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Citation	Tetrahedron Letters, 37(38), 6889-6892 https://doi.org/10.1016/0040-4039(96)01505-5
Issue Date	1996-09-16
Doc URL	http://hdl.handle.net/2115/56158
Type	article (author version)
File Information	(10) B-B + AcO-Allyl (Com).pdf



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A Synthesis of Allylboronates via the Palladium(0)-Catalyzed Cross-Coupling Reaction of Bis(pinacolato)diboron with Allylic Acetates

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Abstract: The cross-coupling reaction of bis(pinacolato)diboron [(Me₄C₂O₂)BB(O₂CMe₄)] with allyl acetates regioselectively provided the pinacol esters of allylboronic acids in high yields. The reaction was efficiently catalyzed by Pd(dba)₂ in DMSO at 50 °C.

Allylboron compounds are useful reagents in organic synthesis, addition of which to the carbon-oxygen or the carbon-nitrogen double bond diastereoselectively provides homoallylic alcohols or amines via a chair-like six-membered cyclic transition state.¹ A number of methods is available for the synthesis of allylboron compounds including the transmetalation of allyllithiums or allylmagnesiums to the boron,² the coupling of 1-alkenyl halides with borylmethylzinc reagents,³ the reaction of halomethylboronates with vinylolithiums,⁴ the mono-hydroboration of 1,2- or 1,3-dienes,⁵ and the one-carbon homologation of 1-alkenylboronates.⁶ The reaction of boryl nucleophiles with allylic electrophiles is a convenient and alternative candidate; however, this protocol has been thoroughly limited due to the lack of suitable boron nucleophiles.⁷ We have recently reported the cross-coupling reaction of bis(pinacolato)diboron (1) with aryl halides giving arylboronates.⁸ As a part of our program on the direct borylation of organic electrophiles with 1, we wish to report here the palladium-catalyzed cross-coupling reaction with allyl acetates (2) which regio- and stereoselectively affords the allylboronic esters (3) under neutral conditions.

The representative results are summarized in Table 1. The reaction of 1 with 2-phenyl-2-propenyl acetate in the presence of Pd(dba)₂ (3 mol %) at 50 °C in DMSO for 16 h gave 3 (89%) together with the dimer (4) of the allyl unit (2,5-diphenyl-1,5-hexadiene, 10%) (Entry 1). The reaction was catalyzed by the palladiums without phosphine ligand, such as Pd(dba)₂ and Pd(OAc)₂, whereas the addition of PPh₃, dppf, or P(OPh)₃ extremely slow downed the coupling rate. Although a combination of Pd(dba)₂ and DMSO exhibited excellent catalytic activity, Pd(dba)₂ in other solvents such as DMF, dioxane, or benzene resulted in quite low yields due to the catalyst decomposition precipitating palladium black at the early stage of the reaction.

A comparison of the representative allyl carboxylates demonstrated the superiority of allyl acetates (Entries 1-4). The reaction with the trifluoroacetate gave good yield of 3 without accompanying its dimer (Entry 2), but the use of trifluoroacetates had no advantage over the acetates because its reactions were extremely slow when using more hindered substrates such as cinnamyl trifluoroacetate. The carbonate predominantly provided its dimer (Entry 4).

The results of other allylic acetates are summarized in Entries 5-10. Allyl acetate itself and its derivatives having methyl or phenyl substituents at the α- or β-carbon provided the corresponding 3 in high yields (Entries 5-7, 9). The reaction with γ-substituted allyl acetates such as cinnamyl acetate required longer reaction periods presumably due to their slow oxidative addition to the palladium(0) (Entries 8 and 10). The boron exclusively coupled to the primary carbon of secondary and tertiary allyl acetates (Entries 7 and 9). Both (E)- and (Z)-3-phenyl-2-propenyl acetate gave (E)-3 as a single isomer (Entries 8 and 10). All attempts to the coupling with 3-methyl-2-butenyl acetate and 2-cyclohexenyl acetate were unsuccessful.

The mechanism for the cross-coupling reaction can be analogous to that of disilanes⁹ or distannanes¹⁰ (Figure 1). The oxidative addition of 2 to palladium(0) complex leads to a p-allylpalladium(II) acetate (5). The transmetalation between 5 and 1 forms a p-allyl(boryl)palladium(II) intermediate (6), followed by the reductive elimination of 3 reproduces the palladium(0) complex.

In contrast to the cross-coupling reaction of organoboron compounds with organic halides,¹¹ the present reaction smoothly proceeded under neutral conditions because the oxidative addition of **2** directly produces an (acetoxo)palladium(II)¹² species (**5**). The high reactivity of oxopalladium complex toward the transmetalation with organoboron compounds can be attributed to both the high reactivity of the Pd-O bond, which consists of a soft acid and a hard base combination, and the high oxophilicity of the boron center. Indeed, the relative reactivity of **2** is in the order of nucleophilicity of the carboxylato ligands in **5** (MeOCO₂ > MeCO₂ > PhCO₂ = CF₃CO₂) which is reverse to that of oxidative addition rate. The exclusive formation of **3** over **4** suggests that the transmetalation of **5** with the diboron is reasonably faster than that with **3**. The coupling with the less hindered allylic carbon (Entries 7 and 9) and the formation of (E)-**3** from (Z)-**2** via the isomerization¹³ of syn-*p*-allylpalladiums (**5** or **6**) to the more stable anti-complexes (Entry 10) are also closely similar to other palladium-catalyzed coupling reactions of allyl electrophiles.¹⁴

The representative procedure: Pd(dba)₂ (dba is dibenzylideneacetone) (29 mg, 0.05 mmol) and **1** (280 mg, 1.1 mmol) were placed in a flask flushed with nitrogen. DMSO (6 ml) and 2-phenyl-2-propenyl acetate (1.0 mmol) were successively added, and the resulting solution was then stirred at 50 °C for 16 h. The product was extracted with benzene, washed with brine, and finally dried over MgSO₄. An analytically pure product was isolated by Kugelrohr distillation. 2-Phenyl-2-propenylboronic acid pinacol ester: ¹H NMR (CDCl₃) δ 1.16 (s, 12 H), 2.16 (s, 2 H), 5.10 (s, 1 H), 5.36 (s, 1 H), 7.2–7.3 (m, 3 H), 7.46 (d, 2 H, J = 8.4 Hz); ¹³C NMR (CDCl₃) δ 24.62, 83.41, 112.22, 125.86, 127.21, 128.05, 141.84, 144.37; ¹¹B NMR (CDCl₃) δ 33.16.

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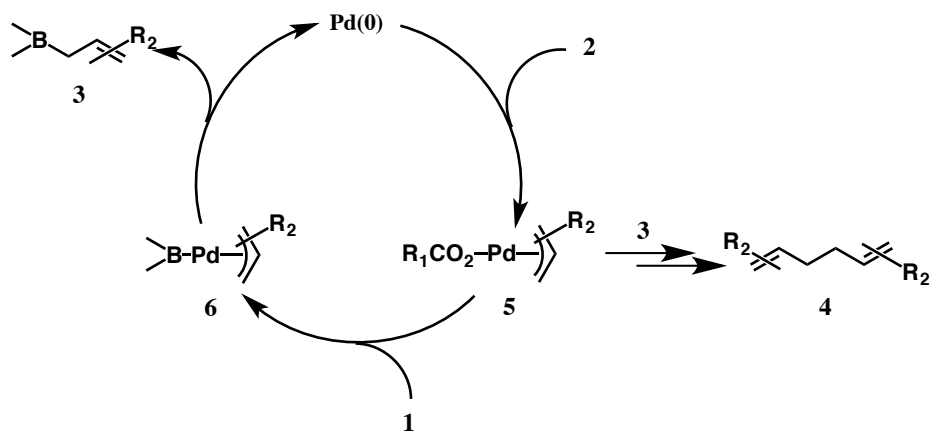
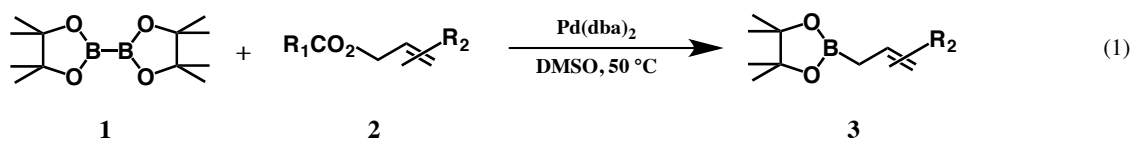


Figure 1. The Catalytic Cycle for the Coupling

Table 1 Cross-Coupling of Allylic Esters with Diboron^a

entry	ester	product	time (h)	yield (%) ^b
1			16	89 ^c
2			22	86
3			18	55
4			16	3 ^c
5			16	68
6			16	70
7			16	83
8			26	73 ^d
9			16	83 ^d
10			24	65 ^d

^a All reactions were carried out in DMSO at 50 °C using diboron (1.1 mmol), ester (1.0 mmol), and Pd(dba)₂ (0.05 mmol).

^b GLC yields based on esters. ^c 0.03 mmol of catalyst was used.

^d (*E*)-isomer over 99% was determined by GLC and ¹H NMR analyses.