J. Am. Chem. Soc. **1998,** *120,* 12303−12309

Theoretical Study of the Concerted and Stepwise Mechanisms of Triazolinedione Diels−Alder Reactions

Jenny S. Chen, K. N. Houk,* and Christopher S. Foote*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

Received June 8, 1998. Revised Manuscript Received October 5, 1998

Abstract: The Diels−Alder (DA) reactions of triazolinedione (TAD) with *s-cis-* and *s-trans-*butadiene have been investigated theoretically with density functional theory. All geometries were fully optimized at the Becke3LYP/6-31G* level. For butadiene, the asynchronous concerted pathway dominates; only stereospecific DA products should be formed. The endo transition structure is 9.7 kcal/mol lower in energy than the exo TS; this exo-lone-pair preference comes from the electrostatic repulsion of the lone pairs on nitrogens with the π-system of butadiene. The stepwise mechanism leads to an aziridinium imide (AI) intermediate. The stepwise formation of AI intermediates is only 2.9−6.0 kcal/mol higher in energy than the asynchronous concerted mechanism. The AI intermediates can open to form a diradical or zwitterion which can react to yield nonstereospecific Diels−Alder, ene, or solvent-trapping products.

Introduction

Triazolinediones (TADs) are highly reactive neutral electrophiles, commonly used to detect unsaturation and to introduce nitrogen functionality.[1] Similar to singlet oxygen in reactivity, TADs undergo Diels−Alder (DA) reactions with dienes,[2−8] and afford [2+2] adducts[8−11] or ene products with alkenes.[5,12] Both theory and experiment agree that the mechanism of the parent DA reaction of butadiene and ethylene is concerted; the alternative stepwise diradical pathway is 2−7 kcal/mol higher in energy.[13−15] Experimentally, the few exceptions to the concerted mechanism are mainly limited to halogenated reactants[16−18] and DA reactions involving very polar components.[13,19,20] Experimental studies with TADs indicate that both concerted and stepwise pathways may occur, depending upon the diene structure.[7,8,21] We investigated these reactions with density functional theory to clarify the nature of the transition states and the occurrence of competing mechanisms. We employed methods that have proven useful in elucidating the mechanisms of TAD ene reactions with propene, 2-butenes, and tetramethylethylene.[22]

Background

Gillis and Hagarty showed that *N*-phenyl-triazolinedione (PTAD) reacts rapidly with a number of different dienes to yield DA products in high yields.[21] However, 2,5-dimethyl-2,4-hexadiene was reported not to afford any DA product; instead, an acyclic addition product containing an acetoxy group was isolated in low yield upon reaction in CH_2Cl_2. This product was suggested to arise from the trapping of a dipolar or diradical intermediate by $Pb(OAc)_4$, used to generate PTAD *in situ* from urazole. Clennan and Earlywine investigated the reactions of PTAD and MTAD (the *N*-methyl derivative) with electron-rich 1,4-di-*tert*-butoxy-1,3-butadienes.[8] The expected DA products were obtained in high yields except with the *Z,Z* isomer. Formation of an aziridinium imide (AI) intermediate was suggested, but no direct experimental evidence was obtained.

Parallel results were observed in a detailed investigation of PTAD reactions with 1,3-butadiene, (*Z,Z*)-, (*Z,E*)-, and (*E,E*)-2,4-hexadiene, and 2,5-dimethyl-2,4-hexadiene by Jensen and Foote.[7] Butadiene, (*E,E*)-, and (*Z,E*)-2,4-hexadiene all react with PTAD to give DA products with expected stereochemistry in high yields in CH_2Cl_2 (Figure 1). In the more sterically hindered dienes, such as (*Z,Z*)-2,4-hexadiene and 2,5-dimethyl-2,4-hexadiene, a mixture of products in addition to the DA products was obtained, including methanol trapping adducts in MeOH

---

[1] Moody, C. J. *Adv. Heterocycl. Chem.* **1982**, *30*, 1 and references therein.

[2] Sauer, J.; Schröder, B. *Chem. Ber.* **1967**, *100*, 678.

[3] Scharf, H.-D.; Plum, H.; Fleischhauer, J.; Schleker, W. *Chem. Ber.* **1979**, *112*, 862.

[4] Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384−6385.

[5] Cheng, C. C.; Seymour, C. A.; Petti, M. A.; Greene, F. D.; Blount, J. F. *J. Org. Chem.* **1984**, *49*, 2910−2916.

[6] Atasoy, B.; Balci, M. *Tetrahedron* **1986**, *42*, 1461−1468.

[7] Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 6376−6385.

[8] Clennan, E. L.; Earlywine, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 7104−7110.

[9] von Gustorf, E. K.; White, D. V.; Kim, B.; Hess, D.; Leitich, J. *J. Org. Chem.* **1970**, *35*, 1155.

[10] Pasto, D. J.; Chen, F. T. *Tetrahedron Lett.* **1973**, 713.

[11] Adam, W.; Griesbeck, A.; Klärner, F.-G.; Schröer, D. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 989−990.

[12] Orfanopoulos, M.; Smonou, I.; Foote, C. S. *J. Am. Chem. Soc.* **1990**, *112*, 3607 and references therein.

[13] Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779 and references therein.

[14] Houk, K. N.; Gonzalez, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81 and references therein.

[15] Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036 and references therein.

[16] Bartlett, P. D.; Mallet, J. J.-B. *J. Am. Chem. Soc.* **1976**, *98*, 143.

[17] Victor, M. *J. Org. Chem.* **1974**, *39*, 3179, 3181.

[18] Bartlett, P. D.; Montgomery, L. K.; Seidel, B. *J. Am. Chem. Soc.* **1964**, *86*, 616.

[19] Little, J. C. *J. Am. Chem. Soc.* **1965**, *87*, 4020.

[20] Gompper, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 312.

[21] Gillis, B. T.; Hagarty, J. D. *J. Org. Chem.* **1967**, *32*, 330.

[22] Chen, J. S.; Houk, K. N.; Foote, C. S. *J. Am. Chem. Soc.* **1997**, *119*, 9852.

10.1021/ja982050y CCC: $15.00

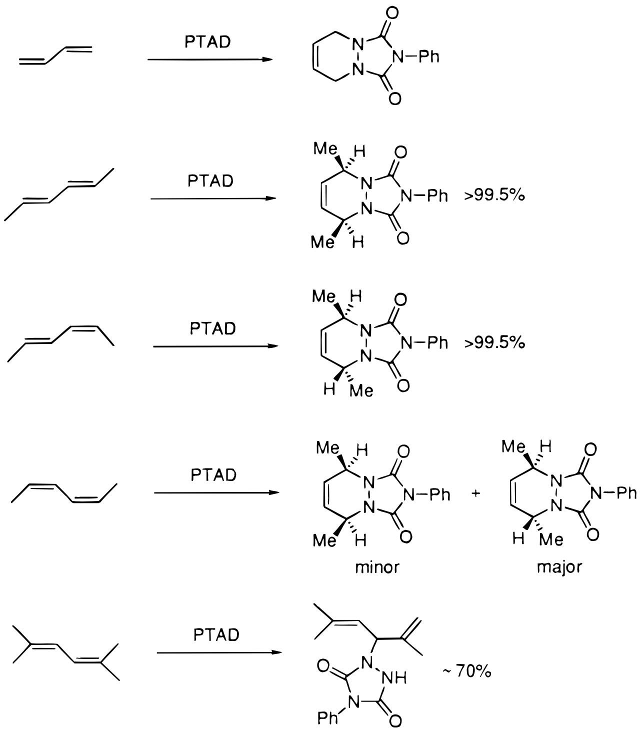


Figure 1. *N*-phenyl-triazolinedione (PTAD) reactions with dienes in CH_2Cl_2.[5]

(Figure 2) and ene products. Methanol adducts were not only obtained from 2,5-dimethyl-1,4-hexadiene and (*Z*,*Z*)-2,4-hexadiene but also from the less sterically hindered (*Z*,*E*)-2,4-hexadiene, suggesting the existence of an intermediate in this case as well. Low-temperature NMR studies with (*Z*,*Z*)-2,4-hexadiene gave evidence for an unstable diazetidine which isomerizes on warming to a mixture of the DA and ene products. A stepwise mechanism involving the initial formation of an AI intermediate which subsequently opens to a 1,4-zwitterion was proposed by the authors.[7]

AI intermediates similar to those proposed in these studies have been observed spectroscopically by low-temperature NMR by several groups.[23−25] Ab initio calculations on TAD ene reactions with alkenes using both RHF/6-31G* and Becke3LYP/6-31G* methods also found a stepwise mechanism with an AI intermediate.[22]

Computational Methodology

Density functional theory was used to explore the potential energy surface for the reaction of TAD with *s-cis-* and *s-trans*-butadiene. DFT has been used with excellent results previously in several studies of pericyclic reactions,[26] including the parent DA reaction.[15,27,28] Calculations were performed with GAUSSIAN94.[29] The Becke3LYP hybrid functional, consisting of the nonlocal exchange functional of Becke's three-parameter set[30] and the nonlocal correlation function of Lee, Yang, and Parr,[31] along with the 6-31G* basis set[32] were used in all calculations. All structures were fully optimized, and frequency calculations were performed to determine the nature of each stationary point. For transition structures, intrinsic reaction coordinate (IRC) calculations were used to follow reaction pathways.[33,34] The CHELPG method was used to calculate the atomic charges on the basis of electrostatic potentials.[35,36]

Table 1. Calculated Relative Energies (kcal/mol) for the Triazolinedione Reaction with 1,3-Butadiene

molecule	B3LYP/ 6-31G*	Δ*S* (eu)	Δ*G* (298 K)[a]
concerted asychronous			
TS **1** − endo	5.5	−42.2	19.8
TS**2** − exo	14.7	−41.3	28.5
concerted synchronous, second-order saddle points			
SOSP **3** - endo	6.6	−47.6	21.9
SOSP **4** − exo	14.9	−46.8	29.8
stepwise			
s-cis-anti			
TS **5**	12.0	−40.7	25.8
AI **6**	5.2	−40.6	20.4
s-trans-syn			
TS **7**	9.3	−41.1	22.7
AI **8**	1.5	−44.0	17.2
s-trans-anti			
TS **9**	10.3	−41.6	23.8
AI **10**	2.4	−44.4	18.3
diradical intermediates			
s-trans **11**[b]	8.8	−39.3	22.2
s-cis **12**[b]	11.1	−34.5	23.7

[a] Free energies are Becke3LYP relative energies corrected for zero-point energy, thermal energy, and entropy at 298 K. [b] UB3LYP.

Results and Discussion

The various possible mechanisms for the reaction of butadiene with TAD are summarized in Figure 3. The concerted transition state may be synchronous or asynchronous, or the reaction may involve AI or zwitterion intermediates.

Concerted Asynchronous Pathway. For the DA reaction of TAD and 1,3-butadiene, both the endo (**1**) and exo (**2**) concerted transition structures were located (Figure 4). The relative energies (Δ*E*) and the free energies (Δ*G*) are summarized in Table 1. The endo TS **1** is 9.2 kcal/mol lower in energy than the exo TS **2**. Both structures are highly asynchronous. In TS **1**, the forming C1−N1 bond is 0.67 Å shorter than the C2−N4 bond. This large degree of asynchronous character is unusual in both all-carbon and hetero DA calculations.[37,38] In DA calculations of butadiene with vinylborane, ethynylborane, and ethynyldichloroborane, asynchronous concerted transition states were predicted, where the difference in the two forming C−C bonds is 0.4−0.5 Å.[38] There is significant twisting between butadiene and TAD, and the TAD ring is tilted

---

(23) Poon, T. H. W.; Park, S.; Elemes, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1995**, *117*, 10468.

(24) Squillacote, M.; Mooney, M.; De Felippis, J. *J. Am. Chem. Soc.* **1990**, *112*, 5364−5365.

(25) Nelsen, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 5548−5549.

(26) Wiest, O.; Houk, K. N.; Black, K. A.; Thomas, B., IV. *J. Am. Chem. Soc.* **1995**, *117*, 8594.

(27) Jursic, B.; Zdravkovski, Z. *J. Chem. Soc., Perkin Trans. 2* **1995**, *311*, 1223.

(28) Barone, V.; Arnaud, R. *Chem. Phys. Lett.* **1996**, *251*, 393.

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Lantham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94 (Revision C.2)* Gaussian, Inc.; Pittsburgh, PA, 1995.

(30) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(31) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(32) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(33) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(34) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 2435.

(35) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.

(36) Chirlian, L. E.; Francl, M. M. *J. Comput. Chem.* **1987**, *8*, 894.

(37) McCarrick, M. A.; Wu, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *58*, 3330.

(38) Leung, S. W.; Singleton, D. A. *J. Org. Chem.* **1997**, *62*, 1955 and references therein.

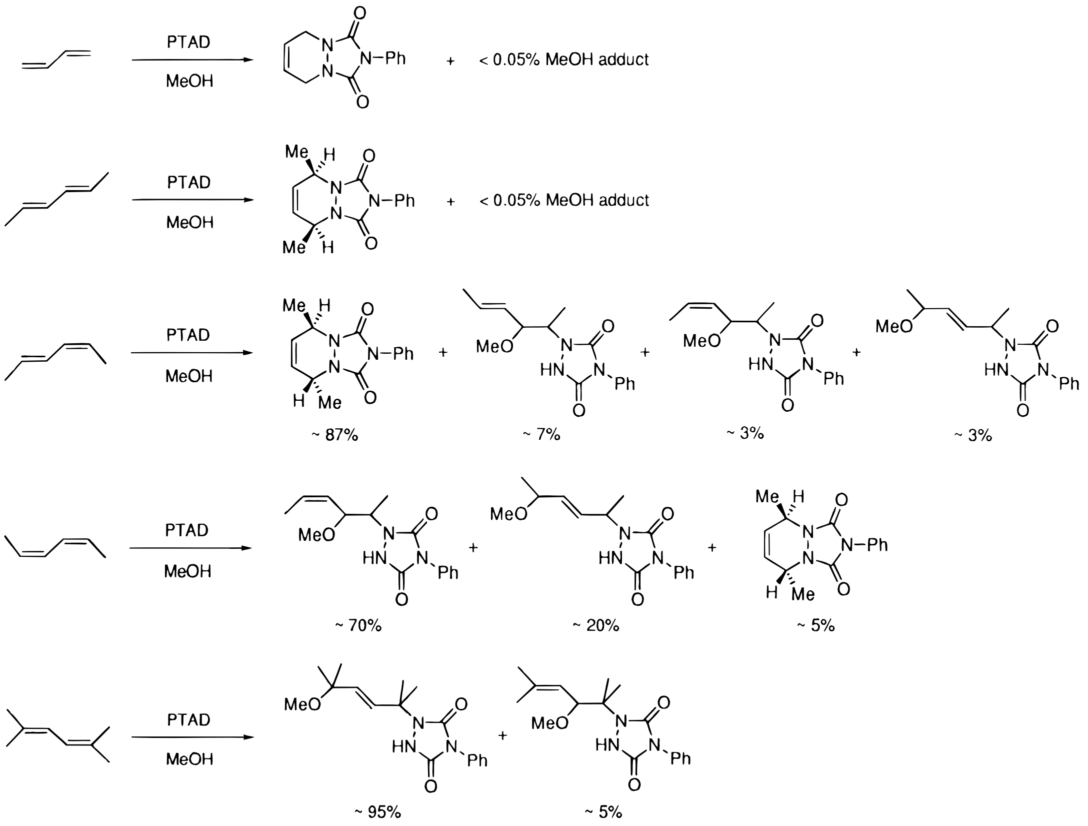


Figure 2. *N*-phenyl-triazolinedione (PTAD) reactions with dienes in MeOH.[5]

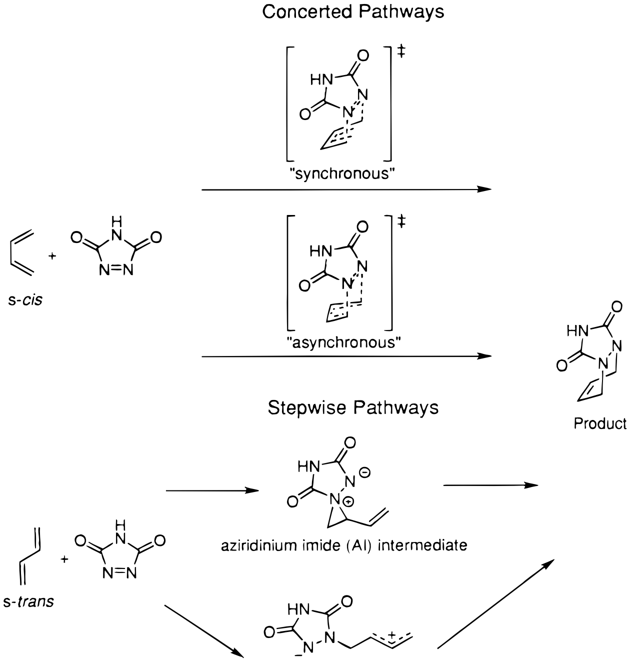


Figure 3. Possible reaction mechanisms for triazolinedione Diels−Alder reactions with 1,3-butadiene.

almost ~40° relative to the plane of butadiene. The TAD ring and the butadiene fragments are quite asymmetric in the transition state, that is, the N1−C bond of the TAD ring is 0.037 Å longer than the N2−C bond, and the corresponding C−N3 bonds differ by 0.025 Å. Also, the C1−C2 bond in the butadiene fragment is 0.026 Å longer than the C3−C4 bond. The CHELPG charges indicate that N1 has a larger negative charge than N2 since the former is more tightly bonded to butadiene. The carbons in the TAD ring also have different charges. In butadiene, the carbon with the shorter C−N bond (C1) is more negative than the other carbon terminus (C4). The differences observed in bond lengths and the CHELPG charges for the TAD ring and the butadiene fragment indicate that TS **1** has some zwitterionic character.

The structural features of TS **1** are also found in the exo TS **2** but to a much lesser degree since TS **2** is less asynchronous. The forming C−N bonds differ by 0.38 Å in this case, and there is almost no twisting of the TAD and butadiene fragments. The separation of charges is also present in TS **2**.

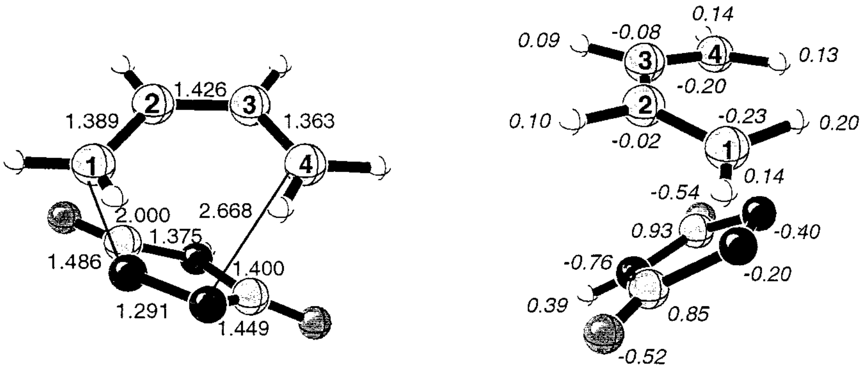
TS **1** and TS **2** are very similar to the transition states calculated for the DA reaction of butadiene and *cis*-diazene, both in terms of geometry and energetics.[37,39] The difference in energy of 9.2 kcal/mol observed here is comparable to the 11.6 kcal/mol for *cis*-diazene, and both preferences can be attributed to electrostatic interactions. In the exo transition structures, the lone pairs on the two nitrogens are positioned endo with respect to the butadiene π-system, causing direct electrostatic repulsion with the π-system of butadiene. The endo structure has little TAD lone pair repulsion with the diene π-system. The preference for endo transition structures (exo lone pairs) is also found in calculations with other aza-dienophiles, for example in butadiene with formaldimine, *N*-methylformaldimine, and nitrosyl hydride.[37] In a recent study of the DA reaction of SO_2 with butadiene and piperylene, an endo preference for the transition state was also evident but to a lesser degree.[40,41] Compared with alkene dienophiles, the magnitude of the endo preference predicted with TADs is considerably larger. In the DA reaction of isoprene or butadiene

---

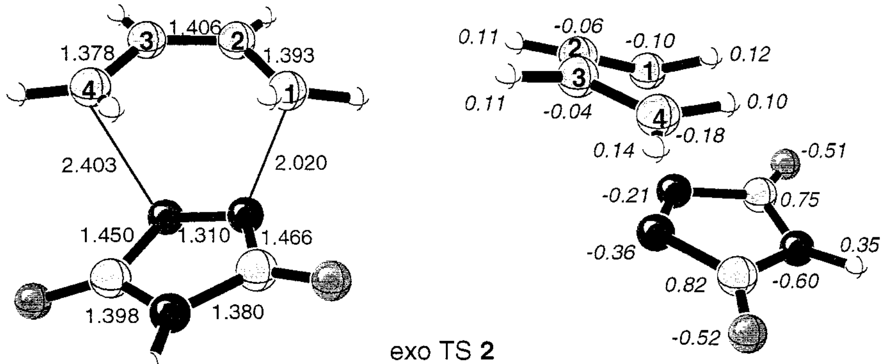
[39] McCarrick, M. A.; Wu, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1499.

[40] Suarez, D.; Iglesias, E.; Sordo, T. L.; Sordo, J. A. *J. Phys. Org. Chem.* **1996**, *9*, 17 and references therein.

[41] Beno, B.; Zipse, H.; Houk, K. N.; Vogel, P., unpublished results.

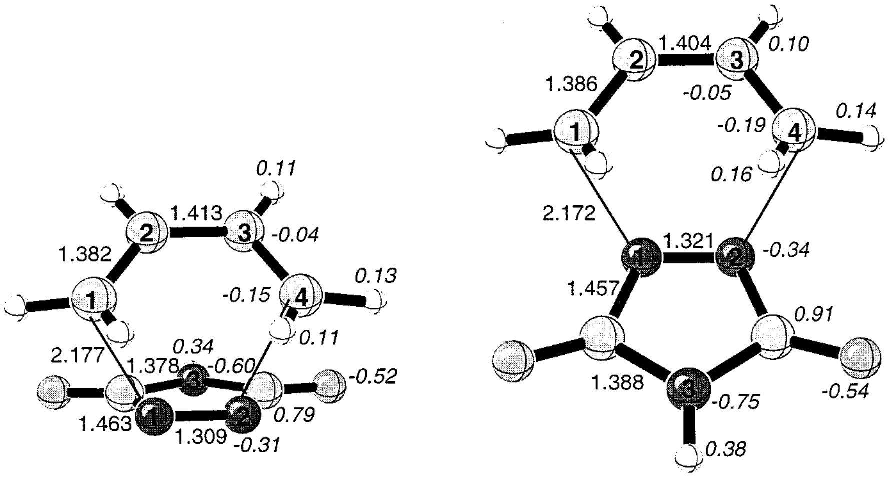


endo TS **1**
$\Delta E^{\ddagger}$ = 5.5 kcal/mol



exo TS **2**
$\Delta E^{\ddagger}$ = 14.7 kcal/mol

Figure 4. Becke3LYP/6-31G* optimized concerted asynchronous transition structures for the Diels–Alder reaction of triazolinedione with 1,3-butadiene. Bond lengths are in angstroms (Å), and CHELPG charges are italic.



endo SOSP **3**
$\Delta E^{\ddagger}$ = 6.6 kcal/mol

exo SOSP **4**
$\Delta E^{\ddagger}$ = 14.9 kcal/mol

Figure 5. Becke3LYP/6-31G* optimized concerted synchronous second-order saddle points for the Diels–Alder reaction of triazolinedione with 1,3-butadiene.

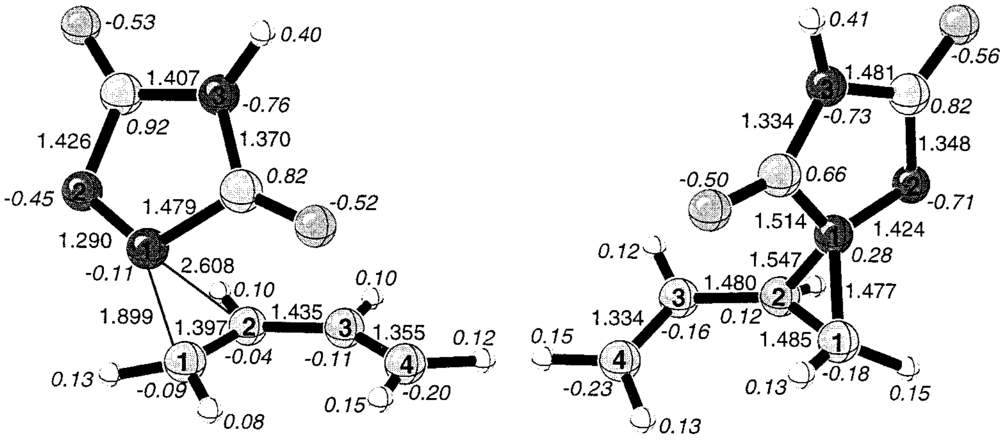
with maleic anhydride, both the calculated and experimental $\Delta\Delta G^{\ddagger}$ were only ~1.2 kcal/mol.[42,43]

Concerted Synchronous Pathway. In attempts to find a concerted synchronous pathway, endo TS **1** and exo TS **2** were constrained to have C_s symmetry and were reoptimized. Only second-order saddle points, endo TS **3** and exo TS **4**, were located (Figure 5). The preference for endo transition structures, with the lone pairs on nitrogen exo to butadiene, still dominates with an energy difference of 8.3 kcal/mol between TS **3** and TS **4**. Constraining the system to C_s symmetry vs C_1 symmetry destabilizes the endo TS by 1.1 kcal/mol and the exo TS by only 0.3 kcal/mol. The potential surface is very flat in the region of the transition structure with respect to this asynchronous motion.

---

(42) Beno, B.; Houk, K. N.; Singleton, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 9984.

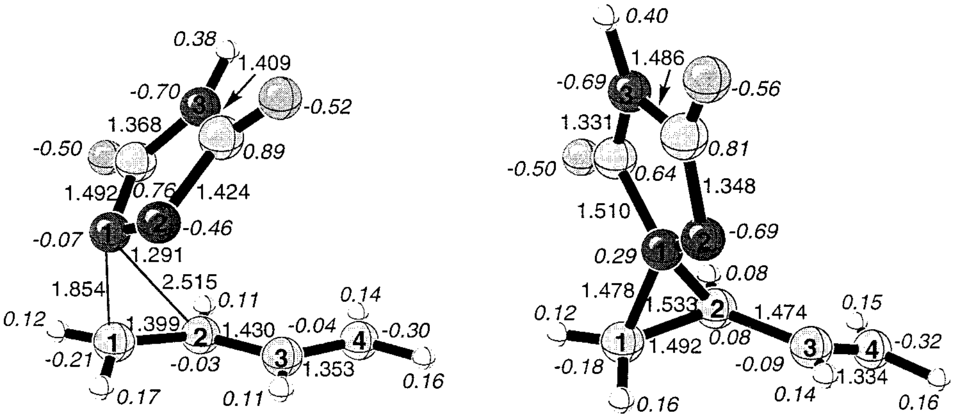
(43) Stephenson, L. M.; Smith, D. E.; Current, S. P. *J. Org. Chem.* **1982**, *47*, 417.



s-*cis*-anti TS **5**
$\Delta E^{\ddagger}$ = 12.0 kcal/mol

s-*cis*-anti AI **6**
ΔE = 5.2 kcal/mol

Figure 6. Becke3LYP/6-31G* optimized stepwise s-cis-anti transition structure and aziridinium imide (AI) intermediate for the Diels−Alder reaction of triazolinedione with 1,3-butadiene.



s-*trans*-syn TS **7**
$\Delta E^{\ddagger}$ = 9.3 kcal/mol

s-*trans*-syn AI **8**
ΔE = 1.5 kcal/mol

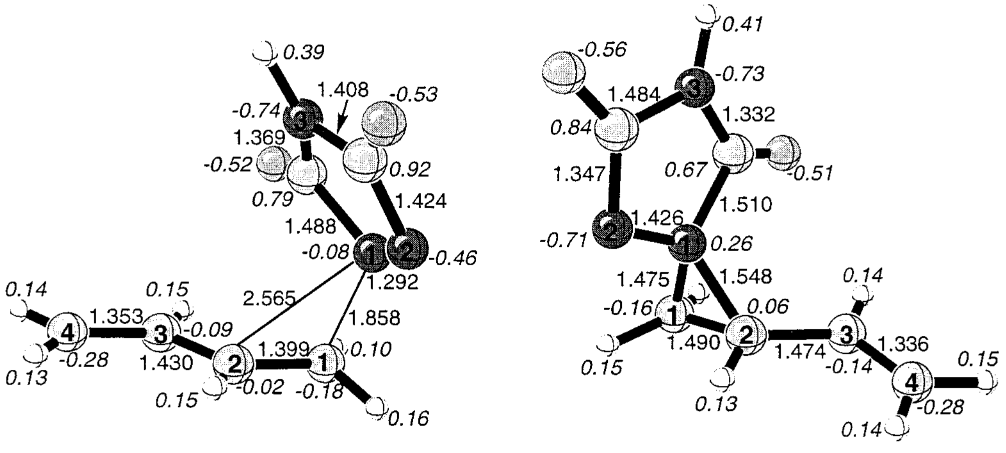
Figure 7. Becke3LYP/6-31G* optimized stepwise s-trans-syn transition structure and aziridinium imide (AI) intermediate for the Diels−Alder reaction of triazolinedione with 1,3-butadiene.

Stepwise Mechanism with Formation of AI Intermediates. We previously reported the formation of AI intermediates in the ene reactions of alkenes.[22] Both *s-cis-* and *s-trans*-butadiene can form AI intermediates with TAD. Depending on the orientation of the C3−C4 double bond on butadiene with respect to N2 of the TAD ring, both syn (N2 and C3−C4 double bond on the same side) and anti (opposite side) AI intermediates are possible. Stepwise transition structures leading to the *s-cis-anti* AI intermediate (TS **5**) as well as both of the *s-trans-syn* (TS **7**) and *s-trans-anti* (TS **9**) AI intermediates were located (Figures 6−8). Efforts to find the *s-cis-syn* AI intermediate were unsuccessful, since the concerted pathway yielding the DA product dominates for this conformation of the butadiene and TAD.

All three transition structures are quite similar in geometry. They are all highly asynchronous, with one C−N bond nearly formed, whereas the other C−N bond distance is over 3.0 Å. The forming C1−N1 bond is ~0.05 Å longer in TS **5** than in TS **7** and TS **9**, indicating a slightly earlier transition state. TS **5** is also lower in energy than the others by 1.2 and 2.3 kcal/mol, respectively. The tilting of the TAD ring relative to the butadiene plane observed in TS **1** is found in all three transition structures here. In addition, the bond lengths in the butadiene and TAD fragments are highly asymmetric, similar to those in TS **1**. For example, the C−N1 and C−N2 bonds in the TAD ring differ by 0.053−0.068 Å in TS **5**, **7**, and **9**, a larger difference than that in TS **1**. Charge separation of the two nitrogens and the carbons on the TAD ring is also greater in these three transition structures. The higher degree of zwitterionic character in TS **5**, **7**, **9** compared with that in the concerted TS **1**−**4** is consistent with the stepwise nature of the transition states.

Following the intrinsic reaction coordinate showed that all three transition structures led to AI intermediates. The corresponding AI intermediates are shown in Figures 7−9; these are 6.8−7.9 kcal/mol lower in energy than the transition states for their formation. The AI intermediates are less asymmetric than the transition states; the C1−N1 bond is ~1.48 Å, while the C2−N bond is ~1.55 Å. There is considerable charge buildup on N1 and N2, and the TAD ring is quite asymmetric. The two C−N3 bond lengths differ by ~0.16 Å in all three AI intermediates.

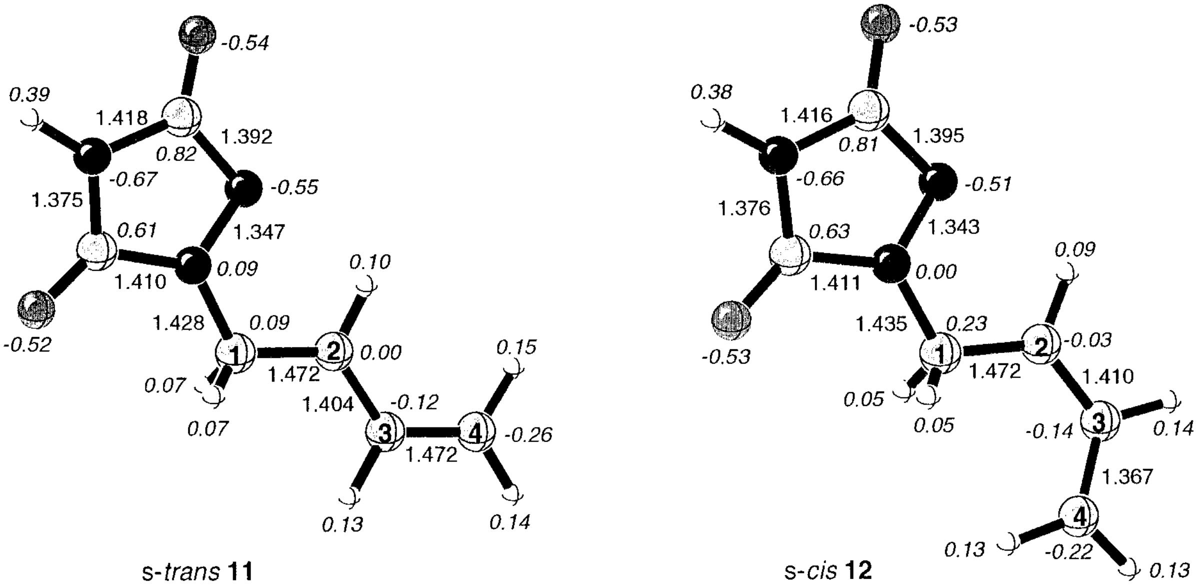
None of the three AI intermediates can form DA product without first either C−N or C−C bond rotation to form the *s-cis-syn* AI intermediate, where N2 of TAD is in the right orientation to attack C4 of butadiene. Efforts to locate such an



s-*trans*-anti TS **9**
$\Delta E^{\ddagger}$ = 10.3 kcal/mol

s-*trans*-anti AI **10**
ΔE = 2.4 kcal/mol

Figure 8. Becke3LYP/6-31G* optimized stepwise s-trans-anti transition structure and aziridinium imide (AI) intermediate for the Diels–Alder reaction of triazolinedione with 1,3-butadiene.



s-*trans* **11**
ΔE = 8.8 kcal/mol

s-*cis* **12**
ΔE = 11.1 kcal/mol

Figure 9. UBecke3LYP/6-31G* optimized *s-trans* and *s-cis* diradical intermediates for the Diels–Alder reaction of triazolinedione with 1,3-butadiene.

AI intermediate only lead to the DA product, suggesting a very small or no barrier for this second step to take place. This finding is similar to that in the parent DA reaction calculations where attempts to find the syn–gauche diradical led only to product formation.[15,44]

The highly substituted dienes such as 2,5-dimethyl-2,4-hexadiene are sterically prohibited from reaching the s-cis conformation. This prohibition should also apply to the AI intermediates. These dienes, after forming the AI intermediate, must go through some type of additional intermediate to yield the corresponding Diels–Alder and ene products. A zwitterionic or diradical intermediate was proposed.[7,8,21] To locate this type of intermediate, one of the C–N bonds of the AI intermediate was rotated such that the N1,N2 on the TAD ring and C1,C2 on the butadiene are in the same plane. The structure was then fully optimized.

Two acyclic intermediates, *s-trans* and *s-cis*, were located with unrestricted B3LYP calculations. These structures, **11** and **12**, have energies of 8.8 and 11.1 kcal/mol, respectively (Figure 9). Frequency calculations confirmed that both of the intermediates are minima. They are much higher in energy than the corresponding AI intermediate, but slightly lower in energy than the stepwise transition states to form AI intermediates. Both intermediates are planar, with respect to the N2–N1–C1–C2 dihedral angle. Compared with the AI intermediate, the N1–C1 bond in both structures is shortened to ~1.43 Å, indicating tighter bonding. The C3–C4 bond is lengthened. CHELPG charges show that N2 is now less negatively charged, while N1 loses some positive charge to become nearly neutral. In the butadiene fragment, C1 becomes positively charged. Taking the charges of the C and attached hydrogens together, C2H and $C4H_2$ are slightly positive, but the overall charges are more characteristic of diradical intermediates. Indeed, the unrestricted B3LYP calculations have $S^2 = 1.0$ in both cases, characteristic

---

(44) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 7478.

of diradical species. This species is expected to become more zwitterionic in solution.

The relative energies (ΔE), entropies (ΔS), and free energies (ΔG) for the system are summarized in Table 1. For the DA reactions of PTAD and *t*-BuTAD with 4,5-dimethylene-1,3-dioxolanes and 2,3-diethoxy-1,3-butadiene, the experimental activation enthalpies ($\Delta H^{\ddagger}$), entropies ($\Delta S^{\ddagger}$), and free energies ($\Delta G^{\ddagger}$) are 7.5−11.8 kcal/mol, −24.9 to −33.3 eu, and 16.1−19.7 kcal/mol, respectively.[3] The calculated values here for $\Delta E^{\ddagger}$ (5.5−12.0 kcal/mol), $\Delta S^{\ddagger}$ (−40.7 to −42.2 eu), and $\Delta G^{\ddagger}$ (19.8−25.8 kcal/mol) are in qualitative agreement with the experimental data.

Comparisons of the relative energies (ΔE) for the concerted and stepwise pathways show that the stepwise transition structures (**5**, **7**, **9**) are 3.8−6.5 kcal/mol higher in energy than the concerted TS **1**. Comparisons of the free energies (ΔG) lower this difference to 2.9−6.0 kcal/mol. Both are qualitatively in the same range as the 2−7 kcal/mol difference found in the parent DA reaction. For dienes where the s-cis conformation is feasible, calculations indicate that the concerted pathway dominates. The energy preference (ΔG) for the concerted (TS **1**) over the stepwise (TS **5**) pathway is 6.0 kcal/mol. Also, both the *s-cis-anti* AI **6** and the *s-cis* **12** intermediates are considerably higher in energy than TS **1**, making the stepwise pathway very unfavorable. These findings are in agreement with the experimental studies, where the dienes that are not sterically prohibited to be in the s-cis conformation all yield Diels−Alder products with the retained stereochemistry.[7,8,21]

For the dienes that are too sterically hindered to achieve a s-cis conformation, the concerted pathway is not possible. Calculations for butadiene indicate that the stepwise pathway is only 2.9−4.0 kcal/mol (ΔG) higher than the concerted transition state for *s-cis*-diene. Thus, the formation of an AI intermediate for this type of diene is favored. The AI intermediate can either react to give the ene product directly[22] in appropriately substituted cases or open to form diradical or zwitterionic intermediates where isomeric Diels−Alder products and ene product can be obtained. This mechanism explains the experimentally observed mixture of Diels−Alder and ene products.[7,8,21] The formation of the AI intermediate can also account for the solvent trapping studies, where MeOH can either add directly to the AI intermediate or trap the subsequent zwitterionic intermediate to give rise to various adducts.[7] The *s-trans-syn* AI such as 8 could rotate about the C2−C3 bond and collapse to form the Diels−Alder adduct.

The results obtained here with butadienes serve as a qualitative model. Additional substitution would lower the energies of both the stepwise transition structures and the corresponding AI intermediates substantially.[12,22,45] In TAD ene reaction calculations, the difference in energy between the first transition state and the corresponding AI intermediate decreases from ∼7.0 kcal/mol in *trans*-butene to ∼3.3 kcal/mol in tetramethylethylene.[22] Thus, for the substituted dienes studied experimentally, the energetics of a stepwise mechanism via AI intermediates would be even more favorable than for butadiene.

Conclusions

Both the concerted and stepwise mechanisms for TAD Diels−Alder reactions with *s-cis-* and *s-trans*-butadiene have been investigated at the Becke3LYP/6-31G* level. For dienes where the s-cis conformation is readily achieved, the concerted pathway dominates, and only stereospecific Diels−Alder products are formed. This is the case in the experimental studies for the less substituted dienes. For the concerted pathway with butadiene, only asychronous transition structures were located. The endo TS is favored over the exo TS by 9.7 kcal/mol (ΔG). This huge preference comes from the electrostatic repulsion of the lone pairs on nitrogens with the π-system of butadiene in the exo TS.

When the dienes are highly substituted and too sterically hindered to be in the s-cis conformation, the stepwise mechanism becomes favored. For butadiene, the stepwise pathway is only 2.9−4.0 kcal/mol higher in energy than the concerted asychronous mechanism. The stepwise transition structures lead to AI intermediates that are 5.5 kcal/mol lower in energy. The AI intermediate can either give ene product directly if there is an alkyl group cis to the AI nitrogen, or open up to form a diradical, or in solution, a zwitterion, which can scramble stereochemistry before closing to the Diels−Alder adduct, or be trapped by solvent to yield different products.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research and the UCLA Office of Academic Computing for computer time.

JA982050Y

---

(45) Houk, K. N.; Williams, K. C.; Mitchell, P. A.; Yamaguchi, K. *J. Am. Chem. Soc.* **1981**, *103*, 949.