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LETTERS

## Palladium-catalyzed cross-coupling reactions between 1-alkynylstibines and acyl chlorides

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### Abstract

1-Alkynyldiphenylstibines react with acyl chlorides in dichloroethane in the presence of a palladium(0) or (II) catalyst to afford alkynyl ketones by cross-coupling reaction in good to moderate yields. These reactions are highly substituent-selective in that only the alkynyl group could be transferred from the antimony compounds, even in the presence of a large excess of acyl chlorides. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* antimony and compounds; alkynes; acylation; coupling reactions; palladium catalyst.

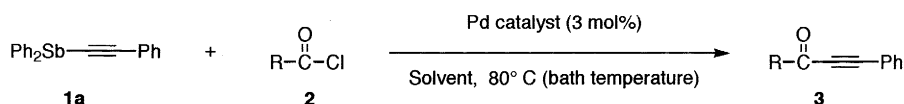
The chemistry of organoantimony compounds has been extensively developed and applications of such compounds to organic synthesis are of current interest.<sup>1</sup> With regard to the carbon–carbon bond-formation by use of organoantimony compounds, a variety of reactions such as self-coupling reactions,<sup>2</sup> cross-coupling reactions,<sup>3–7</sup> carbonylations,<sup>8</sup> and photoreactions<sup>2a,9</sup> have been reported. However, despite the potential of these organoantimony compounds for synthetic reagents, most practical studies have been limited to the use of peraryl antimony derivatives such as triarylstibines and pentaarylstiboranes, mainly because of their high stability and easy availability. In the course of our continuing studies on the synthesis and reactions of organoantimony compounds,<sup>9,10</sup> we were interested in the preparation and synthetic application of trivalent organoantimony compounds bearing alkynyl groups. Here we disclose that treatment of 1-alkynylstibines **1** with acyl chlorides in the presence of a palladium (0) or (II) catalyst resulted in cross-coupling reaction to afford alkynyl ketones **3** in good to moderate yields. These results are the first example of the coupling reaction between trivalent organoantimony compounds and acid halides.

Initially, we examined the reaction between diphenyl(phenylethynyl)stibine **1a**,<sup>11</sup> prepared by the action of phenylethynyllithium on bromodiphenylstibine, and benzoyl chloride in the presence of a variety of Pd(II) or Pd(0) catalysts in various solvents to optimize the reaction conditions. The results are summarized in Table 1. Entry 1 in Table 1 shows that alkynyl ketone **3a** (R=Ph) was produced even in the absence of a palladium catalyst, but the yield was very low. The reaction rates were considerably

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increased in a polar solvent such as acetonitrile and HMPA, but the yields of the product **3a** were not improved (entries 5 and 6). A comparison of the effectivenesses of catalysts showed that  $\text{PhCH}_2\text{PdCl}(\text{PPh}_3)_2$  and  $\text{Pd}(\text{PPh}_3)_4$  were effective (entries 2, 7, and 11), whereas  $\text{PdCl}_2(\text{PhCN})_2$ ,  $\text{Pd}(\text{OAc})_2$ , and  $\text{PdCl}_2$  were less active (entries 8–10). In most cases with Pd(II) catalysts, a catalytic amount of 1,4-diphenyl-1,3-butadiyne was formed in addition to **3a**. Consequently, the best result was obtained when the reaction was carried out in dichloroethane with  $\text{PdCl}_2(\text{PPh}_3)_2$  as a catalyst (entry 2). These reactions were highly substituent-selective in that only the alkynyl group was transferred from the antimony reagent **1a** and no coupling reaction between the phenyl and acyl groups occurred, even in the presence of a large excess of acyl chlorides (5 equiv.). We have also found that triphenyl-, methyldiphenyl-, and diphenyl[(*Z*)- $\alpha$ -styryl]-stibines<sup>12</sup> gave no coupling products under the same reaction condition, although pentavalent organoantimony compounds have been reported to afford coupling products by treatment with acyl halides without a palladium catalyst.<sup>6b,c</sup> These present results are largely different from those of organotin compounds in that a variety of substituents, e.g. alkynyl, vinyl, aryl, and alkyl groups on the tin atom can be coupled with acyl halides in similar reaction.<sup>13</sup>

Table 1  
Palladium-catalyzed cross-coupling reaction of diphenyl(phenylethynyl)stibine **1a** with acyl chlorides **2**<sup>a</sup>



Entry	<b>2</b> / R	Pd Catalyst	Solvent	Reaction time <sup>b</sup> / h	Yield <sup>c</sup> of <b>3</b> / %
1	Phenyl	none	1,2-Dichloroethane	23	5
2			1,2-Dichloroethane	2.5	87
3			Benzene	4.0	77
4	Phenyl	$\text{PdCl}_2(\text{PPh}_3)_2$	Dioxane	4.5	33
5			Acetonitrile	0.7	68
6			HMPA	0.7	58
7		$\text{PhCH}_2\text{PdCl}(\text{PPh}_3)_2$		3.0	82
8		$\text{PdCl}_2(\text{PhCN})_2$		5.0	40
9	Phenyl	$\text{Pd}(\text{OAc})_2$	1,2-Dichloroethane	2.5	51
10		$\text{PdCl}_2$		4.0	41
11		$\text{Pd}(\text{PPh}_3)_4$		2.5	79
12	<i>p</i> -Fluorophenyl			1.8	83
13	<i>p</i> -Chlorophenyl			1.7	82
14	<i>p</i> -Nitrophenyl			0.7	75
15	<i>p</i> -Tolyl			2.5	72
16	<i>p</i> -Methoxyphenyl	$\text{PdCl}_2(\text{PPh}_3)_2$	1,2-Dichloroethane	2.5	77
17	Ethyl			4.0	37
18	<i>n</i> -Hexyl			2.5	47
19	<i>t</i> -Butyl			6.0	26
20	Benzyl			2.5	33
21	Ethyl			1.5	57
22	<i>n</i> -Hexyl	$\text{Pd}(\text{PPh}_3)_4$	1,2-Dichloroethane	1.5	66
23	<i>t</i> -Butyl			6.0	55
24	Benzyl			1.5	46

a; Carried out with **1a** (1 mmol), **2** (1.2 mmol), and a palladium catalyst (3 mol%) in a solvent (5 ml) at 80°C (bath temperature) under an argon atmosphere.

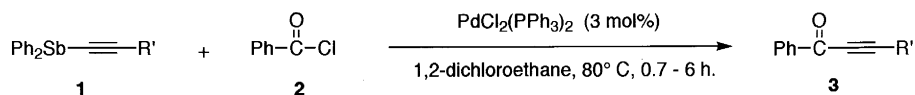
b; Heating of the reaction mixture was terminated with extinction of **1a** on TLC.

c; Yield (%) was calibrated on GLC after removal of polar products by using silica gel column chromatography.

This alkylation procedure could be expanded to a variety of aryl and alkyl acid halides. Aromatic

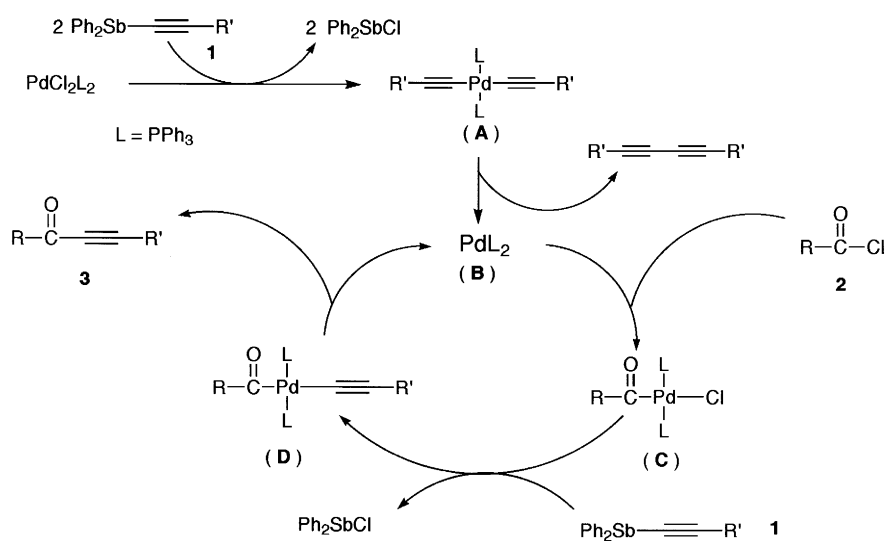
acid chlorides afforded the corresponding alkynyl ketones **3** in good yield (entries 12–16), whereas alkyl acid chlorides gave the products in relatively low yields (entries 17–20). In the latter cases, moderate improvement of the yields of **3** was observed when the reaction was carried out with Pd(PPh<sub>3</sub>)<sub>4</sub> instead of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as a catalyst.

Also proved was that a variety of 1-alkynylstibines **1b–g**<sup>11</sup> could be coupled with benzoyl chloride to produce the corresponding alkynyl ketones **3b–g** (Scheme 1).



Scheme 1. (a) R' = Ph, 87%; (b) R' = *p*-methoxyphenyl, 66%; (c) R' = *p*-fluorophenyl, 71%; (d) R' = TMS, 65%; (e) R' = *n*-butyl, 68%; (f) R' = *n*-hexyl, 65%; (g) R' = benzyloxymethyl, 55%

From the fact that a catalytic amount of 1,3-diyne was formed with Pd(II) catalysts, the initial step of the catalytic cycle in the present reaction would be the generation of Pd(0) species **B** by reductive elimination of 1,3-diyne from the dialkynyl palladium complex **A**, produced by transmetalation between Pd(II) catalysts and 2 equiv. of the 1-alkynylstibines **1**. After oxidative addition of the acyl chlorides to **B** giving rise to the Pd(II) complex **C**, ligand exchange between chloride and the alkynyl group on **1** may occur to afford the intermediate **D**, which presumably undergoes reductive-elimination to give rise to the alkynyl ketone **3**. This elimination also regenerates the active Pd(0) species **B** (Scheme 2). A similar proposal has been offered for the palladium-catalyzed cross-coupling reaction between organotin compounds and acyl halides.<sup>13b</sup>



Scheme 2. Catalytic cycle for Pd-catalyzed coupling reaction of 1-alkynylstibines with acyl chlorides

In summary, we have found that 1-alkynyldiphenylstibines, easily prepared from the reaction of bromodiphenylstibine with alkynyllithium, react with acyl chlorides in the presence of a palladium catalyst to afford the corresponding alkynyl ketones in good to moderate yields. This is the first example of coupling reaction between trivalent organoantimony compounds and acid halides. Further details of the present reactions and the reactions of 1-alkynylstibines with other halogen compounds, e.g. aryl, vinyl, and allyl halides, are currently under study.

## Acknowledgements

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11. Satisfactory elemental analyses and spectroscopic (<sup>1</sup>H NMR and mass) data were obtained for all new compounds. **1a**: 61%, colorless needles, mp 53–55°C (lit.<sup>14</sup> 84–86°C), **1b**: 67%, colorless needles, mp 62–63°C, **1c**: 64%, colorless prisms, mp 42–43°C, **1d**: 75%, colorless oil, **1e**: 69%, colorless oil, **1f**: 71%, colorless oil, **1g**: 40%, colorless oil.
12. When the reaction between benzoyl chloride and diphenyl[(Z)-α-styryl]stibine (mp 54–55°C), prepared by LiAlH<sub>4</sub> reduction of **1a**, was carried out under harder reaction condition [PhCOCl: 1.5 equiv., PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>: 5 mol%, 95°C, 6 h, in HMPA], the formation of *trans*-chalcone (8%) and benzophenone (12%) was observed.
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