

A facile stereoselective synthesis of (E)- α -silylvinylstannanes via hydromagnesiation of alkynylsilanes

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Abstract

(E)- α -Silylvinylstannanes have been synthesized by the hydromagnesiation reaction of alkynylsilanes, followed by the reaction with trialkylstannyl chlorides. (E)- α -Silylvinylstannanes can undergo the cross-coupling reaction with aryl iodides in the presence of a catalytic amounts of Pd(PPh₃)₄ and CuI to afford (Z)-1,2-disubstituted vinylsilanes in good yields.

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1. Introduction

Methodologies for the stereoselective synthesis of vinylstannanes are of considerable interest because the vinylstannanes are proven synthons and very useful building blocks in synthetic organic chemistry [1]. Due to their synthetic utility, a variety of methods have been developed for their preparation including those involving carbonyl addition chemistry [2]; transmetallation of vinylmetallic species [3]; metallometallation of alkynes [4]; and the hydrostannylation of alkynes induced by either radical initiators [5] or Lewis acid [6] or transition metal catalysts [7]. Difunctional group reagents, which have two different functional groups linked to the olefinic carbon atoms, for example, Sn–Al [8], Sn–Cu [9], Sn–Mg [10], Sn–Zr [11] and Sn–Se [12] combinations, play an important role in organic synthesis, especially in developing many convenient methods for the stereoselective synthesis of substituted alkenes. These reagents and their synthetic applications have been re-

ported. Vinylsilanes are also important synthetic intermediates [13], but the difunctional group reagent containing tin and silicon has rarely aroused extensive attention. Mitchell et al. [14] described that the alkynes underwent the regio- and stereospecific addition with (trimethylsilyl)trialkylstannanes in the presence of Pd(PPh₃)₄ catalyst to give (Z)- β -silylvinylstannanes. Hydromagnesiation has emerged as a unique hydrometallation with some attractive features such as the high regioselectivity and stereoselectivity observed with alkynylsilanes [15]. We now wish to report that (E)- α -silylvinylstannanes could be synthesized by hydromagnesiation of alkynylsilanes, followed by treatment with trialkylstannyl chlorides (Scheme 1).

2. Results and discussion

Alkynylsilanes **1** were prepared according to the literature procedure [16]. Hydromagnesiation of alkynylsilanes **1** at 25 °C in diethyl ether for 6 h gave (Z)- α -silylvinyl Grignard reagents **2**, which reacted with tributylstannyl chloride or trimethylstannyl chloride **3**

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Finnigan 8230 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. All solvents were dried, deoxygenated and freshly distilled before use.

3.1. General procedure for the synthesis of (*E*)- α -silylvinylstannanes **4a**, **4b**, **4d**, **4e**, **4g**, **4h**, **4j**

To a solution of isobutylmagnesium bromide (4.5 mmol) in Et₂O (7 ml) was added Cp₂TiCl₂ (50 mg, 0.2 mmol) at 0 °C under Ar, and the mixture was stirred for 30 min at that temperature. To this solution was added alkynylsilane **1** (4.0 mmol), and the mixture was stirred for 6 h at 25 °C. After being cooled to 0 °C, a solution of trialkylstannyl chloride **3** (3.0 mmol) in Et₂O (2 ml) was added and the mixture was stirred at room temperature for 4 h, quenched with saturated aqueous NH₄Cl (25 ml) and extracted with Et₂O (2 × 40 ml). The organic layer was washed with saturated aqueous NH₄Cl (25 ml) and H₂O (3 × 30 ml) and dried (MgSO₄). Removal of solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel using light petroleum ether (bp 30–60 °C) as eluent.

3.1.1. (*E*)-1-Trimethylsilyl-1-tributylstannyl-1-hexene (**4a**)

IR (film): ν (cm⁻¹) 2955, 2926, 2871, 1567, 1464, 1376, 1246, 858, 834. ¹H NMR: δ 6.47 (t, *J* = 6.9 Hz, 1H), 2.25–2.15 (m, 2H), 1.49–1.29 (m, 16H), 0.95–0.82 (m, 18H), 0.12 (s, 9H). ¹³C NMR: δ 159.20, 141.17, 36.37, 31.84, 29.25, 27.38, 22.53, 14.06, 13.68, 10.47, 1.53. MS: *m/z* 445 (M⁺, 3.7), 73 (100). Anal. Found: C, 56.44; H, 10.15. C₂₁H₄₆SiSn Calc.: C, 56.63; H, 10.34%.

3.1.2. (*E*)-1-Trimethylsilyl-1-trimethylstannyl-1-hexene (**4b**)

IR (film): ν (cm⁻¹) 2924, 2855, 1568, 1465, 1378, 1248, 839. ¹H NMR: δ 6.51 (t, *J* = 6.9 Hz, 1H), 2.26–2.19 (m, 2H), 1.45–1.29 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.15 (s, 9H), 0.12 (s, 9H). ¹³C NMR: δ 158.33, 141.78, 36.35, 31.73, 22.52, 14.07, 1.54, –8.01. MS: *m/z* 319 (M⁺, 8.4), 73 (100). Anal. Found: C, 44.96; H, 8.62. C₁₂H₂₈SiSn Calc.: C, 45.14; H, 8.78%.

3.1.3. (*E*)-1-Trimethylsilyl-1-tributylstannyl-5-methyl-1-hexene (**4d**)

IR (film): ν (cm⁻¹) 2955, 2926, 2872, 1567, 1465, 1384, 1366, 1247, 1071, 856, 834. ¹H NMR: δ 6.48 (t, *J* = 6.9 Hz, 1H), 2.25–2.16 (m, 2H), 1.61–1.27 (m, 15H), 0.95–0.83 (m, 21H), 0.13 (s, 9H). ¹³C NMR: δ 159.11, 140.94, 38.90, 34.87, 29.20, 27.99, 27.38, 22.61, 13.69, 10.48, 1.50. MS: *m/z* 459 (M⁺, 4.2), 73 (100). Anal. Found: C, 57.31; H, 10.27. C₂₂H₄₈SiSn Calc.: C, 57.52; H, 10.46%.

3.1.4. (*E*)-1-Trimethylsilyl-1-trimethylstannyl-5-methyl-1-hexene (**4e**)

IR (film): ν (cm⁻¹) 2958, 2925, 2872, 1571, 1465, 1440, 1384, 1367, 856, 839. ¹H NMR: δ 6.51 (t, *J* = 6.9 Hz, 1H), 2.25–2.19 (m, 2H), 1.65–1.56 (m, 1H), 1.34–1.28 (m, 2H), 0.92 (d, *J* = 6.8 Hz, 6H), 0.21 (s, 9H), 0.16 (s, 9H). ¹³C NMR: δ 158.43, 141.92, 38.23, 34.63, 27.88, 22.59, 1.53, –8.02. MS: *m/z* 333 (M⁺, 9.8), 73 (100). Anal. Found: C, 46.62; H, 8.79. C₁₃H₃₀SiSn Calc.: C, 46.85; H, 9.01%.

3.1.5. (*E*)-1-Trimethylsilyl-1-tributylstannyl-1-octene (**4g**)

IR (film): ν (cm⁻¹) 2954, 2926, 2872, 2855, 1567, 1464, 1247, 856, 835. ¹H NMR: δ 6.48 (t, *J* = 6.9 Hz, 1H), 2.25–2.16 (m, 2H), 1.52–1.29 (m, 20H), 0.95–0.82 (m, 18H), 0.13 (s, 9H). ¹³C NMR: δ 159.10, 141.15, 36.83, 31.84, 29.62, 29.20, 29.03, 27.38, 22.62, 14.04, 13.68, 10.49, 1.50. MS: *m/z* 473 (M⁺, 1.8), 73 (100). Anal. Found: C, 58.12; H, 10.41. C₂₃H₅₀SiSn Calc.: C, 58.35; H, 10.57%.

3.1.6. (*E*)-1-Trimethylsilyl-1-trimethylstannyl-1-octene (**4h**)

IR (film): ν (cm⁻¹) 2924, 2856, 1567, 1462, 1376, 1248, 839. ¹H NMR: δ 6.51 (t, *J* = 6.9 Hz, 1H), 2.26–2.17 (m, 2H), 1.41–1.25 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H), 0.15 (s, 9H), 0.12 (s, 9H). ¹³C NMR: δ 158.39, 141.76, 36.65, 31.80, 29.56, 29.12, 22.60, 14.06, 1.54, –8.01. MS: *m/z* 347 (M⁺, 8.2), 73 (100). Anal. Found: C, 48.19; H, 9.04. C₁₄H₃₂SiSn Calc.: C, 48.42; H, 9.22%.

3.1.7. (*E*)-1-Trimethylsilyl-1-tributylstannyl-3-phenyl-1-propene (**4j**)

IR (film): ν (cm⁻¹) 3061, 3018, 2955, 2853, 1579, 1492, 1464, 839, 730, 690. ¹H NMR: δ 7.43–6.94 (m, 5H), 6.51 (t, *J* = 6.9 Hz, 1H), 3.56 (d, *J* = 7.2 Hz, 2H), 1.47–1.29 (m, 12H), 0.93–0.82 (m, 15H), 0.13 (s, 9H). ¹³C NMR: δ 159.21, 140.22, 130.17, 129.11, 128.40, 126.04, 39.55, 29.05, 27.32, 13.63, 9.87, 0.75. MS: *m/z* 479 (M⁺, 1.4), 73 (100). Anal. Found: C, 59.87; H, 9.24. C₂₄H₄₄SiSn Calc.: C, 60.13; H, 9.19%.

3.2. General procedure for the synthesis of (*E*)- α -silylvinylstannanes **4c**, **4f**, **4i**

To a solution of isobutylmagnesium bromide (4.5 mmol) in Et₂O (7 ml) was added Cp₂TiCl₂ (50 mg, 0.2 mmol) at 0 °C under Ar, and the mixture was stirred for 30 min at that temperature. To this solution was added alkynylsilane **1** (4.0 mmol), and the mixture was stirred for 6 h at 25 °C. After removal of the Et₂O under reduced pressure (2 h, r.t./2 Torr), the residue was dissolved in THF (6 ml), and a solution of Ph₃SnCl (3.0 mmol) in THF (4 ml) was added and the reaction mixture was stirred at 60 °C for 8 h, quenched with

saturated aqueous NH_4Cl (25 ml) at 0 °C and extracted with Et_2O (2 × 40 ml). The organic layer was washed with saturated aqueous NH_4Cl (25 ml) and H_2O (3 × 30 ml) and dried (MgSO_4). Removal of solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel using light petroleum ether (bp 30–60 °C) as eluent.

3.2.1. (*E*)-1-Trimethylsilyl-1-triphenylstannyl-1-hexene (**4c**)

IR (film): ν (cm^{-1}) 3064, 3015, 2954, 2871, 2858, 1639, 1568, 1480, 1428, 1247, 1073, 836, 727, 700. ^1H NMR: δ 7.53–7.24 (m, 15H), 6.60 (t, $J = 6.9$ Hz, 1H), 2.27–2.19 (m, 2H), 1.36–1.18 (m, 4H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.18 (s, 9H). ^{13}C NMR: δ 164.17, 140.34, 137.43, 137.08, 128.73, 128.39, 36.87, 31.71, 22.58, 14.09, 1.70. MS: m/z 505 (M^+ , 1.4), 73 (100). Anal. Found: C, 63.93; H, 6.56. $\text{C}_{27}\text{H}_{34}\text{SiSn}$ Calc.: C, 64.16; H, 6.73%.

3.2.2. (*E*)-1-Trimethylsilyl-1-triphenylstannyl-5-methyl-1-hexene (**4f**)

IR (film): ν (cm^{-1}) 3064, 3016, 2955, 2869, 1639, 1568, 1480, 1429, 1384, 1366, 1248, 838, 727, 699. ^1H NMR: δ 7.49–7.22 (m, 15H), 6.57 (t, $J = 6.9$ Hz, 1H), 2.29–2.18 (m, 2H), 1.50–1.36 (m, 1H), 1.20–1.13 (m, 2H), 0.87 (d, $J = 6.4$ Hz, 6H), 0.15 (s, 9H). ^{13}C NMR: δ 164.30, 140.35, 137.46, 137.11, 128.77, 128.44, 38.71, 35.26, 28.22, 22.67, 1.74. MS: m/z 519 (M^+ , 2.2), 73 (100). Anal. Found: C, 64.51; H, 6.85. $\text{C}_{28}\text{H}_{36}\text{SiSn}$ Calc.: C, 64.74; H, 6.94%.

3.2.3. (*E*)-1-Trimethylsilyl-1-triphenylstannyl-1-octene (**4i**)

IR (film): ν (cm^{-1}) 3064, 3016, 2927, 2855, 1638, 1570, 1480, 1429, 1247, 1074, 835, 727, 700. ^1H NMR: δ 7.63–7.35 (m, 15H), 6.65 (t, $J = 6.9$ Hz, 1H), 2.29–2.19 (m, 2H), 1.40–1.19 (m, 8H), 0.84 (t, $J = 7.2$ Hz, 3H), 0.16 (s, 9H). ^{13}C NMR: δ 164.26, 140.36, 137.36, 137.11, 128.76, 128.23, 37.14, 31.63, 29.18, 28.89, 22.53, 14.09, 1.68. MS: m/z 533 (M^+ , 1.7), 73 (100). Anal. Found: C, 65.04; H, 7.21. $\text{C}_{29}\text{H}_{38}\text{SiSn}$ Calc.: C, 65.29; H, 7.13%.

3.3. General procedure for the synthesis of (*Z*)-1,2-disubstituted vinylsilanes (**6a–e**)

To a solution of compound **4** (1.0 mmol), aryl iodide (1.1 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (58 mg, 0.05 mmol) in DMF (5 ml) was added CuI (19 mg, 0.1 mmol) under Ar. The reaction mixture was stirred at room temperature for 48 h, treated with saturated aqueous NH_4Cl (10 ml) and extracted with CH_2Cl_2 (2 × 15 ml). The organic layer was washed with saturated aqueous NH_4Cl (2 × 10 ml), water (3 × 20 ml) and dried (MgSO_4). After removal of the solvent, the residue was purified by column chroma-

tography on silica gel eluting with light petroleum (30–60 °C).

3.3.1. (*Z*)-1-Trimethylsilyl-1-phenyl-1-hexene (**6a**)

IR (film): ν (cm^{-1}) 2956, 2858, 1602, 1598, 1489, 1249, 839. ^1H NMR: δ 7.40–6.91 (m, 5H), 6.01 (t, $J = 7.0$ Hz, 1H), 2.35–2.17 (m, 2H), 1.49–1.23 (m, 4H), 0.91 (t, $J = 7.1$ Hz, 3H), 0.12 (s, 9H). Anal. Found: C, 77.31; H, 10.25. $\text{C}_{15}\text{H}_{24}\text{Si}$ Calc.: C, 77.59; H, 10.34%.

3.3.2. (*Z*)-1-Trimethylsilyl-1-(4-chlorophenyl)-1-hexene (**6b**)

IR (film): ν (cm^{-1}) 2957, 2858, 1605, 1597, 1485, 1249, 839. ^1H NMR: δ 7.08 (d, $J = 8.8$ Hz, 2H), 6.78 (d, $J = 8.8$ Hz, 2H), 5.94 (t, $J = 7.0$ Hz, 1H), 2.32–2.18 (m, 2H), 1.47–1.25 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 3H), 0.15 (s, 9H). Anal. Found: C, 67.66; H, 8.56. $\text{C}_{15}\text{H}_{23}\text{SiCl}$ Calc.: C, 67.54; H, 8.63%.

3.3.3. (*Z*)-1-Trimethylsilyl-1-(4-chlorophenyl)-5-methyl-1-hexene (**6c**)

IR (film): ν (cm^{-1}) 2955, 2870, 1606, 1486, 1384, 1366, 1249, 838. ^1H NMR: δ 7.06 (d, $J = 8.8$ Hz, 2H), 6.74 (d, $J = 8.8$ Hz, 2H), 5.91 (t, $J = 7.0$ Hz, 1H), 2.34–2.16 (m, 2H), 1.67–1.23 (m, 3H), 0.91 (d, $J = 6.4$ Hz, 6H), 0.13 (s, 9H). Anal. Found: C, 68.61; H, 8.99. $\text{C}_{16}\text{H}_{25}\text{SiCl}$ Calc.: C, 68.45; H, 8.91%.

3.3.4. (*Z*)-1-Trimethylsilyl-1-phenyl-1-octene (**6d**)

IR (film): ν (cm^{-1}) 2955, 2855, 1602, 1573, 1488, 1249, 837. ^1H NMR: δ 7.36–6.97 (m, 5H), 5.98 (t, $J = 7.0$ Hz, 1H), 2.41–2.19 (m, 2H), 1.59–1.21 (m, 8H), 0.90 (t, $J = 7.1$ Hz, 3H), 0.11 (s, 9H). Anal. Found: C, 78.22; H, 10.53. $\text{C}_{17}\text{H}_{28}\text{Si}$ Calc.: C, 78.46; H, 10.77%.

3.3.5. (*Z*)-1-Trimethylsilyl-1,3-diphenyl-1-propene (**6e**)

IR (film): ν (cm^{-1}) 2958, 2860, 1605, 1596, 1490, 1249, 839. ^1H NMR: δ 7.46–6.87 (m, 10H), 5.96 (t, $J = 7.0$ Hz, 1H), 3.52 (d, $J = 7.2$ Hz, 2H), 0.12 (s, 9H). Anal. Found: C, 81.07; H, 8.11. $\text{C}_{18}\text{H}_{22}\text{Si}$ Calc.: C, 81.20; H, 8.27%.

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