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

Kou Takahashi, Jun Takagi, Tatsuo Ishiyama and Norio Miyaoura*

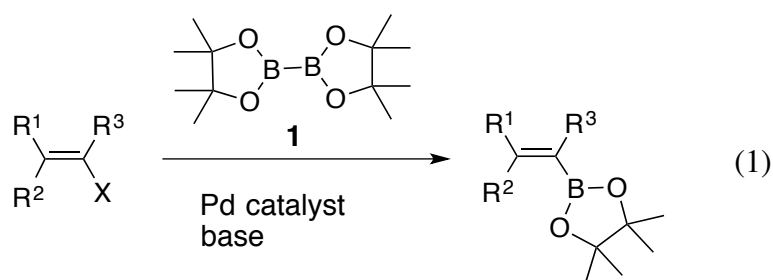
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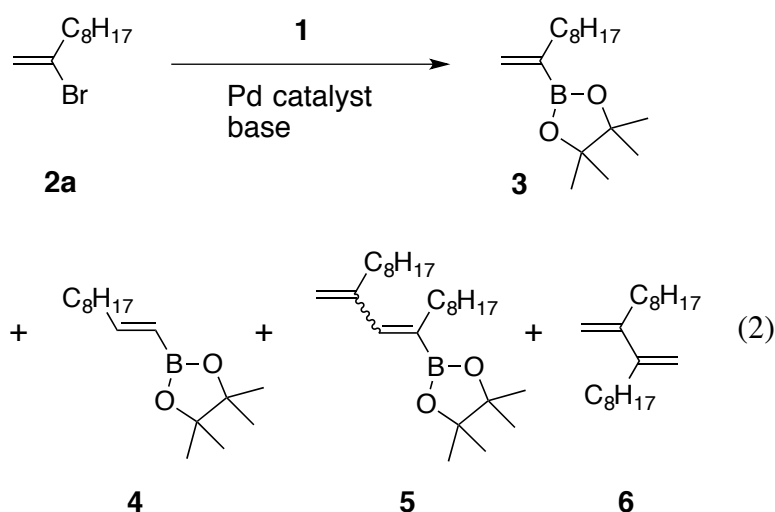
The synthesis of 1-alkenylboronic acid pinacol esters *via* the palladium-catalyzed cross-coupling reaction of 1-alkenyl halides or triflates with bis(pinacolato)diboron [(Me₄C₂O₂)B-B(O₂C₂Me₄)] was carried out in toluene at 50 °C in the presence of potassium phenoxide (1.5 equivalents) and PdCl₂(PPh₃)₂•2PPh₃ (3 mol%).

The transition metal-catalyzed cross-coupling reaction of disilanes and distannanes is an elegant method for the syntheses of organosilicone¹ and -tin² 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 halides³ or triflates⁴, and allylboronates from allyl acetates⁵ *via* a palladium-catalyzed cross-coupling reaction of tetra(alkoxo)diborons. Very recently, Matsuda and Murata⁶ found that pinacolborane (Me₄C₂O₂)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.



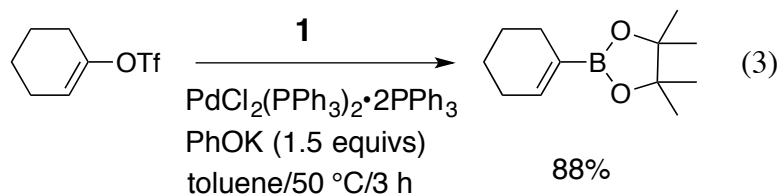
Our initial studies (Eq. 2 and Table 1) were focused on the reaction conditions selectively yielding a vinyl boronate (**3**) because the previous reaction reported for the coupling with aryl halides³ resulted in the formation of an inseparable mixture of several by-products (**4-6**) (entry 1). Thus, the reaction involved the Heck coupling⁸ 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 dimer (**5** and **6**) can be eliminated by changing KOAc or K₂CO₃ (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 K₃PO₄·nH₂O and NaOEt were not effective. The palladium-triphenylphosphine catalyst gave adequately better results than the palladium-dppf complex (entries 3-11).



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 alkynes¹⁰ (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-alkynes¹¹, the coupling reaction of diboron provided an alternative and stereoselective method for synthesizing both isomers with high stereoselectivity over 99% (entries 7 and 8). 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.



References and notes

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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 ₂ CO 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

^aA 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.

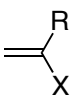
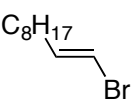
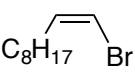

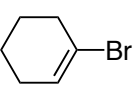
^bGC yields and their compositions were shown in the parentheses.

^cAt 80 °C for 16 h.

^dAt 50 °C for 16 h.

^eAt 50 °C for 5 h.

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

entry	haloalkene	yield/% ^b
		
1	2b: R=C ₈ H ₁₇ , X=I	65 ^d
2	2c: R= <i>t</i> -C ₄ H ₉ , X=Br	69 ^e
3	2d: R=Ph, X=Br	88
4	2e: R=(CH ₂) ₃ Cl, X=Br	85
5	2f: R=(CH ₂) ₃ CN, X=Br	85
6	2g: R=CH ₂ CH(OSi ^{<i>t</i>} BuMe ₂)CH(CH ₃) ₂ , X=Br	70
7		47 ^f
8		74
9		57
10		99

^aA mixture of haloalkene (1.0 mmol), **1** (1.1 mmol), PdCl₂(PPh₃)₂ (0.03 mmol) plus PPh₃ (0.06 mmol), and PhOK (1.5 mmol) in toluene (5 ml) was stirred at 50 °C for 5 h.

^bGC yields. The products were isolated by Kugelrohr distillation or chromatography over silica gel.

^dThe reaction accompanied with (*Z*)-1-dodecenylboronate (3%).

^e(*E*)-1-(2-*t*-butylethenyl)boronate (7%) was also produced.

^f(1-octylethenyl)boronate (6%).

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