Endo−Exo and Facial Stereoselectivity in the Diels−Alder Reactions of 3-Substituted Cyclopropenes with Butadiene

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Received August 18, 2000. Revised Manuscript Received March 21, 2001

Abstract: A computational examination of the four modes of addition in the Diels−Alder reactions of 3-substituted cyclopropene derivatives (substituents: BH_2, CH_3, SiH_3, NH_2, PH_2, OH, SH, F, and Cl) with butadiene have been carried out at the B3LYP/6-31++G(d)//HF/6-31++G(d) level. The degree of stabilization of these derivatives at the ground state correlates with the electronegativity of the substituent. This attenuation of reactivity and differences in steric interactions are the only factors needed to explain both the high facial selectivity and the differences in the endo−exo selectivity seen in these reactions. Furthermore, evidence is presented that indicates that stabilization by an interaction involving the syn C-3 hydrogen of cyclopropene and butadiene is small or irrelevant in controlling the endo−exo selectivity of the Diels−Alder reaction.

Introduction

Diels−Alder reactions of cyclopropene with simple dienes show a considerable preference for endo addition,[1−5] although some additions of cyclopropene to 1,3-diphenylisobenzofuran take place with a modest preference for exo addition.[4,6] However, a careful experimental assessment of the endo−exo selectivity in the simplest reaction, between cyclopropene and butadiene, failed to find any of the exo addition product.[3] Endo selectivity in Diels−Alder reactions is usually explained by a significant favorable overlap of components of frontier molecular orbitals at nonreacting π centers of the diene and the dienophile at the transition state, but more subtle interactions have been invoked to rationalize the endo additions of cyclopropene. Apeloig and Matzner[7] studied the endo selectivity in the additions of cyclopropene to substituted butadienes using the MP2/6-31G(d)//3-21G level of theory. They calculated Mulliken overlap populations (MOP) between the syn hydrogen at C-3 of cyclopropene and C-2 and C-3 of the butadiene moiety, and the data were presented as evidence that a "secondary orbital overlap" (SOI) largely controls the endo selectivity. Jursic[8] examined the reaction of cyclopropene with butadiene by both high-level ab initio and DFT methods. Bond orders and net atomic charges associated with the C-3 hydrogen of cyclopropene led to a conclusion similar to that of Apeloig and Matzner. Dannenberg[9] and co-workers advocated an interaction between the syn hydrogen at C-3 of cyclopropene and the developing π bond between C-2 and C-3 of butadiene as the controlling factor. They suggested a similarity between the H-to-π interaction of cyclopropene with butadiene in the endo transition state and the T-shaped dimer of ethyne. Dannenberg cast some doubt on the accuracy of the calculations of Apeloig and Matzner, which had not included correction for basis set superposition errors (BSSE). Nevertheless, application of BSSE corrections to Dannenberg's data changes the endo−exo ratios by less than 1 $kJ\cdot mol^{-1}$, whereas the difference in the activation energies is about 8 $kJ\cdot mol^{-1}$. Another computational analysis (involving single-point MP2/6-31G(d) and B3LYP/6-31G(d) energies based on RHF/6-31G(d) geometries) of cyclopropene and various dienes was by Fujimoto and co-workers.[10] They concluded that the endo transition state is stabilized by SOI but the degree of stabilization proffered by the SOI contribution (4 $kJ\cdot mol^{-1}$) was not sufficient to explain the level of endo selectivity. They indicated that an electrostatic interaction was another major factor. In a very recent review, Salvatella and co-workers[11] called into question the significance of SOI in most Diels−Alder applications. They pointed out that, in most instances, simple steric interactions could explain the endo−exo selectivity. They discussed the case of cyclopropene at some length, with particular reference to the papers by Dannenberg and Fujimoto, but they stated that deeper investigation was necessary to identify the interactions between cyclopropene and a diene.

Thus, the important question remains: Is a stabilizing interaction between the syn C-3 hydrogen and the π system of butadiene energetically significant, or not? The relative importance of such an interaction should be much better appreciated if molecular variation were brought as close as reasonably

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10.1021/ja0030919 CCC: $20.00
Published on Web 05/16/2001

Table 1. Geometrical and Energetic Data (B3LYP/6-31++G(d)//HF/6-31++G(d)) for 3-Substituted Cyclopropenes[a]

substituent	substituent conformation	group electronegativity[b]	$\Delta E_{isodesmic}$ kJ·mol^{-1}	C-1═C-2 Å	C-1−C-3 and/or C-2−C-3 Å	C-3−H Å	C-3−substituent Å	π^* hartrees	π hartrees
SiH_3	staggered	1.91	7.0	1.2729	1.5153	1.0875	1.8834	0.04323	−0.34727
BH_2	eclipsed	1.93	−15.1	1.2638	1.5350	1.0843	1.5490	0.04442	−0.36200
PH_2	staggered	2.17	−6.3	1.2744	1.5031	1.0833	1.8518	0.04058	−0.34219
H	−	2.20	0	1.2777	1.4974	1.0826	1.0826	0.04655	−0.35973
CH_3	staggered	2.56	−10.8	1.2803	1.4960 1.4856	1.0851	1.5194	0.04318	−0.35638
SH	gauche	2.63	−17.6	1.2784	1.4607	1.0793	1.8198	0.03967	−0.37067[c]
Cl	−	3.05	−32.0	1.2853	1.4914	1.0746	1.8142	0.03850	−0.39208
NH_2	gauche	3.10	−28.0	1.2871	1.4768	1.0811	1.4447	0.04326	−0.37599[c]
OH	staggered	3.64	−41.4	1.2915	1.4726	1.0768	1.3966	0.04184	−0.39406[c]
F	−	4.00	−50.8	1.2899	1.4550	1.0755	1.3811	0.04206	−0.40968

[a] The cyclopropenes are listed in order of increasing electronegativity of the substituent. [b] Group electronegativities are from ref 17. [c] The HOMO for each of these compounds is an a″ orbital.

possible to the C-3 hydrogen in cyclopropene that might engage in the interaction. Therefore, we examined computationally cyclopropenes variously substituted at C-3, and the Diels−Alder reactions of these cyclopropenes with butadiene. Such 3-substituted cyclopropenes also provide the opportunity to assess for the first time facial selectivity in their Diels−Alder reactions.

Computational Methods

Cyclopropene and nine derivatives, monosubstituted at C-3 by BH_2, CH_3, SiH_3, NH_2, PH_2, OH, SH, F, and Cl, and *s-cis*-butadiene as well as their transition-state structures for endo−anti, endo−syn, exo−anti, and exo−syn additions were determined at the HF/6-31++G(d)//HF/6-31++G(d) level employing MUNGAUSS.[12] Gaussian 94[13] was used to obtain single-point B3LYP/6-31++G(d) data and frequencies. Ground-state minima for the substituted cyclopropenes were optimized using Davidon's optimally conditioned method.[14] Transition-state structures were obtained using a minimization of sum-of-squares method.[15] Incompletely converged structures were optimized further using the DIIS method.[16] Many of the substituents introduced at C-3 of cyclopropene are conformationally mobile. All probable rotational minima were optimized to determine the lowest-energy minimum. The terms "staggered," "gauche," and "eclipsed" refer to the relationship between the substituent on C-3 of cyclopropene relative to the hydrogen on C-3 of cyclopropene. C_s symmetry was enforced for optimizations of the staggered and eclipsed forms. Unless otherwise stated, data reported here for the substituted cyclopropenes and the transition states are for the rotational global minima. However, ground-state "butadiene" refers to *s-cis*-butadiene with torsion angle = 39.4°, not the global minimum planar *s-trans* form. Planar *s-cis*-butadiene might appear to be even more amenable to concerted cycloaddition, but planar *s-cis*-butadiene is a first-order saddle-point. All optimized structures for the ground-state molecules had no imaginary frequencies, and all of the transition states were first-order saddle-points.

Results and Discussion

Ground-State Cyclopropenes. Table 1 presents pertinent data on the ground states of the 3-substituted cyclopropenes.

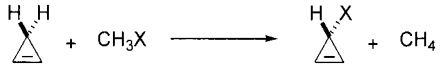

Figure 1. Isodesmic reaction for the quantification of the stabilization of the cyclopropene system by substitution at C-3.

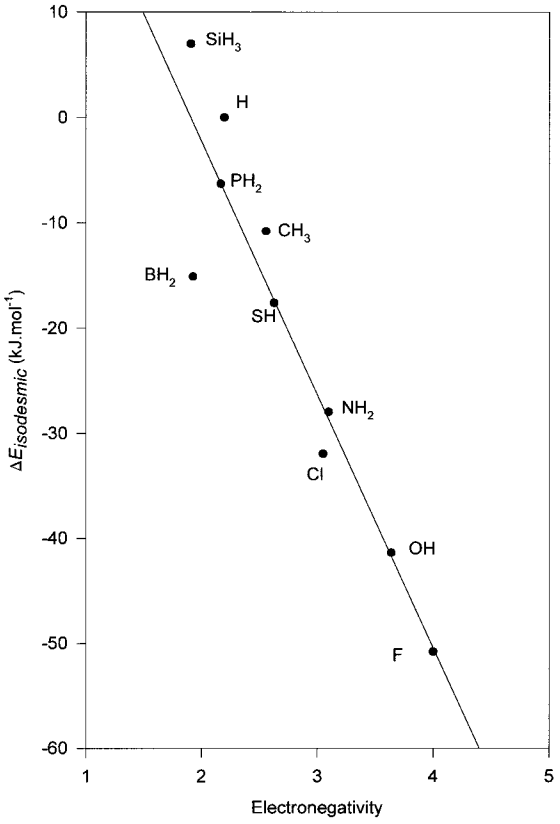

Figure 2. Plot of $\Delta E_{isodesmic}$ (HF/6-31++G(d)//HF/6-31++G(d)) versus the electronegativity of the substituent atom or group.

The isodesmic process depicted in Figure 1 was used to reveal that substitution leads to stabilization of the cyclopropene except for substitution by SiH_3, which shows a positive $\Delta E_{isodesmic}$ (Table 1). The degree of stabilization increases relative to a similarly substituted methane with the electronegativity of the substituent (Figure 2), which suggests that σ-withdrawal is the major factor leading to stabilization. The degree of stabilization by the most electronegative substituents is considerable, that is electronegative groups greatly reduce the gross reactivity of cyclopropenes. The range of $\Delta E_{isodesmic}$ is 57.8 kJ·mol^{-1}. Substitution by an electron-withdrawing group results in a shortening of the C−C single bonds and the C-3-H bond, and

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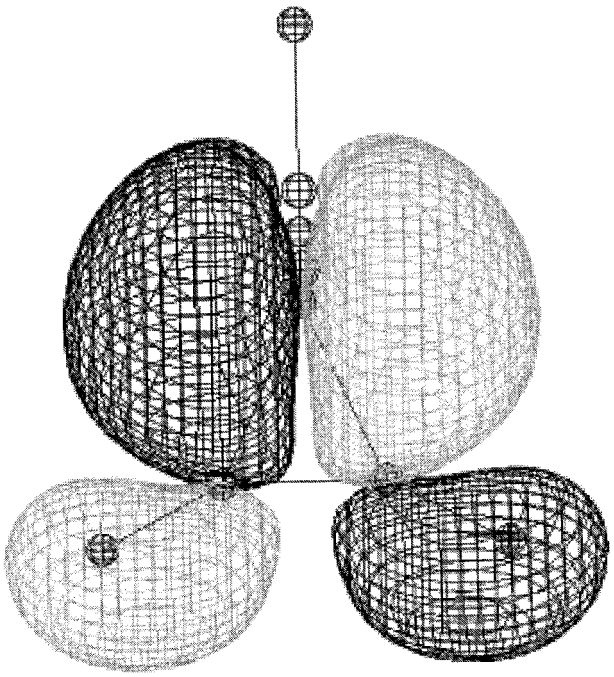

Figure 3. View of the highest occupied a″ orbital for the BH_2-substituted cyclopropene.

in a lengthening of the C═C double bond. Electron donation by PH_2 and, especially, by SiH_3 leads to the opposite effect, that is a lengthening of the C−C and C−H single bonds and a shortening of the C═C double bond. The lowest-energy conformers with SH and NH_2 have no symmetry. With SH the lengths of the two C−C single bonds are similar, but with NH_2 the C−C single bonds are very different in length.

Table 1 includes the energies of the π and π^* orbitals of the cyclopropenes. In every case, the π^* orbital is the LUMO, but the π orbital for these molecules is not always its HOMO. (An orbital arising from a heteroatom lone-pair is the HOMO with SH, NH_2, and OH.) Nevertheless, the π energies do correlate well with the electronegativities of the substituents, and the range of π energies is more than 10 times larger (0.0675 hartrees) than the range of π^* energies. The π energy for cyclopropene falls within the range of those for the substituted cyclopropenes.

Substitution by BH_2 seems anomalous. BH_2 stabilizes the cyclopropene ring, but it results in the shortest double bond, even shorter than that with SiH_3. This is because in its most stable conformation the plane of the BH_2 is aligned such that the boron removes electron density, through an a″ molecular orbital, from the adjacent C−C single bonds. The reduction in the angle strain, in turn, translates into a decrease in the length of the C═C double bond. The highest occupied a″ molecular orbital for this compound shows this interaction (Figure 3). The importance of this effect can be demonstrated by placing BH_2 in the staggered conformation, which is a first-order saddle-point. The result is a shortening of the C−C single bonds by 0.026 Å, and the C═C double bond is 0.016 Å longer. (The C−B bond is also longer by 0.31 Å.)

Overall, geometrical parameters in the ground state, especially the C═C bond length, as well as the π energy, correlate with the electronegativity of the substituent. Substitution by an electronegative group leads to a longer C═C bond, which must be more electron-deficient. Thus, electronegative substituents should enhance Diels−Alder reactions with "normal" electron demand, but the same substituents should retard addition by an inverse-electron-demand mechanism.

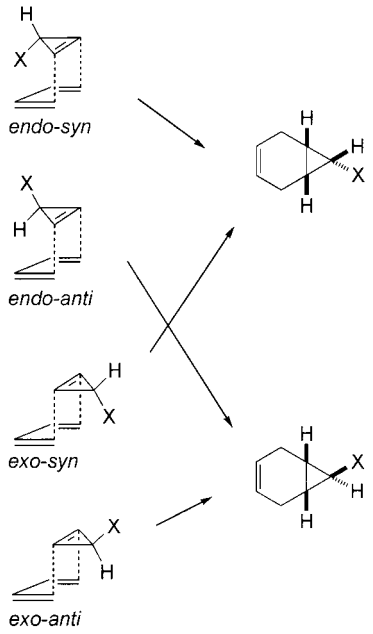

Figure 4. Modes of addition for the Diels−Alder reaction of a 3-substituted cyclopropene to butadiene.

Transition States. Diels−Alder reactions of the substituted cyclopropenes with butadiene can occur in four stereochemically distinct modes (endo−syn, endo−anti, exo−syn, and exo−anti), but these lead to only two diastereomeric adducts, as shown in Figure 4. The computed endo−exo selectivities and the facial (syn−anti) selectivities are essentially the same at HF/6-31++G(d)//HF/6-31++G(d) and at B3LYP/6-31++G(d)//HF/6-31++G(d). The conformation of the substituent is not always the same in all four modes of addition. For cyclopropene itself, the difference in energy between the endo and exo transition states is 7.5 $kJ \cdot mol^{-1}$ at HF/6-31++G(d)//HF/6-31++G(d) and 7.7 $kJ \cdot mol^{-1}$ at B3LYP/6-31++G(d)//HF/6-31++G(d). (The best calculated value in the literature[9] is likely one at QCISD(T)/D95V*//CASSCF/D95V* with correction for CP and ZPVE that gives an endo−exo difference of 7.5 $kJ \cdot mol^{-1}$.) Thus, from the point of view of comparatively studying isodesmic phenomena such as stereoselectivity, both the HF level and the DFT method should give reliable results. The calculations predict synthetically negligible amounts (<2%) of the cis adduct, except with the most electronegative substituents (3.4% with OH and 15.3% with F, calculated at 273.15 K). The cis adducts would be derived by syn addition; therefore, except with the fluorine-substituted analogue, the facial selectivity with 3-substituted cyclopropenes should be extremely high.

Figure 5 shows the activation energies of all four modes of addition plotted against the group electronegativities of the substituents. Initially, it should be pointed out that the cyclopropenes with electronegative substituents generally have higher activation energies in all modes of addition than does cyclopropene. Electropositive substituents accelerate the Diels−Alder reaction, relative to cyclopropene. Thus, the FMO picture would be that these reactions take place by the inverse-electron-demand mechanism.[18] Furthermore, in terms of assessing relative positions along the reaction coordinate, cyclopropenes bearing electronegative substituents would have "later," more-product-like, transition states, and electropositive substituents would have "earlier," more reactant-like, transition states. Later transition

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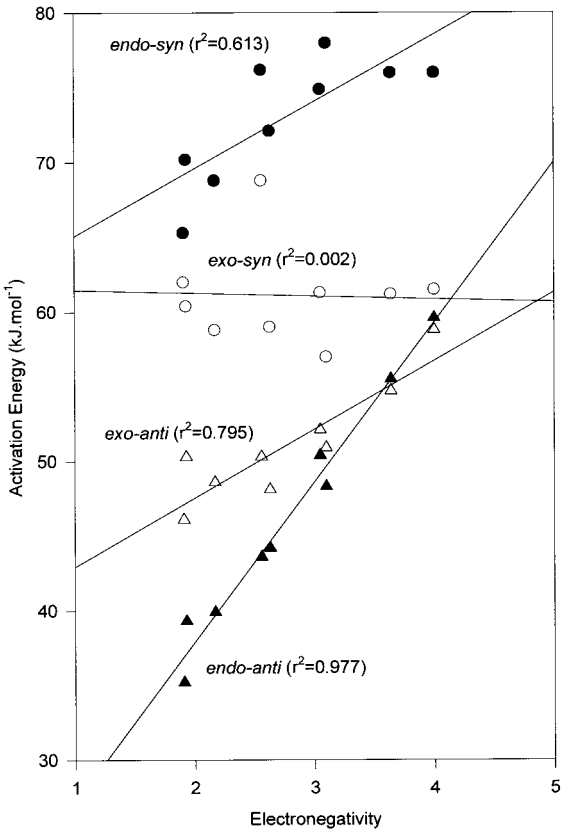

Figure 5. Plots of activation energies (B3LYP/6-31++G(d)//HF/6-31++G(d)) versus the electronegativity of the substituent atom or group for the four modes of addition in the Diels−Alder reactions of 3-substituted cyclopropenes to butadiene. Filled circles are the endo−syn transition states; open circles are the exo−syn transition states, filled triangles are the endo−anti transition states, and open triangles are the exo−anti transition states.

states should have incipient σ bonds that are shorter than for cyclopropene, and earlier transition states should have longer incipient σ bonds. This trend can be seen in the incipient σ bond lengths presented in Table 2. The distinctly scalemic ground-state geometry of the NH_2-substituted cyclopropene is mirrored by plainly unsymmetrical geometries in its gauche transition states.

It is evident from Figure 5 that the syn transition states are higher in energy than the anti transition states, which would translate into the high levels of facial selectivity, especially in endo additions. If the Diels−Alder reactions could occur only via syn addition, the additions would take place much more favorably in the exo geometry, not the endo geometry favored by cyclopropene itself. This implies that Diels−Alder reactions involving 3,3-disubstituted cyclopropene and butadiene should take place mainly by exo addition, which has been observed experimentally.[18,19] However, the syn transition states of the 3-substituted cyclopropenes show marginal or no correlation with the electronegativity (Figure 5), even though the ground-state energies are so intimately linked to the electronegativities of the substituents. This suggests that a second phenomenon, of roughly the same energetic cost but which correlates inversely with electronegativity, also influences reactivity in the syn transition states. The syn transition states have energies in a smaller range than the isodesmic ground-state energies. For the endo−syn additions, the range of activation energies is 12.7 kJ·mol^{-1}. For the exo−syn additions the range is 11.8 kJ·mol^{-1}. Steric interactions must lead to deformation of the addends at the transition state, even though some substituents (e.g. BH_2 and SiH_3) also lower the activation energies for syn addition by changing their conformation from their ground-state conformations. It has been shown with 5-substituted cyclopentadienes that the relative importance of the steric interactions could be estimated by measuring the amount of angular change about the sp^3 carbon (C-5) on going from the ground state to the transition state.[20] A similar analysis of the total angular change about C-3 for the reactions of the 3-substituted cyclopropenes (Table 2) indicates that the syn transition states generally involve more angular change than the corresponding anti transition states and the transition states with cyclopropene itself.[21] The only exception is 3-fluorocyclopropene, which shows no facial selectivity for exo addition. Nevertheless, the angular differences are a strong indication that steric hindrance is very important in determining the facial selectivity. Hence, the syn reactions with the 3-substituted cyclopropenes can be rationalized as follows. Gross reactivity, which is subject to the electronegativity of the substituent influencing the electron density in the C═C double bond, is greatly attenuated (i.e., has higher activation energies) with electronegative substituents. A steric parameter also attenuates reactivity, but in proportions opposite to the attenuation of gross reactivity by electronegativity. Steric hindrance would be a function of the size of the substituent on the dienophile and its distance to the diene. In terms of both size and distance, syn additions should suffer more from steric hindrance when the substituent is electropositive. Electropositive atoms tend to have larger van der Waals radii than do electronegative ones. Also, an electropositive substituent enhances the gross reactivity, which leads to an earlier transition state. Although an earlier transition state has a longer incipient bond, it also involves less rehybridized (i.e., flatter) addends. This, in turn, means a shorter distance and more steric hindrance between parts of the addends that are not the primary reacting carbons.

In contrast with the syn transition states, the energies of the anti transition states do correlate with the electronegativity (Figure 5). The correlation with the endo−anti transition states is extremely good, and the range of activation energies spans 24.4 kJ·mol^{-1}. Although this range is only half of that of the isodesmic ground-state energies, this range is still greater than the range of any other mode of addition. The range in the exo−anti transition states is 14.7 kJ·mol^{-1}, which is similar to the range in the syn additions. For both the endo−anti and exo−anti transition states, the amount of angular change about C-3 of the 3-substituted cyclopropene in going from ground state to transition state is not much different from that for cyclopropene itself. Steric interactions in the anti transition states are not sufficient to negate the order of reactivity that arises from the gross reactivity.

The issue of the endo−exo selectivity with the anti additions now arises. The predominance of endo addition for cyclopropene itself has been attributed to a favorable interaction between the syn hydrogen on C-3 of cyclopropene (hereafter "syn C-3H") and butadiene. This reaction, as well as all of the reactions with

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(21) This angular analysis cannot be used to compare endo and exo transition states since the interacting centers are very different. In an endo transition state, the closest contacts between nonreacting centers are between the endo atom or group at C-3 of cyclopropene and C-2 and C-3 of the butadiene moiety. In an exo transition state, closest nonreacting contacts are between the endo atom or group at C-3 of cyclopropene and the hydrogens on C-1 and C-4 of butadiene.

Table 2. Selected Transition State Properties for the Reaction of 3-Substituted Cyclopropenes with Butadiene (B3LYP/6-31++G(d)//HF/6-31++G(d))[a]

	substituent conformation				incipient bonds				total angular change about C-3[b]			
substituent	endo−syn	endo−anti	exo−syn	exo−anti	endo−syn	endo−anti	exo−syn	exo−anti	endo−syn	endo−anti	exo−syn	exo−anti
SiH_3	eclipsed	staggered	staggered	staggered	2.2758	2.2702	2.2809	2.2686	24.9	5.9	17.5	4.2
BH_2	staggered	eclipsed	eclipsed	eclipsed	2.2895	2.2670	2.2726	2.2655	26.5	4.9	9.5	4.4
PH_2	staggered	staggered	staggered	staggered	2.2537	2.2603	2.2724	2.2623	17.6	6.0	8.5	3.5
H	−	−	−	−	2.2573	2.2573	2.2598	2.2598	6.9	6.9	5.1	5.1
CH_3	staggered	staggered	staggered	staggered	2.2560	2.2585	2.2724	2.2601	14.0	7.2	10.3	4.0
SH	gauche	gauche	gauche	staggered	2.2323	2.2426	2.2440	2.2501	15.8	6.3	8.5	3.0
					2.2523	2.2534	2.2730					
Cl	−	−	−	−	2.2263	2.2302	2.2383	2.2395	17.7	8.6	11.2	3.6
NH_2	staggered	gauche	staggered	gauche	2.2406	2.2360	2.2526	2.2545	9.3	8.1	3.4	3.8
						2.8535		2.2428				
OH	staggered	gauche	gauche	staggered	2.2411	2.2306	2.2434	2.2366	10.8	8.3	10.8	4.7
						2.2365	2.2409					
F	−	−	−	−	2.2184	2.2184	2.2293	2.2305	10.6	9.2	4.0	5.1

[a] The cyclopropenes are listed in order of increasing electronegativity of the substituent. [b] The total angular change is the sum of the changes in angle on going from ground-state to transition-state geometry for the five bond angles about C-3 of the cyclopropene, i.e., with a substituent X, the changes in C-1−C-3−H, C-2−C-3−H, C-1−C-3−X, C-2−C-3−X, and H−C-3−X.

Table 3. Bond Lengths of the Syn Hydrogen to C-3 of the Cyclopropenes or the Syn Substituent to C-3 of the Cyclopropenes and Distances (Anti Additions only) of the Syn C-3 Hydrogen to Butadiene (Closest Contacts) in the Reactions of 3-Substituted Cyclopropenes with Butadiene (HF/6-31++G(d)//HF/6-31++G(d))[a]

substituent	endo−syn C-3−substituent Å	endo−anti C-3−H Å	exo−syn C-3−substituent Å	exo−anti C-3−H Å	endo−anti C-3H−butadiene Å	exo−anti C-3H−butadiene Å
SiH_3	1.8993	1.0929	1.8830	1.0900	2.5214	2.2374
BH_2	1.5777	1.0881	1.5487	1.0868	2.5235	2.2111
PH_2	1.8618	1.0874	1.8512	1.0854	2.5488	2.2586
H	1.0870	1.0870	1.0852	1.0852	2.5812	2.2818
CH_3	1.5186	1.0887	1.5196	1.0871	2.5696	2.2709
SH	1.8254	1.0832	1.8220	1.0825	2.5976	2.3381
					2.5946	
Cl	1.8186	1.0782	1.8259	1.0766	2.6678	2.3805
NH_2	1.4441	1.0844	1.4489	1.0830	2.6227	2.3359
					2.6185	2.3310
OH	1.3888	1.0840	1.4037	1.0786	2.6554	2.3655
					2.6533	
F	1.3764	1.0782	1.3871	1.0777	2.7132	2.4031

[a] The cyclopropenes are listed in order of increasing electronegativity of the substituent.

the 3-substituted cyclopropenes, can be classified as "inverse electron-demand," and the π orbital of the cyclopropene includes a significant component on the syn C-3H, which might mix favorably with the components at C-2 and C-3 of butadiene's π^* orbital. The plots for the anti additions in Figure 5 do not disprove the idea of stabilization of the endo transition state by some H-to-π mechanism. The activation energies for the endo−anti reactions might reasonably correlate with the electronegativity since electron withdrawal or donation from the syn C-3H would provide less or more orbital density with which the π system of butadiene might mix. Activation energies for the endo−anti and the exo−anti reactions are very similar when the substituent is very electronegative. It can be seen in Figure 5 that the plots for the endo−anti and exo−anti transition states meet for the highly electronegative substituents. This would indicate that the stabilizing interaction should be essentially zero with these substituents. The most electropositive substituents have differences in the endo−anti and exo−anti activation energies of about 10 kJ·mol^{-1}, which suggests that these substituents should enhance the stabilizing interaction.

The idea of a stabilizing interaction between the syn C-3H and the π system of butadiene is based on calculated MOPs and bond orders in the transition states.[7,8] The MOP for the fluoro- and silyl-substituted cyclopropenes in endo−anti transition states are 4.6×10^{-3} and 12.2×10^{-3}, respectively, both of which are lower than our value of 30.5×10^{-3} for cyclopropene itself. Cyclopropene is intermediate in endo−exo selectivity. Moreover, the MOP between the fluorine and the π system in the endo−syn transition state of 3-fluorocyclopropene is 21.3×10^{-3}, which would predict that this analogue should have a strong preference for endo−syn addition over all other modes of addition, but endo−syn addition is the one mode that is much higher in activation energy than the other three.

Table 3 shows that the syn C−H bonds of the 3-substituted cyclopropenes are lengthened in the endo−anti transition states.[9] The lengthening is modest but probably significant in the light of the observation that the syn C−H bonds in exo−anti transition states are hardly different from the ground-state C−H bond lengths presented in Table 1. Bond lengthening cannot be taken as evidence of a C-3H-to-π interaction since some C-3-to-substituent bonds are also longer in the endo−syn transition states, yet these analogues show no interest in endo−syn addition. van der Waals attraction in H-to-π systems, for example the type of interaction that is responsible for the edge-to-face associations of aromatic systems,[22] is all much smaller than would account for the endo−exo selectivities. Recently, it was shown that H-to-π interactions are stronger when the H is more acidic.[23] The 3-substituted cyclopropenes present a range of hydrogen acidities for the syn C-3H, and the most acidic syn C-3H must be that of 3-fluorocyclopropene. However, this

(22) (a) Umezawa, Y. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1207. (b) Philp, D. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1643. (c) Samanta, U.; Chakrabarti, P.; Chandrasekhar, J. *J. Phys. Chem. A* **1998**, *102*, 8964. (d) Calhorda, M. J. *J. Chem. Soc., Chem. Commun.* **2000**, 801.

(23) Suezawa, H.; Hashimoto, T.; Tsuchinaga, K.; Yoshida, T.; Yuzuri, T.; Sakakibara, K.; Hirota, M.; Nishio, M. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1243.

Table 4. H-to-π Interaction Energies (kJ·mol^{-1})[a] between the Exo−Anti Transition State of 3-Fluorocyclopropene and Butadiene and the C-3 Hydrogen of Cyclopropene, 3-Fluorocyclopropene, or 3-Silylcyclopropene, As Illustrated in Figure 6

	HF/6-31+G(d)// HF/6-31G(d)			B3LYP/6-31++G(d)//HF/6-31G(d)		
distance[b] Å	cyclopropene	3-fluoro-cyclopropene	3-silyl-cyclopropene	cyclopropene	3-fluoro-cyclopropene	3-silyl-cyclopropene
2.4	15.3	10.7	14.6	9.4	5.7	8.5
2.6	8.2	4.5	7.4	4.6	1.6	3.7
2.8	4.2	1.2	3.5	2.2	−0.3	1.4
3.0	2.0	−0.3	1.3	0.8	−1.1	0.2
3.2	0.9	−1.0	0.2	0.2	−1.3	−0.3
3.4	0.2	−1.3	−0.4	−0.1	−1.2	−0.5

[a] Positive numbers indicate net destabilization, negative numbers mean net stabilization. [b] Distance from the additional cyclopropene C-3 hydrogen to the center of the butadiene C-2−C-3 bond.

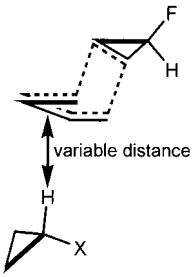

Figure 6. Complex constructed in an attempt to stabilize an exo−anti transition state by the introduction of a C-3H-to-π interaction from a second cyclopropene molecule. The distance between the syn C-3H of the added cyclopropene to the middle of the C-2 to C-3 bond of the butadiene moiety was varied from 2.4 to 6 Å. X may be F, SiH_3, or H.

analogue shows no endo−exo selectivity for anti addition. On the other hand, 3-silylcyclopropene should have the least acidic syn C-3H, and this molecule has the largest endo−exo selectivity for anti addition.

In an attempt to introduce some of the putative stabilizing effect that must be lacking in an exo−anti transition state, we positioned successively three cyclopropenes (3-fluoro-, 3-silyl, and cyclopropene itself) such that a C-3H would subtend C-2 and C-3 of butadiene in its exo−anti transition state with 3-fluorocyclopropene, as shown in Figure 6. The distance between the C-3H and the butadiene π system was varied. The results are summarized in Table 4. The interactions are all repulsive at distances similar to those between the syn C-3H and butadiene in the endo−anti transition states. Even at greater distances, the van der Waals attractive interaction does not exceed 1.3 kJ·mol^{-1}. The cyclopropene analogue that seems to provide the most stabilization[24] is 3-fluorocyclopropene, but this is the analogue that is least endo-selective. In light of these results,[25] it is difficult to associate the H-to-π interaction with a significant role in the control of stereoselectivity in the Diels−Alder reactions of cyclopropene.

Is any stabilizing contribution from a H-to-π interaction necessary to rationalize the endo−exo selectivity with cyclopropene? We wish to present a simple, but less glamorous, explanation for the selectivity. We propose that differences in steric hindrance are sufficient to explain this endo−exo selectivity, just as steric hindrance accounts for the facial selectivity. Indeed, Apeloig and Matzner[7] acknowledged that, in addition to SOI, their plot indicated that there must be 9.6 kJ·mol^{-1} disfavoring exo addition, which they stated is due to differences in steric interactions in the endo and exo transition states.

The correlations between the endo activation energies and electronegativity seen in Figure 5 stem from the ground-state correlation that was even more acute than in the transition states. Stabilizing H-to-π interactions cannot be consistent with diminishing the correlation. Figure 5 shows that the analogues with the more electropositive substituents have greater differences between the endo−anti and exo−anti activation energies than do the analogues with electronegative substituents. If this is not due to a more significant H-to-π interaction in the endo−anti transition states with electropositive substituents, it must mean that steric hindrance is heightened in the exo−anti additions with the same cyclopropenes. In all of the anti additions, the steric hindrance must stem primarily from interactions between the syn C-3H of the cyclopropene and either sp^2 carbons (in the endo transition state) or hydrogens (in the exo transition state) of butadiene. It can be seen in Table 3 that the syn C-3H-to-butadiene closest contacts are always much shorter in the exo−anti transition states when compared with the corresponding endo−anti transition states. Nevertheless, there are marked differences in the distances between the hindering entities. The more reactive cyclopropenes, that is those with electropositive substituents, react via earlier transition states with longer incipient σ bonds than the corresponding incipient σ bonds for cyclopropene itself. The earlier transition states are less rehybridized. As a consequence, the sterically interacting atoms are closer together in both the endo and the exo transition states (Table 3). Therefore, the more reactive analogues are more sensitive to steric differences and show greater endo−exo selectivity. Conversely, the less reactive analogues, which react via later, more rehybridized transition states, are less sensitive to steric differences and show less endo−exo selectivity. The same idea can easily be used to explain differences in endo−exo selectivity with cyclopropene and variously substituted dienes.[7,10] If a substituent on the diene accelerates the reaction, relative to the reaction with butadiene itself, then the endo−exo selectivity increases. Generally, any reduction in reactivity should result in less endo−exo selectivity in the Diels−Alder reactions of cyclopropene or its analogues.

In summary, the rates of Diels−Alder reactions of 3-substituted cyclopropenes are dependent on whether the substituent is electropositive or electronegative. Electropositive substituents destabilize cyclopropene and increase Diels−Alder reactivity, whereas electronegative substituents stabilize cyclopropene and decrease reactivity. Facial selectivity is dominated by steric hindrance, and thus activation energies for anti addition are generally considerably lower in energy than those for the corresponding syn transition states. Endo−exo selectivity can be explained by steric considerations as well, without the need to invoke a H-to-π interaction as an important factor. Endo−exo selectivity is heightened in more reactive systems since the

(24) That the data in Table 4 are not corrected for BSSE does not diminish the validity of this analysis. Application of a counterpoise method for BSSE correction of a transition state is not recommended: Lendvay, G.; Mayer, I. *Chem. Phys. Lett.* **1998**, *297*, 365. Furthermore, BSSE corrections would decrease the stability of the complex shown in Figure 6, so any stabilizing effect would be overestimated by our method.

(25) At distances resembling the H-to-π distance in the endo−anti transition states, the interactions of C-3H of cyclopropenes and ethene are also destabilizing.

hindering atoms are significantly closer in the earlier transition states. Cyclopropenes with most electronegative substituents are essentially devoid of endo−exo selectivity since in their late transition states the potentially hindering groups are further apart than in the transition states of cyclopropene.

Acknowledgment. This research was supported by the Natural Sciences and Engineering Research Council of Canada.

Supporting Information Available: *Z*-Matrices for cyclopropene and its analogues substituted at C-3 by BH_2, CH_3, SiH_3, NH_2, PH_2, OH, SH, F, and Cl in their ground states and in their four Diels−Alder transition states with butadiene (PDF, ASCII). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0030919