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TRANS-VINYLSILANES VIA SUZUKI-MIYAURA COUPLING

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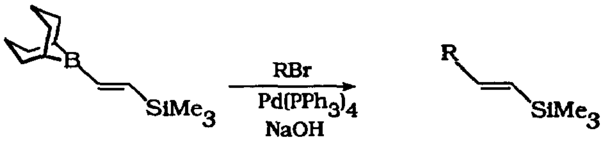
Abstract. *Representative aryl, vinyl and alkynyl bromides undergo efficient Pd-catalyzed cross coupling with trans-1-(9-borabicyclo[3.3.1]non-9-yl)-2-(trimethylsilyl)ethene (1) under basic conditions to produce the corresponding trans styryl-, dienyl- and enynylsilanes (58-89%).*

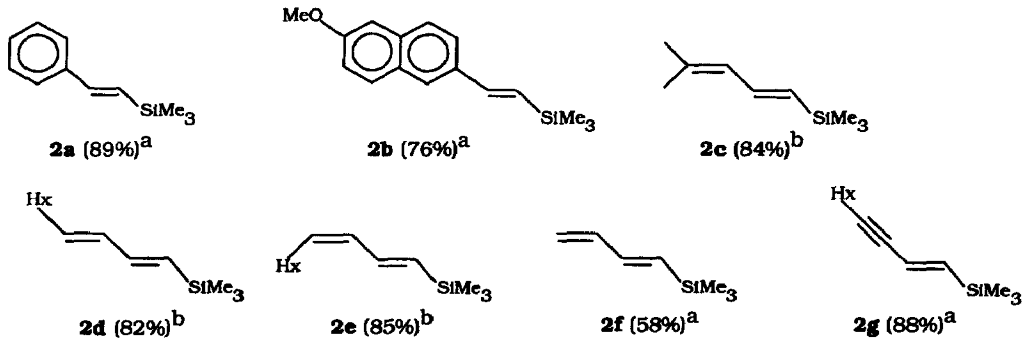
Vinylsilanes undergo numerous and often unique stereoselective conversions which have established an important place for these intermediates in chemical synthesis.[2] As an effective director, the silyl group can be very useful in asymmetric processes such as hydroboration or catalytic dihydroxylation for which we have found the *trans* derivatives to generally provide the best substrates.[3] These vinylsilanes are conveniently prepared through a tin-mediated version of the Crandall reductive alkylation of epoxides.[4] However, with an interest in expanding the scope of our studies to include 1,3-alkadienylsilanes and related systems, this approach appeared neither promising nor practical.

The direct introduction of a *trans*-2-silylvinyl moiety into unsaturated electrophilic substrates can be accomplished through the Stille coupling.[5] However, despite the limited information available on this process, it is apparent that serious problems are encountered in the case of (2-silylvinyl)tin reagents. For example, both stereochemical drift and competitive homocoupling can be observed which leads to low yields (*i.e.* < 30%) and product mixtures. Moreover, the $SnMe_3$ rather than the more convenient and less toxic $SnBu_3$ substitution is required for even a moderately successful coupling. These problems, as well as the formation of regioisomeric products, are also observed in the Heck coupling of vinyltrimethylsilane to vinylic substrates.[6] Our experience with the Suzuki-Miyaura coupling[7] of silylated vinylboranes,[8] suggested that these difficulties may be overcome through the use of vinyl-9-BBN derivatives such as *trans*-2-trimethylsilylvinyl-9-BBN (**1**).[9] However, the hydroboration of trimethylsilylacetylene is plagued by the formation of regioisomeric products or, in the case of 9-BBN-H, an unusually large amount of 2,2-diboryl adducts. Fortunately, **1** can be efficiently prepared (82%) through a new dehydroborylation process.[10] In this Letter, we report its efficient coupling with representative aryl, alkenyl and alkynyl bromides to provide *trans*-1-silyl styrenes, 1,3-dienes and 1,3-enynes (**2**) in both excellent chemical and isomeric purities (Table 1).[11]



1 **2**

Table 1. *trans*-1-Silyl Styrenes, Dienes and Enynes from **1**.



2a (89%)[a] **2b** (76%)[a] **2c** (84%)[b]

2d (82%)[b] **2e** (85%)[b] **2f** (58%)[a] **2g** (88%)[a]

[a] Isolated yields of analytically pure material. [b] GC yield with internal standard (Pure **2** was isolated by prep GC). Complete spectroscopic and analytical data were obtained for **2** in each case.

In all of the systems examined, the cross couplings were very clean producing no homocoupled products. A slight loss of stereochemical purity resulted only in the case of *cis*-hexenyl bromide (*Z/E* = 97:3) which gave **2e** as an *E,Z/E,E* = 93:7 mixture. The *trans* stereochemistry of **1** was rigorously maintained in the Δ^1 double bond in **2** in each combination studied making this a highly useful and efficient process for the simple construction of these versatile vinylsilane intermediates.

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11. The following procedure is representative: A mixture of **1** (2.36 g, 10 mmol), 2-bromo-6-methoxynaphthalene (2.37 g, 10 mmol), NaOH (10 mL of 2 M, 20 mmol), and $Pd(PPh_3)_4$ (0.40 g, 0.30 mmol) in THF (30 mL) was refluxed for 12 h. Oxidation of the residual 9-BBN moiety was effected by the addition of 3 N NaOH (4.5 mL) followed by 30% H_2O_2 (4.5 mL), dropwise. The phases were separated, and the aqueous layer was washed with pentane (30 mL). After concentration *in vacuo*, the organic residue was eluted through neutral alumina (20 g, 150 mesh) and concentrated. Recrystallization from ethanol (95%) gave 1.95 g (76%) of **2b** (mp 52-5 °C). Anal. Calcd for $C_{16}H_{20}OSi$: C, 75.00; H, 7.85. Found: C, 74.76; H, 7.85. ^1H NMR (C_6D_6) δ 0.24 (s, 9H), 3.92 (s, 3H), 6.65 (d, *J* = 19 Hz, 1H), 7.14 (d, *J* = 19 Hz, 1H), 7.16-7.83 (m, 6H); ^{13}C NMR (C_6D_6) δ -0.8, 55.8, 106.9, 119.9, 124.8, 127.5, 128.1, 128.9, 130.1, 130.6, 134.8, 135.7, 145.1, 159.1; IR (KBr) 3100, 1627, 1592, 1480, 1391, 1269, 1243, 1033, 989, 836 cm^{-1}; MS *m/z* (relative abundance) 256 (M^{+}, 93), 241 (100), 226 (34), 215 (24), 184 (11); 152 (13), 139 (18), 59 (39).

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