A Novel and Efficient Route to (*E*)-Alk-1-enyl Boronic Acid Derivatives from (*E*)-1-(Trimethylsilyl)alk-1-enes and a Formal Suzuki–Miyaura Cross-coupling Reaction starting with Vinylsilanes

Gianluca M. Farinola, Vito Fiandanese, Luigia Mazzone and Francesco Naso*

Centro CNR di Studio sulle Metodologie Innovative di Sintesi Organiche, Dipartimento di Chimica, Università di Bari, via Amendola 173, 70126 Bari, Italy

A novel and highly efficient conversion of vinylsilanes into vinyl boronates is described together with their Suzuki–Miyaura cross-coupling reaction, performed without isolating the intermediate resulting from borodesilylation.

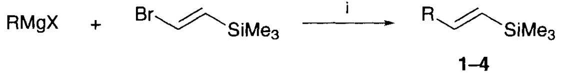
Transition metal-catalysed cross-coupling reactions between organometallic reagents and organic halides represent one of the most efficient methods for carbon–carbon bond formation.[1] Among the array of alkenyl organometallic reagents, alkenyl silicon compounds have also been examined as promising candidates for palladium-catalysed coupling reactions.[2–4] Recently, a method for the palladium-catalysed coupling of alkenyl-trimethylsilanes and -fluorosilanes with unsaturated organic halides in the presence of fluoride ion as an accelerating additive has been reported.[3] Furthermore, alkenylalkoxysilanes have been subjected to Pd-catalysed coupling reactions with organic halides in the presence of fluoride ion.[4] As a whole, the reactions reported so far appear to suffer from lack of availability of the starting materials, insufficient generality and low levels of efficiency and selectivity. As far as the trimethylsilyl derivatives are concerned, a major drawback is their inability to undergo general carbon–carbon bond forming reactions, due to the low polarity of the carbon–silicon bond, compared to other organometallics. As a result of this situation, a relatively limited use of cross-coupling reactions involving alkenylsilanes has appeared in the literature, and the difficulty of performing these reactions, at least with simple trimethylsilyl compounds, has been stressed.[5]

With the aim of overcoming this limitation and in connection with our continued interest in the synthesis of conjugated alkenes by transition metal-catalysed sequential coupling reactions[6] or by means of electrophilic substitution reactions on unsaturated organosilyl derivatives,[7] we have explored the possibility of an easy transmetalation of organic groups from silicon to other metals which have an established ability to form carbon–carbon bonds. In this respect, one of the most useful cross-coupling procedures is the Suzuki–Miyaura[8] process involving organoboranes and organic halides. It is known that phenyltrimethylsilanes,[9] bis-silylated benzenes[9,10] and bis-silylated furans[11] yield, upon treatment with boron trihalides, the corresponding dihaloorganoboranes, which in turn can be transformed into boronic esters by an alcoholysis reaction.[10] These results suggested to us the possibility that the 1-(trimethylsilyl)alkenes could also undergo direct substitution of the trimethylsilyl group with boron trichloride.

In order to confirm experimentally the validity of this approach, we readily synthesized the series of (*E*)-vinylsilanes **1–4**, by coupling reactions of Grignard reagents with (*E*)-1-bromo-2-trimethylsilylethene, in the presence of a Ni^{II} catalyst[12] (Scheme 1). The vinylsilanes **1–4** were treated with boron trichloride in CH_2Cl_2† at 0 °C and it was found that an easy *ipso*-borodesilylation occurred. Moreover, when the solution of the resulting haloborane was added to catechol in benzene[13] at room temperature, the 2-[(*E*)-alk-1-enyl]-1,3,2-benzodioxaboroles **5–8**‡ were obtained in good yields§ (Scheme 2).

To the best of our knowledge these results (see Table 1) represent the first examples of a simple and rapid conversion of vinyltrimethylsilanes into boronic esters. It is noteworthy that both types of compounds, alkenyldichloroboranes[14] and 2-[alk-1-enyl]-1,3,2-benzodioxaboroles,[15] are usually prepared by the monohydroboration of alkynes with dichloroborane ethyl etherate in the presence of BCl_3[14] or with catecholborane (1,3,2-benzodioxaborole).[15] Our methodology should represent an alternative and efficient procedure for the synthesis of these derivatives starting from 1-(trimethylsilyl)alk-1-enes, readily accessible through a variety of simple procedures.[16]

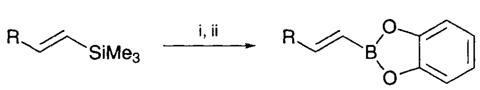
Besides exchanging the silicon for the boron group, for the reasons stated above, we were interested in performing the



1–4

R = alkyl, aryl

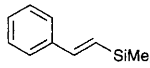
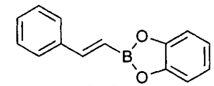
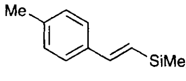
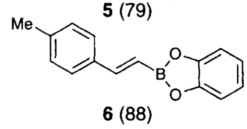
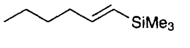
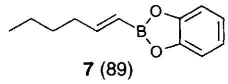
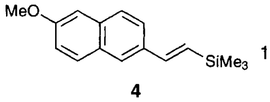
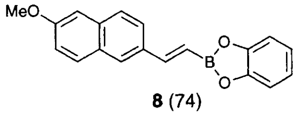
Scheme 1 *Reagents and conditions*: i, $NiCl_2(dppe)$, THF, room temp., 60–72%



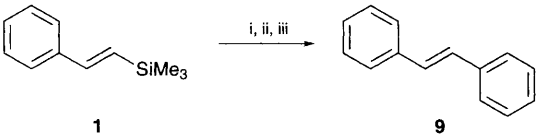
1–4 **5–8**

Scheme 2 *Reagents and conditions*: i, BCl_3, CH_2Cl_2, 0 °C; ii, Catechol, C_6H_6, room temp., 74–89%

Table 1 Conversion of vinylsilanes into boronic esters

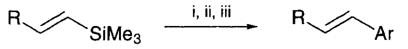
Vinylsilane[a]	BCl_3–CH_2Cl_2[b] reaction time/h	Catechol–C_6H_6 reaction time/h	Boronic esters (overall yield%)[c,d]
 **1**	2.5	1	 **5** (79)
 **2**	1	1.5	 **6** (88)
 **3**	20	1.5	 **7** (89)
 **4**	1	3	 **8** (74)

[a] All reactions of vinylsilanes with BCl_3 were carried out in CH_2Cl_2 at 0 °C. [b] Commercial 1 mol dm^{-3} solutions of BCl_3 in CH_2Cl_2 were used. [c] Yields refer to isolated purified products. [d] ^1H NMR spectral data of all compounds were consistent with the assigned structure.



1 **9**

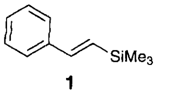
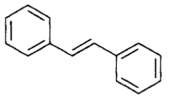
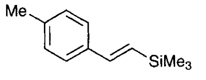
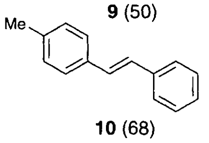
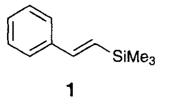
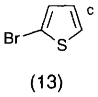
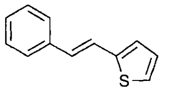
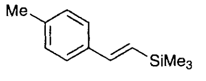
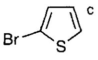
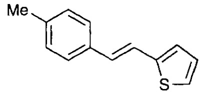
Scheme 3 *Reagents and conditions*: i, BCl_3, CH_2Cl_2, 0 °C; ii, Catechol, C_6H_6, room temp.; iii, C_6H_5Br, $Pd(PPh_3)_4$, NaOH, 86%



1,2 **9–12**

Scheme 4 *Reagents and conditions*: i, BCl_3; ii, EtOH–C_6H_6; iii, ArX, $Pd(PPh_3)_4$, NaOH, 40–68%

Table 2 Suzuki-type cross-coupling reactions of vinylsilanes

Vinylsilane	BCl_3–CH_2Cl_2 reaction time/h	RX reaction time/h	Coupling products (overall yield/%)[a,b]
 **1**	2.5	C_6H_5I[c] (13)	 **9** (50)
 **2**	1	C_6H_5I[d] (18)	 **10** (68)
 **1**	2.5	 (13)	 **11** (45)
 **2**	1	 (12)	 **12** (40)

[a] Yields refer to isolated purified products. [b] ^1H NMR spectral data of all compounds were consistent with the assigned structure. [c] The coupling reaction was performed after treating the product of borodesilylation with EtOH–benzene (1 : 1). [d] The coupling reaction was carried out after dissolving the product of borodesilylation in benzene.

Suzuki–Miyaura cross-coupling reaction.[7] Therefore, we used the boronic ester **5**, without isolating it, for a cross-coupling reaction with bromobenzene, which formed (*E*)-stilbene in 86% yield (Scheme 3). Alternatively, the cross-coupling procedure can be carried out without using catechol, by adding, after evaporation of the solvent, benzene or a benzene–ethanol mixture to the intermediate boron derivative. The actual cross-coupling step was then performed in the usual fashion. Products **9–12** were obtained in fair to good overall yields¶ (Scheme 4; see Table 2).

This clearly shows that it is possible to perform the cross-coupling process using the compounds deriving from the addition of BCl_3 or after transformation with EtOH when the appropriate solvent is used. However, it is noteworthy that the results have not been optimized, (*e.g.* type of catalyst and/or type of base) since we intended only to demonstrate the validity of our approach.

This work was financially supported by National Research Council of Italy (C. N. R.), (Progetto Finalizzato Chimica Fine II) and by Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, 40 and 60%), Rome.

Received, 7th August 1995; Com. 5/05293I

Footnotes

† In order to obtain reproducible results, it is recommended that commercial (Aldrich) solutions of BCl_3 in CH_2Cl_2 be stored under nitrogen in a freezer, where they remain useable for several weeks.

‡ *Selected data* for **6**: ^1H NMR (500 MHz, $CDCl_3$) δ 2.40 (3 H, s), 6.42 (1 H, d, *J* 18.5 Hz) 7.07–7.10 (2 H, m), 7.20 (2 H, d, *J* 8.0 Hz), 7.22–7.26 (2 H, m), 7.49 (2 H, d, *J* 8.0 Hz) and 7.74 (1 H, d, *J* 18.5 Hz); *m/z* 236 (100% M^+), 235 (42), 221 (6), 117 (11), 116 (16), 115 (17) and 91 (20). For **8**: ^1H NMR (500 MHz, $CDCl_3$) δ 3.95 (3 H, s), 6.53 (1 H, d, *J* 18.4 Hz), 7.07–7.12 (2 H, m), 7.13–7.18 (2 H, m), 7.24–7.30 (2 H, m), 7.71–7.80 (3 H, m), 7.87 (1 H, s) and 7.89 (1 H, d, *J* 18.4 Hz).

§ Formation of alk-1-enylboronates **5–8**: a CH_2Cl_2 solution of BCl_3 (1 mol dm^{-3}, 1 cm^3 1 mmol) was slowly added under nitrogen to a stirred CH_2Cl_2 solution (10 cm^3) of the vinylsilane (1 mmol) at 0 °C. The reaction was monitored by GC until no more vinylsilane was detected (a low amount of the protodesilylated product was present). After completion, the solution was transferred *via* syringe, under nitrogen, to a dropping funnel attached to a two-necked flask, equipped with a magnetic stirrer, and containing catechol (1 mmol) in benzene (20 cm^3). After complete addition at room temperature, the mixture was stirred at the same temperature for the times indicated in Table 1. The reaction product was isolated in a sufficiently pure form by simple evaporation of the solvent and treatment of the residue with petroleum ether, in order to eliminate traces (if any) of unreacted catechol.

¶ Synthesis of alkenes **9–12**: a CH_2Cl_2 solution of BCl_3 (1 mol dm^{-3}, 1 cm^3, 1 mmol) was slowly added under nitrogen to a stirred CH_2Cl_2 solution (10 cm^3) of the vinylsilane (1 mmol) at 0 °C. After reaction completion, the solvent was removed under vacuum and the residue was dissolved in EtOH–benzene 1 : 1 (10 cm^3) or in benzene. This solution was then slowly dropped into a stirred (30 min) benzene solution (8 cm^3) containing the organic halide (1 mmol) and the catalyst $Pd(PPh_3)_4$ (3 mol%). An aqueous NaOH solution (2 mol dm^{-3}, 1 cm^3) was then added and the mixture was heated at reflux. After cooling to room temperature and addition of water, the mixture was extracted with ethyl acetate. The combined organic extracts were washed with water, dried (Na_2SO_4) and concentrated. The residue was purified by crystallization (petroleum ether) or by flash chromatography (silica gel, petroleum ether) to give the disubstituted ethenes **9–12** in 40–68% yield.

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