

**THE EFFICIENT STEREOSELECTIVE SYNTHESIS OF Z-VINYLSILANES THROUGH THE SUZUKI-MIYaura COUPLING OF Z-(α -SILYLVINYL)BORINATES**John A. Soderquist* and Gisela León¹

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Abstract: Air-stable Z-(α -silylvinyl)borinates (**2**), easily prepared in a hydroboration-oxidation sequence from **1** provide a particularly effective route to Z-vinylsilanes (**3**, 59-97%) through Suzuki-Miyaura coupling.

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The Suzuki-Miyaura cross coupling of vinylboranes provides a remarkably versatile method for the stereoselective construction of dienes and styrenes, proceeding with clean retention of configuration with respect to both combining partners.² When trialkylsilyl groups are incorporated into the vinylborane, the value of this coupling is further enhanced because the vinylsilane products (e.g. **3**) undergo a variety of useful stereoselective conversions.³ The prerequisite vinylboranes are most conveniently prepared through the hydroboration of 1-silylalkynes (e.g. **1**), and a variety of hydroborating agents (i.e. dicyclohexylborane (DCHB), 9-borabicyclo[3.3.1]nonane (9-BBN-H), dichloroborane (BHCl₂) and catecholborane (CatB-H)), with DCHB being the traditional reagent of choice because it exhibits very clean monohydroboration of **1** under very mild conditions.³ Unfortunately, the dicyclohexyl boron ligation also participates in the coupling process resulting in reductive side reactions which significantly lower the yields of **3**,⁴ a process which for non-silylated systems is solved through the oxidation of the alkyl ligands with trimethylamine N-oxide (TMANO) or better, through the use of CatB-H or BHX₂ to prepare the corresponding vinylboronate derivatives (ViB(OR)₂).^{3c,d} However, we have recently discovered that the coupling process is significantly retarded, at least for alkyl coupling, with increasing oxygenated ligation.⁵ We felt that a better approach to **3** would be through air-stable 9-oxa-10-borabicyclo[3.3.2]decanes (**2**),⁶ easily obtained from the monohydroboration of **1** with 9-BBN-H⁷ followed by clean TMANO oxidation. This would provide, not only, extremely stable spectator boron ligation for the coupling process, but also, a practical compromise between handling convenience and reactivity in the coupling process.

The representative silylated alkynes **1** previously used for the DCHB couplings⁴ were selected for direct comparisons. The vinylborinates **2** (R = Me (77%, bp 100-3 °C (1.5 Torr)), n-Pr (60%, bp

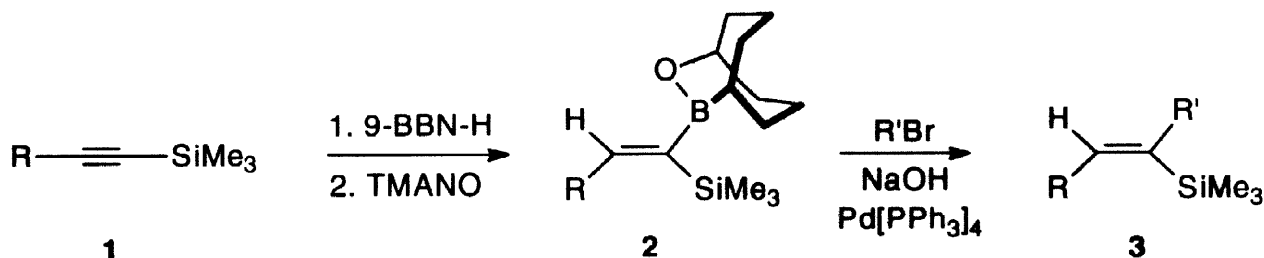
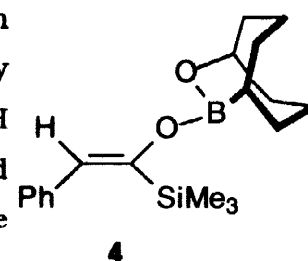


Table 1. Vinylsilanes **3** from Vinylborinates **2** through the Suzuki-Miyaura Coupling.

entry	R	R'	Time (h)	3	Yield ^a	[from DCHB] ^b
1	Me	Ph	8	a	87	[40]
2	Me	<i>p</i> -C ₆ H ₄ OMe	27	b	67	[24]
3	<i>n</i> -Pr	Ph	7	c	76	[66]
4	<i>n</i> -Pr	<i>p</i> -C ₆ H ₄ OMe	7	d	76	[40]
5	Ph	Ph	6	e	59	[40]
6	<i>n</i> -Pr	CH(=CMe ₂)	4	f	88	[61]
7	Me	CMe(=CH ₂)	2	g	83	[40]
8	Ph	2-Pyr	5	h	97	[NA]

^a GC yields employing an internal hydrocarbon standard. ^b Ref. 4. (**3a,d-h** are isolated yields).

140 °C (1.0 Torr)), Ph (71%, bp 170–80 °C (0.9 Torr))) were prepared from the *in situ* oxidation of the *B*-vinyl-9-BBN intermediate, with the exception of the propenyl derivative (R = Me) which was isolated in pure form by distillation prior to its conversion to **2**.⁷ For R = *n*-Pr, the 1:1 **1**/9-BBN-H stoichiometry (neat, 40 °C, 3.5 h) results in little dihydroboration (~5%)⁷ and for R = Ph, the vinylborane is formed exclusively. The styrene derivative requires precisely 1.0 equiv of TMANO in CHCl₃ at 25 °C to avoid further oxidation to the enolborane **4** (91%, 2.0 equiv TMANO).



The cross couplings (2–5 mmol scale) were conducted under standard basic conditions (R'Br (1.0 equiv (~0.4 M in THF), Pd[PPh₃]₄ (3 mol %), **2** (1.1 equiv) and NaOH (3 equiv of 3 M). After the complete disappearance of R'Br, the mixtures were oxidized (30% H₂O₂), and the pentane extracts were chromatographed (SiO₂), concentrated and analyzed by both GC and ¹³C NMR to confirm the product yields and isomeric purities (>98%) employing authentic samples and selected *Z/E* mixtures of each. In all cases, yields of **3** from **2** significantly exceed those obtained from their DCHB counterparts (Table 1). Thus, through the air-stable vinylborinates, **2**, the value of the Suzuki-Miyaura route to these versatile vinylsilanes **3** is significantly enhanced.

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References and Notes

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- Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
- (a) Fleming, I.; Dunoguès, J.; Smithers, R. in *Organic Reactions*; Kende, A. S. (Ed.) J. Wiley & Sons: New York, 1989, Vol. 37, pp 57–576. (b) Soderquist, J. A.; Rane, A. M.; López, C. J. *Tetrahedron Lett.* **1993**, *34*, 1893. (c) Hassner, A.; Soderquist, J. A.; *J. Organomet. Chem.* **1977**, *131*, Cl. (d) Miyaura, N.; Suzuki, A. *Chem. Lett.* **1981**, 879. (e) Soderquist, J. A.; Santiago, B. *Tetrahedron Lett.* **1990**, *31*, 5113.
- Soderquist, J. A.; León-Colón, G. *Tetrahedron Lett.* **1991**, *32*, 43.
- Matos, K.; Soderquist, J. A. *J. Org. Chem.*, **1998**, *63*, 461.
- (a) Soderquist, J. A.; Najafi, M. R. *J. Org. Chem.* **1986**, *51*, 1330. (b) Soderquist, J. A.; Santiago, B. *Tetrahedron Lett.* **1990**, *31*, 5541. (c) Colberg, J. C.; Rane, A.; Vaquer, J.; Soderquist, J. A., *J. Am. Chem. Soc.* **1993**, *115*, 6065. (d) Soderquist, J. A.; Rane, A. M.; Matos, K.; Ramos, J. *Tetrahedron Lett.*, **1995**, *36*, 6847. (e) Soderquist, J. A.; Ramos, J.; Matos, K. *ibid.* **1997**, *38*, 6639.
- Soderquist, J. A.; Colberg, J. C.; Del Valle, L. *J. Am. Chem. Soc.* **1989**, *111*, 4873.