

Theoretical Studies of the [1,5] Sigmatropic Hydrogen Shift in Cyclopentadiene, Pyrrole, and Phosphole

Steven M. Bachrach

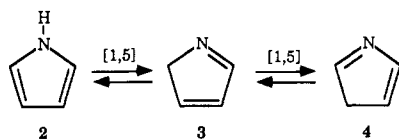
Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received May 10, 1993*

The [1,5] sigmatropic hydrogen shifts in cyclopentadiene, pyrrole, and phosphole were examined using ab initio calculations at the MP2/6-31G* level. The activation enthalpies (corrected for 298 K) for these shifts were computed to be 26.4 kcal mol⁻¹ for cyclopentadiene, 44.5 kcal mol⁻¹ for 1*H*-pyrrole to 2*H*-pyrrole, 26.3 kcal mol⁻¹ for 2*H*-pyrrole to 3*H*-pyrrole, 26.2 kcal mol⁻¹ for 3*H*-pyrrole to 3*H*-pyrrole, 16.0 kcal mol⁻¹ for 1*H*-phosphole to 2*H*-phosphole, 26.9 kcal mol⁻¹ for 2*H*-phosphole to 3*H*-phosphole, and 24.7 kcal mol⁻¹ for 3*H*-phosphole to 3*H*-phosphole. These barrier heights are interpreted in terms of relative stabilities of the isomers, their aromatic character, and their electronic distributions. The calculated barriers are used to understand the reactions of the pyrroles and phospholes.

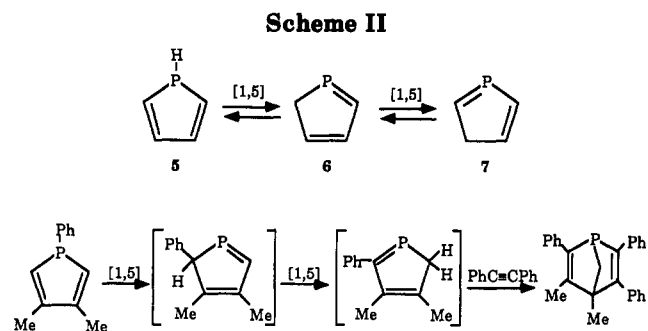
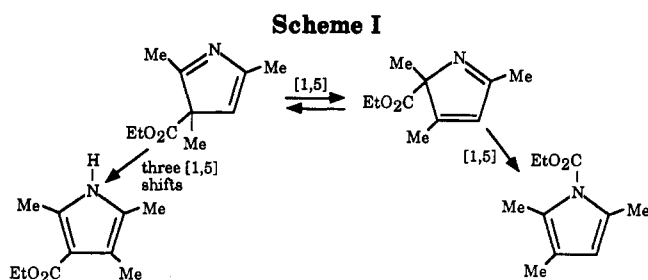
Sigmatropic rearrangements are a subclass of the pericyclic reactions, and the mechanisms for these reactions have been systematized by the Woodward-Hoffmann rules of orbital symmetry.¹ Spangler² reviewed thermal [1,*j*] sigmatropic rearrangements and presented strong evidence concerning the nature of the [1,5] rearrangement. In particular, hydrogen will readily migrate in a [1,5] fashion, particularly in a cyclic system, with suprafacial stereospecificity. The seminal work of Roth explored the thermodynamics of hydrogen migration in cyclopentadiene 1, finding $\Delta H^\ddagger = 23.6$ kcal mol⁻¹ and $\Delta S^\ddagger = -3.3$ eu.³

Recently, there has been growing interest in the sigmatropic rearrangements of heterocycles. In their review article, Sammes and Katritzky⁴ find no evidence for the presence of the 2*H*- (3) and 3*H*-tautomers (4) in equilibrium with 1*H*-pyrrole 2; however, there are examples of the [1,5]



rearrangement converting 3 into 2. Sammes, Chung, and Katritzky⁵ studied the rearrangement of a variety of 3,5-diaryl-2*H*-pyrrole-2,2-dicarboxylic esters to their 1*H*-tautomers, finding the rearrangement is concerted and does not involve charge separation in the transition state. Recently, Chiu and Sammes^{6,7} have shown that 2*H*- and 3*H*-pyrroles can be reversibly interconverted by a [1,5] shift and that each isomer will undergo further [1,5] shifts to the more stable 1*H*-pyrrole (see Scheme I).

Prior to the early 1980s, the analogous [1,5] sigmatropic shift in phospholes was unknown and thought to be highly unlikely. 1*H*-Phosphole 5, whose aromatic character has



been subject to much controversy,⁸⁻¹² is pyramidal and possesses slight aromatic stability. A [1,5] migration to produce 2*H*-phosphole 6 reduces the phosphorus coordination number from 3 to 2, an energetically unfavorable process, and removes the minimal aromatic stabilization.¹³ However, Mathey¹⁴ discovered that the reaction of a substituted 1*H*-phosphole with toluene produced a Diels-Alder product that could only be rationalized by proceeding through a 2*H*-phosphole, see Scheme II. Further studies by Mathey's group have uncovered numerous examples

* Abstract published in *Advance ACS Abstracts*, August 15, 1993.
 (1) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781-853.
 (2) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187-217.
 (3) Roth, W. R. *Tetrahedron Lett.* **1964**, 1009.
 (4) Sammes, M. P.; Katritzky, A. R. *Adv. Heterocycl. Chem.* **1982**, *32*, 234-285.
 (5) Sammes, M. P.; Chung, M. W. L.; Katritzky, A. R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1773-1779.
 (6) Chiu, P.-K.; Sammes, M. P. *Tetrahedron Lett.* **1987**, *28*, 2775-2778.
 (7) Chiu, P.-K.; Sammes, M. P. *Tetrahedron* **1990**, *46*, 3439-3456.

(8) Palmer, M. H.; Findlay, R. H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 974-982.
 (9) Schäfer, W.; Achweig, A.; Mathey, F. *J. Am. Chem. Soc.* **1976**, *98*, 407-414.
 (10) Epitotis, N. D.; Cherry, W. *J. Am. Chem. Soc.* **1976**, *98*, 4365-4370.
 (11) Baldrige, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 4204-4208.
 (12) Hughes, A. N.; Edgcombe, K. E. *Heterocycles* **1992**, *33*, 563-572.
 (13) Mathey, F. *Chem. Rev.* **1988**, *88*, 429-453.
 (14) Mathey, F.; Mercier, F.; Charrier, C. *J. Am. Chem. Soc.* **1981**, *103*, 4595-4597.
 (15) de Lauzon, G.; Charrier, C.; Bonnard, H.; Mathey, F. *Tetrahedron Lett.* **1982**, *23*, 511-514.
 (16) Charrier, C.; Bonnard, H.; de Lauzon, G.; Mathey, F. *J. Am. Chem. Soc.* **1983**, *105*, 6871-6877.

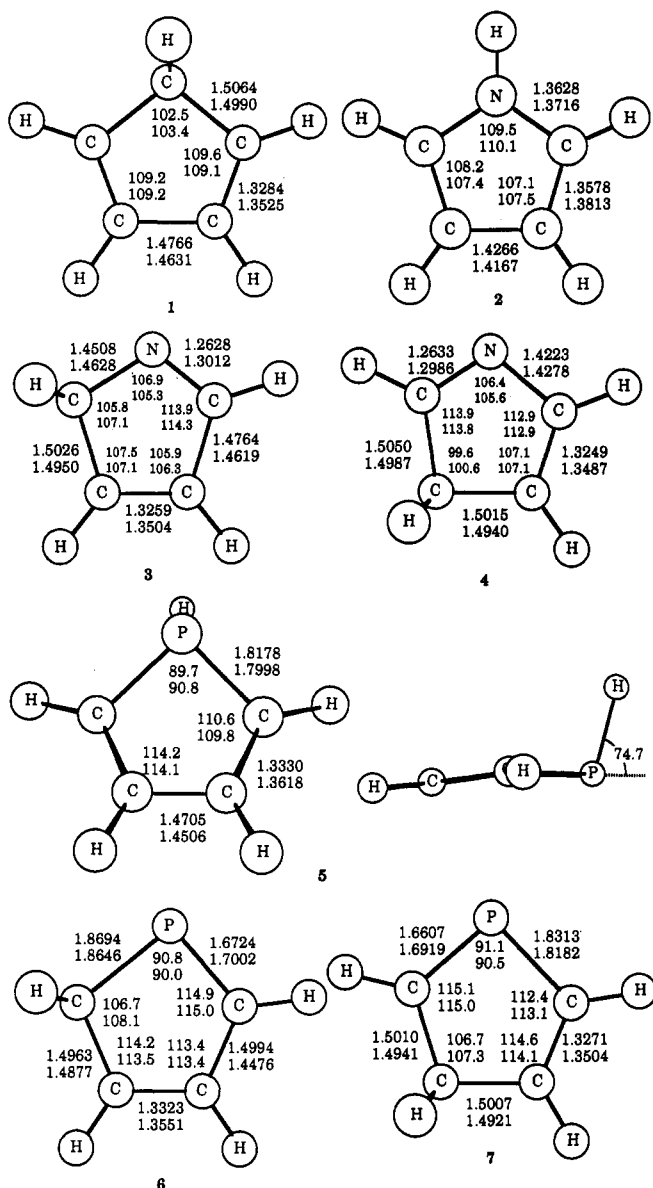


Figure 1. Optimized geometries of 1-7. HF parameters are listed above the MP2 parameters. All distances are in Å and all angles are in deg.

of a 1*H*-phosphole undergoing a [1,5] migration to produce a highly reactive 2*H*-phosphole which is then trapped by a dienophile.¹⁵⁻¹⁸ Mathey has suggested that this migration is relatively facile due to the strong overlap between the π -system and the P-R exocyclic σ -bond.¹³ While most 2*H*-phospholes are inferred by the trapped product, Mathey¹⁹ has been able to obtain a stable 2*H*-phosphole complexed to tungsten and Regitz²⁰ has synthesized a highly substituted 2*H*-phosphole that could be isolated and characterized by NMR.

Continuing our studies of pericyclic reaction of heteroatomic alkenes,²¹⁻²³ we report here *ab initio* calculations of the [1,5] hydrogen migration in pyrrole and phosphole.

(17) Charrier, C.; Bonnard, H.; de Lauzon, G.; Holand, S.; Mathey, F. *Phosph. Sulf.* **1983**, *18*, 51-54.

(18) Mathey, F. *Acc. Chem. Res.* **1992**, *25*, 90-96.

(19) Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1984**, *106*, 826-828.

(20) Zurmühlen, F.; Regitz, M. *J. Organomet. Chem.* **1987**, *332*, C1-C5.

(21) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 209-215.

(22) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 2040-2047.

(23) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 6736-6744.

For comparison, we also examine the degenerate [1,5] hydrogen shift in cyclopentadiene. We report the relative energies of the various isomers and the activation energies for the hydrogen migrations. These results are used to understand the experimental results.

Computational Methods

The geometries of 1-7 were completely optimized at the HF/6-31G*^{24a} level using the standard methods included in GAUSSIAN-90.^{24b} Analytical frequency analysis for all of these structures confirmed them to be local minima. On the basis of our earlier studies of pericyclic reaction of heteroatomic systems,²¹⁻²³ where we found that electron correlation plays an important role in determining activation energies, we reoptimized the geometries of 1-7 at the MP2/6-31G* level.^{24c} A recent study of the [1,5] hydrogen migration in tetrazole²⁶ supports our methodological choice—electron correlation is needed to obtain reasonable activation energies; however, a number of different post-Hartree-Fock calculations gave similar activation energies (within 5 kcal mol⁻¹). We, therefore, chose to use the computationally quick MP2 level for geometry optimization and energy calculations. The optimized geometries of 1-7 are drawn in Figure 1, with the HF results listed above the MP2 results. Since frequency analysis was not conducted at the MP2 level, the MP2 structures are not confirmed to be either ground states or transition states at the MP2 level.

The transition states (TS) for the [1,5] hydrogen migrations were obtained at the HF/6-31G* and MP2/6-31G* level. No symmetry was assumed except for the degenerate [1,5] migration in cyclopentadiene (TSC) and for the rearrangement interconverting the mirror images of the 3*H* isomers (TSN3 and TSP3), which have *C_s* symmetry. The transition state between 2 and 3 and between 3 and 4 will be called TSN1 and TSN2, respectively. Similarly, the transition states between 5 and 6 and between 6 and 7 will be called TSP1 and TSP2, respectively. The transition states for the [1,5] hydrogen shift connecting mirror image isomers of 4 and 7 are called TSN3 and TSP3, respectively. These transition states all have one and only one imaginary frequency at the HF/6-31G* level. The optimized geometries of the transition states are drawn in Figure 2.

The absolute and relative energies of all structures are listed in Tables I and II. The vibrational frequencies have been scaled by 0.89, which are then used to correct the enthalpy for 298 K. Graphical representation of the potential energy surfaces for these systems at MP2/6-31G* are given in Figure 3.

The total electron density was analyzed using the topological methods developed by Bader.²⁸ In particular, we will make use of the values of the electron density at ρ bond critical points, which has been shown to scale with the bond order (BO), using eq 1.^{27,28}

bond type	bond order = $e^{A(\rho-B)}$	
	A	B
C-C ²⁹	6.458	0.252
C-N ³⁰	5.12	0.27
C-P ³¹	19.628	0.153

The ellipticity ϵ is the ratio of the negative eigenvalues of the Hessian matrix of the density evaluated at the bond critical point.²⁸ A small value of the ellipticity indicates symmetrical distribution of the density about the bond path, typical of a single bond. Large values of the ellipticity indicate a preference for electron density buildup in a specific direction perpendicular

(24) (a) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654-3665. (b) Frisch, M.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian, Inc.*: Pittsburgh, PA, 1990. (c) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(25) Wong, M. W.; Leung-Toung, R.; Wentrup, C. *J. Am. Chem. Soc.* **1993**, *115*, 2465-2472.

(26) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, 1990.

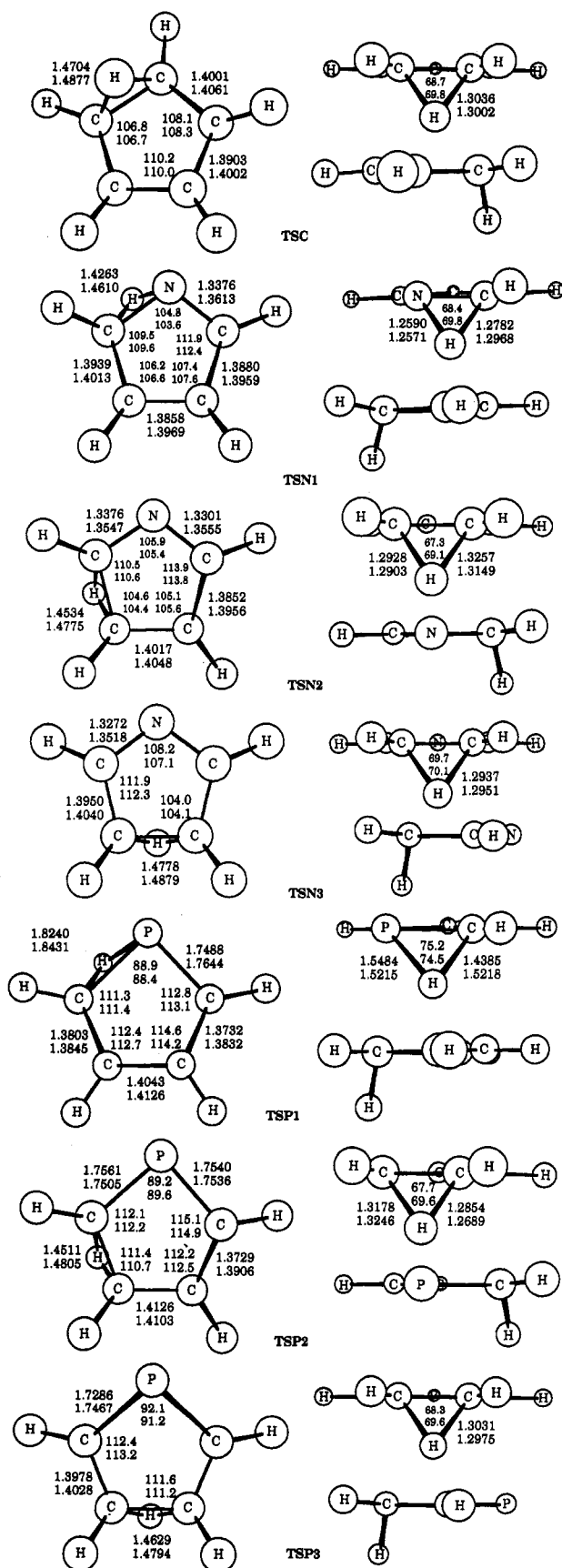


Figure 2. Optimized geometries of the transition states. The two side views for each structure give another orientation: the top figure is a view perpendicular to the bond that has the hydrogen migrating across it and the bottom figure is a Newman projection along that same bond. HF parameters are listed above the MP2 parameters. All distances are in Å and all angles are in deg.

to the bond path, usually found in double bonds. The values of the density ρ and ellipticity at the bond critical points for 1-7 and the TSs at HF/6-31G* are listed in Table III.

The topological method also allows for defining the bond path, the line which follows the ridge of maximum electron density between two adjacent atoms.³² The bond path is the union of the two gradient paths that originate at the bond critical point. The gradient path is found by tracing the gradient of the density, $\nabla\rho$, in the direction of increasing density. The union of all the bond paths in a molecule is called the bond path network, which is typically in a 1:1 correspondence with chemical bond paths. The bond path networks for the TSs are drawn in Figure 4.

Results

Geometries. Cyclopentadiene (1). Cyclopentadiene has been examined by computational methods in the past.³³⁻³⁵ Our discussion here is presented only to assess the computational methods employed. The experimental³⁶ bond distances and angles for cyclopentadiene are as follows: C-C, 1.506 Å; C=C, 1.352 Å; C4-C-C2, 103.2°; C5-C1-C2, 109.3°, and C1-C2-C3, 109.1°. The MP2/6-31G* structure (see Figure 1) is in complete agreement with the experimental structure, lending credence to the computational method selected.

1*H*-Pyrrole (2). The microwave structure of 1*H*-pyrrole was reported in 1969.³⁷ The important distances and angles are as follows: C-N, 1.370 Å; C=C, 1.382 Å; C-C, 1.417 Å; C-N-C, 109.8°; N-C-C, 107.7°; and C-C-C, 107.4°. Our MP2/6-31G* is in remarkably good agreement with this experimental structure and is significantly improved over the previously reported HF/3-21G*¹¹ structure. The molecule is planar at all computational levels, which is also true of the microwave structure and for most substituted 1*H*-pyrroles examined by X-ray crystallography.³⁸ Once again, this comparison confirms that appropriate computational methods are employed here.

2*H*-Pyrrole (3). There have been reports of X-ray crystal structures of three substituted 2*H*-pyrroles.^{39,40} Bond distances and angles in the simplest structure are shown in 8.³⁹ Considering the difference in substituents (none in 3) and phases (gas phase for 3, solid crystalline phase for 8) the agreement between the MP2/6-31G* structure and experiment is again excellent. The only discrepancies of any size, and they are small, occurs about the carbon that bears the bulky *tert*-butyl group in 8. Undoubtedly, the differences in the distances and angles

(27) Bader, R. F. W.; Tang, T. H.; Tal, Y.; Biegler-König, F. W. *J. Am. Chem. Soc.* 1982, 104, 946-952.

(28) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* 1983, 105, 5061-5068.

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

(30) Bachrach, S. M. *J. Comput. Chem.* 1989, 10, 392-406.

(31) Bachrach, S. M. *THEOCHEM* 1992, 255, 207-219.

(32) Runtz, G. R.; Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* 1977, 55, 3040-3045.

(33) Rondan, N. G.; Houk, K. N. *Tetrahedron Lett.* 1984, 25, 2519-2522.

(34) Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* 1983, 105, 4972-4976.

(35) Siggel, M. R. F.; Thomas, T. D.; Saethre, L. J. *J. Am. Chem. Soc.* 1988, 110, 91-96.

(36) Damiani, D.; Ferretti, L.; Gallinella, E. *Chem. Phys. Lett.* 1976, 37, 265-269.

(37) Nygaard, L.; Nielsen, J. T.; Kirchheiner, J.; Maltzen, G.; Rastrup-Andersen, J.; Sorensen, G. O. *J. Mol. Struct.* 1969, 3, 491.

(38) Chadwick, D. J. In *Pyrrroles*; Jones, R. A., Ed.; Wiley: New York, 1990; pp 1-104.

(39) Gambacorta, A.; Nicoletti, R.; Cerrini, S.; Fedeli, W.; Gavuzzo, E. *Tetrahedron Lett.* 1978, 2439-2442.

(40) Kokel, B.; Viehe, H. G. *Tetrahedron Lett.* 1980, 21, 3799-3800.

Table I. Absolute Energies (au) of 1-7 and the Transition States

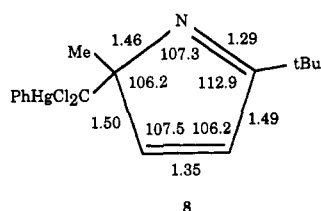
level	1						TSC
HF/6-31G*	-192.791 721						-192.729 916
MP2/6-31G*	-193.449 668						-193.404 072
	2	TSN1	3	TSN2	4	TSN3	
HF/6-31G*	-208.807 854	-208.718 112	-208.793 914	-208.733 515	-208.790 932	-208.726 839	
MP2/6-31G*	-209.504 177	-209.428 625	-209.482 847	-209.437 244	-209.479 029	-209.433 690	
	5	TSP1	6	TSP2	7	TSP3	
HF/6-31G*	-495.059 241	-495.010 362	-495.060 832	-495.002 784	-495.055 659	-494.996 720	
MP2/6-31G*	-495.699 400	-495.671 571	-495.711 633	-495.665 445	-495.705 765	-495.662 718	

Table II. Relative Energies (kcal mol⁻¹) of 1-7 and the Transition States*

level	1						TSC
HF/6-31G*	0.0						38.78
MP2/6-31G*	0.0						28.61
MP2/6-31G* + corr	0.0						26.35
	2	TSN1	3	TSN2	4	TSN3	
HF/6-31G*	0.0	56.31	8.75	46.65	10.62	50.84	
MP2/6-31G*	0.0	47.41	13.38	42.00	15.78	44.23	
MP2/6-31G* + corr	0.0	44.50	13.02	39.36	15.19	41.39	
	5	TSP1	6	TSP2	7	TSP3	
HF/6-31G*	1.00	31.67	0.0	36.43	3.25	40.23	
MP2/6-31G*	7.68	25.14	0.0	28.98	3.68	30.69	
MP2/6-31G* + corr	6.53	22.50	0.0	26.86	3.72	28.41	

* Enthalpy corrections for 298 K make use of the HF/6-31G* frequencies which have been scaled by 0.89.

about this carbon are due to steric interactions with the substituent in 8, which are absent in the unsubstituted 2*H*-pyrrole. The molecule has *C_s* symmetry and is confirmed to be a local energy minimum by frequency analysis.



3*H*-Pyrrole (4). There are no reports of any structures of any 3*H*-pyrrole. Our MP2/6-31G* structure is shown in Figure 1. Since the MP2/6-31G* structures of the tautomers of 3*H*-pyrrole are in excellent agreement with experiment, we believe that our calculated structure should be reasonable. Furthermore, the bond distances and angles in 4 are similar to analogous parameters in 2 and 3. As with the other two pyrroles, 4 has a planar ring.

1*H*-Phosphole (5). In his review of phospholes, Mathey summarizes the X-ray structural data for a number of 1*H*-phospholes.¹³ The simplest compound whose structure has been solved is 1-benzylphosphole.⁴¹ The mean bond distances and angles in 1-benzylphosphole are as follows: P—C, 1.783 Å; C=C, 1.343 Å; C—C, 1.438 Å; C—P—C, 90.7°; P—C—C, 110.0°; and C—C—C, 114.1°. The ring is slightly puckered—the four ring carbon atoms are coplanar and the P atom lies 0.21 Å above this plane. The phosphorus atom is also pyramidal; the benzylic carbon lies 1.36 Å below the carbon plane.

Many theoretical studies of 1*H*-phosphole have been published, mainly aimed at the question of aromaticity.^{8-12,42} The most recent study examined the structure at HF/6-311G*.¹² This geometry is very similar to our HF/6-31G* geometry. However, the MP2/6-31G* geometry better matches the experimental structure than any of the HF structures. The MP2 geometry has a puckered ring and a pyramidal P atom. To compare with the experimental structure, we find the P atom lies 0.18 Å above the carbon plane and the H atom lies 1.11 Å below the ring plane. Again, the agreement between the experimental and calculated geometries is excellent.

2*H*-Phosphole (6) and 3*H*-Phosphole (7). There are no structural reports of a free 2*H*-phosphole. The X-ray structure of a complexed 2*H*-phosphole indicates that there are significant electronic interactions between the phosphole and the metal, leading to a phosphole ring geometry that is likely quite different from the geometry of the free phosphole ligand.¹⁹ There are no reports of an isolated 3*H*-phosphole. Therefore, we cannot compare our calculated structures with experiment.

The calculated structures of 6 and 7 are shown in Figure 1. Both molecules have *C_s* symmetry; i.e., they have planar rings. We can compare the bond lengths in 6 with the bond lengths in 1-phospha-1,3-butadiene⁴³ (at HF/6-31G*): P=C, 1.666 Å; C—C, 1.465 Å; and C=C, 1.325 Å. The only serious difference between these values and those in 6 is the C—C bond length, which is 0.034 Å longer in 6. However, at MP2, this bond contracts greatly, and is in line with the general trends of butadienes (i.e., longer than normal double bonds and shorter than normal single bonds). The bond lengths in 2-phospha-1,3-butadiene⁴³ are as follows: C=P, 1.648 Å; P—C, 1.827 Å; and C=C, 1.322 Å. These distances correspond nicely with the analogous bonds in 7.

TSC. Rondan and Houk³³ reported the HF/3-21G transition state for the [1,5] hydrogen migration in cyclopentadiene. Their structure is very similar to the HF/6-31G* and MP2/6-31G* structures reported here. All the C—C bond lengths are about the same length (1.40 Å) except the C1—C5 bond, over which the hydrogen is migrating. The C1—C5 distance is shorter in the HF/6-31G* geometry than in the 3-21G geometry, while the other C—C bond distances are quite similar in the two optimized structures. As expected, the MP2 geometry has longer bonds, but the essential features noted by Rondan and Houk are unchanged—a near planar carbon ring, a slightly shortened C1—C5 bond relative to cyclopentadiene and nonmigrating hydrogens bent only slightly from the carbon plane.

(41) Coggan, P.; Engel, J. F.; McPhail, A. T.; Quin, L. D. *J. Am. Chem. Soc.* 1970, 92, 5779-5780.

(42) Veszpremi, T.; Nyulaszi, L.; Reffy, J.; Heinicke, J. *J. Phys. Chem.* 1992, 96, 623-626.

(43) Bachrach, S. M.; Liu, M. *J. Am. Chem. Soc.* 1991, 113, 7929-7937.

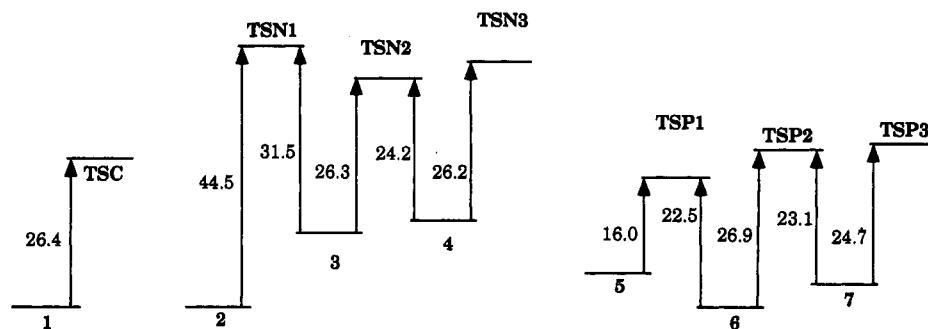


Figure 3. Schematic diagram of the potential energy surface for the [1,5] hydrogen rearrangements in cyclopentadiene, pyrrole, and phosphole. Energies (kcal mol⁻¹) were obtained at the MP2/6-31G* level with scaled ZPE at HF/6-31G*.

Table III. Topological Electron Density Parameters at Bond Critical Points

compd	bond	ϵ	ρ	BO	compd	bond	ϵ	ρ	BO
	C—C(1)	0.0476	0.2654	1.09		C—C(1)	0.2600	0.3151	1.50
	C=C	0.4312	0.3594	2.00		C—C(2)	0.2798	0.3222	1.57
	C—C(3)	0.1022	0.2786	1.19		C—C(3)	0.2836	0.2726	1.14
	N—C	0.1559	0.3901	1.22		P—C	0.1915	0.1605	1.16
	C=C	0.3993	0.3412	1.78		C=C	0.3897	0.3514	1.90
	C—C	0.2123	0.2998	1.36		C—C	0.1016	0.2835	1.22
	N—C	0.0248	0.2881	1.10		P—C	0.0217	0.1505	0.95
	N=C	0.2455	0.4004	1.95		P=C	0.4440	0.1848	1.87
	C—C(3)	0.1087	0.2820	1.21		C—C(3)	0.0907	0.2857	1.24
	C=C	0.4050	0.3605	2.02		C=C	0.4085	0.3586	1.99
	C—C(5)	0.0605	0.2704	1.13		C—C(5)	0.0273	0.2681	1.11
	N—C	0.0154	0.3031	1.18		P—C	0.0558	0.1559	1.06
	N=C	0.2379	0.3999	1.94		P=C	0.4762	0.1880	1.99
	C—C(3)	0.0444	2.6601	1.09		C—C(3)	0.0287	0.2657	1.09
	C—C(4)	0.0446	0.2702	1.12		C—C(4)	0.0409	0.2696	1.12
	C=C	0.4705	0.3636	2.06		C=C	0.4015	0.3577	1.98
	N—C(1)	0.2558	0.2936	1.13		P—C(1)	0.3406	0.1497	0.94
	N—C(2)	0.1940	0.3392	1.42		P—C(2)	0.2307	0.1743	1.52
	C—C(3)	0.2908	0.3267	1.62		C—C(3)	0.2739	0.3303	1.66
	C—C(4)	0.2659	0.3242	1.59		C—C(4)	0.2239	0.3166	1.52
	C—C(5)	0.2593	0.3221	1.57		C—C(5)	0.2668	0.3257	1.61
	N—C(1)	0.1820	0.3597	1.58		P—C(1)	0.3189	0.1600	1.15
	N—C(2)	0.1205	0.3533	1.55		P—C(2)	0.3281	0.1673	1.32
	C—C(3)	0.3063	0.3280	1.63		C—C(3)	0.2778	0.3303	1.66
	C—C(4)	0.2461	0.3131	1.48		C—C(4)	0.2184	0.3104	1.46
	C—C(5)	0.2740	0.2846	1.23		C—C(5)	0.2583	0.2818	1.21
	N—C	0.2038	0.3550	1.54		P—C	0.2822	0.1733	1.49
	C—C(2)	0.2831	0.3215	1.57		C—C(2)	0.2215	0.3148	1.50
	C—C(3)	0.3154	0.2657	1.09		C—C(3)	0.2922	0.2775	1.18

TSN1, TSN2, and TSN3. The structures of the three transition states for [1,5] hydrogen migration about the pyrrole rings are remarkably similar. All three have a nearly planar ring structure. The hydrogens attached to the atoms over which the migration occurs are only bent slightly from the ring plane. The distance between C and the migrating hydrogen is about 1.3 Å, identical to that in TSC. The C—C and C—N bonds that do not have a hydrogen migrating across have bond lengths that are nearly identical in all three TSs. The C—C bonds which have the hydrogen migrating across (C2—C3 in TSN2 and C3—C3' in TSN3) are slightly shorter than the corresponding bonds in 3 and 4. In contrast, the C—N bond over which the hydrogen migrates in TSN1 is much longer than the corresponding bond in 2 and is almost the same

length as the corresponding bond in 3. Outside of this last feature, the structural trends of these TSs are exactly the same as in TSC.

TSP1, TSP2, and TSP3. Like the previously described TSs, the TSs for the hydrogen migration in phospholes all have nearly planar ring structures, and outside of the migrating hydrogen, all hydrogens lie very near the ring plane. However, the phosphole TSs do not show the non-alternation of bond lengths like the previous TSs. In TSP1, the three C—C bond lengths differ by 0.03 Å, and in TSP2, the two C—C bond differ by 0.02 Å.

The trend for the length of the bond over which the hydrogen moves is the same for the phospholes as the pyrroles. The P—C bond is longer in TSP1 than in 5 and nearly as long as the P—C bond in 6. The C—C bonds

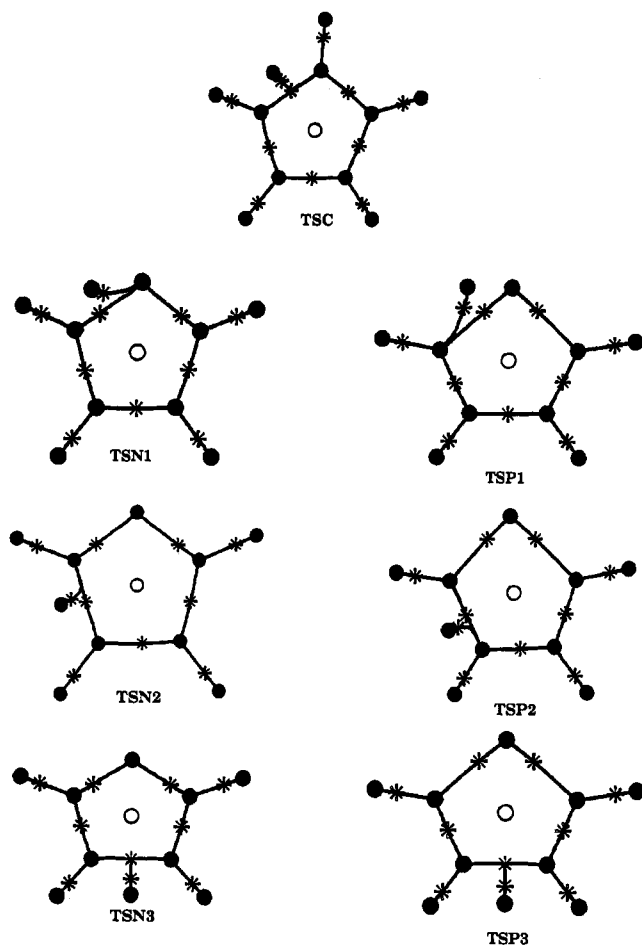


Figure 4. Topological bond path networks of the transition states. Bond and ring critical points are indicated by (*) and (O), respectively. The orientation of the molecules in these plots is similar to those given in Figure 2.

that have the migrating hydrogen in TSP2 and TSP3 are somewhat shorter than the corresponding bonds in 6 and 7.

The distance between carbon and the migrating hydrogen vary among these TSs, a trend not seen in the pyrrole TSs. The long C—H distance in TSP1 might be expected since the P—H distance is longer than a typical C—H bond. The two C—H distances in TSP2 differ by 0.056 Å, while they differ by only 0.025 Å in TSN2. The C—H distance in TSP3 and TSN3 are nearly identical.

Energies. The first task at hand is to evaluate the computational method in terms of how accurately it can predict activation energies. The activation enthalpy for a [1,5] hydrogen shift in a number of substituted cyclopentadienes have been tabulated in Spangler's review article.² The experimental system that is closest to our calculations is the deuterium shift in 1,2,3,4,5-pentadeuterocyclopentadiene, where $\Delta H^\ddagger = 23.6$ kcal mol⁻¹.

Rondan and Houk³³ determined that the energy barrier for the [1,5] shift in cyclopentadiene is 39.7 kcal mol⁻¹ at 3-21G with ZPE corrections. This is 3.2 kcal mol⁻¹ larger than our estimate at HF/6-31G* with thermal corrections (36.5 kcal mol⁻¹). Clearly, the activation energy is basis set sensitive. Previous calculations of pericyclic reactions have indicated a dependence on electron correlation. This is borne out in our study as well (see Table II). The activation energy is reduced to 26.35 kcal mol⁻¹ by inclusion of electron correlation through MP2. This result is still

larger than the experimental activation enthalpy by about 3 kcal mol⁻¹. However, this is certainly good enough agreement (keep in mind that the experiment is for a deuterium migration compared with the our calculation of a hydrogen migration) to expect that relative trends will be reasonably reproduced. On the basis of this, our discussion will refer solely to the MP2/3-21G* energies with thermal corrections.

As anticipated, 2 is the lowest energy isomer of pyrrole, lying 13.02 kcal mol⁻¹ below 3 and 15.19 kcal mol⁻¹ below 4. This reflects, in part, the aromatic stabilization of 2, which is not present in the other isomers. Baldrige and Gordon¹¹ have estimated the stabilization in 2 using a superhomodesmotic reaction as 5.16 kcal mol⁻¹. The difference in energy between 3 and 4 is, in part, due to the difference in delocalization energy in the butadiene fragment of each molecule. We can estimate this difference by comparing the relative energies of the *cis* conformers of *syn*-1-aza-1,3-butadiene (modeling 3) and 2-aza-1,3-butadiene (modeling 4). At MP2/6-31G*,⁴³ the former butadiene is 7.7 kcal mol⁻¹ more stable than the latter, and this is reflected in the greater stability of 3 over 4.

In contrast with the pyrroles, the 1*H*-phosphole is not the most stable form. Rather, 2*H*-phosphole 6 is predicted to be 3.72 kcal mol⁻¹ more stable than 7 and 6.53 kcal mol⁻¹ more stable than 5. This is a surprising result. First, many examples of 1*H*-phospholes have been prepared, isolated, and characterized, while only two examples of 2*H*-phospholes are known and no isolated 3*H*-phospholes have been reported. Second, simple chemical expectations favor 5 over 6—(1) some slight aromatic character is expected in 5 and (2) the P=C bond is weaker than the C=C bond.

Wong, Leung-Toung, and Wentrup²⁵ have noted that the relative energies of tetrazole isomers are basis set and electron correlation dependent. However, basis sets larger than 6-31G* and correlation beyond the MP2 level result in energy changes of less than 3 kcal mol⁻¹. In order to judge the validity of our computational method, we determined the relative energies of 5 and 6 at MP4SDQ/6-31G*/MP2/6-31G*. At this level, 6 is 6.97 kcal mol⁻¹ more stable than 5, only 0.5 kcal mol⁻¹ different from the MP2 result. Therefore, we believe that the relative energetic ordering of the phosphole isomers will not be changed at even higher computational levels.

On the other hand, the aromatic stability of 5 has been questioned. Baldrige and Gordon¹¹ report that there is no delocalization stabilization in 1*H*-phosphole. If we assume that there is no aromatic stabilization in 5, we can then next compare the total bond strengths in 5 vs 6. Summing the average bond strengths for all the bond types in 5 gives an energy of 974 kcal mol⁻¹. If we sum the average bond strengths for all the bonds in 6 except the P=C bond, for which no average value is available, we obtain 870 kcal mol⁻¹. Therefore, if the P=C bond strength is greater than 104 kcal mol⁻¹ then the bond energies of 6 would be greater than 5. Francl, Pellow, and Allen have suggested that the P—C π -bond is very strong (>100 kcal mol⁻¹),⁴⁴ and therefore, simple summation of bond strengths predicts that 6 is more stable than 5. This analysis simply reiterates the care that must be taken when comparing systems on the basis of just one or two of the bonds in the molecules. In moving from 5 to 6, not only

(44) Francl, M. M.; Pellow, R. C.; Allen, L. C. *J. Am. Chem. Soc.* 1988, 110, 3723-3728.

is the C=C bond replaced with a P=C (which presumably is energetically unfavorable), but a weak C—P bond is replaced by a C—C bond and a P—H bond is replaced by a C—H bond. These latter two changes account for an energy of nearly 40 kcal mol⁻¹ in favor of 6 over 5.

Nevertheless, the experimental evidence suggests that 1*H*-phospholes should be more stable than their isomers. We point out that there have been no isolated unsubstituted phospholes. The substituents employed are generally large. Sterics alone would favor substitution on phosphorus, since the P—C distance is much longer than the C—C distance. Further explorations of substituent effects on the isomerization of phospholes are underway.

We now turn our attention to the activation energy for the [1,5] sigmatropic shifts in these heterocyclopentadienes. The relative energies of the ground state species and the TSs are listed in Table II. A schematic drawing of the potential energy surface for these reactions is drawn in Figure 3. This figure also gives the activation energy for all of the sigmatropic shifts. The first item to note is that the activation energy of most of these migrations are very similar. In particular, the activation for the degenerate conversion of cyclopentadiene, 3*H*-pyrrole, and 3*H*-phosphole are 26.4, 26.2, and 24.7 kcal mol⁻¹. The activation energies for the reactions 3 → 4 and 4 → 3 are 26.3 and 24.2 kcal mol⁻¹. In the phosphole system, the activation energies range from 16.0 kcal mol⁻¹ (5 → 6) to 26.9 kcal mol⁻¹ (6 → 7). The only real outlier is the reaction of 2 → 3 (and the reverse reaction) where the activation energy is quite large, 44.5 kcal mol⁻¹ (31.5 kcal mol⁻¹ for the reverse reaction).

Topological Electron Density Analysis. Bader and co-workers have shown that the value of the electron density at the bond critical point correlates with the bond order.^{27,28} An exponential relationship best fits the data, especially in order to properly relate the decrease in bond order as ρ approaches zero. Unfortunately, empirical parameters must be found for all atom pairs. Bader has established these parameters for the C—C bond,²⁹ and we have fit the exponential function for the C—N³⁰ and C—P³¹ bonds. Using eq 1, we can predict the bond order for all the heavy atom bonds in the systems under study here. This calculated bond orders are presented in Table III.

The topological bond orders for cyclopentadiene are in agreement with expectations. The C1—C2 bond order is 2.00 and the C1—C5 bond order is 1.09, indicating a normal double and single bond. The C2—C3 bond order of 1.19 indicates some small double bond character, due to delocalization between the two π -bonds. This is also evident in the ellipticity, where the value is significantly larger for this bond than for the C1—C5 bond, suggesting small π -character between the double bonds.

If 1*H*-pyrrole is aromatic, one would expect that the π -character is spread over all bonds. This behavior is found to some extent. The bond order for the formal C—C double bond is only 1.78, the formal C—C bond has a bond order of 1.36, and the bond order for the C—N bond is 1.22. The values of the ellipticity are all relatively large, supporting the notion of delocalized π -bonding about the ring.

In contrast, the degree of delocalization of the π -bonds in 1*H*-phosphole is substantially less than in 1*H*-pyrrole. The P—C bond order is 1.16 and the C=C bond order is 1.90. The C—C bond order of 1.22 reflects the delocalization of the butadiene fragment. This bond order

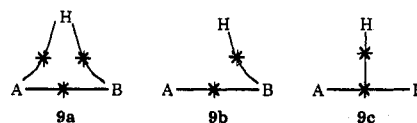
alternation in 5 further supports the nonaromatic nature of this phosphole.

The other pyrroles and phospholes (3, 4, 6, and 7) all express the expected bond orders: normal single and double bonds, with a slightly increased bond order for the single bond between the adjacent double bonds. The values of the ellipticities also indicate alternating single and double bonds. These molecules show no delocalization beyond that seen in a standard butadiene fragment.

The bond orders in the transition states, as determined using the empirical topological relationship, suggest a concerted mechanism for all cases. For example, in TSC, the bond orders for the C—C bonds not bridged by hydrogen are 1.50 and 1.57. For the TSs for the migrations in the pyrroles, the C—C and C—N bond orders (for bonds not bridged by hydrogen) range from 1.42 to 1.63; while the comparable P—C and C—C bond orders in TSP1–3 range from 1.32 to 1.66. The ellipticities are all large, reflecting π character throughout the ring.

The bond order for the bonds across which the hydrogen migrates is 1.1 to 1.2 for all the TSs except TSP1. This reflects the bond shrinkage that accompanies the migration in the TS, again except for TSP1, where the bond lengthens in the TS.

The bond path networks for the seven TSs are presented in Figure 4. While all the networks have a five membered ring and the appropriate number of C—H, N—H, and P—H paths, there are differences concerning the path terminating at the migrating hydrogen. There are three topological possibilities for the bond path network in this migration. The hydrogen might bridge the 1 and 5 centers, having a bond path to each, which would also demand a ring critical point for the ring formed by the migrating hydrogen and the two heavy atoms (see 9a). The hydrogen



may be connected to only one of the centers, indicating that the bond to the other center has not formed in the TS (see 9b). The hydrogen may be connected to the bond critical point of the bond over which it migrates (see 9c).

The seven networks fall into only two of these classes: TSN1, TSN2, TSP1, and TSP2 are isomorphic with 9b while TSC, TSN3, and TSP3 are isomorphic with 9c. There are no bridged structures. The TSs with bond path networks that are isomorphic with 9b were extensively searched for any other critical points in order to confirm that these are not bridged structures.

The networks that are isomorphic with 9b, such as TSN1, indicate that the hydrogen is not transferred synchronously. In other words, in the rearrangement of 2 → 3, the TS is reached with the hydrogen still bonded to nitrogen. Only after the TS state is reached is the hydrogen actually transferred to carbon.

The networks that are isomorphic with 9c have *C*₂ symmetry, which would necessitate either the T-shaped network (9c) or a symmetric bridging structure like 9a. Only the former is found. The T-shaped network has been found oftentimes, usually with π -complexes.^{45,46} These three TSs can be viewed as the interaction of the migrating

hydrogen (acceptor) with the π -system (donor) of the five-membered ring. Note that the bond path between the hydrogen and the heavy atom in the TSs that are isomorphic to **9b** are bent in towards the C–X bond critical point, suggesting some π -like interactions are present in these systems as well. In fact, a point along the intrinsic reaction path from these TSs (TSN1, TSN2, TSP1, and TSP2) has a bond path network isomorphic to **9c** and not **9a**.

Discussion

The recent experiments of Chiu and Sammes^{6,7} suggest that 2*H*-pyrroles and 3*H*-pyrroles can equilibrate and that each will rearrange irreversibly to the 1*H*-pyrrole isomer. The MP2/6–31G* calculations of the unsubstituted series of pyrroles confirms these experiments. We find that **3** is only 2.17 kcal mol⁻¹ lower in energy than **4** and the activation energy for the [1,5] hydrogen migration connecting these isomers is only 26.3 kcal mol⁻¹. This activation energy is comparable to the activation energy for the hydrogen migration in cyclopentadiene. Therefore, **3** and **4** will equilibrate.

Furthermore, **2** is 13.02 kcal mol⁻¹ more stable than **3**, which can be attributed to the aromatic character of **2**. The planar structure of **2** and the bond delocalization, as indicated by the topological bond orders, imply a significant aromatic character to **2**. The barrier for conversion of **2** into **3** is very large, 44.5 kcal mol⁻¹; thus, conversion of **3** or **4** into **2** will be irreversible.

In contrast, the isomers of phosphole are very close in energy. The lowest energy isomer is 2*H*-phosphole, however, for substituted phospholes, the 1*H* isomer is the thermodynamic minimum. We believe that steric interactions favor the 1*H* isomer and are examining this anomaly further.

The activation energy for [1,5] hydrogen shifts among the phospholes range from 16.0 to 26.9 kcal mol⁻¹, which is less than or comparable to the barrier in cyclopentadiene. These low barriers support the proposed mechanism of Mathey¹⁴ to account for the product distribution in Diels–Alder reactions of a variety of phospholes. The first step requires the reactant 1*H*-phosphole to undergo a [1,5] shift to a 2*H*-phosphole. Our studies indicate that this step should be relatively facile.

Finally, we note that the transition states for all of the [1,5] shifts examined here are very similar in their energies, structures, and electron density distributions. The activation energies of these rearrangements are all about 25 kcal mol⁻¹. The lone exception is the shift taking **2** into **3**, which has a larger barrier due to the loss of aromaticity. The TSs have a nearly planar ring and all of the hydrogens (except for the migrating hydrogen) also lie near the ring plane. The electron distribution indicates a delocalization of the π bonds about the ring in the TSs. The bond orders are very similar in the TSs. The bond paths to the migrating hydrogen indicates significant π -type interaction. While the hydrogen does not migrate synchronously in all the TSs (in particular TSN1, TSN2, TSP1, and TSP2) the reaction pathways are very similar among the TSs. Therefore, the mechanisms for the migration in these systems are analogous—a concerted [1,5] hydrogen shift—even in the heterocycles.

Conclusion

This computational study has addressed a number of interesting features of the chemistry of pyrroles and phospholes. 2*H*- and 3*H*-pyrrole are very close in energy and are separated by a barrier of only 26.3 kcal mol⁻¹, supporting the experimental observation of their interconversion. The mechanistic proposal of Mathey to account for the chemistry of 1*H*-phosphole is supported by our calculations. The first step in this mechanism is the conversion of 1*H*-phosphole into 2*H*-phosphole, and we find a low barrier (16.0 kcal mol⁻¹) for this process. Lastly, the [1,5] hydrogen migrations of cyclopentadiene, pyrrole, and phosphole all proceed through transition states having very similar structure and electron density distributions, suggesting that the mechanism for the migration is the same in all these systems—a concerted [1,5] hydrogen shift.

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

Supplementary Material Available: Optimized geometries in the form of Z-matrices for structures 1–7 and the transition states at MP2/6–31G* (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(46) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* 1987, 109, 5909–5916.