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Citation	Tetrahedron Letters, 38(19), 3447-3450 https://doi.org/10.1016/S0040-4039(97)00642-4
Issue Date	1997-05-12
Doc URL	https://hdl.handle.net/2115/55295
Type	journal article
File Information	TetrahedronLetters38_3447.pdf



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A Synthesis of Arylboronates via the Palladium(0)-Catalyzed Cross-Coupling Reaction of Tetrakis(alkoxo)diborons with Aryl Triflates

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Abstract: Tetrakis(alkoxo)diborons cross-coupled with aryl triflates at 80 ˚C in the presence of PdCl2(dppf)-dppf catalyst and KOAc in dioxane, producing arylboronates in excellent yields. The synthetic utility of the method was demonstrated by the tandem coupling between two non-identical aryl triflates to give unsymmetrical biaryls.

Recent studies on the transformations of tetrakis(alkoxo)diborons1 (1) by transition-metal catalysis provide new methodology for the synthesis of organoboron compounds. The addition of 1 to alkynes,2 1,3-dienes,3 and alkenes4 is effectively catalyzed by Pt(0), Rh(I), or Au(I) complex to provide a convenient access to stereodefined bis(boryl)alkenes, bis(allyl)boronates, and bis(boryl)alkanes. The mechanism was postulated to proceed through the oxidative addition of 1 to the low-valent metal complex to form bis(boryl)metal intermediate. Alternative route from 1 to organoboron compounds is the Pd(0)-catalyzed cross-coupling with organic electrophiles, which involves the transmetalation of boryl group from 1 to R-Pd(II)-X intermediate. Haloarenes5 and allyl acetates6 smoothly coupled with 1 in the presence or absence of base to afford the corresponding aryl- and allylboronates. As a part of our program on the direct borylation of organic electrophiles using 1, we wish to report here the Pd(0)-catalyzed cross-coupling reaction of 1 with aryl triflates (2) to give arylboronates (3) (Eq. 1).

Initially, we examined the reaction between bis(pinacolato)diboron 1a (1.1.mmol) and 2 (1.0 mmol) under the conditions utilized in the similar coupling with haloarenes. Although phenyl triflate smoothly underwent the coupling at 80。C in the presence of PdCl2(dppf) catalyst (3 mol%) and KOAc (3 mmol) in DMSO (6 ml) to give a 91% yield of phenylboronate, relatively low yields were obtained when using substituted 2. The coupling of 2 having electron-withdrawing groups such as 4-acetylphenyl triflate was complete within 2 h under the conditions; however, it resulted only a 62% yield of 3 together with 4-hydroxyacetophenone (29%) caused by the base-promoted hydrolysis of 2.7 Electron-donating substituents extremely slowed down the reaction rate. The coupling of 4-methoxyphenyl triflate was incomplete even on prolonged heating (24 h), giving a 64% yield of 3 due to the catalyst decomposition. Presumably, dppf used as a ligand of palladium reacts with 2 to be converted into phosphonium salts.8

Finally, the successfull coupling could be achieved in both cases by the use of dioxane as a solvent and the addition of dppf ligand (3 mol%). When the reactions of 4-acetyl- and 4-methoxyphenyl triflate were conducted under such conditions, the yields of 3 were improved to 92% (6 h) and 93% (13 h), respectively. Less polar solvent is favorable to avoid the hydrolysis of 2, but the use of toluene sufficiently slowed the coupling rate. The addition of LiCl, which is known to suprress the decomposition of catalyst in the Pd(0)-catalyzed cross-coupling of 2 with organostannanes,9 was totally ineffective in the present reaction. Although we have not investigated the effect of base, KOAc can be the most suitable base because stronger bases such as K3PO4 and K2CO3 may promote the further coupling of 3 with 2 leading to biaryls as reported in the similar reaction with haloarenes.5

The procedure could be applied for other alkoxy derivatives of 1. The coupling of tetrakis(methoxo)diboron (1b) with phenyl triflate in the presence of PdCl2(dppf)-dppf catalyst and KOAc in dioxane for 6 h gave an 83% yield of 3 along with biphenyl (14%). For convenience of the analyses, the producs were converted into the corresponding pinacol ester 3 (Eq. 2). On the other hand, the reaction of tetrakis(dimethylamido)diboron (4) was relatively slow resulting a 48% yield of 3.

The representative results of the cross-coupling reaction of 1a with various 2 are summarized in Table 1. 2 including a variety of electron-withdrawing and -donating substutuents can participate in the present coupling to provide 3 in excellent yields. Strong electron-withdrawing property of nitro group was anticipated to enhance the hydrolysis of 2, but the exclusive formation of 3 was observed without such side reaction (Entry 1). ortho-Substituted 3 were also obtained by the reaction with the corresponding 2 (Entries 8 and 9), while all attempts at the coupling of more sterically hindered ortho-disubstituted 2 such as mesityl triflate were unsuccessfull. Synthesis of 2 using Grignard or lithium reagents require the protection of functional groups sensitive to these reagents,10 but the present method is tolerated by various functional groups, e.g., CN, CHO, COMe, and CO2Me (Entries 2-5). Although the coupling of 8-qiunolyl triflate satisfactorily gave the corresponding heteroarylboronates 3 (Entry 11), the similar reaction of 2-quinolyl triflate only gave quinoline resulted by the protodeboration of 3.11

The Pd(0)-catalyzed cross-coupling reaction of arylboron reagents with aryl electrophiles provides a promising route to cunstruct aryl-aryl linkage, which is frequently observed in natural products, pharmaceuticals, and functional polymers.12 Thus, we applied the present method to one-pot synthesis of unsymmetrical biaryls (5) by a tandem cross-coupling reaction between two non-identical 2 (Eq. 3). When 4-acetylphenylboronate generated by the reaction of 1a (1.1 mmol) with corresponding 2 (1.1 mmol) was directly subjected to the next coupling with 4-cyanophenyl triflate (1.0 mmol) in the presence of K3PO4 (3 mmol) and additional PdCl2(dppf) catalyst (3 mol%) at 80 。C for 16 h, the desired 4-(4-acetyphenyl)benzonitrile was produced in 93% yield. The addition of the catalyst was indispesable to achieve high yield because of the catalyst decomposition during the first coupling. Similar tandem coupling between 4-methoxy- and 4-cyanophenyl triflate also afforded an 81% yields of 5. The reaction between 4-methoxy- and 4-methylthiophenyl triflate did not give good result under the conditions (less than 10%), but a 65% yield was achieved by the addition of dppf ligand (3 mol%).

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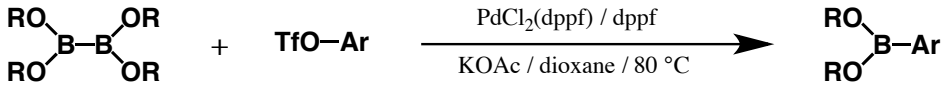
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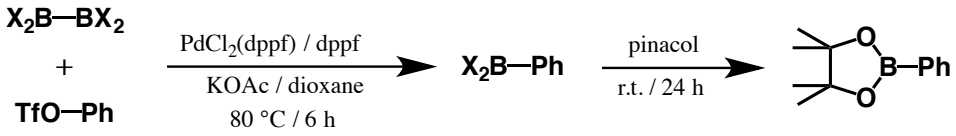
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(1)

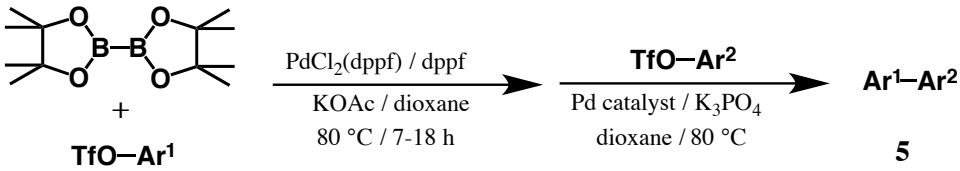
1 **2** **3**



(2)

1b: X = MeO
4: X = Me_2N

X = MeO: 83%
X = Me_2N: 48%



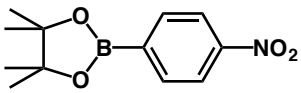
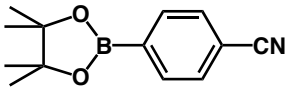
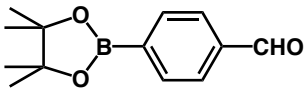
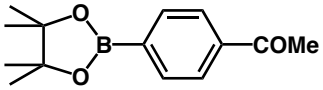
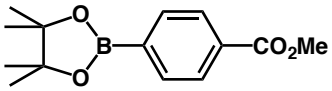
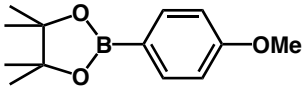
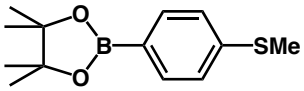
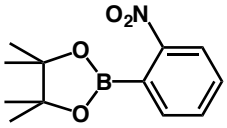
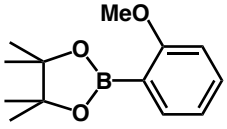
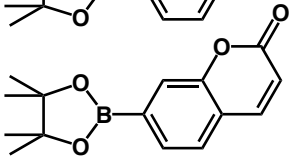
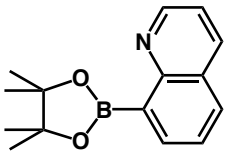
(3)

5

Ar^1	Ar^2	Pd catalyst	Time / h	Yield / %[a]
4-$MeCOC_6H_4$	4-NCC_6H_4	$PdCl_2$(dppf)	16	93
4-$MeOC_6H_4$	4-NCC_6H_4	$PdCl_2$(dppf)	24	81
4-$MeOC_6H_4$	4-$MeSC_6H_4$	$PdCl_2$(dppf) / dppf	24	65

Borylation of **2** (1.1 mmol) was carried out at 80 °C for 7-18 h by using **1a** (1.1 mmol), $PdCl_2$(dppf) (3 mol%), dppf (3 mol%), and KOAc (3 mmol) in dioxane (6 ml) was followed by the next coupling with another **2** (1.0 mmol) at 80 °C in the presence of K_3PO_4 (3 mmol) and additional catalyst (3 mol%). [a]Isolated yields based on **2** employed at the second coupling.

Table 1. The Synthesis of Arylboronates (Eq. 1)[a]

Entry	Triflate (**2**), Ar =	Product (**3**)	Time / h	Yield / %[b]
1	4-$O_2NC_6H_4$		6	86
2	4-NCC_6H_4		15	75
3	4-$HCOC_6H_4$		17	(91)
4	4-$MeCOC_6H_4$		6	(92)
5	4-$MeO_2CC_6H_4$		21	80
6	4-$MeOC_6H_4$		13	(93)
7	4-$MeSC_6H_4$		24	81
8	2-$O_2NC_6H_4$		21	(64)
9	2-$MeOC_6H_4$		16	(80)
10	7-coumaryl		17	84
11	8-quinolyl		39	65

aAll reactions were carried out in dioxane (6 ml) at 80 °C using **1a** (1.1 mmol), **2** (1.0 mmol), $PdCl_2$(dppf) (3 mol%), dppf (3 mol%), and KOAc (3 mmol). [b] Isolated yields based on **2**. and GLC yields are in parentheses.