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Preparation of triarylantimony(V) diacetates and palladium-catalyzed cross-coupling and carbonylative cross-coupling of triarylantimony(V) diacetates and dichlorides with organostannanes

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Abstract

Triarylstibines react with iodobenzene diacetate in dichloromethane to afford triarylantimony(V) diacetates. The cross-coupling and carbonylative cross-coupling of triarylantimony(V) diacetates and dichlorides with organostannanes was accomplished in the presence of $PdCl_2$ (5 mol%) in CH_3CN at room temperature. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Organoantimony compounds; Palladium-catalyzed; Cross-coupling; Carbonylative; Organostannanes

1. Introduction

Organoantimony compounds have been recently applied for synthetic organic reactions [1]. Most of these works are focused on trivalent triarylstibines or tributylstibines [2] as well as pentavalent stibonium compounds such as tetraphenylstibonium iodide and methoxide [3]. Recently, palladium-catalyzed carbonylation [4] of triarylstibines and acylation of triarylstibines have been reported. Coupling reactions of pentaarylantimony with carbon nucleophiles or electrophiles are known [5]. Although different from the other 15 group elements such as phosphorous, arsenic, and bismuth, the reaction of triarylantimony compounds bearing five covalent bonds exhibited unique reactivity in carbon–carbon bond formation [6]. Therefore we wish to describe a novel method of preparation of triarylantimony diacetates, and the palladium-catalyzed cross-coupling and carbonylative cross-coupling of triarylantimony diacetates and triphenylantimony dichloride (Eqs. (1)–(4)).

$$\underset{\mathbf{1a-b}}{Ar_3Sb(OAc)_2} + \underset{R=\text{vinyl, aryl}}{RSnBu_3} \xrightarrow[CH_3CN,\ rt]{PdCl_2\ (5\ mol\%)} Ar\text{–}R \quad (1)$$

$$\underset{\mathbf{1a-b}}{Ar_3Sb(OAc)_2} + RSnBu_3 + CO\ (1\ atm) \xrightarrow[CH_3CN,\ rt]{PdCl_2\ (5\ mol\%)} ArCOR \quad (2)$$

$$\underset{\mathbf{1c}}{Ph_3SbCl_2} + RSnBu_3 \xrightarrow[CH_3CN,\ rt]{PdCl_2\ (5\ mol\%)} Ar\text{–}R \quad (3)$$

$$Ph_3SbCl_2 + RSnBu_3 + CO\ (1\ atm) \xrightarrow[CH_3CN,\ rt]{PdCl_2\ (5\ mol\%)} ArCOR \quad (4)$$

Triarylantimony(V) diacetates are usually prepared by the oxidation of triarylantimony with *t*-butyl hydroperoxide [7], *t*-butyl peracetate [8], and Hg(II) or Cu(II) salts [9]. Herein we wish to report the preparation of triarylantimony(V) diacetates utilizing $PhI(OAc)_2$ as an oxidizing agent. This procedure is more simple and convenient than the method reported. Thus triarylantimony(V) diacetates **1a** and **1c** were prepared by reaction of triarylantimony(III) with $PhI(OAc)_2$ by stirring in CH_2Cl_2 at room temperature for 6–7 h (Eq. (5)) [10].

$$Ar_3Sb + PhI(OAc)_2 \xrightarrow{CH_2Cl_2,\ rt,\ 7\ h} \underset{\begin{array}{l}\mathbf{1a}\ [11]\ Ar=Ph\quad 73\%\\ \mathbf{1b}\ [12]\ Ar=p\text{-Tolyl}\quad 77\%\end{array}}{Ar_3Sb(OAc)_2} \quad (5)$$

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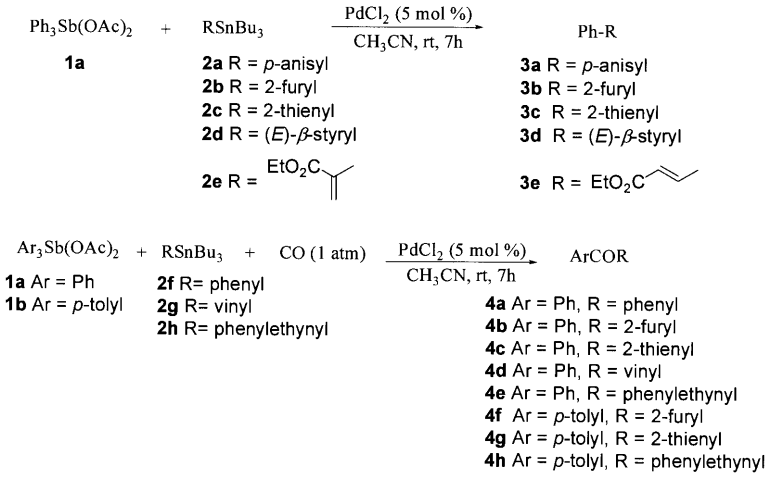
2. Results and discussion

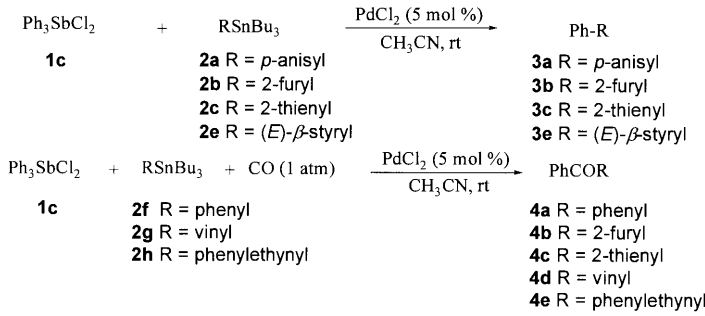
The results of the palladium-catalyzed cross-coupling and carbonylative cross-coupling of triarylantimony(V) diacetates with organostannanes (Scheme 1) are summarized in Table 1. Triarylantimony(V) diacetates (**1a**) [11] reacted with *p*-methoxyphenyltributylstannane (**2a**) in the presence of $PdCl_2$ (5 mol%) in CH_3CN at room temperature for 7 h to afford the coupled product **3a** in 78% yield (entry 1). Among all the catalysts tested [$PdCl_2$, $Pd(OAc)_2$, $Pd_2(dba)_3{\cdot}CHCl_3$, $Pd(PPh_3)_4$], $PdCl_2$ (5 mol%) and $Pd(OAc)_2$ (5 mol%) proved to be the most efficent and $PdCl_2$ (5 mol%) was the preferred catalyst. As a solvent, CH_3CN was the most suitable among the solvents DMF, NMP, MeOH, DME tested. Under the same conditions, the coupling of **1a** with 2-furyl- and 2-thienylstannanes **2b** and **2c** [12] provided the cross-coupled products **3b** [13] and **3c** [14] in 90% yields, respectively (entries 2–3). This coupling method was also applied to alkenyl stannanes **2d** and **2e** to give the substituted alkenes **3d** and **3e** [15] in 80 and 54% yields (entries 4–5). When triphenylantimony(V) diacetate (**1a**) was treated with α-substituted stannane **2e**, (*E*)-cinnamic ester (**3e**) was obtained as the sole product via the mechanism of cine substitution [16] (entry 5). This coupling method was extended to carbonylative cross-coupling to prepare aryl ketones [17]. The palladium-catalyzed carbonylative cross-coupling under atmospheric pressure of carbon monoxide was achieved at room temperature under mild conditions. The reaction of **1a** with phenyltributylstannane (**2f**) under atmospheric pressure of carbon monoxide in the presence of $PdCl_2$ (5 mol%) in CH_3CN at room temperature for 3 h afforded benzophenone (**4a**) in 85% yield (entry 6). Under the same conditions, 2-thienyl- and 2-furylstannanes **2b** and **2c** were readily coupled to give the ketones **4b** [18] and **4c** [19], respectively (entries 7–8). This carbonylative cross-coupling method was also applied to alkenyl- and alkynyl-substituted stannanes. Thus when **2g** and **2h** were treated with **1a** under atmospheric pressure of carbon monoxide, the alkenyl- and alkynyl-substituted ketones **4d** [20] and **4e** [21] were



Scheme 1.

Table 1
The palladium-catalyzed cross-coupling and carbonylative cross-coupling of triarylantimony diacetates with organostannanes

Entry	Organoantimony compounds	Organostannanes	Products	Isolated yields (%)
1	**la**	**2a**	**3a**	78
2	**la**	**2b**	**3b**	90
3	**la**	**2c**	**3c**	90
4	**la**	**2d**	**3d**	80
5	**la**	**2e**	**3e**	54
6	**la**	**2f**	**4a**	85
7	**la**	**2b**	**4b**	81
8	**la**	**2c**	**4c**	81
9	**la**	**2g**	**4d**	83
10	**la**	**2h**	**4e**	77
11	**lb**	**2b**	**4f**	81
12	**lb**	**2c**	**4g**	71
13	**lb**	**2h**	**4h**	75



Scheme 2.

respectively formed in 83 and 77% yields (entries 9–10). For the tri(*p*-tolyl)antimony(V) diacetate (**1b**) [9] the carbonylative coupling with **2b** and **2c** gave the coupled ketones **4f** [22] and **4g** (entries 11–12). Finally, **1b** coupled in the presence of carbon monoxide with alkynyl-substituted stannane **2h** to afford the ketone **4h** in 75% yield (entry 13).

Alternatively, the palladium-catalyzed cross-coupling and carbonylative cross-coupling of the readily available triphenylantimony(V) dichloride (**1c**) with organostannanes (Scheme 2) are summarized in Table 2. **1c** was readily coupled with stannanes **2a**, **2b**, and **2c** to afford the coupled products **3a**–**3c** in 81–90% yields (entries 1–3). When the α-substituted alkenylstannane **2e** was treated with **1c**, the coupled product **3g** with cine substitution was obtained as the sole product (entry 4). This method was also extended to carbonylative cross-coupling. The reaction of triphenylantimony(V) dichloride (**1c**) with stannanes **2f**, **2b**, and **2c** provided the coupled ketones **4a**, **4b**, and **4c** in 88–90% yields (entries 5–7). Finally, **1c** was utilized in carbonylative coupling with alkenyl- and alkynyl-substituted stannanes **2g** and **2h** to afford enone **4d** and ynone **4e** in 81 and 80% yields, respectively (entries 8–9).

Although the detailed mechanism remains to be clarified, it is presumed that oxidative addition of antimony compounds forms the intermediate A, which is subjected to transmetallation and coupling to give the coupled product (Scheme 3).

In conclusion triarylantimony(V) diacetates were prepared conveniently and cross-coupling and carbonylative cross-coupling of triarylantimony(V) derivatives with organostannanes were achieved in the presence of $PdCl_2$ (5 mol%) at room temperature under mild conditions.

3. Experimental

3.1. Materials

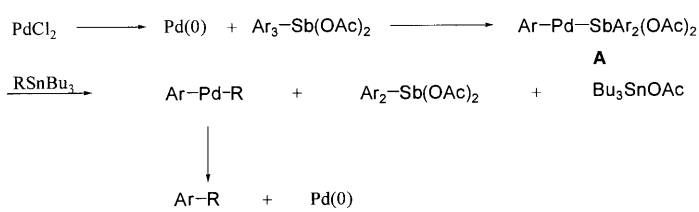
Ph_3SbCl_2 is commercially available from Aldrich Chem. Inc. and was used without further purifications. All solvents were used after distillation. Palladium chloride was purchased from Aldrich Chem. Inc. NMR spectra were recorded on a Varian (500 MHz) spectrometer.

3.2. General procedure for the oxidation of triarylantimony to triarylantimony diacetate

A mixture of triarylantimony (2.00 mmol) and iodobenzene diacetate (2.20 mmol) in dichloromethane (20 ml) was stirred at room temperature for 7 h. The solvent was concentrated under reduced pressure to a small volume. A mixture of diethyl ether–pentane was added and the solution kept overnight at −15°C. The solid was filtered and recrystallized from a mixture of dichloromethane and pentane.

Table 2
The palladium-catalyzed cross-coupling and carbonylative cross-coupling of triphenyl antimony dichloride (**1c**) with organostannanes

Entry	Organostannanes	Products	Isolated yields (%)
1	**2a**	**3a**	81
2	**2b**	**3b**	88
3	**2c**	**R**	90
4	**2e**	**3e**	56
5	**2f**	**4a**	90
6	**2b**	**4b**	88
7	**2e**	**4c**	88
8	**2g**	**4d**	81
9	**2h**	**4e**	80



Scheme 3.

Triphenylantimony(V) diacetate (**1a**): m.p. 210–212°C ([23] 208–209°C), ^{1}H-NMR ($CDCl_3$): δ 1.83 (s, 6H), 7.48 (m, 9H), 7.99 (m, 6H). Tri(*p*-tolyl)antimony-(V) diacetate (**1b**): m.p. 157–159°C, ^{1}H-NMR ($CDCl_3$): δ 1.82 (s, 6H), 2.39 (s, 9H), 7.27 (d, 6H, $J = 8$), 7.86 (d, 6H, $J = 8$ Hz).

3.3. Typical procedure for the cross-coupling of organostannanes with organoantimony(V) compounds

To a mixture of triphenylantimony diacetate (**1a**) (412 mg, 1.00 mmol) and $PdCl_2$ (8.9 mg, 5 mol%) was added 2-(tributylstannyl)thiophene (**2c**) (373 mg, 1.00 mmol) under N_2 charged at room temperature in CH_3CN (20 ml). The reaction mixture was stirred at room temperature for 3 h, extracted with ether (3 × 20 ml), washed with water (3 × 20 ml). The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was separated by SiO_2 column chromatography (Hexanes, $R_f = 0.52$) to afford coupled product 2-phenylthiophene (**3c**) (144 mg, 90%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, 1H, $J = 5.1$, 3.5), 7.27 (m, 2H), 7.32 (dd, 1H, $J = 3.5$ Hz), 7.38 (m, 2H), 7.62 (m, 2H). IR (KBr) = 3070, 1608, 1477, 832, 708 cm^{-1}. MS (EI): *m*/*e* (relative intensity) = 160 (100), 128 (13), 115 (34), 102 (5), 89 (7).

3.4. Typical procedure for the carbonylative cross-coupling of organostannanes with organoantimony(V) compounds

To a mixture of triphenylantimony diacetate (**1a**) (412 mg, 1.00 mmol) and $PdCl_2$ (8.9 mg, 5 mol%) was added 2-(tributylstannyl)furan (**2b**) (358 mg, 1.00 mmol) under atmospheric pressure of CO at room temperature in CH_3CN (20 ml). The reaction mixture was stirred at room temperature for 6 h, extracted with ether (3 × 20 ml), washed with water (3 × 20 ml). The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was separated by SiO_2 column chromatography (EtOAc–hexanes 1: 10, $R_f = 0.46$) to afford coupled product 2-benzoylfuran (**4b**) (139 mg, 81%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.58 (m, 1H), 7.23 (m, 1H), 7.48 (m, 2H), 7.58 (m, 1H), 7.70 (m, 1H), 7.90 (m, 2H). IR (KBr) = 3134, 2342, 1647, 1563, 1464 cm^{-1}. MS (EI): *m*/*e* (relative intensity) = 172 (M^+, 100), 105 (94), 95 (58), 77 (97).

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