Synthesis of 1-Alkenylboronic Esters *via* Palladium-Catalyzed Cross-Coupling Reaction of Bis(pinacolato)diboron with 1-Alkenyl Halides and Triflates

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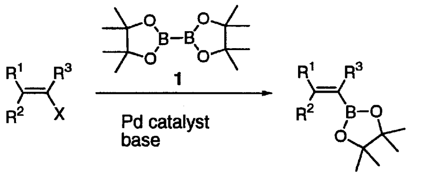
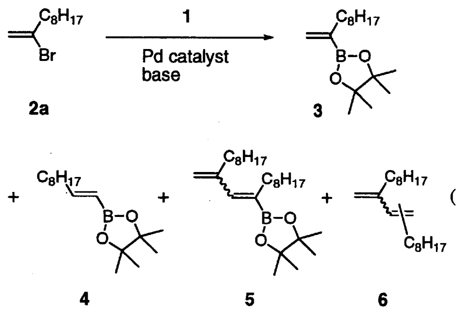
The synthesis of 1-alkenylboronic acid pinacol esters *via* the palladium-catalyzed cross-coupling reaction of 1-alkenyl halides or triflates with bis(pinacolato)diboron [$(Me_4C_2O_2)B$-$B(O_2C_2Me_4)$] was carried out in toluene at 50 °C in the presence of potassium phenoxide (1.5 equivalents) and $PdCl_2(PPh_3)_2$•$2PPh_3$ (3 mol%).

The transition metal-catalyzed cross-coupling reaction of disilanes and distannanes is an elegant method for the synthses of organosilicone[1] and -tin[2] compounds directly from organic electrophiles, but the lack of suitable boron nucleophiles has limited this protocol. We have recently demonstrated the synthesis of arylboronates from aryl halides[3] or triflates,[4] and allylboronates from allyl acetates[5] *via* a palladium-catalyzed cross-coupling reaction of tetra(alkoxo)diborons. Very recently, Masuda and Murata[6] found that pinacolborane $(Me_4C_2O_2)BH$ is an excellent boron-nucleophile for the palladium-catalyzed coupling reaction in the presence of triethylamine. Thus, tetra(alkoxo)diboron and pinacolborane are two nucleophiles now available for the boron cross-coupling reaction.

In this paper, we report the palladium-catalyzed coupling reaction of bis(pinacolato)diboron (**1**) and 1-alkenyl halides or triflates, which provides a one-step procedure for the synthesis of 1-alkenylboronic esters from vinyl electrophiles (Eq. 1).[7]



(1)



(2)

Our initial studies (Eq. 2 and Table 1) were focused on the reaction conditions selectively yielding a vinyl boronate (**3**) because the previous reaction reported for the coupling with aryl halides[3] resulted in the formation of an inseparable mixture of several products (**3**-**6**) (entry 1). Thus, the reaction involved the Heck coupling[8] between **2a** and **3** yielding a small amount of **5**, the homocoupling between **2a** and **3** giving dimer **6**,[9] and an unusual coupling giving a positional isomer **4** together with the desired coupling to afford **3**. Although the formation of positional isomer **4** is not well understood, the Heck product and the dimer (**5** and **6**) can be eliminated by changing KOAc or K_2CO_3 (entries 1 and 2) to a strong base because those side reactions are due to the slow transmetalation of **1** to the vinyl-Pd-Br intermediate. Thus, the selective coupling to give **3** was finally achieved by carrying out the reaction at 50 °C in the presence of a solid PhOK suspended in toluene (entries 10 and 11), whereas other solid bases such as K_3PO_4•nH_2O and NaOEt were not effective. The palladium-triphenylphosphine catalyst gave adequately better results than the palladium-dppf complex (entries 3-11).

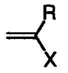
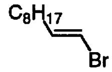
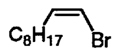
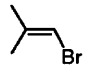
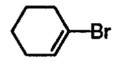
Table 1. Reaction conditions[a]

Entry	Catalyst/Base/Solvent	Yield/%	(**3**/**4**/**5**/**6**))[b]
1	$PdCl_2$(dppf)/AcOK/DMSO	53	(51/11/ 1/37)[c]
2	$PdCl_2$(dppf)/K_2CO_3/DMSO	56	(52/ 2/ 5/41)[d]
3	$PdCl_2$(dppf)/PhOK/DMSO	67	(70/ 2/ 4/24)[d]
4	$PdCl_2$(dppf)/PhOK/DMF	77	(71/ 1/ 4/24)[d]
5	$PdCl_2$(dppf)/PhOK/EtOH	69	(80/ 1/ 9/10)[d]
6	$PdCl_2$(dppf)/PhOK/dioxane	86	(91/ 1/ 4/ 4)[d]
7	$PdCl_2$(dppf)/PhOK/toluene	74	(89/ 7/ 3/ 1)[d]
8	$PdCl_2(PPh_3)_2$/PhOK/DMSO	81	(90/ 1/ 1/ 8)[d]
9	$PdCl_2(PPh_3)_2$/PhOK/DMF	89	(92/ 1/ 1/ 6)[e]
10	$PdCl_2(PPh_3)_2$/PhOK/toluene	78	(97/ 1/ 1/ 1)[e]
11	$PdCl_2(PPh_3)_2$•$2PPh_3$/PhOK/toluene	96	(96/ 1/ 2/ 1)[e]

[a] A mixture of 2-bromodecene **2a** (1.0 mmol), diboron **1** (1.1 mmol), palladium catalyst (0.03 mmol) and base (1.5 mmol) in solvent (6 ml) was stirred at 50 °C or 80 °C. [b] GC yields and their compositions were shown in the parentheses. [c] At 80 °C for 16 h. [d] At 50 °C for 16 h. [e] At 50 °C for 5 h.

The synthesis of 1-alkenylboronates from the representative haloalkenes is summarized in Table 2. The reaction with 2-iododecene **2b** and *t*-butyl derivative **2c** still suffered from the formation of a positional isomer (entries 1 and 2), but other 2-bromoalkenes (**2d**-**2g**) selectively gave alkenylboronates in high yields, which are not available by conventional hydroboration of terminal alkynes[10] (entries 2-6). The use of an insoluble base suspended in toluene can tolerate various functional groups in haloalkenes (entries 4-6). Although (*E*)-1-alkenylboronates have been synthesized by hydroboration of terminal alkynes and (*Z*)-derivatives by a two-step procedure from 1-halo-1-alkynes,[11] the coupling reaction of diboron provided an alternative and stereoselective method for synthesizing both isomers with high stereoselectivity over 99% (entries 7 and 8).

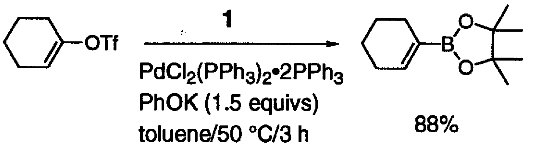
Table 2. Synthesis of 1-alkenylboronates (Eq. 1)[a]

Entry	Haloalkene	Yield/%[b]
		
1	**2b**: $R=C_8H_{17}$, X=I	65[c]
2	**2c**: $R=t\text{-}C_4H_9$, X=Br	69[d]
3	**2d**: R=Ph, X=Br	88
4	**2e**: $R=(CH_2)_3Cl$, X=Br	85
5	**2f**: $R=(CH_2)_3CN$, X=Br	85
6	**2g**: $R=CH_2CH(OSi^tBuMe_2)CH(CH_3)_2$, X=Br	70
7		47[e]
8		74
9		57
10		99

[a]A mixture of haloalkene (1.0 mmol), **1** (1.1 mmol), $PdCl_2(PPh_3)_2$ (0.03 mmol) plus PPh_3 (0.06 mmol), and PhOK (1.5 mmol) in toluene (5 ml) was stirred at 50 °C for 5 h. [b]GC yields. The products were isolated by Kugelrohr distillation or chromatography over silica gel. [c]The reaction accompanied with (*Z*)-1-dodecenylboronate (3%). [d](*E*)-1-(2-t-butylethenyl)boronate (7%) was also produced. [e](1-octylethenyl)boronate (6%).

2,2-Disubstituted 1-alkenylboronate and cyclic 1-alkenylboronate were obtained from the corresponding bromides without any difficulty because the side-reactions observed in Eq. 2 were very slow for these substrates (entries 9 and 10). However, all attempts at the couplings with 4-iodo-3-penten-2-one and methyl 3-bromo-2-methylpropenoate were unsuccessful.

Preliminary results for the cross-coupling of diboron **1** with 1-alkenyl triflate are shown in Eq. 3. Under similar reaction conditions to those used for halides, various triflates provided the corresponding 1-alkenylboronates, which results will be reported elsewhere.



(3)

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7 During the course of our study, a similar cross-coupling reaction of haloalkenes with diboron **1** or pinacolborane was reported: S. M. Marcuccio, M. Rodopoulos, H. Weigold, 10th International Conference on Boron Chemistry, Durham, England, July 1999, PB-35; M. Murata, T. Oyama, S. Watanabe, and Y. Masuda, 76th Annual Meeting of Chemical Society of Japan, March 1999, 2B712.

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