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Palladium-catalyzed Borylation of Aryl Arenesulfonates with Dialkoxyboranes

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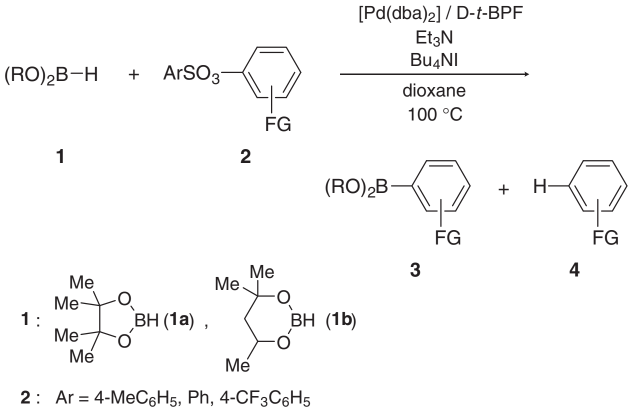
The cross-coupling of aryl arenesulfonates with dialkoxyboranes proceeded in the presence of $\mathrm{Bu_4NI}$ and a catalytic amount of $[\mathrm{Pd(dba)_2}]$/1,1′-bis(di-*tert*-butylphosphano)ferrocene, giving good yields of the corresponding arylboronates. The protocols tolerate a wide range of functional groups, including ester, nitrile, and ketone.

Arylboronic acids and their esters are crucial intermediates for versatile transition-metal-catalyzed C–C bond-forming reactions such as the palladium-catalyzed Suzuki–Miyaura cross-coupling[1] and the rhodium-catalyzed Miyaura conjugate addition.[2] Not surprisingly, the versatility of these methodologies has led to considerable development of C–B bond formation. From environmental and economic points of view, the transition-metal-catalyzed borylation of ubiquitous C–H bonds of arenes is an ultimate goal, however, this method has been a little problematic with regard to the control of regioselectivity to date.[3] In contrast, the borylation of aryl electrophiles has proven to be a regiospecific and powerful method for C–B bond formation.[4] Although these techniques involve the use of tetraalkoxydiborons or dialkoxyboranes **1**, **1** is more cost-effective and atom-economical boron sources.

In 1997, we demonstrated the first examples of the borylation of aryl halides and triflates with pinacolborane (**1a**) by using a suitable palladium catalyst and tertiary amine.[5] Thereafter, numerous catalyst systems have been reported to affect the borylation of aryl halides with **1**.[6–9] Despite several advantages of employing aryl sulfonates, most studies have not focused on the borylation of aryl sulfonates. Recently, Percec has reported the use of aryl mesylates and tosylates as effective electrophiles in the nickel-catalyzed borylation using neopentylglycolborane, although no example of substrates containing ketones has been disclosed.[10] Since these sulfonates are cheaper and more stable than the corresponding triflates, they should be more attractive substrates.

Nonetheless, we would suggest that a drawback of Percec's procedure was that neopentylglycolborane should be prepared in situ, presumably due to its lower stability. In contrast, **1a** and hexyleneglycolborane (**1b**) can be isolated, and a further important point is that these dialkoxyboranes exhibit good reactivity for the palladium-catalyzed borylation of aryl halides.[5–7,11] The purpose of our studies is to explore a substrate scope of the borylation using such dialkoxyboranes **1**. In this paper, we wish to report an efficient protocol for the palladium-catalyzed borylation of aryl arenesulfonates **2** (Scheme 1).



Scheme 1.

Table 1. Palladium-catalyzed borylation of **2a** with **1a**[a]

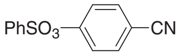
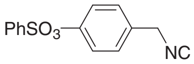
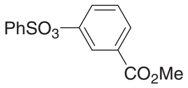
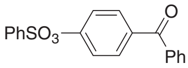
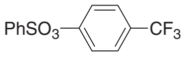
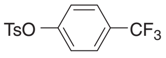
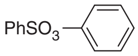
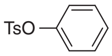
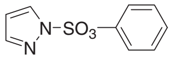
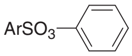
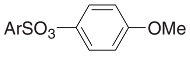
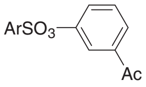
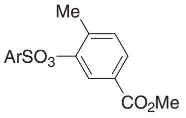
Entry	Ligand	Additive	Yield/%[b]	
			3a	**4a**
1	D-*t*-BPF	none	8	39
2	D-*t*-BPF	$\mathrm{Bu_4NI}$	90	7
3	D-*t*-BPF	$\mathrm{Bu_4NBr}$	37	10
4	D-*t*-BPF	$\mathrm{Bu_4NCl}$	19	22
5	D-*i*-PPF[c]	$\mathrm{Bu_4NI}$	19	28
6	*t*-Bu-DPEphos[d]	$\mathrm{Bu_4NI}$	12	0

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (0.50 mmol), $[\mathrm{Pd(dba)_2}]$ (0.025 mmol), ligand (0.025 mmol), $\mathrm{Et_3N}$ (1.5 mmol), additive (0.55 mmol), in dioxane (2 mL) at 100 °C, 24 h. [b]GC yields are based on **2a**. [c]1,1′-Bis(diisopropylphosphano)ferrocene. [d]Bis[2-(di-*tert*-butylphosphano)phenyl] ether.

As a test for the optimization of reaction parameters, ethyl 4-(phenylsulfonyloxy)benzoate (**2a**) was used as a substrate for the palladium-catalyzed borylation using **1a**. The results are summarized in Table 1. The borylation of **2a** using $[\mathrm{Pd(dba)_2}]$ and 1,1′-bis(di-*tert*-butylphosphano)ferrocene (D-*t*-BPF) as a catalyst gave only 8% yield of the borylated product **3a** due to a strong tendency to produce the reduced arene **4a** (Entry 1). Recently, we reported that addition of an iodide anion source improved the product selectivity on the borylation of aryl chlorides, although we still have no definitive explanation for the role of halide ion.[6b,12] We then examined a treatment with additional tetrabutylammonium halides, and found that the borylation proceeded selectively in the presence of $\mathrm{Bu_4NI}$ (Entry 2). $\mathrm{Bu_4NBr}$ or $\mathrm{Bu_4NCl}$ was less effective as expected (Entries 3 and 4). As for the catalyst system, the combination of $[\mathrm{Pd(dba)_2}]$ and D-*t*-BPF was found to be efficient for this reaction, whereas the use of other ligands such as D-*i*-PPF and *t*-Bu-DPEphos gave lower yields (Entries 5 and 6). $\mathrm{Et_3N}$ as a base and 1,4-dioxane as a solvent, which were extremely effective for the reaction of aryl halides, could also be used with **2a**.[5–7]

After optimization of the reaction conditions, we investigated the scope of the borylation of the aryl arenesulfonates **2**

Table 2. Palladium-catalyzed borylation of representative **2**

Entry	1	2	3	Yield/%[a]
1	**1a**	 (**2b**)	**3b**	77
2		 (**2c**)	**3c**	71
3		 (**2d**)	**3d**	71
4		 (**2e**)	**3e**	87
5		 (**2f**)	**3f**	85
6		 (**2g**)	**3f**	83
7		 (**2h**)	**3g**	24
8		 (**2i**)	**3g**	12
9		 (**2j**)	**3g**	35
10		 (**2k**)[b]	**3g**	80
11		 (**2l**)[b]	**3h**	74
12		 (**2m**)[b]	**3i**	76
13		 (**2n**)[b]	**3j**	65[c]
14	**1b**	**2a**	**3k**	62
15		**2b**	**3l**	70
16		**2m**	**3m**	76

[a]Isolated yields of **3** are based on **2**. [b]Ar = $4\text{-CF}_3\text{-C}_6\text{H}_5$. [c]For 96 h.

using **1** (Table 2).[15] In the first part of this study, **1a** was used as the borylation reagent. Under our standard conditions, electron-deficient aryl benzenesulfonates were efficiently converted to the corresponding products **3** (Entries 1–5). Also, tosylate was a facile leaving group, and **3f** was obtained in good yield (Entry 6). In contrast to the electron-deficient substrates, an electron-neutral aryl sulfonate, phenyl benzenesulfonate (**2h**), did not have enough reactivity and as a consequence **2h** was recovered (Entry 7). Attempts to alleviate this problem through the use of **2i** or **2j**[13] as a substrate also resulted in low conversion to product (Entries 8 and 9). We found however, phenyl 4-trifluoromethylbenzenesulfonate (**2k**) participated in the present palladium-catalyzed borylation to give the desired product **3g** in high yield (Entry 10). Furthermore, the borylation of electron-rich (Entry 11), -deficient (Entry 12), and sterically hindered aryl 4-trifluoromethylbenzenesulfonates (Entry 13) could also be accomplished.[14]

Recently, it was shown that **1b** was a cost-effective borylation reagent for the palladium-catalyzed borylation; however, these studies were limited to aryl halides and triflates.[11] The second portion of this work involved the application of this protocol to the borylation of **2** with **1b**. Several aryl sulfonates having suitable leaving groups were borylated using **1b** without any difficulty (Entries 14–16). Both of the dialkoxyboranes, **1a** and **1b**, were tolerant of a variety of common functional groups. As a result, the presence of functional groups, such as esters (Entries 3, 13, and 14), ketones (Entries 4, 12, and 16), and nitriles (Entries 1, 2, and 15), in the starting **2** did not interfere with the outcome of the present borylation.

In conclusion, we have developed a general method for the borylation of aryl arenesulfonates **2** using dialkoxyboranes **1**. The combination of $[\mathrm{Pd(dba)_2}]$ and D-*t*-BPF was a versatile catalyst system, and the treatment with additional TBAI was critical for the selective borylation. Investigations for mechanistic studies and the extension to other organic electrophiles are currently underway in our laboratory.

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14 The reaction of benzenesulfonate counterparts of **2l**–**2n** gave the corresponding products **3h**–**3j** in ≈20% yields.

15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.