Communications to the Editor

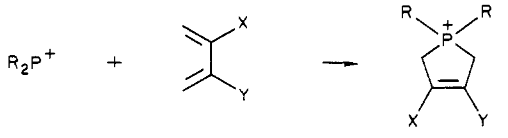
Phosphenium Ions as Dienophiles[†]

Carlton K. SooHoo and S. G. Baxter*

Fred Stark Pearson Memorial Laboratory
Department of Chemistry, Tufts University
Medford, Massachusetts 02155

Received July 11, 1983

The reactivity of carbenes[1] and silylenes[2] has occupied a prominent position in chemical research for a considerable time, and it is likely that it will continue to do so. Phosphenium ions[3] (R_2P^+) constitute a class of molecules that may be considered as isoelectronic to carbenes and silylenes.[4] Although the synthesis[3] and electronic[3d,4] and molecular[5] structures of phosphenium ions have been the subject of intense investigations, their reactivity remains largely unexplored. As shown by Parry and co-workers, phosphenium ions may behave as Lewis acids or bases, as in their reactivity toward phosphines[6] and metal carbonyls,[7] respectively. Perhaps more interestingly, Cowley and co-workers have observed the net insertion of R_2P^+ into a C–H bond in the reaction of $[(i\text{-}Pr_2N)_2P]^+$ with stannocene and plumbocene[8] and the intramolecular rearrangement of $[(Me_5C_5)(t\text{-}Bu)P]^+$,[9] reactions that reflect the carbene character of R_2P^+. A well-known reaction of carbenes and silylenes is the oxidative addition of unsaturated organic compounds, but this type of reactivity is as yet unreported for R_2P^+. We have begun to examine this class of reactions and now report the 1,4-addition of bis(dimethylamino)- and bis(diethylamino)phosphenium tetrachloroaluminate (**1a** and **1b**, respectively) to 1,3-butadienes (**2**) to form the corresponding 3-phospholenium tetrachloroaluminates (**3a**–**c**).



1a, R = Me_2N
b, R = Et_2N

2a, X = H; Y = Me
b, X = Y = Me

3a, R = Me_2N;
X = H; Y = Me
b, R = Et_2N;
X = H; Y = Me
c, R = Et_2N;
X = Y = Me

Table I. NMR Data for Phospholenium Ions 3a–c[a]

nucleus	compound 3a	 3b	 3c
$^{31}P\{^1H\}$	84.2	78.1	71.5
^1H			
R	2.84 (d, 10)	1.22 (t, 7), 2.88–3.43 (m)	1.20 (t, 8), 2.88–3.43 (m)
ring CH_3	1.98 (br)	1.95 (br)	1.88 (br)
ring CH_2	3.07–*b*	2.80–*b*	*b*
vinyl H	5.73 (d, 36)	5.75 (d, 35)	
$^{13}C\{^1H\}$			
R	37.8 (3.9)	14.2, 41.6 (3.9)	14.2, 41.5 (br)
ring CH_3	20.0 (11.7)	19.9 (11.7)	16.5 (13.7)
ring CH_2	27.3 (78.1), 30.4 (82.0)	29.1 (78.3), 32.2 (82.0)	33.7 (80.1)
vinyl C	120.1 (9.8), 137.2 (13.7)	120.2 (7.8), 137.1 (15.6)	128.0 (9.8)

[a] The ^{31}P and ^{13}C NMR spectra were ^1H noise-decoupled and were obtained on a Bruker WP-60 spectrometer. The ^1H NMR spectra were obtained on a Varian EM360 spectrometer. All samples were run as CD_2Cl_2 solutions, and the numbers in parentheses are coupling constants in hertz. [b] Buried by the R signals.

A typical preparation proceeds as follows. One equivalent of the diene is added dropwise to a solution of **1**[10] (~0.1 M) in CH_2Cl_2 at 0 °C, and after warming, **3** is precipitated as a white solid by the addition of pentane. The reactions are carried out on the multigram scale and typically give isolated yields of about 90%, although the ^1H NMR spectra of reaction mixtures indicate that they essentially go to completion. The ^{31}P, ^1H, and ^{13}C NMR data for **3a–c** are contained in Table I, and they are entirely consistent with the 3-phospholenium ion structure.[11] The fact that **3c** shows only one signal each for the ring methyl, methylene, and vinyl carbons in the ^{13}C NMR is consistent only with the symmetry of the 3-phospholenium ion structure and rules out that of the alternative 2-phospholenium ion.

The formation of **3** from **1** and **2** appears to be a useful synthetic approach to five-membered phosphorus heterocycles. Currently, the synthesis of such systems depends largely on the reaction between 1,3-dienes and chlorophosphines, the McCormack reaction.[12] The McCormack reaction is, however, a very sluggish process taking days and sometimes weeks to reach completion. In contrast, the reaction of **1** with **2** proceeds on a more convenient time scale; a ^1H NMR spectrum taken 15 min after the addition of **1b** to **2a** indicates complete formation of **3b**. For comparison, ^1H NMR of a CH_2Cl_2 solution 0.5 M in **2a** and $(Et_2N)_2PCl$ and 0.01 M in cupric stearate shows no reaction after stirring at room temperature for 5 days. We attribute the increased rate of reaction of **1** over that of the chlorophosphines to the greater electrophilicity of **1**.

The addition of **1** to **2** firmly establishes the carbenoid nature of R_2P^+. Although carbenes undergo 1,2-cycloaddition to 1,3-dienes to yield vinyl cyclopropanes, both silylenes (R_2Si)[2] and germylenes (R_2Ge)[13] are known to add to 1,3-dienes in a 1,4 fashion to give silacyclopentenes and germacyclopentenes, respectively. As yet, no such reaction has been reported for stannylenes (R_2Sn).

[†] Dedicated to the memory of Dr. James C. Wilburn, 1953–1981.

(1) See, for example: (a) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971. (b) Jones, M., Jr.; Moss, R. A. "Carbenes"; Wiley: New York, 1973.

(2) Gaspar, P. P. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1978; pp 229–277.

(3) (a) Maryanoff, B. E.; Hutchins, R. O. *J. Org. Chem.* **1972**, *37*, 3475–3480. (b) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534–2540. (c) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Ibid.* **1977**, *16*, 994–1001. (d) For a recent review, see: Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789–797.

(4) Harrison, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 7406–7413.

(5) Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784–7786.

(6) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046–3050.

(7) (a) Montemayor, R. G.; Sauer, D. T.; Fleming, S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231–2233. (b) Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 4289–4293. (c) Hutchins, L. D.; Duesler, E. N.; Paine, R. T. *Organometallics* **1982**, *1*, 1254–1256.

(8) Cowley, A. H.; Kemp, R. A.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 3239–3240.

(9) Cowley, A. H.; Mehrotra, S. K. *J. Am. Chem. Soc.* **1983**, *105*, 2074–2075.

(10) Compounds **1a** and **1b** were prepared by the addition of aluminum chloride to the parent chlorophosphines in CH_2Cl_2 and used directly without isolation.

(11) Products **3a–c** gave satisfactory elemental analysis data.

(12) (a) McCormack, W. B. U.S. Patents 2663737, 2663738, 1953. For reviews, see: (b) Quin, L. D. In "1,4-Cycloaddition Reactions"; Hamer, J., Ed.; Academic Press: New York, 1973; pp 47–96. (c) Quin, L. D. "The Heterocyclic Chemistry of Phosphorus"; Wiley: New York, 1981; pp 30–58.

0002-7863/83/1505-7443$01.50/0

There are several pathways that the mechanism of the cycloaddition may follow. The simplest would be a concerted thermal [2 + 4] cheletropic addition. Alternatively, the reaction may proceed via a two-step addition involving an unstable 1,2 adduct (vinyl phosphiranium ion) which rearranges to give the 1,4 adduct. The former mechanism has been shown to predominate in the case of R_2Ge[13] while the latter holds for R_2Si,[2] both of which are expected to exist as ground-state singlets.[14] There is also the possibility of a nonconcerted addition that passes through a biradical intermediate and is expected for the addition of a triplet species. However, since R_2P^+ is almost certainly a ground-state singlet,[3d,4] this last mechanism is unlikely. At this time, both the [2 + 4] cheletropic and the stepwise addition remain as equally viable candidates.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for support of this work. We also thank Professors William Bachovchin and Michael Blumenstein for the use of their NMR facility.

Registry No. 1a, 61788-01-0; **1b**, 84240-84-6; **2a**, 78-79-5; **2b**, 513-81-5; **3a**, 87712-52-5; **3b**, 87729-01-9; **3c**, 87729-02-0.

---

[13] Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897–901.

[14] (a) Meadows, J. H.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1976**, *98* 4383–4386. (b) Barthelat, J.-C.; Roch, B. S.; Trinquier, G.; Satgé, J. *Ibid.* **1980**, *102*, 4080–4085.

Reaction of Phosphenium Ions with 1,3-Dienes: A Rapid Synthesis of Phosphorus-Containing Five-Membered Rings

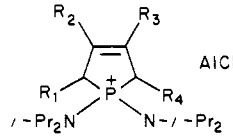
A. H. Cowley,* R. A. Kemp, J. G. Lasch, N. C. Norman, and C. A. Stewart

Department of Chemistry, University of Texas at Austin
Austin, Texas 78712

Received July 27, 1983

In the singlet state, phosphenium ions (R_2P^+) feature both a lone pair and a vacant orbital at the cationic center. The anticipated amphoterism of these cations is evidenced by the fact that they interact with Lewis bases,[1] undergo C–H oxidative addition reactions,[2] and function as ligands.[3] We now report that phosphenium ions react readily with a variety of 1,3-dienes.

Typically, 0.290 g (3.5 mmol) of 2,3-dimethyl-1,3-butadiene was added to a solution of 0.720 g (1.8 mmol) of $[(i\text{-}Pr_2N)_2P]^+[AlCl_4]^-$ (**1**)[4] in 50 mL of CH_2Cl_2 at 0 °C. $^{31}P\{^1H\}$ NMR monitoring of the product, **2a** (δ ^{31}P + 69.6), indicated that the reaction was complete in ~12 h.[5,6] The 3-phospholenium cation structure for **2a** was deduced from the following NMR data: $^{13}C\{^1H\}$ (CH_2Cl_2) (20.0 MHz) δ 16.0 (Me (ring), d, J_{PCCC} = 14.5 Hz), 22.6 (Me (*i*-Pr), s), 37.1 (CH_2, d, J_{PC} = 76.5 Hz), 47.9 (CH (*i*-Pr), d, J_{PNC} = 4.1 Hz), 127.3 (C (ring), J_{PCC} = 11.5 Hz); ^1H NMR (90.0 MHz) (CH_2Cl_2) δ 1.3 (Me (*i*-Pr), d, 12 H, J_{HCCH} = 7.5 Hz), 1.8 (Me (ring), br, 6 H), 3.1 (CH_2, d, 4 H, J_{PCH} = 11.1 Hz), 3.7 (CH (*i*-Pr), m, 4 H). The structure was confirmed by a single-crystal X-ray diffraction study[7] and shows that the double bond is located between C(2) and C(3) (1.313 (5) Å), the other C–C bond lengths averaging 1.517 (5) Å (Figure 1). The $[(i\text{-}Pr_2N)_2P]^+$ unit[4] changes little on coordination: the P–N bond lengths increase by an average of 0.013 (4) Å while the N–P–N angles widen by 1.3 (2)°. The nitrogens remain trigonal planar.



2a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$ (95% yield, mp 132 °C)
b, $R_2 = Me$; $R_1 = R_3 = R_4 = H$ (92% yield, mp 144 °C)
c, $R_1 = R_2 = R_3 = R_4 = H$ (73% yield, mp 153 °C)
d, $R_1 = Me$; $R_2 = R_3 = R_4 = H$ (64% yield, mp 175 °C)
e, $R_1 = R_4 = Me$; $R_2 = R_3 = H$ (55% yield, mp 167 °C)

The times for reaction completion for the other 1,3-dienes are dependent upon steric and electronic factors. Thus, the less activated dienes, isoprene and 1,3-butadiene, require ~24 h at 25 °C and afford the 3-phospholenium cations **2b** (δ ^{31}P + 76.5) and **2c** (δ ^{31}P + 76.0), respectively. The more sterically hindered dienes *trans*-1,3-pentadiene and *trans*-2,*trans*-4-hexadiene produce **2d** (δ ^{31}P + 79.7) and **2e** (δ ^{31}P +88.7) in 3 and 9 days, respectively. Reaction times can be decreased even further by using the less bulky phosphenium ion $[(Me_2N)_2P]^+$. For example, $[(Me_2N)_2P]^+$ reacts with 2,3-dimethyl-1,3-butadiene and isoprene in ~1 h (upon warming) from −78 to 25 °C) affording **3a** (δ ^{31}P +82.7) and **3b** (δ ^{31}P +89.6), respectively. The structures of **3a** and **3b** were shown to be analogous to those of **2a** and **2b** by ^1H and ^{13}C NMR spectroscopy.[6] The chlorophosphenium ion $[(i\text{-}Pr_2N)(Cl)P]^+$ also reacts very cleanly and rapidly (~30 min) with 2,3-dimethyl-1,3-butadiene to afford the corresponding 3-phospholenium cation, **4a** (δ ^{31}P +93.4).

It was first recognized by McCormack[9] that dihalophosphines react with 1,3-dienes and upon hydrolysis produce phospholene oxides. However, the McCormack reactions require several days or weeks for completion. The dramatic reduction in reaction times for the corresponding phosphenium ion reactions is due to their electrophilic nature.

Finally, we note that phosphenium cations are computed to be ground-state singlets.[10] The reactions of these cations with, in particular *trans*-2,*trans*-4-hexadiene show only one product according to ^{31}P NMR spectroscopy, thus suggesting the anticipated stereospecificity of the addition reaction. Further studies of the

---

[1] (a) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046. (b) Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Ibid.* **1981**, *20*, 2916. (c) Baxter, S. G.; Collins, R. L.; Cowley, A. H.; Sena, S. F. *Ibid.*, in press.

[2] Cowley, A. H.; Kemp, R. A.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 3239.

[3] For cationic complexes, see: (a) Thomas, M. C.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994. (b) Montemayer, R. C.; Sauer, D. T.; Fleming, S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231. (c) Bennett, D. W.; Parry, R. W. *Ibid.* **1979**, *101*, 755. (d) Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789. (e) Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 4289. For neutral complexes, see: (f) Light, R. W.; Paine, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 2230. (g) Hutchins, L. D.; Paine, R. T.; Campana, C. F. *Ibid.* **1980**, *102*, 4521. (h) Hutchins, L. D.; Light, R. W.; Paine, R. T. *Inorg. Chem.* **1982**, *21*, 266. (i) Hutchins, L. D.; Duesler, E. N.; Paine, R. T. *Organometallics* **1982**, *1*, 1254.

[4] Cowley, A. H.; Cushner, M.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784.

[5] After reactions were complete all volatiles were removed via vacuum. The phospholenium salts were dissolved in a minimum amount of CH_2Cl_2, and about twice the volume of hexane was layered over the CH_2Cl_2. The two-phase solution was placed at −20 °C. After a few days crystals resulted.

[6] Satisfactory elemental analyses were obtained for all new compounds. These data will be published in a full paper along with ^{13}C and ^1H NMR data.

[7] Crystal data for **2a**: $AlC_{18}Cl_4H_{38}N_2P$ M_r = 482.29, monoclinic, space group $P2_1/c$ (No. 14), a = 9.005 (1) Å, b = 16.134 (4) Å, c = 18.271 (2) Å, β = 96.94 (2)°, U = 2633 (3) Å^3, D_c = 1.216 g cm^{-3}, Z = 4, λ (Mo Kα) (graphite monochromator) = 0.71069 Å, μ (Mo Kα) = 5.5 cm^{-1}. From a total of 5869 unique reflections measured on an Enraf-Nonius CAD-4 diffractometer in the range $2.0 \leq 2\theta \leq 50.0°$, 3214 ($I > 3\sigma(I)$) were used to solve (MULTAN[8] and difference Fourier) and refine (full matrix, least squares) the structure of **2a**. Due to extensive disorder in the $AlCl_4^-$ anion, the structure did not refine well and gave final residuals R = 0.1046 and R_w = 0.1471. The cation was essentially well-behaved during the refinement, and its structure is adequately determined by this experiment. The $AlCl_4^-$ unit was refined as two tetrahedra except for one Cl atom, which did not refine. Positional parameters, occupancy factors, and thermal parameters were refined independently to obtain the best fit. Full details will be published in due course.

[8] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368. Main, P., MULTAN 82, University of York, York, England, 1982.

[9] McCormack, W. B. U.S. Patents 2 663 736, 2 663 737, 1953. *Chem. Abstr.* **1955**, *49*, 7601. For reviews of this reaction, see: Quin, L. D. In "1,4-Cycloaddition Reactions"; Hamer, J., Ed.; Academic Press, New York, 1967; pp 47–96. Quin, L. D. In "The Hetrocyclic Chemistry of Phosphorus"; Wiley-Interscience: New York, 1981; Chapter 2.

[10] Harrison, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 7406.

0002-7863/83/1505-7444\$01.50/0