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Stereospecific Stille-Coupling Reaction of (*Z*)-1,2-*Bis*(trimethylstannyl)ethenes with Hypervalent Iodonium Salts

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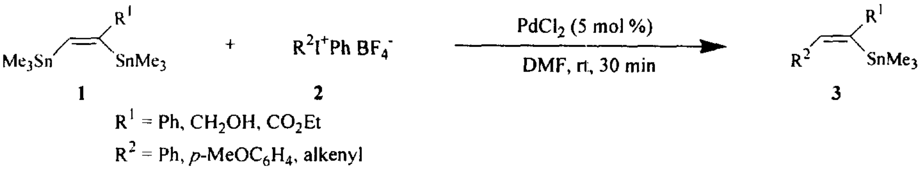
Abstract

The Stille coupling of (*Z*)-1,2-*bis*(trimethylstannyl)ethenes with hypervalent iodonium salts (1 equiv) proceeded stereospecifically in the presence of $PdCl_2$ (5 mol %) in DMF at room temperature to afford partially substituted (*Z*)-vinylstannanes under mild conditions. Alternatively, the use of 2 equivalents of hypervalent iodonium salts afforded tri-substituted alkenes. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: palladium and compounds; hypervalent element; tin and compounds; Stille coupling; regioselection; stereoselection.

The palladium-catalyzed cross-coupling of organostannanes with vinyl or aromatic halides and triflates has become an extremely powerful tool for the construction of carbon-carbon bonds [1]. This coupling reaction has been widely applied in organic synthesis due to the stability of organostannanes and tolerating many functional groups. However, the cross-coupling of bi-metallic reagents such as *bis*organostannanes has received little attention. The stereospecific use of 1,1-*bis*(tributylstannyl)ethene in the Stille coupling has been recently reported by Quayle *et al.* [2]. The (*Z*)-1,2-*bis*(trimethylstannyl)ethene was coupled with *bis*-iodo acetylide to construct enediyne moiety [3]. To the best of our knowledge no systematic and stereospecific coupling of (*Z*)-1,2-*bis*-stannanes was known. We assumed that the stereospecific coupling of 1,2-*bis*-stannanes in a sequential manner provides access to configurationally defined trisubstituted alkenes. In connection with our programs to utilize hypervalent iodonium salts in palladium-catalyzed cross-coupling with organostannanes [4], we have investigated the stereospecific coupling of (*Z*)-1,2-*bis*(trimethylstannyl)ethenes [5], which is shown in Scheme 1.



Scheme 1

The stereospecific palladium-catalyzed cross-coupling of (*Z*)-1,2-*bis*(trimethylstannyl)-ethenes with hypervalent iodonium tetrafluoroborates is summarized in Table 1. The *bis*-

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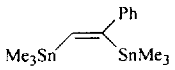
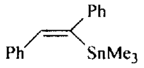
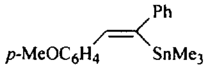
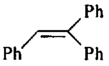
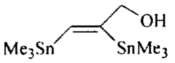
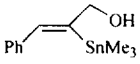
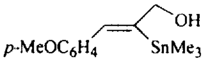
stannane **1a** reacted with diphenyliodonium tetrafluoroborate (**2a**) in the presence of $PdCl_2$ (5 mol %) at room temperature for 30 min to afford the partially substituted stannane **3a** [6] as the sole product in 80% yield (entry 1).[1] As a control experiment the use of iodobenzene instead of diphenyliodonium salt **2a** with *bis*-stannane **1a** in the presence of $PdCl_2$ (5 mol %) at 80 °C for 10 h gave a complex mixture of products without giving the coupled product **3a**. Treatment of **1a** with *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate (**2b**) gave *p*-methoxyphenyl-substituted stannane **3b** stereospecifically (entry 2). When the *bis*-stannane **1a** was coupled with 2 equivalents of **2a**, the trisubstituted olefin **4a** was provided in 68% yield (entry 3).[2] Alternatively, the hydroxymethyl-substituted *bis*-stannane **1b** reacted with 1 equivalent of **2a** and **2b** to afford monosubstituted stannanes **3c** [7] and **3d** in 85 and 72% yields, respectively (entries 4 and 5). Treatment of **2a** (1 equiv) with the carboethoxy-substituted *bis*-stannane **1c** furnished the coupled stannane **3e** in 83% yield (entry 7). For **1c**, reaction with **2b** and 2 equivalents of **2a** gave the coupled products **3f** and **4c** in 81 and 64% yields, respectively (entries 8 and 9). Finally, the *bis*-stannane **1c** was readily coupled with alkenyliodonium salt **2c** (2 equiv) to afford dialkenyl-substituted ester **4d** in 49% yield (entry 10).

Table 1. The Palladium-Catalyzed Cross-Coupling of 1,2-*Bis*(trimethylstannyl)ethenes with Hypervalent Iodonium Salts.

Entry	Substrate	Iodonium Salt	Product	Isolated Yield (%)
1	 **1a**	$Ph_2I^+ BF_4^-$ (1 equiv) **2a**	 **3a**	80
2	**1a**	*p*-$MeOC_6H_4I^+Ph\ BF_4^-$ (1 equiv) **2b**	 **3b**	72
3	**1a**	$Ph_2I^+ BF_4^-$ (2 equiv) **2a**	 **4a**	68
4	 **1b**	**2a** (1 equiv)	 **3c**	85
5	**1b**	**2b** (1 equiv)	 **3d**	72

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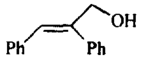
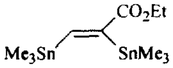
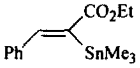
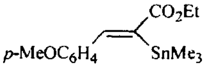
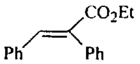
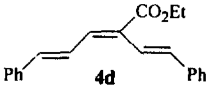
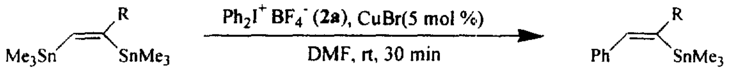
[1] The typical procedure is as follows. To a stirred solution of $Ph_2I^+ BF_4^-$ (**2a**, 70.0 mg, 0.19 mmol) and $PdCl_2$ (1.1 mg, 5 mol %) in DMF (3 mL) at room temperature was added **1a** (81.7 mg, 0.19 mmol). The reaction mixture was stirred for 30 min at room temperature. The mixture was filtered and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (hexanes, $R_f = 0.61$) to afford **3a** (52.1mg, 80%).

[2] To a stirred solution of **2a** (140 mg, 0.39 mmol) and $PdCl_2$ (1.1 mg, 5 mol %) in DMF (5 mL) at room temperature was added **1a** (81.7 mg, 0.19 mmol). The reaction mixture was stirred for 2 h at room temperature. The mixture was extracted with ether and the organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (hexanes, $R_f = 0.43$) to afford **4a** (33.1 mg, 68%).

Table 1 continued.

6	1b	2a (2 equiv)	 **4b**	67
7	 **1c**	**2a** (1 equiv)	 **3e**	83
8	**1c**	**2b** (1 equiv)	 **3f**	81
9	**1c**	**2a** (2 equiv)	 **4c**	64
10	**1c**	 **2c** (2 equiv)	 **4d**	49

It is noteworthy that the stereospecific coupling can be achieved utilizing CuBr (5 mol %) as catalyst instead of using $PdCl_2$ in DMF at room temperature, which is shown in Scheme 2. The *bis*-stannanes **1a** and **1c** were coupled with **2a** to give the partially substituted stannanes **3a** and **3e** in 75 and 72% yields (Scheme 2).



1a R = Ph

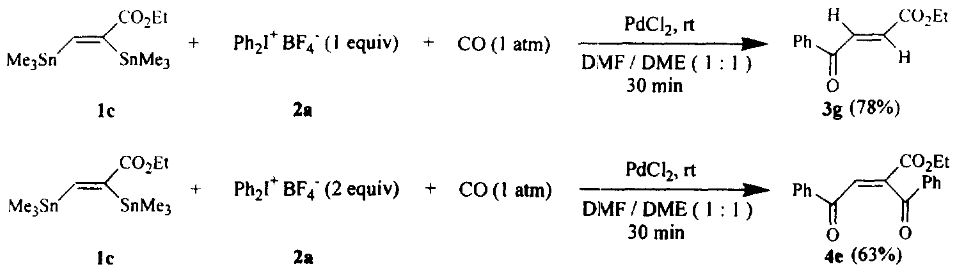
1c R = CO_2Et

3a R = Ph (75%)

3e R = CO_2Et (72%)

Scheme 2

Finally, this stereospecific coupling was applied to carbonylative coupling using carbon monoxide under atmospheric pressure in the presence of $PdCl_2$ (5 mol %) in DMF / DME (1 : 1) at room temperature for 30 min (Scheme 3). Accordingly the *bis*-stannane **1c** was treated with **2a** (1 equiv) to give the ketoolefin **3g** resulting from destannylation during work-up in 78% yield. When the same reaction was conducted with 2 equivalents of **2a**, diketoolefin **4e** was obtained in 63% yield (Scheme 3).



Scheme 3

In conclusion, the stereospecific Stille coupling of 1,2-*bis*(trimethylstannyl)ethenes with hypervalent iodonium salts was accomplished under extremely mild conditions.

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Satisfactory physical and spectral data were obtained in accord with the structure. Selected physical and spectra data as follow. **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.34~7.20 (m, 10H), 0.15~-0.18 (m, 9H). IR (KBr) 3050, 1655, 1594 cm^{-1}. MS (EI): m/e (relative intensity) 342 (M^+, 0.5), 327 (51), 178 (100), 163 (11). **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38~6.84 (m, 10H), 3.82 (S, 3H), 0.12~-0.11 (m, 9H). IR (KBr) 2950, 1600, 1249 cm^{-1}. MS (EI): m/e (relative intensity) 373 (M^+, 5), 358 (100), 209 (94), 178 (31). **3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.30~7.19 (m, 5H), 4.42 (m, 2H), 0.11~-0.03 (m, 9H). IR (KBr) 3398, 1654, 1443, 1067 cm^{-1}. MS (EI): m/e (relative intensity) 296 (M^+, 2), 281 (21), 165 (100), 163 (80), 133 (37). **3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.13 (m, 2H), 6.85 (m, 2H), 4.39 (m, 2H), 3.81 (s, 3H), 0.22~-0.09 (m, 9H). IR (KBr) 3400, 1607, 1508, 1247 cm^{-1}. MS (EI): m/e (relative intensity) 326 (M^+, 1), 296 (8), 166 (100), 162 (61). **3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.35~7.26 (m, 5H), 4.25 (q, 2H, *J* = 7.0 Hz), 1.34 (t, 3H, *J* = 7.0 Hz), 0.14~-0.02 (m, 9H). IR (KBr) 1702, 1635, 1213 cm^{-1}. MS (EI): m/e (relative intensity) 339 (M^+, 0.01), 294 (25), 146 (100), 131 (23), 108 (18). **3f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.24~7.20 (m, 2H), 6.87~6.84 (m, 2H), 4.21 (q, 2H, *J* = 7.0 Hz), 3.81 (s, 3H), 1.29 (t, 3H, *J* = 7.0 Hz), 0.19~-0.02 (m, 9H). IR (KBr) 1700, 1605, 1250, 1171 cm^{-1}. MS (EI): m/e (relative intensity) 369 (M^+, 0.25), 354 (70), 310 (92), 161 (100). **3g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (m, 2H), 7.99 (d, 1H, *J* = 15.0 Hz), 7.62 (m, 1H), 7.53 (m, 2H), 6.88 (d, 1H, *J* = 15.0 Hz), 4.30 (q, 2H, *J* = 7.0 Hz), 1.35 (t, 3H, *J* = 7.0 Hz). IR (KBr) 1720, 1672, 1240 cm^{-1}. MS (EI): m/e (relative intensity) 204 (M^+, 11), 159 (15), 130 (24), 105 (100), 77 (44). **4d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54~6.90 (m, 15H), 4.32 (q, 2H, *J* = 7.0 Hz), 1.39 (t, 3H, *J* = 7.0 Hz). IR (KBr) 1705, 1655, 1622, 1232 cm^{-1}. MS (EI): m/e (relative intensity) 304 (M^+, 67), 258 (70), 230 (100), 154 (16), 77 (19). **4e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.97~7.89 (m, 4H), 7.63~7.44 (m, 6H), 4.28 (q, 2H, *J* = 7.0 Hz), 1.22 (t, 3H, *J* = 7.0 Hz). IR (KBr) 1722, 1669, 1263 cm^{-1}. MS (EI): m/e (relative intensity) 308 (M^+, 1), 165 (100), 77 (33).

Reference and Notes

[1] For reviews, see: (a) Stille JK. Angew. Chem. Int. Ed. Engl. 1986;25:508-524. (b) Mitchell TN. Synthesis 1992;803-815. (c) Farina, V. In Comprehensive Organometallic Chemistry II; Abel EW, Stone FGA, Wilkinson G, Ed. Pergamon Press: New York, 1995; Vol. 12, Chapter 3,4; pp 200-221. (d) Farina V. Pure Appl. Chem. 1996;68:73-78.

[2] Quayle P, Wang J, Xu J, Urd CJ. Tetrahedron Lett. 1998;39:485-488.

[3] (*Z*)-1,2-*bis*(stannyl)ethenes: (a) Shair MD, Yoon T, Danishefsky, SJ. J. Org. Chem. 1994:59:3755-3757. (b) Mitchell TN, Kwetkat K, Rutschow D, Schnelder U. Tetrahedron 1989:45:969-978. (*E*)-1,2-*bis*(stannyl)ethenes: (c) Catellani M, Luzzati S, Musco A, Speroni F. Synthetic Metals 1994:62:223-228. (d) Djuric SW, Haack RA, Yu SS. J. Chem. Soc. Perkin Trans. 1 1989:2133-2134. (e) Haack RA, Penning TD, Djuric SW, Dziuba JA. Tetrahedron Lett. 1988:29:2783-2786.

[4] (a) Kang SK, Lee HW, Kim JS, Choi SC. Tetrahedron Lett. 1996;37:3723-3725. (b) Kang SK, Lee HW, Jang SB, Kim TH, Kim JS. Synth. Commun. 1996;26:4311-4318.

[5] (a) Piers E, Skerlj RT. Can. J. Chem. 1994;72:2468-2482. (b) Mitchell TN, Amamria A, Killing H, Rutschow DJ. Organomet. Chem. 1986;304:257-265.

[6] The compound **3a** was treated with MeOH/AcOH (10 : 1) at room temperature to give *trans*-stilbene in 80% yield.

[7] The (*Z*)-stereochemistry was confirmed by NOE-experiment.