Transition Structures of the Diels–Alder Reaction of Butadiene with Acrolein

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Four transition structures for the Diels–Alder reaction of butadiene with acrolein have been obtained with ab initio quantum mechanical calculations. These calculations correctly reproduce the substituent effects and stereoselectivities observed for related reactions. The degree of asynchronicity is substantial, the formyl substituent causes one forming single bond to be 0.3 Å longer than the other forming single bond. Conformational preferences of acrolein in the ground state and in the transition state of the Diels–Alder reaction and the endo preference of similar reactions are reproduced by these calculations.

Introduction

The Diels–Alder reaction of 1,3-butadiene with ethylene to form cyclohexene has been studied extensively both by ab initio[1–4] and semiempirical techniques.[5–9] Although there has been a major controversy about the mechanism of the prototype Diels–Alder reaction, it now seems clear on the basis of experimental evidence that the parent reaction is concerted.[4] Calculations also indicate that the reaction is synchronous[1,4,10] with equal formation of the two new single bonds in the transition structure.

Although the parent Diels–Alder reaction has been given a great deal of attention, both scientific and rhetorical, the reactions of substituted dienes and dienophiles are of greater interest because of the considerable practical utility of these processes. However, considerations of time and expense have precluded ab initio theoretical investigations of unsymmetrically substituted Diels–Alder reactions. We report here the first ab initio calculations on a reaction of butadiene with an unsymmetrical dienophile. This calculation allows us to address a variety of interesting mechanistic and theoretical questions about Diels–Alder reactions.

We report here the ab initio transition structures for the reaction of butadiene with acrolein using several different basis sets[11] and gradient techniques[12] with optimization of all variables. We have addressed the following points. (1) How asynchronous are the transition structures of Diels-Alder reactions with typical unsymmetrical dienophiles such as acrolein? (2) What factors are important in causing the endo transition structure to be favored over the exo?[13] (3) Why do thermal Diels-Alder reactions proceed through an s-cis conformation of the α,β-unsaturated dienophile, whereas the catalyzed reactions proceed through the s-trans conformation of the dienophile?[14,15] (4) Are gas-phase and solution phase substituent effects on the Diels-Alder reaction opposite, as has been suggested for several reactions on the basis of semiempirical calculations?[10]

Computational Procedure. Four transition structures were located with ab initio RHF calculations and the STO-3G basis set. The potential energy surface was explored starting from the geometry of the STO-3G transition structure for the parent Diels-Alder reaction.[4] The two forming CC bond lengths were fixed at various values and all other variables were optimized. Once a flat region of the potential surface near a single point was located, the constraints on the two forming CC bond lengths were removed, and then a transition-state optimization was carried out. Vibrational frequency calculations were carried out in order to ensure the authenticity of the transition structures. Single-point calculations were then carried out with the 3-21G set. Due to the limits of disk space availability, frequency calculations were not carried out at this level. The two endo transition structures were also determined with full geometry optimizations at the 3-21G level of theory. Single-point calculations at the 6-31G* level revealed that the relative energies of the two endo transition states were independent of whether the STO-3G or 3-21G geometries were used. The 6-31G* single-point calculations for the two exo transition states were therefore performed directly on the STO-3G geometries without prior optimization at the 3-21G level. Single-point 6-

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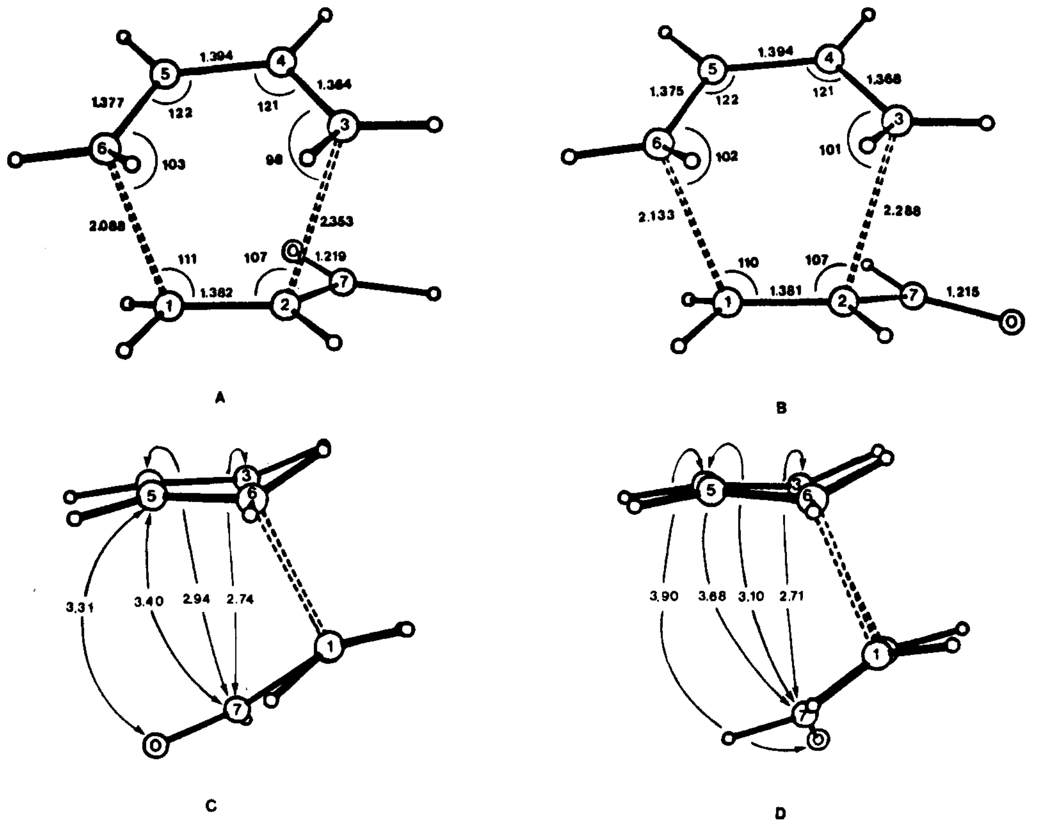

Figure 1. Front and side views of 3-21G transition structures for the butadiene–acrolein reaction.

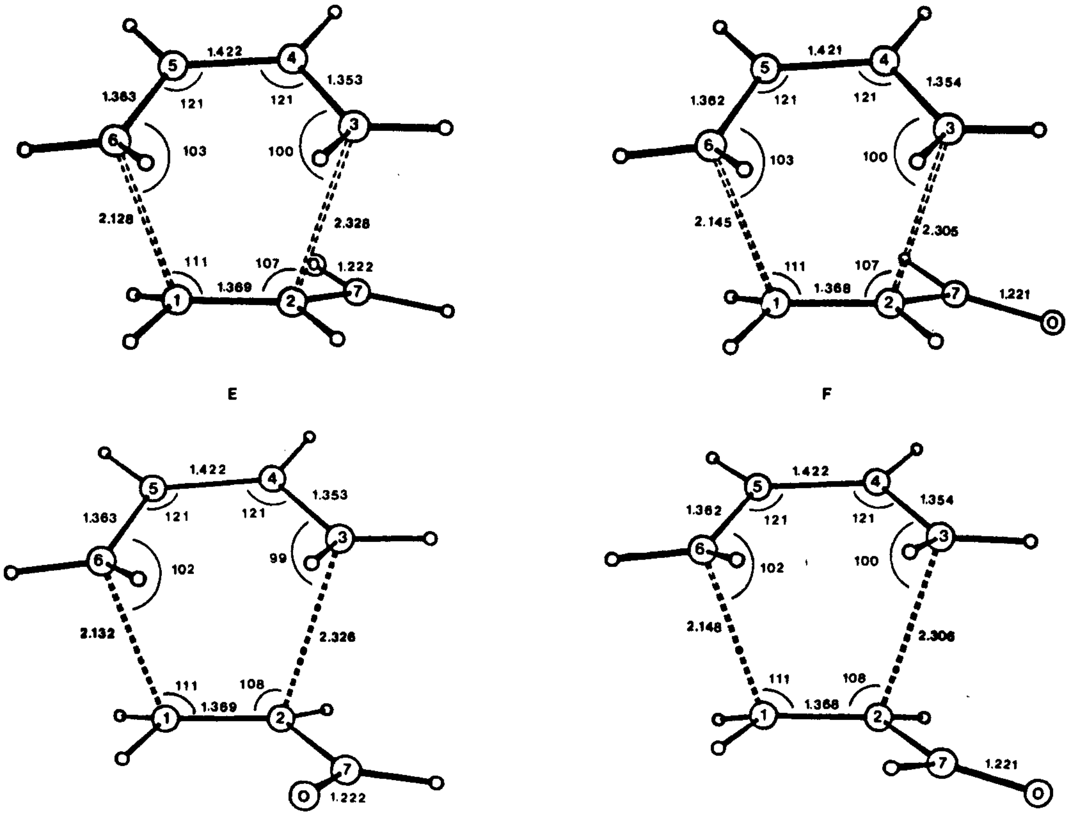

Figure 2. STO-3G geometries of transition structures for the butadiene–acrolein reaction.

31G*//STO-3G calculations were also performed on the two endo transition states for comparison purposes.

Results and Discussion

Energetics. The transition structures are shown in Figures 1 and 2, and the energetics of the reactions are presented in Table I. The experimental activation energy for the reaction of butadiene with acrolein (19.7 kcal/mol) is 18 kcal/mol lower than the STO-3G activation energy of 35.5 kcal/mol.[11] While we know that RHF calculations

Table I. Energetics of the Reactions of Butadiene and Cyclopentadiene with Acrolein[a]

	diene	dienophile	stereochem	E_a	$\Delta H^{\ddagger}$	E_a(rel)	$\Delta S^{\ddagger}$	ΔH_{rxn}
RHF/STO-3G	butadiene	*s-cis*-acrolein	endo	35.5	38.4	0.0	−46.9	
		s-trans-acrolein	endo	35.6	38.5	0.1	−47.0	
		s-cis-acrolein	exo	35.9	38.8	0.4	−46.7	
		s-trans-acrolein	exo	36.2		0.7		
6-31G*//STO-3G		*s-cis*-acrolein	endo	41.5		0.0		
		s-trans-acrolein	endo	42.2		0.7		
		s-cis-acrolein	exo	41.8		0.3		
		s-trans-acrolein	exo	43.5		2.0		
RHF/3-21G		*s-cis*-acrolein	endo	30.5		0.0		
		s-trans-acrolein	endo	32.6		2.1		−39.9
6-31G*//3-21G		*s-cis*-acrolein	endo	41.9		0.0		
		s-trans-acrolein	endo	42.5		0.6		
exptl				19.7[b]	20.7[b]		−35.4[b]	−35.6[c]
MINDO/3[d]	cyclopentadiene	*s-cis*-acrolein	endo		46.4	0.0		
		s-trans-acrolein	endo		47.1	0.7		
		s-cis-acrolein	exo		47.3	0.9		
		s-trans-acrolein	exo		47.2	0.7		
exptl				15.2[b]				
AM1–3X3 CI[e]	butadiene	acrylonitrile			12.6[f]			
		maleonitrile			15.2[f]			
		fumaronitrile			15.4[f]			
		1,1-dicyanoethylene			11.5[f]			

[a] Energies are in kcal/mol. Entropies are in eu (cal/mol·K). The total energies (au) of reactants are *s-trans*-acrolein (C_s) −188.30353 (RHF/STO-3G), −189.68988 (RHF/3-21G), −190.75947 (6-31G*//STO-3G), −190.76154 (6-31G*//3-21G); *s-trans*-butadiene (C_{2h}) −153.02036 (RHF/STO-3G), −154.05946 (RHF/3-21G), −154.91902 (6-31G*//STO-3G), −154.91961 (6-31G*//3-21G). The total energies of the transition structures are endo s-cis −341.26734 (RHF/STO-3G), −343.70076 (RHF/3-21G), −345.61236 (6-31G*//STO-3G), −345.61437 (6-31G*//3-21G); endo s-trans −341.26713 (RHF/STO-3G), −343.69736 (RHF/3-21G), −345.61128 (6-31G*//STO-3G), −345.61341 (6-31G*//3-21G); exo s-cis −341.26668 (RHF/STO-3G), −345.61188 (6-31G*//STO-3G); exo s-trans −341.26620 (RHF/STO-3G), −345.60921 (6-31G*//STO-3G). The total energy of 4-formylcyclohexene is −343.81296 (RHF/3-21G). [b] See ref 13 and 16. [c] Estimated by group additivities found in Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley and Sons, Inc.: New York, 1976. [d] Reference 22. [e] Reference 10. [f] Activation energy from reactants to the second saddle point.

will overestimate the activation energy for such reactions,[4] the experimental value is surprisingly low. The experimental value is obtained from shock tube experiments performed nearly 50 years ago, and it may not be accurate.[16] Using the 3-21G basis set[11] the activation energy is lowered to 30.5 kcal/mol, while the single-point calculation with the 6-31G* basis set[11] raises the activation to 41.9 kcal/mol. The polarization functions cause the energy of the reactants to be lowered more than that of transition structure. The entropy of activation at the 3-21G level is −46.9 eu, which is considerably more negative than the experimental value[16] of −35.4 eu. The differences here are similar to those for the parent Diels–Alder reaction of butadiene with ethylene. At various levels of theory,[4] the calculated activation entropy is −42 eu, while the two experimental values are −30 eu[17] and −41 eu.[18] It is difficult to assess the errors in calculations because of the uncertainties in experimental data. However, the RHF activation energies of various pericyclic reactions are 10–20 kcal/mol higher than experimental values,[19] so that an experimental activation energy in the range of 20–30 kcal/mol is consistent with the calculated activation energy.

In Diels–Alder reactions of normal dienes, it is generally observed that electron-withdrawing substituents on the dienophile lower the activation energies.[13] For example, the experimental activation energy for the Diels–Alder reaction of butadiene with ethylene has been measured as 27.5 and 34.3 kcal/mol,[17,18] as compared to the measured activation energy of 19.7 kcal/mol for the reation of butadiene with acrolein.[16] The same trend is seen with ab initio RHF calculations with a split-valence, or better, basis set. With the minimal STO-3G basis set, the activation energy is only lowered from 36.0 to 35.5 kcal/mol upon replacing ethylene with acrolein. With the split-valence 3-21G basis set the activation energy drops from 35.9 to 30.5 kcal/mol. According to 6-31G*//3-21G calculations, the activation energy drops from 45.9 to 41.9 kcal/mol. For these Diels–Alder reactions it is gratifying to see that ab initio RHF calculations parallel experimental substituent effects, when reasonable basis sets are used. On the other hand, the magnitude of the substituent effect is unreasonably small with the STO-3G set.

Dewar, Olivella, and Stewart have reported MNDO and AM1 studies of the Diels–Alder reaction of butadiene with several substituted cyanoethylenes.[10] Table I presents only the results obtained from the highest level of theory used in that study. The numbers presented are for the second single point corresponding to ring closure of the biradicaloid intermediate. This step was postulated to be rate-determining by the application of a 20 kcal/mol correction factor. The activation energy calculated for the parent Diels–Alder reaction is 16.6 kcal/mol.[10] The activation energies of reactions of maleonitrile (15.2 kcal/mol) and fumaronitrile (15.4 kcal/mol) with butadiene are larger than that of acrylonitrile (12.6 kcal/mol), while that of 1,1-dicyanoethylene is 11.5 kcal/mol. The estimated relative activation enthalpies for the reaction of butadiene with the series ethylene, acrylonitrile, maleonitrile, fumaronitrile, and 1,1-dicyanoethylene are 0.0, −4.0, −1.4, −1.2, and −5.1 kcal/mol. The experimental relative free energies of activation for the analogous reactions of cyclopentadiene with these dienophiles are 0.0, −6.3, −8.9, −8.9, and −12.6 kcal/mol.[10] There is considerable dis-

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agreement between the experimental trends and those derived from the AM1 calculations.[10] The authors proposed that this discrepancy results from solvation effects, and they provide a detailed rationale for why cyano groups should slow down the rates of Diels–Alder reactions, based upon solvation effects. However, there is ample evidence for related reactions that there is little influence of solvation on rates.[13] AM1 and MNDO,[10] like the one example we have by STO-3G, are in error for these substituent effects. The ab initio 3-21G or 6-31G* calculations do reproduce the experimental data observed for the formyl substituent.

Asynchronicity. The question of asynchronicity is one of essential concern in substituted Diels–Alder reactions. Whereas the transition structure for the parent Diels–Alder reaction is symmetrical[1–4] with forming CC bond lengths of 2.2 Å, the transition structure for reaction of butadiene with s-cis acrolein is necessarily unsymmetrical, and so the concerted reaction is asynchronous. The results presented in Figure 1 show this asynchronicity. The forming CC bonds lengths are 2.353 and 2.088 Å, different by 0.27 Å.

In an elegant study of secondary deuterium kinetic isotope effects on the Diels–Alder reactions of isoprene-d_0, -d_2, and -d_4 with four dienophiles—acrylonitrile, fumaronitrile, vinylidene cyanide, and methyl β-cyanoacrylate—Gajewski[20] has concluded that the reaction is not a two-step reaction with the second step rate-determining. Of particular interest to our study is the reaction of isoprene with acrylonitrile. The inverse kinetic isotope effect (KIE) observed at the β site of acrylonitrile is much more inverse than at the α site and is only half of the maximum value expected. This is indicative of an early, unsymmetrical transition state. The results are not consistent with a rate-determining transition state possessing one fully formed bond but instead indicate that each new bond is partially formed, one to a greater extent than the other, as in our calculated transition structures. The results observed for vinylidene cyanide follow the same trend. The KIE for the reaction of fumaronitrile with isoprene-d_4 was twice that with isoprene-d_2, indicating equivalent effects at both the α and β site. The KIEs for methyl β-cyanoacrylate were inverse at both bond-making sites and one-third of the maximum value. The results are consistent with a one-step reaction proceeding through a concerted pathway that is asynchronous, but has partial formation of both bonds in the transition state, not complete formation of one bond. Another recent experimental study uses rates to assess the degree of asynchronicity in Diels–Alder reactions: evidence for nonbiradicaloid transition states is reported.[21] This is precisely what is shown by the calculations on the butadiene–acrolein reaction by our RHF ab initio or Dewar's AM-1 calculations,[10] but not by UHF ab initio or AM1 with 3×3 CI.[10]

Acrolein Transition-Structure Conformation. Recently we reported calculations that support transition-state conformational hypotheses proposed to rationalize the stereoselectivities of catalyzed Diels–Alder reactions of chiral acrylates.[14] Model calculations and experimental studies of thermal Diels–Alder reactions indicate that acrylates have the s-cis conformation in the transition state.[15] Our studies of the ground-state conformational preferences of acrolein, acrylic acid, methyl acrylate, and their Lewis acid complexes indicate that s-cis conformers of acrylic acid and methyl acrylate are slightly more stable than the s-trans conformers.[14] Lewis acid complexation of these acrylates causes the s-trans conformation to become substantially more stable than the s-cis.

Acrolein itself prefers the s-trans conformation by 1.8 kcal/mol, according to 6-31G* calculations. This is in reasonable accord with the experimental 1.9–2.1 kcal/mol preference for the s-trans conformation.[22] Lewis acid complexation was found to increase this preference to 3.2 kcal/mol.[14]

Recent MINDO/3 calculations on the thermal and BF_3-catalyzed reactions of cyclopentadiene and 1-methylbutadiene with acrolein predict that the s-cis conformation of acrolein is preferred in the transition states of both types of reactions.[23,24]

The calculations that we have performed indicate that the endo cisoid transition structure A is 0.6 kcal/mol more stable than the endo transoid B at the 6-31G*//3-21G level. By contrast, the transoid conformation of acrolein is favored in the ground state by 1.7 kcal/mol at this level. Thus, there is a dramatic 2.3 kcal/mol difference between the conformational preferences of the ground-state and the transition structure. In order to understand the origin of this large relative stabilization energy of the s-cis conformation in the transition structure, we carried out single-point energy calculations on the butadiene and acrolein moieties constrained to the geometries of the transition structures A and B. The energies of the acrolein moieties were evaluated by removing the atoms of butadiene followed by the single-point calculations, without altering the transition-state geometry in any way. At the 6-31G*//3-21G level, the acrolein moiety of transition structure B is more stable than that of A by 1.7 kcal/mol. That is, acrolein distorted to the transition-state geometries has an s-trans preference that is identical with that of the ground-state energy difference, and it is only upon interaction with butadiene that the s-cis geometries become favored.

The energies of the butadiene moieties were evaluated in a similar fashion by removing the atoms of the acrolein moieties and performing single-point calculations at the 6-31G*//3-21G level. The butadiene moiety in transition structure A is favored by 1.0 kcal/mol. Analysis of the butadiene moieties in the transition states A and B show that bond lengths and bond angles are nearly identical, but the torsional angles do differ in the two transition states. This arises from the greater asynchronicity of A (see below).

The remaining 1.3 kcal/mol energy difference is due to differences in interactions between the acrolein and butadiene molecules. This is related to the greater asynchronicity of A. Perusal of Figure 1 shows that the C_2C_3 distance is 2.353 Å in A and 2.288 Å in B, while the C_1C_6 distance is 2.088 Å in A and 2.133 Å in B. The s-cis transition structure A is more asynchronous than the s-trans transition structure.

The frontier molecular orbital coefficients and energies of *s-cis-* and *s-trans*-acrolein in the ground state and in the transition-state geometries are shown in Figure 3. The coefficients of the outer part of the 6-31G* π orbitals are

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[24] (a) Branchadell, V.; Oliva, A.; Bertrân, J. *J. Mol. Struct.* (*Theochem*) **1986**, *138*, 117–120; (b) **1985**, *120*, 85–190; (c) *J. Mol. Catal.* **1986**, *35*, 39–46; (d) *Chem. Phys. Lett.* **1985**, *113*, 197–201.

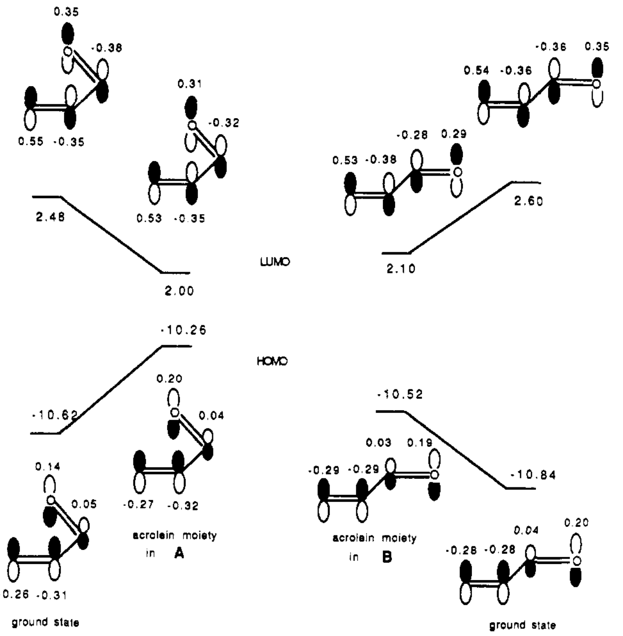

Figure 3. 6-31G*//3-21G HOMO and LUMO of acrolein in the ground-state geometries and of the acrolein moieties in the geometries of transition structures A and B. Coefficients of the heavy atoms are shown.

shown. These differ from others published for acrolein and related systems[25] because of the different calculation technique used to obtain them and because there are two coefficients for each p orbital in a split-valence basis set. For ground-state *s-trans*-acrolein, the highest occupied molecular orbital (HOMO) energy is −10.84 eV and the lowest unoccupied molecular orbital (LUMO) energy is 2.60 eV. For the ground-state conformation of *s-cis*-acrolein, the HOMO energy is higher (−10.62 eV) and the LUMO energy is lower (2.48 eV). The π coefficients of the termini of acrolein have the opposite sign in the HOMO, and consequently, overlap of the termini in the s-cis conformation results in destabilization of the HOMO. The terminal LUMO coefficients have the same sign, so that this orbital is stabilized in the s-cis conformation. In effect, *s-cis*-acrolein takes on some antiaromatic cyclic 4-electron character relative to s-trans. Since *s-cis*-acrolein has a lower energy LUMO, it should be more reactive than *s-trans*-acrolein, because there will be more stabilization upon interaction of this orbital with the HOMO of butadiene. Upon distortion to the transition-state geometries in A and B, this difference is further accentuated.

Single-point calculations were carried out on the radical anion of the acrolein moieties of structures A and B. This calculation gives an estimate of the influence of electron transfer on the conformational preference of acrolein in the transition state. At the 6-31G*//3-21G level, the s-cis radical anion is 0.8 kcal/mol more stable than s-trans. This is the result of the lower energy LUMO of the s-cis conformer of acrolein. In the transition structure, there is donation of 0.1 electron from butadiene to acrolein according to a Mulliken population analysis, and electron donation is more favorable in the cisoid transition structure.

There are also differences in the frontier molecular orbital coefficients on *s-cis-* and *s-trans*-acrolein. As shown in Figure 3, the HOMO of the acrolein moiety in A has a relatively large difference between the coefficient on C_1 (−0.27) and C_2 (−0.32). However, the coefficients on C_1 and C_2 of the acrolein moiety in B are identical, with a value of −0.29. There is also a difference between the coefficients on C_1 and C_2 in the LUMO in the different conformations. The acrolein moiety in A has coefficients of 0.53 and −0.35, a difference in absolute values of 0.18. The acrolein moiety in B has coefficients of 0.53 and −0.38, an absolute difference of 0.15. The coefficients on C_1 of the acrolein moiety in A and B are the same. The greater degree of asynchronicity of bond formation in A as compared to B can be understood by consideration of the interaction between the butadiene HOMO and the acrolein LUMO in the two transition states. The larger difference in the absolute values of the acrolein LUMO orbital coefficients in A leads directly to a larger difference in HOMO/LUMO overlap at the bond-forming positions and thus to a greater degree of asynchronicity in bond formation.

Part of the 1.3 kcal/mol preference for the s-cis conformation in the endo transition state might be a result of the larger secondary orbital interactions that can occur in the s-cis transition structure. This can arise because the oxygen is in position for stabilizing interaction in the endo transition structure. Evidence for secondary orbital interactions comes from differences in geometries of the two transition structures. In A the C_7C_3, C_7C_4, OC_5, and C_7C_5 distances are 2.74, 2.94, 3.31, and 3.40 Å, respectively, as shown in Figure 1. In B the C_7C_3, C_7C_4, OC_4, and C_7C_5 distances are 2.71, 3.10, 3.90, and 3.68 Å, respectively. The Mulliken population analysis, which gives a qualitative indicator of the amount of electron density shared by two atoms, also provides some evidence for interaction. In transition state A the OC_5 overlap density has a positive value of 0.007, indicating an attractive interaction, while the C_7C_3, C_7C_4, and C_7C_5 overlap populations are repulsive with values of −0.019, −0.004, and −0.004, respectively. However, in transition structure B the C_7C_3, C_7C_4, OC_4, and C_7C_5 overlap populations are −0.018, −0.009, 0.000, and 0.000, respectively. The values are small and only the OC_5 in A interaction is attractive. The carbonyl carbon is closer to the butadiene moiety in A than in B, which indicates that there is some attractive interactions between these groups in A.

In summary, the preference for the s-cis conformation is a result of the greater electrophilicity (as well as nucleophilicity) of the s-cis conformer and the greater secondary orbital interaction possible between orbitals on the carbonyl group and those on the diene for this conformer.

Endo Stereoselectivity. We have carried out a number of numerical experiments to determine why endo is favored, but these are unfortunately not very conclusive. Comparisons of the endo and exo transition structures were carried with the 6-31G*//STO-3G calculations, since the relative energies of the two endo transition structures were found to be the same as for the 6-31G*//3-21G calculations. The 6-31G*//STO-3G calculations predit an endo:exo ratio of 67:33, similar to the STO-3G ratio of 69:31 at 25 °C. These calculated values can be compared with the experimental results for the Diels–Alder reaction of cyclopentadiene with maleic anhydride, butadiene with maleic anhydride, and cyclopentadiene with acrolein. An endo:exo ratio of 98.5:1.5 is observed experimentally for the reaction of cyclopentadiene with maleic anhydride at 25 °C.[27] The endo:exo ratio is lowered to 85:15 for reaction of *cis,cis*-1,4-dideuterio-1,3-butadiene with maleic anhy-

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dride at 80 °C.[27] For the reaction of cyclopentadiene with acrolein, Konovalov has shown that the endo:exo ratio is 76:24,[28c] while Kobuke has demonstrated that the product ratio varies from 70:30 at 25 °C to 74:26 at 100 °C.[28d] Semiempirical calculations of the reaction of cyclopentadiene with acrolein, reported by Bertrân et al.,[23] also give an endo:exo ratio of 71:29.

Many explanations have been offered for endo stereoselectivity.[13] Woodward and Hoffmann refined Alder's rule of "maximum accumulation of unsaturation" by proposing that secondary orbital overlap favors the endo product.[29] Others have rationalized the preference by consideration of steric effects,[13] or a combination of steric effects and secondary orbital overlap.[30] Dipole–dipole effects that can be influenced by solvent polarity[31] and the geometrical relationship of the primary centers undergoing bond formation[32] have also been suggested to contribute to the observed stereoselectivity.

As noted, single-point calculations at the 6-31G*//STO-3G level are consistent with the 6-31G*//3-21G calculations, namely, that the endo cisoid acrolein transition structure is favored over the endo transoid acrolein transition structure by 0.6–0.7 kcal/mol (see Table I and Figure 2). In the exo mode of attack the s-cis conformation of acrolein is also preferred in the transition state, now by 1.7 kcal/mol. The two cisoid transition structures are similar: for example, the forming bond lengths in structures E and G are nearly identical. This 0.3 kcal/mol preference of E over G might arise from secondary orbital interactions or electrostatic and van der Waals forces. The preference of E over F can then be attributed to 0.3 kcal/mol of secondary orbital contribution and 0.4 kcal/mol of primary interactions and steric interactions. However, the 6-31G*//STO-3G calculations on structures G and H indicate a 1.7 kcal/mol preference for the exo cisoid transition structure over the exo transoid conformation, and neither of these can have secondary orbital interactions. Although the stereochemical preference is small and of vague origin, the calculated values do compare well with the experimental values for similar systems.[13,15]

On the other hand, there may not be specific interactions of the type described here. The distances between the carbonyl group and butadiene atoms are similar to those present in crystal structures of various molecular complexes. Such "charge-transfer" complexes are believed to be stabilized by electrostatic and van der Waals attractions,[26] so that specific orbital interactions such as implied by the phrase "secondary orbital interactions" are not necessary to stabilize endo transition states relative to exo.

Single-point calculations at the 6-31G* level were performed on all the butadiene and acrolein moieties of the STO-3G transition structures E–H. With transition structures E and F the results are qualitatively the same as the 6-31G*//3-21G single points of the butadiene and acrolein fragments. For example, the butadiene moiety in transition state F is disfavored as compared to the butadiene moiety in E. Single-point calculations on the exo transition structures similarly show that the butadiene moiety in H is disfavored more than the butadiene moiety in G. This again arises from the greater asynchronicity of G over H, as discussed above for the preference of A and B.

Conclusion. RHF calculations give reasonable substituent effects on activation energies and stereochemistries of the Diels–Alder reaction. The asynchronicity caused by one substituent is predicted to give a 0.3 Å difference in the forming bond lengths. The origin of the preference for the s-cis conformation of α,β-unsaturated carbonyl compounds in Diels–Alder transition states is found to be the greater electrophilicity of the s-cis conformation due to narrower FMO energy gaps than for the s-trans conformer. The slight endo preference is probably due to secondary orbital overlap interactions, although electrostatic and van der Waals forces may promote endo cycloaddition just as they stabilize molecular charge-transfer complexes.

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Registry No. 1,3-Butadiene, 106-99-0; acrolein, 107-02-8.

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