Concerted and Diradical Stepwise Mechanisms in the Diels-Alder Reactions of Phosphinine and Phosphinine Sulfide: A DFT Investigation

Raj K. Bansal, Neelima Gupta, and Surendra K. Kumawat

Department of Chemistry, University of Rajasthan, Jaipur 302004, India

Reprint requests to Prof. Raj K. Bansal. E-mail: bansalrk43@yahoo.com

Computations of the concerted and diradical stepwise mechanisms of the Diels-Alder (DA) reactions on the $>C=P-$ functionality of phosphinine and phosphinine sulfide with 1,3-butadiene at the density functional theory level B3LYP/6-311++G**//B3LYP/6-31G** give the values of energy of concert as 10.7 and 2.6 kcal mol^{-1}, respectively. Similarly, the DA reaction of dimethyl acetylene-dicarboxylate (DMAD) with the $-CH=CH-CH=P-$ moiety of phosphinine or its sulfide has been investigated theoretically at the same level of theory. The results reveal that in the DA reaction of phosphinine, the role of sulfur is to oxidize phosphorus to generate a phosphinine sulfide intermediate, which subsequently undergoes DA reaction with 2,3-dimethylbutadiene or DMAD by a concerted mechanism to afford the respective cycloadducts.

Key words: Diels-Alder Reaction, Phosphinine, Phosphinine Sulfide, Reaction Mechanism, DFT Calculations

Introduction

The actual mechanism of the Diels-Alder (DA) reaction has been the subject of intensive theoretical investigations [1, 2]. Depending on the structures of the reactants it may occur *via* either concerted (closed-shell) or stepwise (open-shell) mechanisms. For the parent DA reaction of butadiene and ethylene, it has been found that the concerted mechanism is preferred over the stepwise diradical mechanism only by a few kcal mol^{-1} [1].

In the last few years the synthetic strategy of hetero DA reactions [3 – 8] has been extended to organophosphorus compounds having the $>C=P-$ functionality, namely phosphaalkenes [9, 10], heterophospholes [11, 12], anellated azaphospholes [13, 14], and phosphinines [15, 16]. Several interesting DA reactions have been accomplished successfully on the $>C=P-$ functionality of many of these compounds acting mainly as dienophiles [9 – 17] but in some cases, heterophospholes and λ^3-phosphinines reacted as the diene component as well [15, 16]. Although the mechanistic and theoretical studies of the all-carbon DA reactions have been done extensively [1, 2], investigations of the hetero DA reactions, particularly of those involving organophosphorus compounds, have been reported so far to a limited extent [18, 19]. Furthermore, no comparative studies of the concerted and stepwise diradical mechanisms of the DA reactions involving organophosphorus functionalities have been published yet.

Recently we rationalized theoretically the relative reactivities of 1,4,2-diazaphospholes and 1,3-azaphospholes as dienophiles in their DA reactions [20 – 22], and the role of sulfur in completion of the reaction in the latter case. A lower activation barrier (16 – 19 kcal mol^{-1}) is in accordance with the occurrence of the DA reaction of 1,4,2-diazaphospholes under mild conditions even in the absence of sulfur. But the lower exothermicity of the DA reaction of 1,3-azaphosphole with 1,3-butadiene results in a significant lowering of the activation barrier for the backward reaction and hence a reversible reaction can occur. Here the sulfur appears to oxidize the σ^3-P atom of the initially formed [4+2] cycloadduct, thereby pushing the reaction in the forward direction [20].

In an investigation of the reactivity of 4,5-dimethyl-2-phenylphosphinine (**1b**) towards the DA reactions [23], it was found not to react with 2,3-dimethylbutadiene (**3**) or DMAD (**5**) alone, but on heating in a sealed tube at 100 °C in the presence of sulfur the cycloadducts **4** and **6** were obtained, respectively. The initial generation of the phosphinine sulfide intermediate (**2b**) was postulated, which subsequently undergoes cycloaddition (Scheme 1).
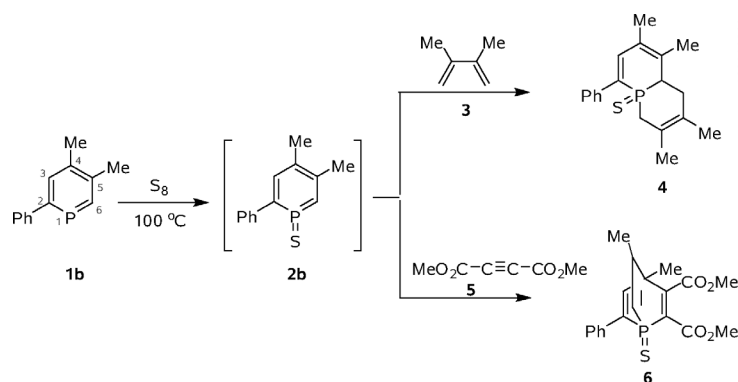
Scheme 1.

In view of our own theoretical results about the role of sulfur in the DA reactions of azaphospholes, it was of interest to investigate theoretically the actual mechanism, concerted or stepwise, and the role of sulfur in the DA reactions of phosphinine. When our studies were in progress, Moores *et al.* [24] published their results of the experimental and theoretical study of phosphinine sulfides. These studies deal mainly with the experimental (X-ray) and theoretical (DFT) determination of the structures of phosphinine sulfides and related compounds, and it was concluded that these species were aromatic in character. Furthermore, the relative reactivities of these compounds as dienes in the DA reaction with acetylene were rationalized by calculating the corresponding activation barriers at the DFT level.

In the present paper, the results of a systematic theoretical investigation of the concerted and stepwise mechanisms of the DA reactions of phosphinines and their sulfides with 1,3-butadiene and with DMAD are reported for the first time. It is now established that the cycloaddition proceeds by a concerted mechanism, and that in contrast to the DA reactions of azaphospholes, sulfurization of phosphinine precedes its cycloaddition with 1,3-diene or DMAD.

Computational Details

All calculations were carried out using the GAUSSIAN-03 suite of programs [25]. Houk and co-workers investigated relative energies for the concerted and stepwise mechanisms of the DA reaction of 1,3-butadiene and ethene with different methods and found Becke's three parameter hybrid functional in conjunction with the correlation functional of Lee, Yang and Parr (B3LYP) with a 6-31G** basis set capable of relatively economical direct comparisons. The reaction enthalpy calculated with this method was within 2 kcal mol^{-1} of the experimental value [2]. With this background, the closed-shell species *s-cis-* and *s-trans-*1,3-butadiene (**7**), phosphinines (**1**), phosphinine sulfides (**2**), the cycloadducts **8 – 11**, and the concerted transition structures (**TSc$_1$–TSc$_{10}$**) were computed at the restricted B3LYP/6-311++G**//B3LYP/6-31G** (hereafter referred to as RB) level, whereas for the stepwise pathway involving diradical intermediates and transition structures, computations were performed at the unrestricted UB3LYP/6-311++G**// UB3LYP/6-31G** (hereafter referred to as UB) level using the guess = (always, mix) option for spin correction. Total energies were calculated by adding unscaled zero-point energy corrections (ZPE) from B3LYP/6-31G** level to the single point energies calculated at the B3LYP/6-311++G** level. Intrinsic reaction coordinate (IRC) calculations [26] starting at the transition structures were performed to establish their connection with the respective reactants and products.

Nucleus-independent chemical shift values [NICS(0)] were calculated at the (3,+1) ring critical points of the electron density topology as defined by Bader [27] of the concerted transition structures at the GIAO-B3LYP/6-311++G**//B3LYP/6-31G** level [28]. For the phosphinines and their sulfides, NICS(1)$_{ZZ}$ were determined at the same level of theory by putting the probe (Bq) at a distance of 1 Å above the (3,+1) critical point of the ring.

Results and Discussion

The concerted mechanism was investigated for ten model DA reactions (Scheme 2), whereas the diradical stepwise mechanism was computed for the reactions of **1a** and **2a** with 1,3-butadiene.
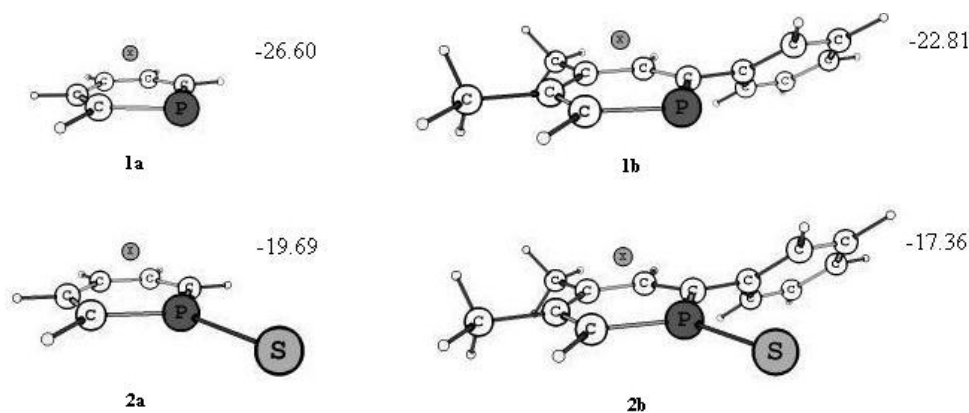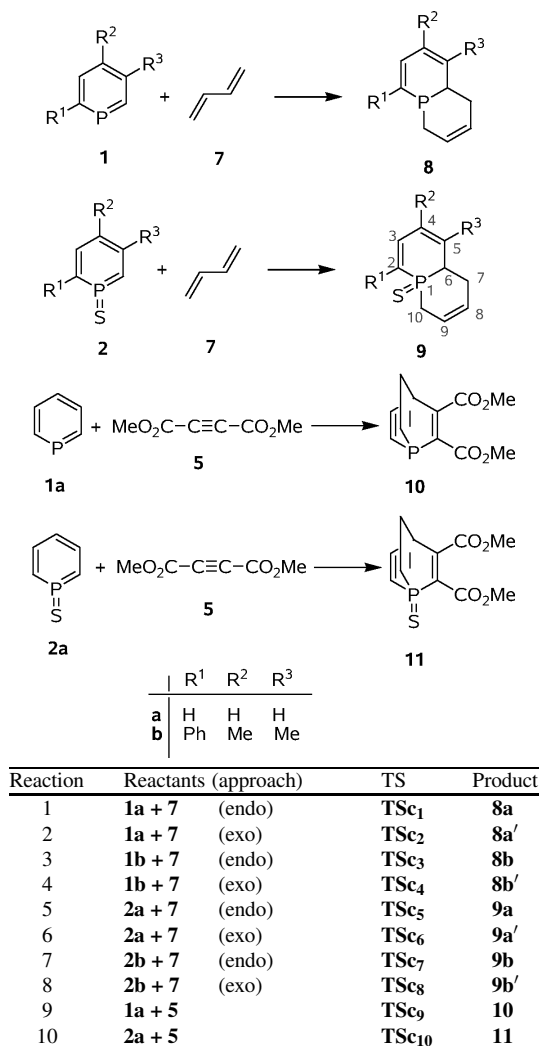
Fig. 1. Structures (RB3LYP/6-31G**) and NICS(1)$_{ZZ}$ (GIAO-RB3LYP/6-311++G**//RB3LYP/6-31G**) values (ppm) of phosphinines and phosphinine sulfides.

Scheme 2.

	R^1	R^2	R^3
a	H	H	H
b	Ph	Me	Me

Reaction	Reactants (approach)		TS	Product
1	**1a + 7**	(endo)	**TSc$_1$**	**8a**
2	**1a + 7**	(exo)	**TSc$_2$**	**8a'**
3	**1b + 7**	(endo)	**TSc$_3$**	**8b**
4	**1b + 7**	(exo)	**TSc$_4$**	**8b'**
5	**2a + 7**	(endo)	**TSc$_5$**	**9a**
6	**2a + 7**	(exo)	**TSc$_6$**	**9a'**
7	**2b + 7**	(endo)	**TSc$_7$**	**9b**
8	**2b + 7**	(exo)	**TSc$_8$**	**9b'**
9	**1a + 5**		**TSc$_9$**	**10**
10	**2a + 5**		**TSc$_{10}$**	**11**

Optimized geometries

The RB optimized geometries of phosphinines **1** and their sulfides **2** along with the NICS(1)$_{ZZ}$ values are given in Fig. 1. The phosphorus-containing six-membered ring of phosphinines and their sulfides is perfectly planar (**1a** and **2a**, all dihedral angles = 0.0°) or almost planar (**1b** and **2b**, ring dihedral angles = 0.01 − 0.96°), the presence of the 2-phenyl group in the latter causing a slight deviation from planarity.

The RB optimized geometries of the concerted transition structures **TSc$_1$–TSc$_{10}$** are given in Fig. 2. Wiberg bond indices [29] of the two new bonds in **TSc$_1$–TSc$_8$** reveal them to be asynchronous, the formation of the P–C10 bond being more advanced (WBI = 0.49 − 0.60) than that of the C6–C7 bond (WBI = 0.24 − 0.37). Asynchronicity, however, diminishes in the transition structures, **TSc$_9$** and **TSc$_{10}$**, resulting from the addition of phosphinine and its sulfide with DMAD.

The NICS(0), which is the negative of the computed magnetic shielding at the centers was first used by Schleyer *et al.* as a parameter to describe the aromaticity of a planar or nearly planar ring [30]. It was subsequently suggested that the isotropic NICS(1) value (*i. e.* at points 1 Å above ring center) was the better indicator of aromaticity [31, 32]. In a recent paper, Schleyer and co-workers have pointed out that NICS(1)$_{ZZ}$ (zz component of the NICS value determined 1 Å above the center) is a readily computable and superior-performing indicator of the aromatic character [33]. In the case of unsymmetrical cyclic systems, however, it has been recommended [34, 35] that NICS values should be determined at the
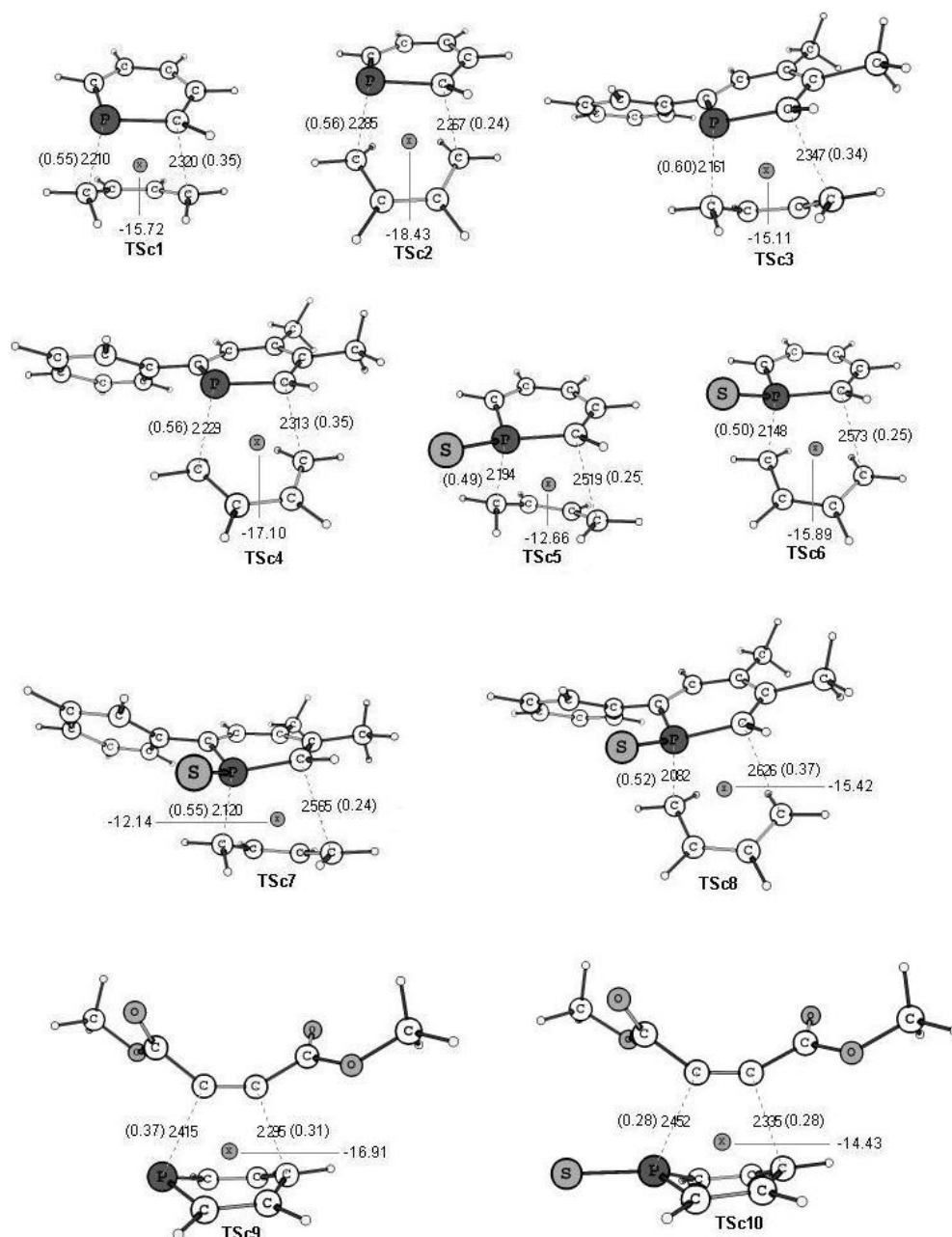
Fig. 2. Structures (RB3LYP/6-31G**) and bond lengths (in Å), Wiberg bond indices (in parentheses) and NICS(0) (GIAO-RB3LYP/6-311++G**//RB3LYP/6-31G**) values (in ppm) of the transition structures, **TSc₁–TSc₁₀**; x denotes the (3,+1) ring critical point of electron density.

(3,+1) ring critical points of the electron density, as defined by Bader [27], as at this point the electron density is a minimum with respect to motion in the plane of the ring, and a maximum with respect to motion perpendicular to the plane defined by the ring.

NICS(0) values of the transition structures **TSc₁**–**TSc₁₀** confirm their aromatic character. Although NICS(1)$_{ZZ}$ values of both phosphinines **1** (-26.60 and -22.81) and phosphinine sulfides **2** (-19.69 and -17.36) reveal their aromatic character, the dimin-
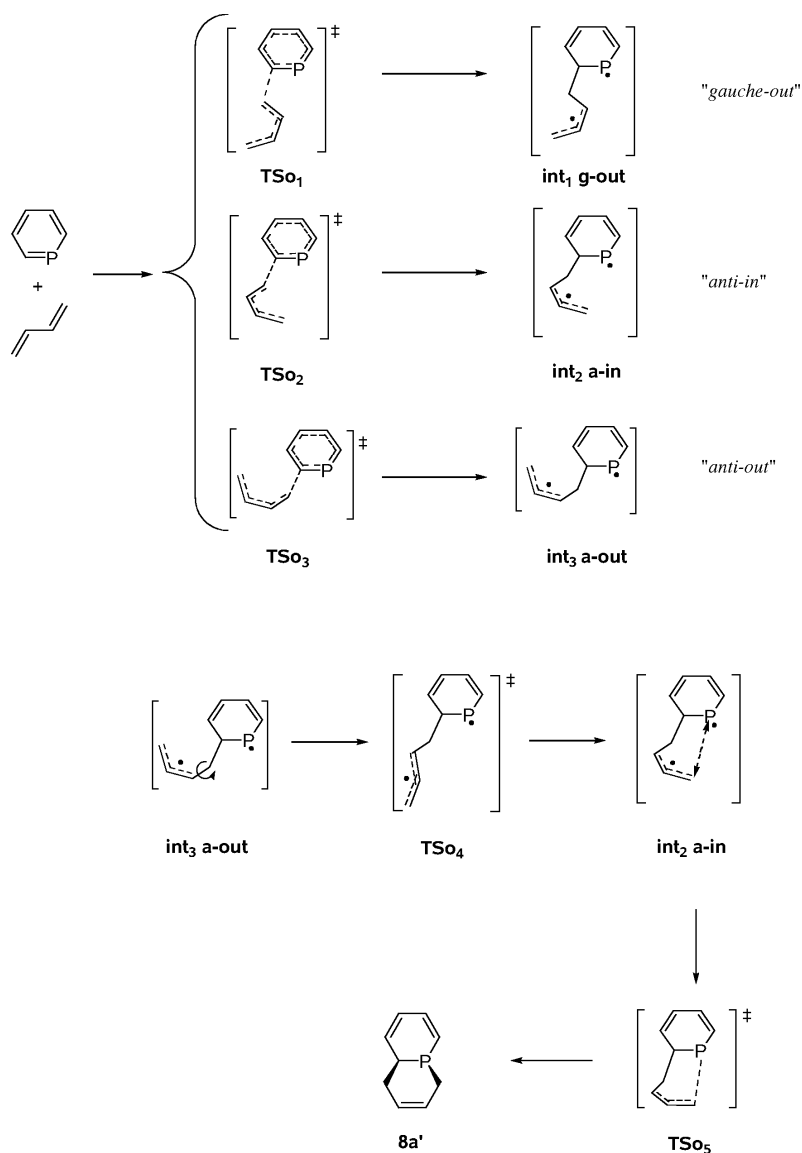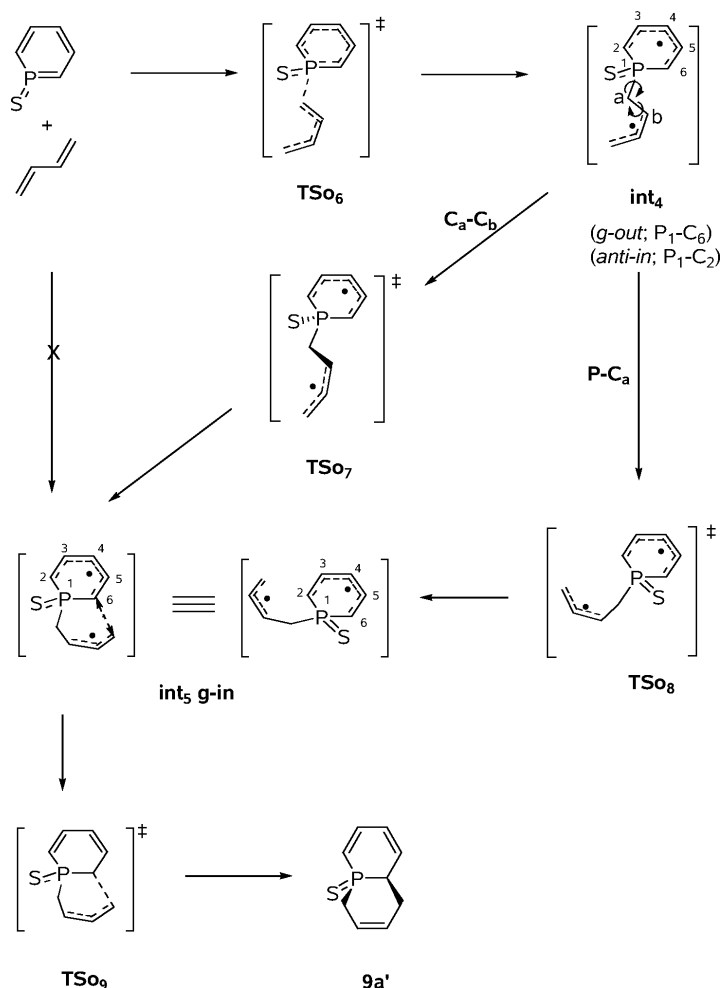
Scheme 3.

ished values in the latter cases indicate their reduced aromatic character.

The diradical stepwise pathways of the DA reactions of phosphinine **1a** and its sulfide **2a** with 1,3-butadiene have also been computed. The singlet diradical intermediate in the DA reaction of the phosphinine with 1,3-butadiene involved an initial C–C bond formation. In contrast, the phosphinine sulfide gave a singlet diradical intermediate with initial P–C bond formation. Phosphinine gives three conformers of the intermediate diradical formed on addition of *s-cis*-butadiene: gauche-out (**int₁ g-out**), anti-in (**int₂ a-in**) and anti-

out (**int₃ a-out**), the last being of the lowest energy and involving the lowest activation barrier (Scheme 3). An attempt to optimize a gauche-in diradical failed; instead this led to the concerted transition structure. A similar observation was made by Houk and co-workers in the case of the parent DA reaction [1]. The "anti-out" diradical intermediate (**int₃ a-out**) changes subsequently into the anti-in intermediate (**int₂ a-in**) through the transition structure **TSo₄** and then closes to the cycloadduct **8a′** *via* the transition structure **TSo₅**. In spite of only a small energy barrier to the closure of **int₂ a-in** to **8a′**, the corresponding transition structure **TSo₅**

Scheme 4.

could be located. The corresponding transition structure in the parent DA reaction could not be located [1].

Phosphinine sulfide on combining with *s-cis*-butadiene leads to only one conformer of the intermediate diradical, namely gauche-out (**int₄ g-out**) (Scheme 4). The latter being symmetrical, it is gauche-out with respect to P–C6, but **anti-in** with respect to P-C2. The **int₄ g-out** on rotation about the bond C_a–C_b changes into the gauche-in intermediate (**int₅ g-in**) through **TSo₇** and subsequently cyclizes into the cycloadduct **9a′** *via* **TSo₉**. The cycloadduct **9a′** can be formed through an alternative pathway *via* **TSo₈** resulting from rotation about the bond P–C_a of the **int₄**. It is found that the latter route is favored by 0.5 kcal mol^{-1}. It is noteworthy that although the transition structure **TSo₉** could be located, its energy is lower than that of **int₅ g-in**, which implies that conversion of the lat-

ter into the cycloadduct does not involve any energy barrier. The UB optimized geometries of all the diradical intermediates and transition structures are shown in Fig. 3.

Energetics

The total energies of the reactants, products and the concerted transition structures along with the relative energies (ΔE_a or ΔE_{rxn}) of the reactions 1 – 10 are given in Table 1, whereas the total energies of the diradical intermediates and the corresponding open-shell transition structures along with the relative energies are given in Table 2. Initial $\langle S^2 \rangle$ values for the diradical stationary points range from 0.52 to 1.07 which become 0.09 to 0.55 after spin annihilation.

The concerted and diradical stepwise pathways of the DA reactions of phosphinine (**1a**) and of phosphi-
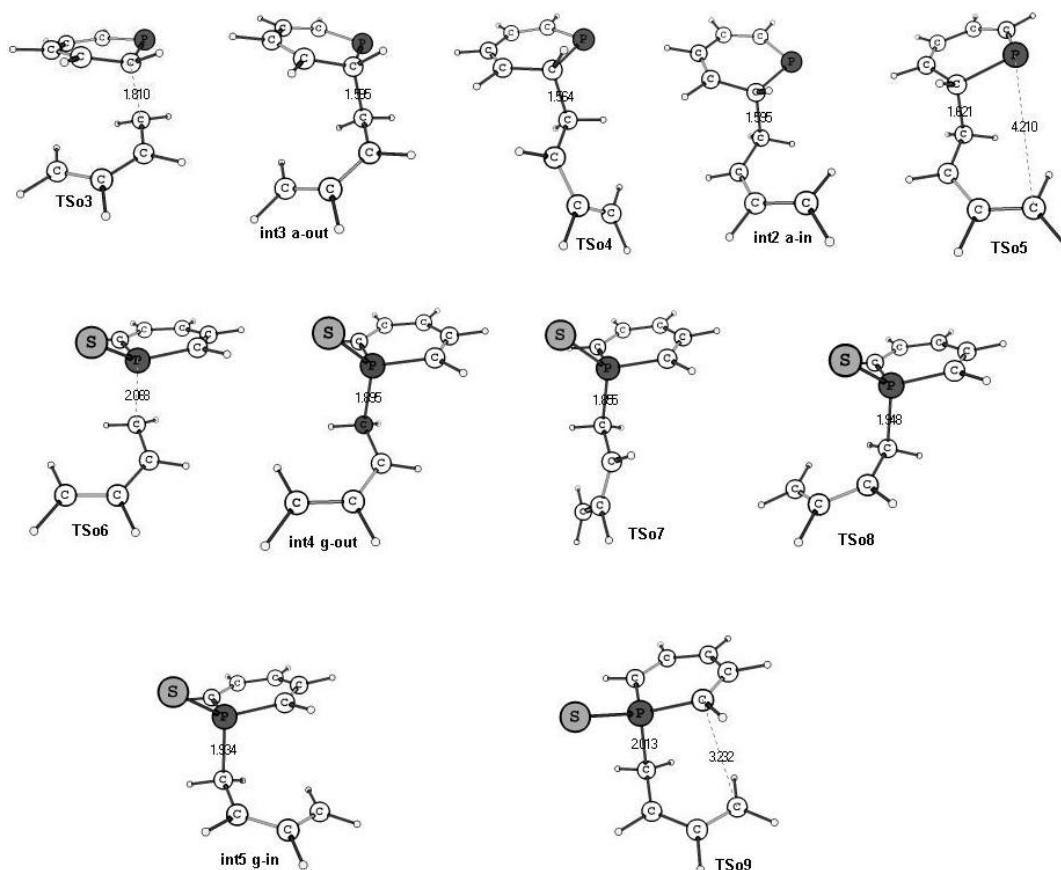
Fig. 3. Structures (UB3LYP/6-31G**) and bond lengths (in Å) in the transition structures and diradical intermediates for the stepwise pathway.
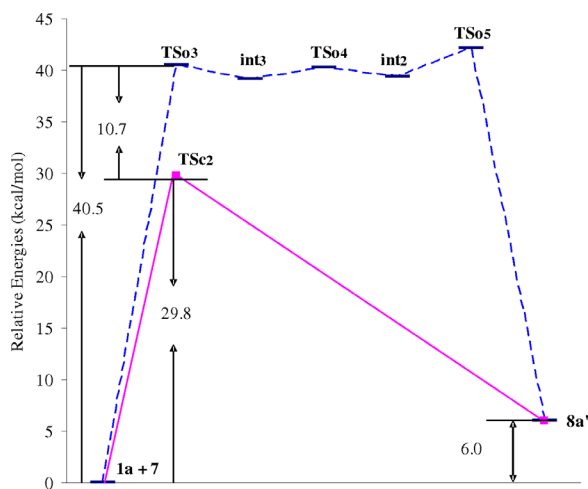

Fig. 4. Potential energy profiles for the concerted (solid line) and stepwise diradical (dotted line) pathways for the DA reaction of **1a** and **7**. The relative energies (kcal mol^{-1}) include zero-point vibrational energy corrections.

nine sulfide (**2a**) with 1,3-butadiene are depicted in Figs. 4 and 5, respectively. We have computed concerted pathways of both *endo* and *exo* approaches of the DA reaction of phosphinines and their sulfides with 1,3-butadiene, whereas diradical stepwise pathways lead to only *exo*-isomers. The energies of concert have therefore been calculated from the activation energies of the *exo*-approach in the concerted mechanism.

A high activation energy barrier of 29.8 kcal mol^{-1} and endothermicity of the concerted DA reaction of phosphinine explain its non-occurrence even at high temperature. An energy of concert of 10.7 kcal mol^{-1} rules out an open-shell pathway also. On the other hand, a lower activation barrier of 24.6 kcal mol^{-1} and high exothermicity of the concerted DA reaction of phosphinine sulfide help this reaction to take place. In this case also the open-shell pathway is unfavorable by 2.6 kcal mol^{-1}.
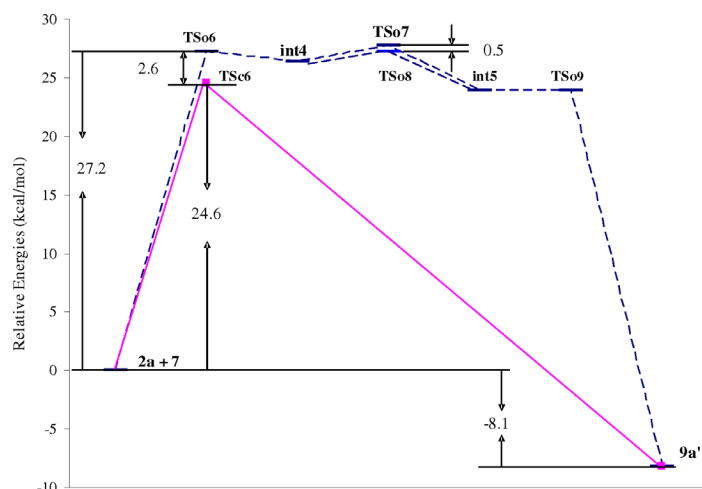
Fig. 5. Potential energy profiles for the concerted (solid line) and stepwise diradical (dotted line) pathways for the DA reaction of **2a** and **7**. The relative energies (kcal mol^{-1}) include zero-point vibrational energy corrections.

Table 1. Total energies and relative energies for stationary points on the closed-shell pathways of DA reactions.

Structure no.	N_{imag}	Total energies[a] (a. u.)	Relative energies (kcal mol^{-1})
7	0	−155.955501	–
1a	0	−534.870848	–
TSc$_1$	1	−690.778965	29.7[b]
8a	0	−690.816287	6.3[b]
TSc$_2$	1	−690.778943	29.8[b]
8a$'$	0	−690.816727	6.0[b]
1b	0	−844.498765	–
TSc$_3$	1	−1000.406975	29.7[b]
8b	0	−1000.441849	7.8[b]
TSc$_4$	1	−1000.406578	29.9[b]
8b$'$	0	−1000.445887	5.3[b]
2a	0	−933.092266	–
TSc$_5$	1	−1089.005509	26.5[c]
9a	0	−1089.061233	−8.4[c]
TSc$_6$	1	−1089.008633	24.6[c]
9a$'$	0	−1089.060735	−8.1[c]
2b	0	−1242.719373	–
TSc$_7$	1	−1398.633865	25.7[c]
9b	0	−1398.687121	−7.7[c]
TSc$_8$	1	−1398.636216	24.3[c]
9b$'$	0	−1398.690920	−10.1[c]
5	0	−533.123643	–
TSc$_9$	1	−1067.950358	27.7[d]
10	0	−1068.004114	−6.0[d]
TSc$_{10}$	1	−1466.178502	23.5[e]
11	0	−1466.236442	−12.9[e]

[a] Energies at B3LYP/6-311++G** + ZPE at B3LYP/6-31G** level; [b] relative to the sum of total energies of **1** and **7**; [c] relative to the sum of total energies of **2** and **7**; [d] relative to the sum of total energies of **1a** and **5**; [e] relative to the sum of total energies of **2a** and **5**.

Table 2. Total energies, relative energies and $\langle S^2 \rangle$ (value of $\langle S^2 \rangle$ after spin-annihilation in parentheses) for stationary points on the open-shell pathway of butadiene plus **1a** or **2a** DA reaction.

	N_{imag}	Total energies[a] (a. u.)	Relative energies (kcal mol^{-1})	$\langle S^2 \rangle$
TSo$_1$	1	−690.759252	42.1[b]	0.65 (0.17)
int$_1$	0	−690.762999	39.8[b]	1.03 (0.50)
TSo$_2$	1	−690.760536	41.3[b]	0.62 (0.15)
int$_2$	0	−690.763561	39.4[b]	1.02 (0.48)
TSo$_3$	1	−690.761769	40.5[b] (10.7)[c]	0.55 (0.11)
int$_3$	0	−690.763949	39.2[b]	1.01 (0.48)
TSo$_4$	1	−690.762119	40.3[b]	1.07 (0.55)
TSo$_5$	1	−690.759225	42.1[b]	1.01 (0.48)
TSo$_6$	1	−1089.004422	27.2[d] (2.6)[c]	0.67 (0.16)
int$_4$	0	−1089.005680	26.4[d]	1.03 (0.48)
TSo$_7$	1	−1089.003597	27.7[d]	1.06 (0.54)
TSo$_8$	1	−1089.004394	27.2[d]	0.87 (0.32)
int$_5$	0	−1089.009578	24.0[d]	0.78 (0.23)
TSo$_9$	1	−1089.009667	23.9[d]	0.52 (0.09)

[a] Energies at UB3LYP/6-311++G** + ZPE at UB3LYP/6-31G** level; [b] relative to the sum of total energies of **1a** and **7**; [c] energy of concert (ΔE_a for open-shell pathway − ΔE_a for closed-shell *exo* pathway); [d] relative to the sum of total energies of **2a** and **7**.

($\sim$ 29 kcal mol^{-1}), whereas those of the corresponding phosphinine sulfides are exothermic (−8 to −10 kcal mol^{-1}) and are characterized by a lower activation energy barrier (24−26 kcal mol^{-1}). These results are consistent with the Bell-Evans-Polanyi (BEP) principle [36, 37] and the Leffler-Hammond postulate (HP) [38, 39].

Both computed model DA reactions of phosphinine and phosphinine sulfide with DMAD are exothermic, but the exothermicity of the reaction of the latter is almost twice the value for the reaction of the former. In accordance with the BEP principle, the activation

The relative energies of the reactions (Table 1) reveal an interesting pattern: all the reactions of phosphinines are endothermic (5−8 kcal mol^{-1}) and have a comparatively higher activation energy barrier

barrier of the reaction of phosphinine sulfide is about 4.2 kcal mol^{-1} lower than that for phosphinine. An attempt to locate an open-shell transition structure in these two reactions failed; it always led to a concerted transition structure.

In summary, the theoretical calculations reveal that the DA reactions of phosphinine sulfides follow a concerted mechanism, and that the role of sulfur is to oxidize phosphinine to generate a phosphinine sulfide intermediate which subsequently reacts with 2,3-dimethylbutadiene or DMAD to afford the corresponding cycloadducts.

Conclusion

Computations of the diradical *versus* concerted mechanisms of the DA reactions of phosphinines and their sulfides confirm the reaction to proceed in a concerted mechanism. The DA reactions of phosphinines are endothermic with a higher activation barrier whereas those of phosphinine sulfides are exothermic with a lower activation barrier. The role of sulfur in the reaction is to convert phosphinine to phosphinine sulfide accompanied by reduced aromatic character, thus making the latter amenable to undergo DA reaction.

[1] E. Goldstein, B. Beno, K. N. Houk, *J. Am. Chem. Soc.* **1996**, *118*, 6036.

[2] K. N. Houk, J. González, Y. Li, *Acc. Chem. Res.* **1995**, *28*, 81, and refs. cited therein.

[3] D. L. Boger, S. N. Weinreb, *Hetero Diels-Alder Methodology in Organic Synthesis*, Academic Press, San Diego, **1987**.

[4] X. Zhang, H. Du, Z. Wang, Y.-D. Wu, K. Ding, *J. Org. Chem.* **2006**, *71*, 2862.

[5] V. Polo, L. R. Domingo, J. Andres, *J. Phys. Chem. A* **2005**, *109*, 10438.

[6] L. R. Domingo, J. Andres, *J. Org. Chem.* **2003**, *68*, 8662.

[7] H. Kunz, W. Pfrengle, *Angew. Chem.* **1989**, *101*, 1041; *Angew. Chem. Int. Ed.* **1989**, *28*, 1067.

[8] E. Vedejs, J. S. Stults, R. G. Wilde, *J. Am. Chem. Soc.* **1988**, *110*, 5452.

[9] R. Appel in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, pp. 157.

[10] L. N. Markovskii, V. D. Romanenko, *Tetrahedron* **1989**, *45*, 6019.

[11] R. K. Bansal, N. Gupta in *Science of Synthesis: Methods of Molecular Transformation (Houben-Weyl)*, Vol. 13 (Eds.: R. C. Storr, T. L. Gilchrist), Thieme, Stuttgart, **2004**, pp. 647, 689, 743.

[12] a) A. Schmidpeter in *Comprehensive Heterocyclic Chemistry-II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**, Vol. 3, pp. 709, 715 and Vol. 4, pp. 771; b) A. Schmidpeter, K. Karaghiosoff in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, pp. 258; c) A. Schmidpeter in *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain* (Ed.: F. Mathey), Elsevier, Oxford, **2001**, pp. 363.

[13] a) R. K. Bansal, N. Gupta, S. K. Kumawat, *Current Org. Chem.* **2007**, *11*, 33; b) R. K. Bansal, J. Heinicke, *Chem. Rev.* **2001**, *101*, 3549; c) R. K. Bansal, N. Gupta, A. Surana, *J. Indian Chem. Soc.* **1998**, *75*, 648; d) R. K. Bansal, K. Karaghiosoff, N. Gandhi, A. Schmidpeter, *Synthesis* **1995**, 361; e) R. K. Bansal, R. Mahnot, G. Pandey, R. Gupta, *J. Indian Chem. Soc.* **1995**, *71*, 415.

[14] R. K. Bansal, K. Karaghiosoff, A. Schmidpeter, *Tetrahedron* **1994**, *50*, 7675.

[15] G. Märkl in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, pp. 220.

[16] G. Märkl in *Methods in Organic Chemistry (Houben-Weyl)*, Vol. 4 (Ed.: M. Regitz), Thieme, Stuttgart, **1982**, pp. 72.

[17] For a recent review, see: R. K. Bansal, N. Gupta, N. Gupta, *Heteroat. Chem.* **2004**, *15*, 271.

[18] C. S. Wannere, R. K. Bansal, P. v. R. Schleyer, *J. Org. Chem.* **2002**, *67*, 9162.

[19] U. Salzner, S. M. Bachrach, D. C. Mulhearn, *J. Comput. Chem.* **1997**, *18*, 198.

[20] R. K. Bansal, N. Gupta, S. K. Kumawat, *Tetrahedron* **2006**, *62*, 1548.

[21] R. K. Bansal, K. Karaghiosoff, N. Gupta, N. Gandhi, S. K. Kumawat, *Tetrahedron* **2005**, *61*, 10521.

[22] R. K. Bansal, N. Gupta, S. K. Kumawat, R. Gupta, *Heteroat. Chem.* **2006**, *17*, 402.

[23] J. Alcaraz, F. Mathey, *J. Chem. Soc., Chem. Commun.* **1984**, 508.

[24] A. Moores, T. Cantat, L. Ricard, N. Mézailles, P. Le Floch, *New J. Chem.* **2007**, *31*, 1493.

[25] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN 03 (revision B.05), GAUSSIAN Inc., Wallingford, CT (USA) **2003**.

[26] C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.

[27] R. F. W. Bader, *Atoms in Molecules – A Quantum Theory*, Clarendon Press, Oxford, **1990**.

[28] K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251.

[29] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083.

[30] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. von Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.

[31] P. v. R. Schleyer, H. Jiao, N. J. R. von Eikema Hommes, V. G. Malkin, O. Malkina, *J. Am. Chem. Soc.* **1997**, *119*, 12669.

[32] For a recent review see: Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.

[33] H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Org. Lett.* **2006**, *8*, 863.

[34] I. Fernández, M. A. Sierra, F. P. Cossío, *J. Org. Chem.* **2007**, *72*, 1488.

[35] I. Fernández, M. A. Sierra, F. P. Cossío, *J. Org. Chem.* **2006**, *71*, 6178.

[36] M. G. Evans, M. Polanyi, *Trans. Faraday Soc.* **1938**, *34*, 11.

[37] R. P. Bell, *Proc. R. Soc. London, Ser. A* **1936**, *154*, 414.

[38] J. E. Leffler, *Science* **1953**, *117*, 340.

[39] G. S. Hammond, *J. Am. Chem. Soc.* **1955**, *77*, 334.