Allylation of Phosphorus, Arsenic, and Antimony Trihalides by Allylic Stannanes. Synthesis, Spectroscopic Characterization, and Quantum Chemical Investigations of Allylic Phosphines, Arsines, and Stibines

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Received June 4, 1997[⊗]

The reaction between an allylic tributylstannane and a phosphorus, arsenic, or antimony trihalide led to the corresponding allylic phosphine, arsine, or stibine dihalides. With phosphorus derivatives, only the γ-regioselection was observed, as shown by the formation of (1-methyl-2-propenyl)- (**2e**,**f)** or (1,1-dimethyl-2-propenyl)dihalophosphines **(2g**,**h)** starting from crotylstannanes **1c**,**c′** or prenylstannane **1d,** respectively, and PCl_3 or PBr_3. On heating at 80 °C, some of these phosphines led to the corresponding thermodynamic products. Allylic dichloroarsines **3a**−**d** were also prepared and kinetic compounds **3c**,**d** completely rearranged at room temperature into the corresponding crotyl- (**3e**,**e′**) and prenyldichloroarsines (**3f**). For antimony derivatives, even at low temperature (−90 °C), crude mixtures containing only the thermodynamic products were observed. While allylic dihalophosphines and -arsines are not efficient allylation reagents of electrophiles, allylic dichlorostibines **4a**,**c** reacted with benzaldehyde to lead to the corresponding homoallyl alcohols. Syn and anti products were mainly produced starting from crotyldichlorostibines (**4e**,**e′**). The primary allylic phosphines **7a**−**f**, arsines **8a**−**f,** and stibines **9a**,**b** have been prepared by the chemoselective reduction of the corresponding allylic dihalophosphines, -arsines, or -stibines with LAH in tetraglyme or with Bu_3SnH as reducing agent and characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. The primary allylic arsines and stibines are the first elements of new classes of compounds. Several allylic phosphines and arsines were investigated by ab initio quantum chemical methods and photoelectron spectroscopy. The most stable structure of these compounds is when the C−E (E = P, As) bond is out of the plane of the allyl system. This conformation is stabilized by the hyperconjugation between the π-orbital and the C−E σ*-bond. Due to this geometrical arrangement, the phosphorus (arsenic) lone pair interacts strongly and unprecedently with the π-system. The strength of this interaction is due to the close proximity of the π and the n_P (n_{As}) levels.

Introduction

It is firmly established that the lone pair of the group 15 elements does not interact with neighboring π-systems, since the lone pair of the heteroatom is mainly of the "s" type and is situated in the nodal surface of the π-bond.[1] It is well-documented that silicone and other group 14 elements exhibit a significant effect if placed in β-position to a π-orbital. This so-called β-effect is the most pronounced at cationic centers; thus, it has a significant impact on reaction rates as rewieved by Lambert.[2] A similar effect has been shown operational on radical cations.[3] Photoelectron spectroscopic investigations also demonstrated this phenomenon.[4] The β-effect is attributed to an interaction between the π-orbital and the σ_{E-C} (E = Si, Sn, etc.) orbitals in case of cationic systems (hyperconjugation). For neutrals and radical cations, the stabilization is achieved by the $\pi-\sigma_{E-C}$* interaction (negative hyperconjugation). In a recent work, Lambert has shown that phosphorus functionalities have this β-effect, comparable in extent to silicone, on cationic centers.[5] Early CNDO/2 calculations together with photoelectron spectroscopic investigation of alkylated allylic phosphines and arsines[4] led Schweig and coworkers to conclude about the importance of such an interaction in case of group 15 compounds as well. The photoelectron spectra of allyldichlorophosphine, allyldibu-

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1997.

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S0022-3263(97)01000-1 CCC: $15.00
Published on Web 01/09/1998

tylphosphine, and allyldimethylarsine have been reported;[4,6] recent quantum calculations appeared on the same compound as well.[7]

The large interaction between C=C and C−Sn bonds of allylic stannanes makes them more reactive than the corresponding silicon derivatives but more selective than lithium or magnesium derivatives. This particular reactivity of the allylic stannanes has generated an impressive amount of work in various areas of the organic and inorganic synthesis.[8] Numerous studies have been devoted to the reactivity of allylic stannanes with aldehydes or imines in the presence of various Lewis acids, and mechanistic considerations have largely been developed. Reaction pathways proceeding or not via a transmetalation have been proposed.[9,10] Some transmetalated products—and particularly the tin derivatives—have been detected by spectroscopy in the reaction mixture.[10,11] When the primary product is the most substituted isomer on the α-carbon, only the rearranged derivative was generally observed. For numerous Lewis acids, such derivatives were only postulated intermediates and the nature of the intermediate was only proposed on the basis of the structure of the final product formed by reaction with an electrophile.[8,12] Among the Lewis acids which have been used, those of the group 15 elements have been poorly investigated and, to our knowledge, only one article has been devoted to the formation of an allylphosphine starting from the corresponding allylstannane and PCl_3.[13] The phosphorus, arsenic, antimony, and bismuth trihalides are very mild or mild Lewis acids;[14] the particular high volatility of PCl_3, PBr_3, or $AsCl_3$ (and of the corresponding derivatives bearing two halogens and a quite small hydrocarbon substituent) is a precious property to study the reactivity of these trihalides with allylic stannanes and to easily isolate the formed product by distillation in vacuo at low temperature. Moreover, the reaction of such isolated compounds with electrophiles could be useful for mechanistic considerations. We report here a study devoted to the preparation of allylic dihalophosphines, -arsines, and -stibines by reaction of allylic stannanes on phosphorus, arsenic, or antimony halides. The thermal rearrangement of the primary γ-products, the chemical properties of the allylic compounds as allylation reagents of aldehydes, and their reduction to form the corresponding primary allylic phosphines, arsines, or stibines are also reported. The structural and electronic properties of different allylic phosphines and allylic arsines have been studied in detail.

Experimental Section

Caution: *Primary allylic phosphines, arsines, and stibines are potentially highly toxic molecules. All reactions and handling should be carried out in a well-ventilated hood.*

Materials. Arsenic trichloride was prepared by reaction of aqueous hydrochloric acid on As_2O_3;[15] LAH, phosphorus trichloride or tribromide, and tetraethyleneglycol dimethyl ether were purchased from Acros Chimica. All chemicals were used without further purification. Antimony trichloride was purchased from Prolabo and distilled in vacuo. Allylic tributylstannanes **1a**−**d** were prepared as previously reported.[16] A mixture of (1-methyl-2-propenyl)triphenylstannane (**1e)** and crotyltriphenylstannane was prepared as previously reported.[17] Fractional crystallization in pentane led to compound **1e** in a 33% yield and with a purity higher than 90%. 1-Phenyl-3-buten-1-ol **(5)** and *syn*- and *anti*-1-phenyl-2-methyl-3-buten-1-ol **(6a**,**b)** were identified by comparison with authentic samples.[18]

Calculations. Quantum chemical calculations were carried out by the Gaussian 94 package.[19] The 6-31G* basis set was used at the HF and at the MP_2 levels of the theory. For As a split valence quality basis was used.[20] The structures were optimized without and with the specified constraint and second derivatives were calculated on the resulting structures to establish whether a real minima was reached.

General. ^{1}H (400 MHz), ^{31}P (162 MHz), and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker spectrometer ARX400. Chemical shifts are given in ppm relative to internal $SiMe_4$ for ^{1}H and ^{13}C spectra and external H_3PO_4 for ^{31}P NMR spectra. High-resolution mass spectrometry (HRMS) experiments were performed on a Varian MAT 311 instrument. To record the mass spectra, the phosphines, arsines, and stibines were directly introduced from a cooled cell into the ionization chamber of the spectrometer. All the new primary phosphines, arsines, and stibines are too reactive to be characterized by combustion analysis. The yields of the unstabilized derivatives were determined by ^{1}H NMR with an internal reference. The half-life ($\tau_{1/2}$) of the unstabilized compounds was determined by ^{1}H NMR for an approximate concentration of 5% in $CDCl_3$.

HeI photoelectron spectra have been measured on an instrument described earlier.[21] The resolution at the Ar $^2P_{1/2}$ line was 40 meV during the measurements. For internal calibration the N_2 and the He^+ peaks were used.

Preparation of Allylic Dichloroarsines 3a−d. General Procedure. In a two-necked round-bottomed flask equipped with a nitrogen inlet was introduced $AsCl_3$ (1.8 g, 10 mmol). The flask was cooled at −20 °C and allylic tributylstannane **1a**−**d** (10 mmol) was slowly added. Thus, the mixture was stirred for 10 min and allowed to warm to 0 °C. Allylic dichloroarsine **3a**−**d** was then purified by distillation in vacuo and kept at low temperature (−20 °C). Such compounds slowly decomposed on standing at room temperature.

Rearrangement of Allylic Dichloroarsines 3c,d. General Procedure. In a two-necked round-bottomed flask equipped with a nitrogen inlet was introduced at room-temperature $AsCl_3$ (1.8 g, 10 mmol). Allylic tributylstannane **1a**−**d** (10 mmol) was then slowly added. The mixture was

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heated to 80 °C and stirred for 1 h. Allylic dichloroarsines **3e**,**f** were then purified by distillation in vacuo. These compounds can also be obtained by heating at 80 °C the corresponding pure arsine precursor **3c**,**d**.

2-Propenyldichloroarsine (3a).[22] Yield: 76%. Bp = 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (d, 2H, J = 8.1 Hz), 5.32 (ddt, 1H, J = 16.9, 1.2, 1.2 Hz), 5.36 (dd, 1H, J = 10.2, 1.2 Hz), 5.96 (ddt, 1H, J = 16.9, 10.2, 8.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.8, 121.6, 128.1. HRMS: calcd for $C_3H_5As^{35}Cl_2$ 185.8985, found 185.899.

(2-Methyl-2-propenyl)dichloroarsine (3b). Yield: 70%. Bp = 138 °C (partially decomposed). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.92 (br s, 3H), 3.32 (br s, 2H), 4.99 (br d, 1H, J = 1.4 Hz), 5.06 (m, 1H, J = 1.4, 1.4, 1.4 Hz) ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 53.9, 116.2, 137.3. HRMS: calcd for $C_4H_7As^{35}Cl_2$: 199.9142, found 199.914.

(1-Methyl-2-propenyl)dichloroarsine (3c). Yield: 84%. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 18 h at rt (slowly rearranged at rt into (*Z*)- and (*E*)-2-butenyldichloroarsines, **3e**,**e′**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.57 (d, 3H, J = 7.0 Hz), 3.17 (dqdd, 1H, J = 7.0, 7.0, 0.9, 0.9 Hz), 5.32 (ddd, 1H, J = 17.2, 0.9, 0.9 Hz), 5.37 (ddd, 1H, J = 10.4, 0.9, 0.9 Hz), 5.93 (ddd, 1H, J = 17.2, 10.4, 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 52.1, 119.5, 134.2. HRMS: calcd for $C_4H_7As^{35}Cl_2$ 199.9142, found 199.914.

(1,1-Dimethyl-2-propenyl)dichloroarsine (3d). Yield: 82%. $Bp_{0.1}$ = 37 °C. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 10 h at rt (slowly rearranged at rt into the (3-methyl-2-butenyl)dichloroarsine**, 3f**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48 (s, 6H), 5.23 (d, 1H, J = 17.4, 1.4 Hz), 5.38 (d, 1H, J = 10.7, 1.4 Hz), 5.95 (dd, 1H, J = 17.4, 10.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 51.6, 118.2, 139.0. HRMS: calcd for $C_5H_9As^{35}Cl_2$ 213.9298, found 213.930.

(Z)*- and *(E)*-2-Butenyldichloroarsines (3e,e′)** (Z:E/30:70). Yield: 67%. Bp 134 °C (partially decomposed), (Z***) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.77 (dm, 3H, J = 6.9 Hz), 3.32 (dm, 2H, J = 8.4 Hz), 5.63 (dt, 1H, J = 10.5, 8.4 Hz), 5.78 (dq, 1H, J = 10.5, = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 43.6, 119.4, 131.0. (***E***) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79 (dd, 3H, J = 6.5, 1.1 Hz), 3.22 (dm, 2H, J = 7.8 Hz), 5.60 (dtq, 1H, J = 15.2, 7.8, 1.5 Hz), 5.78 (dqt, 1H, J = 15.2, 6.5, 1.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.3, 48.2, 120.4, 133.1. HRMS: calcd for $C_4H_7As^{35}Cl_2$ 199.9142, found 199.914.

(3-Methyl-2-butenyl)dichloroarsine (3f). Yield: 84%. $Bp_{0.1}$ = 37 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79 (br s, 3H), 1.84 (br s, 3H), 3.27 (d, 2H, J = 8.4 Hz), 5.36 (t sept, 1H, J = 8.0, 1.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.6, 26.0, 45.0, 113.4, 139.9. HRMS cald for $C_5H_9As^{35}Cl_2$ 213.9298, found 213.930.

Preparation of Allylic Dichlorostibines 4a,b,e−f for NMR Characterization. General Procedure. In a NMR tube were introduced $SbCl_3$ (0.23 g, 1 mmol) and dry $CDCl_3$ (600 μL). The tube was cooled at −40 °C and allylic tributylstannane **1a**−**d** (1 mmol) was added. The tube was shaked a few seconds and directly introduced in the cooled probe (−40 °C) of the NMR spectrometer. On standing at room temperature, allylic stibines gave insoluble brown-black materials.

2-Propenyldichlorostibine (4a). Yield ≈ 45% (crude). $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 20 min at rt. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.53 (d, 2H, J = 7.0 Hz), 5.35 (d, 1H, J = 9.9 Hz), 5.48 (d, 1H, J = 17.0 Hz), 6.07 (ddt, 1H, J = 17.0, 9.9, 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.4, 122.4, 127.7.

(2-Methyl-2-propenyl)dichlorostibine (4b). Yield ≈ 40% (crude). $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 20 min at rt. ^{1}H NMR (400 MHz, $CDCl_3$, −30 °C): δ 1.96 (br s, 3H), 3.58 (br s, 2H), 5.10 (br s, 1H), 5.17 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, −30 °C): δ 24.2, 50.8, 110.6, 142.9.

***(Z)*- and *(E)*-2-Butenyldichlorostibines (4e,e′)**. Yield ≈ 30% (crude). $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 10 min at rt. Two isomers (E and Z) in a 5:1 ratio, the major isomer has not been attributed. ^{1}H NMR (400 MHz, $CDCl_3$, −30 °C): δ (major) 1.82 (m, 3H, J = 5.8 Hz), 3.02 (d, 2H, J = 6.6 Hz), 5.50−5.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, −30 °C): δ 18.6, 46.3, 121.7, 131.0. ^{1}H NMR (400 MHz, $CDCl_3$, −30 °C): δ (minor) 1.83 (d, 3H, J = 3.6 Hz), 3.11 (d, 2H, J = 7.6 Hz), 5.50−5.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, −30 °C): δ 27.0, 41.9, 120.9, 129.1.

(3-Methyl-2-butenyl)dichlorostibine (4f). Yield ≈ 35% (crude). $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 10 min at rt. ^{1}H NMR (400 MHz, $CDCl_3$, −30 °C): δ 1.81 (s, 3H), 1.88 (s, 3H), 3.10 (d, 2H, J = 7.9 Hz), 5.43 (t, 1H, J = 7.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, −30 °C): δ 18.6, 25.8, 43.5, 114.3, 137.8.

Allylation of Benzaldehyde. Method A. Addition of Allyldichlorophosphine (2a), Allyldibromophosphine (2b), Allyldichloroarsine (3a), Allyldichlorostibine (4a), or Crotylstibines (4e,e′) on Benzaldehyde. Compound **2a**,**b**, **3a**, or **4a** (1 mmol) was prepared as reported above and diluted in CH_2Cl_2 (10 mL). The solution was cooled at −78 °C and a solution of benzaldehyde (1 mmol) and CH_2Cl_2 (5 mL) was slowly added. The mixture was stirred for 2 h at this temperature and then hydrolyzed with saturated aqueous $NaHCO_3$. 1-Phenyl-3-buten-1-ol (**5**) was purified by column chromatography (hexane/ether). With phosphorus and arsenic derivatives, the procedure was repeated at room temperature and under reflux of the solvent. Similar experiments were also performed starting from crotylstibines **4e**,**e′** and benzaldehyde.

Method B. Addition of Allylstannane 1a on Benzaldehyde and PCl_3, PBr_3, $AsCl_3$, or $SbCl_3$. Into a 50 mL flask were introduced dry dichloromethane (10 mL); PCl_3, PBr_3, $AsCl_3$, or $SbCl_3$ (1.2 mmol); and benzaldehyde (1.1 g, 1 mmol). The flask was cooled at −78 °C and allyltributylstannane (**1a**) (1 mmol) in CH_2Cl_2 (5 mL) was slowly added. The mixture was stirred 2 h at this temperature and was then hydrolyzed with saturated aqueous $NaHCO_3$. Purification was performed by column chromatography (hexane/ether). With phosphorus and arsenic derivatives, the procedure was reproduced at room temperature and under reflux of the solvent.

1-Phenyl-3-buten-1-ol (**5**) has never been observed in the reactions with phosphorus compounds. Traces of alcohol **5** were detected with arsenic derivatives and using method A. Compound **5** was obtained with antimony compounds in a 78% (method A) and 68% yield (method B). Starting from stibines **4e**,**e′** and benzaldehyde, *syn*- and *anti*-1-phenyl-2-methyl-3-butenol (**6a,b)** were obtained in a 80/20 ratio in a 71% yield (method A) and a 68% yield (method B). Attempts to detect (*Z*)- and (*E*)-1-phenyl-3-penten-1-ol (**6c**,**c′**) were unsuccessful.

Using $BiCl_3$ as Lewis acid, crotylstannane **1c**,**c′**, and benzaldehyde, the alcohols **6a**,**b** were obtained in a 81% yield and with a 90:10 syn:anti ratio.

Preparation of Allylic Arsines 8a−f. General procedure. The apparatus already described for the reduction of alkynyl- and allenylarsines was used.[23] The flask containing the reducing mixture (30 mmol of LAH in tetraglyme or 90 mmol of Bu_3SnH in the presence of small amounts of duroquinone) was cooled at 0 °C, fitted on a vacuum line, and degassed. The dichloroarsine **3a**−**f** (10 mmol) diluted in tetraglyme (10 mL) was then slowly added (10 min) at room temperature with a syringe through the septum. During and after the addition, the product was distilled off in vacuo from the reaction mixture. A cold trap (−60 °C) selectively removed the less volatile products and compound **8a**−**f** was condensed on a coldfinger (−196 °C) which was connected at the bottom to a flask or a NMR tube. A cosolvent can be added at this step. After disconnecting from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen; liquid nitrogen was subsequently removed. The product was collected in a Schlenk flask or a NMR tube and kept at low temperature (< −40 °C) before analysis. The boiling points of arsines **8a**−**f** have been approximately determined (±5 °C) from their temperature of condensation and revaporization in vacuo (0.1 mbar).

Preparation of Allylic Stibines 9a,b. The procedure is similar to this one reported above for allylic phosphines and arsines, but the crude mixture containing the precursor **4a**,**b**

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(≈1 mmol) was quickly prepared, tetraglyme (3 mL) was then added, and the mixture was introduced in the reducing mixture. Compound **9a**,**b** can be separated from SbH_3 by condensation at −100 °C in a trap fitted between the first trap (−40 °C) and the coldfinger (−196 °C), but a loss of product was observed during the revaporization. Attempts to prepare stibines **9e**−**f** starting from the corresponding dichlorostibines **4e**−**f** were unsuccessful.

IR Spectroscopy of Allylphosphine 7a, Allylarsine 8a, and Allylstibine 9a. Special equipment was used for recording the IR spectrum of compounds **7a**, **8a,** and **9a** in the gas phase: a small Pyrex tube (l = 10 cm, i.d. = 3 cm) equipped with a stopcock and sealed at each extremity with a KBr window was connected to the coldfinger of the vacuum line. Compound **7a**, **8a,** or **9a** synthesized as reported below, was condensed without solvent on the coldfinger (−196 °C). After disconnecting from the vacuum line by stopcocks, liquid nitrogen was removed. When the pressure of the product arose to 80 hPa, the cell was disconnected by stopcock from the apparatus and introduced in the IR spectrometer.

Photoelectron Spectroscopy of Allylphosphine 7a and Allylarsine 8a. Compounds **7a** and **8a** were synthesized as described on a separate vacuum line and trapped at liquid nitrogen temperature. The trap was then connected to the spectrometer and immersed in a −35 °C slush bath (1,2-dichloroethane). At this temperature, the compounds were stable enough during the period of the measurement and had enough vapor pressure. Because HCl and HBr were formed during the reaction and had comparable vapor pressure to the phosphine **7a** and arsine **8a**, a few pellets of KOH were placed in the trap to remove these acids. Attempts to record the PE spectra of allylstibines **9a**,**b** were unsuccessful.

2-Propenylarsine (8a). Yield: 72%. $Bp_{0.1} \approx -90$ °C. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 1 h at rt. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (br s, 4H), 4.82 (dd, 1H, J = 9.8, 1.0 Hz), 4.98 (dd, 1H, J = 17.1, 1.0 Hz), 5.98 (dd, 1H, J = 17.1, 9.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.1, 113.1, 139.0. IR (gaseous phase, 80 hPa, cm^{-1}): $\nu_{C=C}$ 1637, ν_{AsH} 2094, $\nu_{C=C-H}$ 3143. HRMS: calcd for C_3H_7As 117.9765, found 117.976.

(2-Methyl-2-propenyl)arsine (8b). Yield: 73%. $Bp_{0.1} \approx -80$ °C. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 1h at rt. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82 (td, 3H, J = 1.3, 0.8 Hz), 2.47 (m, 2H, degenerated system), 2.47 (m, 2H, degenerated system), 4.65 (dtq, 1H, J = 1.8, 1.5, 1.3 Hz), 4.76 (dq, 1H, J = 1.8, 0.8 Hz) ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.1, 23.0, 110.0, 145.8. HRMS: calcd for C_4H_9As 131.9920, found 131.993.

(1-Methyl-2-propenyl)arsine (8c). Yield: 73%. $Bp_{0.1} \approx -80$ °C. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 30 min at rt. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (q, 3H, J = 6.2 Hz), 2.64 (tdq, 2H, J = 13.3, 6.6, 6.2 Hz), 2.92 (dq, 2H, J = 13.3, 5.7 Hz), 4.81 (d, 1H, J = 10.2 Hz), 4.95 (d, 1H, J = 17.0 Hz), 6.01 (ddd, 1H, J = 17.0, 10.2, 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.5, 28.1, 110.3, 144.2. HRMS: calcd for C_4H_9As 131.9920, found 131.992.

(1,1-Dimethyl-2-propenyl)arsine (8d). Yield: 71%. $Bp_{0.1} \approx -70$ °C. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 30 min at rt. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 (s, 6H), 2.87 (s, 2H), 4.79 (dd, 1H, J = 10.5, 0.9 Hz), 4.88 (dd, 1H, J = 17.2, 0.9 Hz), 6.13 (dd, 1H, J = 17.2, 10.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.4, 30.4, 108.1, 148.5. HRMS: calcd for $C_5H_{11}As$ 146.0077, found 146.007.

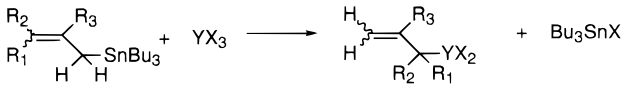
***(Z)*- and *(E)*-2-Butenylarsines (8e,e′)** (Z/E:30/70).Yield: 72%. $Bp_{0.1} \approx -80$ °C. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 1 h at rt, (**Z**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (dd, 3H, J = 5.9, 1.8 Hz), 2.35 (br s, 4H), 5.33 (m, 1H, J = 10.6, 5.9 Hz), 5.62 (m, 1H, J = 10.6, 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 15.3, 122.3, 130.3. (**E**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.67 (dd, 3H, J = 6.1, 1.1 Hz), 2.35 (br s, 4H), 5.43 (m, 1H, J = 14.9, 6.1 Hz), 5.59 (m, 1H, J = 14.9, 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.7, 18.8, 124.0, 131.4. HRMS: calcd for C_4H_9As 131.9920, found 131.992.

(3-Methyl-2-butenyl)arsine (8f). Yield: 73%. $Bp_{0.1} \approx -70$ °C. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 1 h at rt. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.64 (br s, 3H), 1.72 (br s, 3H), 2.30−2.38 (m, 4H), 5.33 (tm, 1H, J = 7.0 Hz) ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 17.0, 25.5, 124.2, 130.6. HRMS: calcd for $C_5H_{11}As$ 146.0077, found 146.007.

2-Propenylstibine (9a). Yield: 35%. $Bp_{0.1} \approx -85$ °C. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 10 min at rt. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (dt, 2H, J = 7.7, 5.4 Hz), 2.65 (t, 2H, J = 5.4 Hz), 4.68 (d, 1H, J = 9.9 Hz), 4.91 (d, 1H, J = 16.9 Hz), 6.07 (ddt, 1H, J = 16.9, 9.9, 7.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.8, 111.9, 139.9. IR (gaseous phase, 80 hPa, cm^{-1}): $\nu_{C=C}$ 1646; ν_{SbH} 1870, $\nu_{C=C-H}$ 3156. HRMS: calcd for $C_3H_6{}^{121}Sb$ [M − H]$^+$ 162.9507, found 162.951.

(2-Methyl-2-propenyl)stibine 9b. Yield: 31%. $Bp_{0.1} \approx -75$ °C. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 10 min at rt. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.81 (s, 3H), 2.58 (t, 2H, J = 5.0 Hz), 2.68 (t, 2H, J = 5.0 Hz), 4.56 (br s, 1H), 4.73 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.0, 22.6, 108.7, 146.7. HRMS: calcd for $C_4H_8{}^{121}Sb$ [M − H]$^+$ 176.9664, found 176.966.

Scheme 1



1a-d **2a-h, 3a-d, 4a-b**

1a : $R_1 = R_2 = R_3 = H$
1b : $R_3 = Me$, $R_2 = R_1 = H$
1c (Z), 1c' (E) : $R_1 = Me$, $R_2 = R_3 = H$
1d : $R_3 = H$, $R_2 = R_1 = Me$

2a : $R_1 = R_2 = R_3 = H$, Y = P, X = Cl
2b : $R_1 = R_2 = R_3 = H$, Y = P, X = Br
2c : $R_1 = R_2 = H$, $R_3 = Me$, Y = P, X = Cl
2d : $R_1 = R_2 = H$, $R_3 = Me$, Y = P, X = Br
2e : $R_2 = R_3 = H$, $R_1 = Me$, Y = P, X = Cl
2f : $R_2 = R_3 = H$, $R_1 = Me$, Y = P, X = Br
2g : $R_3 = H$, $R_1 = R_2 = Me$, Y = P, X = Cl
2h : $R_3 = H$, $R_1 = R_2 = Me$, Y = P, X = Br
3a : $R_1 = R_2 = R_3 = H$, Y = As, X = Cl
3b : $R_1 = R_2 = H$, $R_3 = Me$, Y = As, X = Cl
3c : $R_2 = R_3 = H$, $R_1 = Me$, Y = As, X = Cl
3d : $R_1 = R_2 = Me$, R_3 =H, Y = As, X = Cl
4a : $R_1 = R_2 = R_3 = H$, Y =Sb, X = Cl
4b : $R_1 = R_2 = H$, $R_3 = Me$, Y = Sb, X = Cl

Results and Discussion

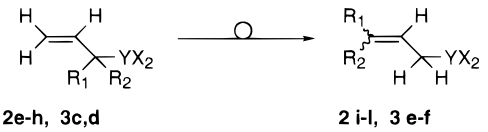
Preparation of Allylic Dihalophosphines, Arsines, and Stibines. Various reactions have been used in the literature to prepare allylic halophosphines: substitution of a halogen or a silyl group by PCl_2,[24] photolysis of alkenes and PBr_3,[25a] photolysis of the 2-propenyltributylstannane with PCl_3,[13] and addition of an allyl Grignard on a dichlorophosphine.[25b] We have studied the reaction of allyl- (**1a**), methallyl- (**1b**), (*Z*)- + (*E*)-crotyl- (**1c**,**c′**), and prenyltributylstannane (**1d**) with PCl_3 or PBr_3. The reaction was performed without solvent and the product was isolated by distillation in vacuo. Thus, 2-propenyldichlorophosphine (**2a**), 2-propenyldibromophosphine (**2b**), methallyldichlorophosphine (**2c**), and methallyldibromophosphine (**2d**) have been easily prepared in good yields (≈80%) (Scheme 1).[26] Starting from (*Z*)- and (*E*)-

(24) Kormachev, V. V., Vasil′eva, T. V.; Bryantsov, B. I.. Kukhtin, V. A. *Z. Obshch Khim.* **1976**, 46, 1264−1268 (*J. Gen. Chim. USSR* **1976**, 1244−1247).

(25) (a) Liorber, B. G.; Khammatova, Z. M.; Razumov, A. I.; Zykova, T. V.; Borisova, T. B. *Z. Obshch Khim.* **1968**, *38*, 878−883 (*J. Gen. Chim. USSR* **1968**, *38*, 843−847). Krivchum, M. N.; Sendyurev, M. V.; Ionin, B. I.; Petrov, A. A. *Z. Obshch. Khim.* **1990,** 60, 2394−2395 (*J. Gen. Chim. USSR* **1991**, *60*, 2140−2141). (b) Gaumont, A.-C.; Bourumeau, K.; Denis, J.-M.; Guenot, P. *J. Organomet. Chem.* **1994**, *484*, 9−12.

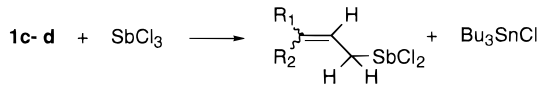
(26) A radical mechanism for the reaction of the allyltributylstannane with PCl_3 has been proposed (ref 13). However we observed that the reaction can be performed in toluene without photolysis, in the presence of duroquinone or acrylonitrile. Thus an anionic process cannot be excluded.

Scheme 2



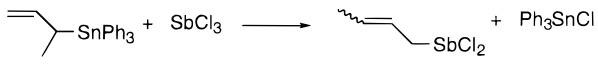
2e-h, 3c,d **2 i-l, 3 e-f**

2e,i (Z) ,i' (E) : R_2 = H, R_1 = Me, Y = P, X = Cl
2f,j (Z),j'(E) : R_2 = H, R_1 = Me, Y = P, X = Br
2g,k : R_2 = R_1 = Me, Y = P, X = Cl
2h,l : R_2 = R_1 = Me, Y = P, X = Br
3c,e (Z),e' (E) : R_2 = H, R_1 = Me, Y = As, X = Cl
3d,f : R_2 = R_1 = Me, Y = As, X = Cl



4 e-f

4e (Z),e' (E) : R_1 = H; R_2 = Me
4f : R_1 = R_2 = Me



1e **4e (Z),e' (E)**

crotyl-(**1c**,**c**′) or prenylstannane (**1d)** and PCl_3 or PBr_3, we only observed the formation of the γ-products, the dichlorophosphines **2e** and **2g** and the dibromophosphines **2f** and **2h,** respectively. Several hours of heating at 80 °C of the dichlorophosphine **2g** only led to small amounts of the rearranged prenylphosphine **2k**. Under similar conditions, and only after 2 h of heating, the dibromophosphine **2h** gave the (3-methyl-2-butenyl)-dibromophosphine **(2l**) in 67% yield (Scheme 2). This difference cannot be attributed only to the nature of the halogens: the heating at 80 °C of the dichlorophosphine **2e** led, in less of 1 h, to the rearranged crotyl compounds **2i**,**i**′ (Z:E/3:7), although, under similar conditions, a mixture of the regioisomers **2f** and **2j**,**j**′ were obtained after heating for 1 day at 80 °C. These results clearly show that the versatility of such rearrangements is dependent on the substituents on the α-carbon atom and the nature of the halogens.

The reaction was modeled by quantum chemical calculations as well with H substituents on Sn instead of Bu groups. For the reactions of an allylic stannane with PCl_3 and $AsCl_3$, a small exothermicity (respectively 8.34 and 6.34 kcal/mol) was obtained. This finding was in accordance with the experimental results, since the temperature of the reaction mixture was somewhat increased in both cases. Comparing the stabilities of **2g** and **2k**, the latter compound has been shown to be more stable by 5.31 kcal/mol, in accordance with the observation that **2g** (which thus must have been the kinetic product) was formed in the reaction and rearranged upon heating to **2k**.

The reaction of stannanes with arsenic halide is well-established. In 1957, Seyferth et al. reported the formation of vinyl- and divinylhaloarsines starting from divinyldibutylstannane and $AsCl_3$ or $AsBr_3$.[27] More recently, some of us have described the preparation of vinyl-, allenyl-, and alkynylchloroarsines starting from arsenic chloride and the corresponding vinyl-, allenyl-, or alkynyltributylstannane.[23,28] However, to our knowledge, the reaction of an allylic stannane with arsenic halide has never been described and only few allylic chloroarsines have been reported.[22,29]

We observed that the reaction of allylic stannanes with arsenic chloride and without solvent was very fast at room temperature; 2-propenyl- (**3a)** and methallyldichloroarsine (**3b)** were prepared in good yields (≈75%) (Scheme 2). In the presence of $AsCl_3$, the (*Z*)- and (*E*)-crotyl- (**1c**,**c**′) and prenylstannane (**1d)** led without isomerization to, respectively, 1-methyl-2-propenyl- (**3c)** and 1,1-dimethyl-2-propenyldichloroarsine **(3d**) when the reaction was performed at −20 °C. At room temperature, compound **3c**,**d** slowly rearranged into the corresponding crotyl- (**3e**,**e**′) (Z:E/3:7) and prenyldichloroarsine (**3f)** (formally the α-products in the reaction of $AsCl_3$ with stannanes **1c**,**c**′ and **1d,** respectively). Compounds **3a**−**f** can be kept at low temperature (−20 °C).

No allylic dihalostibine has been described in the literature. We have prepared the allylic dichlorostibines **4a**,**b**,**e**−**f** by freezing the antimony chloride before addition of the allylic stannanes **1a**−**d**.[30] The same reaction performed in a NMR tube in the presence of $CDCl_3$ as solvent led to the characterization in the crude mixture of the allylic stibines **4a**,**b** by low-temperature (−30 °C) ^{1}H and ^{13}C NMR. Starting from stannanes **1c**,**c**′ and **1d**, only the α-products, the crotyl- (**4e**,**e**′) (Z:E or E:Z/1:5) and prenyldichlorostibine (**4f)** were respectively observed. Compounds **4e**,**e**′ were also observed starting from (1-methyl-2-propenyl)triphenylstannane **(1e**) and $SbCl_3$, but in this case, they are the γ-products and consequently the thermodynamic products of both reactions (Scheme 2). This last reaction clearly indicates that the formation of allylic phosphines **2a**−**h**, arsines **3a**−**f,** and stibines **4a**−**f** proceeds via a similar mechanism, even when γ-products were not observed with antimony derivatives. In the case of stibines **4e**−**f**, the rearrangement occurred at very low temperature. All attempts to purify allylic stibines **4a**,**b**,**e**−**f** were unsuccessful and these compounds exhibited a low stability at room temperature ($\tau_{1/2}$ ≈ 15 min in $CDCl_3$) which cannot be attributed to the sole presence of the allylic group on the antimony atom, triallylstibine being a stable compound at room temperature;[31] the presence of an allylic substituent and halogens on the same antimony atom probably promotes the decomposition into insoluble brown-black products.

All the new compounds **2**−**4** have been analyzed by

(27) Seyferth, D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1957**, *79*, 515−517.

(28) Guillemin, J.-C.; Lassalle, L. *Organometallics* **1994**, *13*, 1525−1527. Guillemin, J.-C.; Lassalle, L.; Dréan, P.; Wlodarczak, G; Demaison, J. *J. Am. Chem. Soc.* **1994**, *116*, 8930−8936.

(29) Childs, A. F.; Plant, S. G. P.; Tompsett, A. L. L.; Weeks, G. A. *J. Chem. Soc. (London)* **1948**, 2180−2183; Kamai, G.; Belorossowa, O. N. *Izv. Akad. SSSR Ser. Khim.* **1947**, 191−196; *Chem. Abstr.* **1948**, 4133f. Pellon, P.; Himdi-Kabbab, S.; Rault, I.; Tonnard, F.; Hamelin, J. *Tetrahedron Lett.* **1990**, *31*, 1147−1150. Some cyclopentadienyldihaloarsines have also been described: Jutzi, P.; Kuhn, M. *Chem. Ber.* **1974**, *107*, 1228−1234.

(30) Similar experiments have already been reported to prepare α-unsaturated halostibines or stannanes: Legoupy, S.; Lassalle, L.; Guillemin, J.-C.; Metail, V.; Senio, A.; Pfister-Guillouzo, G. *Inorg. Chem.* **1995**, *35*, 1466−1471. Lassalle, L.; Janati, T.; Guillemin, J.-C. *J. Chem. Soc., Chem. Commun.* **1995**, 699−700. Guillemin, J.-C.; Bellec, N.; Kiz-Szétsi, S.; Nyulászi, L.; Veszprémi, T. *Inorg. Chem.*, **1996**, *36*, 6586−6591.

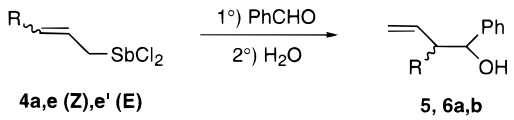
(31) Voskuil, W.; Arens, J. F. *Rec. Trav. Chim. (Pays-Bas*) **1964**, *83*, 1301−1304.

Table 1. ^{1}H Chemical Shifts of Crotonaldehyde on Complexation with Various Lewis Acids

Lewis acid	δ_{H2} (ppm)	$\Delta\delta_{H2}$ (lit.) (ppm)	δ_{H3} (ppm)	$\Delta\delta_{H3}$ (lit.) (ppm)
without LA	6.14	0	6.86	0
PCl_3[a]	6.14	0	6.86	0
PCl_3[b]	6.14	0	6.86	0
$AsCl_3$[a]	6.16	0.02	6.90	0.04
$AsCl_3$[b]	6.17	0.03	6.92	0.06
$SbCl_3$[a]	6.18	0.02	6.93	0.07
$SbCl_3$[b]	6.32	0.18	7.18	0.32
$BiCl_3$[a]	6.17	0.03	6.90	0.04
$SnCl_4$[a]	6.59	0.45 (0.50)[32]	7.80	0.94 (0.87)[32]
BBr_3[a]	6.93[32]	0.79 (0.93)[32]	8.42	1.56 (1.49)[32]

[a] 1 equiv of Lewis acid and 1 equiv of crotonaldehyde. [b] 10 equiv of Lewis acid and 1 equiv of crotonaldehyde.

Scheme 3



4a,e (Z),e' (E) **5, 6a,b**

4a, 5 : R = H
4e (Z),e' (E), 6a,b : R = Me

HRMS and ^{1}H and ^{13}C NMR spectroscopy. The NMR data are typical of allylic systems. By ^{1}H NMR, we observed that the nature of the heteroatom plays a weak role on the chemical shifts: the signals are lightly shifted downfield from phosphorus to arsenic to antimony; the ^{13}C NMR spectra gave similar data independent of the nature of the heteroatom.

Reaction of Compounds 2a,b, 3a, and 4a,e,e′ with Benzaldehyde. The synthesis of homoallyl alcohols or homoallylamines by reaction of an allylic stannane with the corresponding aldehydes or imines in the presence of a Lewis acid has been the subject of numerous works.[8] Depending on the Lewis acid and the experimental conditions, the reaction can proceed via a transmetalation reaction followed by the addition of the transmetalated product on the electrophile[12a] or by direct nucleophilic addition on the electrophile activated by complexation with the Lewis acid.[9,10] To our knowledge, the use of a Lewis acid of group 15 in the allyllation of electrophiles by an allylic stannane has never been reported.

The strength of a Lewis acid has been estimated by the variation of the chemical shifts of the β- and γ-hydrogen signals of *trans*-crotonaldehyde in the presence of 1 equiv of this Lewis acid.[32] As shown in Table 1, we only observed weak differences in the chemical shifts of crotonaldehyde in the presence of 1 equiv of PCl_3, PBr_3, $AsCl_3$, $SbCl_3$, or $BiCl_3$. All these halides should be weak Lewis acids, this effect being dramatically lower than those observed with stronger Lewis acid as $SnCl_4$ or BBr_3.

We then added the dichlorophosphine **2a**,**b** or arsine **3a** to the benzaldehyde. With phosphines **2a**,**b**, we never observed the formation of the corresponding 1-phenyl-3-butenol (**5**) and only traces were detected using arsine **3a**. Mixtures of allylstannane **1a**, benzaldehyde, and PCl_3, PBr_3, or $AsCl_3$ did not give alcohol **5,** even on heating under reflux of dichloromethane. The addition of $SbCl_3$ to stannane **1a** diluted in CH_2Cl_2 (at a temperature where the substitution is quickly performed) followed by the addition of the benzaldehyde led to 1-phenyl-3-butenol (**5)** in a 78% yield (Scheme 3). This result clearly shows that the reaction proceeds by reaction of allyldichlorostibine (**4a)** on the benzaldehyde. The compound **5** was also obtained when $SbCl_3$ was added last. In this case, both mechanisms can be envisaged, but the weak interaction previously observed between crotonaldehyde and $SbCl_3$ could be in favor of the transmetalation. Starting from the (*Z*)- + (*E*)-crotylstannanes **1c**,**c′**, benzaldehyde, and $SbCl_3$, the *syn*- and *anti*-1-phenyl-2-methyl-3-butenol (**6a**,**b)** were obtained in both approaches in a 80/20 ratio. This is also in favor of the formation of crotyldichlorostibines (**4e**,**e′**) as intermediates in the second approach (method B). Moreover, this ratio seems to indicate that the major isomer of crotylstibines **4e**,**e′** was the *Z*-derivative, mainly leading to the syn-isomer.[8] Other experiments using $BiCl_3$ as Lewis acid gave results similar to those obtained with $SbCl_3$.

We tried to understand why the homoallyl alcohol **5** was only efficiently formed with antimony and bismuth trihalides although PCl_3, $AsCl_3$, $SbCl_3$, or $BiCl_3$ led to the same weak deshielding of the chemical shifts of the hydrogens of crotonaldehyde (Table 1). This deshielding is however dependent on the ratio between Lewis acid and aldehyde: using a big excess of Lewis acid (10 equiv), the corresponding signals were shifted downfield with $SbCl_3$ and almost not at all with PCl_3 or $AsCl_3$. Thus the strength of a Lewis acid could be better defined by an extrapolation of such chemical shifts at very high excesses of the Lewis acid. Antimony trichloride presents some similarities with Lewis acids as BCl_3[33] or $SnCl_4$:[11] the allylation by stannanes can be performed at low temperature, most of the formed allylic compounds are unstable at room temperature, and only the thermodynamic products are generally observed. So, the temperature of the rearrangement "kinetic γ-product → thermodynamic α-product" of the allylic compounds **2**−**4** can be correlated with the kinetic stability of these compounds and with their reactivity with an electrophile.

Reduction of Allylic Phosphines 2a−l, Arsines 3a−f, and Stibines 4a,b. Compounds **2, 3,** and **4** can also be considered as potentials precursors of the corresponding primary allylic phosphines, arsines, and stibines, respectively. The reduction of functionalized phosphates, phosphinates, phosphites, or halophosphines into the corresponding primary or secondary phosphines has been largely studied.[34−37] Actually, the use of a reducing agent such as LAH with unsaturated heterohalides led in numerous cases to a concomitant reduction of the heteroatom-halogen group and the C−C multiple bond. So, reducing agents such an AlH_2Cl or $AlHCl_2$ have been used to obtain in a chemoselective reduction α,β-unsaturated phosphines.[36,37] Some of us have recently reported that the reduction of α,β-unsaturated chloroarsines or -stibines into the corresponding primary or secondary arsines and stibines was efficient using a reducing agent like Bu_3SnH,[23,28,30] chloroalanes leading to a mixture of products. In some cases and particularly with alkynyl

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Table 2. Total Energies (in au), Relative Energies (kcal/mol), the Four Lowest Koopmans Ionization Energies (in eV), and Some Important Structural Parameters of the Five Obtained Conformers of Different Allyl Compounds Calculated at the MP_2 Level of Theory

CH_2=$CHCH_2EX_2$		E_{tot}	E_{rel}	IE_1	IE_2	IE_3	IE_4	C=C	C−C	C−E	δ(C=C−C−E)
	I[a]	−458.84844	0.00	9.17	10.51	13.34	13.55	1.339	1.495	1.872	112.9
	II	−458.84795	0.31	9.50	10.02	13.17	13.58	1.339	1.498	1.873	−112.0
CH_2=$CHCH_2PH_2$, **7a**	**III**	−458.84716	0.80	9.45	10.08	13.17	13.38	1.339	1.498	1.875	106.3
	IV	−458.84553	1.82	9.83	9.87	12.66	13.62	1.337	1.505	1.862	−0.03
	V	−458.84497	2.18	9.91	9.94	12.60	13.52	1.339	1.504	1.869	−10.4
	I	−1376.95850	0.71	9.80	10.61	12.41	12.71	1.339	1.494	1.857	109.4
	II	−1376.95922	0.26	9.94	10.67	12.39	12.71	1.340	1.498	1.853	−107.2
CH_2=$CHCH_2PCl_2$, **2a**	**III**[a]	−1376.95963	0.00	10.02	10.68	12.42	12.73	1.340	1.500	1.850	99.3
	IV	−1376.95154	5.07	10.10	10.21	12.47	12.62	1.338	1.509	1.843	−0.1
	V	−1376.95493	2.95	10.32	10.39	12.39	12.58	1.339	1.506	1.847	−18.03
	I[a]	−2350.12628	0.00	8.97	10.48	12.77	12.87	1.340	1.491	1.980	113.1
	II	−2350.12551	0.48	9.26	10.03	12.80	12.90	1.340	1.494	1.982	−108.1
CH_2=$CHCH_2AsH_2$, **8a**	**III**	−2350.12517	0.70	9.26	10.05	12.78	12.86	1.340	1.494	1.983	104.1
	IV	−2350.12430	1.24	9.69	9.81	12.06	12.95	1.338	1.502	1.967	−0.02
	V	−2350.12455	1.08	9.70	9.89	12.07	12.82	1.339	1.501	1.977	−7.4
	I	−3268.26294	1.13	9.61	10.71	12.18	12.41	1.340	1.490	1.965	109.1
CH_2=$CHCH_2AsCl_2$, **3a**	**II**	−3268.26387	0.55	9.77	10.80	12.13	12.46	1.341	1.496	1.959	−96.0
	III[a]	−3268.26474	0.00	9.90	10.74	12.14	12.50	1.342	1.498	1.952	84.5
CH_2=$CHCH_2SiH_3$	*a*	−407.61045	0.00	9.38	12.74	12.77	12.85	1.340	1.500	1.894	104.1
CH_2=$CHCH_2GeH_3$	*a*	−2191.94912	0.00	9.29	12.40	12.41	12.65	1.340	1.496	1.956	100.9

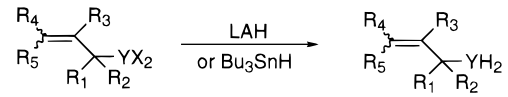
[a] The most stable conformer.

and allenyl derivatives, the addition of a radical inhibitor was necessary to form and isolate the expected products.[30]

The synthesis of the 2-propenylphosphine by reduction of the corresponding phosphonates with LAH or $AlHCl_2$[34] or by addition of a phosphaanion on an allylic halide[38] has already been reported. We prepared primary allylic phosphines **7a**−**f**, arsines **8a**−**f,** and stibines **9a**,**b** using LAH or Bu_3SnH in the presence of small amounts of duroquinone as reducing agent. The C−C double bond of the allylic compounds not being activated by the presence of the YX_2 group (YX_2 = PCl_2, PBr_2, $AsCl_2$, $SbCl_2$), the reduction of the YX_2 group can be performed even with LAH. The allylic function, being sensitive to the presence of radicals, required the presence of a radical inhibitor (duroquinone) with Bu_3SnH, which inhibited the breaking of the C-heteroatom bond. To limit their decomposition, compounds **7**−**9** were distilled off in vacuo from the cooled reaction mixture (−10 °C) during the course of the addition of **2**−**4** and separated from the less volatile products by a cold trap (−60 °C) before condensation (−196 °C).

With LAH or Bu_3SnH, the allylic phosphines **7a**−**f** were obtained in good yields (≈80%) and exhibited a stability similar to those of vinylphosphines;[39] they can be kept several weeks in pure form in a freezer (Scheme 4). The allylic arsines **8a**−**f** were obtained in a 70−75% yield. These compounds are the first derivatives of a new class of compounds. The half-life of **8a**−**f** in $CDCl_3$ ($\tau_{1/2}$ ≈ 1 h) is strongly lower than those of the corresponding allylic phosphines. On standing at room temperature, the allylic arsines **8a**−**f** only led to unidentified decomposition products. The synthesis of primary allylic stibines, which are also the first derivatives of a new class of compounds, was much more difficult. The preparation of the precursors **9a**,**b**,**e**−**f** was done by addition of the corresponding allylic stannane on frozen antimony chloride quickly followed by addition of tetraglyme and then

Scheme 4



2a-i,l, 3a-f, 4a-b **7a-f, 8a-f, 9a-b**

7a : $R_1 = R_2 = R_3 = R_4 = R_5$ = H, Y = P
7b : $R_1 = R_2 = R_4 = R_5$ = H, R_3 = Me, Y = P
7c : $R_2 = R_3 = R_4 = R_5$ = H, R_1 = Me, Y = P
7d : $R_3 = R_4 = R_5$ = H, $R_1 = R_2$ = Me, Y = P
7e (Z), 7e' (E) : $R_1 = R_2 = R_3 = R_4$ = H, R_5 = Me, Y = P
7f : $R_1 = R_2 = R_3$ = H, $R_4 = R_5$ = Me, Y = P
8a : $R_1 = R_2 = R_3 = R_4 = R_5$ = H, Y = As
8b : $R_1 = R_2 = R_4 = R_5$ = H, R_3 = Me, Y = As
8c : $R_2 = R_3 = R_4 = R_5$ = H, R_1 = Me, Y = As
8d : $R_3 = R_4 = R_5$ = H, $R_1 = R_2$ = Me, Y = As
8e (Z), 8e' (E) : $R_1 = R_2 = R_3 = R_4$ = H, R_5 = Me, Y = As
8f : $R_1 = R_2 = R_3$ = H, $R_4 = R_5$ = Me, Y = As
9a : $R_1 = R_2 = R_3 = R_4 = R_5$ = H, Y = Sb
9b : $R_1 = R_2 = R_4 = R_5$ = H, R_3 = Me, Y =Sb

reduction of the crude mixture with LAH in tetraglyme. The 2-propenyl- (**9a)** and methallylstibine (**9b)** were synthesized by this approach, but attempts to prepare the crotyl- (**9c**,**c′**) and prenylstibine **(9d**) were unsuccessful. The kinetic stability of **9a**,**b** in $CDCl_3$ ($\tau_{1/2}$ ≈ 10 min) is much lower than that of the corresponding arsines **7a**,**b,** in opposition with the reported stability of vinylstibines[30] being greater than that of vinylarsines.[28] The different roles played by the presence of a C−C double bond in the α,β- or β,γ-position are thus clearly shown. At room temperature, stibines **9a**,**b** led to insoluble brown-black products. The relative stability of allylic phosphines, arsines, and stibines can be compared to those of the corresponding precursors **2**−**4** and shows their dependence on the presence on the same heteroatom of an allylic substituent and of chlorine or hydrogen atoms. With primary phosphines **7c**,**d** and arsines **8c**,**d**, the corresponding rearranged derivatives **7e**−**f** and **8e**−**f** were never observed in the decomposition products.

Allylic phosphines **7a**−**h**, arsines **8a**−**h,** and stibines **9a**,**b** were characterized by ^1H and ^{13}C NMR spectroscopy

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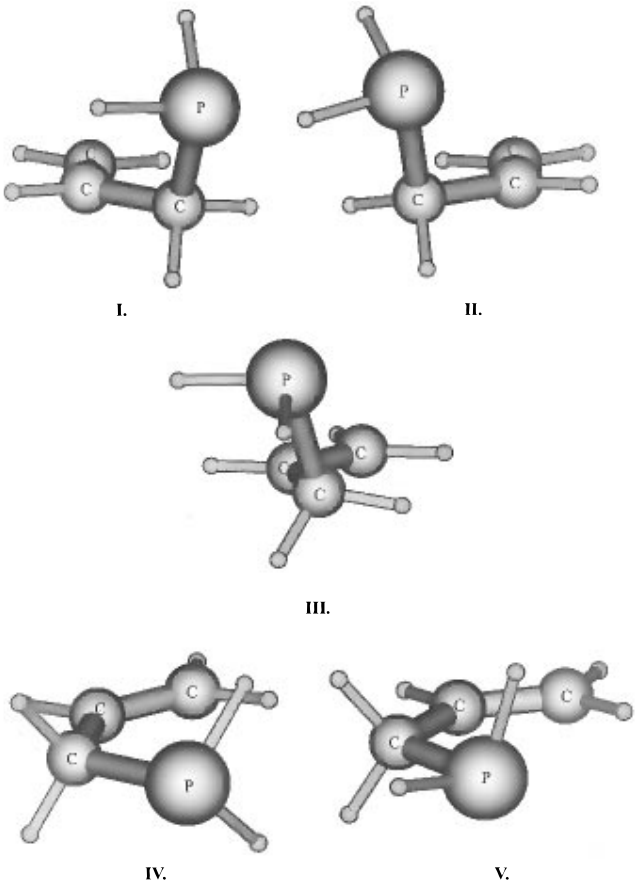

Figure 1. The most stable structure of allylphosphine **7a** as shown by the MOLDEN program.[40]

and HRMS. The FT-IR spectra of the three parent compounds **7a**, **8a,** and **9a** were also recorded. We observed weak differences in the ^{1}H and ^{13}C chemical shifts of the hydrogens and carbons of the allylic function or in the infrared absorptions $\nu_{C=C}$ or $\nu_{C=C-H}$. Only the infrared absorption ν_{Y-H} (ν_{PH} 2200 cm^{-1}, ν_{AsH} 2094 cm^{-1}, ν_{SbH} 1870 cm^{-1}) have data typical of the nature of the heteroatom.[28,30,36]

Calculated Structures. The calculated structural parameters for allylphosphines and allylarsines, as well as for their dichloro derivatives, are compiled in Table 2. As a comparison, calculated data of the most stable structure of allylsilane and allylgermane are also included in Table 2. In most cases five minima were found on the potential energy surface, as shown in Figure 1. The three lowest energy structures are when the phosphorus (arsenic) atom is above the plane of the allylic unit (**I**−**III**) (Figure 1). These structures differ by the rotation of the EX_2 group (E = P, As; X = H, Cl) only; their energy difference is quite small.[41] In case of the "planar" conformer, two further minima (**IV, V**) were located. Among the chloro-substituted derivatives, some of the above structures (**IV**, **V**) could not be found during the geometry optimization at some levels of the theory. Since **I**−**III** show similar structural characteristics and are close in energy, in the following discussion, **I**−**III** will be called **A**. Similarly, **IV**, **V** will be termed the **B** conformer. The hyperconjugation can be realized in the **A** type conformers, which is indeed the most stable allylphosphines, although the stabilization relative to **B** is small. It is worthy to note that the near 2 kcal/mol preference of the **A** type structure with respect to **B** is close to the value obtained for β-substituted ethyl radicals.[42]

In accordance with their very small energy separation, the bond length of the **A** and **B** type structures varies only slightly (see Table 2). The length of the C=C bond is again nearly unchanged when comparing the **A** and **B** type structures. For the **A** type structures, however, slightly shorter C−C and longer P−C bonds are characteristic versus that for the **B** type structures. Such behavior can be expected if hyperconjugation occurs with the P−C σ^* orbitals. Nevertheless, these changes in the bond lengths are quite small, in accordance with the small energy difference of the **A** and **B** structures. Comparing to the isolated structural subunits propene and methylphosphine (C−C 1.498 Å, P−C 1.857 Å, MP_2/6-31G*), the bond lengths are longer in all allylphosphine conformers, while the length of the C=C bond is nearly identical with the value in propene (1.337 Å, MP_2/6-31G*). The general elongation of the bonds indicates some small destabilization in the allylic system, presumably due to some steric repulsion. Comparison of the C=C and the C−C bond lengths of the corresponding phosphorus and arsenic structures shows that in case of the As derivatives the C−C bond is slightly shorter than in case of the P derivatives. Since this difference is similar for both the **A** and the **B** type structures, no considerable increase of hyperconjugative effect could be concluded in case of the arsenic derivative.

When calculating Wiberg bond indices[43] for the most stable conformer (**I**) of allylphosphine, 1.979, 1.031, and 0.927 are obtained for the C=C double, C−C single, and C−P bonds, respectively. From the analysis of the electron density by the method developed by Bader,[44] it can be seen that the ellipticity of the C=C double bond is large (0.47), while it is near zero (0.03) in case of the C−C bond. Since the ellipticity is an indication of how symmetric the electron distribution about the bond is, this behavior indicates that the hyperconjugative effect should be small.

The energy difference of the planar (**B**) and nonplanar structures is small, and there is no significant change in the relative energies by inclusion of the electron correlation. This behavior indicates that the calculated energy ordering is reasonable.

Photoelectron Spectra. The photoelectron spectra of allylphosphine **7a** and allylarsine **8a**, as well as that of their dichloro derivatives **2a** and **3a**, are shown in Figure 2, while the positions of the most important bands are collected in Table 3. All the spectra can be characterized by two low ionization energy bands, which should be attributed to the π-system and the phosphorus/arsenic lone pair ionization. In the case of the halogen-substituted derivatives, further bands appear, which are attributable to the four halogen lone pair ionization energies. The four ionization processes form two bands for most of the compounds, which are broader that the usual narrow halogen lone pair peaks. In case of the bromo compounds, one of the low-energy features is missing,

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(41) Rotation about the P−C and As−C bonds requires small energies only, see ref 1a, 1d, 1e.
(42) Guerra, M. *J. Am. Chem. Soc.* **1992**, *114*, 2077−2085.
(43) Wiberg, K. E. *Tetrahedron* **1968**, *24*, 1083−1096.
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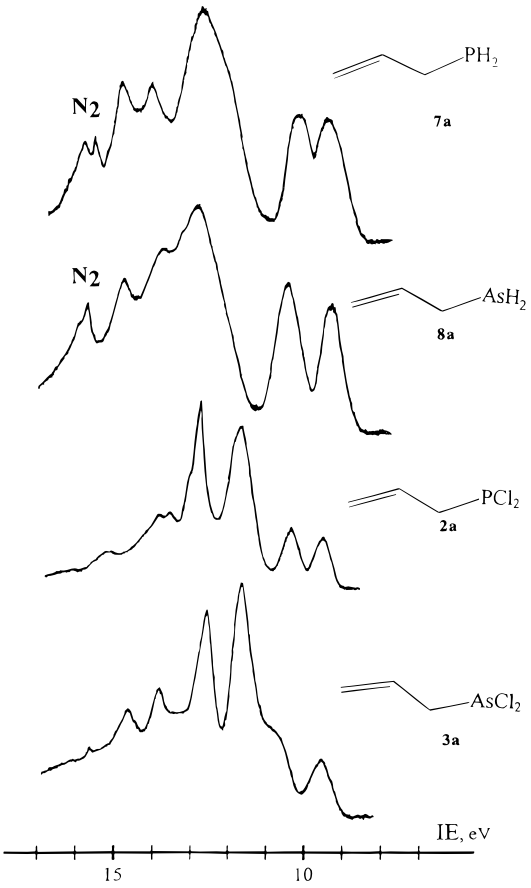

Figure 2. Photoelectron spectra of the investigated compounds.

Table 3. Ionization Energies and Assignment for the Investigated Compounds in EV

compd	substituent	n_E[a]	p	n_X
7a	PH_2	9.32	10.25	
2a	PCl_2	9.58	10.41	11.76, 12.86
8a	AsH_2	9.19	10.37	
3a	$AsCl_2$	9.52	10.90	11.63, 12.62

[a] E = P, As.

apparently it has some overlap with the lowest ionization energy bromine lone pair. The effect of the methyl group attached to the allylic fragment is only minor, and—as usual—is to shift the ionization energies toward the lower values.

To investigate the possible effect of hyperconjugation on the ionization energies, the π-band should be located among the two lowest energy features. Since according to the quantum chemical calculations several conformers are possible with similar energies, it should be investigated whether the spectrum can originate from a mixture of all conformers or if only some of the conformers will dominate. First allylphosphine will be considered. According to the calculations, the orbital energies of all **A** type structures are close to each other. Similarly the ionization energies of the **B** type conformers are nearly the same. The two sets, however, differ considerably from each other. While in case of the **A** conformers, the first two Koopmans ionization energies are separated by about 1 eV from each other (Table 2)—in good agreement with the experimental data—the first two Koopmans ionization energies of the **B** conformer are nearly degenerate. Similarly the HF/6-31G*/MP2/6-31G* ionization

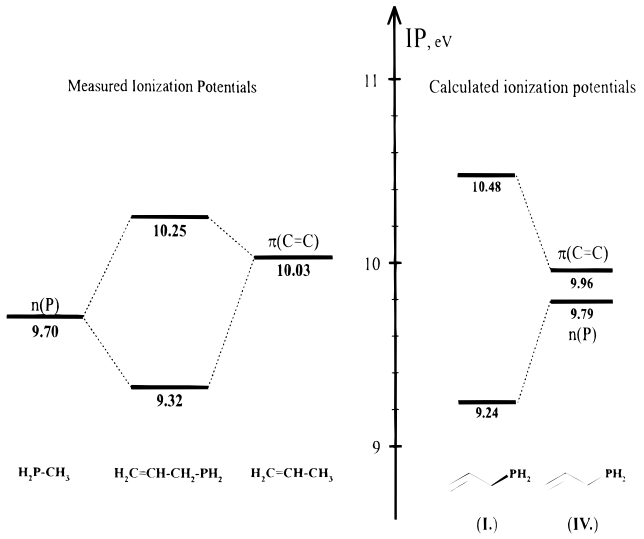

Figure 3. Correlation between observed and calculated ionization energies.

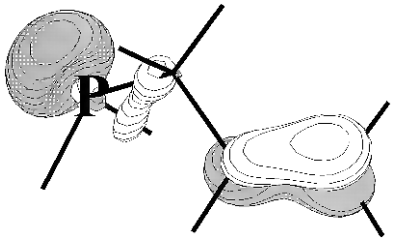

Figure 4. The HOMO of allylphosphine **7a**.[40]

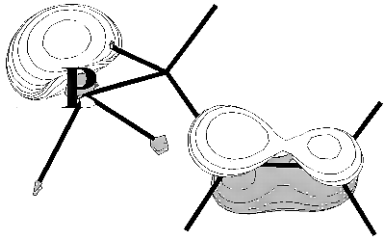

Figure 5. The HOMO-1 orbital of allylphosphine **7a**.[40]

energies of propene and methylphosphine are nearly equal (9.96 and 9.79 eV, respectively). Furthermore, these two values agree well with the observed ionization energies (10.03[45] and 9.70[46] eV, respectively) of the two compounds. This behavior indicates that the present Koopmans ionization energies give a proper description of the experimental data. While the calculated orbital energies of methylphosphine and propene are in good agreement with those of the **B** structure, they differ significantly from the values obtained for the **A** structure. This indicates that there is a large interaction between the π and n_P orbitals in the case of the **A** but not for the **B** structure.

The inspection of the calculated MO's reveals the difference. While in the case of the **B** type structures

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(46) Lappert, M. F.; Pedley, J. B.; Wilkins, B. T.; Stelzer, O.; Unger, E. J. *J. Chem. Soc., Dalton* **1975**, 1207–1214.

(47) Szepes, L.; Nagy, A.; Zanathy, L. PES, of organic derivatives of As, Sb and Bi. In *The chemistry of organic arsenic, antimony and bismuth compounds*; Patai S., Ed.; John Wiley & Sons: New York, 1994.

the first two orbitals are the localized π and heteroatom lone pair MO's, in case of **A** these two MO's are completely mixed, forming a bonding and antibonding combination. Since these combinations are formed between two filled MO's, no energetic stabilization is obtained. This is in agreement with the results of the quantum chemical calculations, where the energy difference of the **A** and **B** type conformers did not exceed 2 kcal/mol (see above). Nevertheless, this interaction is strong, as is shown by the near 1 eV splitting of the ionization energies, because the interacting orbitals are close in energy (cf. the IE's of propene and methylphosphine). The interaction scheme is shown in Figure 3, showing clearly that the photoelectron spectrum is attributable to an **A** but not to a **B** type structure. Such as n$-\pi$ interaction was not observed in the ionization energies of allyldibutylphosphine and allyldimethylarsine.[4] To understand the difference between the H and the alkyl-substituted derivatives the n_E (E = P, As) lone pair orbital energies should be considered. For the trimethylphosphine and -arsine the lone pair appears at 8.6 eV,[46] which is by about 1 eV lower than the corresponding ionization energy of methylphosphine(arsine). As a result, the interaction energy (which is inversly proportional to the energy difference of the interacting levels) should be much smaller for the fully alkylated derivatives than for the hydrogenated system studied here.

The interaction between the phosphorus lone pair and the π-system is not a common phenomenon (see the Introduction). Unlike for the nitrogen-containing systems, the interaction with the phosphorus (arsenic) lone pair orbital happens only if the heteroatom lone pair is separated from the π-system by a CH_2 unit, while in case of the nitrogen-containing systems the heteroatom should be in the α-position with respect to the π-system. A further difference is that in case of a vinylamine or -aniline there is a considerable lone pair$-\pi^*$ orbital interaction, resulting in energetic stabilization, while in case of the heavy element (P, As) substituted allylic systems, no energetic stabilization occurs as a result of the $n_P-\pi$ interaction.

Although the arsine lone pair is somewhat destabilized in comparison with the phosphine lone pair (9.5 eV in case of methylarsine),[47] the spectral data of allylarsine shows larger splitting than those of the allylphosphine (see Table 3), indicating a slightly larger interaction than in the phosphorus case. This increased interaction is presumably attributable to the larger sterical demand of the arsenic lone pair orbital.

The stability of the **A** structure cannot be explained by the $n_P-\pi$ interaction, so the hyperconjugative β-effect should be considered instead. On the basis of the small changes in the bond lengths and the small energy differences between the **A** and **B** systems, this effect should not be large. Further evidence can be gathered, however, from the shape of the HOMO (Figure 4). This MO picture shows that apart from the antibonding combination of the phosphorus lone pair and the π-orbitals a small σ_{PC}^* contribution can be observed, too, which is characteristic for a hyperconjugative interaction. A similar feature cannot be seen in the HOMO-1 (Figure 5). This orbital is more stable by 1 eV than the HOMO, and interacts apparently less with the σ^* orbital of the PC bond than the HOMO.

To see if the interaction of the π and the σ^* MO's results in net energy stabilization or not, an isodesmic reaction was investigated. This reaction

$$CH_2{=}CHCH_2{-}R + CH_4 \rightarrow CH_2{=}CHCH_3 + CH_3{-}R$$

shows if the C$-$C bond is more stable in propene or in the substituted derivative. For R = CH_3, NH_2, SiH_3, PH_2, GeH_3, and AsH_2, -5.86, -4.06, -6.81, -5.42, -4.88, and -3.79 kcal/mol was obtained at the MP2/6-31G*+ZPE level, respectively. From a comparison of the results, it is apparent that in all cases a significant (5 kcal/mol) destabilization was observed. This is in accordance with the observed increase of the bond lengths which was noted above as a possible result of a steric interaction. Therefore, the above isodesmic reaction is not a proper measure of the β-effect in case of the allyl derivatives. The rotation barrier about the C$-$C bond, however (resulting in the **A** and **B** structures), gives a much better estimate. Comparing the energy differences of the **A** and **B** type structures in case of the silyl and the phosphino derivatives, it turns out that the energy difference is somewhat larger in the silyl than in the phosphino case (3.71 kcal/mol at the MP2/6-31G* level of the theory, for allylsilane), indicating that the β-effect of the silyl group is somewhat larger than that of the phosphino group.

Conclusion

Allylic dihalophosphines, -arsines, and -stibines can be prepared by reaction of an allylic stannane on a phosphorus, arsenic, or antimony trihalide, respectively. The reaction leads to the γ-products. The isolation of kinetic (and not thermodynamic) γ-products formed by reaction of an allylic stannane on a Lewis acid has thus been performed for the first time. Depending on the heteroatom, the substituent, and the halogens, a rearrangement can occur to lead to the thermodynamic product. Allylic dichlorostibines are efficient allylation reagents of an electrophile as the benzaldehyde. The chemoselective reduction of these allylic compounds into the corresponding phosphines, arsines, and stibines has been efficiently performed with LAH or Bu_3SnH and the first primary allylic arsines and stibines have thus been prepared. By using ab initio quantum chemical calculations, it has been shown that the preferred structure of allylphosphines and allylarsines are nonplanar, in accordance with a β-effect. From the analysis of the photoelectron spectrum an unusually large interaction between the heteroatom lone pair orbital and the π-system could be concluded. Due to the particular volatility and reactivity of the phosphorus and arsenic halides, this work gives a particular contribution to the study of the substitution or transmetalation of Lewis acid by allylic stannanes. Similar studies with stronger and more usual Lewis acids are currently under progress in our laboratory.

Acknowledgment. OTKA Grant (T014339 and T022032) (Hungary) and the "Programme National de Planétologie" (INSU-CNRS) (France) are gratefully acknowledged for financial support.

Supporting Information Available: 400-MHz ^{1}H NMR, 100-MHz ^{13}C NMR, and 121-MHz ^{31}P NMR spectral data of the allylic dichloro- and dibromophosphines **2a**$-$**j**,**l** and of primary allylic phosphines **7a**$-$**f** and 400-MHz ^{1}H NMR and 100-MHz ^{13}C NMR spectra of the allylic arsines dichlorides **3a**$-$**f** and of primary allylic arsines **8a**$-$**f** (31 pages). This material is containing in libraries on microfiche, immediatly follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO971000T