Synthesis and Characterization of Primary and Secondary Allenyl- and Alkynylarsines

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

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

Received March 31, 1995

Although numerous kinetically stabilized arsaalkenes[1] and one arsaalkyne[2] have been prepared, few examples of unstabilized molecules containing an arsenic atom are known. However, primary vinylarsines,[3] and among them the parent compound, were recently synthesized and the first primary alk-1-ynylarsine has been described; the latter led via a base-induced rearrangement to the first unstabilized arsaalkyne isolated up to now, the ethylidynearsine $CH_3C{\equiv}As$.[4] The potential of allenylarsines and alkynylarsines as ligands in organometallic chemistry or as precursors of carbon−arsenic multiple-bond compounds prompted us to develop a general approach. We report here the preparation of allenylchloroarsines and their chemoselective reduction to the corresponding primary and secondary allenylarsines, a new class of compounds. Also described are the preparation of C- or As-substituted alk-1-ynylarsines and the study of the base-induced rearrangement of the primary derivatives into the corresponding arsaalkynes.

Experimental Section

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

Materials. Arsenic trichloride was purchased from Strem or prepared by reaction of aqueous hydrochloric acid on As_2O_3;[5] *n*-dibutyl ether, 2,2′-azobis(2-methylpropionitrile) (AIBN), and duroquinone were purchased from Acros Chimica; galvinoxyl was purchased from Aldrich. All chemicals were used without further purification. Tributylstannane,[6] allenyltributylstannane **1**[7] and alkynyltributylstannanes **2a**−**d**[7a,8] were prepared as previously reported.

General Methods. ^1H and ^{13}C NMR spectra were recorded on Bruker spectrometers (AC300P and ARX400), and HRMS (high-resolution mass spectrometry) experiments were performed on a Varian MAT 311 instrument. To record the mass spectrum, alkynyl- and allenylarsines were directly introduced from a cooled cell into the ionization chamber of the spectrometer. The yields of the allenyl- and alkynylarsines were determined by ^1H NMR with an internal reference.

Allenylchloroarsines (3a−c). General Procedure. Into a 25 mL two-necked round-bottomed flask equipped with a nitrogen gas inlet were introduced arsenic trichloride, methyl- or ethylarsinous dichloride (10 mmol), propadienyltributylstannane **1** (3.3 g, 10 mmol), and catalytic amounts of AIBN. The mixture was stirred for 30 min at 60 °C. Purification by distillation in vacuo gave propadienylchloroarsines **3a**−**c**. Compounds **3a**−**c** were obtained in the presence of $AsCl_3$, $MeAsCl_2$, and $EtAsCl_2$, respectively, and, due to their instability, crude products were used in the following step without further purification. Allenylchloroarsines **3a**−**c** can be kept in a freezer.

Propadienylarsinous Dichloride (3a). This compound was prepared from arsenic trichloride (1.8 g, 10 mmol) and propadienyltributylstannane **1** (3.3 g, 10 mmol): $bp_{0.1} \approx 30$ °C; yield 75%; ^1H NMR ($CDCl_3$) δ 5.15 (d, 2H, CH_2, $^4J_{HH}$ = 6.7 Hz), 6.30 (t, 1H, CH, $^4J_{HH}$ = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 77.9 (td, CH_2, $^1J_{CH}$ = 170.9 Hz, $^3J_{CH}$ = 7.4 Hz), 96.7 (dt, CH, $^1J_{CH}$ = 186.8 Hz, $^3J_{CH}$ = 7.4 Hz), 208.5 (br s, $H_2C{=}C{=}CH$).

Propadienylmethylarsinous Chloride (3b). This compound was prepared from methylarsinous dichloride (1.6 g, 10 mmol) and propadienyltributylstannane **1** (3.3 g, 10 mmol): $bp_{0.1} \approx 25$ °C; yield 52%; ^1H NMR ($CDCl_3$) δ 1.71 (s, 3H, CH_3), 4.85 (d, 2H, CH_2, $^4J_{HH}$ = 6.9 Hz), 5.93 (t, 1H, CH, $^4J_{HH}$ = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 19.4 (q, CH_3, $^1J_{CH}$ = 135.1 Hz), 74.0 (td, CH_2, $^1J_{CH}$ = 169.2 Hz, $^2J_{CH}$ = 8.0 Hz), 89.6 (dm, CH, $^1J_{CH}$ = 183.1 Hz), 208.4 (br s, $H_2C{=}C{=}CH$).

Propadienylethylarsinous Chloride (3c). This compound was prepared from ethylarsinous dichloride (1.75 g, 10 mmol) and propadienyltributylstannane **1** (3.3 g, 10 mmol): $bp_{0.1} \approx 30$ °C; yield 49%; ^1H NMR ($CDCl_3$) δ 1.28 (t, 3H, CH_3, $^3J_{HH}$ = 7.6 Hz), 2.08 (q, 2H, CH_2, $^3J_{HH}$ = 7.6 Hz), 4.85 (d, 2H, CH_2, $^4J_{HH}$ = 6.7 Hz), 5.89 (t, 1H, CH, $^4J_{HH}$ = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 8.9 (q, CH_3, $^1J_{CH}$ = 127.8 Hz), 28.7 (t, CH_2, $^1J_{CH}$ = 135.6 Hz), 73.7 (td, CH_2, $^1J_{CH}$ = 169.3 Hz, $^3J_{CH}$ = 7.7 Hz), 88.2 (dm, CH, $^1J_{CH}$ = 178.3 Hz); 209.2 (br s, $H_2C{=}C{=}CH$).

Alkynylchloroarsines (4a−e). General Procedure. In a 25 mL two-necked round-bottomed flask equipped with a nitrogen gas inlet was placed arsenic trichloride (2 g, 11 mmol). The reagent was frozen at −60 °C, and the appropriate alkynyltributylstannane (**2a**−**d**) (10 mmol) was added. The solution was then vigorously stirred and allowed to warm to room temperature over 10 min. Purification by trap-to-trap distillation gave pure alkynyldichloroarsine (**4a**−**d**). The products must be kept at low temperature (−40 °C). To prepare **4e**, a similar experiment was performed by starting from ethylarsinous dichloride and ethynyltributylstannane **2a**; the mixture was heated for 20 min at 50 °C before distillation.

Prop-1-ynylarsinous Dichloride (4a). This compound was prepared from arsenic trichloride (2.0 g, 11 mmol) and prop-1-ynyltributylstannane **2a** (3.29 g, 10 mmol): $bp_{0.1} \approx 30$ °C, yield 60%; ^1H NMR ($CDCl_3$) δ 2.13 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 5.8 (q, CH_3, $^1J_{CH}$ = 132.0 Hz), 84.1 (q, CAs, $^3J_{CH}$ = 5.0 Hz), 113.8 (q, $CH_3C{\equiv}C$, $^2J_{CH}$ = 9.5 Hz).

Pent-1-ynylarsinous Dichloride (4b). This compound was prepared from arsenic trichloride (2.0 g, 11 mmol) and pent-1-ynyltributylstannane **2b** (3.56 g, 10 mmol): $bp_{0.1} \approx 40$ °C; yield 58%; ^1H NMR ($CDCl_3$) δ 1.00 (t, 3H, CH_3, $^3J_{HH}$ = 7.3 Hz), 1.62 (tq, 2H, CH_3CH_2, $^3J_{HH}$ = $^3J_{HH}$ = 7.3 Hz), 2.43 (t, 2H, $CH_2C{\equiv}C$, $^3J_{HH}$ = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 13.8 (q, CH_3, $^1J_{CH}$ = 125.6 Hz), 21.3 (t, CH_2, $^1J_{CH}$ = 129.6 Hz), 22.3 (t, CH_2, $^1J_{CH}$ = 126.0 Hz), 85.1 (t, CAs, $^3J_{CH}$ = 5.4 Hz), 117.4 (tt, $CH_2C{\equiv}C$, $^2J_{CH}$ = 9.8 Hz, $^3J_{CH}$ = 6.0 Hz).

((Trimethylsilyl)ethynyl)arsinous Dichloride (4c). This compound was prepared from arsenic trichloride (2.0 g, 11 mmol) and (2-(trimethylsilyl)eth-1-ynyl)tributylstannane **2c** (3.86 g, 10 mmol): $bp_{0.1} \approx 45$ °C; yield 53%; ^1H NMR ($CDCl_3$) δ 0.18 (s, 9H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 0.07 (q, $(CH_3)_3$), $^1J_{CH}$ = 120.0 Hz), 108.2 (s, CAs), 122.8 (m, SiC, $^3J_{CH}$ = 2.2 Hz).

(3-Methoxyprop-1-ynyl)arsinous Dichloride (4d). This compound was prepared from arsenic trichloride (2.0 g, 11 mmol) and (3-methoxyprop-1-ynyl)tributylstannane **2d** (3.59 g, 10 mmol): $bp_{0.1} \approx$ 50 °C; yield 43%; ^1H NMR ($CDCl_3$) δ 3.43 (s, 3H, CH_3), 4.31 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 58.6 (q, CH_3, $^1J_{CH}$ = 148.9 Hz), 60.3 (t, CH_2, $^1J_{CH}$ = 142.7 Hz), 90.9 (t, CAs, $^3J_{CH}$ = 5.5 Hz), 108.7 (t, CH_2C, $^2J_{CH}$ = 6.3 Hz).

Ethynylethylarsinous Chloride (4e). This compound was prepared from ethylarsenic dichloride (1.93 g, 11 mmol) and ethynyltributylstannane **2a** (3.15 g, 10 mmol). Distillation in vacuo of the volatile compounds gave a mixture containing ethynylethylarsinous chloride **4e** (yield (crude product): 35%) in the presence of impurities: $EtAsCl_2$ (40%), $EtAs(C{\equiv}CH)_2$ (20%). Purification of **4e** by trap-to-trap distillation led to a significant loss of product: $bp_{0.1} \approx 25$ °C; ^1H NMR

(1) Jutzi, P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 232−245. Becker, G.; Gutekunst, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 463−464. Klebach, T. C.; van Dongen, H.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 395−396. Grobe, J.; Le Van, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 710−711. Becker, G.; Gutekunst, G. *Z. Anorg. Allg. Chem.* **1980**, *470*, 144−156. Driess, M.; Pritzkow, H.; Sander, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 283−285.
(2) Märkl, G.; Sejpka, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 264.
(3) Guillemin, J. C.; Lassalle, L. *Organometallics* **1994**, *13*, 1525−1527.
(4) Guillemin, J. C.; Lassalle, L.; Dréan, P.; Wlodarczak, G.; Demaison, J. *J. Am. Chem. Soc.* **1994**, *116*, 8930−8936.
(5) Baumhardt, G. C. *Eng. Quim.* **1953**, *5*, 10−11; *Chem. Abstr.* **1954**, *48*, 3833a.
(6) Kuivila, H. G. *Synthesis* **1970**, 499−509.
(7) (a) Keinan, E.; Peretz, M. *J. Org. Chem.* **1983**, *48*, 5302−5309. (b) Aidhen, I. S.; Braslau, R. *Synth. Commun.* **1994**, *24*, 789−797.
(8) Logue, M. W.; Teng, K. *J. Org. Chem.* **1982**, *47*, 2549−2553.

0020-1669/95/1334-5694$09.00/0

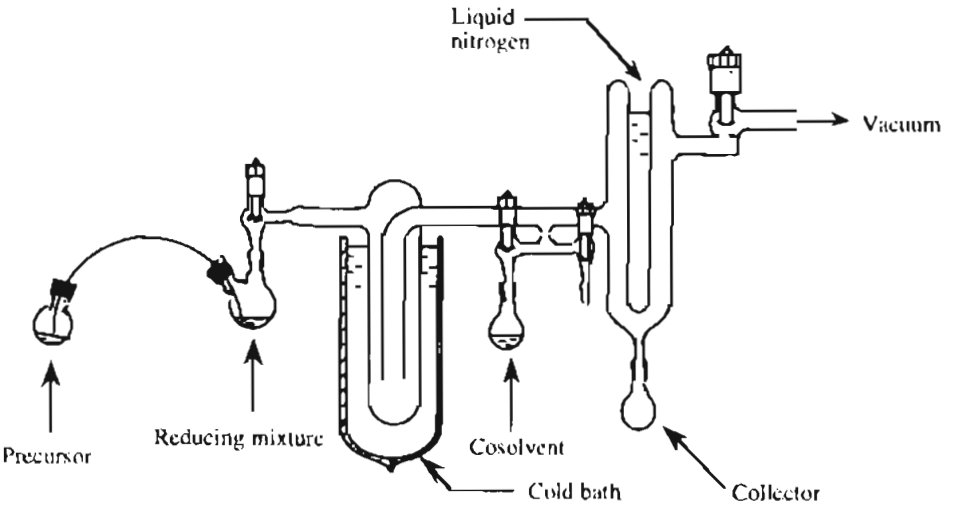


Figure 1.

($CDCl_3$) δ 1.39 (t, 3H, CH_3, $^3J_{HH}$ = 7.6 Hz), 2.18 (q, CH_2, 2H, $^3J_{HH}$ = 7.6 Hz), 3.12 (s, HC, 1H); ^{13}C NMR ($CDCl_3$) δ 9.3 (q, CH_3, $^1J_{CH}$ = 128.2 Hz), 29.6 (t, CH_2, $^1J_{CH}$ = 136.3 Hz), 84.4 (dt, As–$C\equiv$, $^2J_{CH}$ = 44.3 Hz, $^3J_{CH}$ = 4.6 Hz), 97.8 (d, $\equiv CH$, $^1J_{CH}$ = 246.9 Hz).

Allenylarsines (5a–c) and Alkynylarsines (6a–c,e). General Procedure.[9] In a 25 mL two-necked flask were introduced the tributylstannane (4.3 g, 15 mmol) and small amounts of a free-radical inhibitor (galvinoxyl or duroquinone). The flask was fitted on a vacuum line equipped with a stopcock, a cold trap, and a cold finger (Figure 1). The flask was cooled (−20 °C) and degassed; the appropriate chloroarsine (**3a–c**, **4a–c,e**) (4 mmol) was then slowly introduced with a microsyringe or a flexible needle. To limit oligomerization, the propadienylarsine (**5a–c**) or alkynylarsine (**6a–c,e**) was distilled off *in vacuo* from the reaction mixture during the course of the addition of **3** or **4**, respectively. High-boiling impurities were selectively condensed in a cold trap (−60 °C), and arsine **5** or **6** was 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 allowed to warm to room temperature. Compound **5** or **6** was collected in a Schlenk flask or in an NMR tube and was kept at low temperature (−50 °C). Low-temperature analysis showed the presence with the expected allenylarsine (**5a–c**) of propyne (≈10%), the corresponding prop-1-ynylarsine isomer (≈10%), and the corresponding arsine (≈20%) (AsH_3, $MeAsH_2$, or $EtAsH_2$, respectively). $EtAsH_2$ (≈25%) was also observed with **6e**. Purification of **5** and **6** by trap-to-trap distillation led to the pure compound with a significant loss of product. Attempts to prepare (3-methoxyprop-1-ynyl)arsine **6d** by this approach were unsuccessful.

Propadienylarsine (5a): $bp_{0.1} \approx -95$ °C; yield 61%; ^1H NMR ($CDCl_3$, −35 °C) δ 3.12 (dt, 2H, AsH_2, $^3J_{HH}$ = 5.1 Hz, $^5J_{HH}$ = 3.2 Hz), 4.52 (dt, 2H, CH_2, $^4J_{HH}$ = 6.7 Hz, $^5J_{HH}$ = 3.2 Hz), 5.39 (tt, 1H, CH, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 6.7 Hz); ^{13}C NMR ($CDCl_3$, −35 °C) δ 70.1 (dt, CH_2, $^1J_{CH}$ = 169.1 Hz, $^2J_{CH}$ = 7.6 Hz), 71.1 (td, CH, $^1J_{CH}$ = 168.3 Hz, $^2J_{CH}$ = 7.6 Hz), 210.8 (br s, $H_2C{=}C{=}CH$); HRMS ($M^{+\cdot}$) calcd for C_3H_5As 115.9607, found 115.961; *m/z* (%) 117 (1.1), 116 (43.2), 115 (21.8), 114 (14.0), 113 (21.5), 112 (17.9), 101 (61.1), 90 (16.8), 89 (26.7), 88 (21.4), 78 (10.7), 76 (13.6), 75 (13.0), 39 (82.9).

Propadienylmethylarsine (5b): $bp_{0.1} \approx -80$ °C, yield 33%; ^1H NMR ($CDCl_3$, −35 °C) δ 1.14 (d, 3H, CH_3, $^3J_{HH}$ = 7.0 Hz), 3.26 (qdt, 1H, AsH, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 4.4 Hz, $^5J_{HH}$ = 3.6 Hz), 4.58 (dd, 2H, CH_2, $^4J_{HH}$ = 6.8 Hz, $^5J_{HH}$ = 3.6 Hz), 5.45 (td, 1H, CH, $^4J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 4.4 Hz); ^{13}C NMR ($CDCl_3$, −35 °C) δ 1.01 (q, CH_3, $^1J_{CH}$ = 134.2 Hz), 69.3 (dm, CH, $^1J_{CH}$ = 173.2 Hz), 71.7 (td, CH_2, $^1J_{CH}$ = 168.4 Hz, $^2J_{CH}$ = 9.1 Hz), 208.0 (br s, $H_2C{=}C{=}CH$); HRMS ($M^{+\cdot}$) calcd for C_4H_7As 129.9764, found 129.977; *m/z* (%) 130 (38.9), 129 (16.1), 116 (17.3), 115 (95.3), 114 (17.6), 113 (25.2), 112 (16.3), 102 (49.2), 101 (45.5), 90 (23.0), 89 (67.8), 88 (13.8), 87 (17.1), 75 (9.3), 39 (55.9), 38 (10.0), 37 (10.3).

Propadienylethylarsine (5c): $bp_{0.1} \approx -70$ °C; yield 21%; ^1H NMR ($CDCl_3$, −35 °C) δ 1.28 (t, 3H, CH_3, $^3J_{HH}$ = 7.7 Hz), 1.74 (qd, 2H, CH_3CH_2, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 4.4 Hz), 3.33 (tdt, 1H, AsH, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 4.4 Hz, $^5J_{HH}$ = 3.0 Hz), 4.54 (dd, 2H, $C{=}CH_2$, $^4J_{HH}$ = 6.7 Hz, $^5J_{HH}$ = 3.0 Hz), 5.43 (td, 1H, $C{=}CH$, $^4J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 5.2 Hz); ^{13}C NMR ($CDCl_3$, −35 °C) δ 10.9 (t, CH_2, $^1J_{CH}$ = 130.8 Hz), 13.9 (q, CH_3, $^1J_{CH}$ = 126.0 Hz), 69.4 (dm, CH, $^1J_{CH}$ ≈ 170 Hz), 71.2 (td, CH_2, $^1J_{CH}$ = 167.7 Hz, $^2J_{CH}$ = 7.9 Hz), 209.0 (br s, $H_2C{=}C{=}CH$); HRMS ($M^{+\cdot}$) calcd for C_5H_9As 143.9920, found 143.992; *m/z* (%) 144 (11.3), 129 (8.6), 116 (39.4), 115 (30.7), 114 (18.8), 113 (10.4), 112 (6.6), 104 (31.3), 103 (17.3), 102 (9.8), 101 (21.4), 89 (18.0), 39 (16.7), 28 (100).

Prop-1-ynylarsine (6a): $bp_{0.1} \approx -100$ °C; yield 25%; ^1H NMR ($CDCl_3$, −35 °C) δ 1.89 (t, 3H, CH_3, $^5J_{HH}$ = 2.7 Hz), 3.30 (q, 2H, AsH_2, $^5J_{HH}$ = 2.7 Hz); ^{13}C NMR ($CDCl_3$, −35 °C) δ 5.6 (q, CH_3, $^1J_{CH}$ = 126.5 Hz), 63.4 (s, CAs), 101.6 (s, CH_3C); HRMS ($M^{+\cdot}$) calcd for C_3H_5As 115.9607; found 115.961; *m/z* (%) 116 (26.3), 115 (4.6), 113 (5.3), 112 (5.1), 101 (14.4), 89 (7.4), 77 (24.5), 75 (72.8), 36 (15.5).

Pent-1-ynylarsine (6b): $bp_{0.1} \approx -70$ °C; yield 19%; ^1H NMR ($CDCl_3$, −35 °C) δ 0.95 (t, 3H, CH_3, $^3J_{HH}$ = 7.3 Hz), 1.53 (tq, 2H, CH_3CH_2, $^3J_{HH}$ = $^3J_{HH}$ = 7.3 Hz), 2.19 (m, 2H, $CH_2C{\equiv}C$, $^3J_{HH}$ = 7.3 Hz, $^5J_{HH}$ = 1.0 Hz), 3.33 (t, 2H, AsH_2, $^5J_{HH}$ = 1.0 Hz); ^{13}C NMR ($CDCl_3$, −35 °C) δ 13.8 (q, CH_3, $^1J_{CH}$ = 125.6 Hz), 20.5 (t, CH_2, $^1J_{CH}$ = 123.9 Hz), 22.1 (t, CH_2, $^1J_{CH}$ = 125.6 Hz), 63.8 (s, CAs), 106.1 (br s, $CH_2{-}C$); HRMS ($M^{+\cdot}$) calcd for C_5H_9As 143.9920; found 143.992; *m/z* (%) 144 (5.0), 129 (4.0), 116 (8.0), 115 (5.8), 102 (5.3), 101 (6.5), 89 (5.7), 78 (67.9), 77 (15.9), 76 (100), 75 (23.3), 67 (7.0), 43 (5.6), 42 (12.7), 41 (20.7), 39 (11.4).

(Trimethylsilyl)ethynylarsine (6c): $bp_{0.1} \approx -65$ °C; yield 19%; ^1H NMR ($CDCl_3$, −35 °C) δ 0.17 (s, 9H, $(CH_3)_3$), 3.45 (s, 2H, AsH_2); ^{13}C NMR ($CDCl_3$, −35 °C) δ −0.02 (q, $(CH_3)_3$, $^1J_{CH}$ = 119.4 Hz), 93.3 (s, SiC), 113.3 (br s, CAs). Attempts to isolate compound **6c** in pure form to record its mass spectrum resulted in the formation of brown, arsenic-containing decomposition products and arsenic mirrors on the wall of the cell.

Ethynylethylarsine (6e): $bp_{0.1} \approx -80$ °C; yield 19%; ^1H NMR ($CDCl_3$, −35 °C) δ 1.40 (t, 3H, CH_3, $^3J_{HH}$ = 7.6 Hz), 1.81 (qd, 2H, CH_2, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 5.0 Hz), 2.51 (d, 1H, $HC{\equiv}C$, $^4J_{HH}$ = 2.7 Hz), 3.63 (td, 1H, AsH, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 2.7 Hz); ^{13}C NMR ($CDCl_3$, −35 °C) δ 10.9 (t, CH_2, $^1J_{CH}$ = 132.3 Hz), 13.9 (q, CH_3, $^1J_{CH}$ = 126.0 Hz), 77.9 (s, CAs), 92.5 (d, $HC{\equiv}C$, $^1J_{CH}$ = 245.1 Hz); HRMS ($M^{+\cdot}$) calcd for C_4H_7As 129.9764, found 129.977; *m/z* (%) 130 (45.5), 104 (14.3), 102 (26.3), 101 (52.5), 100 (100), 75 (9.2), 29 (15.8), 28 (13.2), 27 (16.7), 26 (6.6).

Propylidynearsine (7a). The reaction was performed under VGSR conditions.[10] Powdered and dried sodium carbonate (15 g) was introduced into a VGSR reactor (l = 30 cm, i.d. = 3.5 cm Pyrex tube)

(9) Similar experiments have already been described to prepare reactive species: (a) Cabioch, J. L.; Denis, J. M. *J. Organomet. Chem.* **1989**, *377*, 227–233. (b) Guillemin, J. C.; Savignac, P.; Denis, J. M. *Inorg. Chem.* **1991**, *30*, 2170–2173.

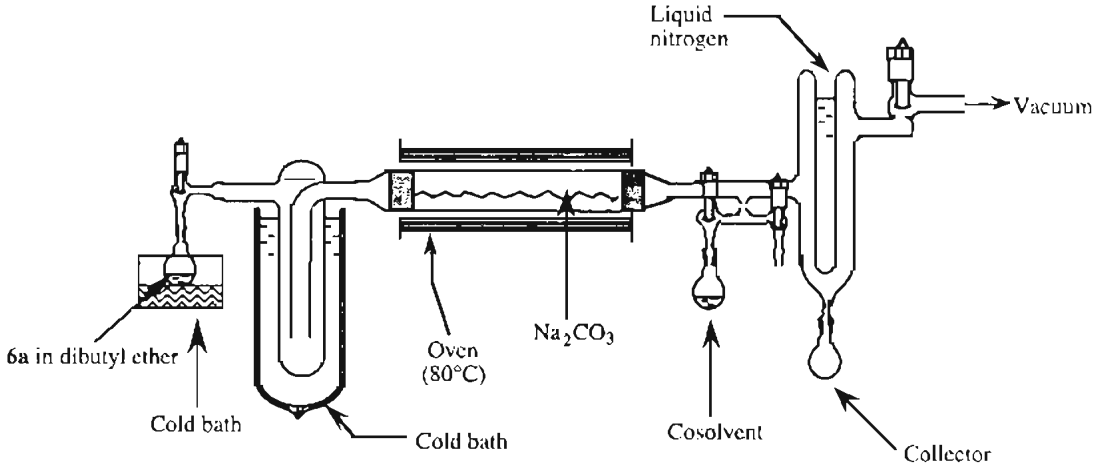


Figure 2.

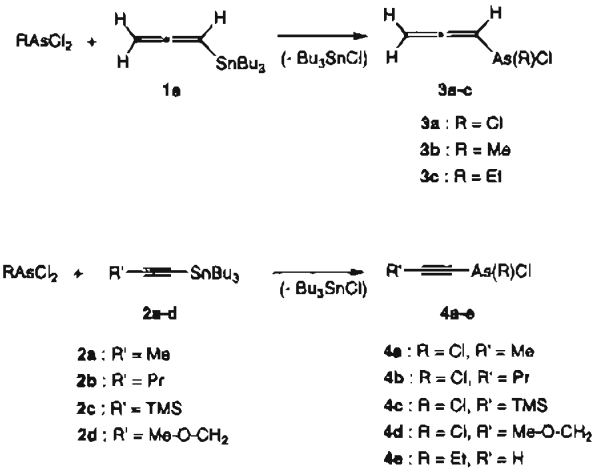
and then horizontally distributed between two pads of glass wool 20 cm apart. This reactor was fitted onto a vacuum line equipped with a cold trap and a cold finger (Figure 2). Propynylarsine **6a** (0.57 g, 5 mmol) diluted in dibutyl ether (10 mL) and cooled at −70 °C was fitted on the vacuum line. Pure propynylarsine was slowly vaporized *in vacuo* through the reactor heated at 80 °C. Propylidynearsine **7a** and a cosolvent were condensed on the cold finger (−196 °C). After disconnection from the vacuum line, the apparatus was filled with dry nitrogen and the cold finger was allowed to warm to room temperature. Compound **7a** was collected in a Schlenk flask or in an NMR tube and was kept at low temperature (−60 °C): $bp_{0.1} \approx -100$ °C; yield 15%; ^{1}H NMR ($CDCl_3$, −35 °C) δ 1.18 (t, 3H, CH_3, $^3J_{HH}$ = 7.4 Hz), 2.33 (q, 2H, CH_2, $^3J_{HH}$ = 7.4 Hz); ^{13}C NMR ($CDCl_3$, −35 °C) δ 15.0 (q, CH_3, $^1J_{CH}$ = 129.3 Hz), 31.6 (t, CH_2, $^1J_{CH}$ = 126.8 Hz), 204.2 (tm, $C{\equiv}As$, $^2J_{CH}$ = 11.6 Hz).

Results and Discussion

No allenylchloroarsine and only one alk-1-ynylchloroarsine[4] containing simple substituents have been described up to now.[11] The preparation of allenylchloroarsines **3a−c** was performed by addition at room temperature of allenyltributylstannane **1**[7] to arsenic trichloride or methyl- or ethyldichloroarsine, followed by 30 min of stirring at 60 °C. Low-temperature distillation in vacuo led to allenylchloroarsines **3a−c** in yields ranging from 49 to 75%, which are stable when kept in a freezer (Scheme 1). Pure alkynyldichloroarsines **4a−d** were easily and quickly prepared by stirring cooled arsenic trichloride with 0.9 equiv of alkynyltributylstannane **2a−d**. From ethyldichloroarsine and **2a**, crude compound **4e** was obtained in a moderate yield (Scheme 1). The presence of a radical inhibitor in the reaction mixture led to the recovery of the starting materials; this result seems to indicate that the reactions proceed *via* a radical reaction. Structures of **3a−c** and **4a−e** were determined by ^{1}H and ^{13}C NMR spectra. The spectra are characteristic of allenyl and acetylenic derivatives, respectively.

The chemoselective reduction of chloroarsines **3** and **4** to the corresponding allenyl- **5** and alkynylarsines **6** was a difficult step: the reducing agent must reduce the As−Cl bond but not react with the carbon−carbon multiple bond of precursors (**3**, **4**) or products (**5**, **6**). The use of tributylstannane[12] as reducing agent had given good results in the preparation of vinylarsines[3]

Scheme 1



and of ethynylarsine.[4] In the same way, we can synthesize allenylarsine **5a** in a 35% yield by reduction of **3a** with Bu_3SnH. However, attempts to prepare allenylarsines **5b−c** and substituted alkynylarsines **6a−e** by a similar approach were unsuccessful and only led to the observation of traces of product, arsine (AsH_3 (**6a−d**), $MeAsH_2$ (**5b**), or $EtAsH_2$ (**5c**, **6e**)), and the corresponding alkyne. The breaking of a carbon−heteroatom bond is usually performed by stannanes in the presence of radical activation (AIBN, UV),[13,14] and this reaction has largely been used to break C−Se[13] and C−S bonds.[14] A similar radical reaction probably occurred with the α-unsaturated chloroarsines in the presence of tributylstannane and promoted the formation of byproducts.[15]

We have observed that the addition of small amounts of a radical inhibitor (galvinoxyl or duroquinone) to Bu_3SnH inhibited the breaking of the C−As bond and led to the formation of the allenylarsines **5a−c** and alkynylarsines **6a−c,e** in

(10) For a review on vacuum gas−solid reaction (VGSR) experiments, see: Billups, W. E.; McCord, D. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1332−1343.

(11) Some allenyl- and alkynylchloroarsines bearing bulky substituents have been described: Märkl, G.; Reithinger, S. *Tetrahedron Lett.* **1990**, *31*, 6331−6334. Yagudeev, T. A.; Dzhakiyaev, G. M.; Nurgalieva, A. N.; Godovikov, N. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 933−935; *Chem. Abstr.* **1982**, *97*, 55935s.

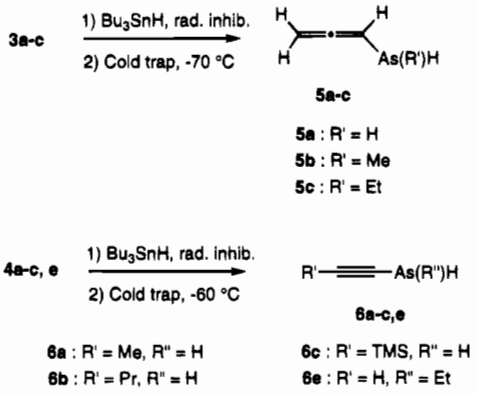
(12) We recently reported the use of this reducing agent to prepare α-unsaturated heterocompounds: Janati, T.; Guillemin, J. C.; Soufiaoui, M. *J. Organomet. Chem.* **1995**, *486*, 57−62 and refs 3 and 4.

(13) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438−4447.

(14) McIntosch, J. M.; Schram, C. K. *Can. J. Chem.* **1977**, *55*, 3755−3757.

(15) Using Bu_3SnH, similar breaking of sp^3- or sp-carbon−heteroatom bonds has already been observed in the preparation of α-unsaturated stannanes and stibines: Lassalle, L.; Janati, T.; Guillemin, J. C. *J. Chem. Soc., Chem. Commun.* **1995**, 699−700. Legoupy, S.; Lassalle, L.; Guillemin, J. C.; Metail, V.; Senio, A.; Pfister-Guillouzo, G. *Inorg. Chem.* **1995**, *34*, 1466−1471.

Scheme 2

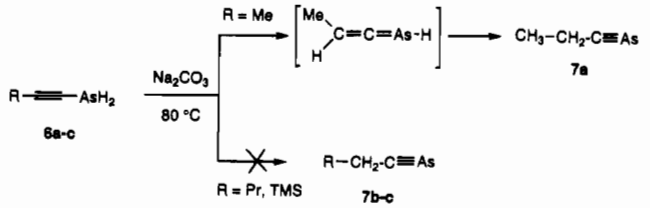


reasonable yields (19−61%) (Scheme 2). However, from **4d**, under these conditions, only the methoxypropyne was observed; this result can be explained by the presence of the ether function, which could promote the formation of radicals. To limit oligomerization, compounds **5a−c** and **6a−c,e** were distilled off *in vacuo* from the cooled reaction mixture (−20 °C) during the course of the addition of **3a−c** and **4a−c,e** and separated from less volatile compounds by a cold trap (−70 °C) before condensation (−196 °C). Except for **6c**, further purification by trap-to-trap distillation could then be performed to remove the corresponding alkynes and arsines (AsH_3, $MeAsH_2$, or $EtAsH_2$).

Arsines **5** and **6** have been characterized on the basis of their spectral data (low-temperature (−35 °C) ^1H and ^{13}C NMR spectroscopy and mass spectrometry). The ^1H and ^{13}C NMR data observed for **5a−c** and **6a−c,e** are similar to those reported for the corresponding alkynyl- and allenylphosphines.[9b,16] Only the hydrogen(s) on the arsenic atom presents (present) a signal at higher field and a $^3J_{HH}$ coupling constant lower than those of the corresponding phosphorus derivatives. This can be attributed to the difference in covalent radius and electronegativity between the arsenic and phosphorus heteroatoms.[17]

We have studied the rearrangement of the alkynylarsines **6a−c** into the corresponding arsaalkynes. The propylidynearsine **7a** was obtained in a 15% yield by base-induced rearrangement of the propynylarsine **6a** on solid sodium carbonate under VGSR conditions (Scheme 3).[10] Characteristic is the ^{13}C NMR signal for the carbon of the As≡C bond (δ: 204.2 ppm), which by its position at very low field reflects the sp hybridization of the carbon and the effect of the neighboring arsenic.[18] Compound **7a** is the third arsaalkyne isolated up to now. However,

Scheme 3



this approach is not general and all attempts to prepare pentylidynearsine **7b** and (trimethylsilyl)ethylidynearsine **7c** under similar conditions failed (Scheme 3). Numerous bases (Li_2CO_3, K_2CO_3, NaOH, KOH, ...) were used but only oligomeric compounds were obtained when the products condensed with $CDCl_3$ as cosolvent on the cold finger were allowed to warm (≈−50 °C). This result cannot be explained by the kinetic instability of the products since pentylidynearsine **7b** and (trimethylsilyl)ethylidynearsine **7c** are probably more stable than the less substituted derivatives **7a** and $CH_3C{\equiv}As$[4] we obtained. A plausible mechanism for the rearrangement **6** → **7** involves the corresponding arsaallene as intermediate; the highly reactive arsaallene could be present in a higher ratio in the rearrangement products of the substituted derivatives **7b,c** and promote the oligomerization we observed. The lower yield of **7a** relative to ethylidynearsine[4] and the presence of insoluble brown materials are consistent with this hypothesis.

The arsines **5a−c**, **6a−c,e** and **7a** exhibit low stability even when kept under nitrogen at room temperature in deuteriochloroform ($\tau_{1/2}$: 30 min) and are not significantly more stable in the presence of a radical inhibitor. An insoluble red or brown arsenic-containing material was slowly formed under these conditions.

In summary, the synthesis of volatile allenyl- and alkynylarsines can be performed by the chemoselective reduction of the corresponding chloroarsines. The primary alk-1-ynylarsines are potential precursors of the corresponding arsaalkynes. However, the synthesis of the latter by this approach seems to be limited to the more volatile compounds. In comparison with the preparation of the easily available corresponding phosphorus derivatives,[19] the synthesis of unstabilized carbon−arsenic multiple-bond compounds is still a challenge.

Acknowledgment. A part of these experiments were performed in the Laboratoire de Physicochimie Structurale (Université de Rennes 1). We thank the Programme National de Planétologie (INSU-CNRS) for financial support.

IC9503747

(16) Guillemin, J. C.; Janati, T.; Denis, J. M.; Guenot, P.; Savignac, P. *Tetrahedron Lett.* **1994**, *35*, 245−248.
(17) Sanderson, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 2259−2261.
(18) Schäfer, W.; Schweig, A.; Dimroth, K.; Kanter, H. *J. Am. Chem. Soc.* **1976**, *98*, 4410−4418.
(19) Guillemin, J. C.; Janati, T.; Guenot, P.; Savignac, P.; Denis, J. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 196−198. Guillemin, J. C.; Janati, T.; Denis, J. M. *J. Chem. Soc., Chem. Commun.* **1992**, 415−416.