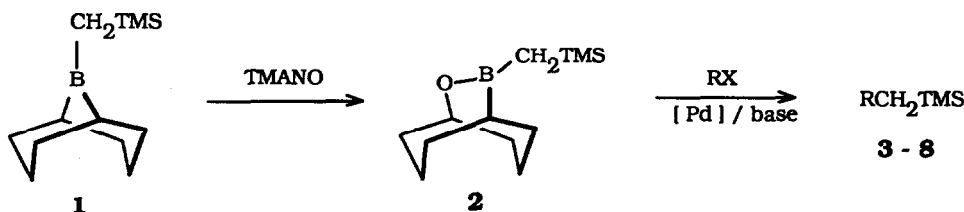


ALLYL, BENZYL AND PROPARGYL SILANES VIA THE SUZUKI REACTION

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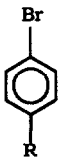

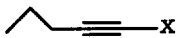
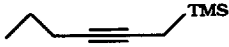
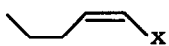
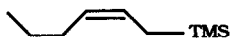
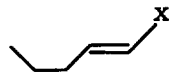
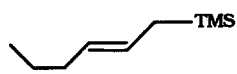
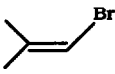
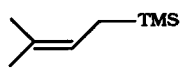
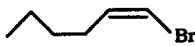

Abstract. The clean, efficient Pd-catalyzed cross-coupling of vinyl, alkynyl and aryl bromides with the air-stable organoborane, 10-trimethylsilylmethyl-9-oxa-10-borabicyclo[3.3.2]decane (**2**) gives excellent yields of the corresponding silylmethylated products, proceeding with complete retention of configuration in the first case.

The oxidation of 9-borabicyclo[3.3.1]nonane (9-BBN) derivatives (e.g. **1**) with 1 equiv of anhydrous trimethylamine N-oxide (TMANO),³ is completely selective, giving the corresponding 9-oxa-10-borabicyclo[3.3.2]decane system (e.g. **2**).⁴ Unlike **1** or their B-alkoxy-9-BBN counterparts,⁵ these liquid borinate esters are remarkably stable toward air oxidation!



The extensive studies of Suzuki and his co-workers have demonstrated the versatile nature of the Pd-catalyzed cross-coupling of aromatic and alkenyl halides and triflates with organoboranes.⁶ Recently, we reported the application of this methodology to the preparation of stereodefined vinylsilanes.⁷ While numerous methods are available for the silylmethylation of organic substrates,⁸ none appeared simpler nor potentially more convenient than the use of **2** with the Suzuki protocol. For one, a variety of groups can be selectively transferred from organoboranes which are derived from 9-BBN, catechol- or distamyl- borane without competitive side reactions from these ligands. Alkyl groups on boron can be coupled to vinylic or aromatic substrates. Moreover, the competitive rearrangement and reduction processes which can be observed with common catalysts such as $\text{Pd}(\text{PPh}_3)_4$, originate from the palladium hydride intermediates formed from *cis*- β -elimination reactions.⁹ However, the TMSCH_2 group contains no *beta* hydrogens so that no special catalysts¹⁰ appeared to be required in this case.^{6b,c} The versatile trimethylsilylmethyl functionality in **2** makes it a particularly attractive candidate for the preparation of a wide variety of functionalized organosilanes (i.e. **3-8**) in a highly efficient manner. This proved to be the case. Our results are presented in Table 1.

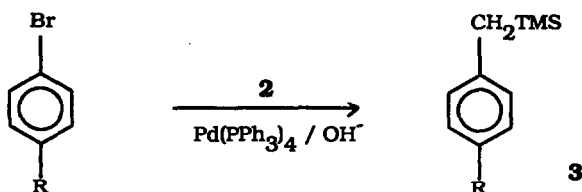
Table 1. Benzyl, Propargyl and Allyl Silanes from **2**.

Substrate	Product		Yield ^a
		3	a: R = H 96 ^b (87) b: R = OMe 96 ^c
		4	X = I 0 X = Br 75 ^d
		5	X = I 68 ^e (>99% Z) X = Br 97 ^b (>99% Z)
		6	X = I 64 ^f (>98% E) X = Br 99 ^b (86) (99% E)
		7	96 ^b
		8	87 ^g (98% Z)

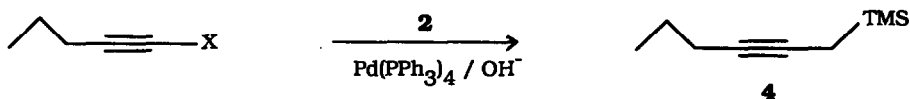
^a GC yield with internal hydrocarbon standard (isolated yield) (isomeric purity). The following reaction times (temp) were required for the complete disappearance of the starting halides: ^b 10 h (65°C). ^c 6 h (70°C). ^d 6 h (67°C). ^e 6 h (62°C). ^f 12 h (68°C). ^g 7 h (70°C).

The preparation of **3a** is representative:

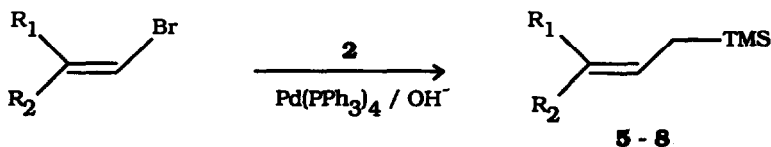
A mixture of **2** (3.57 g, 15.9 mmol), NaOH (2.05 g, 51 mmol), water (12 mL) and THF (18 mL) was added to a solution bromobenzene (2.36 g, 15.0 mmol) and Pd(PPh₃)₄ (0.53 g, 0.46 mmol) in THF (40 mL). After heating at 65°C for 11 h, oxidation of the organoborane residue was accomplished with NaOH (4.5 mL 3N) followed by 30% H₂O₂ (4.5 mL), dropwise. After 2 h at reflux temperature, the organic layer was washed with water (2 x 30 mL) and the combined aqueous material was washed with pentane (2 x 30 mL). Evaporation of the solvents at reduced pressure gave a residue which was eluted through neutral alumina with pentane (70 mL). Distillation at 35 Torr afforded 2.14 g (87%) of **3a** (bp 110-112°C). For GC analysis, a measured quantity of *n*-tridecane was added and the product yield was determined from the corrected peak areas.



The methodology was initially applied to the preparation of simple benzylsilanes with the finding that aryl bromides were smoothly converted to **3** in excellent yields (96%). We did note that products which were sensitive to aqueous base (e.g. *p*-TMSCH₂C₆H₄CHO), while identifiable as intermediates, underwent desilylation to give the corresponding methylated products (e.g. *p*-MeC₆H₄CHO, 8 h (70°C), 60%). Under similar conditions, **3a** was also formed from **1** in yields comparable to those obtained with **2**. However, unlike **2**, **1** is pyrophoric and, as a consequence, is somewhat more difficult to handle. With the synthetic versatility of this benzylsilane functionality¹¹ introduced through such available substrates, their preparation by this efficient methodology should expand greatly their scope of potential applications to synthesis.



The coupling of **2** with 1-bromo-1-pentyne gives a good yield (75%) of the desired silylmethylated product (**4**). However, the related reaction with the iodoalkyne proved complex with the majority of **2** remaining unreacted. Suzuki⁹ had found that diisiamylborane derivatives worked better than their catecholborane counterparts in related conversions. However, even with **1**, only 66% of this trialkylborane was consumed with the disappearance of 1-iodo-1-pentyne (7 h (65°C)) resulting in a 60:40 mixture of **4** and 1,2-*bis*-(trimethylsilyl)ethane. Thus, the bromoalkyne is clearly superior to the iodo compound for this alkylation.



This cross-coupling reaction is particularly suited to the preparation of allylsilanes (5-8 ($R_1, R_2 = \text{alkyl, H}$)). The coupling of vinyl bromides is more efficient than that of the corresponding iodides. With authentic samples of the isomerically-pure allylsilanes, obtained from previous studies,^{7v} we determined that both proceed with complete retention of configuration. Thus, the stereochemical purities of the starting halides are critical to obtain isomerically-pure allylsilanes. As was first shown by Negishi^{7a} with the related Grignard reagent, the Pd-catalyzed cross-coupling of silylmethyl organometallics is a highly effective method to prepare allylsilanes. With the added advantages of air-stability and ease of handling offered by **2**, this is now a particularly convenient synthetic operation.

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2. Graduate student supported by the NSF EPSCoR Program of Puerto Rico.
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