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Suzuki-type cross-coupling reaction of pentavalent triarylantimony diacetates with arylboronic acids without a base

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Abstract—Novel base-free Suzuki-type cross-coupling reaction by the use of triarylantimony diacetates and arylboronic acids in the presence of $Pd(PPh_3)_4$ catalyst led to the formation of biaryl derivatives in moderate to excellent yields. The reaction is applicable to a variety of arylboronic acids bearing base-sensitive functional groups.

The Suzuki–Miyaura cross-coupling reaction is one of the most versatile and utilized reactions for carbon–carbon bond formation, in particular for the synthesis of biaryls.[1] In these reactions, however, it is inevitable to add a stoichiometric or excess amount of bases for smooth transformation, which makes it difficult to apply the reaction to base-sensitive substrates and, moreover, the formation of an equivalent amount of waste salts is unavoidable. Consequently, the development of transition metal-catalyzed cross-coupling reactions of organoboron compounds without bases has been a challenging and urgent issue.[2,3] On the other hand, transition metal-catalyzed coupling reaction by the use of organoantimony compounds has recently been the focus of attention. Among these compounds, pentavalent triarylantimony dichloride and diacetate were known to be effective in carbon–carbon bond formation such as Heck-,[4] Stille-,[5] and Hiyama-type[6] cross-coupling reactions. We have recently reported that the reaction of organoantimony(III) compounds with acid halides, aryl halides, and vinyl halides in the presence of Pd-catalyst resulted in cross-coupling reaction to give alkynyl ketones, diarylacetylenes, and enyne compounds.[7] We present here a novel base-free Pd-catalyzed Suzuki-type cross-coupling reaction of organoantimony(V) compounds, triphenylantimony diacetate, with a variety of arylboronic acids.

We initially focused our attention on the determination of the best experimental conditions for the cross-coupling of organoantimony compounds **1a**–**c** with *p*-methylphenylboronic acid **3a** without any bases. The results including the search for active substrates and suitable catalysts for the reaction are summarized in Table 1. The progress of the reaction was monitored by gas–liquid chromatography (GLC) and the reaction time was determined when the yields of products **4a** and **5** show a maximum value because it is impossible to detect the disappearance of the starting material by thin-layer chromatography (TLC) or GLC. First, we performed the reaction of **3a** (3 equiv) and antimony derivatives, such as triphenylantimony **1a**, triphenylantimony dichloride **1b**, and diacetate **1c**,[4b] to compare the reactivity using 5 mol % of $Pd(OAc)_2$ as a catalyst in 1,4-dioxane at 60 °C (entries 1–3). The expected cross-coupling compound **4a** was obtained in a good yield along with homo-coupling product **5** when **1c** was employed as a substrate. In this reaction, one of the three phenyl groups on antimony is involved in the carbon–carbon bond formation. On the other hand, pentavalent dichloride **1b** was found to be less reactive toward the cross-coupling reaction and the major product was biphenyl **5** formed by the homo-coupling reaction of phenyl group on **1b**. It is also known that pentavalent triarylbismuth dichloride **2b** and diacetate **2c** were effective reagents as a pseudo-halogen compound in carbon–carbon

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Keywords: Base-free; Suzuki-type cross-coupling; Antimony; Triphenylantimony diacetate; Palladium; Biaryl.

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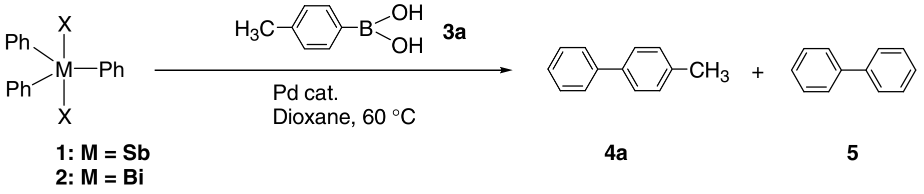
Table 1. Palladium-catalyzed Suzuki-type cross-coupling reaction of organo-antimony **1** and -bismuth **2** compounds with 4-methylphenyllboronic acid **3a**[a]



Entry	Substrate	M	X	Pd cat.	Time (h)	Yield[b,c]	
						4a	**5**
1	**1a**	Sb(III)	—	$Pd(OAc)_2$	12	ND	ND
2	**1b**	Sb(V)	Cl	$Pd(OAc)_2$	12	8	84
3	**1c**	Sb(V)	OAc	$Pd(OAc)_2$	12	92	6
4	**2a**	Bi(III)	—	$Pd(OAc)_2$	12	6	26
5	**2b**	Bi(V)	Cl	$Pd(OAc)_2$	12	3	122
6	**2c**	Bi(V)	OAc	$Pd(OAc)_2$	12	39	97
7	**1c**	Sb(V)	OAc	$PdCl_2$	12	60	3
8	**1c**	Sb(V)	OAc	$PdCl_2(PPh_3)_2$	12	95	2
9	**1c**	Sb(V)	OAc	$Pd(dba)_2$	12	73	4
10	**1c**	Sb(V)	OAc	$Pd(PPh_3)_4$	6	98 (94)[f]	ND (0)
11[d]	**1c**	Sb(V)	OAc	$Pd(PPh_3)_4$	36	91	5
12[e]	**1c**	Sb(V)	OAc	$Pd(PPh_3)_4$	36	95	ND
13	**1c**	Sb(V)	OAc	None	36	ND	ND

[a] Compound **1** or **2** (0.5 mmol), **3a** (1.5 mmol), Pd cat. (5 mol %).

[b] The yields of **4a** and **5** were determined by GLC using tetradecane or octadecane as an internal standard, and the yield 100% correspond to the involvement of one phenyl group on **1** or **2**.

[c] ND: not detected.

[d] Compound **3a** (0.75 mmol).

[e] Pd cat. (1 mol %).

[f] Isolated yield.

bond formation such as Heck-[8] and Stille-type[9] cross-coupling reactions. However, the homo-coupling reaction took precedence over the expected cross-coupling reaction when bismuth agents **2a–c** were used instead of antimony reagents in the present reaction (entries 4–6). These results showed that the reactivity of the metal reagents was considerably affected by not only the valence [(III), (V)] and the kind (Sb, Bi) of the constitutive metal, but also the substituent (Cl, OAc) on the metal. Next, several available palladium catalysts were also screened by means of the reaction between **1c** and **3a** (entries 3, 7–10). All catalysts examined here afforded **4a** in good yields. Among these, $Pd(PPh_3)_4$ appeared to be the best catalyst for this reaction in terms of the yield (98%) of the cross-coupling product **4a** and reaction time (6 h), and no homo-coupling product **5** was formed (entry 10). When the reaction was carried out at rt, **4a** was formed in 41% yield after 24 h. We also tested the reaction without a palladium catalyst, but the formation of coupling products **4a** and **5** was not detected by GLC analysis (entry 13). When loading of boron reagent (1.5 equiv, entry 11) and catalyst (1 mol %, entry 12) was decreased, prolonged time was required to finish the reaction and the formation of **5** was observed in the former reaction. Utilization of other solvents such as toluene (44%) and 5:1 mixture of dioxane–water (5%) gave inferior results under the same reaction conditions (60 °C, 6 h). Consequently, the best result was obtained when **1c** was treated with **3a** (3 equiv) by the use of $Pd(PPh_3)_4$ (5 mol %) in 1,4-dioxane at 60 °C. Similar reactions by the use of tri(*p*-tolyl)antimony diacetate $[(p\text{-}CH_3C_6H_4)_3Sb(OAc)_2]$[4b] and tri(*p*-chlorophenyl)antimony diacetate $[(p\text{-}ClC_6H_4)_3Sb(OAc)_2]$[10] with **3a** afforded 4,4′-dimethylbiphenyl (96%) and 4-chloro-4′-methylbiphenyl **4f** (93%) in good yields (60 °C, 6 h), respectively.

The scope of the present coupling was evaluated by investigating the reaction of **3a** with a variety of arylboronic acids **3b–o**.[11] The reaction was carried out for 6 h for **3b–d** bearing an electron-donating group and for 18 h for **3f–m** having an electron-withdrawing group, because the reaction rate was sensitive to the electronic nature of the acids and the decrease of **1c** in the course of the reaction could not be monitored by TLC and GLC as noted above (Table 2). Thus, **3b–d** afforded the corresponding cross-coupling product **4b–d** in good yields in a shorter reaction time (6 h, entries 1–3), while **3f–m** gave **4f–m** in satisfactory yields in a longer reaction time (18 h, entries 5–12). The results also showed that the present base-free reaction allows employment of acids **3i,j**, and **3l** with a relatively base-sensitive group. Moreover, the reaction can be applied to the cross-coupling-active substrate, 2-bromophenylbronic acid **3g**, whose carbon–bromine bond remained intact (entry 6). Additionally, the reaction of heterocyclic boronic acids **3n** and **3o** gave the corresponding biaryls **4n** and **4o**, respectively (entries 13 and 14). Unfortunately, sterically hindered 2,6-dimethylphenylboronic acid and basic 4-pyridylboronic acid did not afford cross-coupling products.