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LETTERS

THE EFFICIENT STEREOSELECTIVE SYNTHESIS OF Z-VINYLSILANES THROUGH THE SUZUKI-MIYAURA COUPLING OF Z-(α-SILYLVINYL)BORINATES

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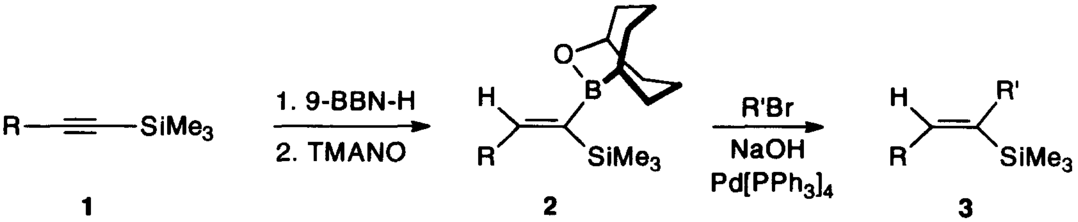
Abstract: *Air-stable Z-(α-silylvinyl)borinates (**2**), easily prepared in a hydroboration-oxidation sequence from **1** provide a particularly effective route to Z-vinylsilanes (**3**, 59-97%) through Suzuki-Miyaura coupling.*

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 ($BHCl_2$) 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 BHX_2 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-H[7] 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 couplings[4] were selected for direct comparisons. The vinylborinates **2** (R = Me (77%, bp 100-3 °C (1.5 Torr)), *n*-Pr (60%, bp



1 **2** **3**

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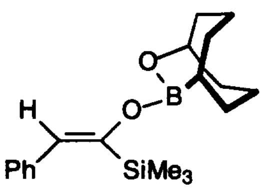
Table 1. Vinylsilanes **3** from Vinylborinates **2** through the Suzuki-Miyaura Coupling.

entry	R	R'	Time (h)	3	Yield[a]	[from DCHB][b]
1	Me	Ph	8	**a**	87	[40]
2	Me	p-C_6H_4OMe	27	**b**	67	[24]
3	*n*-Pr	Ph	7	**c**	76	[66]
4	*n*-Pr	p-C_6H_4OMe	7	**d**	76	[40]
5	Ph	Ph	6	**e**	59	[40]
6	*n*-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 $CHCl_3$ at25 °C to avoid further oxidation to the enolborane **4** (91%, 2.0 equiv TMANO).



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The cross couplings (2-5 mmol scale) were conducted under standard basic conditions (R'Br (1.0 equiv (~0.4 M in THF), $Pd[PPh_3]_4$ (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% H_2O_2), and the pentane extracts were chromatographed (SiO_2), concentrated and analyzed by both GC and ^{13}C 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

1. Graduate student support provided by the NIH-MBRS program (S06-GM08102).
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