Primary Vinyl- and Alkynylstibines: Preparation and Characterization

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Received October 3, 1994[⊗]

Primary unsaturated stibines ethenylstibine (**1a**), *E*-prop-1-enylstibine (**1b**), ethynylstibine (**2a**), and prop-1-ynylstibine (**2b**) are synthesized by reaction of antimony trichloride with the corresponding vinyltributylstannanes **3a,b** and alkynyltributylstannanes **4a,b**, respectively, followed by a chemoselective reduction of the formed dichlorostibines **5a,b** and **6a,b**. Compounds **1a,b** and **2a,b** are characterized on the basis of spectral data (NMR, photoelectron spectroscopy and high resolution mass spectrometry). In particular, the PE spectra display very well-resolved bands (**1a**, 9.3, 10.3, 11.2, 11.9, 13.7, and 15.0 eV; **2a**, 9.7, 10.5, and 11.2 eV). The α-unsaturated stibines exhibit a low stability at room temperature even in the presence of a solvent ($\tau_{1/2}$ *ca.* 1 h) and lead to the formation of oligomeric material or an antimony mirror on the wall of the flask. Attempts to detect C−Sb multiple bond derivatives by a base-catalyzed rearrangement of **1** or **2** were unsuccessful.

Introduction

The preparation of the first α-unsaturated primary or secondary arsines has been reported recently.[2,3] However, the corresponding antimony derivatives, the vinyl- and alkynylstibines, have never been characterized. For the group Va elements (N, P, As, Sb, Bi), the stability of hydrides falls rapidly down the group; so BiH_3 is very unstable thermally.[4] However arsines and stibines possess a similar stability. The average bond energies are in accord with these experimental observations: E_{N-H}, 391; E_{P-H}, 322; E_{As-H}, 247; and E_{Sb-H}, 255 kJ·mol^{-1}.[4a] It is thus of interest to synthesize primary vinyl- and alkynylstibines, to define their spectroscopic characteristics and their stabilities, and to study if such compounds can be considered as potential precursors to the corresponding stibaalkenes or -alkynes.[3,5,6] Moreover, with the lone pair on the heteroatom, the α-unsaturated stibines are potential functionalized ligands in organometallic chemistry. We report here the synthesis of the two parent compounds, ethenylstibine (**1a**) and ethynylstibine (**2a**) and their spectral identification. Also described is the preparation and characterization of methyl derivatives **1b** and **2b**. The photoelectron spectra (PES) of these four compounds have been recorded, and their spectra are compared with those of the corresponding phosphines.

Experimental Section

Caution! Stibines are potentially highly toxic molecules. All reactions and handling should be carried out in a well-ventilated hood.[7]

Materials. Antimony trichloride was purchased from Prolabo (Rhône-Poulenc) and used without further purification. Vinyltributylstannanes,[8] alkynyltributylstannanes,[9] and tributylstannane[10] were prepared as previously reported.

General Data. ^{1}H and ^{13}C NMR spectra were recorded on a Brüker AC-300P spectrometer. IR spectra were obtained using a Perkin-Elmer 1420 spectrometer and HRMS (high resolution mass spectrometry) experiments were performed on a Varian MAT 311 instrument. To record the mass spectrum, stibines **1a,b** and **2a,b** were directly introduced from a cell into the ionization chamber of the spectrometer. Photoelectron spectra were recorded on an Helectros 0078 photoelectron spectrometer equipped with a 127° cylindrical analyzer using 21.21 eV He I and 40.81 eV He II radiation photon sources and monitored by a microcomputer supplemented with a digital analog converter. Helium ionization at 4.98 eV and nitrogen ionization at 15.59 eV were used as references. The pressure in the ionization chamber was *ca.* 10^{-3} mbar. The products were generated according to the general procedure and selectively analyzed as soon as they are formed.

Preparation of Vinyldichlorostibines 5a,b. General Procedure. In a two-necked round-bottomed flask equipped with a nitrogen inlet were introduced $SbCl_3$ (2.3 g, 10 mmol) and vinyltributylstannane **3a,b** (10.5 mmol). Then, the mixture was stirred for 1 h at 60 °C. Vinyldichlorostibine (**5a**) was then purified by distillation *in vacuo*. Attempts to purify **5b** by distillation led to the decomposition of the product.

Ethenyldichlorostibine (5a).[11] Yield: 72%; (purity: 90%); $bp_{0.1}$ ≈ 50 °C. ^{1}H NMR ($CDCl_3$): δ 6.29 (d, 1H, $^3J_{HHtrans}$ = 19.4 Hz); 6.56

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1995.

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(2) Guillemin, J. C.; Lassalle, L. *Organometallics* **1994**, *13*, 1525−1527.

(3) Guillemin, J. C.; Lassalle, L.; Dréan, P.; Wlodarczak, G; Demaison, J. *J. Am. Chem. Soc.* **1994**, *116*, 8930−8936.

(4) (a) Cotton, F. A., Wilkinson, G., *Advanced Inorganic Chemistry*, 5th ed.; J. Wiley & Sons: New York, 1988; Chapter 11, pp 382−391. (b) Amberger, E. *Chem. Ber.* **1961**, *94*, 1447−1452.

(5) Rearrangement of ethenylamine, ethenol, ethenethiol, and ethenylphosphine into the corresponding heteroalkene has been largely studied. See: Gonbeau, D; Lacombe, S.; Lasnes, M. C.; Ripoll, J. L.; Pfister-Guillouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 2730−2735 and ref. cited therein.

(6) (a) Guillemin, J. C.; Janati, T.; Denis, J. M. *J. Chem. Soc., Chem. Commun.* **1992**, 415−416. (b) Gaumont, A. C.; Guillemin, J. C.; Denis, J. M. *J. Chem. Soc., Chem. Commun.* **1994**, 945−946.

(7) Few studies have been devoted to the toxicity of substituted stibines; SbH_3 has shown properties similar to those of AsH_3. Goncharenko, L. E.; Kozyrena, O. I.; Ptitsa, A. N. *Farmakol. Toksikol. (Kiev)* **1970**, *5*, 169−173.

(8) Seyferth, D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1957**, *79*, 515−517. Seyferth, D.; Vaughan, L. G. *J. Organomet. Chem.* **1963**, *1*, 138−152.

(9) Bottaro, J. C.; Hanson, R. N.; Seitz, D. E. *J. Org. Chem.* **1981**, *46*, 5221−5222. Keinan, E.; Peretz, M. *J. Org. Chem.* **1983**, *48*, 5302−5309.

(10) Kuivila, H. G. *Synthesis* **1970**, 499−509.

(11) Maier, L. M.; Seyferth, D.; Stone, F. G. A.; Rochow, E. G. *J. Am. Chem. Soc.* **1957**, *79*, 5884−5889. Ramdsen, H. E.; Patent U.S. 3,010, 983; Appl. July 12, 1957; *Chem. Abstr.* **1958**, *56*, 8750d.

0020-1669/95/1334-1466$09.00/0

(d, 1H, $^3J_{HHcis}$ = 12.3 Hz); 7.50 (dd, 1H, $^3J_{HHtrans}$ = 19.4 Hz, $^3J_{HHcis}$ = 12.3 Hz). ^{13}C NMR ($CDCl_3$): δ 134.8 (t, $^1J_{CH}$ = 159.8 Hz); 152.1 (d, $^1J_{CH}$ = 164.5 Hz).

(*Z*- + *E*-)Prop-1-enyldichlorostibine (5b). *E*/*Z*: 4/1. Yield (crude product): 66%. *E*-isomer. ^{1}H NMR ($CDCl_3$): δ 1.97 (dd, 3H, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.5 Hz); 6.58 (dq, 1H, $^3J_{HH}$ = 19.4 Hz, $^3J_{HH}$ = 6.6 Hz); 7.17 (dq, 1H, $^3J_{HH}$ = 19.4 Hz, $^4J_{HH}$ = 1.5 Hz). ^{13}C NMR ($CDCl_3$): δ 20.7 ($^1J_{CH}$ = 128.4 Hz (q)); 139.6 (d, $^1J_{CH}$ = 168.6 Hz); 144.2 (d, $^1J_{CH}$ = 152.7 Hz). *Z*-isomer. ^{1}H NMR ($CDCl_3$): δ 2.03 (d, 3H, $^3J_{HH}$ = 6.6 Hz); 6.25 (dq, 1H, $^3J_{HHcis}$ = 11.0 Hz, $^4J_{HH}$ = 1.5 Hz); 6.97 (dq, 1H, $^3J_{HHcis}$ = 11.0 Hz, $^3J_{HH}$ = 6.6 Hz). ^{13}C NMR ($CDCl_3$): δ 20.5 (q, $^1J_{CH}$ = 125 Hz); 145.3 (d, $^1J_{CH}$ = 160 Hz); 145.7 (d, $^1J_{CH}$ = 160 Hz).

Preparation of Alkynyldichlorostibines 6a,b. General Procedure. In a 25-mL two-necked round-bottomed flask equipped with a nitrogen inlet was introduced antimony trichloride (2.6 g, 11 mmol). The reagent was frozen at −40 °C, and the alkynyltributylstannane **4a,b** (10 mmol) was added. The solution was then vigorously stirred and allowed to warm to room temperature over 5 min. Thus a crude solution of the alkynyldichlorostibine **6a,b** is obtained. Attempts to purify compound **6a,b** led to the decomposition of the product.

Ethynyldichlorostibine (6a). Yield (crude product): 27%. ^{1}H NMR ($CDCl_3$): δ 3.04 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 99.0 (d, $^1J_{CH}$ = 243.0 Hz); 103.0 (d, $^2J_{CH}$ = 43.2 Hz).

Prop-1-ynyldichlorostibine (6b). Yield (crude product): 25%. ^{1}H NMR($CDCl_3$): δ 2.05 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 3.4 ($^1J_{CH}$ = 132.0 Hz), 81.3, 111.3.

Preparation of Vinylstibines 1a,b. General Procedure. The apparatus already described for the reduction of phosphonates was used.[12] The flask containing the reducing mixture (30 mmol of Bu_3SnH) was cooled at −10 °C, fitted on a vacuum line, and degassed. The vinyldichlorostibine **5a,b** (10 mmol) was then slowly added (10 min) at room temperature with a syringe through the septum. During and after the addition, vinylstibine **1a,b** was distilled off *in vacuo* from the reaction mixture. A cold trap (−60 °C) removed selectively the less volatile products and compound **1a,b** was condensed with a cosolvent on a cold finger (−196 °C) which is connected at the bottom to a flask or a NMR tube. 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 (<−50 °C) before analysis (low temperature NMR spectroscopy).

IR Spectroscopy. Special equipment was used for recording the IR spectrum of **1a,b** 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 cold finger of the vacuum line. Compound **1a,b**, synthesized as reported below, was condensed without solvent on the cold finger (−196 °C). After the cold finger was disconnected from the vacuum line by stopcocks, the liquid nitrogen was removed. When the pressure of vinylstibine arose 80 hPa, the cell was disconnected by stopcock from the apparatus and attached to the IR spectrometer.

Photoelectron Spectroscopy. To record the photoelectron spectra (PES), two cold traps were fitted on a vacuum line (*ca.* 10^{-3} mbar). Compounds **1a,b** were synthesized as reported below. The first cold trap (−60 °C) removed selectively the less volatile products and compound **1** was condensed in the second cold trap (liquid nitrogen bath, −196 °C). At the end of the reaction, this cold trap was allowed to warm to −90 °C to remove traces of SbH_3. After subsequent heating of the trap to the suitable temperature, the analysis of the stibines **1a,b** was completed by recording the photoelectron spectra of the gaseous flow.

Ethenylstibine (1a). Yield: 55%; ^{1}H NMR ($CDCl_3$, −30 °C): δ 3.16 (ddd, 2H, $^3J_{HH}$ = 3.3 Hz, $^4J_{HH}$ = 1.4 Hz, $^4J_{HH}$ = 1.0 Hz); 5.99 (ddt, 1H, $^3J_{HHtrans}$ = 19.4 Hz, $^2J_{HH}$ = 1.9 Hz, $^4J_{HH}$ = 1.4 Hz); 6.28 (ddt, 1H, $^3J_{HHcis}$ = 11.8 Hz, $^2J_{HH}$ = 1.9 Hz, $^4J_{HH}$ = 1.0 Hz); 6.94 (ddt, 1H, $^3J_{HHtrans}$ = 19.4 Hz, $^3J_{HHcis}$ = 11.8 Hz, $^3J_{HH}$ = 3.3 Hz). ^{13}C NMR ($CDCl_3$, −30 °C): δ 121.7 (dm, $^1J_{CH}$ = 159.8 Hz); 136.9 (tm, $^1J_{CH}$ = 156.1 Hz). HRMS: calcd for $(C_2H_5{}^{121}Sb)^{\bullet+}$, 149.9429; found, 149.944. *m/z* (%): 152 (13.8), 151 (6.4), 150 (31.5), 149 (10.9), 148 (17.2), 124 (79.4), 123 (47.8), 122 (100), 121 (34.7). IR (gaseous phase, cm^{-1}): $\nu_{=CH}$ 3058 (s); ν_{Sb-H} 1855 (vs); $\nu_{C=C}$ 1585 (w). The PE spectrum of **1a** displayed six well-resolved sharp bands at 9.3, 10.3, 11.2, 11.9, 13.7, and 15.0 eV. With He II radiation, a strong decrease of the intensity of the first, third, and forth bands was observed.

***E*-Prop-1-enylstibine (1b).** Yield: 62%. ^{1}H NMR ($CDCl_3$, −30 °C): δ 1.83 (ddt, 3H, $^3J_{HH}$ = 5.9 Hz; $^4J_{HH}$ = $^5J_{HH}$ = 1.2 Hz); 3.00 (ddq, 2H, $^3J_{HH}$ = 2.8 Hz, $^4J_{HH}$ = 1.2 Hz, $^5J_{HH}$ = 1.2 Hz); 6.27 (dqt, 1H, $^3J_{HHtrans}$ = 17.6 Hz, $^3J_{HH}$ = 5.9 Hz, $^4J_{HH}$ = 1.2 Hz); 6.45 (dtq, 1H, $^3J_{HHtrans}$ = 17.6 Hz, $^3J_{HH}$ = 2.8 Hz, $^4J_{HH}$ = 1.2 Hz). ^{13}C NMR ($CDCl_3$, −30 °C): δ 24.0 (qm, $^1J_{CH}$ = 126.4 Hz); 111.8 (dm, $^1J_{CH}$ = 156.5 Hz); 147.9 (dm, $^1J_{CH}$ = 158.2 Hz). IR (gaseous phase, cm^{-1}): $\nu_{=CH}$ 3083 (s); ν_{Sb-H} 1850 (vs); $\nu_{C=C}$ 1610 (w). HRMS for $(C_3H_7{}^{121}Sb)^{\bullet+}$: calcd, 163.9586; found; 163.959. *m/z* (%): 166 (7.2), 164 (24.8), 162 (10.1), 161 (5.4), 138 (49.1), 137 (10.4), 136 (66.0), 135 (10.1), 124 (36.2), 123 (35.9), 122 (33.5), 121 (34.7), 86 (10.7), 84 (17.1). On the PE spectrum, six well-resolved bands were observed at 9.0, 9.8, 10.9, 11.6, 12.6, and 14.1 eV. Traces of the Z-isomer have been detected in the ^{1}H and ^{13}C NMR spectra of *E*-prop-1-enylstibine.

Preparation of Alk-1-ynylstibines 2a,b. General Procedure. The procedure described below for the vinylstibines was modified: the flask containing the reducing mixture (30 mmol of Bu_3SnH and small amounts of duroquinone) was cooled at −10 °C, fitted on a vacuum line, and degassed. The crude solution of alkynyldichlorostibine **6a,b** (6 mmol) was then slowly added (10 min) at room temperature with a flexible needle through the septum. During and after the addition, alkynylstibine **2a,b** was distilled *in vacuo* from the reaction mixture. A cold trap (−60 °C) removed selectively the less volatile products and compound **2a,b** and SbH_3 were condensed with a cosolvent on the cold finger (−196 °C). After being disconnected from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen; liquid nitrogen was subsequently removed. The products were collected in a Schlenk flask or in a NMR tube and characterized by spectroscopy. Alkynylstibine **2a,b** can be purified by trap-to-trap distillation but revaporization of crude stibine **2a,b** led to a significant loss of product. However, purification was performed to record the PE spectrum and a procedure similar to this reported for **1a,b** was used. Attempts to record the IR spectrum of **2a,b** in the gaseous phase were unsuccessful.

Ethynylstibine (2a). Yield: 25%; ^{1}H NMR ($CDCl_3$, −30 °C): δ 2.35 (1H, t, $^4J_{HH}$ = 2.4 Hz); 4.04 (2H, d, $^4J_{HH}$ = 2.4 Hz). ^{13}C NMR ($CDCl_3$, −30 °C): δ 65.5 (d, $^2J_{CH}$ = 42.5 Hz); 99.2 (d, $^1J_{CH}$ = 240.7 Hz). HRMS: calcd for $(C_2H_3Sb)^{\bullet+}$, 147.9277; found, 149.927. *m/z* (%): 150 (30.2), 149 (5.5), 148 (100), 147 (13.7), 146 (86.5), 145 (9.7), 124 (79.6), 123 (40.6), 122 (98.5), 121 (83.4). MIKE spectrum of *m/z* 150: 123. CAD-MIKE spectrum of *m/z* 150: 137, 123. On the PE spectrum, three well-resolved bands were observed at 9.7, 10.5, and 11.2 eV.

Propynylstibine (2b). Yield: 22%; ^{1}H NMR ($CDCl_3$, −30 °C): δ 1.97 (3H, t, $^5J_{HH}$ = 2.3 Hz); 3.81 (2H, q, $^5J_{HH}$ = 2.3 Hz). ^{13}C NMR ($CDCl_3$, −30 °C): δ 5.9 (q, $^1J_{CH}$ = 132.1 Hz, CH_3); 56.3 (s, CH_3−C≡*C*); 109.2 (s, CH_3−*C*≡C). HRMS: calcd for $(C_3H_5{}^{121}Sb)^{\bullet+}$, 163.9433; found, 163.944. The PE spectrum displayed three well-resolved bands at 9.2, 9.8, and 10.6 eV.

Results and Discussion

The preparation of the ethenyldichlorostibine **5a** has already been reported: compound **5a** was obtained starting from trivinylstibine and 2 equiv of antimony trichloride.[11] However, the product was never obtained in pure form. We have prepared vinyldichlorostibines **5a,b** in good yield (≈75%) upon heating $SbCl_3$ to 60 °C with 1 equiv of vinyltributylstannane **3a,b** (Scheme 1). Compound **5a** is distilled under reduced pressure; a purity of 90% is usually observed (impurities: $SbCl_3$, divinyl compounds).[11] Attempts to purify stibines **5b** by distillation in vacuo lead to the decomposition of the product and the crude product is directly used in the following step; structures are determined by ^{1}H and ^{13}C NMR spectroscopy.

The alkynyldichlorostibines derivatives **6a,b** represent a new class of compounds and are prepared by freezing $SbCl_3$ before

(12) Cabioch, J. L.; Denis, J. M. *J. Organomet. Chem.* **1989**, *377*, 227−233. Gaumont, A. C.; Morise, X.; Denis, J. M. *J. Org. Chem.* **1992**, *57*, 4292−4295.

Scheme 1

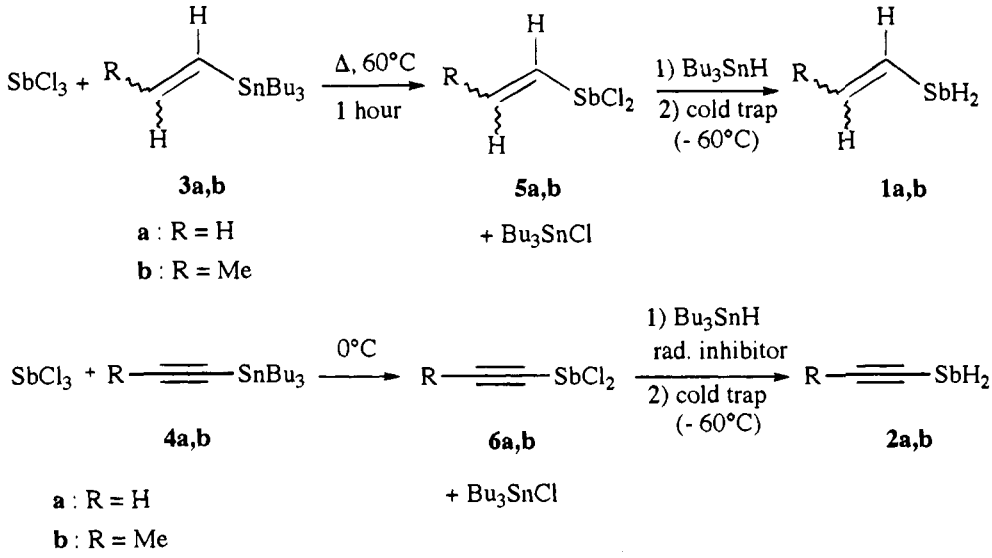
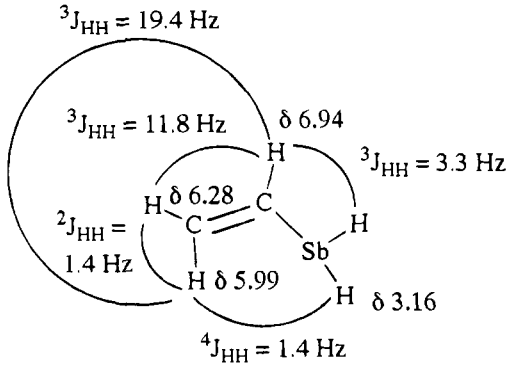
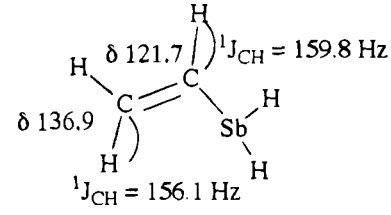


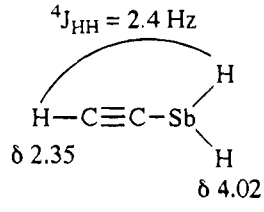
Chart 1



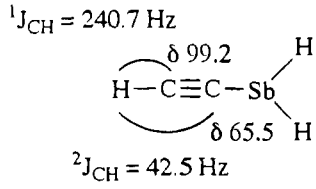
^{1}H NMR chemical shifts and coupling constants of **1a**



^{13}C NMR chemical shifts and coupling constants of **1a**



^{1}H NMR chemical shifts and coupling constants of **2a**



^{13}C NMR chemical shifts and coupling constants of **2a**

addition of the alkynyltributylstannanes **4a,b**.[13] The solution is shaken vigorously and allowed to warm to room temperature to form the unstable dichlorostibines **6a,b**. Attempts to purify compounds **6a,b** were unsucessful and led to the decomposition of the products. The crude solution must be quickly used in the following step.

The chemoselective reduction of chlorostibines **5a,b** is performed using tributylstannane as reducing agent.[14] To limit their decomposition, compounds **1a,b** are distilled off *in vacuo* from the cooled reaction mixture (−10 °C) during the course of the addition of **5a,b** and separated from the less volatile products by a cold trap (−60 °C) before condensation (−196 °C). The vinylstibines **1a,b** are obtained in an essentially pure form in *ca.* 60% yields. Similar results were obtained using $AlHCl_2$ in tetraglyme as reducing agent.[12]

The chemoselective reduction of alk-1-ynyldichlorostibines **6a,b** is difficult and leads, with various reducing agent ($LiAlH_4$, $AlHCl_2$, Bu_3SnH) to the corresponding alkynes and SbH_3 as major products. The use of Bu_3SnH in the presence of a radical

(13) Similar experiments have already been used to prepare ethynylarsine (see ref 3). However, the stibines **5b** and **6a,b** cannot be purified by distillation.

(14) Some of us have recently reported the use of this reducing agent to prepare primary α-unsaturated heterocompounds: See refs 2 and 3 and: Janati, T.; Guillemin, J. C.; Soufiaoui, M. *J. Organomet. Chem.* **1995**, *486*, 57−62.

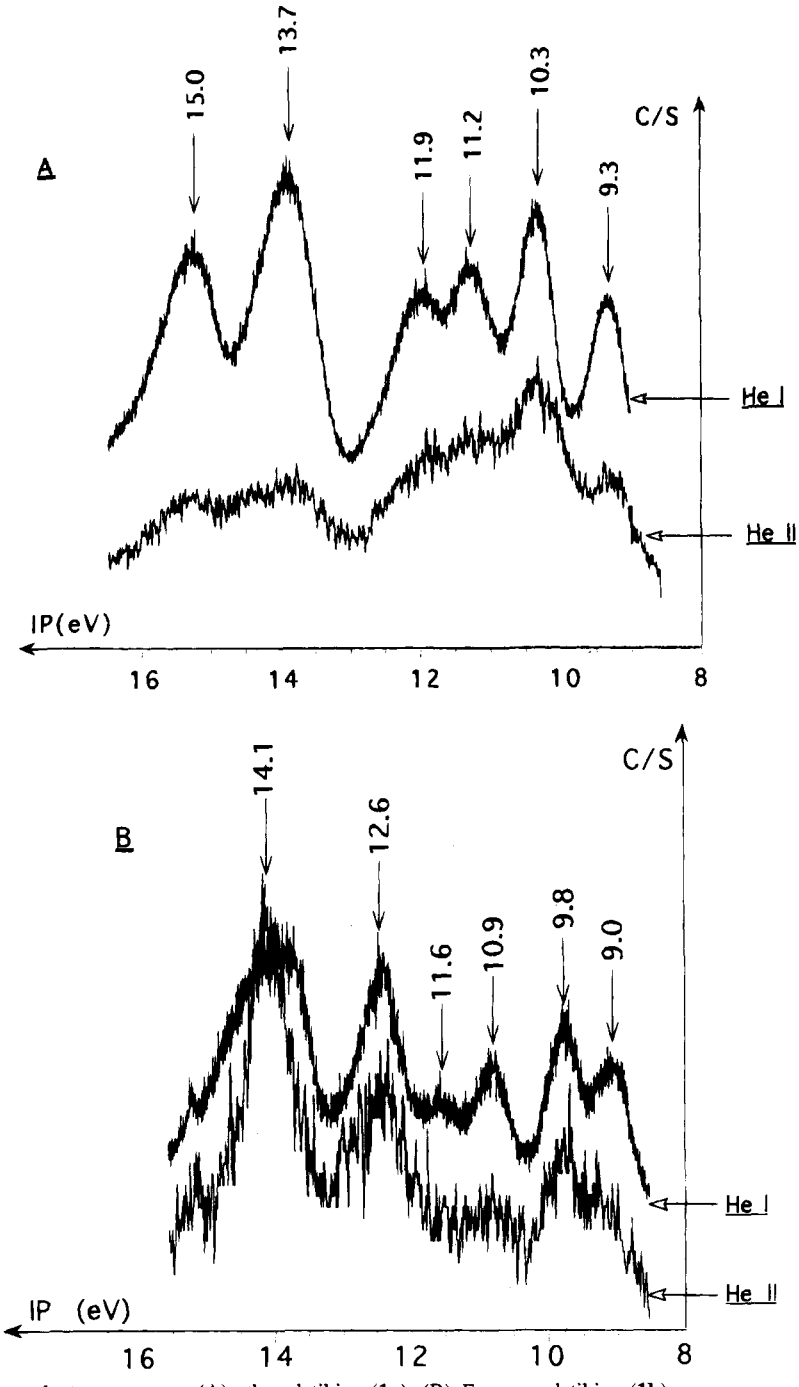


Figure 1. He I and He II photoelectron spectra: (A) ethenylstibine (**1a**); (B) *E*-propenylstibine (**1b**).

inhibitor (hydroquinone, duroquinone, galvinoxyl) gave better results, the breaking of the C−Sb bond probably proceeding *via* a radical reaction.[15] Under these conditions, stibines **2a,b** are obtained in *ca.* 25% yields.

Stibines **1a,b** and **2a,b** are characterized by low temperature ^1H and ^{13}C NMR spectroscopy. The ^1H and ^{13}C NMR data allow an unambiguous structural assignment, since the chemical shifts and coupling constants are typical of ethylenic and acetylenic derivatives respectively.[2,3,12,16] We give as an example the NMR data of ethenylstibine **1a** and of ethynylstibine **2a** (Chart 1). Similar data are obtained for stibines **1a**, **2a** and for the corresponding arsenic[2,3] or phosphorus derivatives.[17,18] However a small downfield shift is observed for the ^1H NMR signals of the protons of the stibines **1a** and **2a** in comparison with those of the corresponding arsines or phosphines. This effect can be attributed to the difference of the covalent radius and of the electronegativity between phosphorus, arsenic and antimony atoms[19] and to the more metallic character of antimony. In the ^{13}C NMR spectra, an inductive effect through the triple bond can explain the observation of a downfield chemical shift for the signal of the carbon on the β-position and an upfield shift for the signal of the carbon on

(15) The use of tributylstannane in the presence of a radical inhibitor has already been reported. Menapace, L. W.; Kuivila, H. G. *J. Am. Chem. Soc.* **1964**, *86*, 3047−3051. Pereyre, M.; Colin, G.; Valade, J. *Bull. Soc. Chim. Fr.* **1968**, *8*, 3358−3370. Godet, J. Y.; Pereyre, M. *Bull. Soc. Chim. Fr.* **1976**, 1105−1109.

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

(17) Lasne, M. C.; Ripoll, J. L.; Thuillier, A. *J. Chem. Soc. Perkin Trans 1* **1988**, 99−104.

(18) Guillemin, J. C.; Savignac, P.; Denis, J. M. *Inorg. Chem.* **1991**, *30*, 2170−2173.

(19) Sanderson, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 2259−2261.

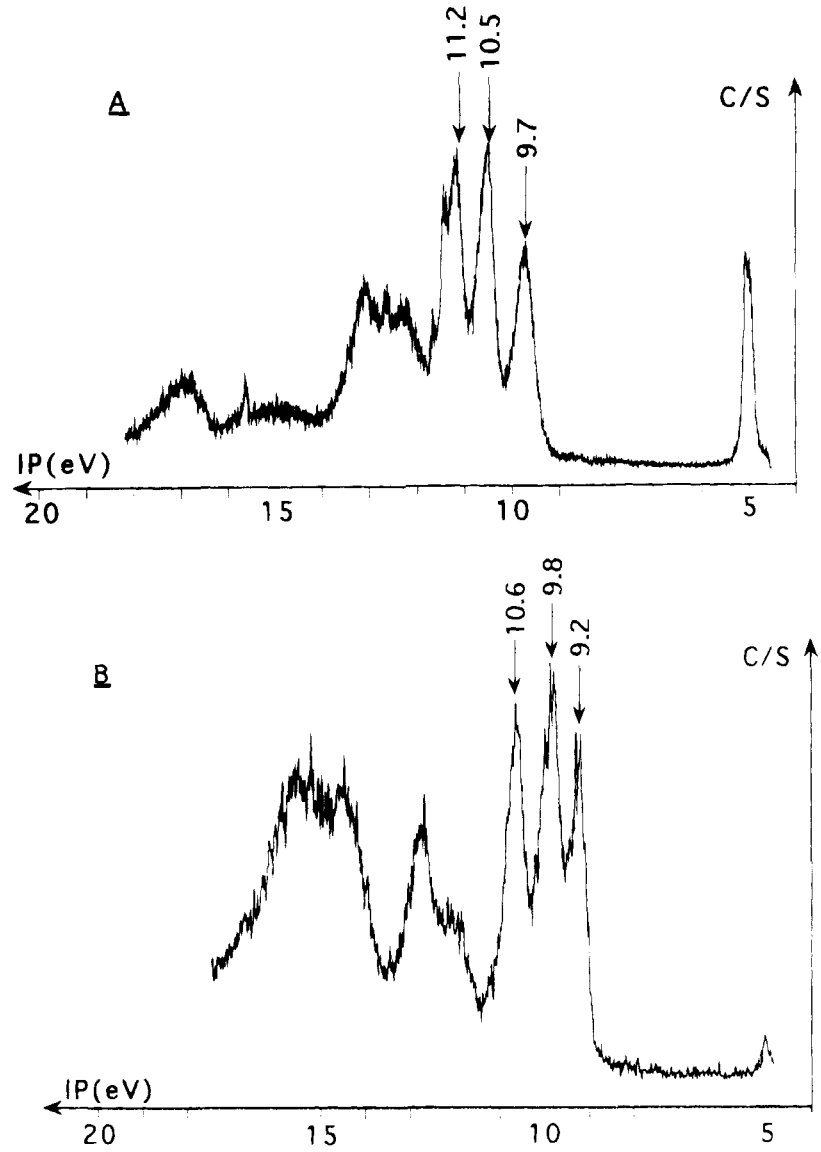


Figure 2. Photoelectron spectra: (A) ethynylstibine (**2a**); (B) propynylstibine (**2b**).

the α-position. The presence of stibines **1a,b** and **2a,b** is confirmed by the observation of the corresponding molecular ion by high resolution mass spectrometry (HRMS). Compounds **1a,b** are also identified by the infrared absorptions [**1a**: (gas phase, 100 mbar) ν_{Sb-H} 1855 cm^{-1} and $\nu_{C=C}$ 1585 cm^{-1}].

PE Spectroscopy. The PE spectra of stibines **1a,b** and **2a,b** (obtained for respective trap temperatures of −80, −70, −70, and −50 °C) display very well-resolved bands (Figures 1 and 2). The two first ionizations of these systems are associated with the ejection of an electron from the two orbitals resulting of the interaction between the lone pair of the heteroatom and the ethylenic system. For ethenylphosphines,[5] the PE spectra were interpreted on the basis of a free rotation of the phosphino group, the observed broadening of the two first bands coming from a population of rotamers with differentiated ionizations (the C−C bond eclipsed by the lone pair for the energetically favored conformation and the lone pair in interaction with the π system in the gauche conformation).

The two first bands for the stibines **1a** and **1b** are sharp and observed at 9.3 and 10.3 eV and 9.0 and 9.8 eV, respectively (Figure 1). Upon He II radiation, only a decrease of the intensity of the first band was observed. This result indicates a significant localization on the lone pair of the antimony atom. Moreover, the substitution by a methyl group induces a strong destabilization of the second ionization, consequently associated with an orbital strongly localized on the ethylenic bond. These observations are interpreted by assuming the presence of the sole rotamer where the C=C bond is eclipsed by the lone pair of the antimony atom or by a large population of this rotamer.

The interaction between the ethylenic system and the lone pair is weak (0.8−1.0 eV) and we observe a destabilization marked for these two first ionizations due to the inductive effect of the SbH_2 group. The 11.2 and 11.9 eV ionizations, which decrease in intensity with the He II radiation, are associated with the σ_{Sb-C}, σ_{Sb-H}, and π_{SbH_2} ionizations. At deeper energies, the ionizations are characteristic for the carbon skeleton.

The cylindrical symmetry of the alkynylstibines **2a** and **2b** leads to the equivalence of the orbital energies of the rotamers. If we choose, as a reference, the two rotamers where the lone pair of the antimony atom interacts with one of the π-acetylenic orbitals, the potential of the unperturbed orbital is of 10.5 eV (11.4 eV for C_2H_2) (Figure 2). This value shows a strong destabilizing effect due to the presence of the stibine group. The values of the two other ionizations (9.7 and 11.2 eV) show a weaker interaction in these systems than in the phosphorus derivatives;[5] these observations can be explained by the longer C−Sb bond length, a pronounced pyramidalization of antimony and a weak 5p−2p overlap.

Upon methylation of the triple bond, the first three bands are shifted by about 0.5 eV at 9.2, 9.8, and 10.6 eV.

Stibines **1** and **2** exhibit a low stability at room temperature even when kept under nitrogen in deuterochloroform ($\tau_{1/2}$ *ca.* 1 h) and a metallic film is slowly formed on the wall of the flask under these conditions. These compounds are considerably less stable than the corresponding phosphines,[17,18] but more stable than the corresponding arsines.[2,3] This property can be attributed to the low energy of the Sb−H bond[4] and weak interactions between the π-orbitals of the C−C multiple bonds and the lone pair of the antimony atom.

We have tried to extend the already reported rearrangements of α-unsaturated phosphines[6] and arsines[3] to antimony derivatives. Several experiments starting from ethynylstibine **2a** were analyzed by PE spectroscopy or low temperature NMR. Addition of a Lewis base to a cooled solution (−50 °C) of **2a** or vaporization of **2a** in VGSR conditions[20] were unsuccessful and resulted in the formation of black materials in each case. It is well-known that the stability of heteroalkynes falls rapidly down in the group V; thus nitriles are stable compouds, arsalkynes are unstable thermally,[3] and, to our knowledge, there is no compound with a C−Sb multiple bond characterized up to now. Ethylidynestibine (**7a**) (or the ethenylidenestibine intermediate) is perhaps too unstable to be isolated under our experimental conditions.

In conclusion, we have developed a mild synthesis of primary vinyl- and alkynylstibines, unknown so far. Extension of this approach to the preparation of other unstabilized antimony derivatives and the study of their chemistry is currently in progress.

Acknowledgment. We acknowledge Maryse Simon for technical assistance. J.-C.G. thanks the "Programme National de Planétologie" (INSU-CNRS) for financial support.

IC941116X

(20) For other vacuum gas−solid reactions (VGSR) experiments, see for example: Lacombe, S.; Pellerin, B.; Guillemin, J. C; Denis, J. M.; Pfister-Guillouzo, G. *J. Org. Chem.* **1989**, *54*, 5958−5963. Guillemin, J. C.; Janati, T.; Guenot, P.; Savignac, P.; Denis, J. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 196−198. Guillemin, J. C.; Cabioch, J. L.; Morise, X.; Denis, J. M; Lacombe, S.; Gonbeau, D.; Pfister-Guillouzo, G.; Guenot, P.; Savignac, P. *Inorg. Chem.* **1993**, *32*, 5021−5028. Billups, W. E.; McCord, D. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1332−1343.