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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 PdCl₂ (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.

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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 crosscoupling 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.



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

0040-4039/99/\$ - see front matter © 1999 Published by Elsevier Science Ltd. All rights reserved. *PII:* S0040-4039(99)00575-4 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).

Entry	Substrate	Iodonium Salt	Product	Isolated Yield (%)
1	Me ₂ Sn SnMe ₃	$Ph_2I^*BF_4^-(1 equiv)$	Ph Ph SnMe ₃	80
	la	2a	3a	
2	1a	p-MeOC ₆ H ₄ I ⁺ Ph BF ₄ ⁻ (1 equiv)	p-MeOC ₆ H ₄ SnMe	72
		2b	3b	
3	la	$Ph_2I^+BF_4^-$ (2 equiv)	Ph Ph	68
		2a	4 a	
4	Me ₃ Sn SnMe ₃	2a (1 equiv)	Ph OH SnMe ₃	85
	1b		~	
5	1b	2b (1 equiv)	<i>p</i> -MeOC ₆ H ₄ SnMe	H 72
			3d	

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

¹ The typical procedure is as follows. To a stirred solution of $Ph_2l^+BF_4^-$ (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 SiO₂ column chromatography (hexanes, $R_f = 0.61$) to afford 3a (52.1 mg, 80%).

To a stirred solution of 2a (140 mg, 0.39 mmol) and PdCl₂ (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 MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography (hexanes, $R_r = 0.43$) to afford 4a (33.1 mg, 68%).



It is noteworthy that the stereospecific coupling can be achieved utilizing CuBr (5 mol %) as catalyst instead of using PdCl₂ 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).



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).



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: 'H NMR (400 MHz, CDCl₃) & 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: ¹H NMR (400 MHz, CDCl₁) § 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: ¹H NMR (400 MHz, CDCI₃) 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: ¹H NMR (400 MHz, CDCl₃) 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: ¹H NMR (400 MHz, CDCl₃) & 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: 'H NMR (400 MHz, CDCl₃) 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: ¹H NMR (400 MHz, CDCl₃) 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), 7.53 (m, 2H), 6.88 (d, 2H), 7.53 (m, 2H), 7.53 (m, 2H), 7.54 (m, 2H), 7.55 (m, 2H), 7 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: ¹H NMR (400 MHz, CDCl₃) & 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: ¹H NMR (400 MHz, CDCl₃) 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

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- [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.

