

# Rhodium-Catalyzed Dehydrogenative Coupling Reaction of Vinylarenes with Pinacolborane to Vinylboronates

Miki Murata, Shinji Watanabe, and Yuzuru Masuda\*

*Department of Materials Science, Kitami Institute of Technology, Kitami 090-8507, Japan*

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## Abstract

The treatment of pinacolborane with vinylarenes in the presence of a catalytic amount of  $[\text{RhCl}(\text{cod})]_2$ , through a dehydrogenative borylation, provides pinacol esters of (*E*)-2-arylethenylboronates.

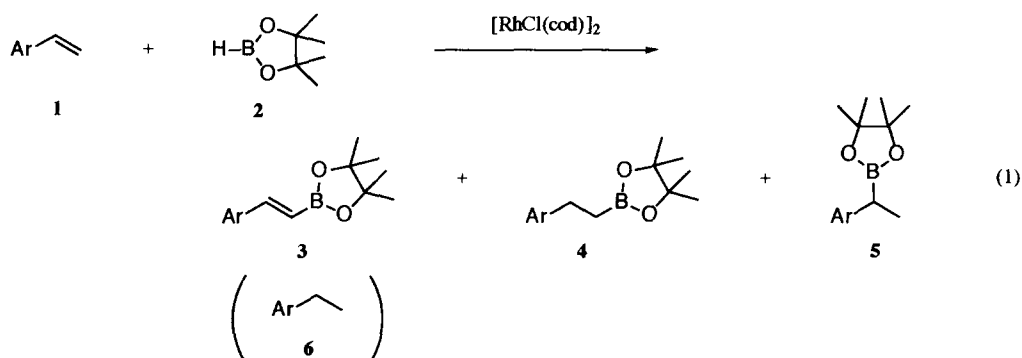
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Alkenylboronates are useful intermediates in organic synthesis, particularly with reactions involving carbon-carbon bond formation through a palladium-catalyzed Suzuki-Miyaura cross-coupling reaction [1]. They can be prepared by several methods, notably by uncatalyzed [2] or transition-metal-catalyzed [3] hydroboration of alkynes with catecholborane. Several authors have observed the formation of dehydrogenated vinylboranes in the catalytic hydroboration of alkenes, suggesting the potential application of that process for preparing vinylboronates [4, 5]. Brown and Lloyd-Jones demonstrated a practical example of the rhodium-catalyzed dehydrogenative coupling reaction of vinylarenes with *N*-isopropyl oxazaborolidine [6]. To our knowledge, however, there has been no report of dehydrogenative borylation using dialkoxyborane to provide a direct procedure for preparing vinylboronates from alkenes.

We herein describe the results of attempting the rhodium-catalyzed dehydrogenative borylation of vinylarenes by using pinacolborane (eq. 1). Recently, pinacolborane has been widely recognized as a potent borane reagent [7], and utilized in the transition-metal-catalyzed hydroboration of alkynes or alkenes [8] and the borylation of aryl halides [9]. Further, the resulting pinacolboronates exhibit good reactivity for conversion of the

boron functionality to other atoms and excellent stability for aqueous workup and chromatography. It is interesting to note that dehydrogenative borylation by pinacolborane in the presence of a phosphine-free rhodium catalyst proceeded predominantly over hydroboration, whereas, commonly, pinacolborane has been applied for the phosphine-containing rhodium-catalyzed hydroboration of alkenes, including vinylarenes. It has hitherto been reported that other borane reagents usual for catalytic hydroboration, such as catecholborane or *N*-methyl oxazaborolidine, were not suitable for selective dehydrogenative borylation [6].



The reaction of styrene **1a** (2 mmol) with pinacolborane **2** (1 mmol) in toluene (4 ml) at ambient temperature in the presence of a catalytic amount of  $[\text{RhCl}(\text{cod})]_2$  (0.005 mmol) caused a dehydrogenative coupling to give (*E*)-2-phenylethenylboronate **3a** (94% GLC yield based on **2**) along with a small quantity of hydroboration products (2-phenylethylboronate **4a**, 3%; 1-phenylethylboronate **5a**, 3%). Concurrently, ethylbenzene **6a** was generated in 46% yield based on **1a**, exhibiting that styrene **1a** acted as a hydrogen acceptor. With regard to catalysts, a variety of transition metal complexes were examined. In comparison with the  $[\text{RhCl}(\text{cod})]_2$ , other phosphine-free complexes such as  $[\text{Rh}(\text{cod})_2]\text{BF}_4$ ,  $\text{Rh}_4(\text{CO})_{12}$ ,  $[\text{IrCl}(\text{cod})]_2$ ,  $\text{Ir}_4(\text{CO})_{12}$ ,  $\text{Ru}_3(\text{CO})_{12}$ , and  $[\text{RuCl}_2(\text{cod})]_n$  were less effective. However, the phosphine containing  $\text{RuCl}_2(\text{PPh}_3)_3$  showed some catalytic activity for the dehydrogenative borylation at 50 °C (**3a**, 60%; **4a**, 21%; **5a**, 16%). Five solvents, including toluene, benzene,  $\text{CH}_2\text{ClCH}_2\text{Cl}$ , THF, and dioxane, were tested, and it was observed that these did not play an important role.

The results obtained with representative vinylarenes are summarized in Table 1 [10]. As shown, the present reaction proceeded regio- and stereoselectively; that is, neither 1-arylethenylboronate nor the (*Z*)-isomer was produced, although **3** was contaminated with a small amount of hydroboration products **4** and **5** in each case. The presence of



alkylboronates such as **4** and **5** were not capable of palladium-catalyzed cross-coupling [12]. Thus, the cross-coupling of **3c** prepared from **1c** (3 mmol) with 4-fluoriodobenzene (1.0 mmol) at 90 °C for 8 h in the presence of PdCl<sub>2</sub>(dppf) (0.03 mmol) and 3M aq. KOH (1 ml) provided the corresponding stilbene in 79% isolated yield based on the iodoarene employed.

In conclusion, the present dehydrogenative borylation of vinylarenes with pinacolborane provides general and synthetically useful access to a wide range of 2-arylethenylboronates. Additional detailed studies in this area are currently underway.

## References and Notes

- \* E-mail: MASUDA-Yuzuru/mtrl@king.cc.kitami-it.ac.jp
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  - [9] Murata, M.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62*, 6458.
  - [10] A representative procedure is as follows. A flask was charged with [RhCl(cod)]<sub>2</sub> (0.005 mmol) and toluene (4 ml) under an argon flow. Pinacolborane **1** (1.0 mmol) and vinylarenes **2** (2.0 mmol) were added successively, and the mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with toluene, washed with water, and dried over MgSO<sub>4</sub>. The solvent was evaporated, and product **3** was isolated by distillation with Kugelrohr or chromatography over silica gel.
  - [11] In the case of aliphatic alkenes such as 1-hexene and 3,3-dimethyl-1-butene, the usual hydroboration only proceeded under the present condition, and trace amounts (less than 5%) of the vinylboronates could be detected by GLC.
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