. Allinger's MM2 force field[23] predicts the geometries of *syn*- and *anti*-sesquinorbornene quite well and

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Table 1. Experimental Top:Bottom Product Ratios for Diels–Alder Reaction of Isodicyclopentadiene and Analogues.[a] Reactions Were Carried Out at 25 °C Unless Otherwise Noted (in Parentheses)

com-pound	substituent R₁	substituent R₂	maleic anhydride	N-phenyl-maleimide	methyl acrylate	benzo-quinone	N-methyl-triazolinedione	phenyl vinyl sulfone	DMAD	methyl propiolate	benzyne	TCNE	N-phenyl-triazolinedione
1a[3a,3b]	H	H	25/75 45/55–65/35[4a]		<3/>97 (42 °C)	<3/>97 (10 °C)	>97/<3 (–78 °C)[b]	<3/>97	<3/>97	<3/>97 (42.°C)	<3/>97 (85 °C)	>97:<3[c]	>97:<3[d]
1b[3j]	H	Me	>97/<3		>97/<3 (42 °C)		93/7 (–78 °C)	>97/<3	30/70				
1c[3j]	Me	Me	>97/<3 (80 °C)	>97/<3 (61 °C)			>97/<3 (–78 °C)		30/70				
1d[3i]	-(CH₂)₂-			<3/>97		<3/>97			<3/>97 (111 °C) <3/>97				
1e[3i]	-(CH₂)₄-		>97/<3	>97/<3	>97/<3 (42 °C)		>97/<3 (–78 °C)	>97/<3 (111 °C)	25/75				
1f[3m]	=C(CH₃)₂		<3/>97	<3/>97					<3/>97	<3/>97 (111 °C)			
2[3j]			<3/>97	<3/>97					<3/>97				
3[5a]			<3/>97						<3/>97				
4a[3a,3b]	H	H	<3/>97		<3/>97 (42 °C)	<3/>97 (40 °C)	<3/>97 (–35 °C)[3e]	<3/>97	<3/>97 (65 °C)	<3/>97 (65 °C)	<3/>97 (85 °C)		
4b[3i]	H	Me	>97/<3 (80 °C)										
4c[3j]	Me	Me		e			56/44 (–78 °C)		<3/>97 (61 °C)				
4d[3l]	-(CH₂)₂-			<3/>97		<3/>97			<3/>97				
4e[3i]	-(CH₂)₄-		66/34				39/61 (–78 °C)		22/78				
4f[3m]	=C(CH₃)₂		<3/>97	<3/>97									
4g[3j]	Me	H	<3/>97 (80 °C)										
5[3a]			20/80[d]	20/80[d]			<3/>97 (78 °C)[3e]		86/14	79/21 (42 °C)	81/19 (85 °C)		
6[3l]				<3/>97		<3/>97	>97/<3 (–78 °C)	<3/>97 (111 °C)	<3/>97				
7[3l]				<3/>97		<3/>97	45/55 (–78 °C)	<3/>97 (111 °C)	6/94				
	E	Z											
8a[5c]	H	Cl, R[f]										85/15 (60 °C)	
8b[5c]	Cl	H, R[f]										80/20 (130 °C)	
8c[5c]	MeO	H, R[f]										>97/<3 (20 °C)	>97/<3 (20 °C)
8d[5c]	MeO	H, R[g]										85/15 (20 °C)	
	Y												
9a[5b]	CH=CH											22/78 (20 °C)	
9b[5b]	CH–CH (exo)											20/80 (20 °C)	
9c[5b]	CH–CH (endo)											40/60 (20 °C)	
9d[5b]	CH₂CH(OH) (exo)											32/68 (20 °C)	
9e[5b]	CH₂CH(OH) (endo)											97/3 (20 °C)	
9f[5b]	CH₂C=O											70/30 (20 °C)	

[a] >97/<3 indicates that a single product was isolated. [b] The result has been revised since the original publication: L. A. Paquette, unpublished results. [c] P. D. Bartlett, unpublished results. [d] L. A. Paquette, unpublished results. [e] Two adducts detected; ratio not reported. [f] R = exo-CH₂Cl. [g] R = methylene.
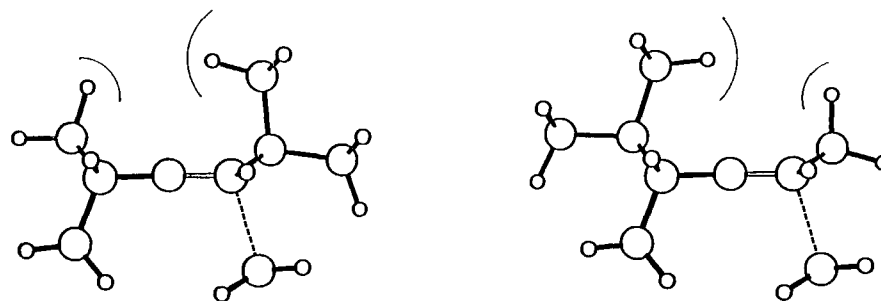

Figure 2. Nonoperative steric effects in cycloadditions of 1c and 2.

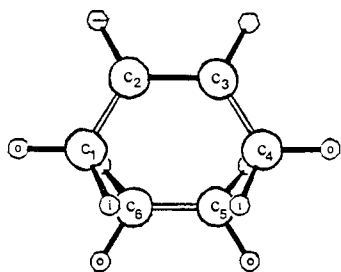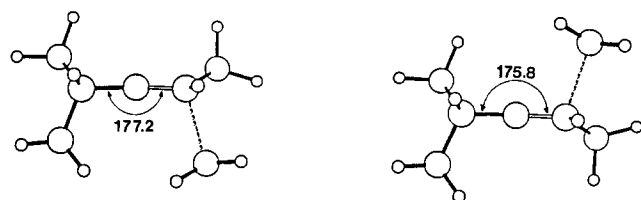**Table II.** The Geometries of the STO-3G and Constrained-Synchronous MNDO Transition Structures[a]

	bond lengths			bond angles			torsional angles	
	STO-3G	MNDO		STO-3G	MNDO		STO-3G	MNDO
C1–C2	1.359	1.389	C1–C2–C3	121.2	123.4	C1–C2–C3–C4	0.0	0.0
C2–C3	1.421	1.420	C1–C6–C5	109.3	111.1	C1–C6–C5–C4	0.0	0.0
C5–C6	1.366	1.388	C6–C1–C2	101.4	100.7	C2–C1–C6–C5	50.9	47.7
C1–C6	2.217	2.163	C2–C1–H$_i$	120.2	119.6	C2–C1–C6–H$_i$	72.2	75.8
C1–H$_i$	1.079	1.091	C2–C1–H$_o$	121.1	119.6	C2–C1–C6–H$_o$	173.0	170.5
C1–H$_o$	1.083	1.091	H$_i$–C1–H$_o$	114.3	112.2	C5–C6–C1–H$_i$	69.8	76.1
C2–H	1.083	1.094	C3–C2–H	117.8	117.0	H$_o$–C1–C2–H	7.7	0.5
C6–H$_i$	1.080	1.094	C1–C2–H	119.3	118.8	C5–C6–C1–H$_o$	176.3	171.9
C6–H$_o$	1.080	1.093	C5–C6–H$_i$	120.3	120.2	H$_i$–C1–C2–H	163.0	154.1
			C5–C6–H$_o$	120.2	120.4	C3–C2–C1–H$_i$	32.1	37.3
			H$_i$–C6–H$_o$	114.9	113.8	C3–C2–C1–H$_o$	172.6	168.0
			C1–C6–H$_i$	89.4	90.2	C4–C3–C2–H	165.1	168.7
			C1–C6–H$_o$	91.8	91.3	C1–C6–C5–H$_i$	104.1	104.7
			C6–C1–H$_i$	84.9	86.6	C1–C6–C5–H$_o$	101.0	103.3
			C6–C1–H$_o$	103.9	103.5	C1–C2–C3–H	165.1	168.7

[a] The activation energies are 39.3 kcal/mol (STO-3G with ZPE correction) and 60.8 kcal/mol (MNDO).

Table III MM2 Calculated Energy Differences ($E = E$(top) − E(bottom) in kcal/mol) and Predicted Isomer Ratios (T/B = Top/Bottom at the Experimental Temperature 25 °C Unless Indicated Otherwise) for the Cycloadditions of Isocyclopentadiene and Derivatives with Ethylene and Maleic Anhydride

	dienophile					
	ethylene			maleic anhydride		
diene	ΔE	T/B theory	T/B exptl[a]	ΔE	T/B theory	T/B exptl
1a	0.5	30:70	<3:>97	1.0	16:84[b] x	25:75 x
1b	−3.9	100:0	30:70	−5.8	100:0 x	>97:<3 n
1c	0.1	46:54	30:70	−1.7	95:5 n	>97:<3 n (80 °C)
1d	0.5	30:70	<3:>97	0.9	18:82 x	<3:>97[c] x
1e	0.1	46:54	25:75	−2.6	99:1 n	>97:<3 n
2[d]	2.6	1:99	<3:>97	3.0	0:100 x	<3:>97 x
4a	0.5	30:70	<3:>97 (65 °C)	1.6	6:94 n	<3:>97 x
4b	−3.8	100:0		2.4	98:2 x	>97:<3 n (80 °C)
4c	0.4	34:66	<3:>97 (61 °C)	1.8	5:95 n	e
4d	0.5	30:70	<3:>97	1.1	14:86 n	<3:>97[c] x
4e	0.3	38:62	22:78	1.9	4:96 n	66:34 n
4q	4.5	0:100		6.1	0:100 n	<3:>97 x (80 °C)

[a] For DMAD reactions. [b] The x (exo) and n (endo) represent the mode of attack on the favored face. [c] For N-phenylmaleimide reactions. [d] Calculations were carried out on 10,10-dimethylisodicyclopentadiene. [e] Two adducts detected; ratio not reported.

Figure 3. Numbering of STO-3G and C_s-constrained MNDO transition structures for the Diels–Alder reaction of butadiene with ethylene. See Table II for geometrical parameters.

Figure 4. MNDO synchronous transition structure models for top and bottom attack of ethylene on isodicyclopentadiene.

gives energy differences which we believe are reasonable.[18] Because of the success of MM2 in this area, we undertook the development of methods to evaluate the energies of the isomeric transition structures by MM2.

MM2 Model Transition Structures for Isodicyclopentadiene Cycloadditions. The MM2 model for the transition structures of

cycloaddition of isodicyclopentadiene and derivatives was constructed in the following manner. The positions of the seven carbon atoms of the cyclopentadiene–ethylene moiety and the hydrogens attached to these carbons were fixed at the MNDO geometries for top and bottom attack on isodicyclopentadiene. This is equivalent to the assumption that the transition states for all of these reactions are synchronous and that the position of the transition state is constant, regardless of the nature of the dienophile or of the substituents on the isodicyclopentadiene. The positions of the two norbornene bridgehead carbons were also fixed, in order to maintain the appropriate bending at the norbornene–cyclopentadiene fusion. The positions of all other atoms were fully optimized, with the normal parameters of Allinger's MM2 force field.[23] The normal parameters for van der Waals interactions were also included for the atoms whose positions were fixed.

In the cases where the dienophile is maleic anhydride rather than ethylene, the anhydride moiety was connected in place of the appropriate dienophile hydrogens. In order to allow some flexibility of the anhydride moiety, the equilibrium angles for the atoms attached to the dienophile carbons were set at the values obtained for the isodicyclopentadiene–ethylene transition state. Bending and stretching parameters for the dienophile carbons were normal values for sp³ carbons.

Since parameters are not available in Allinger's MM2 for the anhydride moiety, the maleic anhydride was treated as follows: the O=C—O—C torsional parameter was given the values V_1 = 1.66, V_2 = 8.98, and V_3 = 0.0, and the C–O–C bending parameter was given the values CS = 0.600 and an equilibrium angle at 107.1°. These values are the MM2 values for alkyl esters.[23]

The computational results for the reaction of ethylene or maleic anhydride with isodicyclopentadiene and several derivatives are

given in Table II. For the reaction of isodicyclopentadiene with ethylene, bottom attack is predicted to be favored by 0.5 kcal/mol, which would give a 30:70 ratio of top/bottom attack at 25 °C. Professor Bartlett has informed us that isodicyclopentadiene reacts with ethylene at 175 atm and 140° to give 2% *anti-* and 10.2% *syn*-sesquinorbornene, corresponding to a 20:80 ratio of top:bottom attack, along with other products.[4c]

Bottom attack is predicted for all ethylene reactions, except for the unsymmetrically substituted derivatives, **1b** and **4b**, where calculations predict a large preference for top attack, away from the methyl group.

There is reasonably good agreement between the calculated ratios (for ethylene) and the experimental results (for DMAD). The only qualitatively incorrect prediction is for **1b**, where exclusive top attack is predicted but bottom attack is preferred experimentally. Our model apparently overemphasizes the steric effects involving repulsions between the bottom methyl on the cyclopentadiene position and the ethylene. That some repulsions are present is reflected in the increases percentage of the product of top attack by DMAD. The model predicts a large preference for top attack because the model is too inflexible to allow proper relief of steric repulsions upon bottom attack, due to the immobility of the saturated carbon of the cyclopentadiene moiety. Indeed, when the saturated carbon of the cyclopentadiene moiety is no longer fixed, the energy difference is reduced from −3.9 to −2.3 kcal/mol.

The predictions for the reactions of maleic anhydride are remarkably good. Only the reaction of **4e** with maleic anhydride, which is predicted to give a 4:96 top:bottom ratio but actually gives 66:34, deviates significantly. This deviation is once again caused by the rigidity of the model. The change from the preferential bottom attack with **1a** and **1d** to top attack with **1b**, **1c**, and **1e** is predicted correctly. Furthermore, as described below, the observed endo/exo preference is also predicted. Since our model includes only torsional and steric effects, these effects are sufficient to account for the selectivities of the reactions of **1b**, **1c**, and **1e** with maleic anhydride. We postulate that the main difference between DMAD and other dienophiles such as maleic anhydride is the relatively bulky nature of the latter, so that steric effects influence the stereoselectivities of reactions of the substituted ethylenic or azo dienophiles. This is described in more detail below.

What is the origin of the stereoselectivity for reactions of **1a** and the derivatives which prefer bottom attack? In order to answer this question, calculations were performed in which the ethylene was removed from the model transition structures, the isodicyclopentadiene moiety was kept in the top or bottom transition structure geometry, and an MM2 calculation was performed on each fragment. The difference in energy between the isodicyclopentadiene moiety bent up for bottom attack or bent down for top attack is 0.4 kcal/mol, with the bent up geometry more stable. For bottom attack, the norbornene moiety is found to bend in an endo direction. This is the bending found in norbornene itself.[18] This endo bending relieves the torsional strain between bonds attached to atoms 2 and 3 and those attached to atoms 1 and 4, because a more staggered arrangements results. For the top attack, these same torsional interactions are increased due to a more eclipsed arrangement in the exo-bent norbornene moiety. This difference is shown in Figure 5. The drawings are Newman projections looking down the bond connecting the bridgehead carbon to the carbon at the intersection between the norbornene and cyclopentadiene moieties. The difference in torsional strain about the 2–3 bond (Figure 5) for these two transition states is 0.3 kcal/mol. Since there are two bonds of this type, torsional strain favors bottom attack by 0.6 kcal/mol.

This torsional energy difference is quite reasonable, considering that the difference in energy for endo vs. exo bending of 3.4° for the olefinic hydrogens in norbornene is 0.8 kcal/mol, using STO-3G calculations, in favor of endo bending.[10a] These same classical torsional effects are present in *syn*-sesquinorbornene and

(24) Kravetz, T. M.; Hathaway, S. J.; Paquette, L. A., *J. Am. Chem. Soc.*, submitted for publication.
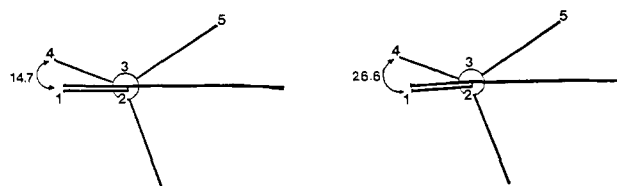

Figure 5. Newman projections showing differences in torsional effects for top and bottom attack on isodicyclopentadiene. Views are from C2 of the diene toward the norbornene bridgehead carbon.

are believed to cause the 16° endo bending of this molecule.[18] These torsional effects will be involved for all reactions of isodicyclopentadiene and related species, although they will be more influential in late transition states than in early ones.

The additional effect which causes the reversals in π-facial selectivity found for reactions of **1b**, **1c**, and **1e** with large dienophiles is steric. When the unsubstituted isodicyclopentadiene reacts with maleic anhydride, or other large dienophiles, the anhydride may attack in the four ways shown in Figure 6. Either the exo-bottom or exo-top attack is relatively unencumbered. The anhydride experiences more steric hindrance when attacking in the endo fashion, either top or bottom, as shown in Figure 6. The values for relevant steric repulsions are given in Figure 6. These were obtained from the MM2 calculations. For the endo-bottom attack of maleic anhydride on isodicyclopentadiene, the steric repulsion between the carbonyl groups of the dienophile and the inside hydrogens on the ethano bride is 1.6 kcal/mol. The endo-top attack has a steric repulsion of 0.5 kcal/mol, involving the lone pairs of the ether oxygen of the anhydride and the inside hydrogen on the methano bridge. The corresponding steric repulsions for the two exo attacks are small and negligible. Thus, steric effects disfavor endo attack, and the preferred exo-bottom stereochemistry observed experimentally is governed by the torsional effects mentioned previously.

Upon substitution of methyl groups on the methylene unit, both of the exo approaches become highly hindered, as shown in Figure 7. The steric repulsions for exo attack are about 1.5 kcal/mol for both the exo-top and exo-bottom attacks. The steric repulsions are not dominated by any one interaction in these cases but rather result from interactions of the entire anhydride with the hydrogens on the methyl groups. Because of these large repulsions, there can only be competition between the two endo approaches. As mentioned earlier for the parent isodicyclopentadiene case the endo-top attack is less hindered than the exo-bottom attack. Thus, the endo-top attack is favored when the substituents are large.[3i]

The torsional arguments developed for the unsubstituted species, **1a**, can be applied to the spirocyclopropane derivative, **1d**. Cycloadditions of **1d** show a preference for bottom attack similar to that found for reaction of **1a**. The hydrogens on the cyclopropane are tied back by the cyclopropane ring in such a way that they cause very little steric hindrance for top or bottom attack. Thus, torsional effects prevail. Reactions of the spirocyclopentane, **1e**, give the top attack, similar to reactions of **1c**. The cyclopentane ring is larger and exhibits the same steric hindrance for exo-top and exo-bottom attack as does the *gem*-dimethyl group. Thus, steric effects control, and the endo-top attack is favored.

Both torsional and steric effects cause **2** to prefer bottom attack. The intramolecular steric interactions[3j] shown in Figure 2 are not of importance, but rather intermolecular steric interactions reinforce the torsional preference for bottom attack. As the dienophile approaches from the top, it encounters the interior methyl group regardless of the size of the dienophile. The bottom approach is as unencumbered as in the unsubstituted case, as shown in Figure 8.

The reactions of "isodicyclopentatriene" **4a**, and various derivatives, were also studied by this procedure. The etheno bridge in **4a** is smaller than the ethano bridge in **1a**, resulting in a decrease in steric interactions for the bottom attack of large dienophiles. The calculations for **4a–f** are given in Table II. The ethylene reactions are predicted to be affected little by the additional unsaturation in **4a–f**. Bottom attack is always favored, except
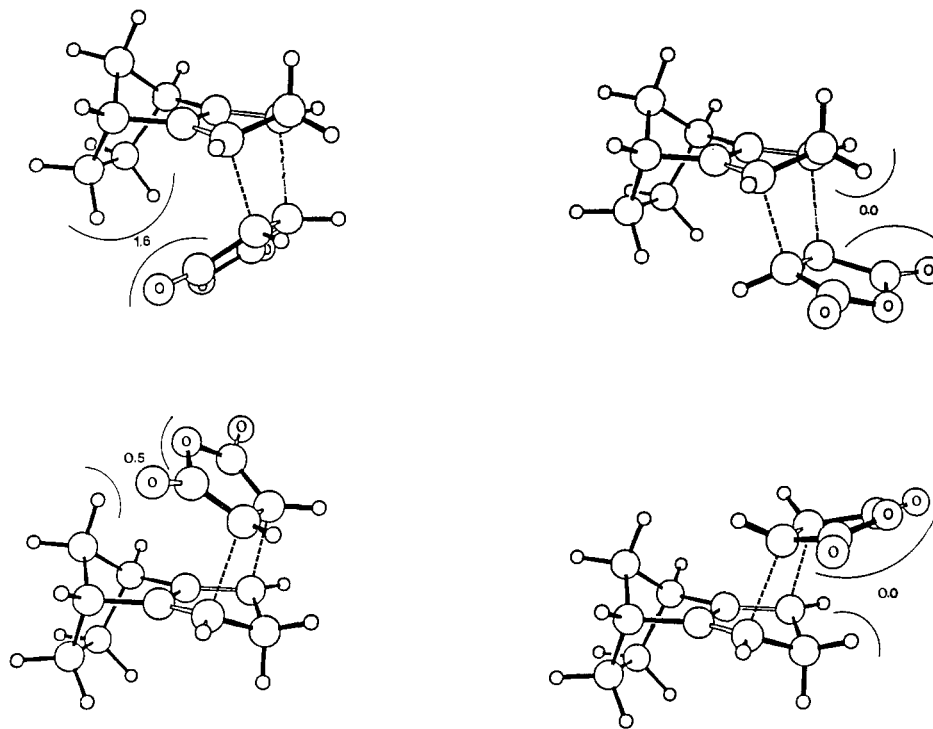
Figure 6. The MM2 model transition structures for the reaction of isodicyclopentadiene (**1a**) with maleic anhydride.

for **4b**. The bottom preference is the same (cf. **1a**, **1d** to **4a**, **4d**), or slightly larger (cf. **1c**, **1e** to **4c**, **4e**).

For the reactions of maleic anhydride, bottom attack is predicted for all cases except **4b**. The experimental results are in accord, except for **4e**, which shows a small preference for bottom attack, whereas calculations predict a small preference for top attack.

The bicyclo[2.2.2]octene derivative, **5**, shows a preference for top attack for acetylenic type dienophiles. This top attack would seem contrary to predictions on the basis of steric arguments since the ethano bridge is sterically more demanding than the etheno bridge. However, steric effects are not governing these reactions, just as steric effects do not control the selectivity found for DMAD with **1a**. Rather, torsional effects are most likely in control in both cases.

To investigate this, bicyclo[2.2.2]octadiene was optimized with MM2. The hydrogens on the etheno bridges bend toward the ethano bridge by 1.2°, comparable to the bending in norbornene but in the opposite direction. MM2 has been found to give reasonable predictions for this bending in norbornene and norbornadiene.[18] The bending of the olefinic hydrogens of bicyclo-[2.2.2]octadiene is a consequence of the greater length of the ethano bridge as compared to the length of the etheno bridge. This situation is exactly opposite to that found in norbornadiene, where the methano bridge is, of course, shorter than an etheno bridge. Whereas the olefinic hydrogens on one etheno bridge in norbornadiene must bend toward the other etheno bridge to relieve eclipsing with bonds to the bridgehead, they must bend away from the other etheno bridge in bicyclo[2.2.2]octadiene to relieve eclipsing. In several substituted derivatives of this type, bending in both this and the opposite direction has been observed in X-ray crystal structures.[5d] Since the bending about a double bond of bicyclo[2.2.2]octadiene is toward the ethano bridge, the attack of small dienophiles on **5** will occur from the side of the ethano bridge. In this way, bending at the cyclopentadiene–bicyclo-octadiene fusion will occur in the direction favored in order to minimize torsional strain in the transition state. Only a sterically demanding but highly reactive dienophile, like a triazolinedione, and presumably TCNE as well, will attack from the less hindered, etheno bridge side of **5**.

Both dimethylenenorbornene derivatives **6** and **7** undergo the expected bottom attack with all dienophiles studied except *N*-methyltriazolinedione, a dienophile which because of its size and

perhaps also due to the earliness of the transition states of this reactive dienophile follows the sterically less hindered course of attack.

The monosubstituted dimethylenenorbornanes **8a–c** give the products resulting from top attack with TCNE. These findings can be explained in terms of steric effects. TCNE has substituents on both sides of the double bond and, therefore, cannot avoid steric repulsions between cyano groups and the etheno-bridge hydrogens upon bottom attack. For top attack, the cyano groups extend out away from the inside methylene hydrogen, minimizing the steric effects for the top attack. We predict that smaller dienophiles will attack **8a–c** from the bottom.

The stereoselectivities of the reactions of the dichlorodi-methylenebicyclooctanes, **9a–f** with TCNE can also be accounted for in steric terms. Bottom attack is favored for **9a–d** while top attack is favored for **9e** and **9f**. The switch from bottom to top attack in **9e** can be attributed to the increase in steric hindrance on the bottom face due to the *endo*-hydroxy group, while the carbonyl in **9f** may also promote top attack.

However, the cycloaddition stereoselectivities in such systems are influenced by the alkene substitutents, and simple generalizations are dangerous. Avenati and Vogel recently reported the cycloadditions of various dienophiles to analogues of **9a**, in which deuterium labels have been introduced in place of the chlorines on the *exo*-methylene groups.[5e] Stereoselectivity varies from a strong bottom (near the ethano bridge) preference with PTAD to no preference for singlet oxygen. The observed bottom/top ratios are 95/5 (PTAD), 75/25 (TUNE), 70/30 (DMAD), 60/40 (MA), and 50/50 ($^1O_2$).[5e] The authors note that this order does not follow expectation based upon pure steric effects.[5e] According to our model, the degree of stereoselectivity should be related to the position of the transition state, the least reactive dienophile giving the greatest selectivity due to torsional effects, but this order can be altered by steric effects.

Related Cycloadditions. After this work was completed, Paquette reported the [4 + 2] reactions of **1a** with diphenyl and tetramethyl oxallyl cations and the [6 + 4] cycloaddition of **1a** with tropone.[24] The major product in each case results from top attack. The top:bottom product ratios are 90:10, 66:34, and 83:17, respectively, for these cycloadditions. This reversal in π-facial selectivity was taken as support for the π-orbital tilting and closed-shell repulsion control of stereoselectivity. That is, the
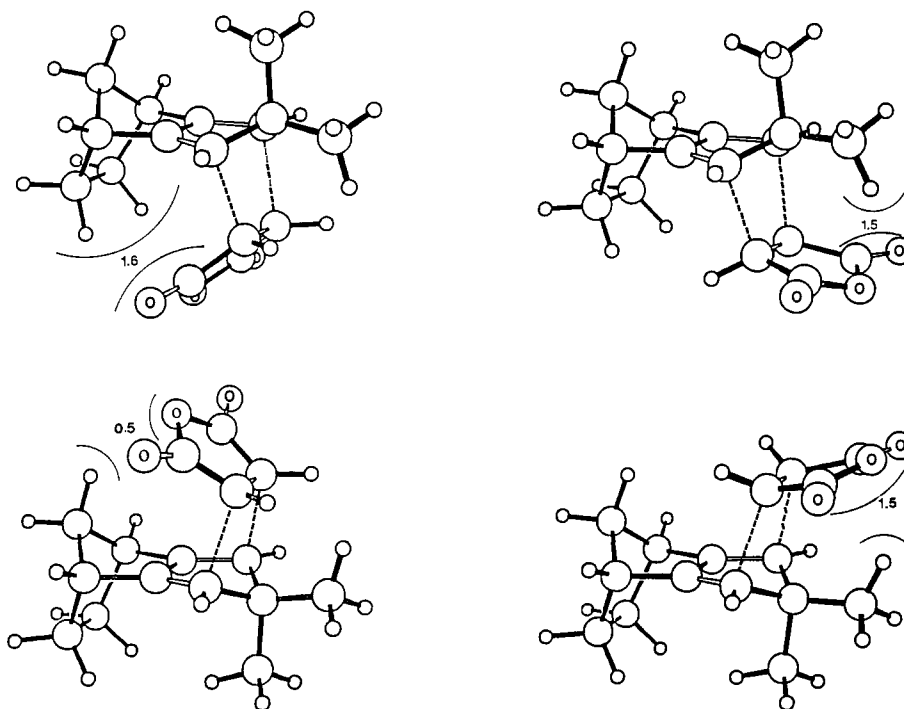
Figure 7. The MM2 model transition structures for the reaction of 4,4-dimethylisodicyclopentadiene (**1c**) with maleic anhydride.
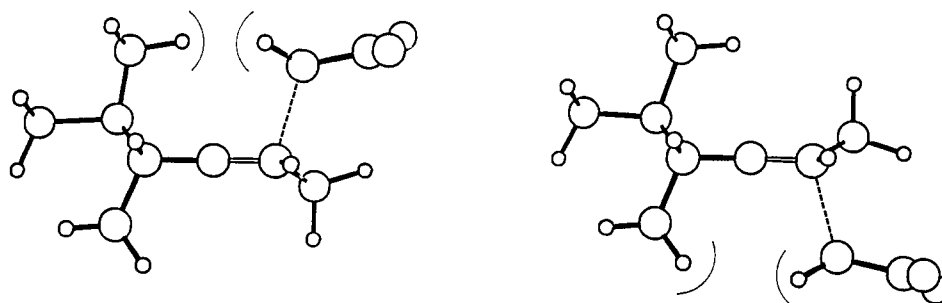

Figure 8. The MM2 exo transition structure models for the reaction of 10,10-dimethylisodicyclopentadiene with maleic anhydride.
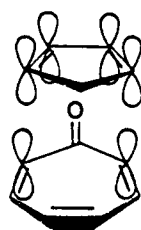

Figure 9. Front view of the tropone–cyclopentadiene [6 + 4] transition state showing the approximate matching of intertermini distances.

distance between the termini of the oxallyl cations or of tropone is now sufficiently large that repulsion between ψ_1 of the diene and symmetrical π orbitals of the oxallyl cation or of tropone should be larger upon bottom attack than top attack.

Although calculations on these systems have not been performed, we believed that the torsional effects which control the π-facial selectivity for reactions of **1a** with alkenes and alkynes no longer exist in oxallyl cations and tropone cycloadditions. As described earlier, these torsional effects are the result of the bending of atoms attached to C2 or C3 of the diene in response to the inward rotation of the diene termini in Diels–Alder reactions. This bending maintains overlap between the p orbitals at C1 and C2 and at C3 and C4. The distances between the termini of an oxallyl cation or tropone are larger than these distances for alkenes. The distances between the oxallyl cation or tropone termini are nearly equal to the distance between the isodicyclopentadiene diene termini. Thus, overlap can be achieved without having to twist

the diene terminal p orbitals, as shown in Figure 9. Therefore, the bending between the norbornene and cyclopentadiene moieties will be reduced, decreasing torsional effects on stereoselectivity. In such a situation, steric effects are expected to be the controlling element.

Conclusion

From the computational evidence presented here, we suggest that the origin of the π-facial selectivity of isodicyclopentadiene is the out-of-plane bending of groups at C2 and C3 of the diene in Diels–Alder transition states. Torsional effects in the norbornane skeleton dictate the preferred direction of attack. These torsional effects can be overcome by steric effects in substituted cases. This explanation is in contrast to the Gleiter–Paquette hypothesis that the origin of π-facial selectivity lies in the orbital tilting of ψ_1 of the diene which can be altered by substituents. This orbital tilting argument implies that the size of the dienophile should have no influence on the stereoselectivity. However, we have shown that the stereoselectivity does change with the size of the dienophile in a predictable way. Our arguments are able to predict the change in stereoselectivity with the change in size of the dienophile, and these predictions are in good agreement with experimental data.