J. Org. Chem. **1995**, 60, 4395–4398

Diels–Alder Reaction of Furan with Cyclopropenone. An ab Initio Study

Steven M. Bachrach

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received March 6, 1995®

The Diels–Alder reaction of furan with cyclopropenone is examined at the MP4SDQ/6-31G*//MP2/6-31G* level. Reactants, transition states, and products were completely optimized at the MP2/6-31G* level. Optimized structures indicate a stabilizing interaction between the ether oxygen and the carbonyl carbon makes the *exo* product the thermodynamic (*exo* favored by 6.35 kcal mol^{-1}) and kinetic (*exo* TS favored by 1.81 kcal mol^{-1}) product. On the basis of topological bond orders, the reaction follows a synchronous concerted pathway.

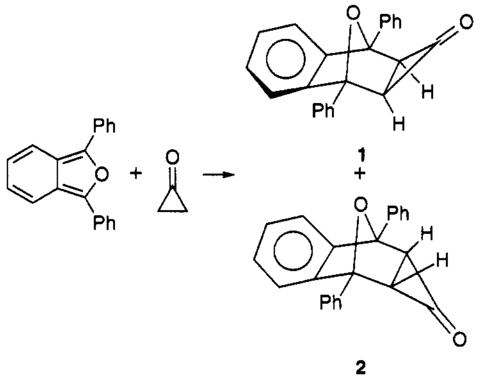
Recently, Cordes, de Gala, and Berson[1] re-examined the reaction of diphenylisobenzofuran with cyclopropenone, first described by Breslow and co-workers in 1970.[2,3] In principle, this Diels–Alder reaction should give two products (Scheme 1), the *exo* isomer **1** and the *endo* isomer **2**. Breslow reported a single, nonaromatic ^{1}H NMR peak at 2.75 ppm and suggested the *exo* isomer.

Berson et al. were able to isolate the product and obtain the crystal structure, which confirms the *exo* structure.[1] They argue that **1** is thermodynamically favored over **2** due to a stabilizing interaction between the furan oxygen and the carbonyl carbon. This distance is only 2.54 Å. Furthermore, the carbonyl carbon is not planar but rather lies 0.035 Å above the plane formed by the neighboring atoms, suggesting, as noted by Bürgi and Dunitz,[4–6] a stabilizing attractive interaction.

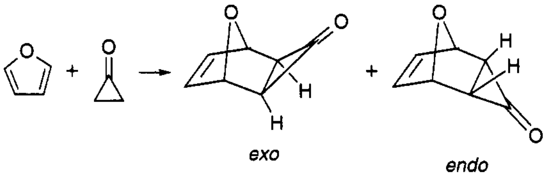
In an effort to observe the *endo* isomer, Berson et al. carried out the Diels–Alder reaction at −30 °C.[1] At this temperature the reaction is quite slow, and they detected a second (weak) NMR signal at 3.30 ppm, which slowly grows in and then diminishes as the reaction nears completion. This peak disappears rapidly upon warming above −20 °C. Based on these observations, they estimate a kinetic rate preference of about 50:1 *exo* over *endo*.

Over the past decade, substantial progress has been made in the theoretical study of Diels–Alder reactions.[7,8] We report here *ab initio* calculations of the parent analogous reaction, Scheme 2, in an attempt to understand the kinetics and thermodynamics of this interesting reaction. Our study indicates a kinetic preference for the *exo* isomer in close agreement with experiment and also supports the notion of a favorable interaction between the ether oxygen and the carbonyl carbon.

Scheme 1



Scheme 2



Computational Method

The geometries of all structures shown in Scheme 2 were optimized at the HF/6-31G* level. These structures were then confirmed to be minima (no imaginary frequencies) or transition structures (one imaginary frequency) by calculating the analytical frequencies. The two transition structures (TS) were assumed to have C_{2v} symmetry, but frequency analysis confirms this symmetry.

Previous studies of Diels–Alder reactions have indicated that activation energies at the HF level are too large and that MP2 calculations underestimate the activation energies.[9–13] However, MP3 and MP4 calculations are in quite reasonable agreement with experimental activation energy values. Therefore, we have reoptimized the geometries of all structures at MP2/6-31G* and carried out single point energy calculations at MP4SDQ/6-31G* with the MP2 geometries (MP4SDQ/6-31G*//MP2/6-31G*). While there is some evidence that ommission of triples from the MP4 calculation leads to activation barriers that are a few kcal mol^{-1} too high,[9] we were unable, due to limited computational facilities, to perform MP4SDTQ

® Abstract published in *Advance ACS Abstracts,* July 1, 1995.

[1] Cordes, M. H. J.; de Gala, S.; Berson, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 11161–11162.

[2] Breslow, R.; Ryan, G.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 988–993.

[3] Breslow, R.; Oda, M. *J. Am. Chem. Soc.* **1972**, *94*, 4787–4788.

[4] Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065–5067.

[5] Bürgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563–1572.

[6] Schweitzer, W. B.; Procter, G.; Kraftory, M.; Dunitz, D. *Helv. Chim. Acta* **1978**, *61*, 2783–2808.

[7] Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682–708.

[8] Houk, K. N.; Gonzalez, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81–90.

[9] Bach, R. D.; McDouall, J. J. W.; Schlegel, H. B. *J. Org. Chem.* **1989**, *54*, 2931–2935.

[10] Houk, K. N.; Loncharich, R. J.; Blake, J. F.; Jorgensen, W. J. *J. Am. Chem. Soc.* **1989**, *111*, 9172–9176.

[11] Jorgensen, W. L.; Lim, D.; Blake, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 2936–2942.

[12] Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 6736–6744.

[13] Bachrach, S. M. *J. Org. Chem.* **1994**, *59*, 5027–5033.

0022-3263/95/1960-4395$09.00/0

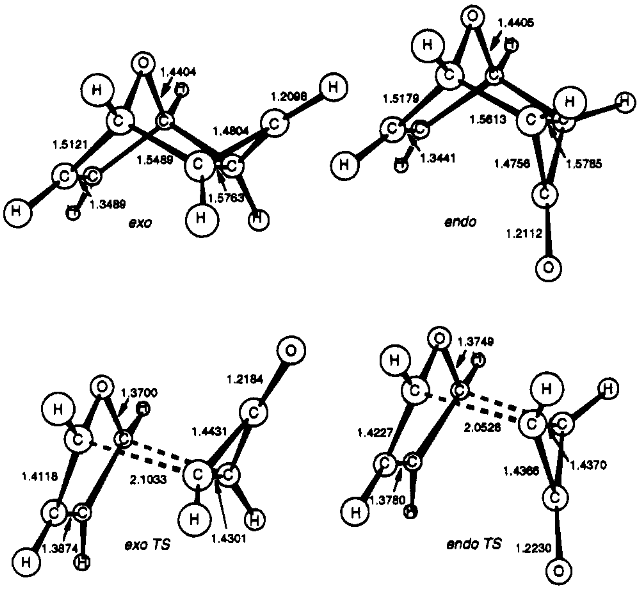
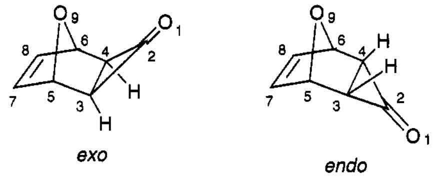


Figure 1. MP2/6-31G* optimized structure of the *endo* and *exo* products and transition structures. All distances are in angstroms.

Table 1. Selected Geometrical Parameters of the Products



		exo		*endo*	
parameter[a]	exp[b]	HF	MP2	HF	MP2
O_1-C_2	1.200	1.177	1.210	1.178	1.211
C_2-C_3	1.471	1.469	1.480	1.466	1.476
C_3-C_4	1.592	1.561	1.576	1.558	1.578
C_3-C_5	1.542	1.547	1.549	1.561	1.561
C_5-C_7	1.526	1.524	1.512	1.526	1.518
C_7-C_8	1.402	1.321	1.349	1.318	1.344
C_5-O_9	1.462	1.410	1.440	1.411	1.440
C_2-O_9	2.54	2.523	2.540	3.213	3.249
$O_1-C_2-C_3$	147.1	147.4	147.5	147.5	147.4
$C_3-C_2-C_4$	65.5	64.2	64.3	64.2	64.7
$C_2-C_3-C_4$	57.2	57.9	57.8	57.9	57.7
$C_2-C_3-C_5$	116.4	115.8	115.7	119.3	119.1
$C_3-C_5-O_9$	100.9	101.1	101.4	100.9	101.4
$C_3-C_5-C_7$	105.0	106.5	105.8	109.1	108.2
$O_9-C_5-C_7$	100.3	101.4	102.1	101.1	101.9
$C_5-C_7-C_8$	105.5	105.3	105.3	105.1	105.0
$C_5-O_9-C_6$	98.9	97.9	96.5	96.9	95.5

[a] All distances are in angstroms and angles in degrees. [b] See ref 1.

calculations. Nevertheless, we expect that triples will affect both TSs to a similar extent and therefore not change our conclusions. The MP2 structures of the *exo* and *endo* products and the TSs leading to these products are drawn in Figure 1. Selected geometrical parameters at the HF and MP2 level for the products and TSs are listed in Tables 1 and 2, respectively. The reaction energetics are listed in Table 3. Zero-point vibration energies (ZPE) have been scaled by 0.89. All calculations were performed using GAUSSIAN-92.[14]

Table 2. Selected Geometrical Parameters of the Transition Structures[a]

	exo TS		*endo* TS	
parameter[b]	HF	MP2	HF	MP2
O_1-C_2	1.1887	1.218	1.191	1.223
C_2-C_3	1.4278	1.443	1.422	1.437
C_3-C_4	1.4080	1.430	1.410	1.437
C_3-C_5	2.1098	2.103	2.094	2.053
C_5-C_7	1.4061	1.412	1.414	1.423
C_7-C_8	1.3699	1.387	1.362	1.378
C_5-O_9	1.3430	1.370	1.345	1.375
C_2-O_9	2.7025	2.714	3.342	3.344
$O_1-C_2-C_3$	150.4	150.29	150.2	149.8
$C_3-C_2-C_4$	59.1	59.4	59.5	60.0
$C_2-C_3-C_4$	60.4	60.3	60.3	60.0
$C_2-C_3-C_5$	108.7	109.6	114.3	114.1
$C_3-C_5-O_9$	92.7	92.4	89.9	90.5
$C_3-C_5-C_7$	95.6	94.8	101.4	100.6
$O_9-C_5-C_7$	108.2	108.6	108.0	108.2
$C_5-C_7-C_8$	105.7	105.9	105.7	105.8
$C_5-O_9-C_6$	104.9	104.2	104.4	103.2

[a] See Table 1 for numbering scheme. [b] All distances are in angstroms and angles in degrees.

Table 3. Reaction Energetics (kcal mol^{-1}) for Scheme 2

	exo		endo	
level	E_a	ΔE	E_a	ΔE
HF/6-31G*	37.02	−8.65	39.74	−1.70
MP2/6-31G*	7.95	−19.46	10.34	−12.85
MP3/6-31G*	19.25	−19.14	21.06	−12.72
MP4SDQ/6-31G*	19.21	−19.82	21.09	−13.34
MP4SDQ/6-31G* + ZPE/HF[a]	20.58	−15.74	22.39	−9.39

[a] ZPE calculated at HF/6-31G* and scaled by 0.89.

Topological electron density analysis[15] was performed using a locally modified version of EXTREME.[16] Of principal use in this paper is the empirical correlation between the value of the electron density at the bond critical point ($\varrho(\mathbf{r}_c)$) and bond order (n(X−Y). This correlation for C−C bonds, with densties calculated at HF/6-31G*, is given by eq 1.[17]

$$n(\text{X}-\text{Y}) = \exp[6.458[\varrho(\mathbf{r}_c) - 0.252]] \qquad (1)$$

Results

Geometry of Products. The optimized structures of the *exo* and *endo* products are drawn in Figure 1, and selected geometric parameters are listed in Table 1. The difference between the HF/6-31G* and MP2/6-31G* geometries are as expected: bond lengths are slightly longer at the correlated level and bond angles are unchanged.

We can compare the geometry of the calculated *exo* structure with the X-ray crystal structure of **1**. While this comparison involves differences in phase and substitution, the agreement between the experimental and theoretical structures is excellent. The MP2 structure agrees slightly better with experiment than does the HF structure (the rms for the bond distances is 0.034 Å for MP2 and 0.065 Å for HF). For this reason, and the fact that the MP2 structure does incorporate some of the

---

(14) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Jouhnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replonge, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. L.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN-92*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(15) Bader, R. F. W. *Atoms in Molecules – A Quantum Theory*; Oxford University Press: Oxford, 1990.

(16) Biegler-Konig, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317–328.

(17) Slee, T. S. In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH Publichers: New York, 1988; p 69.

effects of electron correlation, we will restrict our discussion to the MP2 geometries herewith.

The MP2 structure of the *exo* isomer does show a long C_3-C_4 bond, though not as long as in **1**, and a short C_2-C_3 bond. The rest of the structure reflects typical bond lengths and angles. The only disparity between the structure of **1** and the *exo* isomer is in the C_7-C_8 distance. This distance is 1.321 Å in the *exo* isomer, a typical value for a C=C bond. The corresponding bond in **1** is actually an aromatic C–C bond and is therefore longer: 1.402 Å. This fused benzene ring does not induce any other significant geometrical differences. For example, the C_5-C_7 distance is 1.526 Å in **1** and 1.5121 Å in the *exo* isomer and the $C_5-C_7-C_8$ angle is 105.5° in **1** and 105.3° in the *exo* isomer. Perhaps the most sensitive test for geometrical agreement is the C_2-O_9 distance which depends on a number of bond distances and angles. Further, this distance was used by Berson as evidence for a stabilizing interaction in the *exo* isomer. The C_2-O_9 distance of 2.54 Å is identical in **1** and the *exo* isomer.

Outside of the obvious difference in the relative orientation of the functional groups, best evidenced by the large differences in the C_2-O_9 distance (2.540 Å in *exo*, 3.249 Å in *endo*), the geometries of the *exo* and *endo* isomers are quite similar. Not including the C_3-C_5 bond, the rms difference of the remaining bond lengths is only 0.009 Å. The only significant differences between the *exo* and *endo* isomers are the C_3-C_5 bond length (1.549 Å in *exo*, 1.561 Å in *endo*) and the $C_2-C_3-C_5$ angle (115.7° in *exo*, 119.1° in *endo*).

The extent of the interaction of a nucleophile with a carbonyl carbon can be measured, among other methods, by the distance the carbon lies out of the plane formed by the three atoms to which it is bonded.[4,5] For our case, we are interested in the distance C_2 lies from the plane formed by O_1, C_3, and C_4. This distance is 0.055 Å in the *exo* isomer and 0.044 Å in the *endo* isomer. For comparison, this distance is 0.035 Å in **1**.

Geometry of Transition Structures. The structures of the two TSs are drawn in Figure 1, and selected geometrical parameters are given in Table 2. While we will focus on the MP2 geometries, we note in passing that the differences in the HF and MP2 geometries follow the usual trends, with the exception that the forming C_3-C_5 bond is shorter at MP2 than HF.

As Scheme 2 progresses from reactants to products, we expect that the C_3-C_4 and C_5-C_7 distances will lengthen as they change from double to single bonds and the C_7-C_8 distance contracts as it changes from a single to a double bond. The bond distances in the two TSs reflect these bond changes. The C_3-C_4 bond length in cyclopropenone is 1.214 Å, about 1.44 Å in the TSs, and about 1.58 Å in the products. The C_5-C_7 distance is 1.366 Å in furan, lengthening to about 1.42 Å in the TSs and 1.52 Å in the products. Finally, the C_7-C_8 distance starts at 1.428 Å in furan, contracts to about 1.38 Å in the TSs, and becomes 1.34 Å in the products.

Houk[7] has surveyed a number of transition structures for pericyclic reactions and noted that the reactive bonds tend to fall within small ranges. A forming single bond between two sp^2 carbons is between 1.95 and 2.28 Å long, and the C_3-C_5 distance in the two TSs fall within this range. Partial double bond lengths are in the range 1.34–1.42 Å. The C_7-C_8 distances are within this range and the C_3-C_4 and C_5-C_7 distances are just beyond the expected range. The bond lengths indicate greater progression toward products in the *endo* TS than in the *exo* TS.

Table 4. Bond Orders from Eq 1

bond	furan	cyclo-propene	*exo* TS		*endo* TS		*exo*	*endo*
				Δ[a]		Δ[a]		
C_2-C_3		1.31	1.26		1.29		1.15	1.16
C_3-C_4		1.80	1.33	−0.47	1.32	−0.48	0.85	0.85
C_3-C_5			0.32	0.32	0.32	0.32	0.97	0.93
C_5-C_7	1.95		1.56	−0.39	1.52	−0.44	1.08	1.08
C_7-C_8	1.29		1.69	0.40	1.75	0.46	2.04	2.06
sum	6.99		6.78		6.75		6.99	6.93

[a] Defined as the bond order in the reactant minus the bond order in the TS.

The C_2-O_9 distance is 2.714 Å in the *exo* TS and 3.344 Å in the *endo* TS. The distance that C_2 lies off the plane formed by its neighbors is 0.007 Å in the *exo* TS and 0.037 Å in the *endo* TS.

Energetics. The relative reaction energetics are listed in Table 3. The exothermicity of the reactions are underestimated at the HF level, most probably due to the inability to adequately describe the strain of the products. There is little difference in the reaction energy between the MP2, MP3, and MP4SDQ calculations, though the effect of triples configurations has not been included. We do not expect the effect of the triples to be very large, especially since the energies do not vary much at the different levels. The *exo* product is 6.35 kcal mol^{-1} lower in energy than the *endo* product at our best level of calculation.

The trends in activation energies follows our previous experience; activation energies are too large at HF, too small at MP2, and generally insensitive to higher perturbation order after MP3. Our best estimate is that the activation energy to proceed through the *exo* and *endo* TSs is 20.58 and 22.39 kcal mol^{-1}, respectively. Therefore, the *exo* TS is 1.81 kcal mol^{-1} lower in energy than the *endo* TS.

Bond Orders. Bond orders, calculated using eq 1 with values of the electron density at the C–C bond critical points, are reported in Table 4. The bond orders of the reactants and products are as expected, i.e., either one or two, except for the bonds in the three-membered ring. The C_2-C_3 bond orders are larger than unity. The C_3-C_4 bond order in cyclopropenone is 1.80, less than a typical double bond due to the strain in this bond. (This strain in this bond is apparent in the very long bond path, 1.344 Å, compared to the internuclear distance of 1.327 Å.)[15,18,19] The C_3-C_4 bond order is only 0.85 in the products.

The bond orders in the two TSs are very similar. The forming/breaking bonds all have values intermediate between the reactant and product values.

The extent of reaction can be gauged by the difference in bond orders between reactant and TS. These differences (labeled as Δ in Table 4) indicate that the bonds are made/broken to a very similar extent, ranging (in absolute value) from 0.32 to 0.48.

We have previously noted a conservation of bond order in Diels–Alder reactions.[13,20] While the reactants and products have an identical bond order sum, the sum of

---

(18) Runtz, G. R.; Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* **1977**, *55*, 3040–3045.

(19) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800–3810.

the bond orders in the TSs is only 0.25 less. This small difference may be attributed in part to the difficulty in extrapolating eq 1 to bond orders less than one.

Discussion

The experiments of Cordes, de Gala, and Berson[1] indicated that the *exo* isomer is both the thermodynamic and kinetic product of the Diels–Alder reaction shown in Scheme 1. Our calculations are in complete agreement with this result. While formation of both products is exothermic, we find that the *exo* product is 6.35 kcal mol^{-1} more stable than the *endo* product. The activation energy for producing the *exo* isomer is 20.58 kcal mol^{-1}, 1.81 kcal mol^{-1} less than the activation energy to obtain the *endo* isomer.

Berson estimated[1] that at −30 °C there is a 50-fold kinetic rate preference for formation of the *exo* product. Assuming that the entropy of formation is comparable for the two reactions, we estimate a 42-fold preference for the *exo* isomer, in excellent agreement with experiment.

Berson has argued that the *exo* product is stabilized relative to the *endo* product by two principle factors: a stabilizing, attractive electrostatic interaction between the ether oxygen (O_9) and the carbonyl carbon (C_2) and a staggered conformation about the C_3-C_5 bond, neither of which appear in the *endo* product. The optimized structures of the products supports this argument.

The C_2-O_9 distance is 2.540 Å in the *exo* product, slightly below the van der Waals contact distance. In the *endo* product this distance is 3.249 Å. Bürgi and Dunitz have argued that a measure of the interaction between an incoming nucleophile and a carbonyl carbon is the degree of pyramidalization at the carbon. A practical measure is the distance the carbon lies out of the plane formed by its bonded neighbors. We find that this distance is 0.055 Å in the *exo* product and 0.044 Å in the *endo* product.

The *endo* product is expected to have a near eclipsed conformation about the C_3-C_5 bond, while a near staggered conformation exists for the *exo* product.[21] The torsional angle defined by $H-C_3-C_5-H$ is 22.2° in the *endo* isomer and 67.7° in the *exo* isomer.

These effects manifest themselves in other structural features, principally the C_3-C_5 distance and the $C_2-C_3-C_5$ angle. To maximize the attractive interaction between C_2 and O_9 in the *exo* product, the C_3-C_5 distance and the $C_2-C_3-C_5$ angle are small, bringing the atoms close together. On the other hand, to minimize the torsional interactions about the C_3-C_5 bond in the *endo* product, the C_3-C_5 distance is quite long.

The Hammond postulate predicts that the TS for the reaction leading to the *exo* product should be earlier than for the *endo* product. The geometries of the TSs clearly support this prediction. For example, the forming C_3-C_5 length and the C_7-C_8 bond are shorter and the C_3-C_4 and C_5-C_7 are longer in the *endo* (later) TS. The bond orders (determined using the emprical formula given in eq 1) also support the Hammond prediction, though since the bond orders are so similar in the two TSs, the differences are small. The easiest difference to discern is in the bond orders of the butadiene fragment where the C_7-C_8 bond order in larger and the C_5-C_7 bond order is smaller in the *endo* (later) TS than the earlier *exo* TS.

A common assumption is that earlier TSs will have lower activation energies than later TSs. While this is not strictly true, for very exothermic reactions like Scheme 2, this assumption is valid. For Scheme 2, the earlier TS (*exo*) is lower in energy than the later (*endo*) TS. The same stabilizing effects as described for the products will apply to the TSs, but to a lesser degree since the interacting fragments are farther appart in the TSs than in the products. Therefore, we find an energy difference of 1.81 kcal mol^{-1} for the TSs, relative to 6.35 kcal mol^{-1} for the products.

Finally, we note that Scheme 2 proceeds *via* a synchronous pathway. The absolute values of the changes in bond order for the C_3-C_4, C_5-C_7, and C_7-C_8 bonds in the TSs range only from 0.39 to 0.48. The forming C_3-C_5 bond order lags somewhat behind, but this probably reflects the error in extrapolating to the partial bond region. The near conservation of bond order (which would be nearly exact if a C_3-C_5 bond order more in line with the others were used) strongly supports a synchronous concerted mechanism.

Conclusions

The *exo* product of the Diels–Alder reaction of cyclopropenone with furan is both the thermodynamic and kinetic product. The *exo* product to 6.35 kcal mol^{-1} lower in energy than the *endo* product, and the *exo* TS is 1.81 kcal mol^{-1} below the *endo* TS. This result suggests a kinetic rate ratio of 42:1, in excellent agreement with experiment. Structural analysis of the products supports Berson's[1] suggestion of a favorable interaction between the ether oxygen and the carbonyl carbon in the *exo* product coupled with an unfavorable eclipsed conformation about C_3-C_5 in the *endo* product. These effects also play a limited role in the TSs, where the *exo* TS is earlier than the *endo* TS.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research.

JO9504427

---

(20) Bachrach, S. M.; Mulhearn, D. C. In *First Electronic Computational Chemistry Conference – CDROM*; Bachrach, S. M., Boyd, D. B., Gray, S. K., Hase, W. L., Rzepa, H. S., Eds.; ARInternet: Landover, MD, 1994; in press.

(21) Kinnel, R. B.; Freeman, P. K. *Tetrahedron Lett.* **1973**, 4803–4806.