Synthesis of Allenyl- and Alkynyl-stannanes by Reduction of Allenyl- and Alkynyl-chlorostannanes

Laurent Lassalle, Tajdine Janati and Jean-Claude Guillemin*†

Groupe de Physicochimie Structurale, URA CNRS No. 704, 35042 Rennes, France

Allenyl- **1a,b** and alkynyl-stannanes **2a–c** are synthesized by reaction of the corresponding allenyl- and alkynyl-tributylstannanes with tin tetrachloride or dichlorodimethylstannane followed by a chemoselective reduction of the formed chlorostannanes with tributylstannane in the presence of duroquinone or galvinoxyl, a radical inhibitor.

Compounds containing a heteroatom bonded to hydrogen atoms and to an α-unsaturated system have been the subject of numerous recent investigations. The preparation of primary allenyl and alkynyl derivatives of oxygen,[1,2] sulfur,[3] nitrogen,[4] phosphorus[5] and arsenic[6] have been reported. The interactions between the unsaturated substituent, the hydrogen(s) on the heteroatom and the heteroatom itself lead to the particular properties of these molecules. As an example, the very high acidity of phenylethynylamine or ethynol[1] has been evidenced. Particular emphasis was focussed on the first, second and third derivatives of group 15[4–6] and 16[1–3] elements of the Periodic Table. In contrast, little work has been done on the other elements. Thus, free primary, secondary or tertiary allenyl- and alkynyl-stannanes have not previously been described, and only a nickel-complexed alkynylstannane[7] has been prepared. We report here the synthesis and the characterization of the two parent compounds, allenylstannane **1a** and ethynylstannane **2a**, prepared by a two-step sequence involving the synthesis of the corresponding allenyl- and alkynyl-chlorostannanes and the subsequent chemoselective reduction of these derivatives. Three substituted derivatives are also described.‡

Preparations of allenyl- and alk-1-ynyl-halogenostannanes have been reported.[8,9] Such compounds quickly led, by disproportionation, to mixtures of products, and consequently were never obtained in pure form. We have prepared allenyl- **3a** and alkynyl-chlorostannanes **4a,b**§ by addition of the corresponding allenyl- **5a** or alkynyl-tributylstannane **6a,b** to a stoichiometric amount of frozen (−40 °C) tin tetrachloride; the solution was then vigorously shaken and allowed to warm to room temperature over 10 min. Distillation *in vacuo* at room temperature led to **3a** and **4a,b** in *ca.* 80% yield and *ca.* 90% purity. The dimethyl derivatives **3b** and **4c** were prepared by a similar approach, but the mixture was heated for 45 min at 50 °C before distillation (Scheme 1). Compounds **3a,b** and **4a–c** were characterized on the basis of spectral data (^{1}H and ^{13}C NMR).

Several attempts were then made to reduce **3** and **4** to the corresponding stannanes **1** and **2**. The use of reducing agents like LAH or dichloroalane ($AlHCl_2$)[5b] in an ethereal solution led to the production of traces of the expected products in the presence of the corresponding stannane (SnH_4 or Me_2SnH_2) and allene or alkyne. The allenylstannanes **1a,b** were obtained in *ca.* 20% yield starting from **3a,b**, respectively, and using Bu_3SnH as reducing agent.[10] Under similar conditions, the reduction of alkynylchlorostannanes **4a–c** only led to the detection (^{1}H NMR) of compounds **2a–c**, respectively (yield 2–5%). However, the reduction of **3** or **4** with Bu_3SnH in the presence of small amounts of duroquinone or galvinoxyl, a radical inhibitor, led to the obtention of pure allenylstannanes **1a,b** and alk-1-ynylstannanes **2a–c** in a reasonable yield (33–63%; Scheme 2);¶ the breaking of the C–Sn bond probably proceeds *via* a radical reaction. To limit their decomposition, **1** and **2** were distilled off *in vacuo* from the cooled reaction mixture (−10 °C) during the course of the addition of **3** or **4** and separated from impurities by a cold trap (−60 °C) before condensation (−196 °C). Several mmol of **1a,b** or **2a–c** can be prepared easily.‖

Allenyl- **1a,b** and alkynyl-stannanes **2a–c** have been characterized by ^{1}H, ^{13}C and ^{119}Sn NMR and HRMS.** The ^{1}H and ^{13}C NMR data allow an unambiguous structural assignment, since the chemical shifts and coupling constants are typical of stannanes[10b] and allenic[2,5b] or acetylenic derivatives.[5,6] An upfield shift is observed for the ^{119}Sn NMR signal of alkynylstannane **2a**, δ −420.6 (the ethyl-, ethenyl- or phenylstannane are observed at $\delta_{^{119}Sn}$ −282,[11] −361,[10b] −320,[12] respectively). The presence of the triple bond also leads to an increase in the value of the $^1J_{^{119}SnH}$ coupling constant (**2a**: $^1J_{SnH}$ 2242.4 Hz) in comparison with those usually observed for alkyl- or aryl-stannanes and shows an important s character of the Sn–H bonds for **2a**.[13] The two methyl substituents bonded to the tin atom lead, by their donor effect, to a lower coupling constant for **2c** ($^1J_{SnH}$ 1964.2 Hz). The presence of **1** and **2** is confirmed by the observation of the corresponding molecular ions by HRMS.

Allenyl- **1a,b** and alkynyl-stannanes **2a–c**, which are very unstable species in pure form at room temperature, can be kept indefinitely in solution at −40 °C. Their half-life at room temperature in benzene ranges from one to several hours and is dependent on the substitution on the tin atom, the dialkyl derivatives **1b** and **2c** being more stable than the parent compounds **1a** and **2a**. A black material is slowly formed under these conditions.

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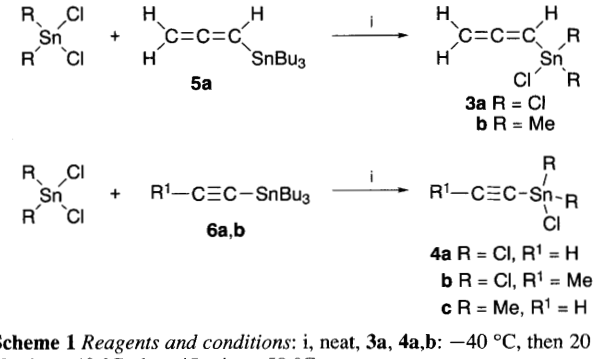
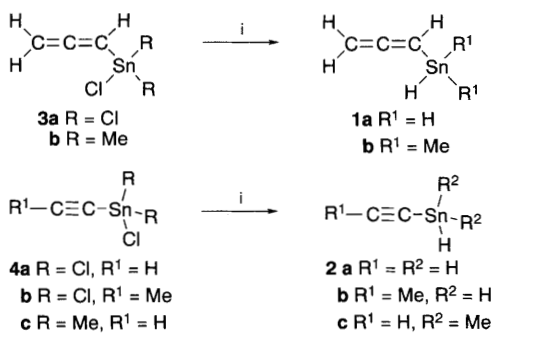


Scheme 1 *Reagents and conditions*: i, neat, **3a**, **4a,b**: −40 °C, then 20 °C; **3b**, **4c**: −40 °C, then 45 min at 50 °C



Scheme 2 *Reagents and conditions*: i, Bu_3SnH, radical inhibitor

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Footnotes

† *Present address*: Laboratoire de Synthèse Organique Biologique, URA CNRS No. 1467, ENSCR, 35700 Rennes, France.

‡ **CAUTION**: low-boiling stannanes are potentially toxic molecules. All reactions and handling should be carried out in a well-ventilated hood.

§ The reaction of ethynyltributylstannane on tin tetrachloride has already been reported [ref. 9(*d*)] and led to the spectroscopic characterization of compound **4a** in the crude mixture.

¶ Otherwise, the use of tributylstannane in the presence of a radical inhibitor can lead to a retardant effect (ref. 14), a different stereoselectivity or chemoselectivity of the reactions (ref. 15 and 16, respectively).

‖ *General procedure*: A two-necked flask containing the reducing mixture (30 mmol of Bu_3SnH and small amounts of duroquinone or galvinoxyl) was cooled at −10 °C, fitted on a vacuum line and degassed. The chlorostannane **3,4** (5 mmol) was then slowly added (10 min) at room temp. with a flexible needle through a septum. During and after the addition, stannane **1,2** was distilled off *in vacuo* from the reaction mixture. A cold trap (−60 °C) selectively removed the less volatile products and compound **1,2** was condensed on a cold finger (−196 °C) which was connected at the bottom to a flask or NMR tube (a cosolvent can be added at this step). After disconnecting from the vacuum line, the apparatus was filled with dry nitrogen; liquid nitrogen was subsequently removed. The product was collected and kept at low temperature (< −80 °C) before analysis.

** *Selected data* for **1a**: Yield 63%. ^{1}H NMR (300 MHz, C_6D_6) δ 4.17 (d, 2H, $^4J_{HH}$ 7.0 Hz), 4.81 (d, 3H, $^3J_{HH}$ 0.6 Hz), 4.73 (tq, 1H, $^4J_{HH}$ 7.0, $^3J_{HH}$ 0.6 Hz). ^{13}C NMR (75.5 MHz, C_6D_6) δ 65.4 [t, $^1J_{CH}$ 167.6, $^3J_{SnC}$ 60 Hz (d)], 67.7 [d, $^1J_{CH}$ 169.2, $^1J_{SnC}$ 488 Hz (d)], 212.7. ^{119}Sn NMR (111 MHz, C_6D_6–C_7H_8, −30 °C) δ −338.4 (q, $^1J_{SnH}$ 2010.3 Hz). HRMS Calc. for $[M - H]^+$ $(C_3H_5{}^{120}Sn)^+$ 160.9413. Found, 160.942. **1b**: Yield: 56%. ^{1}H NMR (300 MHz, C_6D_6) δ 0.11 (d, 6H, $^3J_{HH}$ 2.3 Hz), 4.21 (d, 2H, $^4J_{HH}$ 7.1 Hz), 4.99 (t, 1H, $^4J_{HH}$ 7.1 Hz), 5.25 (m, 1H, $^3J_{HH}$ 2.3 Hz). ^{13}C NMR (75.5 MHz, C_6D_6) δ −11.1 [q, $^1J_{CH}$ 130.3, $^1J_{SnC}$ 379 Hz (d)], 64.8 [t, $^1J_{CH}$ 167.2, $^3J_{SnC}$ 48 Hz (d)], 73.4 [d, $^1J_{CH}$ 164.5, $^1J_{SnC}$ 380 Hz (d)], 210.8. ^{119}Sn NMR (111 MHz, C_6D_6–C_7H_8, −30 °C) δ −118.6 (dd, $^1J_{SnH}$ 1876.9, $^2J_{SnH}$ 57.3 Hz). HRMS Calc. for $[M - H]^+$ $(C_5H_9{}^{120}Sn)^+$, 188.9726. Found, 188.973. **2a**: Yield: 37%. ^{1}H NMR (300 MHz, C_6D_6) δ 1.96 (s, 1H), 4.71 (s, 3H). ^{13}C NMR (75.5 MHz, C_6D_6) δ 77.6 [d, $^2J_{CH}$ 41.8, $^1J_{SnC}$ 517.2 Hz (d)], 99.3 [d, $^1J_{CH}$ 241.5, $^2J_{SnC}$ 115.3 Hz (d)]. ^{119}Sn NMR (111 MHz, C_6D_6–C_7H_8, −30 °C) δ −420.6 (qd, $^1J_{SnH}$ 2242.4, $^3J_{SnH}$ 18.9 Hz). HRMS Calc. for $[M - H]^+$ $(C_2H_3{}^{120}Sn)^+$, 146.9257. Found, 146.926. **2b**: Yield: 33%. ^{1}H NMR (300 MHz, C_6D_6) δ 1.63 (s, 3H), 4.81 (s, 3H). ^{13}C NMR (75.5 MHz, C_6D_6) δ 4.4 (q, $^1J_{CH}$ 131.5 Hz), 70.1, 108.9. ^{119}Sn NMR (111 MHz, C_6D_6–C_7H_8, −30 °C) δ −419.3 (q, $^1J_{SnH}$ 2110.7 Hz). HRMS Calc. for $[M - H]^+$ $(C_3H_5{}^{120}Sn)^+$, 160.9413. Found, 160.942. **2c**: Yield: 43%. ^{1}H NMR (300 MHz, C_6D_6) δ 0.17 (d, 6H, $^3J_{HH}$ 2.0 Hz), 2.10 (s, 1H), 5.34 (spt, 1H, $^3J_{HH}$ 2.0 Hz). ^{13}C NMR (75.5 MHz, C_6D_6) δ −10.4 [q, $^1J_{CH}$ 131.2, $^1J_{SnC}$ 419.4 Hz (d)], 85.3 [dm, $^2J_{CH}$ 41.8, $^1J_{SnC}$ 407.1 Hz (d)], 97.3 [d, $^1J_{CH}$ 234.5, $^2J_{SnC}$ 93.2 Hz (d)]. ^{119}Sn NMR (111 MHz, C_6D_6–C_7H_8, −30 °C) δ −171.2 (d, $^1J_{SnH}$ 1964.2 Hz). HRMS Calc. for $[M - H]^+$ $(C_4H_7{}^{120}Sn)^+$, 174.9570. Found, 174.958.

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