## Z-TRIMETHYLSILYL STYRENES AND 1,3-DIENES VIA THE SUZUKI REACTION

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**Abstract:** Representative vinyl and aryl bromides are cross-coupled, under basic conditions, to Za-trimethylsilylvinylboranes with tetrakis(triphenylphosphine)palladium(0) catalyst to provide the corresponding silylated styrenes and 1,3-dienes (40-60%, >98% Z).



Stereodefined vinylsilanes are of interest to the synthetic chemist because they undergo a variety of stereoselective carbon-carbon bond-forming reactions and functional group conversions.<sup>2</sup> With acylsilane substrates, both the Wittig and Peterson olefinations provide Z-1,2-disubstituted vinylsilanes (3).<sup>3</sup> However, for aroylsilanes, the Wittig approach gives silyl enol ethers rather than 3 ( $\mathbb{R}^1 = Ar$ ).<sup>4</sup> While the isomeric *E*-1-phenylvinylsilanes are available,<sup>5</sup> the only known route to the corresponding Z isomers produces regioisomeric co-products.<sup>6</sup>

The Pd-catalyzed cross-coupling of vinylmetallic reagents with aromatic or vinylic substrates provides a particularly effective entry to stereodefined styrenes and 1,3-dienes.<sup>7</sup> We recently observed that Z-2-borylvinylsilanes also undergo these reactions in a remarkably efficient and stereoselective manner.<sup>8</sup> Both **2** and its vinylalane counterpart are easily accessible in isomerically pure form through the hydrometallation of **1**.<sup>9</sup> Moreover, these intermediates can be converted to **3** ( $\mathbb{R}^1 = alkyl$ ) through organocopper-based procedures.<sup>2,7c</sup> In this Letter, we report the highly stereoselective conversion of **1** to the corresponding  $\alpha$ -arylated and  $\alpha$ -vinylated Z-vinylsilanes (**3**) through the Pdcatalyzed cross-coupling of **2** to vinyl and aryl bromides under basic conditions (Suzuki reaction) (cf. Table 1).<sup>10</sup>

The isolated product yields for **3** range from 40-61%, which are significantly lower than from this process employing  $\beta$ -borylvinylsilanes.<sup>6</sup> Our previous studies had alerted us to the possibility that in such systems, problems could be encountered both with the coupling of  $\alpha$ silylvinyl derivatives and with the stability of **3** under the conditions of its formation. For **3c**, its production was monitored with time, and the only significant co-product was identified as *cis*-1-trimethylsilylpent-1-ene (**4**) (*cf.* Figure 1). After 5 h, the amounts of **4** (21%) and unreacted bromobenzene (17%) are approximately

## Table 1. Z-Vinylsilanes (3) from 1.

R	R'	Yield	of <b>3</b> *
Ме	Ph	a	40
Ме	p-MeOC <sub>6</sub> H <sub>4</sub>	b	(24)
n-Pr	Ph	с	60(66) <sup>b</sup>
n-Pr	<i>p</i> -MeOC <sub>6</sub> H₄	đ	40
Ph	Ph	e	40°
n-Pr	C(=CH <sub>2</sub> )Me	f	40
n-Pr	CH(=CMe <sub>2</sub> )	g	61 <sup>d</sup>

\* Isolated yield of analytically pure material (GC yield). <sup>b</sup> bp 75 °C (0.15 Torr). <sup>c</sup> mp 34-5 °C (from EtOH). <sup>d</sup> bp 70 °C (3 Torr). equal. Since related vinylboranes do not undergo protonolysis under these conditions, 4 probably arises from the reductive elimination of a vinyl(hydrido)palladium(II) species.<sup>11</sup> Neither increasing the amount of added hydroxide nor changing to a different base (*e.g.* NaOEt) proved effective in increasing the yield of 3.

Fortunately, these products were configurationally stable to a carefully performed oxidative work-up and were efficiently isolated in pure form. Several were photoisomerized and the minor *E* component was characterized by GCMS, <sup>1</sup>H and <sup>13</sup>C NMR. Illustrated below for **3c**, it can be noted, that only *ca*. 0.1 ppm differences exist between the *Z* and *E* isomers for the vinylic (*cf.* 6.23 *vs* 6.10 ppm) and SiMe<sub>3</sub> (*cf.* 0.28 *vs* 0.19 ppm) hydrogens. From the <sup>13</sup>C NMR data, the most notable features are the upfield shifts for the SiMe<sub>3</sub> and for the  $\alpha$ carbons in groups which are bonded to the vinylsilane moiety, upon *Z*→*E* isomerization.



Figure 1. Co-production of 3c and 4 with time.

From these studies, pure Z silvlated styrenes and 1,3-dienes are available for the first time. Efforts to develop the chemistry of these interesting systems are currently under investigation.



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10. Under a N<sub>2</sub> atmosphere, 1-trimethylsilyl-1-pentyne (0.70 g, 5.0 mmol) was added to a stirred slurry of dicyclohexylborane (5.0 mmol) in THF (5 mL) at 0 °C, dropwise. After 15 min, the mixture was allowed to warm to 25 °C and stirred for 2.25 h. Concentration *in vacuo* gave 2 (R = n-Pr) which was dissolved in THF (5 mL) and 2 M NaOH (5 mL, 10 mmol) was added. In an amber bottle, a solution of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.058 g, 0.050 mmol) and PhBr (0.70 g, 4.5 mmol) in THF (5 mL) was prepared and after 0.5 h, transferred to the first. Protected from light, this mixture was stirred at reflux temperature for 5 h and oxidized (2 M NaOH (5 mL) followed by 30% H<sub>2</sub>O<sub>2</sub> (2 mL), dropwise). Pentane (ca. 20 mL) was added and after separation, the organic material was chromatographed (SiO<sub>2</sub>,  $C_{\rm s}H_{12}$ ), concentrated and distilled at 0.15 Torr to give 0.59 g (60%) of 3c (bp 75 °C). In most cases, chromatography provided pure 3, and distillation was unnecessary.

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