Allenyl and Divinyl Phosphines, Arsines, and Stibines as Potential Precursors of the Corresponding 1- and 2-Phospha, 1- and 2-Arsa, and 1- and 2-Stiba Dienes

Laurent Lassalle, Stéphanie Legoupy, and Jean-Claude Guillemin*

Laboratoire de Synthèses et Activations de Biomolécules, URA CNRS No. 1467, ENSCR, 35700 Rennes, France

Received February 1, 1996[⊗]

Summary: The base-induced rearrangement of divinylphosphine led to the corresponding 3-phospha-1,3-pentadiene, which is sufficiently stable to be detected at room temperature by ^{31}P NMR spectroscopy. This diene was trapped by addition of 2-propanethiol to the reaction mixture. Under similar conditions, the transient 1-phospha-1,3-butadiene and 3-arsa-1,3-pentadiene were chemically trapped. Divinylstibine and allenylstibine, both new compounds and potential precursors of stibadienes, were also prepared.

Over the last several decades, numerous 1- and 2-aza dienes have been prepared and their chemistry has been studied.[1] However, few studies have been devoted to heterodienes containing other atoms of the group 15 elements: phosphorus, arsenic, and antimony. Such compounds generally are of low stability, which can be attributed to the weak heteroatom−carbon double bond[2] and to the high chemical reactivity of 1,3-diene compounds. Nevertheless, several substituted phospha dienes have been prepared[3] and the two parent compounds, the 1- and 2-phospha 1,3-dienes, have been partially characterized and chemically trapped with a nucleophile.[3b]

Vinylphosphines and -arsines can be rearranged into the corresponding phospha- and arsaalkenes. The base-induced rearrangement of vinylphosphines has been demonstrated for a derivative stabilized with a bulky substituent[4a] or by chemical trapping for the unstabilized derivatives.[4b] The presence of arsaalkenes in the products formed by vaporization of primary vinylarsines on a solid base has been evidenced by analysis of the gaseous flow by photoelectron spectroscopy.[5] (A rearrangement was also observed between alk-1-ynylphosphines and phosphaalkynes[6] or alk-1-ynylarsines and arsaalkynes.[7,8]) Consequently, we thought that the base-induced rearrangement of the allenyl and divinyl derivatives could lead, via a similar rearrangement, to the corresponding 1- and 2-hetero dienes containing a phosphorus, arsenic, or antimony atom. We report here a study devoted to the base-induced rearrangement of the two phosphorus and two arsenic parent compounds (allenylphosphine (**1**), divinylphosphine (**2**), allenylarsine (**3**), and divinylarsine (**4**)), potential precursors of the corresponding 1- and 2-hetero dienes. The preparation of allenylstibine (**5**) and divinylstibine (**6**) and attempts to rearrange them into the corresponding dienes are also described.

Experimental Section

Caution! *Phosphines, arsines, and stibines are toxic compounds. All reactions and handling should be carried out in a well-ventilated hood.*

Materials. Dichloromethane was purified by distillation from P_2O_5 and THF by refluxing and then distillation from Na/benzophenone. Duroquinone was purchased from Acros Chimica. Chlorotributylstannane and galvinoxyl were purchased from Aldrich. All chemicals were used without further purification. Tributylstannane,[9] allenyltributylstannane,[10] vinyltributylstannane,[11] allenylphosphine (**1**),[12] allenylarsine (**3**),[8] and divinylarsine (**4**)[13] were prepared as previously reported.

General Considerations. ^1H (400 MHz), ^{31}P (162 MHz), and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker ARX400 spectrometer. Chemical shifts are given in ppm relative to internal $SiMe_4$ for ^1H and ^{13}C spectra and external H_3PO_4 for ^{31}P NMR spectra. High resolution mass spectrometry experiments (HRMS) were performed on a Varian MAT 311 instrument. To record the mass spectra, the phosphines, arsines, and stibines were introduced directly from a cooled cell into the ionization chamber of the spectrometer. The yields of the unstabilized derivatives were determined by ^1H NMR with an internal reference.

(3-Pentoxy)dichlorophosphine (7). In a three-necked flask equipped with a magnetic stirring bar, a dropping funnel, and a nitrogen inlet were introduced phosphorus trichloride (41.2 g; 0.30 mol) and anhydrous dichloromethane (250 mL). 3-Pentanol (22 g, 0.25 mol) diluted in anhydrous dichloromethane (20 mL) was then added dropwise. Evolution of a

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

(1) Trost, B. M.; Fleming, I.; Paquette, L. A. Heterodiene Additions. In *Comprehensive Organic Chemistry*; Boger, D. L., Ed.; Pergamon Press: Oxford, U.K., 1991; Vol. 5, pp 473−484.

(2) Sowerby, D. B. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; Wiley: New York, 1994; Chapter 2, pp 33−35.

(3) (a) Boyd, B. A.; Thoma, R. J.; Watson, W. H.; Neilson, R. H. *Organometallics* **1988**, *7*, 572. Martin, G.; Ocando-Mavarez, E. *Heteroat. Chem.* **1991**, *2*, 651. Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: New York, 1990; Vol. 2, p 651. Appel, R.; Knoch, F.; Kunze, H. *Chem. Ber.* **1984**, *117*, 3151. Markovskii, L. N.; Romanenko, V. D.; Pidvarko, T. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *53*, 1502. (b) Guillemin, J.-C.; Cabioch, J.-L.; Morise, X.; Denis, J.-M.; Lacombe, S.; Gonbeau, D.; Pfister-Guillouzo, G.; Savignac, P.; Guenot, P. *Inorg. Chem.* **1993**, *32*, 5021.

(4) (a) Mercier, F.; Hugel-Le Goff, C.; Mathey, F. *Tetrahedron Lett.* **1989**, *30*, 2397. (b) Gaumont, A.-C.; Guillemin, J.-C.; Denis, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 945.

(5) Métail, V.; Senio, A.; Lassalle, L.; Guillemin, J.-C.; Pfister-Guillouzo, G. *Organometallics* **1995**, *14*, 4732.

(6) Guillemin, J.-C.; Janati, T.; Denis, J.-M. *J. Chem. Soc., Chem. Commun.* **1992**, 415.

(7) Guillemin, J.-C.; Lassalle, L.; Dréan, P.; Wlodarczak, G.; Demaison, J. *J. Am. Chem. Soc.* **1994**, *116*, 8930.

(8) Lassalle, L.; Legoupy, S.; Guillemin, J.-C. *Inorg. Chem.* **1995**, *34*, 5694.

(9) Kuivila, H. G. *Synthesis* **1970**, 499.

(10) Keinan, E.; Peretz, M. *J. Org. Chem.* **1983**, *48*, 5302. Aidhen, I. S.; Braslau, R. *Synth. Commun.* **1994**, *24*, 789.

(11) Seyferth, D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1957**, *79*, 515. Seyferth, D.; Vaughan, L. G. *J. Organomet. Chem.* **1963**, *1*, 138.

(12) Guillemin, J.-C.; Savignac, P.; Denis, J.-M. *Inorg. Chem.* **1991**, *30*, 2170.

(13) Guillemin, J.-C.; Lassalle, L. *Organometallics* **1994**, *13*, 1525.

S0276-7333(96)00066-0 CCC: $12.00

gas (HCl) was observed. At the end of the addition, the solvent was removed in vacuo and compound **7** was purified by distillation: bp_{45} 73 °C; yield 86%. ^{31}P NMR ($CDCl_3$): δ 175.1. ^1H NMR ($CDCl_3$): δ 0.94 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_3); 1.74 (qd, 4H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 5.8 Hz, CH_2); 4.68 (d quint, 1H, $^3J_{PH}$ = 15.1 Hz, $^3J_{HH}$ = 5.8 Hz, C*H*). ^{13}C NMR ($CDCl_3$): δ 9.3 (q, $^1J_{CH}$ = 126.3 Hz, *C*H_3); 27.1 (td, $^1J_{CH}$ = 127.0 Hz, $^3J_{PC}$ = 1.5 Hz, *C*H_2); 85.2 (dd, $^1J_{CH}$ = 146.9 Hz, $^2J_{PC}$ = 9.7 Hz, *C*H). Anal. Calcd for $C_5H_{11}Cl_2OP$: C, 31.77; H, 5.87. Found: C, 32.01; H, 6.02.

Divinyl(3-pentoxy)phosphine (8). In a three-necked flask equipped with a magnetic stirring bar, a dropping funnel, and a nitrogen inlet was introduced vinylmagnesium bromide in THF (11.5 mL, 2 M, 23 mmol). The solution was cooled to −50 °C, and $Et_2CHOPCl_2$ (2.1 g, 11 mmol) diluted in THF (25 mL) was added dropwise. At the end of the addition, the mixture was stirred for 30 min at −50 °C and then warmed to room temperature. Pentane (50 mL) was added to precipitate the magnesium salts, which were removed by filtration under nitrogen. Purification was performed by distillation in vacuo (0.1 mbar), condensation of **8** at −55 °C, and then revaporization: yield 63%. ^{31}P NMR ($CDCl_3$): δ 107.3. ^1H NMR ($CDCl_3$): δ 0.89 (t, 6H, $^3J_{HH}$ = 7.3 Hz, CH_3); 1.55 (dq, 4H, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 6.3 Hz, CH_2CH$_3$); 3.59 (d quint, 1H, $^3J_{PH}$ = 10.2 Hz, $^3J_{HH}$ = 6.3 Hz, −OC*H*); 5.73 (ddd, 2H, $^3J_{HHcis}$ = 14.7 Hz, $^3J_{PH}$ = 9.4 Hz, $^2J_{HH}$ = 2.1 Hz, =CH_2); 5.79 (ddd, 2H, $^3J_{HHtrans}$ = 18.3 Hz, $^3J_{PH}$ = 12.1 Hz, $^2J_{HH}$ = 2.1 Hz, =CH_2); 6.41 (ddd, 2H, $^3J_{HHtrans}$ = 18.3 Hz, $^3J_{HHcis}$ = 14.7 Hz, $^2J_{PH}$ = 2.7 Hz, =C*H*−). ^{13}C NMR ($CDCl_3$): δ 9.7 (q, $^1J_{CH}$ = 125.5 Hz, *C*H_3); 28.2 (td, $^1J_{CH}$ = 125.5 Hz, $^3J_{PC}$ = 4.9 Hz, *C*H_2); 83.7 (dd, $^1J_{CH}$ = 143.8 Hz, $^2J_{CP}$ = 17.0 Hz, *C*HO); 125.8 (td, $^1J_{CH}$ = 158.7 Hz, $^2J_{CP}$ = 26.3 Hz, *C*H_2=CH); 141.2 (dd, $^1J_{CH}$ = 155.2 Hz, $^1J_{CP}$ = 18.7 Hz, CH$_2$=*C*H). HRMS: calcd for $C_9H_{17}OP$ 172.1017, found 172.102.

Allenyldichlorostibine (9). In a 25-mL two-necked round-bottomed flask equipped with a nitrogen inlet was introduced antimony trichloride (1.3 g, 5.5 mmol). The reagent was frozen at −40 °C, and allenyltributylstannane (1.65 g, 5 mmol) was added. The solution was vigorously stirred and warmed to room temperature over 5 min. Thus, a crude solution of allenyldichlorostibine (**9**) was obtained. Attempts to purify compound **9** led to the decomposition of the product, and the crude solution must be kept at low temperature (−40 °C): yield (crude) 33%. The NMR spectra were obtained by addition of 1 equiv of allenyltributylstannane in a cooled (−20 °C) NMR tube containing 1 equiv of $SbCl_3$ in CD_3CN. ^1H NMR (CD_3CN, −30 °C): δ 4.74 (d, 2H, $^4J_{HH}$ = 6.9 Hz, CH_2); 5.93 (t, 1H, $^4J_{HH}$ = 6.9 Hz, C*H*). ^{13}C NMR (CD_3CN, −30 °C): δ 73.5 (t, $^1J_{CH}$ = 169.1 Hz, *C*H_2); 99.2 (d, $^1J_{CH}$ = 180.1 Hz, *C*H); 209.8 (s, C=*C*=C).

Divinylchlorostibine (10). In a two-necked round-bottomed flask equipped with a nitrogen gas inlet were introduced 1 equiv of $SbCl_3$ (1.14 g, 5 mmol) and 2.0 equiv of vinyltributylstannane (3.2 g, 10 mmol). Heating to 70 °C over 3 h followed by distillation in vacuo led to divinylchlorostibine (**10**). This compound must be kept at low temperature (−30 °C): $bp_{0.1}$ ∼40 °C; yield 71%. ^1H NMR ($CDCl_3$): δ 6.00 (dd, 2H, $^3J_{HHtrans}$ = 19.5 Hz, $^2J_{HH}$ = 1.2 Hz, CH_2); 6.38 (dd, 2H, $^3J_{HHcis}$ = 12.2 Hz, $^2J_{HH}$ = 1.2 Hz, CH_2); 7.19 (dd, 2H, $^3J_{HHtrans}$ = 19.5 Hz, $^3J_{HHcis}$ = 12.2 Hz, C*H*). ^{13}C NMR ($CDCl_3$): δ 134.6 (t, $^1J_{CH}$ = 158.5 Hz, *C*H_2); 143.8 (d, $^1J_{CH}$ = 159.1 Hz, *C*H).

General Procedure for the Preparation of Phosphine 2 and Stibines 5 and 6. In a 25 mL two-necked flask was introduced the reducing agent (**8**, $AlHCl_2$ (20 mmol) in tetraglyme (10 mL);[12] **9** or **10**, tributylstannane (4.3 g, 15 mmol) with small amounts of duroquinone or galvinoxyl).[8] The flask was fitted on a vacuum line equipped with a stopcock, a cold trap, and a cold finger. The flask was degassed, and compound **8**, **9**, or **10** (4 mmol) was slowly introduced onto the reducing mixture with a microsyringe or a flexible needle. To limit oligomerization, compounds **2**, **5**, and **6** were distilled off *in vacuo* from the reaction mixture during the course of the addition of **8**−**10**, respectively. High-boiling impurities were selectively trapped in a cold trap (−70 °C) and compounds **2**, **5**, and **6** were condensed with a cosolvent on the cold finger (−196 °C). After disconnection from the vacuum line, the apparatus was filled with dry nitrogen and the cold finger was warmed to room temperature. Thus, the product was collected in a Schlenk flask or in an NMR tube and kept at low temperature (<−40 °C).

Divinylphosphine (2). Yield: 65%. ^{31}P NMR ($CDCl_3$): δ −62.3. ^1H NMR ($CDCl_3$): δ 4.39 (dtm, 1H, $^1J_{PH}$ = 216.1 Hz, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.8 Hz, $^4J_{HH}$ = 1.0 Hz, P*H*); 5.73 (dddd, 2H, $^3J_{HHtrans}$ = 18.4 Hz, $^3J_{PH}$ = 13.9 Hz, $^2J_{HH}$ = $^4J_{HH}$ = 1.8 Hz, CH_2); 5.81 (dddd, 2H, $^3J_{PH}$ = 30.4 Hz, $^3J_{HHcis}$ = 11.7 Hz, $^2J_{HH}$ = 1.8 Hz, $^4J_{HH}$ = 1.0 Hz, CH_2), 6.33 (dddd, 2H, $^2J_{PH}$ = 13.6 Hz, $^3J_{HHtrans}$ = 18.4 Hz, $^3J_{HHcis}$ = 11.7 Hz, $^3J_{HH}$ = 5.1 Hz, C*H*). ^{13}C NMR ($CDCl_3$): δ 128.8 (td, $^1J_{CH}$ = 154.5 Hz, $^2J_{CP}$ = 19.4 Hz, *C*H$_2$); 131.4 (dd, $^1J_{CH}$ = 156.5 Hz, $^1J_{CP}$ = 11.8 Hz, *C*H). IR (CCl_4, cm^{-1}): ν_{PH} 2272 (s), $\nu_{C=C}$ 1595 (m), 1450 (m), 1380 (s), 1335 (m), 1180 (s), 1140 (m), 1010 (m), 985 (m). HRMS: calcd for C_4H_7P 86.02854, found 86.0286. MS *m*/*z* (%): 86 (30.6), 85 (6.8), 59 (12.5), 58 (42.2), 57 (50.4). MIKE: 85, 84, 71; CAD-MIKE: 85, 84, 83, 71, 58.

Allenylstibine (5). Yield: 21%. ^1H NMR ($CDCl_3$): δ 3.63 (dt, 2H, $^3J_{HH}$ = 3.9 Hz, $^5J_{HH}$ = 2.7 Hz, SbH_2); 4.39 (dt, 2H, $^4J_{HH}$ = 6.8 Hz, $^5J_{HH}$ = 2.7 Hz, CH_2); 5.53 (tt, 1H, $^4J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 3.9 Hz, C*H*). ^{13}C NMR ($CDCl_3$): δ 61.4 (d, $^1J_{CH}$ = 170.4 Hz, *C*H); 68.4 (t, $^1J_{CH}$ = 168.4 Hz, *C*H_2); 211.7 (s, C=*C*=C). HRMS: calcd for $(C_3H_5{}^{121}Sb)^{\bullet+}$ 163.9433, found 163.944. MS *m*/*z* (%): 138 (4.7), 123 (2.6), 121 (3.2), 41 (5.6), 40 (5.5), 39 (8.4).

Divinylstibine (6). Yield: 65%. ^1H NMR ($CDCl_3$): δ 4.50 (m, 1H, $^3J_{HH}$ = 3.3 Hz, $^4J_{HH}$ = 1.4 Hz, $^4J_{HH}$ = 0.9 Hz, Sb*H*); 5.90 (ddd, 2H, $^3J_{HHtrans}$ = 19.5 Hz, $^2J_{HH}$ = 2.0 Hz, $^4J_{HH}$ = 1.4 Hz, CH_2); 6.30 (ddd, 2H, $^3J_{HHcis}$ = 12.0 Hz, $^2J_{HH}$ = 2.0 Hz, $^4J_{HH}$ = 0.9 Hz, CH_2); 6.92 (ddd, 2H, $^3J_{HHtrans}$ = 19.5 Hz, $^3J_{HHcis}$ = 12.0 Hz, $^3J_{HH}$ = 3.3 Hz, C*H*). ^{13}C NMR ($CDCl_3$): δ 129.0 (d, $^1J_{CH}$ = 155.9 Hz, *C*H); 136.0 (t, $^1J_{CH}$ = 156.9 Hz, *C*H_2). HRMS: calcd for C_4H_7Sb 175.9586, found 175.958. MS *m*/*z* (%): 176 (12.1), 151 (5.3), 150 (75.1), 149 (12.0), 148 (100), 124 (27.3), 123 (23.4), 122 (41.3), 121 (40.7), 55 (84.8), 53 (7.0), 28 (40.6), 27 (19.4).

Spectroscopic Characterization of (*E*)-/(*Z*)-3-Phospha-1,3-pentadiene (12). In a NMR tube were introduced divinylphosphine (**2**; 30 mg) and a deuterated solvent (CD_3CN, 600 μL). Diazabicycloundecene (DBU; 10 μL) was added and the tube was then introduced into the NMR probe and analyzed by ^{31}P NMR at room temperature. After some hundreds of scans, two small signals corresponding to the two isomers of **12** were observed in a 4:1 ratio. ^{31}P NMR (CD_3CN): δ 240.8 (m); 224.2 (m).

Chemical Trapping of the Dienes 11−13. General Procedure. In a 25 mL flask equipped with a magnetic stirring bar and a rubber septum and cooled to −50 °C were introduced the phosphine **1** or **2** or the arsine **4** (2 mmol) and 2-propanethiol (5 mL). Then DBU (30 μL; for **1**, **2**) or DABCO (30 mg; for **4**) was added. The mixture was warmed to room temperature over 30 min, and compounds **14**−**16**, respectively, were purified by trap-to-trap distillation.

2-Propenyl(2-propylthio)phosphine (14).[3b] Yield: ∼5%.

Ethylvinyl(2-propylthio)phosphine (15). Yield: 60%. ^{31}P NMR ($CDCl_3$): δ 18.8. ^1H NMR ($CDCl_3$): δ 1.06 (dt, 3H, $^3J_{PH}$ = 15.2 Hz, $^3J_{HH}$ = 7.6 Hz, CH_3CH$_2$); 1.27 (dd, 6H, $^3J_{HH}$ = 6.6 Hz, $^4J_{PH}$ = 3.6 Hz, CH_3CH); 1.64 (qd, 2H, $^3J_{HH}$ = 7.6 Hz, $^2J_{PH}$ = 4.6 Hz, CH_2CH$_3$); 2.96 (d sept, 1H, $^3J_{PH}$ ≈ $^3J_{HH}$ = 6.6 Hz, SC*H*); 5.69 (ddd, 1H, $^3J_{PH}$ = 29.0 Hz, $^3J_{HHcis}$ = 12.2 Hz, $^2J_{HH}$ = 2.0 Hz, =CH_2); 5.70 (ddd, 1H, $^3J_{HHtrans}$ = 17.8 Hz, $^3J_{PH}$ = 11.7 Hz, $^2J_{HH}$ = 2.0 Hz, =CH_2); 6.29 (ddd, 1H, $^3J_{HHtrans}$ = 17.8 Hz, $^2J_{PH}$ = 16.7 Hz, $^3J_{HHcis}$ = 12.2 Hz, =C*H*). ^{13}C NMR ($CDCl_3$): δ 9.6 (qd, $^1J_{CH}$ = 127.4 Hz, $^2J_{CP}$ = 13.4 Hz, *C*H$_3$CH$_2$); 22.3 (td, $^1J_{CH}$ = 139.6 Hz, $^1J_{CP}$ = 14.1 Hz, CH$_3$*C*H$_2$); 25.5 (qd, $^1J_{CH}$ = 122.1 Hz, $^3J_{CP}$ = 6.7 Hz, *C*H$_3$CH); 25.6 (qd, $^1J_{CH}$ = 122.1 Hz, $^3J_{CP}$ = 6.7 Hz, *C*H$_3$CH); 37.5 (dd, $^1J_{CH}$ = 141.9 Hz, $^2J_{CP}$ =

20.2 Hz, S*C*H); 125.8 (td, $^1J_{CH}$ = 158.3 Hz, $^2J_{CP}$ = 20.2 Hz, *C*H_2=CH); 138.7 (dd, $^1J_{CH}$ = 155.2 Hz, $^1J_{CP}$ = 25.9 Hz, CH_2=*C*H). IR ($CDCl_3$, cm^{-1}): 2998 (s), 2960 (s), 2903 (s), $\nu_{C=C}$ 1630 (w), 1470 (s), 1400 (m), 1385 (m), 1260 (s), 1215 (s), 1130 (s), 990 (s), 927 (s). HRMS: calcd for $C_7H_{15}PS$ 162.0632, found 162.063. MS *m*/*z* (%): 120 (6.3), 118 (13.9), 117 (22.2), 108 (22.6), 91 (5.5), 75 (24.9), 74 (7.3), 66 (5.8), 63 (10.4), 59 (14.6), 55 (12.7), 43 (100). Anal. Calcd for $C_7H_{15}PS$: C, 51.83; H, 9.32. Found: C, 51.67; H, 9.26.

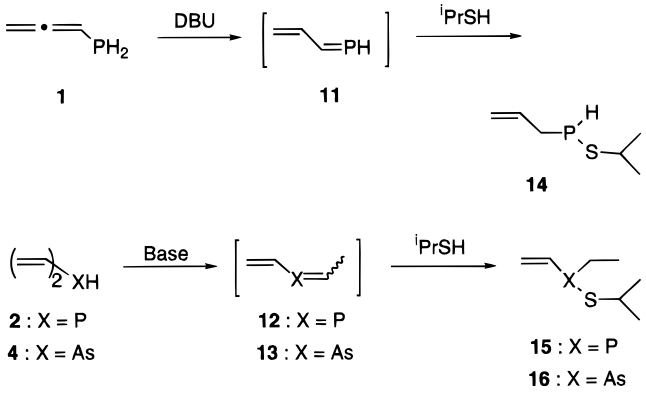
Ethylvinyl(2-propylthio)arsine (16). Yield: 38%. ^{1}H NMR ($CDCl_3$): δ 1.23 (t, 3H, $^3J_{HH}$ = 7.7 Hz, C*H*$_3$CH$_2$); 1.36 (d, 6H, $^3J_{HH}$ = 6.7 Hz, (C*H*$_3$)$_2$CH); 1.77 (q, 2H, $^3J_{HH}$ = 7.7 Hz, CH$_3$C*H*$_2$); 3.09 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, SC*H*); 5.81 (d, 1H, $^3J_{HHtrans}$ = 18.6 Hz, =C*H*$_2$); 5.93 (d, 1H, $^3J_{HHcis}$ = 11.6 Hz, =C*H*$_2$); 5.67 (dd, 1H, $^3J_{HHtrans}$ = 18.6 Hz, $^3J_{HHcis}$ = 11.6 Hz, CH$_3$C*H*$_2$). ^{13}C NMR ($CDCl_3$): δ 10.3 (q, $^1J_{CH}$ = 127.0 Hz, *C*H$_3$-CH$_2$); 21.9 (t, $^1J_{CH}$ = 136.6 Hz, CH$_3$CH$_2$); 26.4 (q, $^1J_{CH}$ = 129.4 Hz, *C*H$_3$CH); 26.5 (q, $^1J_{CH}$ = 131.7 Hz, *C*H$_3$CH); 36.1 (d, $^1J_{CH}$ = 141.4 Hz, *C*HS); 127,4 (t, $^1J_{CH}$ = 158.9 Hz, *C*H$_2$=CH); 140.5 (d, $^1J_{CH}$ = 159.8 Hz, CH$_2$=*C*H). HRMS: calcd for $C_7H_{15}AsS$ 206.0110, found 206.011. MS *m*/*z* (%): 206 (47.0), 177 (28.6), 164 (13.9), 163 (5.5), 137 (17.8), 135 (100), 134 (5.6), 131 (6.0), 130 (5.6), 109 (13.4), 107 (19.5), 102 (19.8), 101 (30.4), 55 (54.0). Anal. Calcd for $C_7H_{15}AsS$: C, 40.78; H, 7.33. Found: C, 40.74; H, 7.43.

Preparation of an Authentic Sample of Ethylvinyl(2-propylthio)arsine (16). Ethylvinylchloroarsine (17). In a two-necked 25 mL flask cooled to 0 °C and equipped with a magnetic stirring bar and a nitrogen inlet was introduced vinyldichloroarsine[13] (1.73 g, 10 mmol). Diethylmercury (2.58 g, 10 mmol) was then slowly added, and the formation of a solid (EtHgCl) was observed (a small amount of azobis(isobutyronitrile) can be added to start the reaction). The mixture was warmed to room temperature and stirred for 1 h. Chloroarsine **17** was then purified by distillation. Yield 89%; bp_{760} 127 °C. ^{1}H NMR ($CDCl_3$): δ 1.27 (t, 3H, $^3J_{HH}$ = 7.7 Hz, C*H*$_3$); 2.04 (q, 2H, $^3J_{HH}$ = 7.7 Hz, CH$_3$C*H*$_2$); 5.93 (d, 1H, $^3J_{HHtrans}$ = 18.7 Hz, =C*H*$_2$); 6.07 (d, 1H, $^3J_{HHcis}$ = 11.5 Hz, CH=C*H*$_2$); 6.87 (dd, 1H, $^3J_{HHtrans}$ = 18.7 Hz, $^3J_{HHcis}$ = 11.5 Hz, CH$_2$=C*H*). ^{13}C NMR ($CDCl_3$): δ 8.9 (q, $^1J_{CH}$ = 127.7 Hz, *C*H$_3$); 28.5 (t, $^1J_{CH}$ = 134.6 Hz, *C*H$_2$); 129.8 (t, $^1J_{CH}$ = 159.9 Hz, CH$_2$=CH); 142.1 (d, $^1J_{CH}$ = 163.8 Hz, CH$_2$=*C*H). HRMS: calcd for $C_4H_8As^{35}Cl$ 167.9500, found 165.953. MS *m*/*z* (%): 166 (27.5), 138 (9.0), 137 (21.6), 131 (5.8), 130 (5.6), 111 (6.3), 110 (22.5), 103 (18.3), 102 (59.5), 101 (17.2), 75 (5.0), 55 (62.5). Anal. Calcd for C_4H_8ClAs: C, 28.86; H, 4.84. Found: C, 28.46; H, 4.68.

Ethylvinyl(2-propylthio)arsine (16). In a two-necked 25 mL flask cooled to 0 °C and equipped with a magnetic stirring bar and a nitrogen inlet were introduced the chloroarsine **17** (0.83 g, 5 mmol) and dry acetonitrile (5 mL). Then, the 2-propanethiol sodium salt (0.78 g, 8 mmol) diluted with acetonitrile (3 mL) was added dropwise. The mixture was stirred for 1 h at room temperature. The ethylvinyl(2-propylthio)arsine (**16**) was then purified by distillation in vacuo, condensed at −60 °C, and then revaporized. Yield: 45% (see the above spectroscopic data).

General Procedure for the Preparation of Deuterated Phosphines, Arsines, and Stibines. In an NMR tube were introduced the phosphine **1** or **2**, the arsine **3** or **4**, or the stibine **5** or **6** (about 0.2 mmol), CD_3CN (600 μL), and D_2O (100 μL). The solution was shaken, and the tube was introduced in the NMR probe. Starting from phosphines **1** and **2**, we observed in the ^{31}P NMR spectrum signals corresponding to the deuteriophosphines **1′** and **2′** (**1′**, $^1J_{PD}$ = 33.7 Hz (t); **2′**, $^1J_{PD}$ = 31.0 Hz (quint)). Similar experiments with arsines **3** and **4** followed by ^{1}H NMR led to deuterioarsines **3′** and **4′**, respectively, but the rate of the exchange was considerably slower. In the case of the stibine **6**, the addition of DABCO (30 mg) was needed to observe the deuteriodivinylstibine **6′**; compound **5** was quickly decomposed when the base was added.

Scheme 1



Results and Discussion

The first primary allenylphosphines[12] and secondary divinylphosphines[14] have been prepared only recently. Allenylphosphine (**1**) has been synthesized by a chemoselective reduction of the corresponding phosphonate.[12] We prepared the divinylphosphine **2** in a two-step sequence: the reaction of 2 equiv of vinylmagnesium bromide with 1 equiv of $Et_2CHOPCl_2$ led to the corresponding divinyl(3-pentoxy)phosphine (**8**), which was reduced by dichloroalane in tetraglyme.

The base-induced rearrangement of compounds **1** and **2** to the corresponding phospha dienes **11** and **12** was first studied by ^{31}P NMR spectroscopy. With **2** as the starting material, in the presence of a Lewis base (DBU), the reaction led to the formation of 3-phospha-1,3-pentadiene (**12**), which was characterized by two ^{31}P NMR signals attributed to the two stereoisomers (δ 240.8 and 224.2 ppm) and comparison of these data with those reported in the literature.[15] With **1** as starting material, even at low temperature, neither the 1-phospha 1,3-diene **11** nor the corresponding cyclic isomer[16] was observed.

The chemical trapping of the dienes **11** and **12** was performed by addition of small amounts of DBU to the corresponding phosphines **1** and **2** diluted in 2-propanethiol. Allyl(2-propylthio)phosphine (**14**) and ethylvinyl(2-propylthio)phosphine (**15**) were respectively obtained (Scheme 1). The structure of **14** was confirmed by comparison of its spectra with those reported in the literature.[3b] The two expected products of a 1,4-addition, the (*Z*)- and (*E*)-1-propenyl(2-propylthio)phosphines, were not observed. Phosphine **15** was characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy and HRMS. The greater instability of 1-phospha 1,3-dienes with respect to 2-phospha 1,3-dienes has already been reported,[3,17] and this could explain the low yield (~5%) observed for the product **14** and the nondetection of compound **11** by ^{31}P NMR.

Thus, the base-induced rearrangements of vinyl- and alkynylphosphines to the corresponding phosphaalkenes[4] and -allenes[18] or -alkynes[6] can be extended to

(14) Haber, S.; Le Floch, P.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1992**, 1799. Guillemin, J.-C.; Janati, T.; Lassalle, L. *Adv. Space Res.* **1995**, *16*, 85.
(15) Morise, X. Ph.D. Thesis, University of Rennes 1 (France), No. 625, 1991.
(16) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 209.
(17) Appel, R.; Kündgen, U.; Knoch, F. *Chem. Ber.* **1985**, *118*, 1352.
(18) Guillemin, J.-C.; Janati, T.; Denis, J.-M.; Guenot, P.; Savignac, P. *Tetrahedron Lett.* **1994**, *35*, 245.

these of allenyl- and divinylphosphines into 1- and 2-phospha 1,3-dienes, respectively.

The tendency to form the pπ-hybridized state with coordination number 2 is still less pronounced with arsenic than with phosphorus. In comparison to the corresponding phosphorus derivatives, relatively few compounds with two-coordinate arsenic are known, and all of them are stabilized by bulky groups or by the presence of oxygen, nitrogen, or fluorine atoms directly bonded to the carbon atom of the C=As bond.[19] Such compounds are less stable than those of phosphorus, and few studies have been devoted to their chemistry.[20]

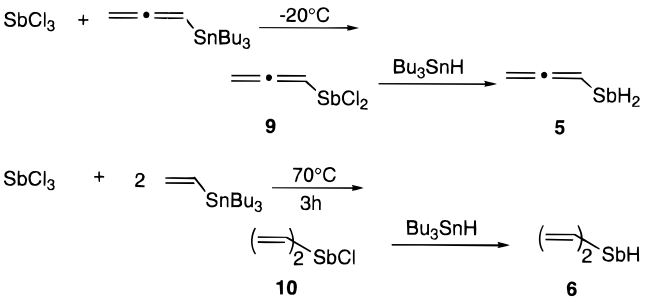
Attempts to trap, with a thiol as nucleophile, the products of rearrangement of vinyl-[13] and alkynylarsines[7,8] were unsuccessful, and only a brown solid was obtained. These results can be attributed to a fast decomposition of the arsaalkene and -alkyne intermediates. We performed then a similar reaction with divinylarsine (**4**), potential precursor of 3-arsa-1,3-pentadiene (**13**). In the presence of 2-propanethiol and of small amounts of DABCO, arsine **4** led to ethylvinyl 2-propylthioarsine (**16**) in 38% yield (Scheme 1). With a stronger base such as DBU or a weaker one such as triethylamine, compound **16** was not detected. The thioarsine **16** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and HRMS and by comparison of these data with those obtained from an authentic sample. This compound was obtained by reaction of diethylmercury with vinyldichloroarsine followed by addition of the sodium salt of 2-propanethiol to the resulting arsine **17** (Scheme 1).

All our efforts to trap the 1-arsa-1,3-butadiene **18** by rearrangement of the allenylarsine **3** were unsuccessful. 1-Arsa diene **18** is probably much less stable than 3-arsa-1,3-pentadiene (**13**), and these results seem to confirm for the arsenic derivatives the higher stability of 2-hetero dienes with respect to 1-hetero dienes, already reported for phosphadienes.

Except for a few stibabenzenes where the λ^3, σ^2 double bond is stabilized in an aromatic cyclic system,[21] only one stibaalkene has been synthesized to date. This 2,3-distiba 1,3-diene[22] is stabilized with bulky substituents and trimethylsiloxy groups on the sp^2 carbons. To extend our study to the antimony derivatives, we needed to prepare allenylstibine (**5**) and divinylstibine (**6**), compounds unknown so far.

The stibine **5** was prepared in a two-step sequence. Allenyltributylstannane is added to a stoichiometric amount of frozen $SbCl_3$ to give allenyldichlorostibine (**9**). Attempts to purify compound **9** led to the decomposition of the product, and the crude mixture was quickly used in the following step. The chemoselective reduction of

Scheme 2



chlorostibine **9** was performed with Bu_3SnH in the presence of small amounts of a radical inhibitor (duroquinone and galvinoxyl) to avoid the cleavage of the C−Sb bond.[23] Allenylstibine (**5**), obtained in a 21% overall yield, is the parent compound of a new class of products. It was characterized by low-temperature ^{1}H and ^{13}C NMR spectroscopy and HRMS. The ^{1}H and ^{13}C NMR data allow an unambiguous structural assignment, since the chemical shifts and coupling constants are typical of allenic derivatives. The presence of stibine **5** was confirmed by the observation of the corresponding molecular ion by HRMS. Divinylstibine (**6**) was prepared in a two-step sequence starting from 1 equiv of $SbCl_3$ and 2 equiv of vinyltributylstannane. The reduction of the formed divinylchlorostibine (**10**) was similar to that previously described to prepare stibine **5** (Scheme 2). Stibines **5** and **6** had low stability at room temperature, even when kept under nitrogen in a solvent (half-life ~1 h). An insoluble black, oligomeric material and antimony mirrors on the walls of the flask were slowly formed under these conditions. As already observed for primary vinyl- and alkynylstibines,[23] compounds **5** and **6** are more stable than the corresponding arsenic derivatives.[8,13]

We failed in our attempts to trap the rearrangement products of allenylstibine **5** and divinylstibine **6** with 2-propanethiol in the presence of a base (Et_3N, DABCO, or DBU), stibines **5** and **6** being quickly decomposed. In the first step, a proton on the heteroatom was probably removed but either the migration of the double bond did not occur or the formed C−Sb double-bond derivative was too unstable to be trapped by a nucleophile. This deprotonation of the antimony atom of **6** was confirmed in the presence of D_2O: the deuteriodivinylstibine **6′** was only formed when small amounts of a base (DABCO) were added.

In summary, we have shown that the base-induced rearrangement of α-unsaturated phosphines and arsines can be used to detect or to trap 1- and 2-phospha and 2-arsa dienes, respectively. Allenylstibine, parent compound of a new class of products, and divinylstibine have been isolated. However, the ability of antimony derivatives to rearrange into the corresponding stibaalkenes has not been demonstrated. This work illustrates, once again, that the stability of derivatives with a C=X bond (X = P, As, Sb) decreases rapidly as one goes down group 15.

Acknowledgment. We thank the "Programme National de Planétologie" (INSU-CNRS) for financial support.

OM960066W

(19) Becker, G.; Gutekunst, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 463. Klebach, T. C.; van Dongen, H.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 395. Becker, G.; Gutekunst, G. *Z. Anorg. Allg. Chem.* **1980**, *470*, 144. Grobe, J.; Le Van, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 710.

(20) Sowerby, D. B. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; Wiley: New York, 1994; Chapter Chap. 2, pp 813−881. The chemical trapping of a stabilized 1-arsadiene intermediate has been reported: Pellon, P.; Himdi-Kabbab, S.; Rault, I.; Tonnard, F.; Hamelin, J. *Tetrahedron Lett.* **1990**, *31*, 1147.

(21) Ashe, A. J., III. *Acc. Chem. Res.* **1978**, *11*, 153. Ashe, A. J., III; Drone, F. J. *Organometallics* **1985**, *4*, 1478.

(22) Hitchcock, P. B.; Jones, C.; Nixon, J. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 492.

(23) Legoupy, S.; Lassalle, L.; Guillemin, J.-C.; Metail, V.; Senio, A.; Pfister-Guillouzo, G. *Inorg. Chem.* **1995**, *34*, 1466.