

# Stereoselective synthesis of 1,3-dienylstannanes by palladium catalyzed cross-coupling reactions

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Received 10 June 2003; received in revised form 4 September 2003; accepted 4 September 2003

## Abstract

(*Z*)- $\alpha$ -Bromovinylstannanes are new difunctional group reagents, which undergo palladium catalyzed cross-coupling reactions with (*E*)-alkenylzirconium complexes to give stereoselectively 1,3-dienylstannanes in good yields.

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**Keywords:** Palladium; Zirconium; 1,3-Dienylstannane; Cross-coupling reaction

## 1. Introduction

The stereocontrolled synthesis of conjugated dienes is of considerable interest in organic synthesis since such dienes are often encountered in natural compounds, such as insect sex pheromones and Achilla amide [1]. The synthesis of dienes for use in the Diels–Alder reaction is still an important challenge in organic synthesis [2] although other elegant uses of these compounds have been developed [3]. Conjugated dienes are usually prepared by utilizing either a Wittig type approach [4] or coupling reactions of stereodefined vinyl halides with vinyl organometallic compounds catalyzed by transition metals [5]. The synthesis of 1,3-dienes containing functional groups is of great interest in recent years. The stereoselective synthesis of 1,3-dienylsilanes [6], 1,3-dienyl sulfides [7], 1,3-dienyl selenides [8] has already been described in the literature. Dienylstannanes serve as valuable versatile intermediates since vinylstannanes are pivotal intermediates in a wide range of carbon–carbon bond forming reactions [9]. The stereoselective synthesis of 1-stannyl-substituted 1,3-dienes has been described in the literature [10], however, the stereoselective synthesis of 2-stannyl-substituted 1,3-dienes has received less attention [11].

The (*E*)-alkenylzirconium complexes, obtained by hydrozirconation of 1-alkynes, can be cross-coupled with alkenyl halides in the presence of a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> or Ni(PPh<sub>3</sub>)<sub>4</sub> to form 1,3-butadienes [12]. In this paper, we wish to report that 1,3-dienylstannanes could be synthesized by cross-coupling reaction of (*Z*)- $\alpha$ -bromovinylstannanes with (*E*)-alkenylzirconium complexes in the presence of a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub>.

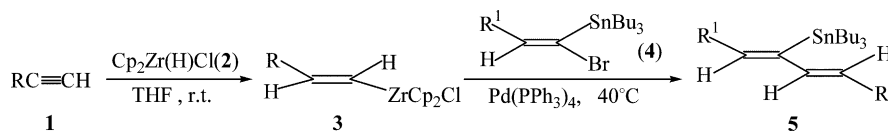
## 2. Results and discussion

(*Z*)- $\alpha$ -Bromovinylstannanes (**4**) were conveniently prepared in good yields with high stereoselectivity by the hydrozirconation of alkynylstannanes and the successive reaction with NBS [13]. Hydrozirconation of 1-alkynes (**1**) at r.t. in THF gave (*E*)-alkenylzirconium complexes (**3**), which were cross-coupled with (*Z*)- $\alpha$ -bromovinylstannanes (**4**) at 40 °C in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst to afford 1,3-dienylstannanes (**5**) in good yields (Scheme 1). The experimental results are summarized in Table 1.

It is well documented that the cross-coupling reaction of alkenylzirconium complexes with alkenyl halides in the presence of a palladium catalyst occurs with retention of configuration [12]. The *E*-configuration of the compounds **5** has been proved by their <sup>1</sup>H-NMR spectra

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Scheme 1.

Table 1  
Synthesis of 1,3-dienylstannanes **5a–i**

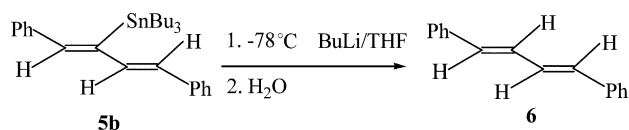
R	R <sup>1</sup>	Product <b>5</b>	Yield (%) <sup>a</sup>
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Ph	<b>5a</b>	78
Ph	Ph	<b>5b</b>	64
CH <sub>3</sub> OCH <sub>2</sub>	Ph	<b>5c</b>	58
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<b>5d</b>	80
Ph	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<b>5e</b>	72
CH <sub>3</sub> OCH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<b>5f</b>	77
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub> OCH <sub>2</sub>	<b>5g</b>	76
Ph	CH <sub>3</sub> OCH <sub>2</sub>	<b>5h</b>	68
CH <sub>3</sub> OCH <sub>2</sub>	CH <sub>3</sub> OCH <sub>2</sub>	<b>5i</b>	71

The products were identified by <sup>1</sup>H-NMR, IR, MS and elemental analyses.

<sup>a</sup> Isolated yield.

which show a doublet at  $\delta = 6.2\text{--}7.2$  with a coupling constant of 15–16 Hz, and this is also the evidence of the retention of the *E*-configuration of the starting compounds **3**. In addition, the configuration of the 1,3-dienylstannane (**5b**) could be confirmed from compound **6** which was obtained by treatment of **5b** with *n*-butyllithium in THF followed by hydrolysis, a reaction which occurs stereoselectively (Scheme 2) [14]. The stereochemistry of compound **6** was easily established, since <sup>1</sup>H-NMR spectrum (500 MHz) of **6** gives rise to a doublet–doublet at  $\delta = 6.97$  with coupling constants of 14.7 and 9.1 Hz and a doublet–doublet at  $\delta = 6.68$  with coupling constants of 14.6 and 9.0 Hz, which is consistent with an (*E,E*)-configuration. The melting point of compound **6** was determined to be 148–149 °C which is also consistent with (*E,E*)-configuration [15].

In conclusion, the palladium catalyzed cross-coupling reaction of (*Z*)- $\alpha$ -bromovinylstannanes with (*E*)-alkenylzirconium complexes provides a direct route to 1,3-dienylstannanes (**5**). The method has some attractive advantages such as mild reaction conditions, a simple procedure and good yields. Investigations into the synthetic applications of 1,3-dienylstannanes (**5**) are currently in progress.



Scheme 2.

### 3. Experimental

<sup>1</sup>H-NMR spectra were recorded on an AZ-300 (300 MHz) or a Bruker AC-P500 (500 MHz) spectrometer with TMS as internal standard using CDCl<sub>3</sub> as the solvent. IR spectra were determined on a Perkin–Elmer 683 spectrophotometer. Mass spectra were obtained on a Finigan 8230 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. All reactions were carried out in pre-dried glassware (150 °C, 4 h) and cooled under a stream of dry nitrogen. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl immediately before use. Cp<sub>2</sub>Zr(H)Cl was prepared according to the literature method [16].

#### 3.1. General procedure for the synthesis of **4**

A mixture of Cp<sub>2</sub>Zr(H)Cl (1 mmol) and alkynylstannane (1 mmol) in THF (5 ml) was stirred at r.t. for 40 min to yield a clear solution. Into the resulting solution was added NBS (1 mmol) at 0 °C, and the mixture was stirred for 30 min, then at r.t. for 30 min. The solvent was removed by rotary evaporator under reduced pressure. The residue was extracted with light petroleum (3 × 10 ml) and filtered through a short plug of silica gel. After evaporation of the filtrate, the residue was purified by column chromatography on silica gel eluting with light petroleum.

##### 3.1.1. (*Z*)-1-Bromo-1-tributylstannyl-2-phenylethene (yield: 76%)

IR (film):  $\nu$  (cm<sup>-1</sup>) 3058, 3023, 2956, 2921, 2871, 2853, 1600, 1489, 1463, 1376, 1072, 754, 722, 695; <sup>1</sup>H-NMR:  $\delta$  8.18 (s, 1H), 7.46–7.11 (m, 5H), 1.47–0.79 (m, 27H); Anal. Found: C, 50.60; H, 6.83. C<sub>20</sub>H<sub>33</sub>SnBr Calc.: C, 50.85; H, 6.99%.

##### 3.1.2. (*Z*)-1-Bromo-1-tributylstannyl-1-hexene (yield: 83%)

IR (film):  $\nu$  (cm<sup>-1</sup>) 2957, 2928, 2872, 2855, 1596, 1463, 1377, 1073, 693; <sup>1</sup>H-NMR:  $\delta$  6.85 (t, *J* = 7.8 Hz, 1H), 1.97 (m, 2H), 1.67–0.85 (m, 34H); Anal. Found: C, 47.54; H, 8.03. C<sub>18</sub>H<sub>37</sub>SnBr Calc.: C, 47.79; H, 8.19%.

##### 3.1.3. (*Z*)-1-Bromo-1-tributylstannyl-3-methoxy-1-propene (yield: 82%)

IR (film):  $\nu$  (cm<sup>-1</sup>) 2957, 2922, 2872, 2853, 1606, 1464, 1377, 1117; <sup>1</sup>H-NMR:  $\delta$  7.00 (t, *J* = 6.5 Hz, 1H),

3.79 (d,  $J = 6.4$  Hz, 2H), 3.33 (s, 3H), 1.65–0.76 (m, 27H); Anal. Found: C, 43.42; H, 7.37.  $C_{16}H_{33}OSnBr$  Calc.: C, 43.64; H, 7.50%.

### 3.2. General procedure for the synthesis of **5a–i**

A mixture of  $Cp_2Zr(H)Cl$  (1 mmol) and alkyne (**1**) (1 mmol) in THF (6 ml) was stirred at r.t. for 30 min to yield a clear solution. Into the resulting solution were added  $Pd(PPh_3)_4$  (0.05 mmol) and (*Z*)- $\alpha$ -bromovinylstannane (**4**) (1 mmol), and the mixture was stirred at 40 °C for 24 h. The mixture was diluted with diethyl ether (40 ml) and the mixture was filtered through a short plug of silica gel and concentrated to give a residue. The residue was purified by flash chromatography on silica gel eluting with light petroleum ether.

#### 3.2.1. (*1Z*, *3E*)-1-Phenyl-2-tributylstannyl-1,3-octadiene (**5a**)

IR (film):  $\nu$  ( $cm^{-1}$ ) 3056, 2925, 2871, 1630, 1598, 1489, 1463, 1376, 960, 750, 699.  $^1H$ -NMR:  $\delta$  7.41–7.18 (m, 6H), 6.43 (d,  $J = 16.0$  Hz, 1H), 5.63 (dt,  $J = 16.0, 7.2$  Hz, 1H), 2.13 (m, 2H), 1.76–0.68 (m, 34H). MS:  $m/z$  475 [ $M^+$ , 1.5], 419 (23), 129 (41.7), 105 (100), 91 (63.2), 77 (78.1), 57 (63.4). Anal. Found: C, 65.42; H, 9.13.  $C_{26}H_{44}Sn$  Calc.: C, 65.68; H, 9.26%.

#### 3.2.2. (*1Z*, *3E*)-1,4-Diphenyl-2-tributylstannyl-1,3-butadiene (**5b**)

IR (film):  $\nu$  ( $cm^{-1}$ ) 3058, 3022, 2925, 2870, 1615, 1597, 1489, 1463, 1376, 957, 744, 692.  $^1H$ -NMR:  $\delta$  7.46–7.19 (m, 11H), 7.15 (d,  $J = 15.6$  Hz, 1H), 6.54 (d,  $J = 15.6$  Hz, 1H), 1.71–0.77 (m, 27H). MS:  $m/z$  496 [ $M^+$ , 1.4], 439 (5.4), 207 (18.3), 206 (100), 128 (44.9), 105 (52.7), 91 (86.3), 77 (83.5). Anal. Found: C, 67.63; H, 8.19.  $C_{28}H_{40}Sn$  Calc.: C, 67.88; H, 8.08%.

#### 3.2.3. (*1Z*, *3E*)-1-Phenyl-2-tributylstannyl-5-methoxy-1,3-pentadiene (**5c**)

IR (film):  $\nu$  ( $cm^{-1}$ ) 3058, 3023, 2925, 2871, 1635, 1598, 1489, 1463, 1376, 1120, 962, 752, 699.  $^1H$ -NMR:  $\delta$  7.41–7.19 (m, 6H), 6.58 (d,  $J = 15.8$  Hz, 1H), 5.72 (dt,  $J = 15.8, 7.1$  Hz, 1H), 4.01 (d,  $J = 6.4$  Hz, 2H), 3.36 (s, 3H), 1.50–0.71 (m, 27H). MS:  $m/z$  464 [ $M^+$ , 2.7], 407 (8.4), 265 (51.6), 177 (69.4), 115 (95), 77 (47), 57 (66.3), 45 (100). Anal. Found: C, 62.05; H, 8.49.  $C_{24}H_{40}OSn$  Calc.: C, 62.20; H, 8.64%.

#### 3.2.4. (*5Z*, *7E*)-6-Tributylstannyl-5,7-dodecadiene (**5d**)

IR (film):  $\nu$  ( $cm^{-1}$ ) 3024, 2925, 2872, 1587, 1464, 1377, 960.  $^1H$ -NMR:  $\delta$  6.22 (m, 2H), 5.45 (dt,  $J = 15.4, 7.0$  Hz, 1H), 2.04 (m, 4H), 1.53–0.78 (m, 41H). MS:  $m/z$  456 [ $M^+$ , 1.5], 399 (38), 287 (30.1), 177 (52.8), 67 (100), 57 (66.9), 55 (92.8), 43 (72.1). Anal. Found: C, 63.44; H, 10.61.  $C_{24}H_{48}Sn$  Calc.: C, 63.30; H, 10.55%.

#### 3.2.5. (*1E*, *3Z*)-1-Phenyl-3-tributylstannyl-1,3-octadiene (**5e**)

IR (film):  $\nu$  ( $cm^{-1}$ ) 3059, 3024, 2926, 2871, 1618, 1599, 1576, 1491, 1463, 1376, 956, 747, 691.  $^1H$ -NMR:  $\delta$  7.48–7.21 (m, 5H), 6.94 (d,  $J = 15.8$  Hz, 1H), 6.45 (t,  $J = 7.0$  Hz, 1H), 6.35 (d,  $J = 15.8$  Hz, 1H), 2.18 (m, 2H), 1.72–0.79 (m, 34H). MS:  $m/z$  475 [ $M^+$ , 1.6], 419 (10.6), 335 (27.5), 177 (41), 131 (88.4), 103 (59.4), 77 (73.2), 57 (100). Anal. Found: C, 65.49; H, 9.10.  $C_{26}H_{44}Sn$  Calc.: C, 65.68; H, 9.26%.

#### 3.2.6. (*2E*, *4Z*)-1-Methoxy-4-tributylstannyl-2,4-nonadiene (**5f**)

IR (film):  $\nu$  ( $cm^{-1}$ ) 2926, 2872, 1637, 1588, 1464, 1378, 1122, 962.  $^1H$ -NMR:  $\delta$  6.40 (d,  $J = 16.1$  Hz, 1H), 6.31 (t,  $J = 7.1$  Hz, 1H), 5.52 (dt,  $J = 16.1, 7.0$  Hz, 1H), 3.92 (d,  $J = 6.4$  Hz, 2H), 3.31 (s, 3H), 2.09 (m, 2H), 1.54–0.81 (m, 34H). MS:  $m/z$  444 [ $M^+$ , 1.8], 387 (8.3), 291 (9.8), 265 (64.3), 177 (67.2), 57 (66.2), 45 (100). Anal. Found: C, 59.37; H, 9.82.  $C_{22}H_{44}OSn$  Calc.: C, 59.59; H, 9.93%.

#### 3.2.7. (*2Z*, *4E*)-1-Methoxy-3-tributylstannyl-2,4-nonadiene (**5g**)

IR (film):  $\nu$  ( $cm^{-1}$ ) 2925, 2871, 1594, 1464, 1376, 1116, 960.  $^1H$ -NMR:  $\delta$  6.33 (t,  $J = 7.2$  Hz, 1H), 6.24 (d,  $J = 15.6$  Hz, 1H), 5.53 (dt,  $J = 15.6, 7.0$  Hz, 1H), 3.92 (d,  $J = 6.5$  Hz, 2H), 3.34 (s, 3H), 2.11 (m, 2H), 1.55–0.82 (m, 34H). MS:  $m/z$  443 [ $M^+$ , 1.7], 291 (10.4), 265 (53.2), 177 (56.4), 151 (34.7), 57 (62.3), 45 (100). Anal. Found: C, 59.41; H, 9.80.  $C_{22}H_{44}OSn$  Calc.: C, 59.59; H, 9.93%.

#### 3.2.8. (*1E*, *3Z*)-1-Phenyl-3-tributylstannyl-5-methoxy-1,3-pentadiene (**5h**)

IR (film):  $\nu$  ( $cm^{-1}$ ) 3060, 3024, 2925, 1642, 1599, 1493, 1449, 1376, 1091, 958, 692.  $^1H$ -NMR:  $\delta$  7.48–7.18 (m, 5H), 7.04 (d,  $J = 15.4$  Hz, 1H), 6.48 (d,  $J = 15.4$  Hz, 1H), 6.42 (t,  $J = 7.2$  Hz, 1H), 4.02 (d,  $J = 6.4$  Hz, 2H), 3.38 (s, 3H), 1.51–0.79 (m, 27H). MS:  $m/z$  463 [ $M^+$ , 1.4], 407 (11.3), 291 (14.8), 265 (63.5), 177 (65.4), 115 (88.7), 77 (46.3), 45 (100). Anal. Found: C, 62.37; H, 8.52.  $C_{24}H_{40}OSn$  Calc.: C, 62.20; H, 8.64%.

#### 3.2.9. (*2Z*, *4E*)-1,6-Dimethoxy-3-tributylstannyl-2,4-hexadiene (**5i**)

IR (film):  $\nu$  ( $cm^{-1}$ ) 2921, 2871, 1594, 1458, 1376, 1113, 962.  $^1H$ -NMR:  $\delta$  6.44 (d,  $J = 16.3$  Hz, 1H), 6.40 (t,  $J = 7.0$  Hz, 1H), 5.59 (dt,  $J = 16.3, 7.0$  Hz, 1H), 3.96 (m, 4H), 3.34 (s, 3H), 3.32 (s, 3H), 1.50–0.81 (m, 27H). MS:  $m/z$  432 [ $M^+$ , 3.1], 375 (10.7), 291 (21.5), 265 (59.8), 177 (62.4), 45 (100). Anal. Found: C, 55.41; H, 9.12.  $C_{20}H_{40}O_2Sn$  Calc.: C, 55.68; H, 9.28%.

### 3.3. The synthesis of (1*E*, 3*E*)-1,4-diphenyl-1,3-butadiene **6**

BuLi (1 ml, 1.1 M hexane solution) was added to a THF (5.0 ml) solution of **5b** (1.0 mmol) at  $-78^{\circ}\text{C}$ . After stirring for 30 min, the mixture was hydrolyzed with saturated aq.  $\text{NH}_4\text{Cl}$  and extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 15$  ml). The organic extract was dried with  $\text{MgSO}_4$ , filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel, eluting with light petroleum to give (1*E*,3*E*)-1,4-diphenyl-1,3-butadiene **6** (yield: 83%) as a solid. M.p.  $148-149^{\circ}\text{C}$ , lit. [15] m.p.  $149-150^{\circ}\text{C}$ . IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3054, 3015, 1635, 1593, 1490, 992, 739, 690.  $^1\text{H-NMR}$ : (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45 (d,  $J=7.5$  Hz, 4H), 7.22–7.35 (m, 6H), 6.97 (dd,  $J=14.7, 9.1$  Hz, 2H), 6.68 (dd,  $J=14.6, 9.0$  Hz, 2H).

### Acknowledgements

Project 20062002 was supported by the National Natural Science Foundation of China and this work was also supported by the Natural Science Foundation of Jiangxi Province in China.

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