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1,6-Diphospha-1,5-hexadiene and the Phospha-Cope Rearrangement: An ab Initio Investigation

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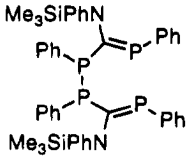
The phospha-Cope rearrangement converting 1,6-diphospha-1,5-hexadiene into 3,4-diphospha-1,5-hexadiene was examined at the MP4SDTQ(fc)/6-31G*//MP2(fc)/6-31G* and QCISD(T)(fc)/6-31G*//MP2(fc)/6-31G* levels of theory. In agreement with experiment, the equilibrium was found to lie on the side of 3,4-diphospha-1,5-hexadiene. The reaction energy of 1.73 kcal mol^{-1} is mainly due to ZPE correction which amounts to 1.30 kcal mol^{-1}. Both 1,6-diphospha-1,5-hexadiene and 3,4-diphospha-1,5-hexadiene have several conformational and, in the case of the former, configurational isomers with relative energies within 1 kcal mol^{-1}. The actual structures of substituted analogs will thus be influenced by steric effects. The activation energy for the Cope-rearrangement of 1,6-diphospha-1,5-hexadiene is 15.63 kcal mol^{-1}, significantly smaller than that for the parent Cope-rearrangement. The geometry and electron distribution of the transition state points to a concerted reaction in accordance with the orbital symmetry rules. The inversion barrier at phosphorus in 3,4-diphospha-1,5-hexadiene is 25.6 kcal mol^{-1} , which is smaller than the inversion barrier in nonconjugating phosphines. In the planar inversion transition state, conjugation between the P lone pair and the C=C bond is weak.

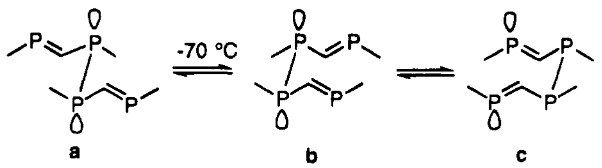
With the development of synthetic methodologies to prepare stable phosphaalkenes came the systematic exploration of the chemistry of the C=P bond.[1] A number of experimental studies of the pericyclic reactions of phosphaalkenes have been published, including the phospha-Cope rearrangement. Appel and coworkers have prepared a variety of phosphorus-substituted hexadienes that undergo an apparent Cope rearrangement.[2]

The earliest example is the rearrangement of a substituted 1,3,4,6-tetraphospha-1,5-hexadiene **I**, which exists in the *meso* form **a** below −70 °C but which converts into the racemate **b,c** at higher temperatures (Scheme 1).[3] The structure of the *meso* compound has been obtained via X-ray crystallography. Appel suggests that below −70 °C the *meso* compound exists primarily in the conformation where the lone pairs on P are arranged *anti* about the P−P bond. This positions the two double bonds too far from each other for a rearrangement to proceed. Above −70 °C, inversion at phosphorus, aided by presumed interaction between the phosphorus p orbital and the π-bond, occurs giving **b**, which can then undergo a Cope rearrangement to produce **c**. Using a fluorinated analogue, Appel has estimated that the activation energy of the phospha-Cope rearrangement is about 15 kcal mol^{-1}.[2]

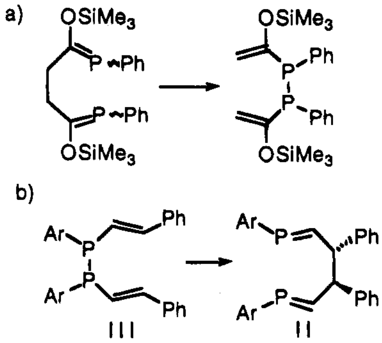


I

Scheme 1



Scheme 2



Ar = 2,4,6-tris(t-butyl)phenyl

1,6-diphospha-1,5-hexadienes will undergo a Cope rearrangement so rapidly that the rate cannot be measured (Scheme 2a).[4–6] Only when very bulky substituents are placed on phosphorus, thereby inducing large steric interactions in **III**, can a stable 1,6-diphospha-1,5-hexadiene **II** be produced by a Cope rearrangement (Scheme 2b).[7] Using simple bond additivity arguments, Appel estimates that 3,4-diphospha-1,5-hexadiene is approximately 4 kcal mol^{-1} more stable than 1,6-diphospha-1,5-hexadiene.[2]

1,3-Diphospha-1,5-hexadienes undergo an inversion process at phosphorus and at temperatures above 40 °C

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.

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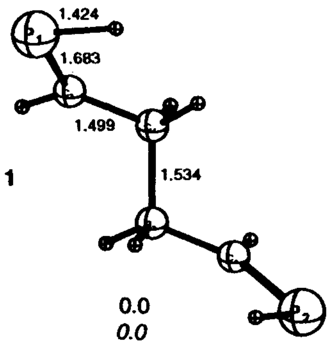

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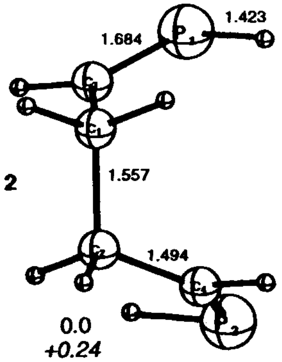

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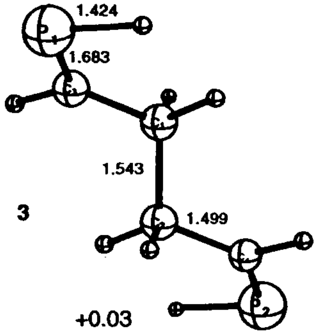

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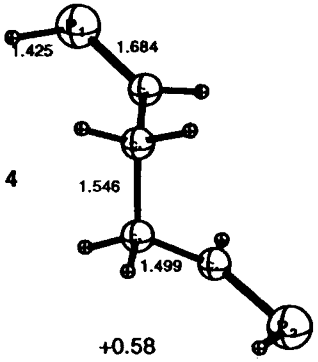

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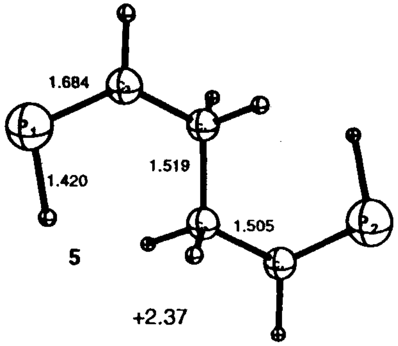

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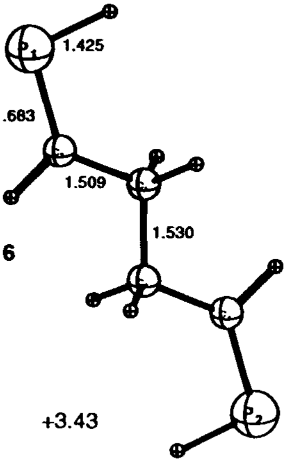

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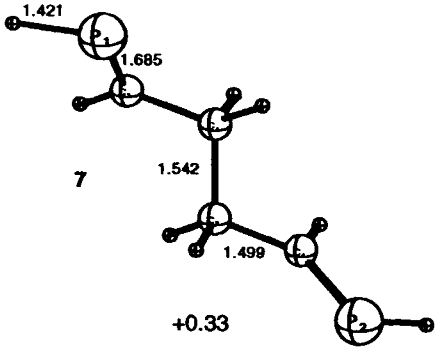

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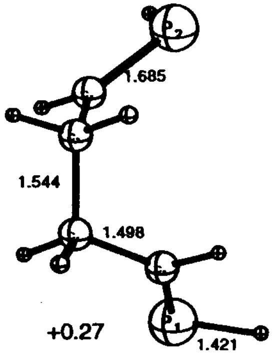

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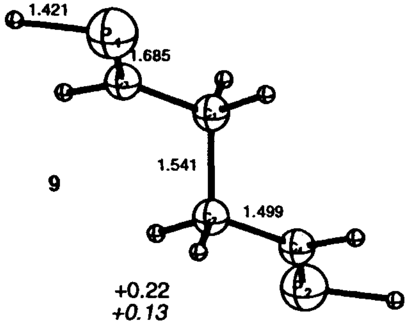

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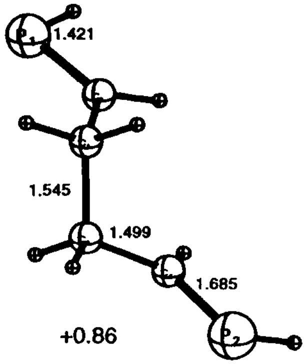

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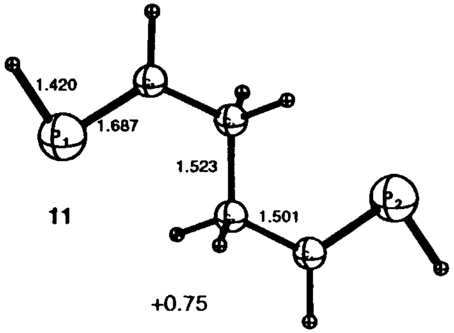

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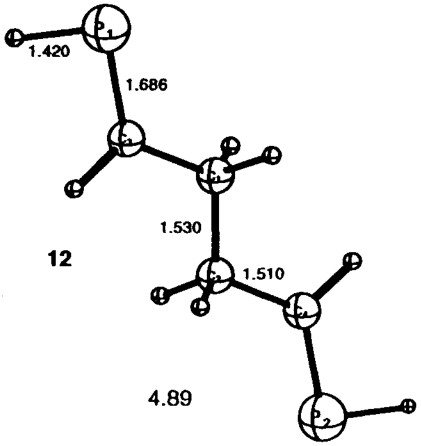

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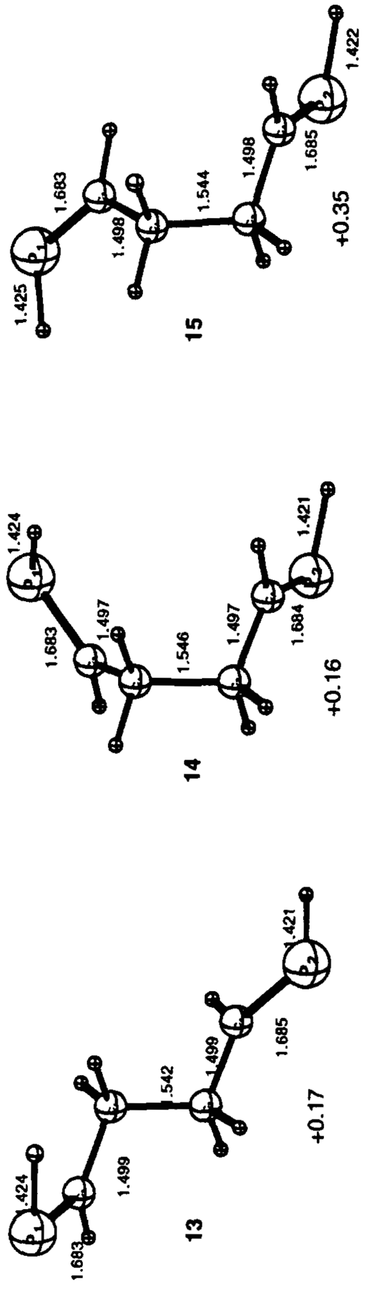
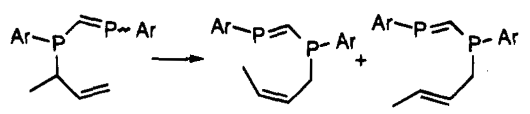
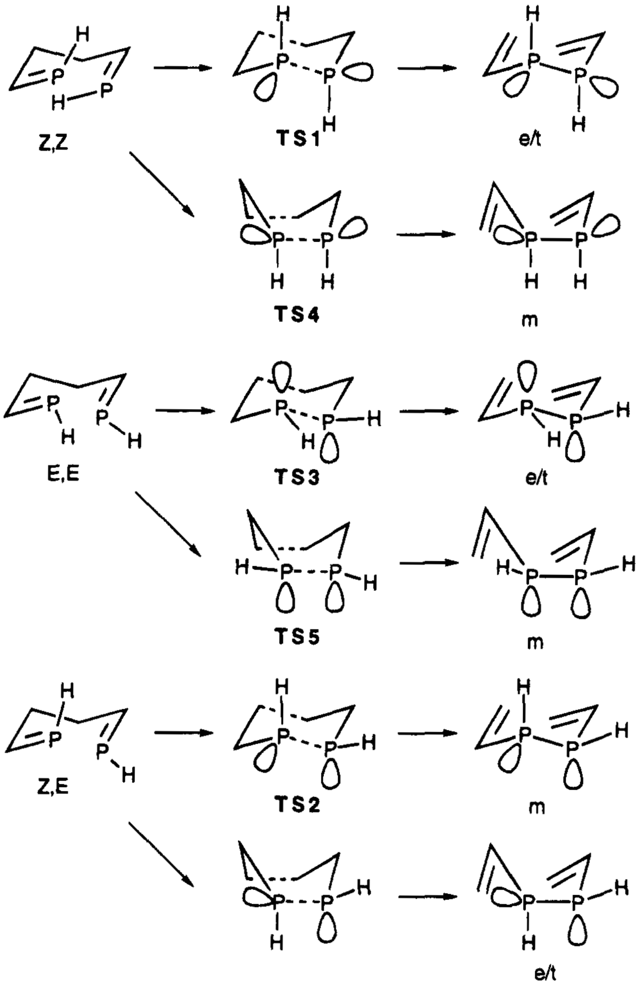


Figure 1. MP2(fc)/6-31G* optimized geometries of 1,6-diphospha-1,5-hexadiene. Relative energies (kcal mol^{-1}) at MP4SDTQ(fc)/6-31G*//MP2(fc)/6-31G* and QCISD(T)(fc)/6-31G*//MP2(fc)/6-31G* (in italics).

Scheme 3



Scheme 4



they rearrange (Scheme 3).[8] Both the reactant and the *E* product have been isolated and examined by X-ray crystallography.

We have a long-standing interest in the pericyclic reactions of phosphaalkenes.[9-15] Our studies have suggested that pericyclic reactions of the phosphaalkenes proceed under orbital symmetry control, through remarkably synchronous transition structures. The stereochemical control and negative entropy of activation observed by Appel indicate that the phospha-Cope rearrangement occurs through a concerted process. We therefore report here our theoretical examination of the phospha-Cope rearrangement of 1,6-diphospha-1,5-hexadiene into 3,4-diphospha-1,5-hexadiene, reaction 1 (Scheme 4). This system was selected to afford a reasonable comparison with the experimental work and also to maximize the

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symmetry in the expected transition structures. We find that the phospha-Cope rearrangement occurs along a concerted reaction pathway.

Computational Methods

Before we discuss the computational methods employed here, we briefly review recent calculations of the parent Cope rearrangement. The controversy surrounding these calculations has centered on whether the reaction proceeds through a single, concerted transition state TS or through a stable intermediate of diradicaloid character. Semiempirical methods and ab initio calculations with small basis sets favored a biradical intermediate.[16,17] CASSCF(6,6)/6-31G* calculations indicated an extremely flat surface with the biradicaloid intermediate only 1.9 kcal mol^{-1} below the concerted TS, with the TS leading to the intermediate only 0.6 kcal mol^{-1} below the concerted TS.[18] Very recently, two papers have shed considerable light on the problem. Using multireference perturbation theory, Borden[19] and Davidson[20] independently discovered that the CASSCF surface is quantitatively and qualitatively wrong and that only one TS exists. The multireferenece methods overestimates the importance of the biradical (biradicaloid) character. Davidson[20] further showed that correlated wavefunctions built from a single configuration, such as MP4, CCD, and QCISD, produce a single TS is close geometric and energetic agreement with the MRMP2 results, and only the MP2 surface is in error, having a structure that is similar in structure to the TS at higher levels, but in fact has no imaginary frequencies.[20]

On the basis of these results, and our[11,13-15] previous studies of pericyclic reactions of phosphaalkenes, we decided to employ single-reference techniques. The geometries of reactants (fifteen isomers **1**−**15**), products (nine conformers **16**−**24**), and transition states (three chair conformations **TS1**−**TS3** and two boat conformations **TS4, TS5**) for reaction 1 were fully optimized at HF/6-31G* and MP2(fc)/6-31G* and zero point energies were evaluated with analytical frequencies computed at HF/6-31G*. The nature of the lowest energy transition state **TS1** for the Cope rearrangement was reconfirmed with analytical frequencies at the MP2 level. Single-point energies were calculated at MP4SDTQ(fc)/6-31G*//MP2(fc)/6-31G* and at QCISD(T)(fc)/6-31G*//MP2(fc)/6-31G* in order to correct for electron correlation. All calculations were performed using GAUSSIAN-92.[21]

Table 1. Relative Energies (kcal mol^{-1}) of Isomers of 1,6-Diphospha-1,5-hexadiene and 3,4-Diphospha-1,5-hexadiene at Various Theoretical Levels

	HF[a]	MP2[b]	MP4SDTQ[c]	QCISD(T)[d]	ZPE[e]
			1,6-Diphospha-1,5-hexadiene		
1	0.0	0.0	0.0	0.0	0.0
2	0.61	−0.56	0.02	0.26	−0.02
3	0.0	0.07	0.04	0.03	−0.01
4	0.68	0.30	0.46		0.14
5	2.99	2.79	2.37		0.0
6	3.90	4.60	4.04		−0.61
7	0.25	0.14	0.35		−0.02
8	0.72	−0.08	0.29		−0.02
9	0.09	0.06	0.24	0.15	−0.02
10	1.04	0.41	0.76		0.10
11	1.90	0.99	0.90		−0.15
12	5.52	5.94	5.47		−0.58
13	0.11	0.06	0.16		−0.01
14	0.70	−0.12	0.19		−0.03
15	0.69	0.08	0.32		0.03
			3,4-Diphospha-1,5-hexadiene		
16	−12.11	0.29	0.90	−0.43	−1.30
17	−11.08	0.39	1.04	−0.17	−1.33
18	−11.47	1.42	1.90		−1.37
19	−10.73	0.41	1.10	−0.06	−1.38
20	−11.82	0.66	1.29	−0.01	−1.23
21	−11.55	0.92	1.59		−1.38
22	−10.86	1.15	1.79		−1.40
23	−11.12	2.05	2.55		−1.41
24	−9.04	1.95	2.51		−1.21

[a] HF/6-31G*//HF/6-31G*. [b] MP2(fc)/6-31G*//MP2(fc)/6-31G*. [c] MP4SDTQ(fc)/6-31G*//MP2(fc)/6-31G*. [d] QCISD(T)(fc)/6-31G*//MP2(fc)/6-31G*. [e] ZPE (at HF/6-31G*) scaled by 0.89.

Electronic structures of ground and transition states were analyzed with Bader's topological analysis[22] and with the NBO[23,24] method. Charge densities at bond critical points were obtained employing a locally modified version of EXTREM.[25] Bond orders were calculated using the empirical relationship eq 1, where $\rho(\mathbf{r}_c)$ is the value of the electron density at the bond critical point.

$$n(X\text{-}Y) = \exp\,[A\,[\,\rho(r_C) - B\,]\,] \qquad \text{eq. 1}$$

X-Y	A	B
C-P[26]	19.628	0.153
C-C[27]	6.458	0.252

Results

Energies. As indicated in Scheme 4 there are three geometric isomers of 1,6-diphospha-1,5-hexadiene: the *Z,Z*-, *E,E*-, and *E,Z*- isomers. Each of these isomers have many conformational isomers. Gung, Zhu, and Fouch[28] recently discussed the conformational surface of 1,5-hexadiene. Using MP2/6-31G* structures and energies, they determined that there are many conformers with very similar energies. Instead of exploring all possible conformers of each geometric isomer, we have chosen to examine a few of the structures that correspond to the low energy conformers of 1,5-hexadiene. Depicted in Figure 1 are six conformers of the *Z,Z*-isomer **1**−**6**, six conformers of the *E,E*-isomer **7**−**12**, and three isomers of the *E,Z*-isomer **13**−**15**. The relative energies of these isomers are reported in Table 1.

At MP4SDTQ/6-31G*//MP2/6-31G* with ZPE corrections, there are 12 structures of 1,6-diphospha-1,5-hexa-

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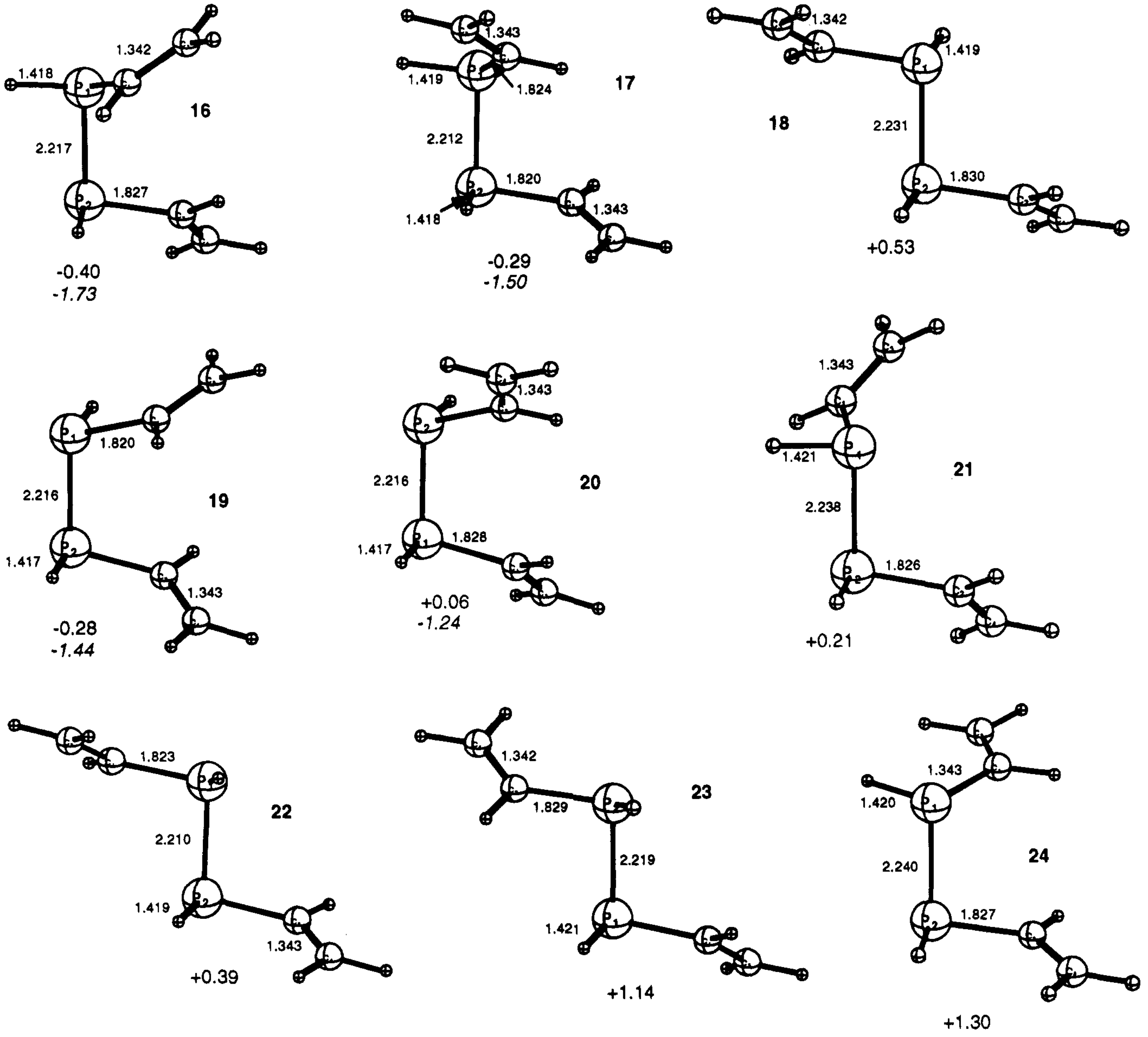

Figure 2. MP2(fc)/6-31G* optimized geometries of 3,4-diphospha-1,5-hexadiene. Relative energies (kcal mol^{-1}) at MP4SDTQ-(fc)/6-31G*//MP2(fc)/6-31G* and QCISD(T)(fc)/6-31G*//MP2(fc)/6-31G* (in italics).

diene within 1.0 kcal mol^{-1}, 9 of them within 0.5 kcal mol^{-1}. The relative energies are sensitive to the computational level, but at every theoretical level employed, the energy differences are so small that it can only be concluded that there are many essentially equivalent energy forms. The energy differences between *E*- and *Z*-configurations at the C=P bond are small for most of the conformers. *Z*-Configurations are favored by about 0.2–0.3 kcal mol^{-1}. While our search of the conformational space has not been exhaustive, we have sampled enough of the space to conclude that it is unlikely that any other conformer would be considerably more stable than these. The favored structures of substituted analogs will depend strongly on the steric demands of the substituents.

Like 1,6-diphospha-1,5-hexadiene, 3,4-diphospha-1,5-hexadiene (**16**–**24**) has many isomers with similar energy. Structures **16**–**18** are *meso* while **19**–**24** are *erythro*/*threo*. Seven structures are found within 1 kcal mol^{-1}, four of them within 0.5 kcal mol^{-1}. The two lowest lying conformers have the carbons, the hydrogens, and the lone pairs at the phosphorus atoms oriented gauche with respect to each other. In the next two stable conformers only the small hydrogens are trans to each other, while the carbons and the lone pairs remain gauche. Trans orientation of the phosphorus lone pairs is least favorable. Again, it is unlikely that any other conformer will be much lower in energy than the conformers displayed in Figure 2.

At HF/6-31G* 3,4-diphospha-1,5-hexadiene is about 12 kcal mol^{-1} more stable than 1,6-diphospha-1,5-hexadiene. The relative energies are, however, very sensitive to the improvement of the correlation treatment. At MP4SDTQ 3,4-diphospha-1,5-hexadiene is 0.9 kcal mol^{-1} higher in energy than 1,6-diphospha-1,5-hexadiene, while at QCISD(T) it lies 0.43 kcal mol^{-1} lower in energy. Correlation thus favors the 1,6-diphospha-1,5-hexadiene. (Inclusion of triples turns out to be crucial. Without triples the correlation effect is underestimated by about 2 kcal mol^{-1} using perturbation theory and by about 0.8–0.9 kcal mol^{-1} employing QCI.) Zero point energy corrections, on the other hand, favor 3,4-diphospha-1,5-hexadiene by 1.1–1.3 kcal mol^{-1}. Our best estimate at QCISD(T)/6-

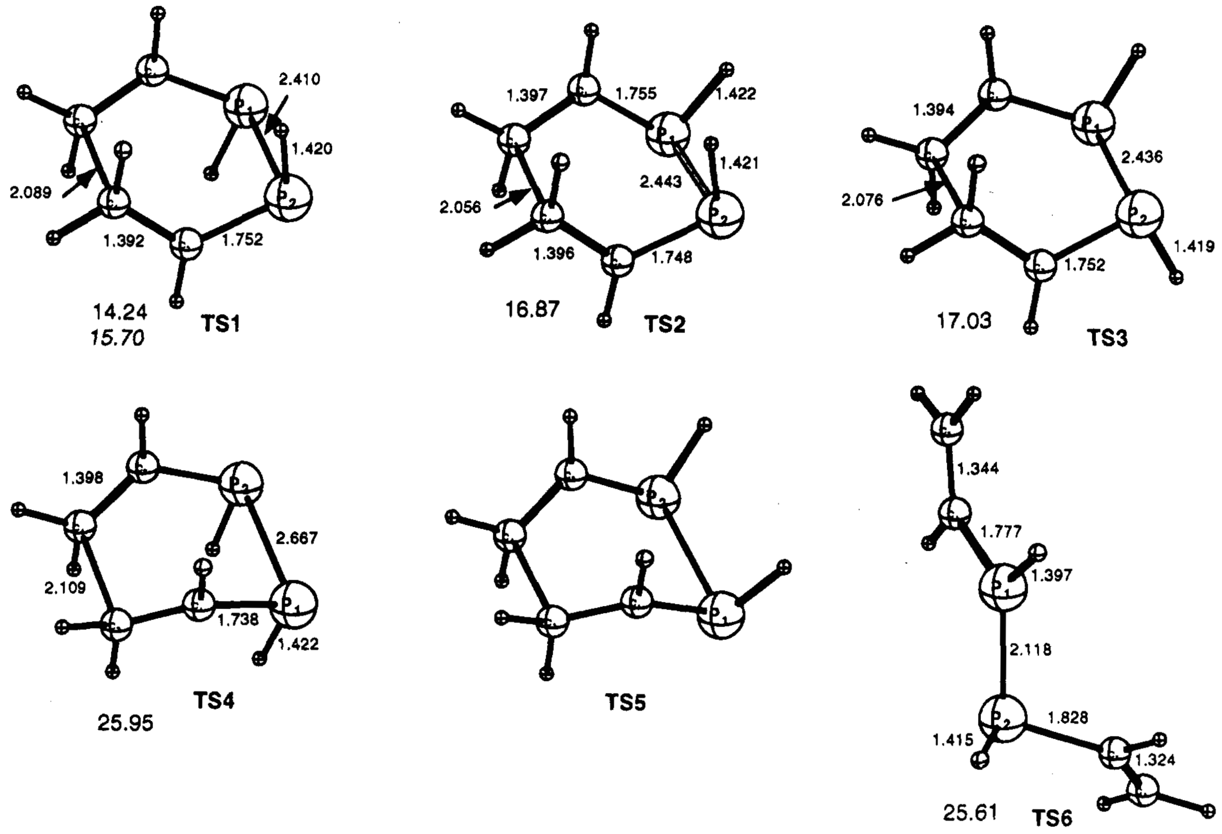

Figure 3. MP2(fc)/6-31G* optimized geometries of **TS1**–**TS6**. Activation energies (kcal mol^{-1}) at MP4SDTQ(fc)/6-31G*//MP2-(fc)/6-31G* and QCISD(T)(fc)/6-31G*//MP2(fc)/6-31G* (in italics).

31G*//MP2/6-31G*+ZPE indicates that the equilibrium lies on the side of 3,4-diphospha-1,5-hexadiene by about 1.6 kcal mol^{-1}. This energy difference is mainly due to the 1.2 kcal mol^{-1} ZPE correction.

In analogy to the parent Cope rearrangement, we looked for boat and chair concerted transition states and biradicaloid intermediates. We were unable to locate any intermediates, but it is well known that single-reference methods favor closed-shell systems[18] and therefore are unlikely to locate biradicaloid intermediates. The TSs we did locate are shown in Figure 3. Assuming that the phospha-Cope rearrangement proceeds according to orbital symmetry rules,[29] the *Z,Z*-isomer could react through a chair **TS1** or boat **TS4** transition state. The activation energy through **TS1** is 14.24 kcal mol^{-1} at MP4SDTQ+ZPE (15.70 kcal mol^{-1} at QCISD(T)+ZPE). The boat TS lies 7.5 kcal mol^{-1} above the chair TS at HF, and this difference increases to 12.9 kcal mol^{-1} at MP2 and 12.2 kcal mol^{-1} at MP4SDTQ.

TS1 is a true transition structure on both the HF and MP2 potential energy surfaces, as determined by analytical frequency analysis. For the parent Cope rearrangement, MP2 gives a structure that is similar to the TS obtained by other methods, but analytical frequency analysis shows it to be a true minimum, not a TS.[20] Analytical frequencies were obtained at the HF level only for the other TSs, and all cases had one and only one imaginary frequency.

Table 2. Activation Energy (kcal mol^{-1}) for the Phospha-Cope Rearrangement through TS1–TS5, Relative to 1

	HF^a	MP2^b	MP4SDTQ^c	QCISD(T)^d	ZPE^e
TS1	26.20	10.02	14.79	16.25	−0.55
TS2	29.17	12.87	17.73		−0.85
TS3	29.75	13.26	18.00		−0.93
TS4	33.66	22.91	27.01		−1.06
TS5	38.77				

^{a} HF/6-31G*//HF/6-31G*. ^{b} MP2(fc)/6-31G*//MP2(fc)/6-31G*. ^{c} MP4SDTQ(fc)/6-31G*//MP2(fc)/6-31G*. ^{d} QCISD(T)(fc)/6-31G*//MP2(fc)/6-31G*. ^{e} ZPE (at HF/6-31G*) scaled by 0.89.

The *E,E*-isomer proceeds through the chair form **TS3** or the boat form **TS5**. The activation energy for reaction through **TS3** is 17.03 kcal mol^{-1}, 2.8 kcal mol^{-1} more than through **TS1**. This is likely to be due to the positions of the phosphorus lone pairs, which are both equatorial in **TS1** and axial in **TS3**. The boat form **TS5** lies 9.0 kcal mol^{-1} (HF/6-31G*) above **TS3**. Since the boat isomer is so unfavorable we did not pursue higher-order calculations.

The *E,Z*-isomer can proceed through a chair or boat TS. Clearly, the boat TSs are unfavorable and we did not search for the boat TS coming from the *E,Z*-isomer. The activation energy through the chair **TS2** is 16.87 kcal mol^{-1}, between the activation energies through **TS1** and **TS3**.

In the reactions of 1,3,4,6-tetraphospha-1,5-hexadienes and 1,3-diphospha-1,5-hexadienes Appel has suggested that an inversion at phosphorus can occur allowing the two double bonds to approach each other.[3,8] While inversion at phosphorus is rather large (estimated as 38.2 kcal mol^{-1} in dimethylphosphine[30] and 36.5 kcal mol^{-1} in methylphosphine[31]), Appel suggested that a favorable

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

(28) Gung, B. W.; Zhu, Z.; Fouch, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 1783–1788.

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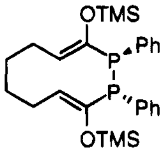
interaction between the phosphorus lone pair and the adjacent π-bond might reduce the inversion barrier. We optimized the TS for inversion through one phosphorus atom in **18**, shown in Figure 3 as **TS6**. This inversion barrier is 25.6 kcal mol^{-1}, 10 kcal mol^{-1} less than the inversion barrier in the nonconjugating phosphines.

Geometries and Electronic Structures. Optimized structures of phosphaalkenes at HF/6-31G* and MP2/6-31G* are in excellent agreement with experiment. We have every reason to believe that our optimized structures of 1,6-diphospha-1,5-hexadiene and 3,4-diphospha-1,5-hexadiene should be quite reasonable. While the parent (unsubstituted) compounds are unknown, the crystal structure of **II**[7] and **IV**[5] have been reported. The P=C distance in **II** is 1.635 Å, about 0.05 Å shorter than in our calculated structures of 1,6-diphospha-1,5-hexadiene. The angles about P and the double bonded C in **II** are 101.1° and 123.6°, respectively, while these angles are 98° and 122.5° in the calculated structures. In **IV**, the P−P distance is 2.254 Å while the C−P bond is 1.820 Å and the C=C bond is 1.352 Å. These compare quite well with our calculated values of about 2.2 Å for P−P, 1.83 Å for C−P and, 1.34 Å for C=C for 3,4-diphospha-1,5-hexadiene. Considering the vastly different substituent pattern and phase difference, the calculated structures agree remarkably well with experiments.



IV

The central C−C bond distances in 1,6-diphospha-1,5-hexadiene are between 1.52 and 1.56 Å. The shortest bonds occur when the phosphavinyl groups are trans and the molecule has a plane of symmetry. As the vinyl groups approach each other, the central C−C bond lengthens, the longest being in **2**, where the phosphavinyl groups are gauche and the hydrogens point toward each other. Similarly, the C−C distances between the central carbons and the alkene carbons appear to respond to steric hindrance. The C=P distances are essentially constant, regardless of the stereochemistry about the bond.

In 3,4-diphospha-1,5-hexadiene the P−P bond lengths are between 2.21 and 2.24 Å. The P−P bond is longest in the conformations when lone pairs are trans as in **18** and **21**. The P−P distance is shortest in the all gauche conformation. The P−C and C=C bond lengths are almost constant.

The forming C−C bond distance in **TS1** is 2.09 Å at MP2/6-31G*. This value is 0.3 Å larger than that for the parent Cope rearrangement. The forming P−P bond distance is 2.41 Å. Compared to reactant, the C−C bond is stretched by 0.5−0.7 Å, while compared with product the P−P is only 0.2 Å longer. The P−C bond length is 1.75 Å. This is 0.08 Å shorter than the P−C bond in 3,4-diphospha-1,5-hexadiene and 0.06 Å longer than the P=C bond in 1,6-diphospha-1,5-hexadiene. The C−C bond length of 1.39 Å is more alkene-like. Compared to reactant and product, it is 0.11 Å shorter than the averaged single bonds but only 0.05 Å longer than the C=C bonds. Thus, the geometry of transition state **TS1** is productlike. The bond orders according to Bader analysis confirm this. The bond order of the breaking C−C bond is 0.34, that of the former C=C bond is 1.49, and that of the C−P bond is 1.63. For the P−P bond no parameters for the charge density/bond order relationship are available.

The bond lengths in **TS2** and **TS3** are very similar to those in **TS1** with two exceptions: the P−P bond is 0.03 Å longer and the breaking C−C bond is 0.01 Å shorter in the former two TSs. Thus, **TS2** and **TS3** are slightly earlier than **TS1**. The P−P distance appears to correlate with the position of the lone pair—the distance decreases as the lone pairs occupy the more favorable equatorial position.

The boat transition state **TS4** has the phosphorus lone pairs eclipsing, leading to a very long P−P and C−C distances, substantially longer than in the chair TSs.

TS6 , the transition state for inversion at phosphorus, shows characteristic bond lengths changes. The P−P bond is shortened by about 0.11 Å, the P−C is shortened by 0.06 Å, and the P−H bond at the planar P atom is shortened by about 0.02 Å compared to the corresponding ground state **18**. That all three bonds around the planar phosphorus shorten simultaneously indicates that this contraction is mainly due the change in hybridization rather than conjugation. The lone pair of planar P is a pure p-orbital in contrast to pyramidal P where the lone pair has significant s-character. The bonds around a planar phosphorus in turn have increased s-character. Since s-electrons are more tightly bound than p-electrons, the bonds shorten. If π-conjugation were more important, the C−P bond would shorten most strongly and the conjugated C=C bond would lengthen. The potential conjugating double bond in **TS6** is only 0.002 Å longer than in **18**, though the other C=C has contracted by nearly 0.02 Å. This interpretation is confirmed by NBO analysis. There is only a comparatively weak interaction present between the phosphorus lone pair and the C−C-π-bond which leads to a shift of 0.1 electron into the C=C antibond. For comparison, in the allyl anion 0.44 electrons are transferred from the lone pair to the double bond, and the interaction energy is about five times larger than that in **TS6**. The same conclusion is obtained from Bader analysis. The bond orders around the planar P atom are 1.27 for the P−C single bond and 1.96 for the C=C bond. This can compared to the values of 1.10 and 2.03, respectively, in **18**. The single bond is thus strengthened, but the double bond is only slightly weakened. Thus, geometries and electronic structure analysis indicate that π-donation from the lone pair of the planar phosphorus atom is weak.

Discussion

Appel has reported that unless heavily substituted on phosphorus, 1,6-diphospha-1,5-hexadiene will rearrange irreversibly to 3,4-diphospha-1,5-hexadiene.[2] A rough estimate suggests that this reaction is exothermic by about 4 kcal mol^{-1}. Our calculations indicate that the energy difference is much smaller. Our best estimate (QCISD(T)/6-31G*//MP2/6-31G* +ZPE(HF)) is that 3,4-diphospha-1,5-hexadiene is about 1.7 kcal mol^{-1} more stable than 1,6-diphospha-1,5-hexadiene, with most of this difference due to zero-point energy. This result agrees with the experiments on the less substituted

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examples. However, with such a small energy difference, substituents should be able to alter the equilibrium of this phospha-Cope rearrangement.

Higher order calculations do agree that the equilibrium slightly favors 3,4-diphospha-1,5-hexadiene over 1,6-diphospha-1,5-hexadiene. Calculations at the HF level are in dramatic disagreement, greatly overestimating the stability of 3,4-diphospha-1,5-hexadiene. Exclusion of the effect of triples substitution favors the wrong isomer.

As was found for 1,5-hexadiene,[28] we find a number of conformations of 1,6-diphospha-1,5-hexadiene and 3,4-diphospha-1,5-hexadiene of very similar energy. While we have not determined rotational barriers about the central C−C or P−P bond, there is no clear conformational preference in these compounds. Appel[3] has suggested that there is a preference for having the adjacent phosphorus lone pairs anti; while we do not find this preference, substituents will certainly play a strong role in determining the conformational surface. The typical bulky substituent on phosphorus will certainly favor the anti P−P conformations (**18**−**20**).

The activation energy of the phospha-Cope rearrangement of reaction 1 depends on the reaction path. Reaction through **TS1** is favored, with an activation energy of 14.2 kcal mol^{-1} at MP4SDTQ. (This increases slightly, to 15.7 kcal mol^{-1} at QCISD(T).) The activation energy for reaction through **TS2** is 2.9 kcal mol^{-1} greater than through **TS1**, while reaction through **TS3** is another 0.3 kcal mol^{-1} higher still. The reaction through a boat TS is even less favorable: the activation energy for **TS4** is 26.9 kcal mol^{-1}, about 12.2 kcal mol^{-1} above that of **TS1**. This is greater than the difference between the chair and boat TSs in the hydrocarbon Cope rearrangement, which is estimated at about 5−6 kcal mol^{-1}.[18,32]

The activation energy of the phospha-Cope rearrangement is roughly half that of the parent reaction, 16 vs 31−34 kcal mol^{-1}.[20] This finding is in line with results for Diels−Alder reactions where activation energies dropped by roughly 10 kcal mol^{-1} for every C atom in a participating π-bond replaced by P.[11,14] The lower activation energies of phosphorus systems are probably due to the weak C=P bonds. The very small activation energy for the phospha-Cope rearrangement explains the rapid rearrangement reported by Appel.[4−6] This result can also be extended to the tetraphospha system, which should have a small activation barrier.

The lack of any intermediates suggests that the phospha-Cope rearrangement is concerted. (Again, it is worth remarking that single-configuration methods are likely to disfavor diradical intermediates, and the fact that we did not locate any does not necessarily prove that intermediates are not present. However, the recent MRMP2[20] and CASPT2N[19] calculations on the parent Cope rearrangement strongly cast doubt on the existence of diradical intermediates.) This begs the question of stereocontrol and whether the reaction obeys orbital symmetry rules, as outlined in Scheme 4. The intrinsic reaction coordinate through **TS1** connects (*Z,Z*)-1,6-diphospha-1,5-hexadiene to *erythro*-3,4-diphospha-1,5-buutadiene, exactly as predicted by orbital symmetry rules. We did not trace the other reaction coordinates; however, inspection of the mode corresponding to the imaginary frequency clearly indicates that **TS3** connects the *E,E* isomer to the erythro isomer and **TS2** connects the *E,Z* isomer to the *meso* isomer, in agreement with orbital symmetry arguments. As we have observed in a variety of pericyclic reactions of phosphaalkenes, orbital symmetry rules can be successfully utilized to understand and predict the outcome of the phospha-Cope rearrangement.

Since this phospha-Cope rearrangement is slightly exothermic, we expect the TS to productlike. This is confirmed by the bond orders in **TS1** as determined using eq 1. Starting from 1,6-diphospha-1,5-hexadiene, the former C=C bond has a bond order of 1.49, a loss of about one-half. The C−P bond has a bond order of 1.63 and an increase of about 0.6, and the breaking C−C bond has decreased by about 0.6 to 0.37. The electron distribution indicates a late TS, but one that displays a fairly synchronous change in the bonding. We have noted previously that the pericyclic reaction of phosphaalkenes are remarkably synchronous.[12−15]

Finally, Appel[2,3] has suggested that inversion at the saturated phosphorus in polyphosphahexadienes may be reduced due to conjugation between a vinyl group and the phosphorus lone pair. We have determined that the barrier is dramatically reduced (by over 10 kcal mol^{-1}) relative to nonconjugating phosphines. The inversion barrier is larger than the barrier for rearrangement, indicating that if inversion must occur first, as suggested by Appel, the subsequent rearrangement must be exceptionally rapid. This behavior has been observed in the tetraphosphahexadiene. One should however keep in mind that substituents, especially the bulky ones employed in the experiments, may affect the inversion barrier and the activation barrier for the Cope rearrangement.

While the inversion barrier is reduced in the conjugating phosphines, the TS does not show significant interaction between the phosphorus lone pair and the π-bond. The three short bonds about phosphorus reflect the change in hybridization from sp^3 to sp^2 in the TS. The bond orders of the C−P and C=C bonds in the TS are 1.27 and 1.96, respectively, which combined with the NBO results suggest little charge transfer.

Conclusions

Both 1,6-diphospha-1,5-hexadiene and 3,4-diphospha-1,5-hexadiene can adopt various conformations and configurations with similar energies. The system is thus very flexible, and the structures of substituted analogs are expected to vary according to steric demands of the substituents.

Inversion at phosphorus in 3,4-diphospha-1,5-hexadiene requires an activation energy of 25 kcal mol^{-1}, significantly reduced from the inversion barrier in nonconjugating phosphines. However, π-conjugation between the P lone pair and the C=C bond is present, but weak. This is reflected in geometry changes upon planarization of phosphorus and can be extracted from NBO and Bader analysis.

The Cope rearrangement of 1,6-diphospha-1,5-hexadiene proceeds through a chairlike concerted transition state. The three isomers of 1,6-diphospha-1,5-hexadiene rearrange through isomeric chair transition states, producing stereospecific products in accord with orbital symmetry rules. The reaction is exothermic but only by 1.7 kcal mol^{-1}. Substituent effects should be able to alter the equilibrium, particularly through large steric interac-

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(32) Dupuis, M.; Murray, C.; Davidson, E. R. *J. Am. Chem. Soc.* **1991**, *113*, 9756−9759.

tions. The activation energy is significantly lower than that of the parent Cope rearrangement, 16 kcal mol^{-1} for the phospha-Cope vs 31 kcal mol^{-1} for the Cope rearrangement of 1,5-hexadiene. As seen in other pericyclic reactions of phosphaalkenes, the weak C=P bond results in a reduced activation energy relative to analogous hydrocarbon systems.

The geometry and electron density distribution in **TS1** indicate a concerted reaction that is quite synchronous. While this TS is productlike, as expected for an exothermic reaction, the forming and breaking bonds have changed to similar extents. In all regards, the phospha-Cope rearrangement is analogous to the parent Cope rearrangement.

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