J. Org. Chem. **1997,** *62,* 5801−5803

Diels−Alder Reaction of an Ene−Phospha−Yne

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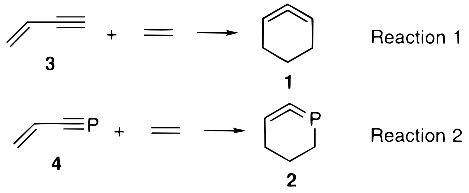
Received February 18, 1997[⊗]

The Diels−Alder reactions of ethylene with but-3-en-1-yne (reaction 1) or 1-phosphabut-3-en-1-yne (Reaction 2) were examined at the MP4SDTQ/6-311G**/MP2/6-311G** level. While reaction 1 is exothermic ($\Delta G_{\mathrm{rxn}} = -2.70$ kcal mol^{-1}), reaction 2 is endothermic ($\Delta G_{\mathrm{rxn}} = 9.38$ kcal mol^{-1}, though $\Delta H_{\mathrm{rxn}} = -3.23$ kcal mol^{-1}). The activation barrier for reaction 2 is, however, 4 kcal mol^{-1} lower than for reaction 1 ($\Delta G^{\ddagger} = 35.14$ vs 39.22 kcal mol^{-1}, respectively). The ring strain energies for the two cyclic cumulene products are 29.56 kcal mol^{-1} for 1,2-cyclohexadiene and 23.24 kcal mol^{-1} for 1-phospha-1,2-cyclohexadiene.

The recent discovery of naturally occurring enyne species has rekindled interest in the pericyclic chemistry of this functional group.[1] Recently, Johnson and coworkers reported on the apparent intramolecular Diels−Alder reactions involving enyne and diyne moieties acting as the diene component.[2] Their theoretical calculation on reaction 1 supports the intermediacy of this unusual Diels−Alder reaction, even though the product appears to be quite strained. Much progress has been made recently in the preparation of phosphaalkynes, and these species are now readily accessible.[3] Our work in phosphaalkyne chemistry, especially the finding that the C=P and C≡P bonds lower activation barriers by about 10 kcal mol^{-1} in Diels−Alder reactions relative to the all-carbon case,[4−8] suggested that the phosphorus analogue (reaction 2) may be easier to observe. We report here a high-level ab initio calculation comparing the energetics of these two reactions.



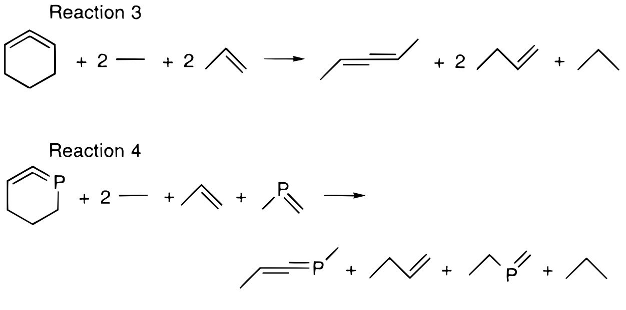
We first wish to address the concern of the proper computational method for examining these strained cumulene systems. In order to judge the methods, we compare the energies of allene with the energy of allene having its central angle fixed to 132.93°, the value we obtain for the cumulene angle in 1,2-cyclohexadiene. We have optimized both structures (i.e., the linear and bent forms) at MP2/6-311G** and have listed in Table 1 single-point energy differences using a variety of methods. Clearly, there is little variation in these correlated energy differences, with the MP4SDTQ/6-311G** results in close agreement with those provided by the very largest methods. Therefore, cognizant of the size of the calculations at hand, we will report here all energies evaluated at MP4SDTQ/6-311G**//MP2/6-311G** and refer to them simply as MP4.

Table 1. Energy Difference (kcal mol^{-1}) between Linear and Bent Allene[a]

level	ΔE
HF/6-31G*//HF/6-31G*	24.38
MP2/6-311G**	18.97
MP4SDTQ/6-311G**	17.79
QCISD/cc-pVTZ	19.38
QCISD(T)/cc-pVTZ	18.04
CCSD/cc-pVTZ	19.43
CCSD(T)/cc-pVTZ	18.05

[a] All structures optimized at MP2/6-311G** except the HF entry. The bent allene has its C=C=C angle fixed to 132.93°.

We begin by examining the ring strain energy (RSE) of both products. Using the group equivalent reactions[9] defined in reactions 3 and 4 and MP4 energies (with zero-point vibrational energy calculated at HF/6-31G* scaled by 0.89) for each molecule, we find that the strain energy for 1,2-cyclohexadiene **1** is 29.56 and 23.24 kcal mol^{-1} for 1-phospha-1,2-cyclohexadiene **2**. The structures of these molecules are drawn in Figure 1.



The principal cause for strain in these rings is the distortion from linearity about the cumulene carbon. In order to assess this strain for the carbon system, we determined the energy difference between 1,3-dimethylallene with the angle about C_2 equal to 180° (the ground state) and equal to 132.93° (the angle in **1**). This latter structure was optimized at MP2/6-311G**, keeping the central angle fixed. This energy difference is 15.68 kcal mol^{-1}. For the phosphorus system, we determined a

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

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S0022-3263(97)00304-6 CCC: $14.00

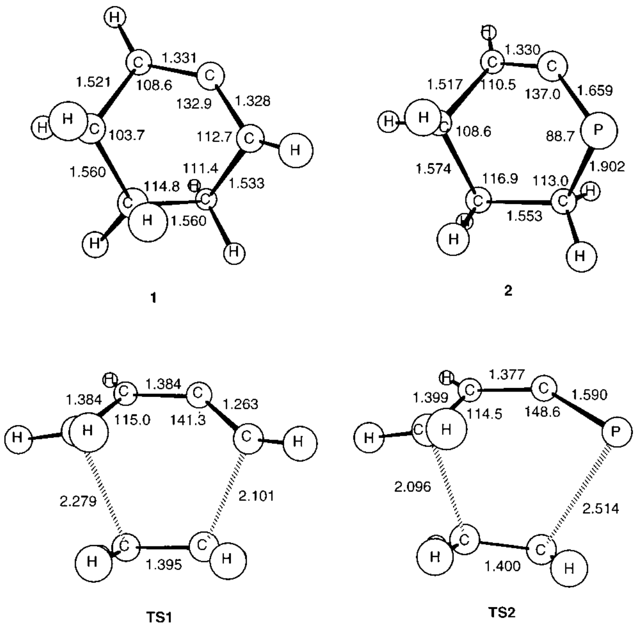

Figure 1. Optimized structures (MP2/6-311G**) of the products and transition states of reactions 1 and 2. All distances are in Å and all angles are in deg.

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

	reaction 1	reaction 2
ΔH_{rxn}	−15.61	−3.23
$T\Delta S_{rxn}$	−12.91	−12.61
ΔG_{rxn}	−2.70	9.38
$\Delta H^{‡}$	26.86	22.88
$T\Delta S^{‡}$	−2.36	−12.26
$\Delta G^{‡}$	39.22	35.14

similar energy difference for 1,3-dimethyl-1-phosphaallene except with the angle about C_2 fixed to 136.97°, the angle about the cumulene C in **2**. The energy for bending this phosphacumulene is 13.79 kcal mol^{-1}, about 2 kcal mol^{-1} less than in the carbon case.

The difference in the strain energies of **1** and **2** is mainly due to the smaller distortion from linearity about the cumulene carbon in the phosphorus compound. We have established that small ring phosphorus compounds are less strained than their carbon analogues primarily due to the ability of phosphorus to accommodate small angles due to the large p-character in its bonds.[10-13] This allows angles about other atoms in the ring to widen and become less strained. The angle in **2** about C_2 is 4.1° wider than in **1**. Further, the angle at C_3 is also larger in **2** than in **1**. The drawback to P substitution is the long C_4-C_5 bond, but we note that this bond is long in both cyclocumulenes.

Given that **2** is about 6 kcal mol^{-1} less strained than **1**, we anticipated that reaction 2 would be more exothermic than reaction 1. The reaction energies are listed in Table 2. The enthalpy for reaction 1 is 3 kcal mol^{-1} more exothermic than the value found using a smaller basis set: −12.7 kcal mol^{-1} at MP4SDTQ/6-31G*//MP2/6-31G*. There are also small differences in the entropies determined at the two diffferent levels. This leads to our prediction that the free energy for reaction 1 is actually slightly negative, as opposed to the slight positive value found by Johnson.[2] Reaction 2 is only slightly exothermic, with $\Delta H_{rxn} = -3.23$ kcal mol^{-1}, contrary to our expectations.

The near thermoneutrality for reaction 2 rests on the relative stabilities of phosphaalkynes vs phosphacumulenes. If we compare the energy of allene with propyne (reaction 5), we find that at MP4/6-311G** with ZPE corrections, propyne is only 0.26 kcal mol^{-1} more stable. Comparing phosphaallene with 1-phosphapropyne (reaction 6) shows that the alkyne is 21.28 kcal mol^{-1} more stable at MP4. This is probably due, in large part, to the significantly stronger C−H than P−H bond.

$$H_2C{=}C{=}CH_2 \longrightarrow H_3C{-}C{\equiv}CH \qquad \text{Reaction 5}$$

$$H_2C{=}C{=}PH \longrightarrow H_3C{-}C{\equiv}P \qquad \text{Reaction 6}$$

Furthermore, the C≡P is highly polar with carbon bearing a large negative charge.[14] Placing a vinyl group on this carbon will allow for delocalization of that charge, further stabilizing this reactant. (Delocalization is evident in the structure of **4** — its C−C bond is 0.009 Å shorter and its C=C is 0.026 Å longer than the comparable bonds in **3**.) Therefore, reaction 2 is less exothermic than reaction 1 due to the relative stabilities of the reactants.

We now turn to the transition states for these two Diels−Alder reactions. The optimized structures of the two TSs (**TS1** and **TS2**) are drawn in Figure 1. The structure of **TS1** is in accordance with previous studies of Diels−Alder reactions. The forming C···C distances are at the high end of the typical range found in pericyclic reactions.[15] The C_2-C_3, C_3-C_4, and C_5-C_6 distances are very close, all suggestive of a synchronous concerted reaction. The $C_1-C_2-C_3$ angle is 141.3°, 8.4° wider than in the product **1**. Similarly, the structure of **TS2** is in accord with previous studies, with the forming C···C distance a bit shorter than usual. The forming C···P distance of 2.514 Å is typical for pericyclic reactions.[4-8]

Comparing the C−C distances in **TS2** with those in **TS1** indicates that **TS2** is the later TS. The C_2-C_3 bond, which is becoming a double bond, is shorter in **TS2** than in **TS1**. The C_3-C_4 and C_5-C_6 bonds, which are becoming single bonds, are longer in **TS2**. However, the bond about C_2 still must deform more in **TS2** than in **TS1**. Nevertheless, most of the evidence indicates that **TS2** is the later TS, which is in accordance with the Hammond postulate, since reaction 2 is less exothermic than reaction 1.

Lastly, we examine the activation barriers for the two reactions. The activation enthalpy for reaction 1 is 26.86 kcal mol^{-1}, about 4 kcal mol^{-1} lower than that determined at MP4SDTQ/6-31G*//MP2/6-31G*. This barrier is larger than for the reaction of butadiene with ethylene. This certainly reflects some strain build up in the TS.

The activation enthalpy for reaction 2 is 22.88 kcal mol^{-1}. This is 4 kcal mol^{-1} below the barrier for reaction 1. The activation entropy for reactions 1 and 2 are nearly identical and quite negative, as expected for a cyclization reaction.

Previous studies of phosphaalkenes and phosphaalkynes involved in Diels−Alder reactions have indicated a

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reduction in the barrier by approximately 10 kcal mol^{-1} relative to the all-carbon case.[4−8] The C−P π-bond is much weaker than the C−C π-bond, which leads to its more reactive nature. However, in the previous cases examined, a cumulene is not the product as it is here. Phosphacumulene, as noted above, is destabilized relative to phosphaalkyne so that its partial formation in the TS offsets the normal reduction (due to P substitution) of the activation barrier.

Nevertheless, even though the activation energy of reaction 2 is not as reduced relative to reaction 1 as for other phospha-Diels−Alder reactions, its barrier is still lower than for the carbon case. In fact, the barrier is in the range of typical Diels−Alder reactions. Therefore, if the appropriate precursor is prepared, perhaps analogous to the system developed by Johnson,[2] the ab initio calculations suggest that this unusual phospha-Diels−Alder reaction should be observed. We look forward to experimental study of this system.

Computational Methods

All molecules present in reactions 1−6 were completely optimized at the HF/6-31G* level, and analytical frequencies were obtained. The structures were then reoptimized at MP2/6-311G**. Single-point energies were evaluated at MP4SDTQ/6311G**//MP2/6-311G**, which we denote simply as MP4. Thermal corrections and entropies were obtained at the HF/6-31G* level scaled[16] by 0.9135 assuming a temperature of 298.15 K and a pressure of 1 atm. All ab initio calculations were performed using GAUSSIAN-94.[17]

Acknowledgment is made to the National Science Foundation for support of this research. This paper was written while the author was visiting Profs. Truhlar and Cramer, and he thanks them for their hospitality.

JO970304C

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