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Synthesis of 1-Alkenylboronic Esters viaPalladium-CatalyzedCross-CouplingReaction of Bis(pinacolato)diboron with1-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 PdCl₂(PPh₃)₂•2PPh₃ (3 mol%).

The transition metal-catalyzed cross-coupling reaction of disilanes and distannanes is an elegant method for the synthses of organosilicone¹ 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 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 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 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 but other 2-bromoalkenes (2d-2g) selectively gave 2), 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)
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)
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/toluen	e 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.

^{*d*}At 50 °C for 16 h.

^{*e*}At 50 °C for 5 h.

entry	haloalkene	yield/% ^b
	$= \stackrel{R}{\underset{X}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}}{\overset{R}{\overset{R}{\overset{R}}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}}{\overset{R}}{\overset{R}}{\overset{R}}}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}}{\overset{R}}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}{\overset{R}}{\overset{R}}{\overset{R}}{\overset{R}}{\overset{R}}{\overset{R}}}}{\overset{{}}{\overset{R}}}}{{\overset{R}}{{}}}{\overset{{}}}{{}}}$	
1	2b : R=C ₈ H ₁₇ , X=I	65^d
2	2c : R=t-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>i</i>} BuMe ₂)CH(CH ₃) ₂ , X=Br	70
7	C ₈ H ₁₇ Br	47 <i>f</i>
8	C ₈ H ₁₇ Br	74
9) Br	57
10	── Br	99

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

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^{*a*}A 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 $^{\circ}$ C for 5 h. ^bGC yields. The products were isolated by Kugelrohr distillation or chromatography over silica gel. ^{*d*}The reaction accompanied with (*Z*)-1-dodecenylboronate (3%). e(E)-1-(2-*t*-butylethenyl)boronate (7%) was also produced. f(1-octylethenyl)boronate (6%).

Synthesisof1-AlkenylboronicEstersviaPalladium-CatalyzedCross-CouplingReactionofBis-(pinacolato)diboronwith1-AlkenylHalidesandTriflates

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