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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. © 2004 Elsevier B.V. All rights reserved.

Keywords: Hydromagnesiation; Alkynylsilane; (E)-α-Silylvinylstannane; Cross-coupling reaction; Stereoselective synthesis

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-

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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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at room temperature for 4 h to afford (E)- α -silylvinylstannanes 4 in high yields. The intermediates 2 were found to possess low reactivity with triphenylstannyl chloride and the Mg/Sn metathesis reaction did not occur in diethyl ether at 30 °C. However, the Mg/Sn metathesis reaction proceeded smoothly in THF at 60 °C and the corresponding (E)- α -silylvinylstannanes 4 were obtained in good yields (Entry 3, 6, 9) after 8 h. The typical results are summarized in Table 1.

The hydromagnesiation of alkynylsilanes 1 at 25 °C in ether is almost 100% regio-and stereoselective as previously described [15]. We observed that the Mg/Sn metathesis reaction on intermediates 2 occurs with total retention of the configuration. Investigations of the crude products 4 by ¹H NMR spectroscopy (400 MHz) showed their isomeric purities to be more than 98%, one olefinic proton signal of 4a-j splits characteristically into one triplet with a coupling constant of J = 6.9 Hz, which indicated that the hydromagnesiation of alkynylsilanes had taken place with strong preference for the addition of the magnesium atom at the carbon adjacent to the silvl group. The configuration of compound 4a could be confirmed from compound 5 which was obtained by treatment of 4a with *n*-butyllithium in THF followed by hydrolysis, a reaction which occurs stereoselectively (Scheme 2) [17]. The stereochemistry of compound 5 was easily established, since ¹H NMR spectrum (400 MHz) of 5 gives rise to a doublet at δ = 5.44 with a coupling constant of 11.5 Hz, which is consistent with an Z-configuration.

We have also carried out the cross-coupling reaction of compounds **4** with aryl iodides. We observed that

Table 1	
Synthesis of (E)-α-silvlvinylstannanes	4a-j

-					
Entry	R	\mathbf{R}^1	Product ^a	Yield (%) ^b	
1	n-C ₄ H ₉	$n-C_4H_9$	4a	90	
2	$n-C_4H_9$	CH ₃	4b	87	
3	$n-C_4H_9$	Ph	4c	69	
4	i-C5H11	n-C ₄ H ₉	4d	89	
5	i-C ₅ H ₁₁	CH ₃	4 e	86	
6	i-C5H11	Ph	4f	72	
7	<i>n</i> -C ₆ H ₁₃	$n-C_4H_9$	4g	88	
8	<i>n</i> -C ₆ H ₁₃	CH ₃	4h	85	
9	<i>n</i> -C ₆ H ₁₃	Ph	4i	70	
10	PhCH ₂	$n-C_4H_9$	4j	81	

^a All the compounds **4** were characterized by IR, ¹H NMR, ¹³C NMR, MS and elemental analyses.

^b Isolated yield based on the trialkylstannyl chloride used.



Scheme 3.

Table 2 Synthesis of (Z)-1,2-disubstituted vinylsilanes **6** according to Scheme 3

Entry	R	\mathbf{R}^1	Ar	Product	Yield ^a (%)
1	n-C ₄ H ₉	CH ₃	Ph	6a	78
2	$n-C_4H_9$	CH ₃	$4-ClC_6H_4$	6b	83
3	i-C5H11	n-C ₄ H ₉	$4-ClC_6H_4$	6c	71
4	<i>n</i> -C ₆ H ₁₃	CH_3	Ph	6d	84
5	PhCH ₂	n-C ₄ H ₉	Ph	6e	75

^a Isolated yield based on the 4 used.

when $(E)-\alpha$ -silylvinylstannanes **4** were allowed to react with aryl iodides in the presence of a catalytic amounts of Pd(PPh₃)₄ and CuI in DMF at room temperature under Ar, the corresponding (Z)-1,2-disubstituted vinylsilanes **6** were obtained in good yields according to Scheme 3 and Table 2.

In summary, our results showed that the hydromagnesiation–stannylation sequence of the alkynylsilanes has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and high yields. The investigation on the synthetic applications of compounds **4** is in progress.

3. Experimental

¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker AC 400 MHz spectrometer with TMS as an internal standard. Chemical shifts are given in ppm and spin–spin coupling constants, *J*, are given in Hz. IR spectra were obtained on a Perkin–Elmer 683 instrument as neat films. Mass spectra were determined on a 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 Et_2O (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 $(2 \times 40 \text{ ml})$. 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): v (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): v (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-1hexene* (*4d*)

IR (film): v (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 (**4***e*)

IR (film): v (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): v (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): v (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): v (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, 12 H), 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 NH₄Cl (25 ml) at 0 °C 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.

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

IR (film): v (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). ¹³C 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. C₂₇H₃₄SiSn 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). ¹³C 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. C₂₈H₃₆SiSn Calc.: C, 64.74; H, 6.94%.

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

IR (film): v (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). ¹³C 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. C₂₉H₃₈SiSn Calc.: C, 65.29; H, 7.13%.

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

To a solution of compound 4 (1.0 mmol), aryl iodide (1.1 mmol) and Pd(PPh₃)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 NH₄Cl (10 ml) and extracted with CH₂Cl₂ (2 × 15 ml). The organic layer was washed with saturated aqueous NH₄Cl (2 × 10 ml), water (3 × 20 ml) and dried (MgSO₄). 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): v (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. C₁₅H₂₄Si Calc.: C, 77.59; H, 10.34%.

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

IR (film): v (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. C₁₅H₂₃SiCl Calc.: C, 67.54; H, 8.63%.

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

IR (film): v (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. C₁₆H₂₅SiCl Calc.: C, 68.45; H, 8.91%.

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

IR (film): v (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. C₁₇H₂₈Si Calc.: C, 78.46; H, 10.77%.

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

IR (film): v (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. C₁₈H₂₂Si Calc.: C, 81.20; H, 8.27%.

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