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Molecular Orbital Study of the Vinylphosphinidene to Phosphapropyne Rearrangement

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MNDO and *ab initio* studies of interconversions on the C_2H_3P potential surface point to 1-phosphapropyne (**1**) as the global minimum and suggest that, under vigorous reaction conditions, vinylphosphinidene **2** will interconvert with its ring-closed isomer **5**. At the reported experimental temperature of 700 °C, the conversion of **2** or **5** to phosphaallene (**3**) will occur much more rapidly than their conversion to **1**. The lowest-energy pathway for conversion of **3** to **1** involves reversion of **3** to **2**, and subsequent rearrangement of **2** to **1**. It is predicted that, at high temperatures, an equilibrium mixture of **2**, **5**, and **3** will be depleted by the conversion of **2** to **1**. Thus, the net reaction will be the direct rearrangement of **2** to **1**, in which a hydrogen shifts away from an electron-deficient center. These results agree well with experimental studies in which the flash vacuum thermolysis of vinylphosphirane at 700 °C led to **1** as the sole product.

Recently, Mathey, Le Floch, and Haber (MLFH) found that the flash vacuum thermolysis (FVP) of vinylphosphirane at 700 °C leads to the production of phosphapropyne (**1**), presumably via rearrangement of vinylphosphinidene (**2**).[1] The direct rearrangement of **2** to **1** would be an unusual reaction for a carbene-like species, in that a hydrogen atom is moving *away* from the electron-deficient center. Thus, the mechanism for the rearrangement of **2** to **1** is of considerable interest. **2** is the phosphinidene analog of vinylmethylene, possible rearrangements of which have received detailed theoretical scrutiny by Yoshimine, Pacansky, and Honjou (YPH).[2] Since YPH predicted that vinylmethylene rearranges to propyne via allene, it was decided to see whether molecular orbital calculations lead to the same predicted pathway for **2** (Scheme 1).

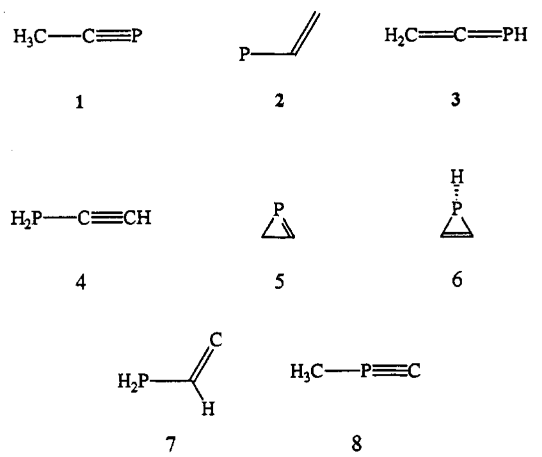
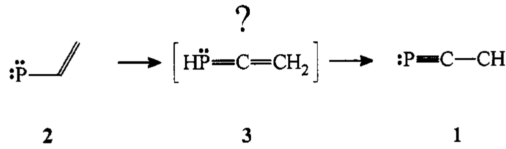


Figure 1. Initial geometries assumed for MNDO geometry optimizations on the C_2H_3P potential surface.

Scheme 1



We carried out semiempirical and *ab initio* studies upon several isomers of C_2H_3P, guided by the work of YPH. The isomers considered here are shown in Figure 1. The work consisted of three parts. First, all geometries were fully optimized, using MNDO at the RHF-SCF level, in both singlet and triplet states. Next, using the relative energies of the local minima as a guide, the singlet MNDO potential surface was searched for saddle points between likely reactants or intermediates in the vinylphosphinidene to phosphapropyne rearrangement. Finally, independent *ab initio* studies were performed on selected points on the potential surface described by the semiempirical treatment.

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[1] Haber, S.; Le Floch, P.; Mathey, F. *J. Chem. Soc., Chem. Commun.* 1992, 1799.

[2] (a) Honjou, N.; Pacansky, J.; Yoshimine, M. *J. Am. Chem. Soc.* 1985, *107*, 5332. (b) Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* 1989, *111*, 2785. (c) Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* 1989, *111*, 4198.

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Computational Details

1. Semiempirical Methods. Semiempirical studies were performed using MNDO[3] as implemented by the MOPAC package, versions 5.0 and 6.0.[4] All work was performed at the restricted Hartree–Fock SCF level except that limited configuration interaction was used in order to compare the two lowest singlet states of **2** with those obtained by *ab initio* methods. The configurations mixed are those resulting from excitation of 0, 1, and 2 electrons, respectively, from the HOMO of the RHF closed-shell singlet to the LUMO.

Initial molecular geometries were constructed according to Figure 1 using the SYBYL Molecular Graphics package[5] and fully optimized; where appropriate, geometries were then reoptimized using symmetry (e.g. in calculating the geometry of **1** which is C_{3v} in the singlet state).

Transition states were fully optimized by eigenvector following[6] at the RHF-SCF level in MOPAC 6.0, after being obtained either as saddle points along the MOPAC-generated reaction coordinate between two fully optimized local minima[7] or, in the case of the interconversion of **2** and **5** (*vide infra*), by optimizing points along a reaction coordinate defined by variation of the P–C–C angle.

Vibrational analysis was performed on each transition state to confirm that it had one and only one imaginary frequency and that the frequency corresponded to the probable reaction coordinate. The imaginary vibrational modes of transition states were also visually examined in order to confirm that the transition states made physical sense. This was done using HyperChem Release 3 for DOS.[8]

2. *Ab Initio* Methods. All stationary points on the C_2H_3P potential energy surface were initially located by using SCF gradient techniques,[9] except for the C_s symmetry $^1A'$ state of vinylphosphinidene (**2**), where two-configuration SCF (TCSCF) methods were used.[10] Analytic SCF[11] and TCSCF[12] second derivative methods were then employed to determine the nature of the stationary points obtained. Subsequently, these structures were refined at correlated levels of theory. In particular, configuration interaction methods including all single and double excitations (CISD) from the SCF[13] or TCSCF[14] reference were adopted. Final relative energy estimates from the CI methods were obtained after appending the Davidson correction[15] for unlinked quadruple excitations (CISD+Q) or its multireference analog (TC-CISD+Q).

Because there are two nearly isoenergetic singlet states of vinylphosphinidene in C_s symmetry ($^1A'$ and $^1A''$, both derived from the $^1\Delta$ state of PH) that are freely mixed in C_1 symmetry where the transition states involving **2** are expected to lie, we have used special methods in our *ab initio* transition state searches. Thus, after initially obtaining transition state geometries at the SCF level of theory, the structures were refined using the Davidson–Stenkamp method[16] for ground states (equivalent to a TCSCF with both orbitals of the same symmetry) and the highly-correlated single-reference coupled cluster singles-and-doubles (CCSD) method.[17]

The one particle basis set used in this research is of polarized double-ζ (DZP) quality. Specifically, the Huzinaga–Dunning basis sets[18] for carbon (9s5p/4s2p), phosphorus (11s7p/6s4p), and hydrogen (4s/2s) (scaled by 1.2) have been supplemented with polarization functions as follows: $\alpha_d(P) = 0.6$, $\alpha_d(C) = 0.75$, and $\alpha_P(H) = 0.75$.

Results and Discussion

Results of MNDO geometry optimization are shown in Figure 2, and *ab initio* geometries are shown in Figures 3 and 4; relative enthalpies are shown in Table 1. MNDO and *ab initio* energies are within 3 kcal/mol where both are available, except for phosphinoacetylene (**4**), where the disagreement is 6 kcal/mol. Some of these molecules have been previously studied by Nguyen, Vansweevelt, and Vanquickenborne;[19] we have included their MP4-derived energies, which are somewhat higher than ours, in Table 1. In each case, the molecules appear in the same order of energy with similar energetic differences. It should be noted that, for the relative energies which form the basis of this study, the agreement between the present *ab initio* results and the earlier MP4 results is no better than the agreement between the *ab initio* and MNDO results reported here.

Geometries derived from MNDO and *ab initio* methods are not always in such good agreement, but this does not affect our conclusions concerning the current mechanistic problem. The discussion that follows is based primarily on the MNDO results, and is, of course, therefore qualitative; *ab initio* results are included where appropriate.

Phosphapropyne (**1**) is the global minimum. This is consistent with the experimental results reported.[1] FVP experiments at 700 °C are conducive to thermodynamic control of product formation. It would therefore have been surprising had **1** not been the thermodynamic sink. This theme will be elaborated in the discussion of various transition states between the local minima, and the mechanism that they imply.

The energies of phosphaallene (**3**), ethynylphosphine (**4**),[20] and 3*H*-phosphirene (**5**) are not far above that of **1**. 1*H*-Phosphirene (**6**) is found, by both MNDO and *ab initio*, to be ca. 10 kcal/mol above 3*H*-phosphirene (**5**); this result

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[3] (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Dewar, M. J. S.; McKee, M. L.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 3609.

[4] Stewart, J. J. P. QCPE catalog No. 455; Indiana University: Bloomington, IN.

[5] TRIPOS, Inc., St. Louis, MO.

[6] Baker, J. *J. Comput. Chem.* **1986**, *7*, 385.

[7] Dewar, M. J. S.; Healy, E. F.; Stewart, J. J. P. *J. Chem. Soc., Faraday Trans. 2*, **1984**, *3*, 227.

[8] Autodesk, Inc., Scientific Modeling Division, 2320 Marinship Way, Sausolito, CA 94965–9910.

[9] (a) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 4, p 53. (b) Dupuis, M.; King, H. F. *J. Chem. Phys.* **1978**, *68*, 3998.

[10] Goddard, J. D.; Handy, N. C.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *71*, 1525.

[11] Saxe, P.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1982**, *77*, 5647.

[12] (a) Yamaguchi, Y.; Osamura, Y.; Fitzgerald, G.; Schaefer, H. F. *J. Chem. Phys.* **1983**, *78*, 1607. (b) Yamaguchi, Y.; Osamura, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 7506.

[13] (a) Saxe, P.; Fox, D. J.; Schaefer, H. F.; Handy, N. C. *J. Chem. Phys.* **1982**, *77*, 5584. (b) Brooks, B. R.; Laidig, W. D.; Saxe, P.; Goddard, J. D.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1980**, *72*, 4652. (c) Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *85*, 963.

[14] Lee, T. J.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 7062.

[15] Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

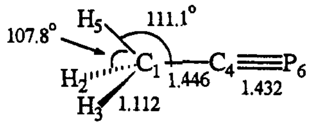
[16] (a) Davidson, E. R.; Stenkamp, L. Z. *Int. J. Quant. Chem. Symp. Ser.* **1976**, *10*, 21. (b) Fitzgerald, G.; Schaefer, H. F. *J. Chem. Phys.* **1985**, *83*, 1162.

[17] (a) Scuseria, G. E.; Scheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *86*, 2881. (b) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1988**, *89*, 7382. (c) Scheiner, A. C.; Scuseria, G. E.; Rice, J. E.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 5361.

[18] (a) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Huzinaga, S. Approximate Atomic Functions II. Department of Chemistry Report; University of Alberta: Edmonton, Alberta, Canada, 1971. (c) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823. (d) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 3, p 1.

[19] Nguyen, M. T.; Vansweevelt, H.; Vanquickenborne, L. G. *Chem. Ber.* **1992**, *125*, 923.

[20] We expected 4 to be the global minimum. These results, however, are consistent with MNDO calculations on CH_3CN vs $NH_2C{\equiv}CH$. Pauling's bond dissociation energy data also predict that acetonitrile is lower in energy than ethynylamine. Pauling, L. *The Nature of the Chemical Bond*, 2nd ed.; Cornell University Press; Ithaca, NY, 1960.



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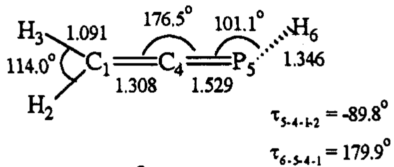

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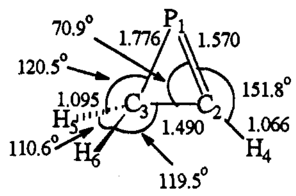

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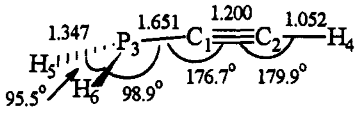

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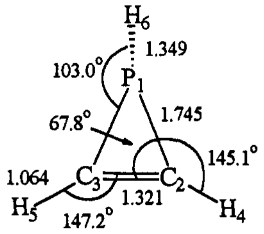

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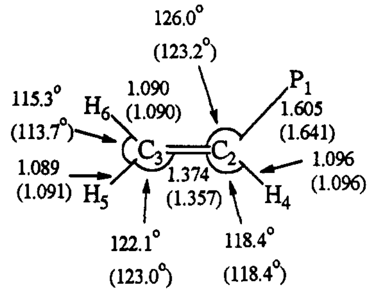

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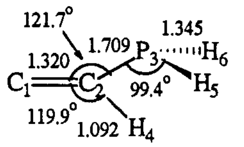

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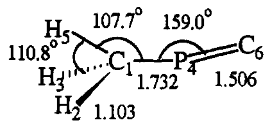

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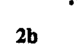
Figure 2. MNDO RHF-optimized singlet-state geometries of molecules on the C_2H_3P potential surfaces. Numbers for **2** are for CI- and (RHF)-optimized geometries. τ is a torsion angle.

is as expected from qualitative bond-energy considerations[21] and previously published experimental studies on substituted phosphirenes.[22]

Next in energy is vinylphosphinidene (**2**). The ground state is a triplet, as would be expected for a group 15 neutral six-valence-electron species. The lowest-lying MNDO singlet state had biradical character, as represented by **2a**, approximately corresponding to the *ab initio* $^1A''$ state

2a



2b

(*vide infra*). The MNDO energies reported in Table 1 place this state 11 kcal/mol below the closed-shell state **2b**, but this energy difference may be exaggerated by the limited CI included in the optimization of **2a** but not **2b**. High-level *ab initio* studies have shown this to be the ordering of the lowest singlet states for phenylnitrene,[23]

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[21] In going from **6** to **5** one "gains" the energy advantage of a C—H over a P—H bond and "loses" the energy advantage of a C═C π-bond over a C═P π-bond; this rough estimate favors **5** over **6** by 1–3 kcal/mol. Furthermore, **6** is expected to be destabilized by any interaction of the phosphorus lone pair with the C═C π-bond. For D_0(C—H) see: Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. No. 1. For D_0(P—H) see: Berkowitz, J.; Curtiss, L. A.; Gibson, S. T.; Greene, J. P.; Hillhouse, G. L.; Pople, J. A. *J. Chem. Phys.* **1986**, *84*, 375. for C═C and C═P π-bond energies see: Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217.

[22] For a rearrangement of a 1*H*- to a 3*H*-phosphirene, see: Wagner, O.; Ehle, M.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 225; *Angew. Chem.* **1989**, *101*, 227. See also: Wagner, O.; Ehle, M.; Birkel, M.; Hoffmann, J.; Regitz, M. *Chem. Ber.* **1991**, *124*, 1207. Typically, however, 1*H*-phosphirenes are synthesized with substituents other than hydrogen at phosphorus; this usually precludes rearrangement to the thermodynamically more stable form. See also ref 19, a study of the stabilization of 1*H*-phosphirenes by halo substitution at phosphorus.

[23] Kim, S.-J.; Hamilton, T. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1992**, *114*, 5349.

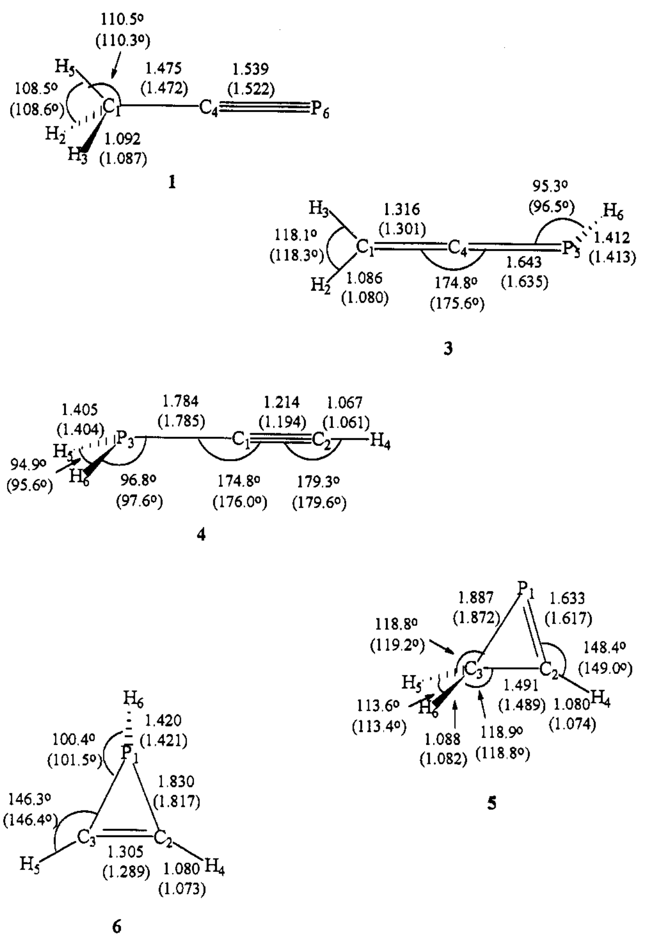

Figure 3. *Ab initio* SCF- and CISD-optimized singlet-state geometries of molecules on the C_2H_3P potential surface. Values in parentheses refer to SCF calculations.

though not for vinylmethylene.[2b] The MNDO RHF (**2b**) and CI (**2a**) geometries for **2** are shown in Figure 2.

Ab initio methods find two nearly isoenergetic singlet biradical states of **2**. The lower is a $^1A''$ state; the other is a $^1A'$ state. We found the energy difference to be less than 3 kcal/mol. Three *ab initio* structures for **2** are shown in Figure 4: the ground $^3A''$ state at the CISD level; the nonplanar ^1A state optimized at the CCSD level; and the TCSCF-CISD-optimized $^1A'$ state. Obviously, extensive electron correlation must be included in a single-reference method to recover a planar geometry.

Finally, isomeric structures **7** and **8** lie quite high on the semiempirical potential surface and are therefore probably not of any importance in the reactions of vinylphosphinidene.

We therefore obtained semiempirical transition states for the following rearrangements: **2b** to **1**, **3**, **5**, and **6**; **3** to **1**, **4**, and **6**; **4** to **6**; **5** to **1**, **3**, and **6**; and **6** to **1**. Since all the structures considered except vinylphosphinidene (**2**) have closed-shell lowest singlet states, RHF calculations were employed. The enthalpic results are given in Table 2; MNDO-derived structures are shown in Figures 5–7. *Ab initio* SCF, TCSCF, and CCSD structures of the transition states for **2** to **1** and **2** to **3** were also obtained. The SCF and CCSD results are shown in Figure 8. Notice that the CCSD optimization for **2** to **1**, which started at the C_1 symmetry SCF structure, converged to a C_s symmetry geometry. The TCSCF optimization for **2** to **1** (not shown) also converged to a C_s symmetry transition state geometry.

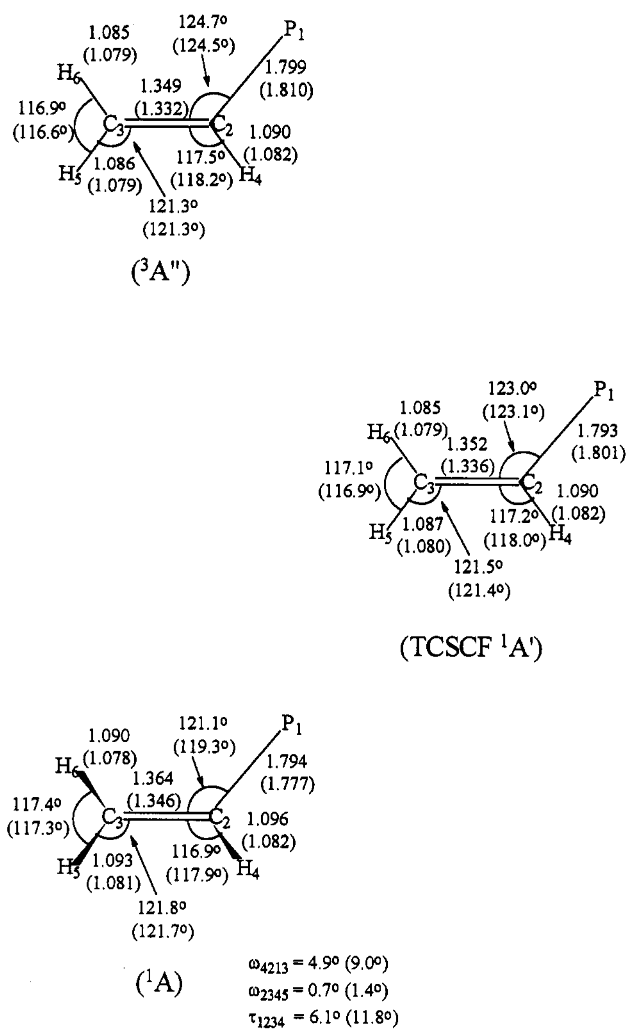

Figure 4. *Ab initio* geometries for **2**. ω is an out-of-plane angle; τ is a torsion angle. $^3A''$ geometries are from CISD and (SCF) studies; $^1A'$ geometries are from TC-CISD and (TCSCF) studies; ^1A geometries are from CCSD and (SCF) studies.

Table 1. MNDO[a] and *Ab Initio* Enthalpies of Several Isomers of C_2H_3P, Relative to Phosphapropyne 1

molecule	MNDO singlet ΔE (kcal/mol)	MNDO triplet ΔE (kcal/mol)[b]	*ab initio* singlet ΔE (kcal/mol)[c]
1	0.0	68.7	0.0 (0.0)
3	17.3	43.9	20.5 (24.1)
5	19.4	45.0	22.8 (24.4)
4	20.1	104.4	25.8 (31.8)
6	29.7	67.2	32.4 (35.6)
2a	41.9[d]	27.2	51.0[e] [triplet, 25.1][f]
2b	52.6		
8	81.6		
7	87.1	124.7	

[a] MNDO energies given here were obtained at the RHF level, except as noted. [b] Relative to singlet **1**. [c] Optimized at the CISD level. Numbers in parantheses are MP4 results using the frozen-core approximation, from ref 17, Table 2. [d] Calculated employing the limited configuration interaction (see text). [e] $^1A'$ state energy, TCCISD+Q. [f] $^3A''$ state energy, CISD+Q, relative to CISD+Q singlet to **1**.

There is general agreement between the structures predicted by the two methods, but bond angles differ by as much as 5°. MNDO predicts energy barriers ca. 10 kcal/mol higher than the *ab initio* values, but there is good agreement regarding the energy *difference* between the two transition states **2** → **1** and **2** → **3**. Both methods predict that the barrier for **2** → **3** will be 12–14 kcal/mol less than that for **2** → **1**.

Table 2. MNDO[a] and *Ab Initio* Enthalpies of Activation for Various Reactions on the C_2H_3P Surface, Relative to the End Point of Each Reaction

initial point	final point	MNDO $\Delta E^{\ddagger}$ (kcal/mol) (init → final)	MNDO $\Delta E^{\ddagger}$ (kcal/mol) (final → init)	*ab initio* $\Delta E^{\ddagger}$ (kcal/mol)[b] (init → final)
2b	**1**	29.8	82.4	18.4
2b	**3**	15.6	51.0	6.1
2b	**5**	1.9	35.1	ca. 0[c]
2	**6**	59.3	82.2	
3	**1**	103.7	120.9	
3	**4**	78.4	75.6	
3	**6**	78.4	65.9	
4	**6**	59.0	49.3	
5	**1**	63.0	82.4	
5	**3**	48.8	51.0	
5	**6**	92.5	82.2	
6	**1**	52.7	82.4	

[a] MNDO energies were obtained at the RHF level. [b] Calculated for **2** → **1** and **2** → **3** at the CCSD level. TC-CISD+Q energies obtained at TCSCF-optimized geometries give 15.6 kcal/mol for **2** to **1** and 8.0 kcal/mol for **2** to **3**. [c] Due to a very flat potential energy surface, no transition state was found for **2** → **5** at the CCSD level of theory; this is in qualitative agreement with the MNDO result in that the activation enthalpy should therefore be very small.

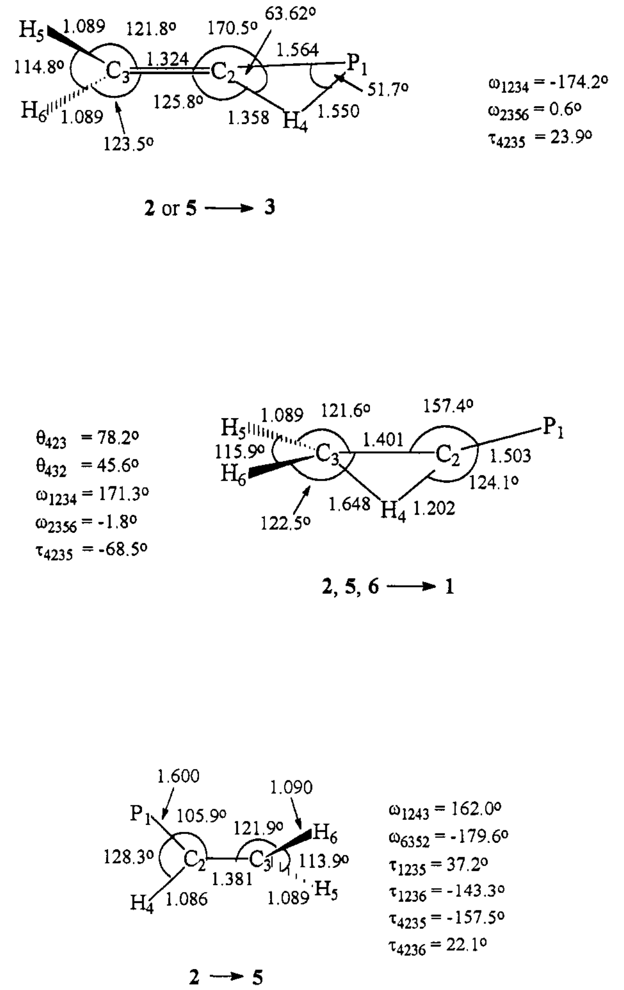

Figure 5. MNDO-optimized transition-state geometries for conversions on the C_2H_3P potential surface. θ is a bond angle; ω is an out-of-plane angle; and τ is a torsion angle.

Despite extensive searches for an *ab initio* transition state between **2** and **5** at the CCSD level of theory, no stationary point was found. It was clear from this search, however, that the barrier must be small, in accord with the MNDO result.[24]

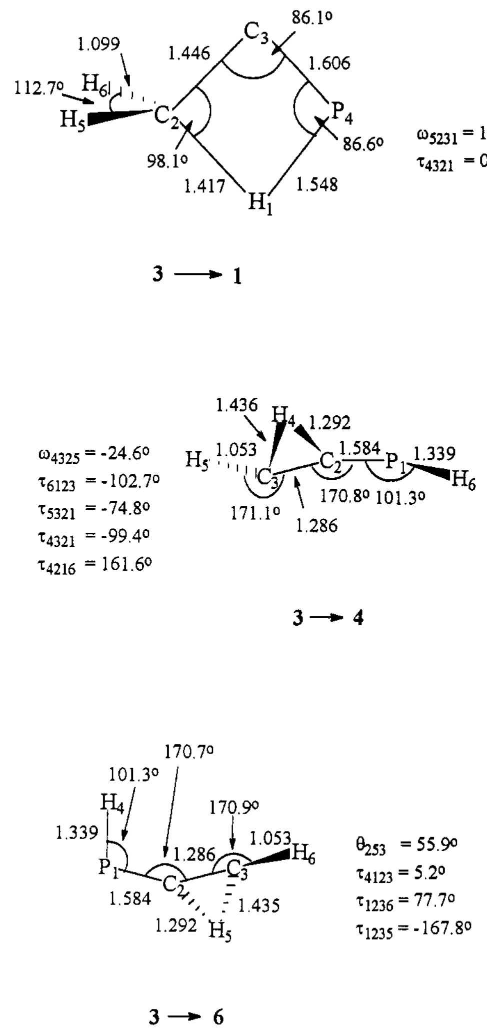

Figure 6. MNDO-optimized transition-state geometries for conversions on the C_2H_3P potential surface. ω is an out-of-plane angle; τ is a torsion angle.

The semiempirical results (Table 2), supported in part by *ab initio* calculations, allow us to make several qualitative predictions.

First, we found that transition state structures and energies for the conversion of **5** to **3**, **1**, and **6** were identical to those obtained for the conversion of **2** into **3**, **1**, and **6** (Figures 5 and 7). This is not unexpected given that **2** and **5** are geometrically so similar. In other words, although under extremely mild conditions the sole product from the generation of **2** should be **5** since the barrier to reversion is predicted to be 35 kcal/mol, the only path found for the conversion of **5** to either **3** or the actual product, **1**, was via **2**. Thus, **2** should be considered as an intermediate between **5** and **3**, between **5** and **1**, and between **3** and **1**.

It was also found that the transition state for the conversion of **5** to **6** was identical to that for conversion of **2** to **6**. Furthermore, **6** cannot convert directly into **1**; the transition state located between **6** and **1** was identical to that for the conversion of **2** to **1**.

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[24] In response to a suggestion by one reviewer, it seems that since there is generally good agreement between our MNDO and *ab intio* results for molecules and transition states studied by both methods, there is, with regard to the present mechanistic discussion, no need to further investigate those reactions which were found by semiempirical methods to have large barriers. Only an unprecedently large difference between MNDO and *ab intio* results could change any of the arguments presented in this paper.

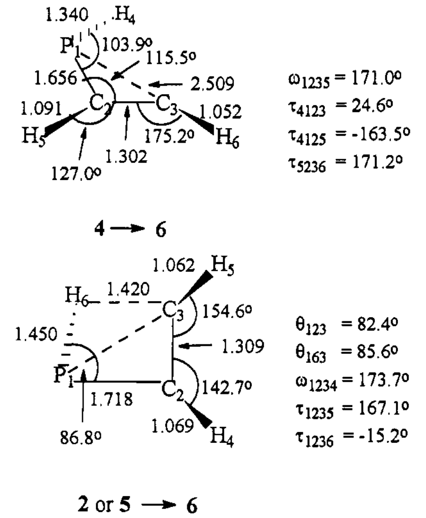


Figure 7. MNDO-optimized transition-state geometries for conversions on the C_2H_3P potential surface. θ is a bond angle; ω is an out-of-plane angle; and τ is a torsion angle.

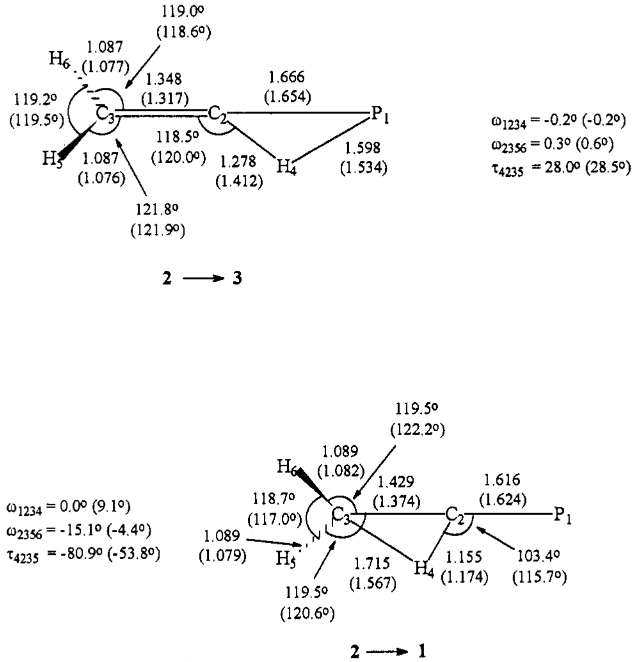


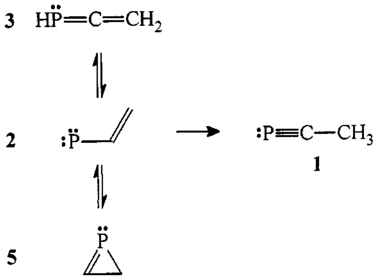
Figure 8. *Ab initio* SCF- and CCSD-optimized geometries for selected transition states. ω is an out-of-plane angle; τ is a torsion angle. Values in parantheses are from SCF calculations. Note that the CCSD transition state for **2** to **1** has converged to C_s symmetry. Starting from the C_1 symmetry SCF structure, the TCSCF transition state (not shown) also converged to C_s symmetry.

Second, conversion of **2** into **3** will be more rapid than conversion of **2** into **1**. This is as expected; a hydrogen shift *toward* an electron-deficient atom should be more facile than a shift *away* from it.

Third, while conversion of **2** to **5** is even more rapid than rearrangement of **2** to **3**, it is suggested that, under vigorous conditions such as those used by MLFH (FVP at 700 °C),[1] **2** and **5** will interconvert more rapidly than **5** can rearrange to an isomer which could survive at this temperature.

Fourth, the fact that neither phosphaallene (**3**) nor 3*H*-phosphirene (**5**) was detected in the experiments reported[1] is explained by relative energies and barriers for reversion. The heat of formation of **1** is 15.6 and 19.4 kcal/mol lower than those of **3** and **5**, respectively. Under conditions of thermodynamic control, very little **2** or **5** will be formed relative to **1**. The reversion of **3** to **2** has a barrier some 30 kcal/mol lower than that for reversion of **1** to **2**, and reversion of **5** to **2** has a barrier that is lower yet, by another 15 kcal/mol. This suggests that, under the experimental conditions (700 °C) employed by MLFH,[1] phosphaallene (**3**), 3*H*-phosphirene (**5**), and vinylphosphinidene (**2**) will interconvert rapidly compared to any isomerization of **1** to **2**. Therefore **1**, is expected to be more stable than **3** or **5** kinetically as well as thermodynamically. Under the reaction conditions, **3** and **5** are expected to rapidly isomerize to **1** by equilibrating with **2**, which is drained off to form **1**.

Scheme 2



On the other hand, it is extremely unlikely that any **3** will be directly converted into **1**. The transition state for direct conversion of **3** to **1** is so high in energy that this rearrangement should be very slow.

Finally, the participation of **6** in the reaction is disfavored, since transition states leading to **6** from any of the other molecules likely to be present are comparatively high-lying; in particular, the enthalpy barrier for rearrangement of **2** to **6** is ca. 20 kcal/mol higher than for conversion of **2** to **1**.

The same is true of ethynylphosphine (**4**); it is surrounded by relatively high potential barriers and is unlikely to play an important role in any series of interconversions on this potential surface.

The mechanism suggested by the present results is shown in Scheme 2. **2** interconverts with phosphaallene (**3**) and 3*H*-phosphirene (**5**). Under the reaction conditions **3** and **5** interconvert via **2**, which is drained off to form **1**. It should be noted that this mechanism is predicted to apply only under vigorous conditions such as those used by MLFH.[1]

Note also that this mechanism calls for the formation of **1** directly from **2** rather than via **3** or **5**. This is an unusual instance of product formation as a result of hydrogen atom transfer *away* from an electrophilic center. It is further predicted that this will prove to be an exception to the general rule, found only under forcing conditions.

Conclusions

MNDO and *ab initio* studies of the C_2H_3P potential surface have been performed in order to elucidate the mechanism of the vinylphosphinidene rearrangement. There is generally good agreement between semiempirically- and *ab initio*-derived energies. However, it should be remembered that, as the potential surface has been probed largely by semiempirical MO methods and the role of *ab initio* has been to buttress the most important points, the predictions reported here are still qualitative.

The ground state of vinylphosphinidene (**2**) is predicted to be a triplet, with the lowest-lying singlet state a biradical. Once formed, **2** will, under vigorous conditions, interconvert with its thermodynamically more stable isomer **5** and with phosphaallene (**3**). At high temperatures, all **3** and **5** formed will be converted to **1** via reversion to **2**. Hence a 1,2-shift of a hydrogen *away* from an electron-deficient phosphorus atom is the mechanism for the rearrangement of vinylphosphinidene to 1-phosphapropyne.

These results explain the observation that only **1** is found under conditions which presumably generate **2**: the FVP of vinylphosphirane at 700 °C.[1] It is predicted that, as conditions for the generation of **2** are made less vigorous, the yield of **1** should decrease and the yields of **3** and **5** should increase.[25]

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(25) Note that this mechanism applies only to the unsubstituted, isolated system. Bulky substituents, electronegative substituents (see ref 19), or other stabilizing interactions should, of course, profoundly affect the course of this reaction.