Primary and Secondary Vinylarsines: Synthesis, Stability and Characterization

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Primary and Secondary Vinylarsines: Synthesis, Stability, and Characterization

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*Summary: Primary unsaturated arsines, vinylarsine (**1a**), isopropenylarsine (**1b**), (Z + E)-prop-1-enylarsine (**1c**), and secondary divinylarsine (**1d**) are synthesized by reaction of arsenic trichloride with vinyltributylstannane derivatives **2a–c** followed by a chemoselective reduction of the corresponding chloroarsines **3a–d**. Compounds **1a–d** are characterized from their spectral data and tungsten complex derivative (**1a**). The arsines 1 exhibit a low stability at room temperature even in a solvent ($\tau_{1/2}$ ca. 30 min).*

Although many studies have been carried out on vinyl alcohols,[1] ethenethiols,[2] vinylamines,[3] and vinylphosphines,[4,5] the corresponding primary and secondary vinylarsines have been only postulated as intermediates.[6] It is thus of interest to synthesize these species and to define their spectroscopic characteristics and their stability. Moreover, vinylarsines are of synthetic importance in the field of coordination chemistry[7] and can be considered as potential precursors of the corresponding arsaalkenes.[8] We report here the synthesis of ethenylarsine (**1a**), its spectral identification, and the corresponding tungsten complex. Also described is the preparation and characterization of some substituted derivatives **1b–d**.

Experimental Section

Caution: *Arsines are potentially highly toxic molecules. All reactions and handling should be carried out in a well-ventilated hood.*

Materials. Arsenic chloride was purchased from Strem; bis(2-ethoxyethyl) ether and decahydronaphthalene were purchased from Janssen. All chemicals were used without further purification. Ethenyltributylstannanes[9,10] and tributylstannane[11] were prepared as previously reported.

General. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 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. Special equipment was used for recording the IR spectrum of **1a–d** 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 filled with pure ethenylarsine to a pressure of 100 mbar. To record the mass spectrum, ethenylarsine 1 was directly introduced from a cell into the ionization chamber of the spectrometer.

Ethenyldichloroarsines 3a–c. General Procedure. In a two-necked round-bottomed flask equipped with a nitrogen inlet, were introduced $AsCl_3$ (1.8 g, 10 mmol), ethenyltributylstannane **2a–c** (10.5 mmol), and catalytic amounts of azobis(isobutyronitrile) (AIBN). Thus, the mixture was stirred 3 h at 60 °C. Distillation *in vacuo* led to pure vinyldichloroarsine **3a–c**.

Ethenyldichloroarsine (3a).[12] Yield: 82%. Bp: 61 °C/40 mmHg. ^{1}H NMR ($CDCl_3$): δ 6.08 (d, 1H, $^3J_{HH}$ = 18.8 Hz), 6.15 (d, 1H, $^3J_{HH}$ = 11.3 Hz), 7.21 (dd, 1H, $^3J_{HH}$ = 18.8 Hz, $^3J_{HH}$ = 11.3 Hz). ^{13}C NMR ($CDCl_3$): δ 130.3 ($^1J_{CH}$ = 160.4 Hz (t)), 146.3 ($^1J_{CH}$ = 170.2 Hz (d)).

(1-Methylethenyl)dichloroarsine (3b). Yield: 85%. Bp: 78 °C/40 mmHg. ^{1}H NMR ($CDCl_3$): δ 2.29 (3H, t, $^4J_{HH}$ = 1.3 Hz), 5.72 (q, 1H, $^4J_{HH}$ = 1.3 Hz), 5.79 (q, 1H, $^4J_{HH}$ = 1.3 Hz). ^{13}C NMR ($CDCl_3$): δ 18.3 ($^1J_{CH}$ = 129.2 Hz (q)), 125.9 ($^1J_{CH}$ = 160.4 Hz (t)), 154.4 ($^2J_{CH}$ = 7.2 Hz (q)). HRMS for $(C_3H_5AsCl_2)^{\bullet+}$: calcd 185.8984; found 185.897. Anal. Calcd for $C_3H_5AsCl_2$: C, 19.28; H, 2.70. Found: C, 18.89; H, 2.50.

(Z + E)-Prop-1-enyldichloroarsine (3c) (Z/E: 3/1). Yield: 86%. Bp: 81 °C/40 mmHg. (*Z*): ^{1}H NMR ($CDCl_3$) δ 2.03 (dd, 3H, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.4 Hz), 6.54 (dq, 1H, $^3J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 7.1 Hz), 6.87 (dq, 1H, $^3J_{HH}$ = 10.8 Hz, $^4J_{HH}$ = 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 18.1 ($^1J_{CH}$ = 127.2 Hz (q)), 139.9 ($^1J_{CH}$ = 163.7 Hz (d)), 142.9 ($^1J_{CH}$ = 155.3 Hz (d). (*E*): ^{1}H NMR ($CDCl_3$) δ 1.99 (dd, 3H, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.5 Hz), 6.48 (dq, 1H, $^3J_{HH}$ = 19.4 Hz, $^3J_{HH}$ = 6.6 Hz), 6.92 (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 ($^1J_{CH}$ = 168.6 Hz (d)), 144.2 ($^1J_{CH}$ = 152.7 Hz (d)). HRMS for $(C_3H_5AsCl_2)^{\bullet+}$: calcd 185.8984; found 185.898. Anal. Calcd for $C_3H_5AsCl_2$: C, 19.28; H, 2.70. Found: C. 18.95; H, 2.46.

Diethenylchloroarsine (3d).[12] Compound **3d** was prepared starting from 1 equiv of $AsCl_3$ and 2.1 equiv of ethenyltributylstannane (**2a**) in the presence of catalytic amounts of AIBN. Heating at 70 °C during 12 h followed by distillation led to **3d**. Yield: 67%. Bp: 105 °C/760 mmHg. ^{1}H NMR ($CDCl_3$): δ 5.91 (d, 2H, $^3J_{HH}$ = 18.6 Hz), 6.05 (d, 2H, $^3J_{HH_{cis}}$ = 11.4 Hz), 6.87 (dd, 2H, $^3J_{HH}$ = 18.6 Hz, $^3J_{HH}$ = 11.4 Hz). ^{13}C NMR

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($CDCl_3$): δ 130.0 ($^1J_{CH}$ = 159.4 Hz (t)), 141.9 ($^1J_{CH}$ = 164.4 Hz (d)).

Ethenylarsines 1. General Procedure. The apparatus already described for the reduction of phosphonates was used.[5] The flask containing the reducing mixture (30 mmol of Bu_3SnH in 20 mL of decahydronaphthalene) was cooled at −20 °C, fitted on a vacuum line, and degassed. Then, the ethenylchloroarsine **3** (10 mmol in 5 mL of decahydronaphthalene) was slowly added (10 min) at room temperature with a flex-needle through the septum. During and after the addition, ethenylarsine **1** and the carried away solvent were condensed into a cold trap (−120 °C). When the reaction was complete (20 min), the cold trap was allowed to warm to −60 °C and the volatile species were condensed with a cosolvent onto the cold finger (77 K). After disconnection 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 and characterized by spectroscopy.

Ethenylarsine (1a). Yield: 55%. ^1H NMR ($CDCl_3$, −30 °C): δ 3.00 (ddd, 2H, $^3J_{HH}$ = 4.4 Hz), 5.81 (ddt, 1H, $^3J_{HH_{trans}}$ = 18.5 Hz, $^2J_{HH}$ = 1.7 Hz, $^4J_{HH}$ = 1.7 Hz), 5.92 (ddt, 1H, $^3J_{HH_{cis}}$ = 11.2 Hz, $^2J_{HH}$ = 1.7 Hz, $^4J_{HH}$ = 1.1 Hz), 6.59 (ddt, 1H, $^3J_{HH_{trans}}$ = 18.5 Hz, $^3J_{HH_{cis}}$ = 11.2 Hz, $^3J_{HH}$ = 4.4 Hz). ^{13}C NMR ($CDCl_3$, −30 °C): δ 126.2 (dm, $^1J_{CH}$ = 160.8 Hz), 131.5 (tdd, $^1J_{CH}$ = 157.3 Hz, $^2J_{CH}$ = $^3J_{CH}$ = 7.6 Hz). HRMS for $(C_2H_5As)^{\bullet+}$: calcd 103.9607; found 103.960. MS, *m/z* (%): 104 (47.4), 103 (6.0), 102 (100), 101 (44.2), 100 (17.9), 76 (24.9), 75 (18.5). IR (gaseous phase, cm^{-1}) $\nu_{=CH}$ 3060 (m), ν_{As-H} 2100 (s), $\nu_{C=C}$ 1591 (m).

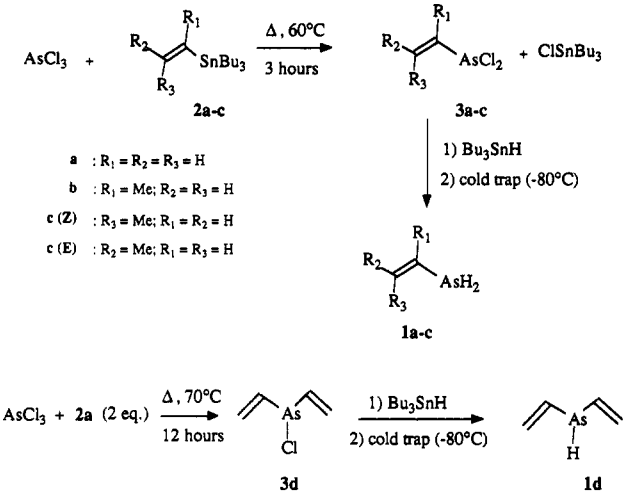
(1-Methylethenyl)arsine (1b). Yield: 52%. ^1H NMR ($CDCl_3$, −30 °C): δ 2.11 (m, 3H, $^4J_{HH}$ = 1.6 Hz), 3.03 (m, 2H), 5.29 (1H, m, $^4J_{HH}$ = 1.0 Hz, $^2J_{HH}$ = 1.6 Hz), 5.45 (dq, 1H, $^2J_{HH}$ = $^4J_{HH}$ = 1.6 Hz). ^{13}C NMR ($CDCl_3$, −30 °C): δ 30.8 ($^1J_{CH}$ = 126.9 Hz (q)), 125.7 ($^1J_{CH}$ = 153.9 Hz (t)), 138.8. HRMS for $(C_3H_7As)^{\bullet+}$: calcd 117.9764; found 117.976. MS, *m/z* (%): 118 (74.7), 116 (15.5), 101 (33.5), 90 (100), 89 (24.3), 75 (12.7), 41 (74.8). IR (gaseous phase, cm^{-1}): $\nu_{=CH}$ 3055 (m), ν_{As-H} 2095 (s).

(*Z* + *E*)-Prop-1-enylarsine (1c). Yield: 62% (*Z*/*E*: 3/1). (Z): ^1H NMR ($CDCl_3$, −30 °C) δ 1.77 (ddt, 3H, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = $^5J_{HH}$ = 1.2 Hz), 2.77 (m, 2H, $^3J_{HH}$ = 3.9 Hz), 6.15 (dm, 1H, $^3J_{HH_{cis}}$ = 10.8 Hz), 6.30 (dqt, 1H, $^3J_{HH_{cis}}$ = 10.8 Hz, $^3J_{HH}$ = 6.5 Hz, $^3J_{HH}$ = 3.9 Hz); ^{13}C NMR ($CDCl_3$, −30 °C) δ 17.6 ($^1J_{CH}$ = 125.9 Hz (q)), 116.5 ($^1J_{CH}$ = 163.7 Hz (d)), 139.5 ($^1J_{CH}$ = 154.8 Hz (d)); IR (gaseous phase, cm^{-1}) $\nu_{=CH}$ 3010 (m), ν_{As-H} 2090 (s), $\nu_{C=C}$ 1615 (w). (E): ^1H NMR ($CDCl_3$, −30 °C) δ 1.77 (dd, 3H, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = $^5J_{HH}$ = 1.2 Hz), 2.89 (m, 2H), 6.15 (m, 1H), 6.30 (m, 1H); ^{13}C NMR ($CDCl_3$, −30 °C) δ 21.8 ($^1J_{CH}$ = 126.5 Hz (q)), 116.3 ($^1J_{CH}$ = 163.7 Hz (d)), 142.9 ($^1J_{CH}$ = 155.1 Hz (d)). HRMS (*Z* + *E*) for $(C_3H_7As)^{\bullet+}$: calcd 117.9764; found 117.976. MS, *m/z* (%): 118 (23.1), 116 (9.2), 101 (12.5), 90 (78.5), 89 (29.4), 76 (56.2), 75 (19.8), 43 (69.7), 41 (100).

Diethenylarsine (1d). Yield: 65%. ^1H NMR ($CDCl_3$, −30 °C): δ 4.00 (m, 1H, $^3J_{HH}$ = 4.1 Hz), 5.73 (ddd, 2H, $^3J_{HH_{trans}}$ = 18.5 Hz, $^2J_{HH}$ = $^4J_{HH}$ = 1.6 Hz), 5.95 (ddd, 2H, $^3J_{HH_{cis}}$ = 11.3 Hz, $^2J_{HH}$ = 1.6 Hz, $^4J_{HH}$ = 1.0 Hz), 6.63 (ddd, 2H, $^3J_{HH_{trans}}$ = 18.5 Hz, $^3J_{HH_{cis}}$ = 11.3 Hz, $^3J_{HH}$ = 4.1 Hz). ^{13}C NMR ($CDCl_3$, −30 °C): δ 129.9 ($^1J_{CH}$ = 157.6 Hz (t), $^3J_{CH}$ = 7.0 Hz (d)), 132.7 ($^1J_{CH}$ = 162.8 Hz (d)). HRMS for $(C_4H_7As)^{\bullet+}$: calcd 129.9764; found 129.976. MS, *m/z* (%): 130 (26.0), 115 (27.8), 102 (100), 101 (69.6), 100 (13.2), 75 (11.5). IR (gaseous phase, cm^{-1}): $\nu_{=CH}$ 3070 (m), ν_{As-H} 2095 (s), $\nu_{C=C}$ 1590 (w).

(Ethenylarsine)pentacarbonyltungsten (4). In a Pyrex two-necked round-bottomed flask equipped with a nitrogen inlet and a magnetic stirrer, were introduced tungsten hexacarbonyl (0.46 g, 1.3 mmol) and tetrahydrofuran (100 mL). The mixture was photolyzed 3 h through the Pyrex wall with a medium pressure mercury lamp. To this solution was added a cooled (−30 °C) THF (10-mL) solution of arsine **1a** (1 mmol). The mixture was slowly allowed to warm to room temperature and stirred overnight. Concentration *in vacuo* led to crude (ethenylarsine)-pentacarbonyltungsten (**4**). Attempts to purify it by silica gel chromatography only led to decomposition products (yield (crude product): 47%). ^1H NMR ($CDCl_3$, −30 °C): δ 4.34 (d, 2H, $^3J_{HH}$ = 3.2 Hz), 5.96 (dt, 1H, $^3J_{HH_{trans}}$ = 18.0 Hz, $^4J_{HH}$ = 1.1 Hz), 6.10 (dm, 1H, $^3J_{HH_{cis}}$ = 10.8 Hz), 6.50 (ddt, 1H, $^3J_{HH}$ = 18.0 Hz, $^3J_{HH_{cis}}$ = 10.8 Hz, $^3J_{HH}$ = 3.2 Hz). ^{13}C NMR ($CDCl_3$, −30 °C): δ 122.8 ($^1J_{CH}$ = 168.2 Hz (d)), 134.1 ($^1J_{CH}$ = 159.6 Hz (t)), 196.0, 198.6.

Scheme 1



Results and Discussion

The vinylarsenic dichlorides **3a–c** are prepared in very good yields (≈85%) upon heating arsenic trichloride to 60 °C with 1 equiv of vinyltributylstannane **2a–c**[9,10] in the presence of catalytic amounts of azobis(isobutyronitrile) (Scheme 1).[13] Divinylarsenic chloride (**3d**) is obtained by a similar approach starting from $AsCl_3$ and 2 equiv of **2a**. Compounds **3a–d**[12] are purified by distillation under reduced pressure, and the structures are determined by ^1H and ^{13}C NMR spectroscopy.

When the reduction of chlorovinylarsines **3a–d** is performed using lithium aluminum hydride,[14] a complex mixture containing alkylated arsines and AsH_3 is obtained. The reduction is found to be chemoselective using tributylstannane (Bu_3SnH) without solvent or diluted in a high boiling solvent like bis(2-ethoxyethyl) ether or decahydronaphthalene; in these conditions, only arsines **1a–d** are formed (Scheme 1).[15] To limit their decomposition, compounds **1a–d** are distilled off *in vacuo* from the cooled reaction mixture (−20 °C) during the course of the addition of **3a–d** and separated from the carried away solvent by a cold trap (−60 °C) before condensation (77 K). Arsines **1a–d** are obtained in a essentially pure form in *ca.* 60% yields and characterized by low temperature ^1H and ^{13}C NMR spectroscopy. The ^1H NMR data allow an unambiguous structural assignment, since the chemical shifts and coupling constants are typical of vinylarsenic derivatives.[16] We give as an example the NMR data of the parent compound **1a** (Chart 1): the chemical shifts of the vinylic protons are observed between 5.8 and 6.6 ppm ($^3J_{H_aH_c}$ = 18.5 Hz and $^3J_{H_bH_c}$ = 11.2 Hz) and the signals corresponding to the sp^2 carbons at δ_{C_2} (126.2 ppm) and δ_{C_1}: (131.5 ppm). The presence of vinylarsines **1a–d** is confirmed by the observation of the corresponding molecular ion by high resolution mass spectrometry (HRMS).

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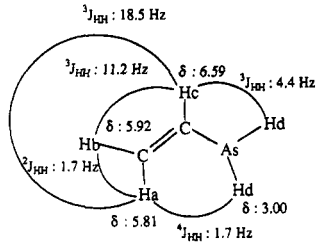
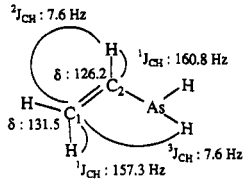
(16) Goedken, V. L.; Brough, L. F.; Rees, W. S., Jr. *J. Organomet. Chem.* **1993**, *449*, 125.

Chart 1

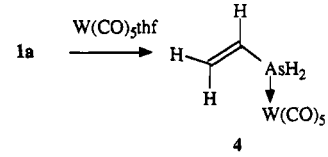


^{1}H NMR chemical shifts and coupling constants of **1a**



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

Compounds **1** are also identified by the infrared absorptions [**1a**: (gas phase, 100 mbar) ν_{As-H} 2100 cm^{-1} and $\nu_{C=C}$ 1591 cm^{-1}]. Treatment of **1a** in THF with (tetrahydrofuran)pentacarbonyltungsten leads to complex **4** which is characterized spectroscopically (eq 1).



(1)

Arsines **1a–d** exhibit a low stability at room temperature even when kept under nitrogen in a solvent (half-life ≈ 30 min). An insoluble brown polymeric material is slowly formed under these conditions.

In conclusion, we have developed a mild synthesis of primary and secondary vinylarsines, unknown so far. Extension of this approach to the preparation of other unstabilized arsenic derivatives is currently under progress.

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Supplementary Material Available: Figures of the ^{1}H and ^{13}C NMR spectra of the vinylarsines **1** (15 pages). Ordering information is given on any current masthead page.

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