A Practical One-Pot Synthesis of Vinylstannanes from Ketones

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General Experimental

All reactions were carried out under argon using flame-dried glassware. NMR data were recorded on 300 MHz instruments in CDCl₃ unless otherwise specified. Couplings to ¹¹⁷Sn and ¹¹⁹Sn are reported as averages of the two values. THF was distilled from Na/benzophenone, diisopropylamine was distilled from CaH₂, and acetone was distilled from B₂O₃. Bu₃SnH was prepared from Bu₃SnOSnBu₃ and NaBH₄.¹ Alkynyl ketones **1h** and **1i** were prepared by reaction of the appropriate alkynyllithium with dimethylacetamide.² *n*-BuLi was titrated using *N*-benzylbenzamide.³

General procedure for preparation of vinylstannanes 2. To a cold (0 °C), stirred solution of diisopropylamine (5 mmol, 1.0 eq) in THF (15 mL) was added *n*-BuLi (1.6 M in hexanes, 5 mmol, 1.0 eq). The solution was stirred at 0 °C for 10 min then Bu₃SnH (5 mmol, 1.0 eq) was added and the resulting yellow solution was stirred at 0 °C for an additional 10 min. The solution was then cooled to -78 °C and the ketone (5 mmol, 1.0 eq) was added dropwise. After 10 minutes, Et₃N (40 mmol, 8 eq) and MsCl (20 mmol, 4 eq) were added. The reaction mixture was then allowed to warm to rt. After 30 min at rt, hexanes (200 mL) was added and the organic layer was washed with CH₃CN (3 x 100 mL). Concentration of the hexanes layer provided crude vinylstannanes. Traces of Bu₃SnH could be removed by stirring the sample with a small amount of AIBN in CHCl₃ (15 mL per gram of crude material) at 40 °C for 4 h followed by flash chromatography on silica gel (10 g per gram of crude material). Alternatively, purification could be effected using flash column chromatography on reverse-phase silica gel^{4,5} using 40% CH₂Cl₂ in CH₃CN. In all cases, vinylstannanes were isolated as colorless liquids.

1-Tributylstannylcyclohexene (2a).^{6,7,8,9,10} ¹H NMR δ 5.78 (1H, s, J_{Sn-H} = 68.9 Hz), 2.70 – 2.50 (4H, m), 2.14 – 2.04 (4H, m), 1.54 - 0.82 (27H, m)

1-Tributylstannylcyclopentene (2b).^{7,9} ¹H NMR δ 5.86 (1H, t, J = 2.1 Hz, J_{Sn-H} = 35.2 Hz), 2.50 – 2.28(2H, m), 2.39 – 2.34 (4H, m), 1.58 - 0.86 (27H, m)

4-tert-Butyl-1-tributylstannylcyclohexene (2c).¹¹ ¹H NMR δ 5.78 (1H, s, $J_{\text{Sn-H}} = 66.8$ Hz), 2.31 – 1.65 (7H, m), 1.55 – 0.84 (36H, m); ¹³C NMR δ 140.0, 137.5, 44.1, 33.7, 32.4, 29.4, 29.3, 27.5 ($J_{\text{Sn-C}} = 60.4$ Hz), 27.2, 13.8, 8.9 ($J_{\text{Sn-C}} = 326.0$ Hz)

6-Methyl-1-tributylstannylcyclohexene (2d).^{9,10} ¹H NMR δ 5.73 (1H, m, $J_{\text{Sn-H}} = 70.2$ Hz), 2.24 (1H, m), 2.00 (2H, m), 1.85 – 1.60 (4H, m), 1.57 – 0.82 (30H, m); ¹³C NMR δ 146.9, 137.0, 35.2, 32.0, 30.7, 29.3, 27.5 ($J_{\text{Sn-C}} = 60.4$ Hz), 23.0, 20.5, 13.8, 9.8 ($J_{\text{Sn-C}} = 339.6$ Hz)

1-Tributylstannyl-3,4-dihydronaphthalene (2e). ¹H NMR δ 7.11 (3H, m), 6.94 (1H, d, $J = 7.2$ Hz), 6.23 (1H, t, $J = 4.3$ Hz, $J_{\text{Sn-H}} = 59.6$ Hz), 2.71 (2H, t, $J = 7.8$ Hz), 2.27 (2H, m), 1.55 – 0.84 (27H, m); ¹³C NMR δ 140.5, 139.9, 138.7, 136.0, 127.8, 126.4, 126.3, 29.2, 28.2, 27.4 ($J_{\text{Sn-C}} = 65.3$ Hz), 24.8, 13.8, 10.1 ($J_{\text{Sn-C}} = 326.3$ Hz); IR (neat) 2871, 2853, 1463, 754 cm^{-1} ; MS (EI) m/z 420 (M^+ , 1%), 363 ($M - n\text{Bu}$, 100%); Anal. Calcd for $\text{C}_{22}\text{H}_{36}\text{Sn}$: C, 63.03; H, 8.66. Found: C, 63.00; H, 8.66.

1-Tributylstannyl-1-indene (2f). ¹H NMR δ 7.50 (1H, d, $J = 7.2$ Hz), 7.36 (1H, d, $J = 7.4$ Hz), 7.27 (1H, t, $J = 7.3$ Hz), 7.17 (1H, t, $J = 7.3$ Hz), 6.68 (1H, s, $J_{\text{Sn-H}} = 31.2$ Hz), 3.46 (2H, s), 1.58 – 0.85 (27H, m); ¹³C NMR δ 150.0, 145.0, 144.8, 143.9, 126.2, 124.2, 123.6, 122.4, 41.5 ($J_{\text{Sn-C}} = 48.3$ Hz), 29.3, 27.4 ($J_{\text{Sn-C}} = 72.4$ Hz), 13.8, 9.5 ($J_{\text{Sn-C}} = 350.2$ Hz); IR (neat) 2871, 2859, 1604, 1456, 774 cm^{-1} ; MS (EI) m/z 406 (M^+ , 0.7%), 349 ($M - n\text{Bu}$, 100%); Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{Sn}$: C, 62.25; H, 8.46. Found: C, 62.20; H, 8.26.

1-Tributylstannyl-1-phenylethylene (2g).¹² ¹H NMR δ 7.31–7.16 (5H, m), 6.03 (1H, d, $J = 2.4$ Hz, $J_{\text{Sn-H}} = 130.6$ Hz), 5.42 (1H, d, $J = 2.4$ Hz, $J_{\text{Sn-H}} = 60.8$ Hz), 1.55 – 0.82 (27H, m); ¹³C NMR δ 154.7, 146.5, 128.3 (2C), 126.8, 126.4 (2C), 126.3, 29.1, 27.4 ($J_{\text{Sn-C}} = 60.4$ Hz), 13.7, 10.3 ($J_{\text{Sn-C}} = 350.6$ Hz)

2-Tributylstannyl-dec-1-en-3-yne (2h). ¹H NMR δ 6.10 (d, 1H, $J = 3.3$ Hz, $J_{\text{Sn-H}} = 117.8$ Hz), 5.42 (d, 1H, $J = 3.4$ Hz, $J_{\text{Sn-H}} = 55.2$ Hz), 2.33 (t, 2H, $J = 6.6$ Hz), 1.55 – 0.85 (m, 38H); ¹³C NMR δ 135.1, 133.9, 95.6, 84.3, 31.3, 28.9, 28.8, 28.5, 27.4 ($J_{\text{Sn-C}} = 60.3$ Hz), 22.5, 19.7, 13.9, 13.6, 10.0 ($J_{\text{Sn-C}} = 338$ Hz); IR (neat) 2856, 1464, 668 cm^{-1} ; MS (EI) m/z 426 (M^+ , 0.5%), 369 ($M - n\text{Bu}$, 100%); Anal. Calcd for $\text{C}_{22}\text{H}_{42}\text{Sn}$: C, 62.13; H, 9.95. Found: C, 61.92; H, 9.89.

2-Tributylstannyl-4-trimethylsilylbut-1-en-3-yne (2i). ^1H NMR δ 6.23 (d, 1H, $J = 3.3$ Hz, $J_{\text{Sn-H}} = 112.5$ Hz), 5.53 (d, 1H, $J = 3.3$ Hz, $J_{\text{Sn-H}} = 54.0$ Hz), 1.52 – 0.84 (m, 27H), 0.15 (s, 9H); ^{13}C NMR δ 136.3, 134.7, 108.9, 99.3, 28.9, 27.4 ($J_{\text{Sn-C}} = 57$ Hz), 13.8, 10.3 ($J_{\text{Sn-C}} = 320$ Hz), 0.2; IR (neat) 2854, 2109, 842 cm^{-1} ; MS (EI) m/z 414 (M^+ , 0.4%), 357 ($\text{M} - \text{nBu}$, 100%); Anal. Calcd for $\text{C}_{19}\text{H}_{38}\text{SiSn}$: C, 55.21; H, 9.27. Found: C, 55.35 ; H, 9.50.

2-Tributylstannylpropene (2j).⁸ ^1H NMR δ 5.67 (1H, s, $J_{\text{Sn-H}} = 138.1$ Hz), 5.07 (1H, s, $J_{\text{Sn-H}} = 66.0$ Hz), 1.95 (3H, s, $J_{\text{Sn-H}} = 42.0$ Hz), 1.56 - 0.85 (27H, m); ^{13}C NMR δ 150.2, 125.4 ($J_{\text{Sn-C}} = 28.4$ Hz), 29.0 ($J_{\text{Sn-C}} = 19.9$ Hz), 27.3 ($J_{\text{Sn-C}} = 55.1$ Hz), 13.5, 9.0 ($J_{\text{Sn-C}} = 321$ Hz).

2-Tributylstannyl-3-methyl-1-butene (2k).⁸ ^1H NMR δ 5.66 (1H, s, $J_{\text{Sn-Htrans}} = 143.1$ Hz), 5.01 (1H, s, $J_{\text{Sn-Hcis}} = 66.0$ Hz), 2.46 (1H, septet, $J = 6.8$ Hz), 1.52 - 0.85 (33H, m); ^{13}C NMR δ 162.5, 121.7 ($J_{\text{Sn-C}} = 28.5$ Hz), 38.6 ($J_{\text{Sn-C}} = 42.7$ Hz), 29.0 ($J_{\text{Sn-C}} = 21.0$ Hz), 27.3 ($J_{\text{Sn-C}} = 57.0$ Hz), 23.0 ($J_{\text{Sn-C}} = 14.8$ Hz), 13.5, 10.0 ($J_{\text{Sn-C}} = 315.8$ Hz).

4-Tributylstannyl-3,6-dihydro-2H-pyran (2l).¹³ ^1H NMR δ 5.78 (1H, m, $J_{\text{Sn-H}} = 64.3$ Hz), 4.11 (2H, m), 3.74 (2H, t, $J = 5.3$ Hz), 2.24 (2H, m), 1.55 - 0.84 (27H, m); ^{13}C NMR δ 137.7 (Sn-C), 135.9 ($J_{\text{Sn-C}} = 18.0$ Hz), 66.7 ($J_{\text{Sn-C}} = 49.7$ Hz), 64.6 ($J_{\text{Sn-C}} = 27.7$ Hz), 31.6 ($J_{\text{Sn-C}} = 27.2$ Hz), 29.0 ($J_{\text{Sn-C}} = 19.9$ Hz), 27.2 ($J_{\text{Sn-C}} = 54.7$ Hz), 13.6, 8.7 ($J_{\text{Sn-C}} = 325.4$ Hz).

4-Tributylstannyl-3,6-dihydro-2H-thiopyran (2m).¹³ ^1H NMR δ 5.90 (1H, m, $J_{\text{Sn-H}} = 66.9$ Hz), 3.11 (2H, m), 2.65 (2H, t, $J = 5.6$ Hz), 2.43 (2H, m), 1.48 - 0.82 (27H, m); ^{13}C NMR δ 141.9 ($J_{\text{Sn-C}} = 395.9$ Hz), 132.4 ($J_{\text{Sn-C}} = 25.5$ Hz), 31.5 ($J_{\text{Sn-C}} = 35.2$ Hz), 28.9 ($J_{\text{Sn-C}} = 19.7$ Hz), 27.3 ($J_{\text{Sn-C}} = 55.5$ Hz), 26.4 ($J_{\text{Sn-C}} = 58.1$ Hz), 25.1 ($J_{\text{Sn-C}} = 33.4$ Hz), 13.6, 8.8 ($J_{\text{Sn-C}} = 323.0$ Hz).

1-*t*-Butoxycarbonyl-4-Tributylstannyl-1,2,3,6-tetrahydropyridine (2n).¹³ ^1H NMR δ 5.69 (1H, s, $J_{\text{Sn-H}} = 63.0$ Hz), 3.86 (2H, s), 3.40 (2H, t, $J = 5.4$ Hz), 2.22 (2H, s), 1.42 (9H, s), 1.52 - 0.82 (27H, m); ^{13}C NMR δ 154.8, 138.7, 133.4, 79.1, 45.1, 39.8, 39.0, 31.5, 28.9 ($J_{\text{Sn-C}} = 19.9$ Hz), 28.3, 27.2 ($J_{\text{Sn-C}} = 54.4$ Hz), 13.5, 8.9 ($J_{\text{Sn-C}} = 325.5$ Hz).

Addition of Bu₃SnLi to 2-methylcyclohexanone (1d). To examine the stereochemistry of addition of Bu₃SnLi to ketone **1d**, an experiment was carried out in which the general procedure described on page S2 was followed but saturated aqueous NH₄Cl was added instead of MsCl/Et₃N. The resulting unstable hydroxystannanes were isolated after standard aqueous workup and immediately treated with excess MOMCl/*i*-Pr₂NEt. Examination of the ¹H NMR spectrum of the crude reaction mixture indicated a 95:5 mixture of 2 diastereomers. These diastereomers were readily separated by flash chromatography on silica gel.

The major, more polar (R_f = 0.38, hexanes-ether, 10:1) isomer was assigned as the “axial” isomer based on data previously reported for the Bu₃SnLi adducts to 4-*t*-butylcyclohexanone (**1c**).¹⁴ Of particular significance is ³J_{Sn-C} for C3 which is ~0 when the Bu₃Sn group is axial and ~40 Hz when the Bu₃Sn group is equatorial, values consistent with a Karplus relationship.

¹H NMR δ 4.70, 4.67 (OCH₂O, 2H, AB quartet, J_{AB} = 6.9 Hz), 3.34 (OCH₃, s, 3H), 2.18 (H6 eq, br d, 1H, J = 12.2 Hz), 1.73-0.85 (CCH₂CH₂CH₂CH₂, m, 7H), (Sn-nBu, m, 27H), 0.96 (CHCH₃, d, 3H, J = 6.6 Hz); ¹³C NMR δ 93.9 (C1, J_{Sn-C} = 435.4 Hz), 92.2 (OCH₂O, J_{Sn-C} = 24.7 Hz), 55.4 (OCH₃), 41.6 (C2, J_{Sn-C} = 26.0 Hz), 36.8 (C6, J_{Sn-C} = 31.7 Hz), 32.6 (C3, J_{Sn-C} ~ 0 Hz), 29.3 (SnCH₂CH₂CH₂CH₃, J_{Sn-C} = 19.5 Hz), 27.7 (SnCH₂CH₂CH₂CH₃, J_{Sn-C} = 59.4 Hz), 25.4 (C5, J_{Sn-C} ~ 0 Hz), 24.9 (C4, J_{Sn-C} = 7.5 Hz) 20.2 (CHCH₃, J_{Sn-C} = 19.5 Hz), 13.6 (SnCH₂CH₂CH₂CH₃), 11.3 (SnCH₂CH₂CH₂CH₃, J_{Sn-C} = 282.7 Hz)

The minor, less polar (R_f = 0.49, hexanes-ether, 10:1) isomer was assigned as the “equatorial” isomer:

^1H NMR δ 4.66, 4.57 (OCH_2O , 2H, AB quartet, $J_{\text{AB}} = 6.6$ Hz), 3.36 (OCH_3 , s, 3H), 2.26 (H_6 eq, br d, 1H, $J = 11.5$ Hz), 1.65-0.80 ($\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, m, 7H), (Sn-nBu , m, 27H), 0.94 (CHCH_3 , d, 3H, $J = 6.6\text{Hz}$); ^{13}C NMR δ 94.7 (OCH_2O , $J_{\text{Sn-C}} = 19.2$ Hz), 85.8 (C1), 55.9 (OCH_3), 41.1 (C2), 36.2 (C6, $J_{\text{Sn-C}} = 21.7$ Hz), 29.6 (C3, $J_{\text{Sn-C}} = 34.7$ Hz), 29.4 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $J_{\text{Sn-C}} = 19.3$ Hz), 27.7 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $J_{\text{Sn-C}} = 57.4$ Hz), 26.5 (C4), 20.6 (CHCH_3 , $J_{\text{Sn-C}} = 19.5$ Hz), 20.4 (C5, $J_{\text{Sn-C}} = 40.0$ Hz), 13.6 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 10.5 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $J_{\text{Sn-C}} = 280.9$ Hz).

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