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Diels–Alder Reactions of Aza- and Phospha-1,3-butadienes with Ethylene. An ab Initio Study

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The Diels–Alder (DA) reactions of ethylene with 1,3-butadiene, (*Z*)-1-aza-1,3-butadiene, (*E*)-1-aza-1,3-butadiene, 2-aza-1,3-butadiene, (*Z*)-1-phospha-1,3-butadiene, (*E*)-1-phospha-1,3-butadiene, and 2-phospha-1,3-butadiene were examined using ab initio calculations. All structures, including the transition structures, were completely optimized at HF/6-31G* and MP2/6-31G* with single-point energies evaluated at MP4SDQ. Electron correlation beyond MP2 is needed to obtain reasonable activation energies, but the HF- and MP2-optimized structures are only marginally different. The activation energies for the DA reactions of the phosphabutadienes are small (20–28 kcal mol^{-1}) and these reactions are very exothermic (about −43 kcal mol^{-1}). In contrast, the DA reactions of the azabutadienes are less exothermic and have larger activation barriers. These results are consistent with frontier molecular orbital theory and experiments. The diastereomeric reactions of the (*E*)- and (*Z*)-1-aza-1,3-butadienes have activation barriers that differ by 3.27 kcal mol^{-1}, which is attributed to the buildup of lone-pair–π-bond repulsion during the DA reaction of the *Z* isomer. This lone-pair effect is smaller in the 1-phospha-1,3-butadiene case because the phosphorus lone pair, having large s-character, is less diffuse than the nitrogen lone pair. The degree of synchronicity of these reactions is discussed with the aid of electron density analysis.

Perhaps the most widely used, versatile, and studied reaction in organic chemistry is the Diels–Alder cycloaddition. The ability to create two new σ-bonds, potentially set four stereocenters, and predict the regio- and stereochemical outcome using orbital symmetry considerations makes the Diels–Alder (DA) reaction the ideal tool for the construction of rings. It is somewhat surprising that exploitation of this methodology for preparing heteocycles is a relatively recent development.

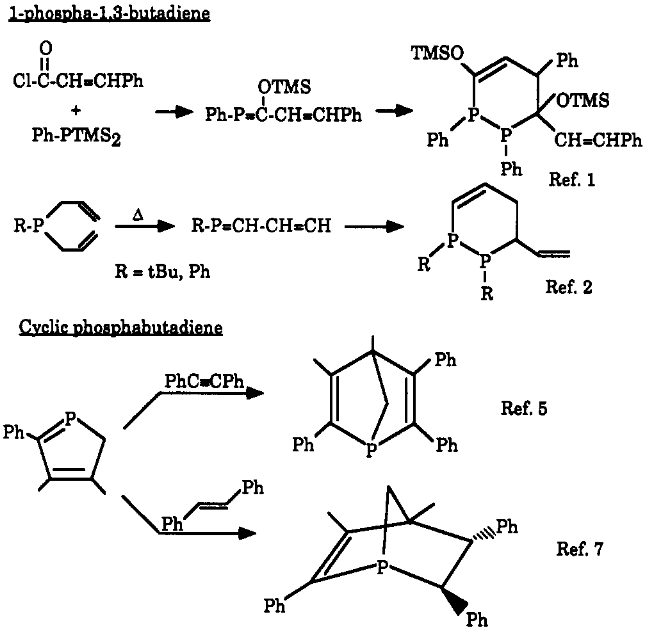
In this paper, we employ ab initio calculations to understand the course of the Diels–Alder cycloaddition involving aza- and phospha-1,3-butadienes as the diene reactant. Complete optimizations of all transition structures at very high theoretical levels indicate that these reactions are concerted and follow frontier orbital theory. Reaction barriers are estimated to be comparable to the prototypical Diels–Alder reaction: ethylene + 1,3-butadiene → cyclohexene. These calculations strongly suggest that further development of pericyclic reactions involving heteroatoms may be quite fruitful.

Background

(1) Experimental Motivations. While phosphaalkenes are a relatively new class of organic compound, a number of phosphabutadienes have been prepared. The use of phosphabutadienes in Diels–Alder reactions is, however, very limited. Appel has described the preparation of a series of 1-phospha-1,3-butadienes, which were not isolated, but inferred from the products.[1] These products suggested that a [4 + 2] dimerization of the phosphabutadiene had occurred. Martin and Ocando-Maravez prepared two 1-phosphabutadienes having no substituents on the carbons; these also rapidly dimerized via a [4 + 2] path and were identified solely on the basis of this product (Scheme I).[2] It is well known that phosphaalkenes will undergo a [2 + 2] dimerization unless bulky substituents are present to hinder this process.[3]

Appel also prepared two 2-phospha-1,3-butadienes which were isolated and characterized.[1] These dienes do not dimerize and, when exposed to cyclopentadiene, undergo a [4 + 2] reaction as the *dienophile* component.

Scheme I



On the other hand, phosphabutadienes contained within a ring will readily undergo Diels–Alder chemistry.[4] Mathey's group has pioneered the [4 + 2] chemistry of phospholes; a couple of examples are shown in Scheme I.[5–8]

The lack of DA chemistry of acyclic phosphabutadienes may be attributable to one of many factors. The DA reaction may be thermodynamically unfavorable. The activation barrier may be very large. The butadiene fragment of the DA reaction must be in the s-cis conformation. Appel[1] suggested that the bulky substituents on the phosphabutadienes may preclude the s-cis conformer. We

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[1] Appel, R.; Knoch, F.; Kunze, H. *Chem. Ber.* **1984**, *117*, 3151–3159.

[2] Martin, G.; Ocando-Mavarez, E. *Heteroatom Chem.* **1991**, *2*, 651–654.

[3] (a) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731–744. (b) Appel, R. *Pure Appl. Chem.* **1987**, *59*, 977–982. (c) Markovski, L. N., Romanenko, V. D. *Tetrahedron* **1989**, *45*, 6019–6090.

[4] Markl, G.; Lieb, F.; Martin, C. *Tetrahedron Lett.* **1971**, 1249–1252.

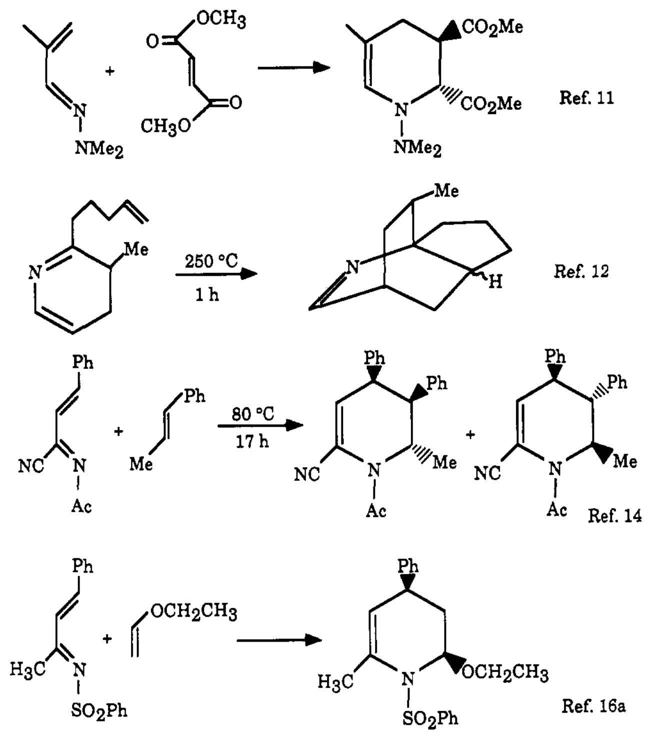
[5] Mathey, F.; Mercier, F.; Charrier, C. *J. Am. Chem. Soc.* **1981**, *103*, 4595–4597.

[6] de Lauzon, G.; Charrier, C.; Bonnard, H.; Mathey, F. *Tetrahedron Lett.* **1982**, *23*, 511–514.

[7] Le Goff, P.; Mathey, F.; Ricard, L. *J. Org. Chem.* **1989**, *54*, 4754–4758.

[8] Mathey, F. *Acc. Chem. Res.* **1992**, *25*, 90–96.

Scheme II

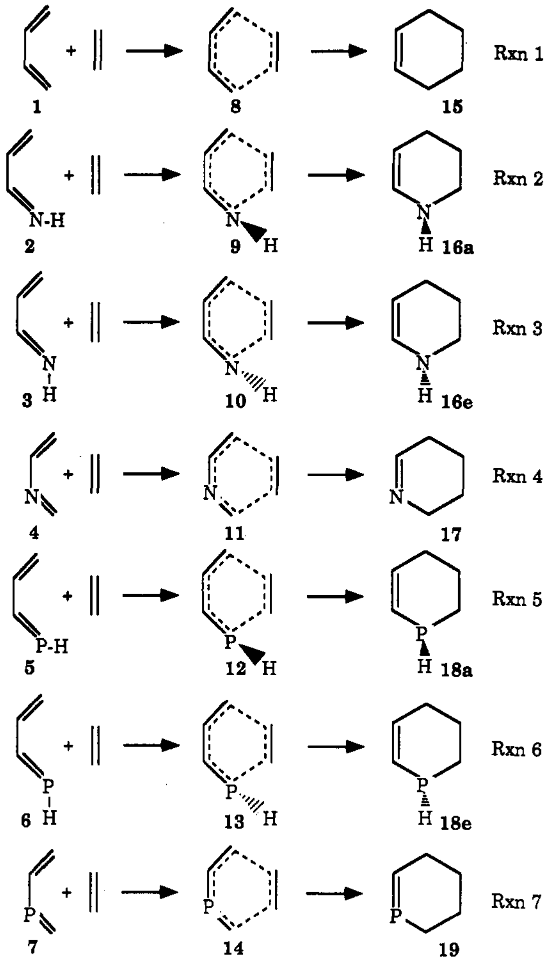


explored the rotational surfaces of mono- and diphosphabutadienes and found them to have typical rotational barriers.[9] There is no intrinsic electronic reason to forbid access to the necessary s-cis conformation. We report here studies addressing the first two factors: the activation and reaction energies of the DA reactions of phosphabutadiene with ethylene.

For comparison purposes, the chemistry of azabutadienes is relevant. The use of azabutadienes as the diene fragment of the Diels–Alder reaction has been reviewed by Boger and Weinreb.[10] They argued that the slow development of azabutadiene Diels–Alder chemistry (besides the difficulty in preparing these reagents) was the electrophilic character of the azabutadiene. This requires the inverse demand DA reaction, which is accelerated by electron-withdrawing substituents on the azabutadiene. However, the normal demand DA is the more commonly employed method, using very electrophilic dienophiles and azabutadienes having electron-donating substituents. Boger and Weinreb[10] list a number of examples of both 1-aza- and 2-aza-1,3-butadienes in DA reactions. A couple of examples are shown in Scheme II.[11,12]

Since Boger and Weinreb's review, a few additional examples of azabutadiene DA reactions have appeared. A promising approach is the use of N-acyl-α-cyano-1-aza-1,3-butadienes, developed by Teng and Fowler (see Scheme II).[13,14] They find the intramolecular DA prefers the exo approach of the dienophile, but the intermolecular DA prefers the more usual endo approach. The mechanism for this reaction appears to be concerted, having a single transition state. The nature of the TS depends on the substituents: it can be either dipolar or diradical. An alternative approach is the development of inverse electron demand DA where electron-withdrawing groups are placed on the N of 1-aza-1,3-butadienes.[15,16] Excellent yields and a strong preference of the endo product are noted.

Scheme III



The calculations presented in this paper will address the thermodynamic properties of the DA reaction involving both 1-aza- and 2-aza-1,3-butadienes with ethylene. These results will be compared with the phosphorus analogues and the prototype DA reaction.

(2) Theoretical Motivations. The prototype DA reaction (1,3-butadiene + ethylene → cyclohexene) has been well studied by theoreticians. Even though this reaction has been understood since the development of orbital symmetry rules,[17] controversy still remains within the theoretical community concerning the exact nature of the TS. All ab initio calculations (both at the HF[18-20] level and at post-HF[21-23] levels) locate a symmetric TS that is syn-

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[9] Bachrach, S. M.; Liu, M. *J. Am. Chem. Soc.* **1991**, *113*, 7929–7937.

[10] Boger, D. L.; Weinreb, S. M. *Hetero Diels-Alder Methodology in Organic Synthesis*; Academic Press, Inc.: San Diego, 1987.

[11] Serckx-Poncin, B.; Hesbain-Frisque, A.-M.; Ghosez, L. *Tetrahedron Lett.* **1982**, *23*, 3261–3264.

[12] Hasan, I.; Fowler, F. W. *J. Am. Chem. Soc.* **1978**, *100*, 6696–6699.

[13] Teng, M.; Fowler, F. W. *Tetrahedron Lett.* **1989**, *30*, 2481–2484.

[14] Teng, M.; Fowler, F. W. *J. Org. Chem.* **1990**, *55*, 5646–5653.

[15] Boger, D. L.; Kasper, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 1517–1519.

[16] (a) Boger, D. L.; Corbett, W. L.; Curran, T. T.; Kasper, A. M. *J. Am. Chem. Soc.* **1991**, *113*, 1713–1729. (b) Boger, D. L.; Curran, T. T. *J. Org. Chem.* **1990**, *55*, 5439–5442. (c) Boger, D. L.; Corbett, W. L.; Wiggins, J. M. *J. Org. Chem.* **1990**, *55*, 2999–3000.

[17] Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

[18] Brown, F. K.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 4609–4612.

[19] Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554–556.

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

[21] Bernardi, F.; Bottoni, A.; Robb, M. A.; Field, M. J.; Hillier, I. H.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1051–1052.

[22] Bernardi, F.; Bottoni, A.; Field, M. J.; Guest, M. F.; Hillier, I. H.; Robb, M. A.; Venturi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3050–3055.

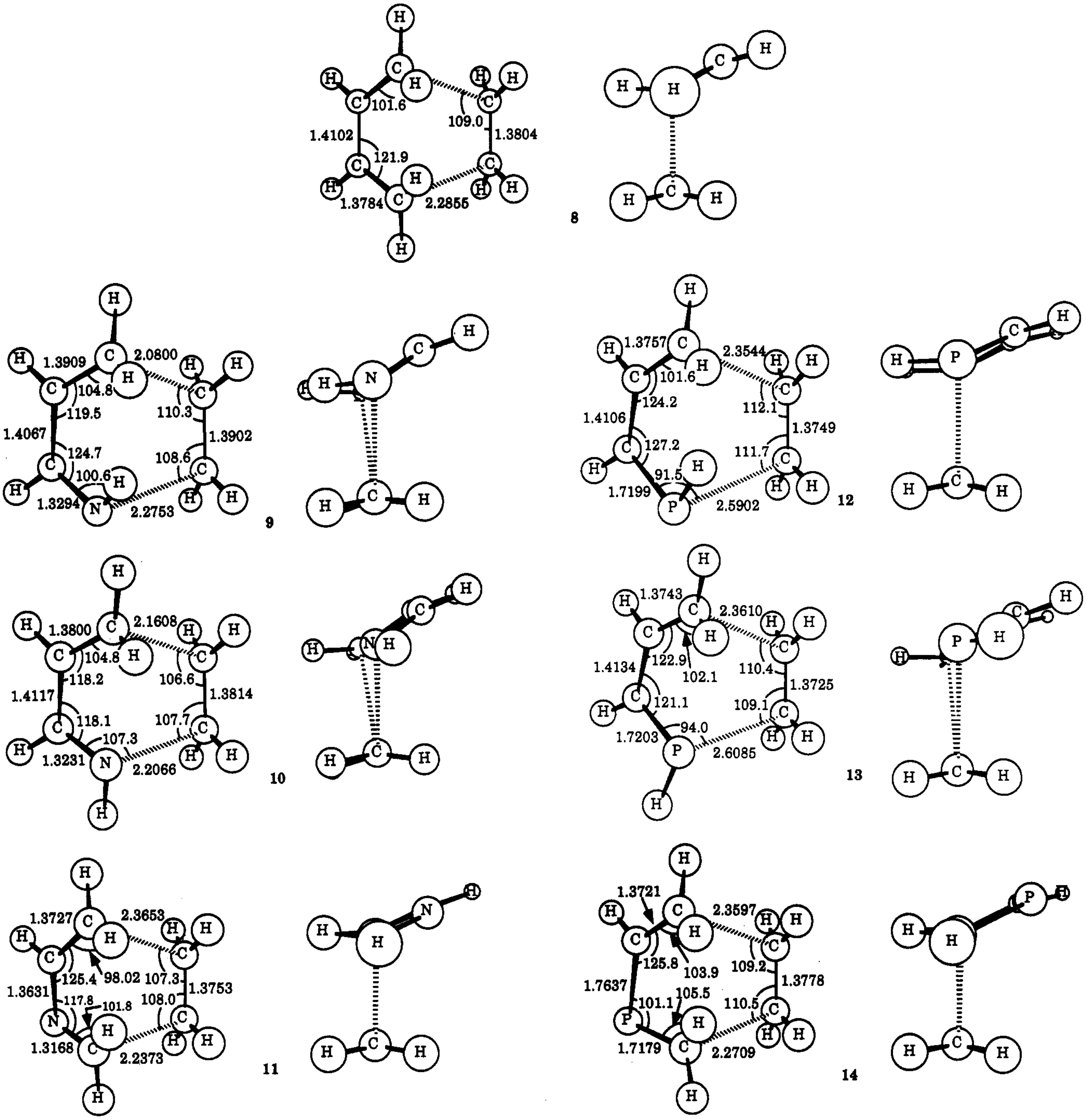

Figure 1. MP2/6-31G* optimized geometries of the transitions structures 8–14 in a top and side view. All distances are in angstroms and all angles are in degrees.

chronous. MINDO/3 calculations locate an asynchronous TS.[24,25] Dewar found that AM1 predicts a synchronous TS, but argues that this is an artifact of the RHF method.[26] Houk claims that the semiempirical calculations inordinately bias the results by inherently favoring diradicals and that the very large-scale CI calculations (which lead to the synchronous TS) offer a well-balanced electronic description.[19,20,27]

No theoretical studies of the DA reactions of phosphabutadienes have been reported. The transition structure for the DA reaction of *anti*-1-aza-1,3-butadiene with ethylene at STO-3G and 3-21G was obtained by Tran Huu Dau et al.[28] Since the C4⋯C5 distance was found to be 0.052 Å shorter in this TS than in the TS of the prototype DA reaction, these authors claim that the TS for the azabutadiene reaction is later.

Houk recently published an ab initio study of the DA reaction of butadiene with formaldimine and diazene.[29] The reaction with formaldimine is concerted but asynchronous. Of note is the stereochemistry of this reaction.

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

[24] Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 5650–5659.

[25] Dewar, M. J. S.; Griffin, A. C.; Kirchner, S. *J. Am. Chem. Soc.* **1974**, *96*, 6225–6226.

[26] Dewar, M. J. S.; Olivella, S.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1986**, *108*, 5771–5779.

[27] Caramella, P.; Houk, K. N.; Domelsmith, L. N. *J. Am. Chem. Soc.* **1977**, *99*, 4511–4514.

[28] Tran Huu Dau, M. E.; Flament, J.-P.; Lefour, J.-M.; Riche, C.; Grierson, D. S. *Tetrahedron Lett.* **1992**, *33*, 2343–2346.

[29] McCarrick, M. A.; Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1499–1500.

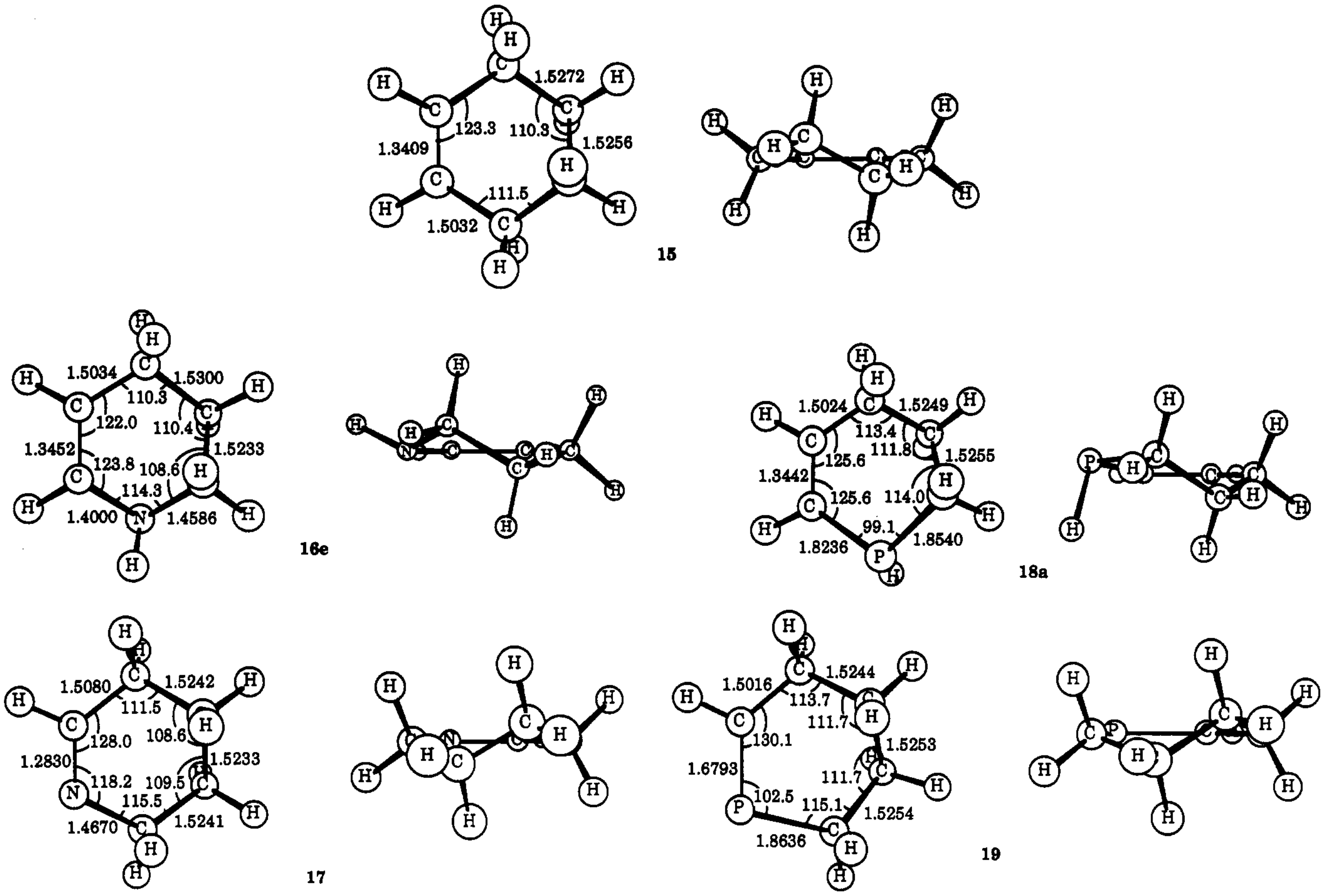

Figure 2. MP2/6-31G* optimized geometries of the products **15**–**19** in a top and side view. All distances are in angstroms and all angles are in degrees.

The reaction with the nitrogen lone pair exo has a lower barrier (15.2 kcal mol^{-1}) than when the lone pair is endo (20.1 kcal mol^{-1}). This exo-lone-pair effect leads to a very asynchronous TS in the reaction of butadiene with *trans*-diazene. The TS where the lone pairs of *cis*-diazene are exo is 12 kcal mol^{-1} lower than the endo case.

The substitution of a heteroatom into the butadiene chain inherently breaks the symmetry of the DA reaction and must result in an asynchronous TS. We will examine the TSs for the DA reactions of the phospha- and azabutadienes using geometric and density features to assess the degree of synchronicity in these reactions. We will also compare the extent of reaction at the TS for these DA reactions.

A comment regarding the appropriate computational level is necessary. The calculations must be able to reproduce experimental values for the activation and reaction energy of the prototype DA reaction and supply TS structures that are self-consistent and in accord with experiment.

Bach has shown that electron correlation is essential for obtaining reasonable activation energy for the prototype DA reaction.[23] The experimental value of E_a ranges from 32.8 to 34.3 kcal mol^{-1}.[30-32] The value of E_a is 35.9 kcal mol^{-1} at HF/3-21G and 45.04 kcal mol^{-1} at HF/6-31G*. Inclusion of electron correlation through MP2 decreases the barrier to 16.58 kcal mol^{-1}. Clearly, higher order corrections are required. MP3 and MP4SDQ calculations give more reasonable estimates of 26.85 and 28.97 kcal mol^{-1}, respectively. Inclusion of zero-point energy and internal energy will increase the calculated value by a few kilocalories per mole. The barrier is 32.0 kcal mol^{-1} at 4.31G/CAS1/STO-3G/CAS1.[22] The reaction enthalpy is 49.1 kcal mol^{-1} at MP4SDQ/6-31G*.

The study by Bernardi located both a synchronous and asynchronous (diradical) TS. The former is 1.3 kcal mol^{-1} lower in energy than the latter.[22] All ab initio calculations have favored the synchronous TS, and frequency analysis[19]

Table I. Energies (au) of 1–19

compound	HF/6-31G*[a]	MP2/6-31G*[b]	MP4SDQ/6-31G*[c]
ethylene	−78.031 718	−78.294 286	−78.311 386
1	−154.914 813	−155.437 443	−155.460 155
2	−170.914 737	−171.469 089	−171.487 507
3	−170.916 029	−171.469 946	−171.488 237
4	−170.907 804	−171.462 903	−171.480 335
5	−457.170 886	−457.682 577	−457.700 279
6	−457.170 849	−457.682 644	−457.700 249
7	−457.168 145	−457.682 151	−457.699 392
8	−232.879 606	−233.707 903	−233.724 878
9	−248.867 763	−249.732 060	−249.747 271
10	−248.877 856	−249.738 659	−249.753 001
11	−248.877 693	−249.735 251	−249.753 460
12	−535.155 650	−535.966 089	−535.984 326
13	−535.156 621	−535.967 043	−535.985 657
14	−535.134 737	−535.953 260	−535.970 307
15	−233.019 655	−233.820 564	−233.852 770
16	−249.005 496	−249.836 762	−249.864 090
17	−249.014 816	−249.846 503	−249.874 294
18	−535.279 332	−536.060 594	−536.088 522
19	−535.275 075	−536.068 656	−536.094 586

[a] HF/6-31G*//HF/6-31G*. [b] MP2/6-31G*//MP2/6-31G*. [c] MP4SDQ/6-31G*//MP2/6-31G*.

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(30) Uchiyama, M.; Tomioka, T.; Amano, A. *J. Phys. Chem.* **1964**, *68*, 1878.

(31) Tsang, W. J. *J. Chem. Phys.* **1965**, *42*, 1805.

(32) Tardy, C.; Ireton, R.; Gordon, A. S. *J. Am. Chem. Soc.* **1979**, *101*, 1508.

Table II. Activation and Reaction Energy (kcal mol^{-1}) for Reactions 1–7

	HG/6-31G*[a]		MP2/6-31G*[b]		MP4SDQ/6-31G*[c]		with ZPE[d]	
rxn	E_a	E_{rxn}	E_a	E_{rxn}	E_a	E_{rxn}	E_a	E_{rxn}
1	42.00	−45.89	14.95	−55.74	29.28	−50.97	31.76	−44.87
2	49.38	−37.05	19.65	−46.05	32.39	−40.91	35.07	−34.94
3	43.86	−36.24	16.05	−45.51	29.26	−40.45	31.80	−34.37
4	38.80	−47.25	13.77	−56.05	24.01	−51.82	26.59	−45.71
5	29.46	−48.15	6.76	−52.54	17.16	−48.23	19.49	−43.02
6	28.83	−48.17	6.20	−52.50	16.30	−48.25	18.30	−43.01
7	40.87	−47.20	14.54	−57.87	25.40	−52.59	27.91	−46.40

[a] HF/6-31G*//HF/6-31G*. [b] MP2/6-31G*//MP2/6-31G*. [c] MP4SDQ/6-31G*//MP2/6-31G*. [d] MP4SDQ/6-31G*//MP2/6-31G* with ZPE at HF/6-31G*//HF/6-31G*.

has confirmed that these geometries are real transition structures. Therefore, the smallest appropriate computational level must include some electron correlation beyond MP2 and a basis set that has polarization functions. We report here optimized geometries at MP2/6-31G* and single-point calculations at MP4SDQ.

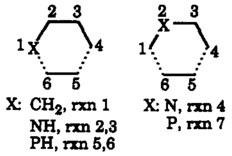
Computational Method

The Diels–Alder reactions of ethylene with the following dienes have been examined: 1,3-butadiene (**1**), (*Z*)-1-aza-1,3-butadiene (**2**), (*E*)-1-aza-1,3-butadiene (**3**), 2-aza-1,3-butadiene (**4**), (*Z*)-1-phospha-1,3-butadiene (**5**), (*E*)-1-phospha-1,3-butadiene (**6**), and 2-phospha-1,3-butadiene (**7**). These reactions 1–7 are shown in Scheme III. All structures were initially completely optimized at the HF/6-31G* level and characterized by analytical frequency analysis. The TSs **7–14** had one imaginary frequency while all other structures had only real frequencies. Our earlier studies of electrocyclic ring closures of aza- and phosphabutadienes[33] indicated that the MP2-optimized TS geometries were only slightly different from the HF geometries. However, since the activation energy of these ring closure reactions[33,34] and of reaction 1[23] are strongly dependent on electron correlation, we decided to completely optimize all structures at MP2/6-31G*. Single-point energy calculations were performed at MP4SDQ/6-31G* to more completely incorporate the correlation energy. We previously reported the MP2 optimized structures of the dienes **1–7**.[9] The MP2-optimized structures of the TSs **8–14** and the products **15–19** are drawn in Figures 1 and 2. The total energies of **1–19** are listed in Table I. The activation and reaction energies of reactions 1–7 are given in Table II. GAUSSIAN-90[35] was used for all calculations.

Table III. Energy (au) of the HOMO and LUMO of 1–7

compound	HOMO	LUMO
1	−0.3305	0.1389
2	−0.3893	0.1054
3	−0.3558	0.1147
4	−0.3484	0.1111
5	−0.3151	0.0530
6	−0.3121	0.0532
7	−0.3296	0.0687

Table IV. Extent of Reaction at TS Using eq 1[a]



Progress Ratio Using $\rho(r_c)$

rxn	1–2	2–3	3–4	5–6	4–5	1–6
1	32.19	51.09	32.19	35.29	23.41	23.41
2	43.16	58.48	39.86	39.42	30.24	20.87
3	38.77	55.38	36.63	36.12	28.27	22.29
4	24.75	45.25	27.55	33.24	20.66	24.96
5	21.15	48.19	29.25	31.67	19.54	30.82
6	23.10	48.62	29.72	28.58	9.91	29.92
7	48.22	40.45	25.94	34.33	18.80	25.71

Progress Ratio Using Bond Distances

rxn	1–2	2–3	3–4	5–6
1	23.06	45.48	23.06	23.82
2	37.52	52.98	30.73	29.31
3	31.95	47.97	24.48	24.64
4	42.67	36.93	19.46	21.40
5	23.53	43.15	20.01	20.94
6	22.68	40.75	19.13	19.69
7	22.75	41.67	18.35	22.49

[a] Numbering scheme used for this table only.

Table V. Bond Orders in TSs 8–14 Using eq 2

	1–2	2–3	3–4	5–6	4–5	1–6	sum
8	1.65	1.57	1.65	1.60	0.29	0.29	7.05
9	1.61	1.62	1.57	1.57	0.32	0.34	7.03
10	1.64	1.60	1.61	1.61	0.31	0.34	7.11
11	1.66	1.50	1.71	1.63	0.28	0.30	7.08
12	1.66	1.53	1.68	1.63	0.27	0.13	6.90
13	1.64	1.54	1.67	1.67	0.23	0.12	6.87
14	1.47	1.39	1.51	1.61	0.27	0.30	6.55

The topological electron density method[36] was used in order to characterize the extent of the reaction at the TS and the degree of synchronicity in the TS. The bond path traces out the path of maximum electron density between two bonded atoms.[37] The bond critical point is the point along the bond path having the least density.[38] The value of the electron density at the bond critical point $\rho(r_c)$ correlates with bond order n(X–Y) according to eq 1.

$$n(\mathrm{X{-}Y}) = \exp[A[\rho(r_c) - B]] \qquad (1)$$

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(33) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 209–215.

(34) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 2040–2047.

(35) Frisch, M.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *GAUSSIAN-90*; Gaussian, Inc.: Pittsburgh, PA, 1990.

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

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

(38) Bader, R. F. W.; Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1389–1395.

X-Y	A	B
C-P[40]	19.628	0.153
C-C[41]	6.458	0.252
C-N[42]	5.12	0.27

A locally modified version of EXTREME was used to obtain $\rho(r_c)$.[39]

We use eq 2 to estimate the extent of reaction at the TS. The parameter x can be either the bond distance or $\rho(r_c)$.

$$\text{progress ratio} = \frac{x_{\text{reactant}} - x\ \text{TS}}{x_{\text{reactant}} - x_{\text{product}}} \times 100 \qquad (2)$$

Results

Geometries. Reactants 1–7. The structures of the dienes 1–7 were reported and discussed in our previous papers and will not be repeated here.[9,33] For all reaction energy calculations, we take the s-gauche (or perhaps s–cis, if it is more stable) as the conformation of the reactant diene, even though the s-trans conformation may be lower in energy.

Cyclohexene 15. The structure of cyclohexene has been reported before and its conformational analysis recently reviewed.[43] The MP2/6-31G* structure of 15 is in the familiar half-chair conformation. This structure differs minimally from the HF/6-31G* structure—the bond distances are slightly longer and ring bond angles slightly smaller in the MP2 structure.

1,2,3,4-Tetrahydropyridine (16) and 2,3,4,5-Tetrahydropyridine (17). While a number of substituted examples of 16 and 17 are known[15,16,44] the parents have not been prepared. We will fully discuss the structures and conformations of these compounds elsewhere and mention here only the highlights.

While in principle 16 may exist in two forms, having the H on N pseudo-axial **16a** or pseudo-equatorial **16e**, only the latter could be located at MP2/6-31G*. The conformation of **16e** is the expected half-chair which enables conjugation between the C=C and the N lone pair. This conjugation results in a short C–N bond [compare $r(\text{N–C}_2) = 1.4000$ Å vs $r(\text{N–C6}) = 1.4586$ Å]. This structure is very similar the X-ray structure of a substituted 1,2,3,4-tetrahydropyridine.[15] In the experimental structure the C=C, N—C6, and N—C2 distances are 1.315, 1.440, and 1.479 Å, respectively, and the C-N-C angle is 114.9°.

The local minimum energy structure of 17 is also the half-chair. The C=N bond length is 1.2830 Å. This value agrees with the C=N distance of 1.262 Å found in the X-ray crystal structure of a substituted analogue of 17.[45] The other ring bond distances and angles in the calculated and X-ray structure are also in excellent agreement. Bond distances and angles about the two tetrahydropyridine and cyclohexene rings are very similar. In fact, these three rings are quite comparable in overall geometry and shape.

1,2,3,4-Tetrahydrophosphorin (18) and 2,3,4,5-Tetrahydrophosphorin (19). A handful of substituted examples of 18 have been synthesized and characterized via spectroscopic techniques, but no geometric parameters are known. No examples of 19 have been reported.

The MP2/6-31G* structures of 18 and 19 are shown in Figure 2. Both occur in the half-chair conformation, like 15–17. Just like 16, 18 can potentially have two local minima structures: **18a**, which has the H attached to P in the pseudo-axial position, and **18e**, which has the H in the pseudo-equatorial position. We could only locate the former conformation **18a**, while for the nitrogen analogue, we could only find the pseudo-equatorial conformer **16e**. The geometry of **16e** allows for conjugation of the N lone pair with the π-bond, leading to a short C N bond. In **18a**, the P lone pair is in the pseudo-equatorial position, directed away from the ring, allowing for little overlap with the π-bond. The P–C2 bond distance is 1.8236 Å, slightly shorter than typical C–P distances of 1.86 Å, but very close to the C–P distance in vinylphosphine (1.8324 Å).[46] The P–C6 distances in both **18a** and 19 are typical. The P=C distance in 19 is 1.6793 Å, just above the typical range of P=C distances (1.65–1.67 Å).[46]

The other bond distances in **18e** and 19 are standard. Ring bond angles at C are larger in these tetrahydrophosphorins than in 15–17. Since the bond angles at P are so small, the angles about C open up.

Transition Structure for Reaction 1 (8). The TS for reaction 1 has been discussed many times.[19–23] We will mention here only the comparison of our MP2/6-31G* structure with the HF/6-31G* of Bach.[23] In fact, these two geometries are extremely similar. The MP2 TS is slightly earlier than the HF TS. The C–C distances in the butadiene fragment are 1.3784 and 1.4102 Å at MP2 and 1.377 and 1.393 Å at HF. The C–C distance in the ethylene fragment is 1.3804 Å at MP2 and 1.383 Å at HF. The forming C–C bond length is 2.2855 Å at MP2 and 2.201 Å at HF. As was reported for other electrocyclic reactions, the differences between the HF and MP2 TSs are very small.[33,47,48]

Transition Structures for Reactions 2 and 3 (9 and 10). The diastereomeric TSs 9 and 10 (see Figure 1) differ by the location of the nitrogen H—syn in 9, anti in 10. Besides this difference, the two TSs are very similar. The end groups of the diene have undergone a disrotatory motion in both TSs. The diene backbones in both are nearly planar. The N-C–C–C dihedral angle is −5.3° in 9 and −1.3° in 10.

The TSs have no symmetry element, due to the introduction of the heteroatom. This translates into the two forming σ-bonds having different lengths. In 9, the forming C–N and C–C distances are 2.2753 and 2.0800 Å, respectively, while in 10 these distances are 2.2066 and 2.1608 Å, respectively. The other C–C and C–N distances in 9 and 10 are similar. For example, the C–C distance in the ethylene fragment is 1.3902 Å in 9 and 1.3814 Å in 10. The distances in 9 reflect a somewhat greater change than the distances in 10 suggesting a later TS.

We can also compare our MP2/6-31G* structure of 10 with the previously reported HF/3-21G structure of Tran Huu Dau et al.[28] The structures have similar overall features. They find that $r(\text{N}\cdots\text{C6}) = 2.103$ and $r(\text{C4}\cdots\text{C5})$

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

(40) Bachrach, S. M. *J. Mol. Struct.* (*THEOCHEM*) **1992**, *255*, 207–219.

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

(42) Values obtained using limited data reported in ref 46.

(43) Anet. F. A. L. In *Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*; Rabideau, P. W., Ed.; VCH Publishers, Inc.: New York, 1989; pp 1–46.

(44) (a) Beeken, P.; Fowler, F. W. *J. Org. Chem.* **1980**, *45*, 1336–1338. (b) Jones, T. H.; Blum, M. S.; Fales, H. M. *Tetrahedron* **1982**, *38*, 1949–1958. (c) Cadogan, J. I. G.; Kickson, C. L.; McNab, H. *J. Chem. Res.* (*S*) **1983**, 243.

(45) Damon, D. B.; Hoover, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 6439–6441.

(46) Bachrach, S. M. *J. Comput. Chem.* **1989** *10*, 392–406.

(47) Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3412–3416.

(48) Yu, H.; Chan, W.-T.; Goddard, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 7529–7537.

= 2.158 Å, which differ by −0.103 and +0.01 Å from our results. The other bond distances differ by less than 0.01 Å and the angles differ by no more than 2°.

Transition Structure for Reaction 4 (11). As with the other TS, 11 involves disrotatory motion at the termini of the diene. The diene backbone is nearly planar; the C–N–C–N dihedral angle is −5.5°. The C–C distance of 1.3753 Å in the ethylene fragment is shorter than in 8–10.

The TS for reaction 4 is distinctly asynchronous. The forming C–C bonds differ in length by 0.13 Å: 2.2373 vs 2.3653 Å. This asymmetry is caused by the heteroatom. These forming bonds are longer than the forming C–C bonds in either 9 or 10.

Transition Structures for Reactions 5 and 6 (12 and 13). The transition structures for reactions 5 and 6 differ by the relative position of the hydrogen bonded to phosphorus. In 12, this hydrogen is inside the ring, while in 13, this hydrogen is outside the ring. The terminal groups have rotated in a disrotatory direction. The diene backbone is nearly planar in each: the P–C–C–C dihedral angle is 3.0° in 12 and 0.8° in 13.

These two TSs have very similar geometric structures. The length of the forming C–P bond is 2.5902 Å in 12 and 2.6085 Å in 13. The forming C–C bond is 2.3544 Å in 12 and is only 0.0066 Å longer in 13. The other distances differ by no more than 0.0028 Å.

These TSs are asynchronous, on the basis of bond lengths, and are earlier than the TSs in reactions 2 and 3. The forming C–C bonds are longer than in the nitrogen analogues. This is a result of forming the long C–P vs the shorter C–N bond. However, in a more direct comparison, the C–C distance in the ethylene fragment of 12 and 13 is shorter than in 9 and 10.

Transition Structure for Reaction 7 (14). The TS for reaction 7 has the familiar geometric features of the other TSs: disrotatory end groups, planar diene backbone (C–P–C–C dihedral angle is −0.4°), and asynchronous bond changes. The two forming C–C bonds are 2.2709 and 2.3597 Å. These differ by less than 0.04 Å from the corresponding bonds in the nitrogen case 11. The C1–P and C3–P distances are close, but differ by a greater margin than the corresponding bonds in either 11 or 8. The C–C distance in the ethylene fragment is slightly longer than in 11 or the other phosphorus TSs.

Energetics. The calculated total energies of 1–19 are listed in Table I. The activation and reaction energies of reactions 1–7 are listed in Table II.

The first issue we need to address is the effect of electron correlation. Bach et al. have reported the activation energy of reaction 1 at a number of computational levels: 41.14 kcal mol^{-1} at HF/6-31G*//HF/6-31G*, 12.98 kcal mol^{-1} at MP2/6-31G*//HF/6-31G*, 25.53 kcal mol^{-1} at MP4SDQ//HF/6-31G*, and 18.42 kcal mol^{-1} at MP4SDTQ//HF/6-31G*.[23] Our complete optimization at MP2/6-31G* leads to an activation energy of 14.95 kcal mol^{-1}. This value is very close to Bach's MP2 result, not surprising since the geometries are little affected by reoptimization at MP2 (vide supra). While optimization at correlated levels may not be critical in obtaining reasonable geometries, it is absolutely essential in order to obtain reasonable energies. The HF activation energy is too high, and the MP2 result is too small. Correlation must be included through at least MP4SDQ; inclusion of the triples is probably wise, but due to limitations of computational resources, they were neglected here. Inclusion of zero-point energy (scaled by 0.9) leads to our best estimate of 31.76 kcal mol^{-1} for the E_a of reaction 1. The reaction energy is −44.87 kcal mol^{-1}.

The reaction energies of reactions 2 and 3 are −34.37 and −34.97 kcal mol^{-1}, the difference being the relative energies of 2 and 3. The activation energy of reaction 3 is 31.80 kcal mol^{-1}, 3.27 kcal mol^{-1} lower than for reaction 2. Outward rotation of the nitrogen lone pair (reaction 3) leads to a lower barrier than rotation inward (reaction 2).

Reaction 4 is much more exothermic (−45.71 kcal mol^{-1}) than the reactions involving 1-aza-1,3-butadiene. Its E_a (26.59 kcal mol^{-1}) is also smaller than for reactions 2 or 3.

The DA reactions of the phosphabutadienes are more exothermic than the azabutadienes. The E_as of reactions 5 and 6 are very small, 18.30 and 19.49 kcal mol^{-1}, respectively. Just as for the nitrogen analogues, the outward rotation (reaction 6) of the heteroatom lone pair leads to the lower E_a, although for the phosphorus case, the difference is small—only 1.19 kcal mol^{-1}.

While the DA reaction of 2-phospha-1,3-butadiene is more exothermic (−46.40 kcal mol^{-1}) than the DA reaction of 1-phospha-1,3-butadiene, the activation energy (27.91 kcal mol^{-1}) is larger. This trend is opposite that of the azabutadienes.

Discussion

The reaction energies for reactions 1, 4, and 7 are very close, approximately −45 kcal mol^{-1}. This can be easily rationalized in terms of the bond changes that occur in these reactions. For all three reactions, in simple terms, two C–C π-bonds are broken and replaced by two new C–C σ-bonds. The heteroatom makes one single bond and one double bond to carbon in both the diene and the product.

The reaction energies for the DA reaction involving 1-aza-1,3-butadiene are less exothermic than the others. Again, taking a simple bond energy approach, the net bond change in these two reactions are the formation of a new C–C (81 kcal mol^{-1}) and C–N (69 kcal mol^{-1}) σ-bond while breaking a C–C (67 kcal mol^{-1}) and a C–N (79 kcal mol^{-1}) π-bond. By using these standard bond energies,[49] the estimated reaction energy is −4 kcal mol^{-1}, while the estimated energy for reaction 1 is −28 kcal mol^{-1}. The formation of the relatively weak C–N bond at the expense of breaking the relatively strong C–N π-bond leads to a less exothermic reaction. The fact that our reaction energies do not agree with these estimated values reflects other changes (geometries, hybridization, conjugation, etc.) that are not included in the simple model. The DA reactions of 1-phospha-1,3-butadiene is more exothermic than of 1-aza-1,3-butadienes, a result of the much weaker C–P π-bond relative to the C–N π-bond.

While the MP4SDQ/6-31G*+ZPE activation energy for reaction 1 is in reasonably good agreement with experiment, these values should be used with some discretion. Consistent with earlier theoretical studies of pericyclic reactions, inclusion of electron correlation *beyond* MP2 is necessary to obtain reasonable activation energies. Certainly, the trends among these seven reactions are useful. The DA reactions of the phosphabutadienes all have E_as well below the E_a of the prototype DA reaction. The energy barrier for reactions 2 and 3 is comparable to or larger than the barrier for reaction 1, while it is lower for reaction 4.

Previous studies of the DA reactions of heterobutadienes have stressed the energy of the frontier orbitals.[10,13,14,16,28] In Table III, we list the HOMO and LUMO energies of the dienes 1–7. Normal electron demand DA reactions are $\mathrm{HOMO}_{\mathrm{diene}}$ controlled. The HOMO energies of the aza-

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[49] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987.

butadienes are lower than the HOMO of 1,3-butadiene, suggesting that strong electron-donating groups are needed to activate these dienes toward DA reactions.

It was suggested,[10] and recently confirmed,[15,16] that inverse-demand (LUMO$_{\text{diene}}$-controlled DA reactions of azabutadienes may be successful. The LUMOs of 2 and 3 are somewhat lower in energy than the LUMO of 1, but certainly offer a more feasible approach than the very low lying HOMOs of these dienes. Boger's inverse demand DA of 1-aza-1,3-butadienes all have strong electron-withdrawing substituents to further lower the LUMO energy.

In contrast, the HOMOs of the phosphabutadienes are quite high and their LUMOs are very low, indicating a strong propensity toward DA reactions with low activation energy. The very low E_as of reactions 5 and 6, consistent with the FMO analysis, suggest that DA reactions should be possible. The lack of isolated 1-phospha-1,3-butadienes with small substituents,[1,2] but rather isolation of the apparent DA product, is completely consistent with our calculations.

The difference in E_a between the DA reaction of 1-aza- vs 2-aza-1,3-butadienes and 1-phospha- vs 2-phospha-1,3-butadienes can also be explained in FMO terms. The HOMO of 4 is higher than the HOMOs of 2 or 3, and its LUMO is lower than the others. Likewise, the HOMO of 7 is lower than the HOMOs of 5 or 6, and its LUMO higher than the others. FMO theory, originally designed for hydrocarbon systems, correctly orders the E_as of the hetero-DA reactions.

The diastereomeric DA reactions of 1-aza-1,3-butadiene (reactions 2 and 3) have activation energies that differ by 3.27 kcal mol^{-1} (reaction 3 lower). The TS for these two reactions differ by the position of the nitrogen lone pair. In reaction 2, the lone pair rotates inward toward the ethylene fragment, while in reaction 3, the lone pair rotates away from the ethylene fragment. The relief of lone-pair, π-electron repulsion in 10 compared to 9 leads to a shorter N–C6 distance and consequently a lower energy in the former. This same effect was noticed by Houk in the DA reaction of formaldimine or cis-diazene with 1,3-butadiene.[29] Note that this implies that even though *two* orbitals on the nitrogen (the π- and the lone-pair orbital) can interact with the dienophile, the preferred path rotates the lone pair away from the reaction zone. Only the π-orbital participates in forming the new C–N bond.

The diastereomeric reactions of 1-phospha-1,3-butadiene also exhibit this preference for the rotation of the phosphorus lone pair away from the ethylene fragment (reaction 6). However, the energy difference between reactions 5 and 6 is only 1.19 kcal mol^{-1}, smaller than the selectivity in the nitrogen case. The phosphorus lone pair has more s-character than the nitrogen lone pair and is, therefore, more compact and less likely to interact with the dienophile.

The geometries of the transition states 8–11 are very similar. Thus, the geometric relationship of the diene to the dienophile does not change upon replacement of a carbon with a nitrogen atom in the diene. This fact reflects the noninvolvement of the nitrogen lone pair in forming the new C–N bond in reactions 2 and 3. While we have not tested the curvature of the potential energy surfaces about the transition states to test the relative sensitivity of approach of the dienophile to the diene, the strong preference for the nitrogen lone pair to rotate away from the dienophile suggests that the freedom in the attack angles will be limited. Thus, the geometric demands of the azadiene Diels–Alder reactions should be nearly identical to the demands in the prototype DA reaction.

The last issue we address here is whether the TSs are synchronous or not. These reactions appear to be concerted; we located only one TS for each reaction and confirmed that it was a true TS on the basis of frequency analysis. However, a concerted reaction need not be synchronous. Bonds do not have to form nor break to the same extent in the TS of a concerted reaction.

Dewar[50] has noted that the prototype DA reaction may, in fact, be synchronous, due to the symmetry plane maintained during the reaction. This, he claims, is an exception to the more general case where a symmetry plane is absent due to substituent groups or, in our case, the introduction of a heteroatom.

In order to ascertain whether these reactions are synchronous, we have calculated the "progress ratio", defined in eq 2, using two separate parameters. In Table IV, we report the "progress ratio" using bond distances and the value of the electron density at the bond critical point $\rho(r_c)$. In general, the values of the "progress ratio" determined in these two methods are similar, since $\rho(r_c)$ correlates with bond distance.[51] The use of $\rho(r_c)$ allows for the determination of a "progress ratio" for breaking or forming σ-bonds, where use of the bond distance makes no sense.

For reaction 1, the "progress ratio" for the C1–C2 and C3–C4 bonds are identical, due to the symmetry plane. These bonds have progressed to nearly the same extent as the C5–C6 bond, but not as far as the C2–C3 bond. The differences in the "progress ratios" for the bonds in the other reactions are much more dissimilar. For example, in reaction 7 the "progress ratios" for the breaking π-bonds of C1–P2, C3–C4, and C5–C6 are 48.22, 25.94, and 34.33, respectively, and the ratio for the forming π-bond of P2–C3 is 40.45. These ratios suggest that the reactions are asynchronous.

The "progress ratios" for reactions 2 and 3 are larger than for the other four reactions, suggesting a somewhat later TS. This is in accord with the Hammond postulate which claims a later TS for the less exothermic reaction.

An alternative approach to assessing synchronicity is to determine the bond orders in the TS. Using eq 2, we calculate the bond orders in 8–14, listed in Table V. What is most striking in this table is the similarity in the bond orders for the 1–2, 2–3, 3–4, and 5–6 bonds—about 1.6 for all seven TSs. The bond orders for the forming σ-bonds (4–5 and 1–6) are about 0.3 for all TSs. These values strongly suggest that the electronic distribution, in bonding terms, is nearly perfectly synchronous. The double bonds break (going from 2.0 to 1.6) and while the new σ-bonds form (going from 0.0 to 0.3) to nearly the same extent in these TSs.

Another interesting feature is the conservation of bond order during the reaction. The heavy atom bond order in the reactants sum to seven—three double bonds and one single bond (C2–C3). The product also has a sum of the heavy atom bond order of seven—five single bonds and one double bond. The transition state does *not* have to sum to seven. For example, if the diene and dienophile preferentially form one of the σ-bonds before the other (say 1–6 before 4–5 leading to a diradical) then the sum of the bond orders will be less than seven. For TSs 8–13, the sum of the bond orders is very close to seven, well within the errors due to limitations of eq 2. This bond-order conservation suggests no diradical character for the TS. The sum for 14 does not quite show this conservation of bond order.

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

(51) Bader, R. F. W.; Tang, T. H.; Tal, Y.; Biegler-Konig, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 946–952.

Conclusion

Our high-level calculations of the Diels–Alder reactions of aza- and phospha-1,3-butadienes reveal a number of interesting conclusions. Reasonable estimation of activation energies requires inclusion of electron correlation beyond the MP2 level. However, the TS geometry is little affected by correlation.

Geometric and density analysis based on the "progress ratio" of reactions 2–7 indicate that these reactions are asynchronous. However, estimates of the bond orders in the TSs suggest that these reactions are synchronous. Further study on this issue is clearly needed to determine the errors and biases imposed by these two methods. However, direct analysis of the electron density in the TS may prove to be more appropriate for understanding the bonding changes that occur in a reaction. For these systems, such an analysis argues for synchronous reactions.

The difficulty in having 1-aza-1,3-butadienes undergo DA reactions can be attributed to two energetic factors. First, the DA reactions of 2 and 3 are less exothermic than the prototype DA reaction. Second, the activation energy of these reactions is quite large, which is attributable to a low-lying HOMO. Thus, Boger's recent development of inverse electron demand DA methodology, taking advantage of the low LUMO, is quite appropriate.[15,16] The success of FMO theory in predicting the relative ordering of the activation energies of the reactions further supports the notion of extending this mechanistic theory from hydrocarbon systems to heteroatomic systems.

The energetics of DA reactions of phosphabutadienes are quite favorable. The activation energy of reactions 5–7 are small, less than 20 kcal mol^{-1} for 1-phospha-1,3-butadiene and 28 kcal mol^{-1} for 2-phospha-1,3-butadiene. These reactions are strongly exothermic. These calculated energies are completely consistent with the albeit scant available synthetic literature. Phosphabutadienes with small substituents readily undergo [4 + 2] self-addition and the isolated diene is not observed.[1,2]

On the other hand, phosphabutadienes with large substituents can be isolated and they do not react as dienes in cycloaddition reactions.[1] These calculations indicate that there is no large barrier or unfavorable reaction energy for the DA reaction of phosphabutadienes. Our previous study of the rotational barrier of phosphabutadienes revealed only normal energy barriers between the s-trans and s-gauche conformers.[9] However, bulky substituents will increase this barrier and disfavor the s-cis conformer. Phosphabutadienes contained within a ring, and thus restricted to the s–cis conformation, readily undergo DA chemistry.[8] The inability of the heavily substituted acyclic phosphabutadienes to access the s-cis conformation appears to be the only reasonable explanation for their inability to act as the diene fragment of the DA reaction. Balancing the need to preclude the self-DA reaction while still allowing access to the s-cis conformation for other DA chemistry on the basis of steric alone appears to be self-defeating, outside of restricting the diene to be in a ring.

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Supplementary Material Available: Optimized geometries in the form of Z Matrices for structures 8–19 at the HF/6-31G* and MP2/6-31G levels (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Molecular Recognition through C–H•••O Hydrogen Bonding in Charge-Transfer Crystals: Highly Selective Complexation of 2,4,7-Trinitrofluorenone with 2,6-Dimethylnaphthalene

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Treatment of a dimethylnaphthalene (DMN) isomer mixture with 2,4,7-trinitrofluorenone (TNF) resulted in the predominant formation of 2,6-DMN·TNF (1:1) complex (3) accompanied by a small amount of 2,7-DMN·TNF (1:1) (4). X-ray structural analyses of these charge-transfer crystals showed that coplanar "ribbon"-like networks are formed by C–H···O hydrogen bonding of TNF and that 3 is thermodynamically more stable than 4 due to the larger interactions through C–H···O contacts.

Hydrogen bonding through the short C–H···O contacts in crystals has been known to play a significant role in determining the molecular packing of organic solids.[1–3] This weak bonding has proven effective in steering flat molecules into the adoption of layered crystal structures,[4,5] and an electrostatic stabilization of at least 1.8 kcal mol^{-1} was estimated experimentally.[6] On the other hand,

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(1) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063. It was reported that C–H groups which are adjacent to nitrogen atoms are particularly likely to participate in this bonding.

(2) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290.

(3) Typical values for the H···O and C···O distances are 2.4–3.0 Å (ref 1) and 3.3–3.8 Å (ref 2), respectively, in C–H···O hydrogen bonding.

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