J. Am. Chem. Soc. **1989**, *111*, 9172–9176

Å versus 1.927 (3) Å). This is in accordance with the earlier observed effect that bonds adjacent to carbonyl groups are longer than those adjacent to ethylene groups. The same effect is observed when comparing r(C–Cl) in 2-chloropropenal[7] (1.723 (2) Å) and in oxalyl chloride[3] (1.745 (2) Å), and also when comparing the two carbon–chlorine distances in 2-chloropropenoyl chloride[6] (1.731 (3) Å versus 1.773 (3) Å). A general shortening has been observed in r(C=O) when comparing the bond lengths of acid halides with those for aldehydes. Halogen substitution has not, however, been found to produce a similar shortening of a carbon–carbon double bond, and the results for 2-bromopropenal confirm this.

Using the harmonic approximation, values for the torsional force constants for the two conformers may be estimated from the rms torsional amplitudes ($k = RT/\sigma^2$). The obtained values are $k_{\text{anti}} = 0.027$ and $k_{\text{syn}} = 0.022$ mdyn·Å·rad^{-1} with standard deviations of 0.012 mdyn·Å·rad^{-1}. The torsional wavenumbers corresponding to these force constants are $\omega_{\text{anti}} = 84$ ($2\sigma = 38$) cm^{-1} and $\omega_{\text{syn}} = 70$ ($2\sigma = 39$) cm^{-1}. No spectroscopic observations of these vibrations have been made.

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Registry No. 2-Bromopropenal, 14925-39-4.

Supplementary Material Available: Tables listing total intensities, final backgrounds, average molecular intensities, symmetry coordinates, and force constants (6 pages). Ordering information is given on any current masthead page.

Substituent Effects and Transition Structures for Diels–Alder Reactions of Butadiene and Cyclopentadiene with Cyanoalkenes

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Abstract: The transition structures for the reactions of butadiene with ethylene, acrylonitrile, maleonitrile, fumaronitrile, and 1,1-dicyanoethylene have been located with ab initio calculations using the 3-21G basis set. The transition structures for the reactions of cyclopentadiene with ethylene and acrylonitrile have also been located at the AM1 and 3-21G levels of theory. Relative activation energies with ab initio techniques follow the same trend as those obtained experimentally by Sauer et al. for the analogous reactions of cyclopentadiene and 9,10-dimethylanthracene with these dienophiles. Limited asynchronicity is obtained for the transition structures with unsymmetrical dienophiles.

The Diels–Alder reaction of butadiene with ethylene is a synchronous concerted reaction.[1-4] A C_s symmetrical transition structure is obtained by a variety of calculations. The calculations[5-10] that predict diradical intermediates appear to be in error. Unsymmetrical substitution will cause the transition structures of such reactions to become asynchronous, and it has been suggested that the mechanism will then involve diradical intermediates or at least biradicaloid transition structures.[5,9] We now present quantum mechanical calculations that address the role of unsymmetrical substitution upon the reaction mechanism.

The major points of interest of this study are as follows: (1) What is the degree of asynchronicity in the transition structures of the Diels–Alder reaction of butadiene and cyclopentadiene with unsymmetrically substituted cyanoethylenes? (2) Are the incorrect AM1 predictions of the trends in the activation energies for cyanoalkene Diels–Alder reactions an inherent failing of that method or do they support the biradical mechanism, as Dewar claims?[5] How do ab initio calculations perform? (3) Do Diels–Alder reactions of the more electron-rich cyclopentadiene give lower activation energies than the corresponding Diels–Alder reactions of butadiene in accordance with experimental observations,[11] and how do these transition structures vary?

Computational Method

Transition structures were obtained with Pople's GAUSSIAN 82 and 86 programs[12,13] via RHF calculations with the STO-3G and 3-21G basis sets.[14] All structures were optimized with analytical gradient methods. Single-point calculations with the 6-31G* basis set and MP2 correlation

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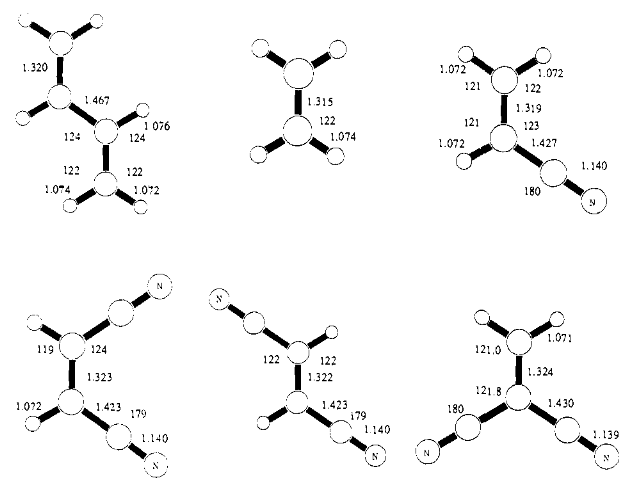

Figure 1. 3-21G optimized geometries of butadiene, ethylene, acrylonitrile, maleonitrile, fumaronitrile, and 1,1-dicyanoethylene.

energy calculations[14] were performed only on the transition structures of butadiene with acrylonitrile. In addition, three transition structures for the reactions with cyclopentadiene were located with Dewar's semiempirical AM1 method.[15]

Results and Discussion

Energetics. The geometrical features of the dienophiles are shown in Figure 1, and the transition structures are shown in Figures 2 and 3. The calculated energetic results are presented in Table I, and some comparisons of experiment and theory are given in Table II. RHF ab initio calculations predict that the activation energies are lowered by substitution with cyano groups. For reaction of butadiene with the cyanoethylenes the activation energy is lowered even further with vicinal substitution (maleonitrile and fumaronitrile), and still further by geminal substitution (1,1-dicyanoethylene). These RHF calculations also predict that the activation energy for the reaction of butadiene with ethylene is higher by 6 kcal/mol than for the reaction of cyclopentadiene with ethylene. Furthermore, the activation energy for the exo reaction of butadiene with acrylonitrile is higher by 7.4 kcal/mol than that for the corresponding reaction of cyclopentadiene with acrylonitrile. Thus, the calculations predict that the more electron-rich and *s-cis*-constrained cyclopentadiene is more reactive than butadiene. The activation energy of cyclopentadiene with the electron-poor acrylonitrile is lowered even further. These trends are precisely what is observed by experiment.[11] On the other hand, even at the MP2/6-31G*//3-21G level, the endo transition state for the butadiene–acrylonitrile reaction is slightly disfavored over the exo alternative, whereas it is slightly favored experimentally, at least for the cyclopentadiene–acrylonitrile reaction. This discrepancy is general for all cases in Table I. It is possible that the origin of the discrepancy even by MP2/6-31G*//3-21G calculations arises from the fact that CC bonds are too short by 3-21G calculations. Consequently, the endo transition structure is too crowded, and unstable, by MP2/6-31G* calculations.

We have also performed AM1 calculations on three transition structures of Diels–Alder reactions with cyclopentadiene. The activation enthalpies for reaction of cyclopentadiene with ethylene,

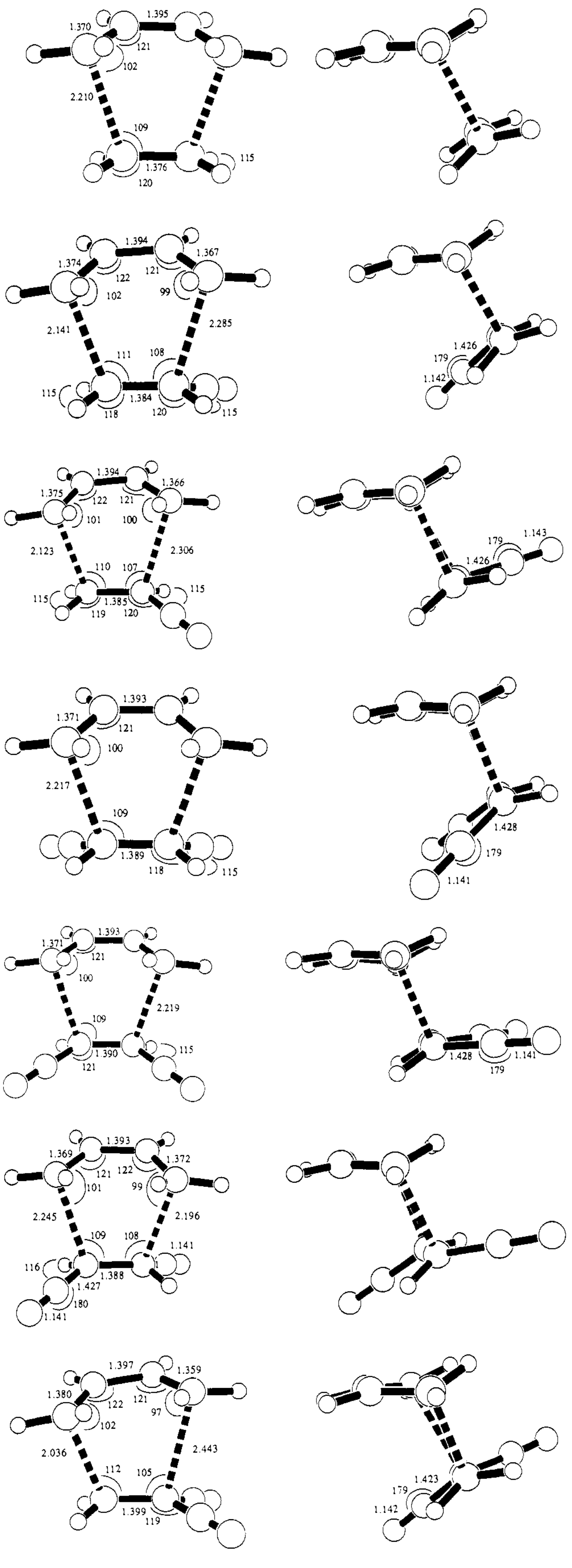

Figure 2. 3-21G optimized geometries of the transition structures of butadiene–ethylene, *endo*- and *exo*-butadiene–acrylonitrile, *endo*- and *exo*-butadiene–maleonitrile, butadiene–fumaronitrile, and butadiene–1,1-dicyanoethylene reactions.

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

theory level	diene	dienophile	stereochem	E_a	$\Delta H^{\ddagger}$	E_a(rel)	$\Delta S^{\ddagger}$	ΔH_{rxn}
AM1	cyclopentadiene	ethylene			28.5	0.0		−27.6
	cyclopentadiene	acrylonitrile	endo		29.2	+0.7		−23.0
		acrylonitrile	exo		28.8	+0.3		−23.5
RHF/STO-3G	butadiene	ethylene		36.0				
	butadiene	fumaronitrile		36.7				
RHF/3-21G	butadiene	ethylene		35.9[b]		0.0		
		acrylonitrile	endo	33.7		−2.2		
		acrylonitrile	exo	33.1		−2.8		
		maleonitrile	endo	32.2		−3.7		
		maleonitrile	exo	31.8		−4.1		
		fumaronitrile		31.2		−4.7		
		1,1-dicyanoethylene		28.5		−7.4		
	cyclopentadiene	ethylene		30.1		0.0		−32.0
	cyclopentadiene	ethylene		30.1		0.0		−32.0
		acrylonitrile	endo	26.0		−4.1		−32.6
		acrylonitrile	exo	25.7		−4.4		−33.1
RHF/6-31G*//3-21G	butadiene	ethylene		45.9		0.0		
		acrylonitrile	endo	42.9		−3.0		
		acrylonitrile	exo	42.4		−3.5		
MP2/6-31G*//3-21G	butadiene	ethylene		15.9		0.0		
		acrylonitrile	endo	13.0		−2.9		
		acrylonitrile	exo	12.9		−3.0		
AM1-3X3 CI[c]	butadiene	ethylene			16.6[e]	0.0		
		acrylonitrile	*d*		12.6[e]	−4.0		
		maleonitrile	*d*		15.2[e]	−1.4		
		fumaronitrile			15.4[e]	−1.2		
		1,1-dicyanoethylene			11.5[e]	−5.1		
experimental	butadiene	ethylene		27.5[f] (26–28)				
	cyclopentadiene	ethylene		23.7[g]		0.0		
	cyclopentadiene	acrylonitrile	endo	13.2[h] (15.2)[i]		−10.5 (−8.5)		
			exo	13.4[h]		−10.3 (−8.3)		
		maleonitrile		11.4[i]	10.8	−12.3	−35	
		fumaronitrile		12.6[i]	11.6	−11.1	−33	
		1,1-dicyanoethylene		ca. 8		ca. −16		

[a] Energies are in kcal/mol. The total energies (au) of reactants are as follows: *s-trans*-butadiene (C_{2h}) −153.02036 (RHF/STO-3G), −154.05946 (RHF/3-21G), −154.91961 (RHF/6-31G*//3-21G), −155.42069 (RMP2/6-31G*//3-21G); cyclopentadiene −191.7108 (RHF/3-21G); ethylene (D_{2h}) −77.60099 (RHF/3-21G), −78.03169 (RHF/6-31G*), −78.28410 (RMP2/6-31G*//3-21G); acrylonitrile (C_s) −168.82040 (RHF/3-21G), −169.76776 (RHF/6-31G*//3-21G), −170.29328 (RMP2/6-31G*//3-21G); maleonitrile (C_{2v}) −260.03133 (RHF/3-21G); fumaronitrile (C_{2h}) −258.17548 (RHF/STO-3G), −260.03294 (RHF/3-21G); 1,1-dicyanoethylene (C_{2v}) −260.02773 (RHF/3-21G). The total energies of the transition structures are the following: butadiene with ethylene (C_s) −231.60321 (RHF/3-21G), −232.87822 (RHF/6-31G*//3-21G), −233.67951 (RMP2/6-31G*//3-21G); *endo*-butadiene with acrylonitrile −322.82617 (RHF/3-21G), −324.61900 (RHF/6-31G*//3-21G), −325.69318 (RMP2/6-31G*//3-21G); *exo*-butadiene with acrylonitrile −322.82706 (RHF/3-21G), −324.61986 (RHF/6-31G*//3-21G), −325.69334 (RMP2/6-31G*//3-21G); *endo*-butadiene with maleonitrile (C_s) −414.03950 (RHF/3-21G); *exo*-butadiene with maleonitrile (C_s) −414.04017 (RHF/3-21G); butadiene with fumaronitrile −411.14001 (RHF/STO-3G), −414.04269 (RHF/3-21G); butadiene with 1,1-dicyanoethylene −414.08719 (RHF/3-21G); *endo*-cyclopentadiene with acrylonitrile −360.49611 (RHF/3-21G); *exo*-cyclopentadiene with acrylonitrile −360.49654 (RHF/3-21G). The total energies of the products are as follows: *endo*-5-cyanonorbornene −360.58948 (RHF/3-21G); *exo*-5-cyanonorbornene −360.59022 (RHF/3-21G). [b] Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554–556. [c] Reference 5. [d] Not reported. [e] Activation energy from reactants to the second saddle point. [f] Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198–213. The estimated E_a at 0 K is 25.1 kcal/mol. [g] Walsh, R.; Wells, J. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 52. [h] Reference 18. [i] Reference 19. [j] Reference 17.

endo-acrylonitrile, and *exo*-acrylonitrile are 28.5, 29.2, and 28.8 kcal/mol. Notably, the activation energy increases with cyano substitution, contrary to experiment, and once again the exo transition state is incorrectly predicted to be favored by a small amount.

The experimental activation energy for the reaction of butadiene with ethylene has been measured as 27.5 kcal/mol[16] and also as 24.2–26.7 kcal/mol.[17] The activation energy is lowered to 13.2 kcal/mol for the reaction of cyclopentadiene with acrylonitrile.[18] The activation energy is further lowered to 12.6 kcal/mol for the reaction of cyclopentadiene with fumaronitrile,[19,20,21] and to 11.4 for reaction with maleonitrile.[19] The activation energy for 1,1-dicyanoethylene is estimated as only 8 kcal/mol.[19] These trends are followed quite closely in the ab initio calculations on reactions with butadiene.

The 3-21G ab initio relative activation energies for the reactions of butadiene with the series of dienophiles ethylene, acrylonitrile, maleonitrile, fumaronitrile, and 1,1-dicyanoethylene are 0.0, −2.8, −4.1, −4.7, and −7.4 kcal/mol, respectively. These results can now be compared directly to the MNDO and AM1 studies of the corresponding Diels–Alder reactions of butadiene with the substituted cyanoethylenes reported by Dewar, Olivella, and Stewart.[5] Table I presents only the results obtained from the highest level of theory used in that study. The numbers presented are for the second saddle point corresponding to ring closure of the biradicaloid intermediate which is believed not to actually be a minimum.[5] The activation energy calculated for the parent Diels–Alder reaction was 16.6 kcal/mol.[5] The relative activation enthalpies

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(16) Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198–213. The estimated E_a at 0 K is 25.1 kcal/mol.

(17) Calculated from E_a of cyclohexene cycloreversion and the experimental heat of reaction: Uchiyama, M.; Tomioka, T.; Amano, A. *J. Phys. Chem.* **1964**, *68*, 1878. Tsang, W. *J. Chem. Phys.* **1965**, *42*, 1805. Tardy, D. C.; Ireton, R.; Gordon, A. S. *J. Am. Chem. Soc.* **1979**, *101*, 1508.

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(19) Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183–3207.

(20) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209–219.

(21) Borden, W. T.; Loncharich, R. J.; Houk, K. N. *Annu. Rev. Phys. Chem.* **1988**, in press.

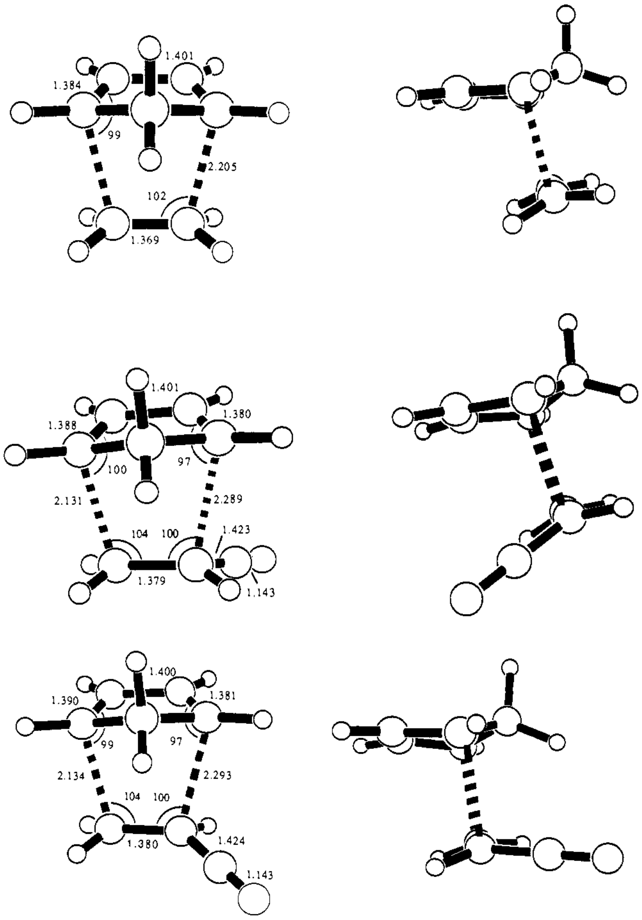

Figure 3. 3-21G optimized geometries of the transition structures of cyclopentadiene–ethylene and *endo*- and *exo*-cyclopentadiene–acrylonitrile reactions.

Table II. Comparisons of Calculated and Experimental Activation Energies

diene	dienophile	stereochem	ΔE (3-21G) − 10[a]	E_a(exptl)[b]
butadiene	ethylene		25.9	27.5 (26–28)
cyclopentadiene	ethylene		20.1	23.7
	acrylonitrile	endo	16.0	13.2 (15.2)
		exo	15.7	13.4
butadiene	acrylonitrile	endo	23.7	21[c]
		exo	23.1	
	fumaronitrile		21.2	20.6[c]
	maleonitrile	endo	22.2	19.4[c]
		exo	21.8	
	1,1-dicyanoethylene		18.5	16[c]

[a] A constant 10 kcal/mol has been subtracted from the 3-21G ΔE in order to estimate crudely the correlation energy plus zero-point energy correction. The 10 kcal/mol is the order of magnitude of these corrections for other pericyclic reactions.[21,25] [b] See Table I for the origin of these numbers. [c] These are 8 kcal/mol more than Sauer's measured activation energies for reactions of cyclopentadiene with these dienophiles. The correction factor was estimated from the calculated activation energies for the reactions of butadiene and cyclopentadiene with acrylonitrile.

for the reaction of butadiene with the series ethylene, acrylonitrile, maleonitrile, fumaronitrile, 1,1-dicyanoethylene are 0.0, −4.0, −1.4, −1.2, and −5.1 kcal/mol, respectively. The relative energies of activation for the analogous reactions of cyclopentadiene with these dienophiles are given in Table II. The experimental trends in activation energies along the series are predicted by the ab initio calculations, except for the exo/endo difficulty already described and the difference between maleonitrile and fumaronitrile. However, the AM1 3X3 CI calculations err in predicting acrylonitrile to be more reactive than the vicinal dicyanoethylenes and almost as reactive as 1,1-dicyanoethylene.[5] It should be noted that standard RHF AM1 calculations (without the CI) yield synchronous transition states, but the reactivity order with butadiene is ethylene > 1,1-dicyanoethylene, acrylonitrile > maleonitrile > fumaronitrile.[5] The authors of the semiempirical study proposed that the discrepancies with the CI results come from solvation effects, and they provide a detailed rationale for why cyano groups should retard 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.[11] This includes an experimental study by Dewar and Pyron[11c] on the reaction of maleic anhydride with isoprene that led to the following conclusion: "the rate of reaction varies little with the solvent; the total range of rates is only about 10:1." It is proposed that "cyano substituents would be expected to retard the reaction if it involved a synchronous mechanism."[5] The calculations reported here predict reasonable substituent effects and geometrical changes (see below), and there is no reason to believe that either solvation effects or asynchronicity beyond that described below is necessary to explain the experimental results.

The experimental activation energies cited above for these reactions are in some doubt. The agreement between theoretical and experimental *changes* in activation energies is only qualitative. A referee proposed that this indicates that there might be a different transition state, a diradical with one bond formed and another not, for the substituted reactions. This is certainly possible. The work of Bernardi et al. gave both biradical and concerted transition structures for the butadiene–ethylene reaction with MCSCF calculations.[1] The 4-31G calculations using four-orbital, four-electron MCSCF indicated that a very asynchronous transition structure, with one forming bond length of 1.66 Å and the other unspecified, is 2 kcal/mol above a synchronous transition structure which is very similar to the results of our calculations. As the authors have shown for the fulminic acid–acetylene reaction, and as they cite, a large MCSCF calculation and configuration interaction will further disfavor the asynchronous transition structure relative to the synchronous structure. The variable transition state, with considerable asynchronicity induced by asymmetric substituents, is supported by experimental isotope effects.[22]

Asynchronicity. Substitution of an electron-withdrawing group on the dienophile necessarily makes the transition structures asynchronous. The central issue in the theoretical studies of these reactions is the degree of asynchronicity. Dewar has maintained that multibond reactions cannot normally be synchronous.[20] His semiempirical UHF or 3X3 CI studies with AM1 predict very asynchronous structures, indeed biradicaloid geometries with only one appreciably developed bond.[5] Opposing views have recently been expressed by Borden et al.[21] MCSCF calculations performed with a sufficiently large basis set[1] agree with the RHF calculations that the reaction of butadiene with ethylene is concerted and synchronous. While much larger calculations than can currently be performed must be carried out for definitive proof, the RHF/3-21G calculations appear to capture the trends in activation energy upon substitution and are, so far, the only available calculations that do this. The substituent effects do seem to be too small.

At the 3-21G basis level, the parent Diels–Alder reaction of butadiene with ethylene is synchronous with forming CC bond lengths of 2.210 Å (Figure 2).[4] Substitution with a cyano group causes the transition structure to become asynchronous with forming CC bond lengths of 2.141 and 2.285 Å, a difference of 0.14 Å. The transition structure for the endo reaction of butadiene with maleonitrile has forming CC bond lengths of 2.217 Å, synchronous but slightly earlier than the reaction with ethylene. The transition structure for the reaction of butadiene with fumaronitrile is barely asynchronous, with forming CC bond lengths of 2.196 and 2.245 Å; the more fully formed bond is at the terminus with the endo cyano group. The 1,1-dicyanoethylene

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[22] Gajewski, J. J.; Peterson, K. B.; Kagel, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5545–5546.

transition structure is the most asynchronous of the series, with forming bond lengths of 2.036 and 2.443 Å, a difference of 0.41 Å.

The ab initio 3-21G transition structure for reaction of cyclopentadiene with ethylene has forming CC bond lengths of 2.205 Å, very slightly shorter than for the butadiene reaction. The transition structures for endo reaction of cyclopentadiene with acrylonitrile have forming bond lengths of 2.131 and 2.289 Å, a difference of 0.16 Å. It should be noted that the RHF AM1 and 3-21G results for the transition-state structures are very similar, as shown in Figure 3. The forming bonds are consistently 0.1 Å longer with AM1.

Of special interest is the fact that the asynchronous transition structures always have one bond shorter and one bond longer than the synchronous ones. The average bond length only varies from 2.210 to 2.239 Å in all of the 3-21G transition structures reported here for reactions with butadiene, and from 2.107 and 2.120 Å with cyclopentadiene.

How do these results compare with experiment? There are no direct experimental measures of transition-state distances, but in an elegant study of the secondary deuterium kinetic isotope effects on the Diels–Alder reactions of isoprene-d_0, -d_2, and -d_4 with four dienophiles, acrylonitrile, fumaronitrile, 1,1-dicyanoethylene, and methyl β-cyanoacrylate, Gajewski[22] has concluded that the reaction is not a two-step reaction with the second step rate determining but rather an asynchronous concerted process, as predicted by these calculations. 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 only half of the maximum value expected, and the inverse effect at the α position is even smaller. This is indicative of an early, unsymmetrical transition state. The results observed for vinylidene cyanide follow the same trend. The KIEs for the reaction of fumaronitrile with isoprene-d_4, were twice that with isoprene-d_2, indicating equivalent effects at both the α and β sites. 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 nearly complete formation of one bond. Results from another recent experimental study that used rate coefficients to measure the degree of asynchronicity in Diels–Alder reactions also support nonbiradicaloid transition states.[23]

Stereoselectivity. Our results show that the exo transition structures of butadiene or cyclopentadiene with acrylonitrile are more asynchronous than the endo structures. However, the difference in forming bond lengths is very small. For example, in the case of reaction of butadiene with *endo*-acrylonitrile the forming bond lengths are 2.141 and 2.285 Å. For reaction of butadiene with *exo*-acrylonitrile the forming bond lengths are 2.123 and 2.306 Å. The exo transition structure appears earlier along the reaction path and results in an activation energy that is slightly lower than that of the endo structure at all levels of theory studied. At our highest level of theory (MP2/6-31G*//3-21G), the exo transition structure for reaction of butadiene with acrylonitrile is favored by only 0.1 kcal/mol. For the reaction of cyclopentadiene with acrylonitrile, the endo configuration is favored experimentally by 0.2 kcal/mol at 30 °C in benzene.[18] At 40 °C in a variety of solvents, the endo:exo ratio is 1.1 to 2.2 with free energy differences of 0.07 to 0.5 kcal/mol.[24] Thus the calculations err in the slight preference for exo reaction. It will be interesting to ascertain the level of ab initio theory that is required to reproduce the endo selectivity.[25]

Frontier Molecular Orbitals. The rates of normal Diels–Alder reactions are increased by adding electron-withdrawing substituents to the dienophile.[11] The substituent lowers the energy of both the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) relative to ethylene. It is of interest here to examine the frontier molecular orbitals of the dienophiles ethylene, acrylonitrile, maleonitrile, fumaronitrile, and vinylidene cyanide. In proceeding along the series the energy of the HOMO is −10.33, −10.88, −11.19, −11.22, and −11.31 eV, and the energy of the LUMO is 5.08, 2.85, 1.16, 1.09, and 1.04 eV, in accord with previous deductions.[11b]

Conclusion

The present calculations show that at the ab initio RHF level, reasonable substituent effects are obtained for the activation energies of Diels–Alder reactions. The accord between ab initio theory and experiment provides a basis for confidence in the computed structures for the transition states. The asynchronicity caused by one substituent is predicted to give a small difference in forming CC bond lengths. Vicinal substitution as in the case of butadiene with fumaronitrile gives a nearly synchronous transition state. The largest asynchronicity (Δr = 0.4 Å) is predicted for geminal substitution in 1,1-dicyanoethylene. The stereoselectivity for reaction of butadiene or cyclopentadiene with acrylonitrile is predicted to favor the exo mode of reaction by very small amounts (0.1–0.3 kcal/mol), opposite to expectation from experimental data.

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Registry No. Cyclopentadiene, 542-92-7; ethylene, 74-85-1; acrylonitrile, 107-13-1; butadiene, 106-99-0; fumaronitrile, 764-42-1; maleonitrile, 928-53-0; 1,1-dicyanoethylene, 922-64-5.

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