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Regio- and stereoselective synthesis of allylboranes via platinum(0)-catalyzed borylation of allyl halides with pinacolborane

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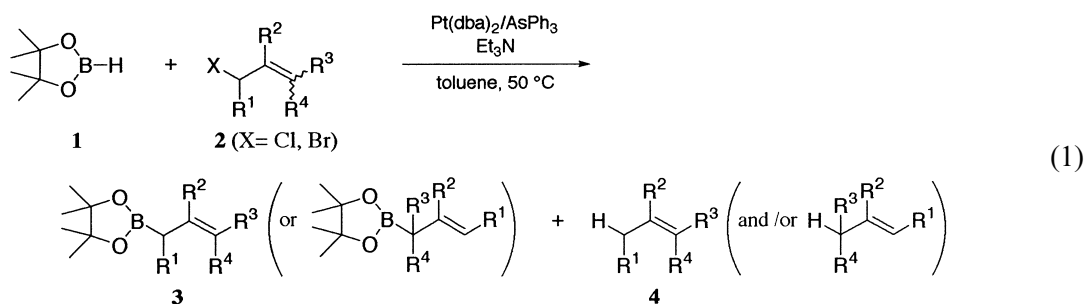
Abstract

Various allyl halides were borylated with pinacolboranes in the presence of NEt_3 and a catalytic amount of $\text{Pt}(\text{dba})_2$ and AsPh_3 to afford regio- and stereodefined allylboranes in good yields. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: pinacolborane; allylborane; allyl halides; platinum catalyst; coupling reactions.

Allylmetal reagents have been shown to be versatile intermediates in organic synthesis. Particularly, the reaction with carbonyl compounds affords homoallyl alcohol derivatives. Among other reagents, the reaction of allylboranes proceeds diastereospecifically due to the formation of a cyclic six-membered transition state.¹ Accordingly, much attention has been paid to the stereoselective synthesis of allylboranes.² Recently, palladium-catalyzed coupling reactions of allyl electrophiles with tetraalkoxydiboron³ and triethylborane⁴ were reported, respectively, which provided a one-step procedure for the preparation of allylboranes. We have developed the metalation of organic halides utilizing dialkoxyboranes⁵ or trialkoxysilanes⁶ as metalating reagents in the presence of palladium(0) complexes. During the course of our studies, we found an efficient stereoselective synthetic route to allylboranes. We describe here a novel platinum(0)-catalyzed coupling reaction of allyl halides **2** with pinacolboranes **1** to provide the corresponding allylboranes **3** (Eq. (1)).

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The reaction conditions were optimized using cinnamyl chloride (**2a**) as a substrate (Table 1). At 50°C in toluene, the reaction of **2a** with 1.5 equiv. of pinacolborane **1** in the presence of Pt(dba)₂ (dba = dibenzylideneacetone), AsPh₃, and Et₃N gave the corresponding (*E*)-cinnamylboronate **3a** (79% yield based on **2a**) regio- and stereoselectively along with a small amount of β-methylstyrene **4a** (2%) and allylbenzene **4a'** (6%) (entry 1). Triphenylarsine, which weakly coordinated with transition metals,⁷ stabilized the complex to prevent the precipitation of platinum black during the reaction, although a reasonable yield was obtained with the ligand-free platinum catalyst (entry 2). On the other hand, the use of a phosphine ligand such as PPh₃ in place of triphenylarsine retarded the reaction (entry 3).

Table 1
Reaction of cinnamyl chloride **2a** with pinacolborane **1**^a

entry	catalyst	ligand	base	solvent	yield / % ^b		
					3a	4a	4a'
1	Pt(dba) ₂	AsPh ₃	Et ₃ N	toluene	72	6	21
2	Pt(dba) ₂	none	Et ₃ N	toluene	59	20	20
3	Pt(dba) ₂	PPh ₃	Et ₃ N	toluene	0	9	28
4	Pd(dba) ₂	AsPh ₃	Et ₃ N	toluene	0	24	44
5	Ni(cod) ₂	AsPh ₃	Et ₃ N	toluene	0	0	0
6	Pt(dba) ₂	AsPh ₃	pyridine	toluene	0	20	30
7	Pt(dba) ₂	AsPh ₃	KOAc	toluene	9	17	52
8	Pt(dba) ₂	AsPh ₃	Et ₃ N	CH ₂ ClCH ₂ Cl	66	6	16
9	Pt(dba) ₂	AsPh ₃	Et ₃ N	dioxane	52	6	25

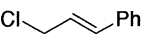
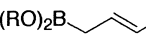
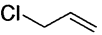
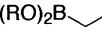
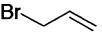
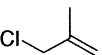
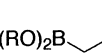
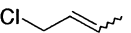
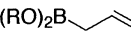
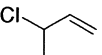
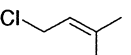
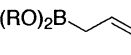
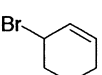
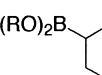
^a Reactions of 3-chloro-1-phenyl-1-propene **2a** (1.0 mmol) with **1** (1.5 mmol) were carried out at 50 °C for 16 h in 4 mL of solvent by using 3 mol % of catalyst and base (3 mmol). ^b GLC yields based on **2a** used.

With regard to catalysts, a variety of transition metal complexes were examined. As we reported recently, aryl halides couple with **1** successfully in the presence of a palladium catalyst and Et₃N to give arylboronates.⁵ However, the coupling reaction of **2a** by using Pd(dba)₂ catalyst gave only the corresponding reduced product **4** (entry 4).⁸ The base also played an important role in affecting the yields and the selectivity. Tertiary amine, Et₃N, was recognized to be the most effective base for the selective formation of **3**. In contrast, the use of potassium acetate caused the reductive cleavage of the C–Cl bond of **2a** to form the C–H bond of **4a** exclusively (entry 7).

The results of Pt(dba)₂-catalyzed borylation of representative allyl halides **2** are summarized in Table 2.⁹ The differences in yields and in selectivity from the nature of halides were not very

significant (entries 2 and 3); however, allyl acetates were less reactive toward the borylation.¹⁰ Although the starting crotyl chloride was a mixture of (*E*)- and (*Z*)-isomers, the borylation of such aliphatic allyl electrophiles proceeded regio- and stereoselectively to give (*E*)-crotylboronates **3e** exclusively (entry 5). Also, 3-chloro-1-butene afforded the same product **3e** (entry 6), suggesting a process via π -allyl platinum intermediacy. It is interesting to note that the present platinum-catalyzed borylation afforded regio- and stereodefined allylboronates, whereas the palladium-catalyzed borylation of such aliphatic allyl electrophiles proceeded in modest stereoselectivity.⁴ Alicyclic allyl halides also afforded the corresponding boronates in high yield (entry 8).

Table 2
Borylation of representative **2** with **1** (Eq. (1))^a

entry	substrate 2	product	yield ^b (%)	<i>E/Z</i> ^c
1	 2a	 3a	(72)	>99
2	 2b	 3b	(70)	–
3	 2c	3b	(77)	–
4	 2d	 3d	78	–
5	 2e^d	 3e	67	>99
6	 2f	3e	78	>99
7	 2g	 3g	49	–
8	 2h	 3h	81	–

^a All reactions were conducted in toluene (1–4 mL) at 50 °C for 16 h using **1** (1.5 mmol) and **2** (1.0 mmol) in the presence of Pt(dba)₂ (0.03 mmol), AsPh₃ (0.12 mmol), and Et₃N (3 mmol). ^b Isolated yields of **3** were based on **2**. GLC yields were shown in parentheses. ^c Determined by GLC and ¹H NMR analysis of isolated products. ^d *E/Z* = 87/13.

Organometallic reagents such as an iridium complex are known to react with dialkoxyborane to give the organoboronates.¹¹ Analogous to this reaction, the π - and/or σ -allylplatinum species generated by the oxidative addition of **2** to Pt⁰ may react with **1** to form the B–C bond in the present process. Actually, the treatment of $[(\eta^3\text{-C}_3\text{H}_5)\text{PtCl}]_4$ ¹² with **1** at 50 °C in the presence of Et₃N gave the corresponding allylboronate **3b** (yield, 6%), although the reaction conditions were not optimized.¹³

In conclusion, we have found a new and stereoselective synthesis of allylboronates **3** in which pinacolborane **1** acts specifically as a boron source for the coupling reaction with allyl halides **2** in the presence of a platinum catalyst and the tertiary amine. Investigations on further mechanistic aspects are currently in progress.

Acknowledgements

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9. A representative procedure is as follows: A flask was charged with Pt(dba)₂ (0.03 mmol), AsPh₃ (0.12 mmol), toluene (1–4 ml), and Et₃N (3 mmol) under an argon flow. Pinacolborane **1** (1.5 mmol) and allyl halide **2** (1.0 mmol) were added successively, and the mixture was stirred at 50°C for 16 h. The reaction mixture was diluted with toluene, washed with water, and dried over MgSO₄. The solvent was evaporated, and product **3** was isolated by distillation with Kugelrohr.
10. Under the present conditions, the borylation of cinnamyl acetate gave only 21% yield of **3a** along with **4a** (23%) and **4a'** (6%).
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13. A mixture of [(C₃H₅)PtCl]₄ (0.0125 mmol), AsPh₃ (0.1 mmol), **2** (0.25 mmol), and Et₃N (0.25 mmol) in toluene (1 ml) was stirred at 50°C for 16 h. GLC analysis of the reaction mixture indicated formation of the corresponding **3b**.