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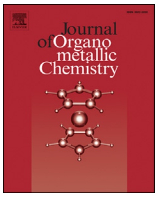

Palladium-catalyzed cross-coupling reactions of triarylbismuthanes with terminal alkynes under aerobic conditions

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ABSTRACT

A simple Pd-catalyzed Sonogashira-type cross-coupling reaction using of triarylbismuthanes is described. The reaction of triarylbismuthanes with terminal alkynes in the presence of 5 mol% of $Pd(OAc)_2$, 6 equiv. AgF and 6 equiv. K_3PO_4 at room temperature afforded the coupling products in good to excellent yield. The reaction proceeded effectively under aerobic conditions, and all three aryl groups on bismuth could be transferred to the coupling products. The reaction was sensitive to the electronic nature of the triarylbismuthanes: substrates bearing an electron-withdrawing group on the aromatic ring showed higher reactivity than those having an electron-donating group.

1. Introduction

The copper(Cu)-palladium(Pd)-catalyzed coupling reaction of terminal alkynes with aryl or vinyl halides to give enynes is known as the Sonogashira reaction, and it has become an extremely powerful tool for constructing conjugated acetylenes [1–4]. The Sonogashira reaction conventionally employs a Pd-phosphine complex as the catalyst, along with a Cu salt as the co-catalyst and excess amine as the solvent and base [1–5]. However, the Cu co-catalyst sometime lead to the Glaser-type homo-coupling of terminal alkynes to form 1,3-diynes under aerobic conditions [6,7]. Moreover, amines have a characteristic foul smell and pungent flavor. In the past decades, various modifications of the Sonogashira reaction have been developed. For example, the use of different aryl substances as the pseudo-halide component and silver reagents as additives has been investigated for C(Ar)–C(sp) bond formation. In 2003, Zou et al. reported a procedure for constructing internal alkynes through the cross-coupling reaction of terminal alkynes and arylboronic acids catalyzed by a $Pd(dppf)Cl_2$–AgO system [8]. Since then, this type of reaction using arylboronic acids has been developed from research of catalyst and ligand by several groups [9–12]. Recently, Zhu et al. carried out the reaction of terminal alkynes with hypervalent aryl iodonium salts using a $PdCl_2$–AgI system [13]. Furthermore, Cheng et al. reported that aryl trimethoxysilanes are useful arylating agents when using a $Pd(dppf)Cl_2$–AgF system [14].

Organobismuth compounds are typically non-toxic, environmentally benign, and potentially useful candidates as synthetic reagents [15–17]. The utility of trivalent organobismuth compounds such as triarylbismuthanes [Ar_3Bi] has attracted much attention in recent years, particularly through their use in the Pd-catalyzed C(Ar)–C(Ar, sp^2) bond formation reaction with aryl or vinyl halides [18–22]. Two methods are known for the synthesis of internal alkynes using the Pd-catalyzed coupling reaction of organobismuth compounds. Shimada et al. reported the reaction of aryl halides with Bi-phenylethynyl-tetrahydrodibenz[c,f] [1,5] azabismocines catalyzed by a $Pd(OAc)_2$/dppf system and CsF under an inert atmosphere [23]. Rao et al. have developed the domino reaction of 1,1-dibromo-1-alkenes with triarylbismuthanes in the presence of $Pd(PPh_3)_4$ catalyst with a base under an inert atmosphere [24]. However, to be best of our knowledge, Pd-catalyzed C(Ar)-C(sp) bond formation by the reaction of terminal alkynes with triarylbismuthanes under aerobic conditions has not hitherto been reported. Herein, we report a novel Sonogashira-type reaction

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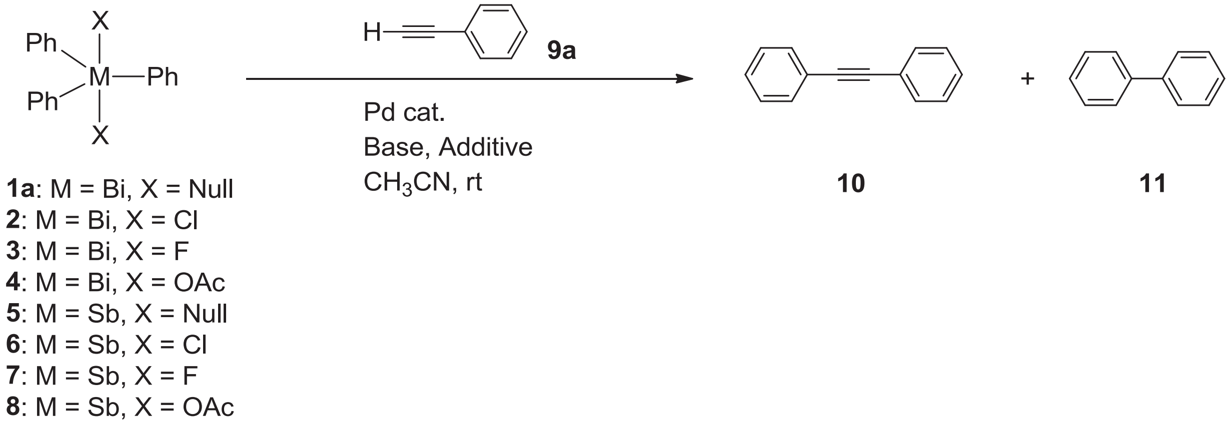
using triarylbismuthanes as pseudo-halides in the presence of a silver salt and base under aerobic conditions.

2. Results and discussion

We initially focused on the determination of the best experimental conditions for the cross-coupling of phenyl acetylene (**9a**) with organobismuth and organoantimony compounds (**1**–**8**), such as Ph_3Bi (**1a**), Ph_3BiCl_2 (**2**), Ph_3BiF_2 (**3**), $Ph_3Bi(OAc)_2$ (**4**), Ph_3Sb (**5**), Ph_3SbCl_2 (**6**), Ph_3SbF_2 (**7**) and $Ph_3Sb(OAc)_2$ (**8**). The results including screening of suitable catalysts, bases, additives, and active aryl substances are summarized in Table 1. We fiest performed the reaction of **9a** (3 equiv.) with organobismuth such as **1a**, **2**, **3**, and **4** to compare their reactivity, using 5 mol% of $Pd(OAc)_2$, AgF (6 equiv.) and K_3PO_4 (6 equiv.) in acetonitrile at room temperature under aerobic conditions (entries 1–4). The expected cross-coupling compound **10** was obtained in high yields when **1a** was employed as a substrate (entry 1). Moreover, all three phenyl groups on bismuth in **1a** participated in this reaction. It is known that 2 and 4 are effective reagents as pseudo-halide compounds in C(Ar)–C(Ar, sp^2) bond formation, for example, in Heck- [25] and Stille-type [26] cross-coupling reactions. In this reaction however, pentavalent organobismuth compounds **2**, **3**, and **4** were found to be less reactive (entries 2–4). We also evaluated the reaction using organoantimony compounds, such as **5**, **6**, **7**, and **8** (entries 5–8). However, all these compounds gave the product **10** in poor yield. These results show that the reactivity of the metal reagents is considerably affected by the valence [(III), (V)] and the kind (Bi, Sb) of the constitutive metal. Several available palladium catalysts were then screened in the reaction between **1a** and **9a** (entries 1, 9–11).

Table 1
Pd-catalyzed cross-coupling reaction of organobismuth and antimony compounds **1**–**8** with phenylacetylene **9a**.[a]



Entry	Substrate	Pd cat.	Base (equiv)	Additive (equiv)	Time (h)	Yield (%)	
						10[b]	11[b]
1	**1a**	$Pd(OAc)_2$	K_3PO_4 (6)	AgF (6)	2	99 (96)[c]	<1
2	**2**	$Pd(OAc)_2$	K_3PO_4 (6)	AgF (6)	24	29	<1
3	**3**	$Pd(OAc)_2$	K_3PO_4 (6)	AgF (6)	24	2	ND
4	**4**	$Pd(OAc)_2$	K_3PO_4 (6)	AgF (6)	24	1	<1
5	**5**	$Pd(OAc)_2$	K_3PO_4 (6)	AgF (6)	24	5	ND
6	**6**	$Pd(OAc)_2$	K_3PO_4 (6)	AgF (6)	24	<1	ND
7	**7**	$Pd(OAc)_2$	K_3PO_4 (6)	AgF (6)	24	2	<1
8	**8**	$Pd(OAc)_2$	K_3PO_4 (6)	AgF (6)	24	7	<1
9	**1a**	$PdCl_2$	K_3PO_4 (6)	AgF (6)	24	94	<1
10	**1a**	$PdCl_2(PPh_3)_2$	K_3PO_4 (6)	AgF (6)	2	72	1
11	**1a**	$PdCl_2$(dppf)	K_3PO_4 (6)	AgF (6)	2	67	<1
12	**1a**	$Pd(OAc)_2$	$NaHCO_3$ (6)	AgF (6)	4	57	<1
13	**1a**	$Pd(OAc)_2$	AcOK (6)	AgF (6)	4	53	ND
14	**1a**	$Pd(OAc)_2$	K_2CO_3 (6)	AgF (6)	24	52	<1
15	**1a**	$Pd(OAc)_2$	Na_2CO_3 (6)	AgF (6)	24	43	<1
16	**1a**	$Pd(OAc)_2$	^{t}BuOK (6)	AgF (6)	24	<1	<1
17	**1a**	$Pd(OAc)_2$	K_3PO_4 (6)	AgOAc (6)	24	34	<1
18	**1a**	$Pd(OAc)_2$	K_3PO_4 (6)	$AgNO_3$ (6)	24	6	<1
19	**1a**	$Pd(OAc)_2$	K_3PO_4 (6)	Ag_2O (6)	24	4	1
20	**1a**	$Pd(OAc)_2$	K_3PO_4 (6)	CsF (6)	24	<1	<1
21	**1a**	$Pd(OAc)_2$	K_3PO_4 (6)	$TBAF\cdot H_2O$ (6)	24	<1	<1
22	**1a**	$Pd(OAc)_2$	K_3PO_4 (3)	AgF (6)	24	65	<1
23	**1a**	$Pd(OAc)_2$	–	AgF (6)	24	60	6
24	**1a**	$Pd(OAc)_2$	K_3PO_4 (6)	AgF (3)	24	31	2
25	**1a**	$Pd(OAc)_2$	K_3PO_4 (6)	–	24	<1	4
26[d]	**1a**	$Pd(OAc)_2$	K_3PO_4 (6)	AgF (6)	24	29	<1
27[e]	**1a**	$Pd(OAc)_2$	K_3PO_4 (6)	AgF (6)	2	82	2

[a] Condition: **1**–**6** (0.5 mmmol), **7a** (1.5 mmol), Pd cat (0.025 mmol), base (3 mmol), additive (3 mmol).
[b] GC yield using dibenzyl as internal standard. The yield 100% corresponds to the formation of 1.5 mmol of **10** and 0.75 mmol of **11**.
[c] Isolated yield.
[d] Pd. cat (1 mol%).
[e] Under Ar.