J. Org. Chem. **1994**, *59*, 5027–5033 **5027**

Ab Initio Study of the Diels–Alder Reaction between Phospholes and Ethyne

Steven M. Bachrach

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

Received April 14, 1994[®]

The reaction of cyclopentadiene with ethyne (reaction 1) and 1*H*-, 2*H*-, and 3*H*-phosphole with ethyne (reactions 2–4) were examined at the MP4SDQ/6-31G*//MP2/6-31G* level. The quality of this computational level was evaluated by comparison of the geometries and energetics of reaction 1 with experimental results. The activation energies of reactions 1–4 are 27.94, 30.62, 17.93, and 28.14 kcal mol^{-1}. These reactions all proceed through a common mechanism—the classic concerted [4 + 2] cycloaddition—as determined by analysis of the geometry, activation energy, and electron distribution. These calculations are then used to evaluate the mechanistic proposal of Mathey concerning the reactions of substituted 1*H*-phosphole with alkynes.

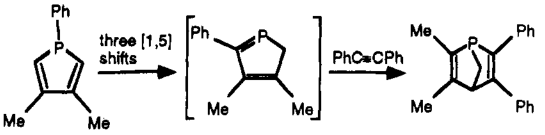
The Diels–Alder reaction is one of the most powerful tools in synthetic chemistry, bringing together two disparate groups, forming two new bonds, and potentially setting four new stereocenters. The Diels–Alder reaction is the prototype [4 + 2] pericyclic reaction and as such has been widely studied by experimentalists and theoreticians alike. Due to the ability to create new cyclic systems in the Diels–Alder reaction, there has been growing interest in applying this methodology to heteroatomic systems, with the goal of developing new schemes for preparing heterocyclic molecules.

In 1981, Mathey and co-workers[1] reported a novel synthesis of a 1-phosphabicyclo[2.2.1]hepta-2,5-diene by the reaction of a 1*H*-phosphole with diphenylethyne (Scheme 1). Mathey suggested that the 1*H*-phosphole first rearranges to the 2*H*-phosphole before undergoing a Diels–Alder reaction (Scheme 1), presuming that the 2*H* isomer is more reactive toward a dienophile than is the 1*H* isomer. Mathey has shown that a variety of substituted 1*H*-phospholes will undergo a Diels–Alder reaction with substituted ethynes and ethenes.[2–6]

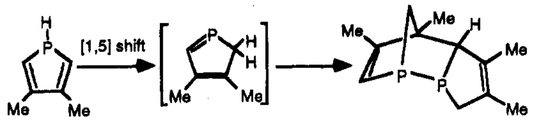
In related work, Mathey demonstrated that 1*H*-phospholes can dimerize by first converting to the 2*H* isomer and then undergoing a self-Diels–Alder reaction (Scheme 2).[7–10] This reaction gives the endo product only, as expected from applying the Woodward–Hoffmann rules and secondary orbital considerations.

Mathey's mechanism for these reactions presumes the formation of an intermediate 2*H*-phosphole, which Mathey was never able to directly detect. Zurmühlen and Regitz[11] were able to prepare a stable substituted 2*H*-phosphole which smoothly reacted with a dienophile to give the Diels–Alder product (Scheme 3).

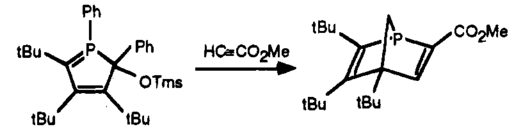
Scheme 1



Scheme 2



Scheme 3



We have been interested in studying the chemistry of phosphaalkenes by theoretical methods.[12–15] In particular, we have focused on the phospha-Diels–Alder reaction. In our study of the Diels–Alder reaction of phospha-1,3-butadienes with ethene, we found that the activation energy for the reaction of (*Z*)- and (*E*)-1-phospha-1,3-butadiene with ethene is 19.49 and 18.30 kcal mol^{-1}, respectively, at MP4SDQ//MP2/6-31G* with correction for zero-point energy (ZPE), while the activation energy for the reaction with 2-phospha-1,3-butadiene is 27.91 kcal mol^{-1}.[16] In comparison, the reaction of 1,3-butadiene with ethene has an activation energy of 31.76 kcal mol^{-1} at the same computational level. We concluded that Diels–Alder reactions of phosphabutadienes should be rapid and exothermic (the three Diels–Alder reactions studied had ΔE of about -44 kcal mol^{-1}).

Recently, we examined the first step in Mathey's mechanistic proposal, the rearrangement of the phosphole by a [1,5] hydrogen shift.[17] At MP2/6-31G* the

---

[®] Abstract published in *Advance ACS Abstracts*, August 1, 1994.

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

[2] Mathey, F.; Mercier, F. *Tetrahedron Lett.* **1981**, *22*, 319–322.

[3] Charrier, C.; Bonnard, H.; Mathey, F. *J. Org. Chem.* **1982**, *47*, 2376–2379.

[4] Mathey, F. *Chem. Rev.* **1988**, *88*, 429–453.

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

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

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

[8] de Lauzon, G.; Charrier, C.; Bonnard, H.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 1272–1273.

[9] Charrier, C.; Bonnard, H.; de Lauzon, G.; Mathey, F. *J. Am. Chem. Soc.* **1983**, *105*, 6871–6877.

[10] Charrier, C.; Bonnard, H.; de Lauzon, G.; Holand, S.; Mathey, F. *Phosph. Sulf.* **1983**, *18*, 51–54.

[11] Zurmühlen, F.; Regitz, M. *J. Organomet. Chem.* **1987**, *332*, C1–C5.

[12] Bachrach, S. M. *J. Comput. Chem.* **1989**, *10*, 392–406.

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

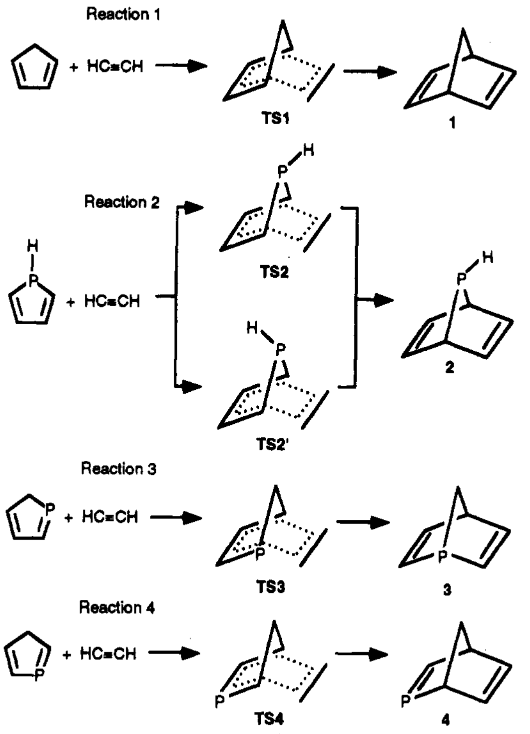
[14] Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 209–215.

[15] Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 2040–2047.

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

0022-3263/94/1959-5027$04.50/0

Scheme 4



barrier for rearrangement from 1*H*-phosphole to 2*H*-phosphole is only 16.0 kcal mol^{-1}. Also of interest is our finding that 2*H*-phosphole is 6.53 kcal mol^{-1} lower in energy than 1*H*-phosphole. Mathey has noted that mesitylvinylphosphine will reaarange to the corresponding phosphaalkene at low temperatures[18] and recent ab initio calculations[19] indicate that 1-phosphapropene is 2 kcal mol^{-1} more stable than vinylphosphine. These results suggest that since 1*H*-phosphole is not aromatic, the isomers of phosphole will be close in energy, perhaps even favoring the C=P isomer. Further ab initio studies of substituted phospholes indicated that substituents favor the 1 position over the 2 position, just as found in experiments.[20]

In order to complete our examination of Mathey's mechanistic proposal outlined in Scheme 1, in this paper we report high-level ab initio calculations of the Diels–Alder reactions of the unsubstituted 1*H*-, 2*H*-, and 3*H*-phosphole with ethyne, which is a model for the reagents used in Mathey's experiments. These calculations are in complete agreement with Mathey's mechanism—2*H*-phosphole is more reactive toward the dienophile than the other two isomers. In fact, the activation energy for the reaction of 2*H*-phosphole with ethyne is predicted to be 10 kcal mol^{-1} less than that for the prototype reaction: the cycloaddition of cyclopentadiene with ethyne. We examine the nature of the transition structures (TS) for these reactions and compare them with the prototype reaction in order explain the reactivity of these species.

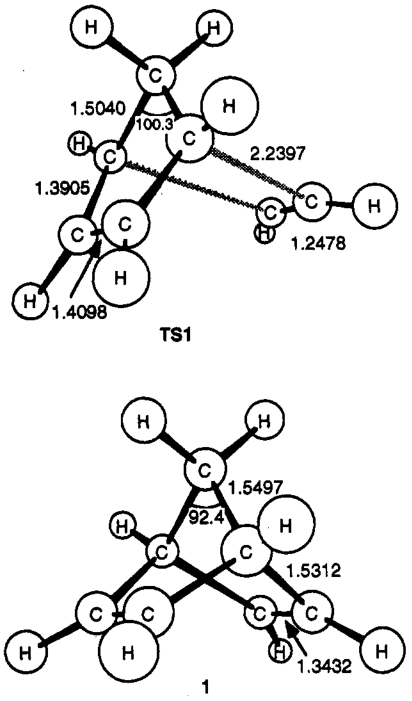


Figure 1. Optimized geometries of **TS1** and **1** at MP2/6-31G*. All distances are in angstroms and all angles are in degrees.

Computational Method

The four reactions examined here are drawn in Scheme 4. All calculations were performed using the GAUSSIAN-92[21] program on a Silicon Graphics Personal Iris 4D35GT. Reaction 1 is the cycloaddition of cyclopentadiene with ethyne, which is included as a reference. Since there are no experiments reported concerning the cycloaddition of phosphole with ethyne, we will use reaction 1 as a basis for judging the quality of our calculations. We have previously reported the optimized structures and energies of cyclopentadiene and 1*H*-, 2*H*-, and 3*H*-phospholes at the HF/6-31G* and MP2/6-31G* levels.[17] The MP2/6-31G* geometries are in excellent agreement with experiment, partially justifying this choice of computational level. We have optimized the geometries of the cycloaddition products norbornadiene (**1**), 7-phospha[2.2.1]bicyclohepta-2,5-diene (**2**), 1-phospha[2.2.1]bicyclohepta-2,5-diene (**3**), and 2-phospha[2.2.1]bicyclohepta-2,5-diene (**4**) at the HF/6-31G* level and confirmed that they are all local minima by analytical frequency analysis. In order to account for some of the electron correlation, we have also optimized these structures at the MP2/6-31G* level. These MP2 geometries are drawn in Figures 1 and 2.

The transition structures for reactions 1–4 were optimized at the HF/6-31G* level using the appropriate symmetry constraints. There are two possible transition structures for reaction 2: one has the hydrogen on phosphorus syn to the incoming ethyne (called **TS2**) and the other has this hydrogen anti to the incoming ethyne (called **TS2'**). All five of the transition structures have one and only one imaginary frequency, as determined at HF/6-31G*. These transition structures were reoptimized at the MP2/6-312G* level and these geometries are drawn in Figures 1 and 3.

Many theoretical studies of Diels–Alder reactions have demonstrated that activation energies are very sensitive to electron correlation.[16,22–24] Specifically, HF activation energies are too large and MP2 overcorrects, giving activation energies that are too small. However, MP3 and MP4 activation

---

[17] Bachrach, S. M. *J. Org. Chem.* **1993**, *58*, 5414–5421.

[18] Mercier, F.; Hugel-Le Goff, C.; Mathey, F. *Tetrahedron Lett.* **1989**, *30*, 2397–2398.

[19] Nguyen, M. T.; Landuyt, L.; Vanquickenborne, L. G. *Chem. Phys. Lett.* **1993**, *212*, 543–546.

[20] Bachrach, S. M.; Perriott, L. *J. Org. Chem.* **1994**, in press.

[21] 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.

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

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

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

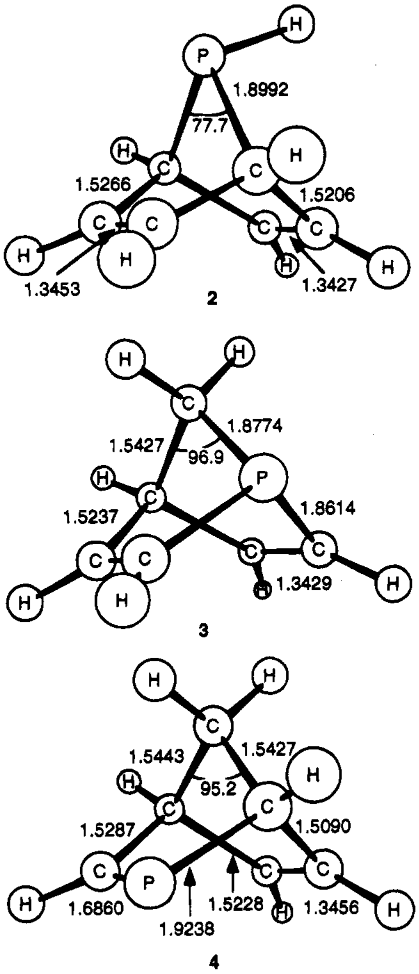


Figure 2. Optimized geometries of **2**−**4** at MP2/6-31G*. All distances are in angstroms and all angles are in degrees.

energies are quite reasonable. Therefore, we have determined the energies of all species in reactions 1−4 at MP4SDQ/6-31G*//MP2/6-31G*. The activation energies and overall reaction energy for reactions 1−4 are reported in Tables 1 and 2. We have included the zero-point vibrational energies, calculated at HF/6-31G* and scaled by 0.89.

The total electron density was analyzed using the topological method developed by Bader.[25] Specifically, we will make use of the empirical correlation between the value of the electron density at bond critical points ($\varrho(\mathbf{r}_c)$) and bond order (n(X−Y)), eq 1. The values of $\varrho(\mathbf{r}_c)$ were obtained using a locally modified version of EXTREME.[26]

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

X-Y	A	B
C-P[27]	19.628	0.153
C-C[28]	6.458	0.252

Results

Evaluating the Method. Cyclopentadiene + Ethyne → Norbornadiene, Reaction 1. Since no experimental evidence exists for reactions 2−4 and no thermochemical data exist for any of the Diels−Alder reactions of phospholes, we must choose an analogous reaction to evaluate the computational method. The simplest analogue for which there is experimental data is the reaction of cyclopentadiene with ethyne to yield norbornadiene, reaction 1.

We first examine the structure of norbornadiene. The MP2/6-31G* optimized geometry is drawn in Figure 1. The geometry of norbornadiene has been examined by electron diffraction[29] and recently a high-quality microwave structure[30] was reported. The structure of norbornadiene has also been determined at the HF/6-31G* level.[31] There are only minor differences between the HF and MP2 geometries; most notably, the C_2−C_3 distance is 0.024 Å longer in the MP2 structure, which is now in excellent agreement with the experimental value of 1.3362 Å. The agreement between our MP2 structure and the microwave structure is excellent: for example, the experimental results are $r(C_1{-}C_2) = 1.5304$ Å, $r(C_1{-}C_7) = 1.5567$ Å, and the C_1−C_7−C_4 angle is 91.9°, all of which are very close to the MP2 results shown in Figure 1.

The optimized geometry of the transition structure for reaction 1 (**TS1**) is shown in Figure 1. Analysis of this structure is probably most instructive by comparison with the calculated transition structures for the Diels−Alder reactions of butadiene[16] and cyclopentadiene[24] with ethene and butadiene with ethyne.[32] In particular, we will focus on the lengths of the forming and breaking bonds. The forming C−C σ-bond in the reaction of butadiene with ethene is 2.286 Å, very comparable to the forming C−C σ-bond length of 2.193 Å in the reaction of cyclopentadiene with ethene. In terms of the diene fragment, the major difference between these two transition structures is the loss of bond alternation in the cyclopentadiene reaction: 1.389 and 1.392 Å in the cyclopentadiene fragment versus 1.378 and 1.4102 Å in the butadiene fragment. The forming C−C σ-bond length in the transition structure for the reaction of butadiene with ethyne is 2.198 Å, and the butadiene fragment shows alternation with bond lengths of 1.373 and 1.396 Å. On the basis of these results, we would expect to find a C−C σ-bond length of about 2.2 Å and little bond alternation in the cyclopentadiene fragment. The MP2/6-31G* optimized structure has the new C−C σ-bond length of 2.2397 Å and little bond alternation−1.3905 and 1.4098 Å. In other words, our transition structure is consistent with other related structures.

The kinetics and thermodynamics of the reaction of cyclopentadiene with ethyne has been examined by Walsh and Wells.[33,34] They determined that the activation energy of reaction 1 is 24.2 kcal mol^{-1} and the heat of reaction is −28.36 kcal mol^{-1}. These are values are of particular appropriateness here since these are gas-phase values which can be directly compared to our calculations.

The reaction and activation energy of reaction 1 calculated at a variety of computational levels are listed

---

[25] Bader, R. F. W. *Atoms in Molecules−A Quantum Theory*; Oxford University Press: Oxford, 1990.

[26] Biegler-Konig, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317−328.

[27] Bachrach, S. M. *J. Mol. Struct. (THEOCHEM)* **1992**, *255*, 207−219.

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

[29] Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2356−2363.

[30] Knuchel, G.; Grassi, G.; Bauder, A. *J. Am. Chem. Soc.* **1993**, *115*, 10845−10848.

[31] Zgierski, M. Z.; Zerbetto, F. *J. Chem. Phys.* **1993**, *98*, 14−20.

[32] Coxon, J. M.; Grice, S. T.; Maclagan, R. G. A. R.; McDonald, D. Q. *J. Org. Chem.* **1990**, *55*, 3804−3807.

[33] Walsh, R.; Wells, J. M. *J. Chem. Thermodynamics* **1975**, *7*, 149−154.

[34] Walsh, R.; Wells, J. M. *Int. J. Chem. Kin.* **1975**, *7*, 319−329.

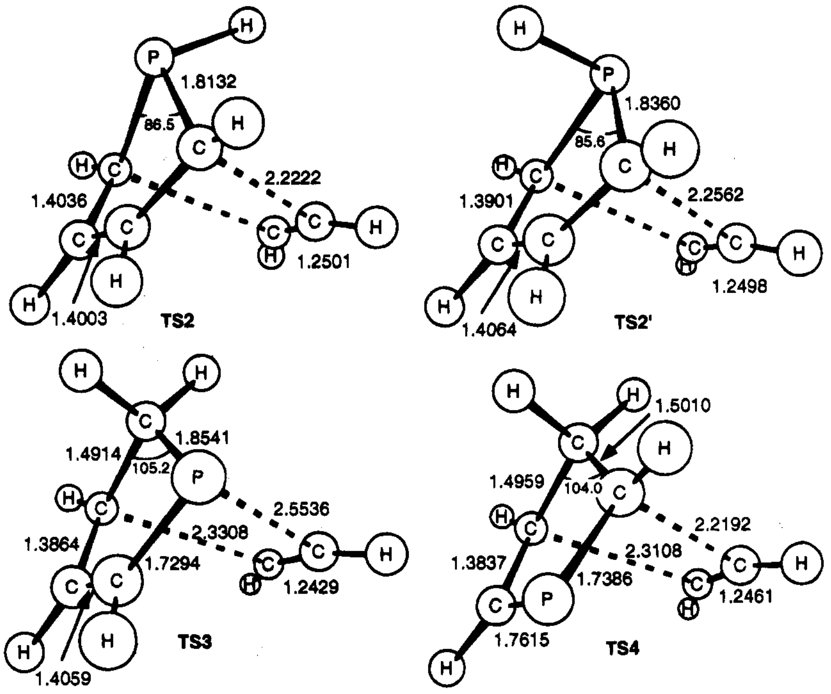


Figure 3. Optimized geometries of **TS2–TS4** at MP2/6-312G*. All distances are in angstroms and all angles are in degrees.

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

level	E_a	ΔE
HF/6-31G*//HF/6-31G*	42.98	−26.96
HF/6-31G*//HF/6-31G* + ZPE[a]	44.54	−21.66
MP2/6-31G*//MP2/6-31G*	14.87	−39.06
MP3/6-31G*//MP2/6-31G*	25.54	−37.47
MP4SDQ/6-31G*//MP2/6-31G*	26.38	−36.00
MP4SDQ/6-31G*//MP2/ 6-31G* + ZPE[a]	27.94	−30.70
exp[b]	24.2	−28.36

[a] Zero-point energy determined at HF/6-31G* and scaled by 0.89. [b] See refs 33 and 34.

Table 2. Reaction Energy and Activation Energy (kcal mol^{-1}) for Reactions 2–4

	reaction 2			reaction 3		reaction 4	
level	E_a(**TS2**)	E_a(**TS2'**)	ΔE	E_a	ΔE	E_a	ΔE
HF[a]	48.19	47.01	−25.57	29.83	−37.94	43.28	−32.13
MP2[b]	18.96	18.50	−37.93	6.53	−43.31	15.23	−46.18
MP4[c]	30.65	29.40	−35.43	16.60	−42.03	26.69	−42.20
MP4 + ZPE[d]	31.98	30.62	−30.45	17.93	−37.19	28.14	−36.71

[a] HF/6-31G*//HF/6-31G*. [b] MP2/6-31G*//MP2/6-31G*. [c] MP4SDQ/6-31G*//MP2/6-31G*. [d] Zero-point energy determined at HF/6-31G* and scaled by 0.89.

in Table 1. As anticipated, the HF activation energy (44.54 kcal mol^{-1} with ZPE correction) is too large. Again consistent with earlier studies, the MP2 activation energy (16.43 kcal mol^{-1} with ZPE correction) is too small. Inclusion of correlation through MP3 or MP4 produces an activation energy that is in satisfactory agreement with experiment. Our best estimate for the activation energy is 27.9 kcal mol^{-1}. The reaction energy is also somewhat dependent on the inclusion of electron correlation, but not to the same extent as with the activation energy. Our best estimate of the reaction energy is −30.7 kcal mol^{-1}, only 2.4 kcal mol^{-1} above the experimental value.

In summary, the excellent agreement between the MP2/6-31G* structures with experiment and the very reasonable agreement in the thermochemistry for reaction 1 using the MP4SDQ energies justifies the use of this method for studying the Diels–Alder reactions of the phospholes.

Geometry. The geometries of the phospholes were previously reported[17] and are in excellent agreement with the limited experimental data available.

Phosphanorbornadienes 2–4. While **2–4** have not been synthesized, a substituted analogue of **3** has been prepared and its X-ray crystal structure reported.[1] This is the only known structure of any of the phosphanorbornadienes and must serve as the sole comparison of our computed structures. We note that the geometry of **2** has been optimized at the HF/6-311G(d,p) level but no structural details were reported.[35]

The X-ray crystal structure of 4,5-dimethyl-2,3,6-triphenyl-1-phosphabicyclo[2.2.1]hepta-2,5-diene was reported by Mathey and co-workers.[1] We can compare the phosphanorbornadiene framework with our computed structure of **3**, but realize that some difference are likely since the compounds differ considerably in substitution and phase. Nevertheless, our computed structure is in reasonable agreement with the experimental structure. The $P-C_2$ and $P-C_7$ distances in the crystal structure are 1.869 and 1.835 Å, which compare to our values of 1.8614 and 1.8774 Å, respectively. The two C=C distances are 1.327 and 1.341 Å in the experimental structure and 1.3429 Å in the MP2 structure. The C–C single bond lengths are $r(C_3-C_4)$ = 1.553 Å, $r(C_4-C_5)$ = 1.544 Å, and $r(C_4-C_7)$ = 1.540 Å compared to the MP2 distances of 1.5237, 1.5237, and 1.5427 Å. Comparison of the bond angles is quite favorable—$\theta(C_2-P-C_6)$, 96.1° (expt) and 94.9° (MP2); $\theta(C_7-P-C_6)$, 85.5° (expt) and 85.6° (MP2); and $\theta(P-C_7-C_4)$, 97.6° (expt) and 96.9° (MP2).

Some of the MP2-optimized geometric parameters for **2–4** are listed in Figure 2. The overall structures of these compounds are similar and simple trends can be

---

(35) Chesnut, D. B.; Quin, L. D.; Moore, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 11984–11990.

observed. The bonds to the atom occupying the 7 position are longer than normal, since this atom must bear a significant portion of the molecular strain energy. This is apparent in the small 1–7–4 angle. This angle is particularly small (77.7°) in **2** where phosphorus, being able to better accommodate small bond angles than carbon, occupies the 7 position. This angle is wider in **3** and **4** than in the hydrocarbon **1**. This reflects less strain in the 7 position in the phosphanorbornadienes since the longer C—P bonds allows the bridging carbon to expand its interior angle.

The bond distance for all the other bonds in these molecules are very similar. The C═C bonds range from 1.3427 to 1.3456 Å and the C—C distances range from 1.5228 to 1.5287 Å. The C—P and C═P distances are typical,[12] except for the C_1—P distance in **4**, which is unusually long. This long distance is the result of the attempt to relieve some of the strain at the (formally) sp^2 P atom, where the interior angle is only 87.8°.

Transition Structures TS2–TS4. The MP2-optimized geometries of the transition structures for reactions 2–4 are drawn in Figure 3. There are two possible transition structures for reaction 2. The hydrogen atom attached to phosphorus can be oriented syn (**TS2**) or anti (**TS2′**) to the incoming ethyne molecule.

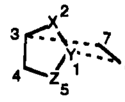
The geometries of these four transition structures, along with **TS1**, possess many similarities. The five-membered ring puckers with the 7 position moving away from the ethyne fragment. The C—C distance in the ethyne fragment ranges only from 1.2429 to 1.2501 Å in these TSs. The H—C—C angles in the ethyne fragment range from 154.5° to 159.9°. Perhaps most striking is the very similar distance for the forming C—C bond: 2.2397 Å in **TS1**, 2.2222 Å in **TS2**, 2.2562 Å in **TS2′**, 2.3308 Å in **TS3**, and 2.2192 and 2.3108 Å in **TS4**. Houk[36] has suggested that a forming C—C bond to an sp center typically has a bond length of 1.90–2.25 Å. The only outliers are when phosphorus participates in the diene, and then the distance is not much beyond the expected range, even in the case of **TS3** where the forming C—P bond is very long (2.5536 Å), demanding that the forming C—C distance be long.

One other interesting structural feature is the general lack of bond alternation in the diene fragment of the five-membered ring. This was previously observed in Diels–Alder reactions of cyclopentadiene.[23,24] The C—C distances of the diene fragment in **TS2** and **TS2′** differ by only 0.0033 and 0.01063 Å, respectively. The C—C distances of the diene in **TS3** differ by only 0.0205 Å and the C—P distances in **TS4** differ by only 0.0229 Å. Direct comparison of the C—C and C—P bond lengths in these last two TS is impossible, but we can make this comparison using bond orders, which we will discuss below.

Topological Electron Density Analysis. In order to address the degree of bond making/breaking in the transition structures of reactions 1–4, we have determined the value of the total electron density at the bond critical points $\varrho(\mathbf{r}_c)$ in each transition structure. Using the empirical relationship between bond order and $\varrho(\mathbf{r}_c)$ given in eq 1, we can estimate the bond orders for all C—C and C—P bonds in **TS1–TS4**. These estimated bond orders are listed in Table 3.

Examination of this table reveals that the bond orders for analogous bonds are very similar in all five transition states. The bond orders for the bonds to the bridging atom (position 2) are about 1.1 for all TSs. The bond order in the ethyne fragment is about 2.7. The forming bonds all have bond orders of about 0.3, except for the forming P—C bond in **TS3** which has a bond order of 0.13. Finally, the bond orders of the diene fragment are all about 1.6, except for the P—C bonds in **TS4** where the bond orders are about 1.4. The use of the bond orders allows us to determine if there is any bond alternation in the diene component of **TS3** and **TS4**. In fact, for **TS1–TS3** the bond orders show no bond alternation, consistent with the bond distance results. For **TS4**, the two P—C bonds have the same bond order, but it is considerably smaller than the C_3—C_4 bond order.

Table 3. Bond Order in TS1–TS4 Determined Using Eq 1



TS1: X=CH_2, Y=Z=CH
TS2, **TS2′**: X=PH, Y=Z=CH
TS3: X=CH_2, Y=P, Z=CH
TS4: X=CH_2, Y=CH, Z=P

bond	TS1	TS2	TS2′	TS3	TS4
1–2	1.09	1.13	1.06	1.07	1.08
2–3	1.09	1.13	1.06	1.11	1.12
3–4	1.61	1.54	1.60	1.65	1.66
4–5	1.57	1.62	1.59	1.56	1.41
1–5	1.61	1.54	1.60	1.61	1.40
1–6	0.29	0.29	0.29	0.13	0.31
3–7	0.29	0.29	0.29	0.28	0.27
6–7	2.64	2.64	2.65	2.70	2.66
sum[a]	8.01	7.92	8.02	7.93	7.71

[a] Summation of the bond orders of the active bonds, i.e., the last six listed in this table.

Energies of Reactions 2–4. The activation and reaction energies for reactions 2–4 are listed in Table 2. There are no experimental measurements of the thermochemistry of the Diels–Alder reaction involving phospholes, so we use the results for reaction 1 as a guideline. Therefore, the trend in the activation energies as electron correlation is added is completely expected. The HF activation energies are very large; the MP2 energies are drastically reduced. The MP4 energies, corrected for ZPE contributions, are the best estimates for the activation energy we determined.

The activation energy leading through **TS2′** is 1.36 kcal mol^{-1} less than through **TS2**. The activation energy for reaction 4 (28.14 kcal mol^{-1}) is slightly less than for reaction 2 (30.62 kcal mol^{-1}). However, the activation energy for reaction 3 is much lower still: $E_a = 17.93$ kcal mol^{-1}.

The reaction energies parallel the activation energies. Reaction 2 has the highest activation energy and is the least exothermic of the three reactions. Reaction 3 has the lowest activation energy and is the most exothermic, though reaction 4 is only 0.48 kcal mol^{-1} less exothermic.

Discussion

Houk, Li, and Evanseck have suggested that bond lengths in transition structures of pericyclic reactions fall within small ranges.[36] The typical distance for a forming C—C bond to an sp and sp^2 center is 1.90–2.25 Å, partially broken triple bonds have a typical distance of 1.22–1.27 A, and partially broken double bonds range from 1.34 to 1.42 Å. All of the bond distances in **TS1–TS4** fall within this range except for the forming C—C bond in **TS3** and one of the forming C—C bonds in **TS4**, and these distances are only just beyond the range.

---

(36) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 682–708.

We have previously examined the Diels–Alder reaction of phosphabutadiene with ethene[16] and some interesting comparisons can be made between those TSs and the ones obtained in this work. In the TS for the reaction of *syn*-1-phospha-1,3-butadiene with ethene, the forming C–C and C–P bond lengths are 2.3544 and 2.5902 Å, respectively. These compare quite favorably with the analogous bond distances in **TS3**–2.3308 and 2.5536 Å. The P–C_2, C_2–C_3, and C_3–C_4 distances are 1.7199, 1.4106, and 1.3757 Å, respectively, very similar to the analogous bonds in **TS3** of 1.7294, 1.4059, and 1.3864 Å.

There is similar strong agreement in the bond distances in **TS4** and the TS for the reaction of 2-phospha-1,3-butadiene with ethene. In the latter TS, the forming C–C bond lengths are 2.2709 and 2.3597 Å. Just as in **TS4**, the forming bond to the carbon adjacent to phosphorus is the shorter of the pair. The C_1–P, P–C_3, and C_3–C_4 distances in the TS of the phosphabutadiene are 1.7179, 1.7637, and 1.3721 Å, compared to 1.7386, 1.7615, and 1.3837 Å in **TS4**. Constraining the diene to a ring does not induce any serious changes in the geometries of the TSs relative to the acyclic systems.

The geometries of the transition structures for reactions 2–4 are remarkably similar to each other and to the prototype **TS1**. This similarity begs the question of whether these reactions are proceeding through a common mechanism—particularly the classic concerted, [4 + 2] cycloaddition mechanism. This mechanism has a single transition structure (no intermediates). Though a synchronous reaction is not a requirement of the [4 + 2] cycloaddition, some degree of both bond making and bond breaking should occur in the transition state.

Examination of the geometries of **TS2**–**TS4** indicate that the double bonds of the diene fragments have lengthened while the interior single bond has shortened, and the C≡C of the ethyne fragment has lengthened. The bond lengths of the diene fragment are very close, suggesting little bond alternation or, in other terms, an aromatic-like structure. While bond lengths can give some insight into the electronic structure of the system, bond orders can more directly probe this issue, along with allowing for direct comparison of the degree of bonding in C–C and C–P bonds and the extent of formation of the new σ bonds.

Using the empirical bond orders based on the topological density analysis, we can evaluate the degree of bond making/breaking in the TSs. The bond orders in the diene fragment of the TSs are all very similar (about 1.6) except for the C–P bonds in **TS4**, which have bond orders of 1.4. There is little bond alternation. The bond order in the ethyne fragment of the TSs are all about 2.65. The forming C–C bond orders are all about 0.3 in the TSs, while the forming C–P bond in **TS3** is only 0.13. What is striking is how synchronous these reactions are: the double bonds of the diene started out with bond order just below 2[17] and decreased by about 0.4; the single bond of the diene component started out with a bond order of about 1.2[17] and increased by about 0.4; the triple bond of the ethyne started out with bond order 3 and reduced by about 0.35; the new C–C bonds have a bond order of about 0.3. Not only are these reactions concerted, they are remarkably synchronous.

The bond orders in **TS3** and **TS4** are nearly identical to the bond orders found in the TSs for the reactions of 1- and 2-phospha-1,3-butadiene with ethene.[16] For example, the corresponding bond orders for the reaction of 1-phospha-1,3-butadiene with ethene are $n(3-4)$, 1.68; $n(4-5)$, 1.53; $n(1-5)$, 1.66; $n(1-6)$ 0.13; and $n(3-7)$, 0.27. Again, the cyclic and acyclic diene is participating equivalently in these Diels–Alder reactions.

In our previous paper,[16] we noted a conservation of bond order in the Diels–Alder reactions of phospha- and azabutadienes. Since the active bonds of the reactants are one triple bond, two double bonds, and one single bond, the sum is eight. In Table 3, we have added together the bond orders of the active bonds in the TSs. We note that the TSs have bond order sums nearly equal to eight, confirming a conservation of bond order in these Diels–Alder reactions.

Therefore, the geometric and bond order data suggest a concerted, near synchronous [4 + 2] cycloaddition for reactions 2–4. We turn our attention to the energetics of these reactions to see if it is compatible with this mechanism.

First, we note that **TS2** is slightly higher in energy than **TS2′**. We note that based on the geometric parameters and the bond orders in these TSs, **TS2′** is reached earlier along the reaction path than **TS2**. For a single reaction that can proceed along a number of different paths, the earliest TS is expected to be the lowest in energy. **TS2′** can also be rationalized as having the lower energy. In a traditional FMO analysis, the most important interaction is between the HOMO of ethyne and the LUMO of the phosphole. These orbitals can also interact favorably with the phosphorus lone pair in **TS2′**, since the lone pair is oriented toward the dienophile. On the other hand, in **TS2** the lone pair is oriented opposite the incoming dienophile and will not stabilize the frontier MO interactions.

The activation energies for the Diels–Alder reactions of butadiene with ethene and cyclopentadiene[37–39] with ethyne[33,34] are approximately 33 and 24 kcal mol^{-1}, respectively. The calculated values for these reactions are 31.76[16] and 27.94 kcal mol^{-1}, in reasonable agreement with experiment. The activation energies of reactions 2 and 4 and the reaction of 2-phospha-1,3-butadiene[16] with ethene are similar to the activation energies of the hydrocarbon analogues. The only outliers are reaction 3 (with an activation energy of 17.93 kcal mol^{-1}) and the reaction of 1-phospha-1,3-butadiene with ethene[16] (with an activation energy of 19.49 kcal mol^{-1}).

The reason for the far lower activation energy for reaction 3 and the reaction of 1-phospha-1,3-butadiene with ethene can be understood in terms of bond strengths. For these reactions a weak[40] and very reactive C–P π-bond is broken. This should be easier to accomplish than the loss of the C–C π-bonds in reactions 1 and 2 (and the reaction of butadiene with ethene). In reaction 4 and the reaction of 2-phosphabutadiene with ethene, the C–P π-bond is broken and reformed, for no net gain. The activation energies of these reactions are consistent with a concerted reaction.

We now turn our attention to the question of Mathey's mechanism for the Diels–Alder reaction of 1-phosphole with ethyne. To aid in understanding the mechanism, we present the energy diagram for reactions 2–4 with all energies plotted relative to the energy of 1*H*-phosphole and ethyne (Figure 4).

---

[37] Uchiyama, M.; Tomioka, T.; Amano, A. *J. Phys. Chem.* **1964**, *68*, 1878.

[38] Tsang, W. *J. J. Chem. Phys.* **1965**, *42*, 1805.

[39] Tardy, C.; Ireton, R.; Gordon, A. S. *J. Am. Chem. Soc.* **1979**, *101*, 1508.

[40] Wiberg, K. B.; Nakaji, D. *J. Am. Chem. Soc.* **1993**, *115*, 10658–10664.

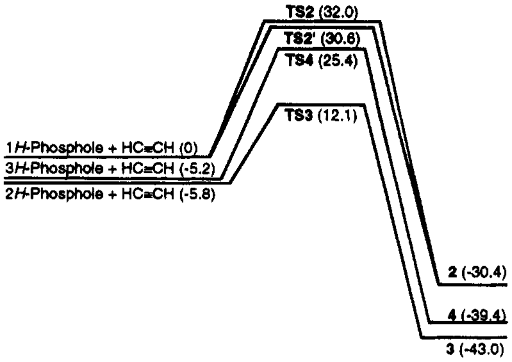


Figure 4. Energy diagram for reactions 1–4. All energies (kcal mol^{-1}) are relative to the energy of 1*H*-phosphole + ethyne.

Mathey proposed that the 2*H*-phosphole is more reactive than 1*H*-phosphole. This is confirmed on the basis of our calculated activation energies of reaction 2 (30.62 kcal mol^{-1}) and reaction 3 (17.93 kcal mol^{-1}). However, realizing that 2*H*-phosphole is more stable than 1*H*-phosphole, the activation energy through **TS3** is only 12.1 kcal mol^{-1} above the starting 1*H*-phosphole and ethyne. In fact, **TS3** is 18.5 kcal mol^{-1} lower than **TS2′** and 13.3 kcal mol^{-1} lower than **TS4**. If the barrier for the sigmatropic rearrangement of 1*H*-phosphole to 2*H*-phosphole is relatively small, than the cycloaddition through **TS3** is the most favored pathway. Our previous calculations[17] determined that the barrier between 1*H*-phosphole and 2*H*-phosphole is only 16.0 kcal mol^{-1}. If this rearrangement takes place, then there is *more* than enough energy for reaction 3 to proceed. Reaction 3 is kinetically favored over the alternatives.

3 is also the thermodynamic product, probably due to less ring strain energy than in **2** or **4**. In **3**, phosphorus occupies the bridgehead position and can contribute to reducing ring strain in all cycles in the molecule.

One minor point is that substituted 1*H*-phosphole are found experimentally to be the most favored isomer. We examined methyl- and vinyl-substituted phospholes and found that substitution favors the 1 position.[20] However, this results in only a few kcal mol^{-1} difference in the relative energies of the reactants, while the difference in the TSs is nearly 20 kcal mol^{-1}. Therefore, substitution is unlikely to alter the ordering of the TSs and **TS3** will remain the lowest energy TS. Our calculations are, therefore, completely consistent with Mathey's proposal as shown in Scheme 1.

Conclusions

The reaction of phospholes with alkynes produce products which suggest a Diels–Alder reaction of the 2*H* isomer only. Mathey suggested that 1*H*-phospholes first undergo a sigmatropic rearrangement to the 2*H*-phosphole, which then undergoes the cycloaddition reaction. Our MP4SDQ/6-31G*//MP2/6-31G* calculations corroborate this mechanism. The activation energy for the reaction of 2*H*-phosphole is 18.50 kcal mol^{-1} lower than the activation for the reaction involving the 1*H* isomer and is 13.3 kcal mol^{-1} lower than the reaction of the 3*H* isomer. Since the activation energy for the sigmatropic rearrangement is estimated to be 16 kcal mol^{-1}, the lowest energy pathway is the one proposed by Mathey.

The lower activation energy for the reaction of the 2*H*-phosphole is expected, since this reaction involves the breaking of the weak and reactive C–P π-bond. The reaction of the other isomers either involves only C–C π-bonds (reaction 2) or the breaking and reforming of the C–P π-bond.

Of more general interest is that these reactions follow the classic concerted [4 + 2] cycloaddition mechanism. The activation energies are consistent with other Diels–Alder reactions. The geometries of the TSs indicate partially formed and broken bonds. Electron density analysis also indicates this concerted bond breaking and forming in the TS. In fact, the bond orders in these TSs, along with other Diels–Alder reactions, suggest that these transition states are not only concerted, but quite synchronous as well.

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

Supplementary Material Available: Optimized *Z*-matrices at MP2/6-31G* of **1–4** and **TS1–TS4** (5 pages). This material is contained in 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.