

# Cycloaddition reactions between 2*H*-phosphole and phosphaketene: ab initio examination of [2 + 2] and [4 + 2] pathways

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## Abstract

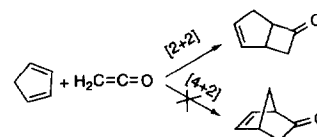
Staudinger ([2 + 2]) and Diels–Alder ([4 + 2]) addition reactions between 2*H*-phosphole and phosphaketene were examined at the MP4SDQ/6-31G\*//MP2/6-31G\* + ZPE level. Electronic structures were analyzed with topological electron density and NBO analyses. The Diels–Alder reaction is favored kinetically by 6 kcal mol<sup>-1</sup> and thermodynamically by 4 kcal mol<sup>-1</sup> over the Staudinger reaction. This is in contrast to the reaction between ketene and cyclopentadiene, for which the Diels–Alder reaction requires a 12 kcal mol<sup>-1</sup> higher activation energy than the Staudinger reaction. In both Staudinger and Diels–Alder reactions phosphaketene reacts at P=C rather than at C=O, as does ketene in the parent Staudinger reaction. The transition structure of the phospho Staudinger reaction is a closed ring, but the second bond is formed employing the phosphaketene phosphorus lone pair rather than the former P=C bond. The reaction mechanism is therefore not [ $\pi^2_s + \pi^2_a$ ].

**Keywords:** Diels–Alder reaction; Staudinger reaction; Phosphole; Ab initio; Phosphaketene

## 1. Introduction

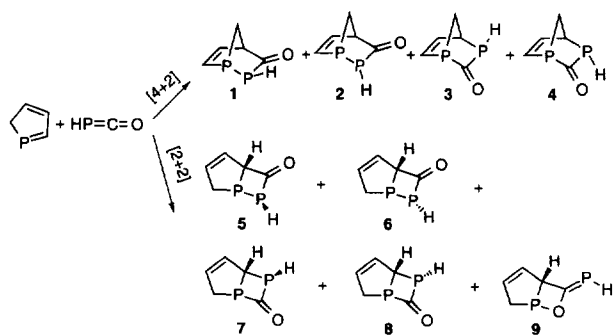
Reaction mechanisms involving phosphalkenes are remarkably similar to those involving alkenes. Phosphalkenes undergo pericyclic reactions, such as the Diels–Alder reaction and the Cope rearrangement, for which the mechanisms agree with the Woodward–Hoffmann rules [1]. The diradical character of the transition state of the phospho Cope rearrangement is actually lower than that of the transition state for the parent reaction [2]. Diels–Alder and Cope reactions involving phosphorus systems require significantly lower activation energies than the parent reactions [1–5]. The Diels–Alder addition of phosphalkene to 2*H*-phosphole proceeds with an activation energy as low as 5 kcal mol<sup>-1</sup> [5]. Like ketene, phosphaketene dimerizes in a [2 + 2] fashion [6]. The activation energy of the phosphaketene dimerization is similar to that of the ketene dimerization [7]. In contrast to the parent reaction, the mechanism of the phosphaketene dimerization is at least topologically in agreement with the [ $\pi^2_s + \pi^2_a$ ] pathway.

In contrast to alkenes, ketenes react with cyclopentadiene (CP) to give the [2 + 2] addition product (the Staudinger reaction) rather than the [4 + 2] addition product (the Diels–Alder reaction) (Scheme 1) [8,9]. In a previous investigation [10] we showed that for the reaction of CP with ketene, the activation energy for the Staudinger reaction is 12 kcal mol<sup>-1</sup> lower than that for the Diels–Alder reaction and 1 kcal mol<sup>-1</sup> lower than that for the Diels–Alder reaction between CP and ethene. We argued that ketenes favor the [2 + 2] pathway for two reasons. First, the Diels–Alder pathway is disfavored for ketenes compared with alkenes since the  $\pi^*_{C=C}$  orbital is significantly higher in energy in the former. Second, the [2 + 2] pathway involves the low lying  $\pi^*_{C=O}$  orbital. The transition state for the [2 + 2] addition is biradicaloid with partial charge separation. The reaction mechanism is concerted but not syn-



Scheme 1.

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Scheme 2.

chronous and does not correspond to the  $[\pi^2_s + \pi^2_a]$  pathway proposed by Woodward and Hoffmann [11].

Since the activation energy of the Diels–Alder reaction between 2*H*-phosphole and phosphathene is significantly lower than that of the parent carbon system, and the activation energy for phosphaketene dimerization is about the same as for the parent carbon system, it seems possible that phosphaketene might preferentially undergo a Diels–Alder reaction with 2*H*-phosphole and not the [2 + 2] pathway like the parent system. The goal of the present study is to examine the products and transition states for [2 + 2] and [4 + 2] additions of phosphaketene with 2*H*-phosphole (Scheme 2) and compare them with the parent reactions.

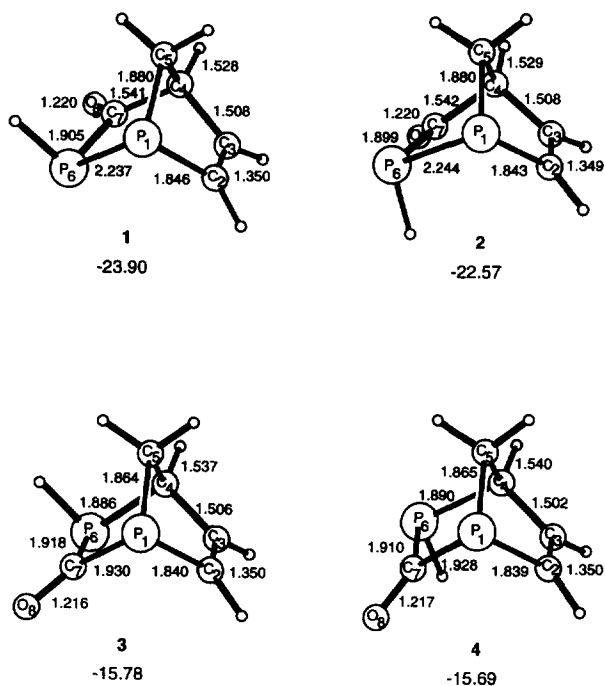


Fig. 1. MP2/6-31G\* optimized geometries of 1–4. All distances are in angstroms and all angles are in degrees.

## 2. Methods

Geometries of reactants, products, and transition states for the structures shown in Scheme 2 were optimized at the HF/6-31G\* and MP2/6-31G\* levels of theory. The MP2 geometries for the products are given in Figs. 1 and 2, and the geometries of the transition states are shown in Figs. 3 and 4. Frequency calculations were carried out at the HF level in order to determine the nature of the stationary points and to evaluate the zero point energy (ZPE) corrections. ZPEs were scaled by 0.89. Reaction and activation energies were obtained at the MP4SDQ/6-31G\*\*//MP2/6-31G\* + HF/ZPE level. All calculations were performed with GAUSSIAN-92 [12].

The [2 + 2] reaction may be biradical or biradicaloid, and perhaps a multiconfigurational wavefunction would be more appropriate. We have rejected using an MC-SCF procedure for a number of reasons. First, recent high-level calculations of the Cope rearrangement have shown that energies from correlated wavefunctions built

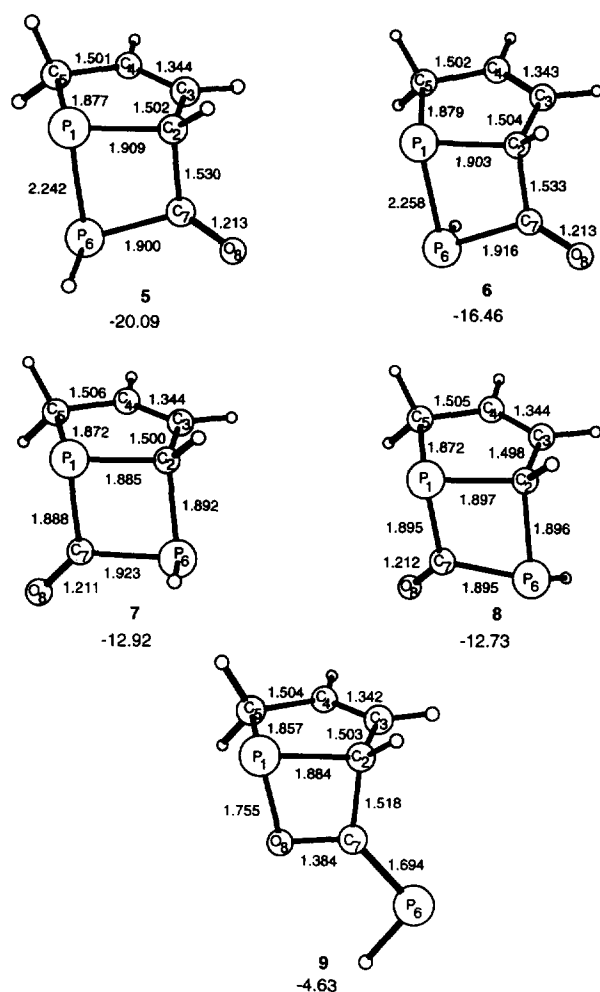


Fig. 2. MP2/6-31G\* optimized geometries of 5–9. All distances are in angstroms and all angles are in degrees.



Table 1

Reaction energies ( $\text{kcal mol}^{-1}$ ) leading to the products of the Diels–Alder reaction (1–4) and the Staudinger reaction (5–9) between 2*H*-phosphole and phosphaketene. Relative ZPEs are scaled by 0.89

Product	HF	MP2	MP4SDQ	ZPE	MP4SDQ + ZPE
1	-32.77	-28.31	-28.17	4.27	-23.90
2	-31.08	-26.82	-26.78	4.21	-22.57
3	-22.49	-19.90	-19.65	3.87	-15.78
4	-22.18	-19.86	-19.59	3.90	-15.69
5	-28.66	-23.33	-23.91	3.82	-20.09
6	-24.84	-18.77	-20.12	3.66	-16.46
7	-20.46	-15.55	-16.41	3.49	-12.92
8	-20.04	-15.66	-16.28	3.55	-12.73
9	-9.15	-7.87	-8.28	3.65	-4.63

There are only minimal structural differences between 5 and 6, the largest being the P–P distance, which is 0.016 Å shorter in 5. The structures of 7 and 8 are also similar, though the P<sub>6</sub>–C<sub>7</sub> distance differs by 0.028 Å. The P–P/C–C bonded isomer 5 from the Staudinger addition is 7.2  $\text{kcal mol}^{-1}$  more stable than the most stable C–P/C–P bonded form 7. Comparison of 5 with 6 and 7 with 8 shows that it is more favorable when the hydrogen at phosphorus of the phosphaketene fragment is *exo*. 5 is lower in energy than 6 due to the *anti* arrangement of the phosphorus lone pairs in 5, thereby reducing their repulsions, relative to their *syn* relationship in 6. This can be seen in the longer P–P bond in 6 than in 5. The energy difference between 7 and 8 is very small due to the large distance between the phosphorus atoms, which results in minimal lone pair repulsion in either isomer.

Lactone 9 is 19  $\text{kcal mol}^{-1}$  less stable than 1 and the reaction is mildly exothermic. We therefore did not attempt to optimize a second isomer in which the P–H bond is *trans* to the C–O bond.

Under thermodynamic control the expectation is to observe formation of 1 only, the P–P/C–C bonded *exo* product of a [4 + 2] addition.

### 3.2. Transition state energies

Activation energies at HF/6-31G\* through MP4SDQ/6-31G\*//MP2/6-31G\* are summarized in Table 2. The trend in activation energies in going from HF to MP2 to MP4SDQ is consistent with previous results: HF activation energies are too large, MP2 activation energies are too small, and MP4 energies are in reasonable agreement with experiment [20,21]. We will discuss only the MP4SDQ (with ZPE correction) energies.

All four transition states for the Diels–Alder additions are lower in energy than those for the Staudinger reaction. The lowest activation energy, 19.3  $\text{kcal mol}^{-1}$ , is computed for transition state II, which leads to the

P–P bonded *endo* isomer 2. This is consistent with experimental [22] and theoretical [5] results regarding Diels–Alder reactions involving 2*H*-phosphole. The activation energy for formation of the P–P bonded *exo* isomer 1, however, is only 0.3  $\text{kcal mol}^{-1}$  higher. The *endo* preference is smaller than that for the Diels–Alder reaction between 2*H*-phosphole and phosphoethene, by about 1.4  $\text{kcal mol}^{-1}$  [5]. Activation energies for transition states leading to C–P/C–P structures are 4.4 and 4.9  $\text{kcal mol}^{-1}$  higher than those leading to the corresponding P–P/C–C isomers.

The activation energy for the Staudinger reaction is 25.5  $\text{kcal mol}^{-1}$ , 6.2  $\text{kcal mol}^{-1}$  higher than that of the Diels–Alder reaction. The [2 + 2] transition states leading to the P–P/C–C bonded isomers are about 0.8  $\text{kcal mol}^{-1}$  higher than those leading to the P–C/P–C bonded isomers.

We also calculated the energy difference between I and VIII at MP4SDQ/6-31G\*//MP2/6-31G\* to determine the effect of triple configurations. This energy difference is 5.78  $\text{kcal mol}^{-1}$ , marginally different from the MP4SDQ difference of 5.86  $\text{kcal mol}^{-1}$ . One last test of the computational method was comparison of this energy difference computed at MP2/6-311+G\*\*//MP2/6-31G\*. Here we examine the effect of the basis set size. The energy difference is 10.17  $\text{kcal mol}^{-1}$  with the large basis, compared with 9.12  $\text{kcal mol}^{-1}$  at MP2/6-31G\*. While exhaustive confirmation of the method is beyond our computational resources, the effect of triples and large basis sets is very small. Given the caveats discussed in Section 2, we believe that these results should adequately reflect the relative energy differences between the [4 + 2] and [2 + 2] reactions.

The Diels–Alder addition is therefore favored both thermodynamically and kinetically over the Staudinger addition. In contrast to the parent carbon reaction, the cycloaddition between 2*H*-phosphole and phosphaketene will yield only [4 + 2] addition products. The

Table 2

Activation energies ( $\text{kcal mol}^{-1}$ ) for through transition structures for the Diels–Alder reaction (I–IV) and the Staudinger reaction (V–IX) between 2*H*-phosphole and phosphaketene. Relative ZPEs are scaled by 0.89

TS	HF	MP2	MP4SDQ	ZPE	MP4SDQ + ZPE
I	24.51	8.80	18.47	1.20	19.67
II	23.90	8.65	18.00	1.33	19.33
III	30.32	14.42	23.36	1.17	24.53
IV	29.40	13.17	22.38	1.37	23.75
V	33.24	19.20	25.51	1.12	26.63
VI	34.58	19.06	25.44	0.90	26.34
VII	33.04	22.78	27.66	1.19	28.85
VIII	31.43	17.92	24.11	1.42	25.53
IX	49.28	37.04	42.50	1.09	43.59

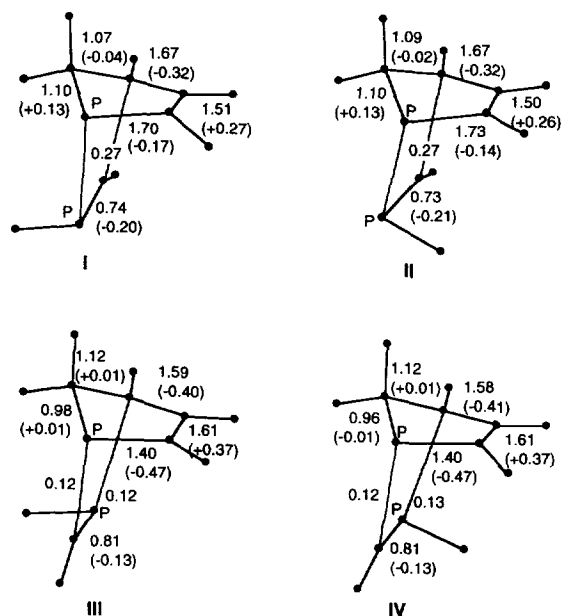


Fig. 5. Representation of the bond path network for I–IV. Bond orders determined by Eq. (1) are listed with the differences from reactants given in parentheses.

P–P bonded *endo* product will be favored, but some P–P bonded *exo* adduct is also expected.

### 3.3. Geometries and electronic structure analyses of transition states

The geometries of the Diels–Alder transition states (I–IV) are shown in Fig. 3. These transition structures are similar to transition structures obtained for other Diels–Alder reactions of phospholes [3,5]. The forming P–P, C–C, and C–P distances are consistent with previous observations. The bond distances within the phosphole fragment are very similar for all four TSs.

Bond orders obtained using Eq. (1) (Fig. 5) provide some ability to distinguish the nature of the TSs I–IV. The bond orders in the phosphole fragment of the transition states leading to P–P/C–C bonded isomers are earlier than those leading to P–C/P–C bonded isomers, i.e. the former double bonds have higher bond orders and the former single bonds have lower bond orders in transition states I and II than in III and IV. This is in agreement with the Hammond postulate that the more exothermic reaction has the earlier transition state. The double bond in the phosphole fragment next to the carbonyl carbon is always weaker than that next to the phosphaketene phosphorus. This indicates that bond formation at the carbonyl carbon is more advanced. The P–C bond orders in the phosphaketene fragments are quite low, between 0.81 and 0.73. This is, however, not surprising considering that the bond order of the P–C "double bond" in free ketene is only 0.94 (see Table 3).

Table 3

Charge densities at bond critical points ( $\rho(r_c)$ ) and bond orders (BO) according to Eq. (1) for ketene and phosphaketene, and for the ketene fragments of the transition states of Diels–Alder and Staudinger reactions between ketene and cyclopentadiene (CP) and between phosphaketene and 2*H*-phosphole

Compound	C–C/P–C		C–O
	$\rho(r_c)$	BO	$\rho(r_c)$
ketene	0.328	1.63	0.470
ketene + CP [4 + 2] TS	0.316	1.51	0.455
ketene + CP [2 + 2] TS	0.339	1.75	0.412
P-ketene	0.150	0.94	0.444
I	0.137	0.73	0.473
IV	0.144	0.84	0.474

The changes in bond orders in progressing from reactant to TS indicate an asynchronous reaction through TS I and II – the bond orders of the active bonds in the phosphole fragment change by from  $-0.15$  for the P<sub>1</sub>–C<sub>2</sub> bond to  $-0.32$  for the C<sub>3</sub>–C<sub>4</sub> bond. In contrast, TSs III and IV are more synchronous, with changes in the range of  $+0.37$  for the C<sub>2</sub>–C<sub>3</sub> bond to  $-0.47$  for the P<sub>1</sub>–C<sub>2</sub> bond.

The TS for the [2 + 2] reaction leading through V and VI appears to follow the  $[\pi^2s + \pi^2a]$  pathway. There is the twisted arrangement between the reacting  $\pi$  bonds. There are bond paths for the two forming new single bonds (Fig. 6). The bond order of the former P=C double bond in phosphole has been reduced by about 0.15. Unfortunately, we cannot assess the bond

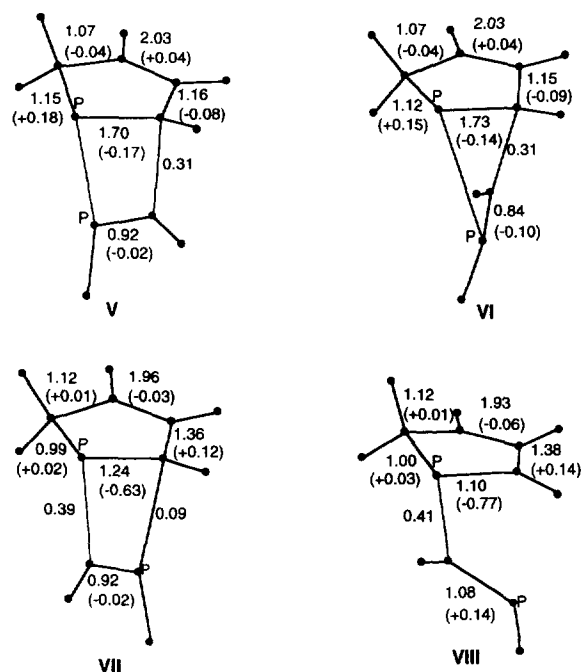


Fig. 6. Representation of the bond path network for V–VIII. Bond orders determined by Eq. (1) are listed with the differences from reactants given in parentheses.

orders of the forming P–P bonds, though the value  $\rho(r_c)$  in these TSs is less than in the Diels–Alder TSs I and II (0.038 vs.  $0.043 e^- au^{-3}$ ).

TS VII also appears to follow the  $[\pi^2_s + \pi^2_a]$  pathway, having a twisted relationship of the reacting  $\pi$ -bonds and bond paths for the new C–P bonds. In contrast, VIII does not possess a bond path between phosphorus of the ketene fragment and C<sub>2</sub>. This distance is longer in VIII than in VII. For both VII and VIII, the new C–P bonds form to much different extents in the TSs, with much more developed interaction between P<sub>1</sub> and the carbonyl carbon than between C<sub>2</sub> and phosphorus in ketene. The P=C<sub>2</sub> bond order indicates that the  $\pi$ -bond is nearly completely destroyed in both TSs. The increased C<sub>2</sub>–C<sub>3</sub> bond order of nearly 1.4 suggests some allylic character, which stabilizes these TSs. This allylic stabilization is not present in either V or VI.

The strong P<sub>1</sub>–C<sub>2</sub> bond and the shorter P–C distance in the ketene fragments of V and VI indicate that these TSs are earlier than VII and VIII. This is consistent with the Hammond postulate.

Table 3 compares charge densities at bond critical points of free ketene and free phosphaketene with those of the ketene fragments in the lowest energy transition states for [2 + 2] and [4 + 2] additions between ketene and cyclopentadiene and between phosphaketene and 2*H*-phosphole. Bond orders for C–C and P–C bonds are computed according to Eq. (1); no empirical relationship is available for computing C–O bond orders. In the hydrocarbon system, the C–C bond order in the [4 + 2] transition state decreases compared with free ketene, while it increases in the [2 + 2] transition state. For the phosphorus system, the P–C bond order decreases in both reactions. The charge density of the C–O bond is less in the [4 + 2] and [2 + 2] TSs (relative to free ketene) for the hydrocarbon case. The charge density of the C–O bond of phosphaketene is larger in both TSs. We previously argued that the C=O bond of ketene is involved in the Staudinger reaction of ketene and CP. The above data suggest that phosphaketene employs the P=C bond in both reaction types, and that the C=O bond is not involved in either reaction.

In agreement with the above Bader analysis, NBO analysis indicates that in the transition states for both the phospho Diels–Alder and phospho Staudinger reactions the P=C bonds are broken and the C=O bonds are intact. In the [2 + 2] transition states for reaction between ketene and CP, the C=O bonds in the ketene fragments are broken while the C=C bonds are only weakened. Although the reaction begins at the carbonyl carbon in all four transition states of the phospho [2 + 2] additions, phosphaketene appears to employ the P=C bond for bond formation. To form the second bond with the phosphole ring, the phosphorus atom of phosphaketene employs an orbital that is perpendicular to

the former P=C bond which lies in the same plane as the C=O bond. This is clearly the phosphorus lone pair. The [2 + 2] addition between 2*H*-phosphole and phosphaketene thus follows a different reaction mechanism to the carbon analog.

#### 4. Discussion

The reaction of CP and ketene yields exclusively the [2 + 2] addition product. In an earlier paper [10] we showed that the Staudinger reaction is kinetically favored by  $12 \text{ kcal mol}^{-1}$  over the Diels–Alder reaction. In sharp contrast to these results, the [4 + 2] pathway is kinetically favored over the [2 + 2] pathway by  $6.2 \text{ kcal mol}^{-1}$  for the reaction between 2*H*-phosphole and phosphaketene. Thermodynamically, the Diels–Alder reaction is favored in both the hydrocarbon and phosphorus cases.

The activation energy of the Diels–Alder addition for the phosphorus system ( $19.33 \text{ kcal mol}^{-1}$ ) is almost  $17 \text{ kcal mol}^{-1}$  lower than that of the parent system, but  $14 \text{ kcal mol}^{-1}$  higher than that of the Diels–Alder reaction between 2*H*-phosphole and phosphoethene. The activation energy for the Diels–Alder reaction between CP and ketene is  $11 \text{ kcal mol}^{-1}$  higher than that involving ethene. The activation energy for the [2 + 2] addition is slightly lower in the parent than in the phosphorus reaction,  $25.0 \text{ kcal mol}^{-1}$  vs.  $25.5 \text{ kcal mol}^{-1}$ .

The lowering of the activation energy for the Diels–Alder reaction involving phosphorus is consistent with previous results [2–5,10,21], which showed that each substitution of C by P in one of the participating bonds lowered the activation energy by roughly  $10 \text{ kcal mol}^{-1}$ . The increase in reactivity can be rationalized by the smaller energy difference between the frontier orbitals in the phosphorus system. As pointed out in the preceding paper [10], the relevant frontier orbitals for Diels–Alder reactions involving ketenes are LUMO(CP) – HOMO(KET) and HOMO(CP) – LUMO + 1(KET), since the LUMO of ketene is essentially  $\pi_{C=O}^*$ . LUMO(CP) – HOMO(KET) is  $26 \text{ kcal mol}^{-1}$  smaller than HOMO(CP) – LUMO + 1(KET), and is thus the dominant interaction. The LUMO(CP) – HOMO(KET) energy difference is  $60 \text{ kcal mol}^{-1}$  smaller in the phosphorus system compared with the carbon system, while the HOMO(CP) – LUMO + 1(KET) difference is  $47 \text{ kcal mol}^{-1}$  smaller in the phosphorus system.

The strongest frontier orbital interaction between cyclopentadiene and ketene, however, is HOMO(CP) – LUMO(KET). The HOMO(CP) – LUMO(KET) gap is  $33 \text{ kcal mol}^{-1}$  smaller than the LUMO(CP) – HOMO(KET) gap. Since the LUMO of ketene is essentially  $\pi_{C=O}^*$ , which is perpendicular to  $\pi_{C=C}^*$ , ketene prefers to approach CP in a plane perpendicular to that required for Diels–Alder addition. For the phosphorus

system HOMO(CP) – LUMO(KET) is only 7 kcal mol<sup>-1</sup> smaller than LUMO(CP) – HOMO(KET). In terms of frontier orbital control there is a strong preference to react at C=O over C=C for the carbon system, but only a slight preference to react at C=O over P=C in the phosphorus case, suggesting that both should react via a [2 + 2] pathway.

While the Diels–Alder reaction for the phosphorus system has a substantially lower activation energy relative to that of the parent, the activation energies for the Staudinger reactions of the parent system and the phosphorus systems are similar, 25.0 and 25.5 kcal mol<sup>-1</sup>. According to frontier orbital control, one might expect that the Staudinger reaction involving phosphorus would have a lower activation energy, since the HOMO(CP) – LUMO(KET) gap is 34 kcal mol<sup>-1</sup> smaller for the phosphorus system compared with the parent system. That this is not the case results from several reasons. The most favorable transition structure (II in fig. 2 of our previous paper) for the parent Staudinger reaction first creates the new  $\sigma$ -bond between the carbonyl carbon and C<sub>1</sub> of the CP ring, which allows for allylic stabilization. The ketene fragment orients in a way such as to minimize steric repulsion. This approach yields the vinylcyclobutanone with the keto group opposite the remaining double bond in the CP fragment. The corresponding transition state for the phosphorus system is VIII, which is the most favorable TS. VIII, however, leads to the C–P/C–P bonded isomer 8. All previous studies of cycloadditions involving phosphorus systems show that P–P/C–C bond formation is thermodynamically and kinetically favored. For example, Diels–Alder reactions examined here kinetically favor formation of P–P/C–C bonded isomers by more than 4 kcal mol<sup>-1</sup>. Since all [2 + 2] additions of carbon and phosphorus systems start at the carbonyl carbon, phosphaketene has to attack C<sub>2</sub> of phosphole instead of P<sub>1</sub> in order to form the P–P/C–C bonded isomers. This approach corresponds to transition states V and VI, which are 0.8–1.0 kcal mol<sup>-1</sup> higher in energy than VIII. Reaction at C<sub>2</sub>, however, does not allow for allylic stabilization within the phosphole ring. We have seen for the parent carbon reaction that attack at C<sub>2</sub> is disfavored by about 12 kcal mol<sup>-1</sup> compared with attack at C<sub>1</sub>. There exists no [2 + 2] pathway for the reaction of phosphaketene with 2*H*-phosphole that combines all the favorable interactions that make the [2 + 2] cycloaddition of ketene with CP the preferred pathway.

Finally, we would like to address the question of why phosphaketene seems to avoid employing the C=O bond in the [2 + 2] addition. The C=O antibond is 7 kcal mol<sup>-1</sup> lower in energy than the P=C antibond, and it lies in the same plane as the phosphorus lone pair. NBO analysis reveals that the two orbitals of phosphaketene which form bonds with phosphole are perpendicular, and that the P=C rather than the C=O

bond is involved in bond formation. It is most easily seen for transition state VI in Fig. 4 that the phosphaketene fragment tilts and twists to allow for employing the two perpendicular orbitals. Apparently, in the Staudinger reaction phosphaketene sacrifices reacting at the lower lying C=O bond to gain additional stabilization from involvement of the phosphorus lone pair. This lone pair is not available in ketene.

## 5. Conclusions

The Diels–Alder reaction between phosphaketene and 2*H*-phosphole is kinetically favored over the Staudinger reaction by 6.2 kcal mol<sup>-1</sup>. This is in contrast to the reaction between ketene and cyclopentadiene, where the Staudinger reaction is kinetically favored over the Diels–Alder reaction by 12 kcal mol<sup>-1</sup> [10]. In general, Diels–Alder reactions that involve a P=C bond have activation energies about 10 kcal mol<sup>-1</sup> lower than the hydrocarbon analogs [2–5,10,20,21]. This trend holds for the case examined here, the Diels–Alder reaction of phosphaketene with 2*H*-phosphole, which has an activation energy 19.3 kcal mol<sup>-1</sup> lower than for the reaction of ketene with cyclopentadiene.

The activation energies for the Staudinger reactions between ketene and cyclopentadiene and between phosphaketene and 2*H*-phosphole are similar, 25.0 and 25.5 kcal mol<sup>-1</sup>. That the activation energy of the [2 + 2] addition involving phosphorus is not lower compared with the parent system results from the fact that the most favorable reaction pathway, in which phosphole reacts at P and is stabilized by allylic conjugation, leads to the kinetically and thermodynamically unfavorable P–C/P–C bonded isomer.

Therefore, the change in reaction preference in moving from the hydrocarbon to the phosphorus case results from the standard reduction in activation energy for the Diels–Alder TS coupled with no change in activation energy for the Staudinger reaction.

The geometries of the transition states for [2 + 2] addition involving phosphorus are in agreement with those expected for the [ $\pi^2s + \pi^2a$ ] mechanism. Topological analysis indicates that the forming C–P bonds are not created to the same extent in VII and VIII. NBO analyses indicate that in all four [2 + 2] transition states the bond between the phosphaketene phosphorus and the phosphole fragment is formed involving the phosphorus lone pair rather than the former P=C bond. Like the parent reaction, the phosphorus Staudinger reaction does not follow the [ $\pi^2s + \pi^2a$ ] pathway.

Finally, the orbital interactions for the [2 + 2] reactions in the parent and phosphorus case differ. In the former case, the  $\pi_{C=O}$  bond is broken first, allowing for allylic stabilization within the ketene fragment. In the reaction of phosphaketene, the  $\pi_{C=P}$  bond is broken

first. This allows the phosphorus lone pair to be involved in the formation of the second bond.

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