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Copper- and base-free Sonogashira-type cross-coupling reaction of triarylantimony dicarboxylates with terminal alkynes under an aerobic condition

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ABSTRACT

A simple copper- and base-free palladium-catalyzed Sonogashira-type cross-coupling by the use of triarylantimony dicarboxylates is described. Reaction of triarylantimony diacetates with terminal alkynes in the presence of 1 mol % of $PdCl_2(PPh_3)_2$ catalyst led to the formation of cross-coupling products in good to excellent yields. The reaction proceeded effectively under an aerobic condition, in that two of the three aryl groups on antimony could be transferred to the coupling products, whereas only one of them was involved in the reaction in an argon atmosphere. The reaction is sensitive to the electronic nature of the diacetates, and those bearing an electron-withdrawing group on the aromatic ring showed higher reactivity than those having an electron-donating group.

The copper(Cu)-palladium(Pd)-catalyzed coupling reaction of terminal alkynes with aryl and vinyl halides to give enyne is known as the Sonogashira cross-coupling, and has become an extremely powerful tool for constructing conjugated acetylenes.[1] The conventional reaction protocol of the Sonogashira cross-coupling employs the Pd–phosphine complex as a catalyst and the Cu salt as a co-catalyst with a large amount of amine as solvent and base.[1,2] However, Cu co-catalysts sometimes lead to the Glaser-type homo-coupling of terminal alkynes to form 1,3-diyne by exposure of the Cu acetylide intermediate to air or other oxidizing agents.[3,4h,5f] Moreover, amines have a characteristic foul smell and pungent flavor. Thus, many improved methodologies, such as Cu-free[4] and Cu- as well as amine-free[5] reactions, were reported recently. To the best of our knowledge, the development of alternative electrophiles to aryl halides and triflates in Cu-free Sonogashira-type cross-coupling reaction has not been reported so far except for tetraarylphosphonium halides. Chang and co-workers have reported that tetraarylphosphonium halides were useful arylating agents for a wide range of terminal alkynes without Cu co-catalyst, however, triethylamine was required as a base.[6] On the other hand, Pd-catalyzed coupling reaction by use of organoantimony compounds has recently been the focus of attention. Triarylantimony dicarboxylates were known to be effective in transition metal-catalyzed carbon–carbon bond forming reactions such as Heck-,[7] Stille-,[8] and Hiyama-type[9] cross-couplings. Among them, Kang et al. reported the Cu salt-mediated Pd-catalyzed cross-coupling of alkynylsilanes with triarylantimony diacetates to give arylated alkynes.[9] We have also found that triarylantimony diacetates is an efficient aryl donor in Pd-catalyzed aryl–aryl bond formation with arylboronic acids, which can be conducted under mild conditions without any base.[10] As a further extension of this work, we investigated the Sonogashira-type sp–sp^2 bond formation of terminal alkynes with triarylantimony diacetates. Here we wish to report a Cu- and base-free Pd-catalyzed cross-coupling of various terminal alkynes with a variety of triarylantimony diacetates to give the corresponding arylated alkynes, in that two of the three aryl groups on the antimony can participate in the formation of coupling product when the reaction is run under an aerobic condition or dioxygen atmosphere.

At the beginning of this research program, we found that the reaction of triphenylantimony diacetate **1a** and phenyl acetylene **2a** in 1,4-dioxane in the presence of $PdCl_2(PPh_3)_2$ catalyst resulted in Sonogashira-type cross-coupling to form diphenylacetylene **3** without Cu reagent and base. It is known that Pd-catalyzed cross-coupling reactions of organoantimony compounds were facilitated under oxidative conditions.[7,11] Thus, in order to elucidate the influence of the reaction atmosphere, we first examined the reaction of **1a** with **2a** (3 equiv) in an argon, air, and dioxygen atmospheres, using 5 mol % $PdCl_2(PPh_3)_2$ as a catalyst in 1,4-dioxane at 80 °C

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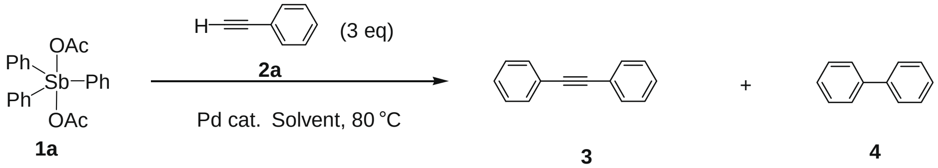
(Table 1, entries 1–3). The reaction in an argon atmosphere gave the cross-coupling product **3** in 93% yield based on **1a**. On the other hand, in an air or a dioxygen atmosphere, the yields of **3** increased to 193% and 198%, respectively. These results show that, in an inert atmosphere, only one of the three phenyl groups on **1a** was involved, whereas two of them could be transferred to **3** in an oxidative atmosphere in the present reaction. However, the third phenyl group on **1a** could not take part in the reaction, even when the reaction was carried out using a large excess amount of **2a** (6 equiv) with prolonged reaction time (24 h).

Next, several Pd catalysts were screened under aerobic conditions (entries 6–11). These results showed that the Pd complexes having phosphine ligand gave **3** in moderate to high yields, and monodentate ligand (triphenylphosphine) was superior to bidentate ligand such as 1,3-bis(diphenylphosphino)propane (entries 7 and 8). Among them, $PdCl_2(PPh_3)_2$ was proved to be the best catalyst for the reaction in terms of the yields of the expected cross-coupling product **3** (193%) and the homo-coupling by-product **4** (<0.5%). These results were in contrast to those of the Heck-type reaction of **1** with alkenes reported by Moiseev et al.,[7b] in that only the Pd catalysts having no phosphine ligand, such as $PdCl_2$ and $Pd(OAc)_2$, were effective in the reaction and no formation of the coupling products was observed when phosphine-ligated Pd catalyst, such as $PdCl_2(PPh_3)_2$, was employed. When the reaction was carried out at room temperature, **3** was formed in 39% yield after 48 h (entry 12). Also apparent was that the decrease of catalyst loading from 5 mol % to 1 mol % did not affect the result and **3** was formed in 199% yield, although a prolonged reaction time was required (entry 4). The screening of a suitable solvent showed that the reaction took place effectively in 1,4-dioxane, DME, NMP, and toluene, whereas other solvents such as CH_3CN, EtOH, and 1,2-DCE gave inferior results (entries 1 and 13–18). It is noteworthy that the formation of 1,4-diphenylbutadiyne resulting from homo-coupling reaction of **2a** was suppressed to less than 1% yield, because no Cu salt which brought about Glaser-type homo-coupling reaction was employed as a co-catalyst in the present reaction. In practice, the reaction of **1a** with **2a** by the use of $PdCl_2(PPh_3)_2$/CuI (5 mol %) catalyst gave a considerable amount of 1,4-diphenylbutadiyne (32% yield) along with **3** (115% yield) (1,4-dioxane, 80 °C, 3 h). We also examined a similar reaction using other antimony compounds, such as $Ph_3Sb(OBz)_2$, $Ph_3Sb(OTs)_2$, Ph_3SbCl_2, Ph_3SbBr_2, Ph_5Sb, and Ph_3Sb. However, all these compounds gave **3** in miserably poor yields (1–6% yields) except for the benzoate $Ph_3Sb(OBz)_2$ (142% yield). The reaction under an aerobic condition is simple and easy to operate. Thus, the best reaction condition was determined to be as follows: triphenylantimony diacetate **1a** was treated with phenyl acetylene **2a** by the use of $PdCl_2(PPh_3)_2$ as a catalyst in 1,4-dioxane without any Cu reagent and base under an aerobic condition.

In order to understand the scope and limitations of the above-mentioned Sonogashira-type reaction, we examined the reactions of various triarylantimony diacetates **1a–j**[12] and terminal alkynes **2a–k** under optimized reaction conditions. The results are summarized in Table 2, in that the yields of the coupling products were calculated from two of the three phenyl groups taking part in the reaction.[13] Initially, triphenylantimony diacetate **1a** was reacted with a variety of terminal alkynes **2b–k** (2.5 equiv) by the use of 1 mol % of $PdCl_2(PPh_3)_2$ in 1,4-dioxane at 80 °C for 18 h under an aerobic condition (entries 1–10). Terminal alkynes with aryls **2b–e**, heteroaryls **2f, g**, and vinyl **2h** groups afforded the corresponding coupling products **5–11** in yields of 68–99%. It should be emphasized that the terminal alkynes **2i–k** having silyl moiety also gave the expected coupling products **12–14** with the silyl groups on **2i–k** being intact. These results were inconsistent with those of Kang's

Table 1
Pd-catalyzed Sonogashira-type coupling of triphenylantimony diacetate **1a** with phenylacetylene **2a**[a]



Entry	Pd cat.	Mol %	Atmosphere	Solvent	Time (h)	Yield [b]	
						3	4
1	$PdCl_2(PPh_3)_2$	5	Ar	1,4-Dioxane	3	93 (90)[g]	<0.5
2	$PdCl_2(PPh_3)_2$	5	Air		3	193 (192)[g]	1
3	$PdCl_2(PPh_3)_2$	5	O_2		3	198 (195)[g]	1
4	$PdCl_2(PPh_3)_2$	1	Air		18	199	<0.5
5	$PdCl_2(PPh_3)_2$	0.1	Air		32	112	<0.5
6	$Pd(PPh_3)_4$	5	Air		3	186	2
7	$Pd(OAc)_2$/dppp	5	Air		3	149	1
8	$Pd(dba)_2$/dppp	5	Air		3	145	7
9	$PdCl_2$	5	Air		3	34	13
10	$Pd(OAc)_2$	5	Air		3	38	56
11	$Pd(dba)_2$	5	Air		3	55	4
12[c]	$PdCl_2(PPh_3)_2$	5	Air		48	39	1
13	$PdCl_2(PPh_3)_2$	5	Air	DME [d]	3	185	1
14	$PdCl_2(PPh_3)_2$	5	Air	NMP [e]	3	186	1
15	$PdCl_2(PPh_3)_2$	5	Air	toluene	6	177	3
16	$PdCl_2(PPh_3)_2$	5	Air	CH_3CN (65C)	6	137	1
17	$PdCl_2(PPh_3)_2$	5	Air	C_2H_5OH	6	124	2
18	$PdCl_2(PPh_3)_2$	5	Air	1,2-DCE [f]	6	121	1

[a] **1a** (0.5 mmol), **2a** (1.5 mmol).

[b] GC yields using octadecane as an internal standard. The yields 100% for **3** and **4** correspond to the involvement of one phenyl group on **1a**.

[c] Room temperature.

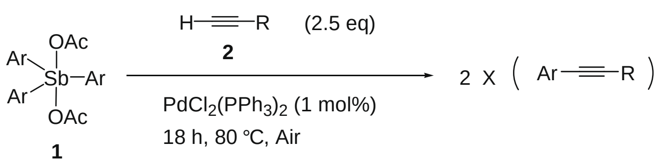
[d] 1,2-Dimethoxyethane.

[e] *N*-Methyl-2-pyrroridone.

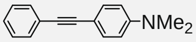
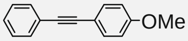
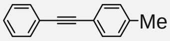
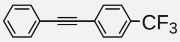
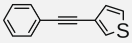
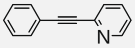
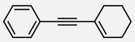
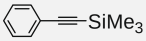
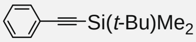
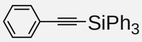
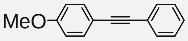
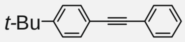
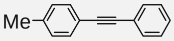
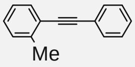
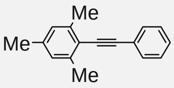
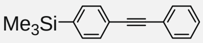
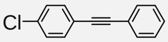
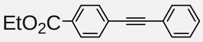
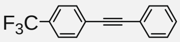
[f] 1,2-Dichloroethane.

[g] Isolated yield.

Table 2
Cu- and base-free Pd-catalyzed Sonogashira-type coupling of triarylantimony diacetates **1** with alkynes **2**[a]



1a: Ar = Phenyl
b: Ar = 4-Methoxyphenyl
c: Ar = 4-*tert*-Butylphenyl
d: Ar = 4-Methylphenyl
e: Ar = 2-Methylphenyl
f : Ar = 2,4,6-trimethylphenyl
g: Ar = 4-Trimethylsilylphenyl
h: Ar = 4-Chlorophenyl
i : Ar = 4-Ethoxycarbonylphenyl
j : Ar = 4-Trifluoromethylphenyl

Entry	Sb reagents	Alkynes	R	Product		Yield (%)[b]
1	**1a**	**2b**	4-Dimethylaminophenyl		**5**	74
2		**2c**	4-Methoxyphenyl		**6**	91
3		**2d**	4-methylphenlyl		**7**	99
4		**2e**	4-Trifluoromethylphenyl		**8**	98
5		**2f**	3-Thienyl		**9**	87
6		**2g**	2-Pyridyl		**10**	68
7		**2h**	1-Cyclohexenyl		**11**	89
8[c]		**2i**	Trimethylsilyl		**12**	75
9		**2j**	*tert*-Butyldimethylsilyl		**13**	80
10		**2k**	Triphenylsilyl		**14**	89
11	**1b**	**2a**	Phenyl		**6**	86
12	**1c**				**15**	94
13	**1d**				**7**	99
14	**1e**				**16**	68
15	**1f**				**17**	3
16	**1g**				**12**	75[c]
17	**1h**				**18**	90
18	**1i**				**19**	75
19	**1j**				**8**	99

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[a] **1** (0.5 mmol), **2** (1.25 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.005 mmol).
[b] Isolated yield. The yield 100% corresponds to the involvement of two phenyl groups on **1**.
[c] In sealed tube filled with oxygen. GC yields using octadecane as an internal standard.

report,[9] in that trimethylsilylacetylene derivatives were employed as alternatives to terminal alkynes and the reaction of **1** with aryltrimethylsilylacetylenes by the use of Pd(0)–Cu(I) catalyst gave rise to the corresponding diarylacetylenes. When 1,4-diethynylbenzene (0.9 equiv) was employed as a coupling partner in the present reaction, the expected double arylation occurred to give 1,4-bis(phenylethynyl)benzene in good yield (78%). However, the reaction of **1a** with aliphatic alkynes, such as electron-deficient ethyl propargylate and electron-rich 2-methyl-3-butyn-2-ol, furnished the corresponding arylated products in 27% and less 1% yields, respectively.

Various triarylantimony diacetates **1b–j**[13] were reacted with phenyl acetylene **2a** under the same reaction conditions. The diacetates **1b–j** with electron-donating and electron-withdrawing groups on the aromatic ring also afforded the corresponding cross-coupling products in excellent to good yields except **1f** (entries 11–19). In the methyl-substituted series of antimony reagents, the influence of the steric hindrance of the antimony reagents **1** was remarkable and the most bulky mesityl derivative **1f** was practically inactive: 4-methylphenyl **1d** (99%) > 2-methylphenyl **1e** (68%) ≫ 2,4,6-trimethylphenyl **1f** (3%). It is known that electron-rich aryl bromides (e.g., 4-bromoanisole) are less reactive aryl donors in the Sonogashira reaction.[1b] However, no noticeable difference in the electronic nature of the diacetates between electron-rich **1b–d**, **g** and electron-poor **1h–j** was observed in the 4-substituted series of antimony reagents. Thus, we examined the competitive reaction using electron-rich **1b** and electron-poor **1j**. The reactions of 1:1:2 (1:1:4) mixture of **1b**, **1j**, and **2a** under the same reaction conditions given in Table 2 gave the coupling products **6** and **8** in 25% (68%) and 74% (96%) yields, respectively. This result indicates that **1j** having an electron-poor aryl group shows higher reactivity than **1b** bearing an electron-rich aryl group.

Possible mechanisms of the present Sonogashira-type coupling are shown in Fig. 1 (1st cycle) and Fig. 2 (2nd cycle). The catalytic cycle of the present reaction would be similar to that of the Heck-type C-arylation of alkenes with **1** reported by Moiseev et al.[7b] and Cu-free Sinogashira coupling proposed by Ljungdahl et al.[4d]

As noted above, only one aryl group on the antimony reagent was involved in the coupling reaction in an argon atmosphere, whereas two of them could participate in the reaction under an oxidative condition. In practice, the reaction of **1a** with **2a** in an argon atmosphere [PdCl$_2$(PPh$_3$)$_2$: 1 mol %, 80 °C, 1,4-dioxane] gave **3** in 99% yield after 3 h, and successive reaction of the mixture under an aerobic condition furnished **3** in 183% yield after 12 h. Taking these results into account, we considered the following two-stage reaction process in the present arylation (Figs. 1 and 2). The initial step of the reaction in an argon atmosphere would be the generation of Pd(0) species **A** by the reaction of PdCl$_2$(PPh$_3$)$_2$ with solvents, substrates, and/or ligand, followed by oxidative addition of Ar$_3$Sb(OAc)$_2$ **1** to **A** to form ArPdSb complex **B**. The complex **B** thus formed is transformed to ArPdOAc complex **C** accompanied by elimination of Sb(III) species Ar$_2$SbOAc **D**. Finally, ligand exchange reaction of **C** with alkynes **2** gives ArPd-alkyne intermediate **E**, which undergoes reductive elimination to form the coupling product **3** and regenerates the Pd(0) species **A**. In the reaction in an argon atmosphere, no further arylation of **2** was observed and the reaction can afford the coupling product **3** in 100% yields at its maximum (Fig. 1).

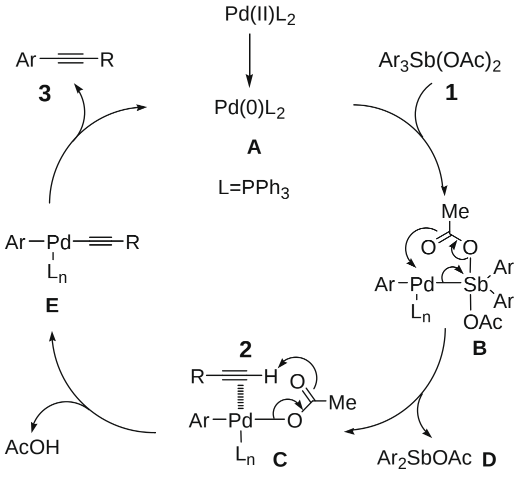

Figure 1. Reaction in an argon atmosphere (1st cycle).

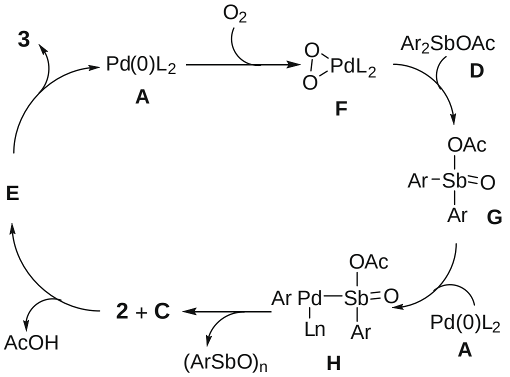

Figure 2. Reaction in an oxidative condition (2nd cycle).

On the other hand, the second aryl group can participate in the reaction under oxidative condition. Recently, generation and involvement of Pd-η^2-peroxo complex have been proposed in a variety of Pd-catalyzed oxidative reactions.[14] Thus, the key step of the second aryl group involvement would be the generation of Pd-peroxo complex **F** from Pd(0) and dioxygen, followed by the oxidation of Ar$_2$SbOAc **D** to pentavalent Ar$_2$Sb(O)OAc **G** by the peroxide **F**. Similar to the diacetate **1**, the Sb(V) species **G** thus formed would function as a aryl donor giving rise to the coupling product **3** (Fig. 2). This interpretation would be supported by the fact that the reaction of Ph$_2$Sb(OBz) with **2** (3 equiv) under an aerobic condition [PdCl$_2$(PPh$_3$)$_2$: 5 mol %, 80 °C, 6 h, 1,4-dioxane] gave **3** in 97% yield. It should be noted that the acetoxy group on the antimony reagent plays an important role in the present reaction, because the reaction of Ph$_3$SbCl$_2$ and Ph$_3$SbBr$_2$ with **2** under the same reaction conditions gave no coupling product **3** (<1%). These results imply that the acetoxy group would work as a base to facilitate the deprotonation of terminal alkynes presented in Fig. 1 **C**.

In summary, we found that triarylantimony diacetates are a new class of electrophiles for Cu- and base-free Sonogashira-type cross-coupling reaction. When the reaction was conducted under an aerobic condition, two of the three aryl groups on the diacetates could be involved in the reaction, and the diacetates with various electron-donating and electron-withdrawing functional groups afforded the corresponding cross-coupling product in satisfactory yields. Synthetic application of this reaction including the use of the third aryl group on the diacetates and detailed reaction mechanisms are in progress.

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References and notes

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12. Triarylantimony diacetates **1a–h** were prepared according to the reported procedure.[10a] Compound **1c**: 50% yield, mp 280–283 °C; **1g**: 63% yield, mp 177–182 °C.
13. *Typical experiment:* a solution of triarylantimony diacetate **1** (0.5 mmol), terminal alkynes **2** (1.25 mmol), and $PdCl_2(PPh_3)_2$ (0.005 mmol) in 1,4-dioxane (3 mL) was heated at 80 °C for 18 h under air. After dilution with ether (20 mL) and water (20 mL), the reaction mixture was separated and the aqueous layer was extracted with ether (20 mL). The combined organic layer was washed with water, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by short column chromatography on silica gel to give the corresponding diarylacetylene derivatives **3** and **5–19**.
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