A Catalytic Method for the Conversion of Silanes to Stannanes

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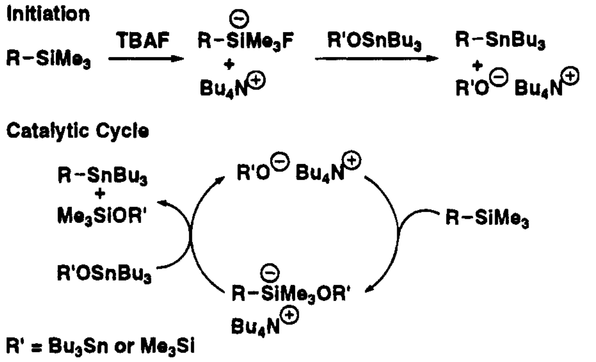
In the course of our studies of organo-main group compounds, we desired ready access to aryl(alkynyl)-boranes. One of the most useful routes to such compounds was from the aryl(silyl)acetylenes generated by the palladium-mediated coupling of an aryl halide and (trimethylsilyl)acetylene.[1] The trimethylsilyl group would then be converted to a tributylstannyl group and then to the corresponding alkynylborane.[2] Rather than the usual two step methods for converting alkynylsilanes to alkynylstannes,[3] we reasoned that the trimethylsilyl group could be removed under appropriate conditions, and the resulting anion would react with bis(tributyltin) oxide. This reaction would generate a new alkoxide, and the cycle would be repeated. We found that tetrabutylammonium fluoride (TBAF) is an excellent catalyst for the process, the presumed course of which is shown in Scheme 1.[4]

We believe that this method for generating alkynylstannanes from silanes has advantages in terms of cost and ease of use. This reaction utilizes inexpensive bis(tributyltin) oxide rather than the more costly and moisture-sensitive tributyltin chloride.[5] The reaction allows the conversion of alkynylsilanes, as well as allyl- and benzyltrimethylsilane, to the corresponding tributylstannanes in one step, as opposed to desilylation and isolation of the terminal alkyne.[3] Finally, the product is isolated in quantitative yield with removal of the volatile bis(trimethylsilyl) oxide the only purification needed.[6]

The reaction was carried out by first charging a sealable Schlenk tube with an appropriate silane (1–1.05[7] equiv), bis(tributyltin) oxide (0.5 equiv), and THF. A small amount of TBAF (0.02 equiv) was then added and the solution was heated at 60 °C for 2.5 h (16 h for allyl- and benzylsilane), at which time the solvent and bis(trimethylsilyl) oxide are removed *in vacuo*. Allyl,[8] benzyl, and alkynylsilanes all react to generate the corresponding stannanes in excellent yields without further purification (Table 1).

Scheme 1



In summary, we have developed an efficient method for the conversion of alkynyl-, benzyl-, and allylsilanes to the corresponding stannanes.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity-300, Varian XL-300, Varian XL 301, or Bruker AC-250 Fourier transform spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 series Fourier transform spectrometer. Electron impact high-resolution mass determinations (HRMS) were recorded on a Finnegan MAT System 8200. Elemental analyses were performed by Desert Analytics; air sensitive samples were sent in sealed vials under nitrogen.

Tetrahydrofuran (THF) was dried and deoxygenated by refluxing and distilling from sodium/benzophenone ketyl under an argon atmosphere. All reagents, unless otherwise stated, are commercially available and were used as received. Yields refer to isolated yields of products of greater than 95% purity as estimated by ^{1}H NMR spectrometry, and are an average of two or more separate experiments.

Representative Procedures. A flame-dried sealable Schlenk flask under argon was charged with **1a** (0.348 g, 2.0 mmol), $(Bu_3Sn)_2O$ (0.596 g, 1.0 mmol), and THF (5 mL). TBAF (0.040 mL, 1 M in THF) was added, and the flask was sealed and stirred at 60 °C for 2.5 h, at which time the volatiles were removed *in vacuo* to yield **1b** as a colorless oil with no further purification necessary (0.764 g, 98%).

Compounds **1a**–**4a**, **9a**, and **10a** were purchased from Aldrich Chemical Co., Inc. Compounds **5a**–**8a** were prepared according to the literature. The spectral data for **6a**,[9] **1b**,[10] and **2b**[11] have been reported in the literature. Compounds **3b** and **9b** were compared with material purchased from Aldrich Chemical Co., Inc.

5a:[1] ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.26 (s, 9H), 7.54 (d, J = 18.0 Hz, 2H), 7.57 (d, J = 18.0 Hz, 2H); IR (film) alkyne 2158, nitrile 2234 cm^{-1}.

7a:[12] ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.18 (s, 9H), 1.59 (m, 4H), 2.11 (m, 4H), 6.18 (m, 1H); IR (film) alkyne 2146 cm^{-1}.

8a:[1] ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.34 (s, 18H), 7.28 (dd, J = 5.7, 3.3 Hz, 2H), 7.51 (dd, J = 5.7, 3.3 Hz, 2H); IR (film) alkyne 2161 cm^{-1}.

4b:[13] ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.89 (t, J = 7.5 Hz, 9H), 1.00 (t, J = 8.3 Hz, 6H), 1.30 (m, 6H), 1.55 (m, 6H); ^{13}C NMR

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[2] Wrackmeyer, B.; Nöth, H. *Chem. Ber.* **1977**, *110*, 1086.

[3] Cf. Williamson, B. L.; Tykwynski, R. R.; Stang, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 93 and references therein.

[4] Nakamura, E.; Kuwajima, I. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 498.

[5] Tributyltin chloride is $47.59/mole and bis(tributyltin) oxide is $33.65/mole of tributyltin from Aldrich Chemical Co., Inc. Prices are from the 1992–93 catalog and are derived from the largest sized bottles listed.

[6] We note that the stannanes generated can be used without purification or removal of solvent and volatiles, in Stille reactions. For example, **1a** was converted to **1b**, and then 1 equiv of iodobenzene, 0.025 equiv of palladium(II) acetate, and 0.05 equiv of triphenylphosphine were added. After heating the reaction mixture to 60 °C for 14 h, followed by aqueous workup and flash chromatography, diphenylacetylene was isolated in 81% yield. Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. Cummins, C. H. *Tetrahedron Lett.* **1994**, *35*, 857.

[7] Solutions of TBAF contain 5% water, which protonates some of the silane or stannane. For alkynylstannanes, this reaction is reversible, but for allyl- and benzyltrimethylsilane, a small amount of material was unavoidably lost.

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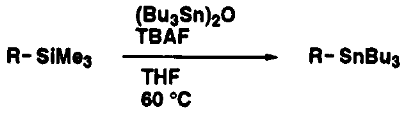
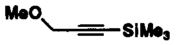
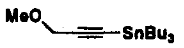
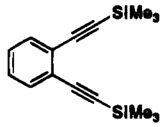
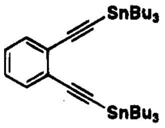
Table 1



$$\mathrm{R{-}SiMe_3} \xrightarrow[\text{THF, 60 °C}]{(\mathrm{Bu_3Sn})_2\mathrm{O},\ \mathrm{TBAF}} \mathrm{R{-}SnBu_3}$$

	substrate[a]		product	yield[c]
1a	$\mathrm{Ph{-}C{\equiv}C{-}SiMe_3}$	**1b**	$\mathrm{Ph{-}C{\equiv}C{-}SnBu_3}$	97%
2a	$\mathrm{Me{-}C{\equiv}C{-}SiMe_3}$	**2b**	$\mathrm{Me{-}C{\equiv}C{-}SnBu_3}$	98%
3a	$\mathrm{Me_3Si{-}C{\equiv}C{-}SiMe_3}$	**3b**	$\mathrm{Bu_3Sn{-}C{\equiv}C{-}SnBu_3}$	98%
4a	$\mathrm{Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3}$	**4b**	$\mathrm{Bu_3Sn{-}C{\equiv}C{-}C{\equiv}C{-}SnBu_3}$	98%
5a	p-NC-Ph$\mathrm{{-}C{\equiv}C{-}SiMe_3}$	**5b**	p-NC-Ph$\mathrm{{-}C{\equiv}C{-}SnBu_3}$	99%
6a		**6b**		98%
7a		**7b**		97%
8a		**8b**		99%
9a[b]		**9b**		95%
10a[b]		**10b**		95%

[a] Reaction run for 2.5 h except as noted. [b] Reaction run for 16 h. [c] Yields refer to isolated product of >95% purity as estimated by ^{1}H NMR.

(75 MHz, $\mathrm{CDCl_3}$) δ 92.91, 83.94, 28.79, 26.97, 13.57, 11.36; IR (film) alkyne 2036 cm^{-1}.

5b: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.91 (t, J = 7.3 Hz, 9H), 1.07 (t, J = 8.0 Hz, 6H), 1.36 (m, 6H), 1.6 (m, 6H), 7.51 (d, J = 8.2 Hz, 2 H), 7.53 (d, J = 8.2 Hz, 2 H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 132.2, 131.7, 128.7, 118.5, 110.5, 108.0, 99.9, 28.9, 27.0, 13.7, 11.3; IR (film) nitrile 2363, alkyne 2228 cm^{-1}; HRMS calcd for $\mathrm{C_{21}H_{31}NSn}$ 417.1478, found 417.1476.

6b:[14] ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.88 (t, J = 7.5 Hz, 9H), 0.99 (t, J = 8.1 Hz, 6H), 1.32 (m, 6H), 1.53 (m, 6H), 3.37 (s, 3H), 4.09 (s, 2H); IR (film) alkyne 2149 cm^{-1}.

7b:[15] ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.89 (t, J = 7.2 Hz, 9H), 0.98 (t, J = 8.1 Hz, 6H), 1.34 (m, 10H), 1.57 (m, 10H), 2.09 (m, 4H), 6.10 (m, 1H); IR (film) alkyne 2126 cm^{-1}.

8b: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.92 (t, J = 7.2 Hz, 18H), 1.06 (t, J = 12 Hz, 12H), 1.36 (m, 12H), 1.6 (m, 12H), 7.17 (dd, J = 5.7, 3.4 Hz, 2 H), 7.42 (dd, J = 5.8, 3.4 Hz, 2 H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 132.6, 127.2, 126.3, 108.5, 97.4, 28.9, 27.0, 13.6, 11.2; IR (film) alkyne 2135 cm^{-1}. Anal. Calcd for $\mathrm{C_{34}H_{58}Sn_2}$: C, 57.99; H, 8.3. Found: C, 57.97; H, 8.58.

10b:[16] ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.81 (t, J = 7.8 Hz, 6H), 0.87 (t, J = 7.4 Hz, 9H), 1.28 (m, 6H), 1.4 (m, 6H), 2.3 (t, $J_{\mathrm{Sn{-}H}}$ =27 Hz, 2H), 6.9 (m, 3 H), 7.16 (m, 2 H).

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Supplementary Material Available: Copies of ^{1}H and ^{13}C NMR spectra for **5b** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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