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

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Abstract

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

Keywords: Boron and compounds; Alkenes; Rhodium and compounds; Dehydrogenation; Suzuki reactions

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

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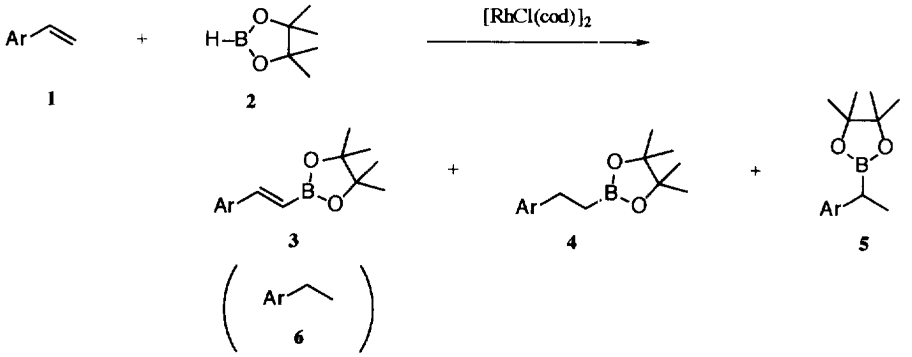
boron functionality to other atoms and excellent stability for aqueous workup and chromatography. It is interesting to note that dehydrogenative borylation by pinacolborane in the presence of a phosphine-free rhodium catalyst proceeded predominantly over hydroboration, whereas, commonly, pinacolborane 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].



(1)

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 $[RhCl(cod)]_2$ (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 $[RhCl(cod)]_2$, other phosphine-free complexes such as $[Rh(cod)_2]BF_4$, $Rh_4(CO)_{12}$, $[IrCl(cod)]_2$, $Ir_4(CO)_{12}$, $Ru_3(CO)_{12}$, and $[RuCl_2(cod)]_n$ were less effective. However, the phosphine containing $RuCl_2(PPh_3)_3$ showed some catalytic activity for the dehydrogenative borylation at 50 °C (**3a**, 60%; **4a**, 21%; **5a**, 16%). Five solvents, including toluene, benzene, CH_2ClCH_2Cl, 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

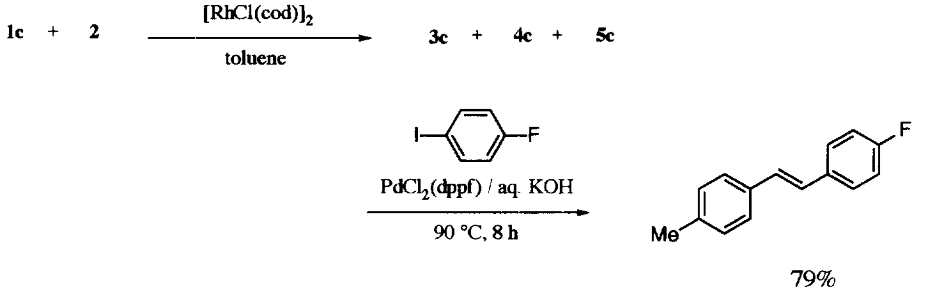
Table 1. Reaction of Representative 1 (Eq 1)[a]

			ratio (%)[c]		
entry	alkene **1**	yield (%)[b]	**3**	**4**	**5**
1	$PhCH=CH_2$ (**1a**)	84	96	3	1
2	$4\text{-}MeOC_6H_4CH=CH_2$ (**1b**)	90	95	4	1
3	$4\text{-}MeC_6H_4CH=CH_2$ (**1c**)	93	95	3	2
4	$4\text{-}ClC_6H_4CH=CH_2$ (**1d**)	87	95	3	2
5	$4\text{-}MeO_2CC_6H_4CH=CH_2$ (**1e**)	86	93	4	3
6	vinylferrocene (**1f**)	85	85	15	0

[a] All reactions were conducted in toluene (4 ml) at room temperature for 4 h using **1** (2.0 mmol) and **2** (1.0 mmol) in the presence of $[RhCl(cod)]_2$ (0.005 mmol). [b] Isolated yields of a mixture of **3**, **4** and **5** by Kugelrohr distillation. [c] Determined by GLC analysis of isolated products.

functional groups such as $MeCO_2$ in the initial **1** did not interfere with the outcome of the present reaction (entry 5), corroborating that **2** was inert to many functional groups [7-9]. In addition, the differences in yields and in selectivity among vinylarenes having electron-donating or electron-withdrawing groups were not significant (entries 2-5). Interestingly, the present application for vinylferrocene **1f**, which previously resulted in a low yield in the case of employment of *N*-isopropyl oxazaborolidine [6], also gave the corresponding **3** without significant difficulty (entry 6). On the other hand, all attempts at the dehydrogenative borylation of other alkenes except for vinylarenes were unsuccessful [11].

Finally, the potential versatility of the present borylation was demonstrated by the one-pot synthesis of stilbenes (eq. 2). Although the dehydrogenative borylation of **1** provided a mixture of the major alkenylboronates and a small amount of alkylboronates, the resulting solution could be used directly for the next Suzuki-Miyaura reaction, since



(2)

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-fluoroiodobenzene (1.0 mmol) at 90 °C for 8 h in the presence of PdCl$_2$(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.

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[10] A representative procedure is as follows. A flask was charged with [RhCl(cod)]$_2$ (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$_4$. 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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