

# Palladium-catalyzed regioselective arylation of silyloxy compounds with triarylantimony diacetates

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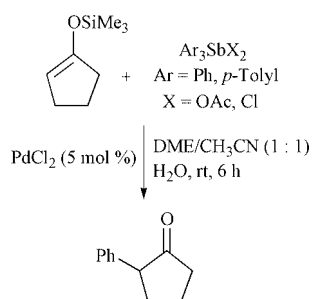
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The palladium-catalyzed arylation of enol silyl ethers, siloxydienes, silyloxycyclopropane with triarylantimony diacetates was carried out in the presence of  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  (5 mol%) in DME- $\text{CH}_3\text{CN}$  at room temperature under mild conditions.

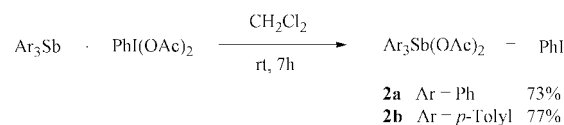
The arylation of ketones to synthesize  $\alpha$ -aryl ketones has received much attention in recent years.<sup>1</sup> The palladium-catalyzed arylation of silyl enol ethers or trimethylsilyl acetals with aryl bromides is known.<sup>2</sup> As an alternative to the use of an organic electrophile, phenyl-substituted hypervalent iodonium salts have been employed in the arylation of silyl enol ethers.<sup>3</sup> Main group metals such as aryl-substituted bismuth<sup>4</sup> and lead<sup>5</sup> compounds have been utilized in the arylation of ketones and active methylene compounds. Recently, Buchwald<sup>6</sup> and Hartwig<sup>7</sup> reported palladium-catalyzed  $\alpha$ -arylation of ketones. In connection with our program to utilize pentavalent antimony diacetates in palladium-catalyzed coupling reactions,<sup>8</sup> we wish to report here the arylation of silyl enol ethers and silyl dienol ethers, and ketene trimethylsilyl acetals with triarylantimony diacetates to give the aryl-substituted ketones or esters (Scheme 1).



Scheme 1

The results of the arylation of silyl enol ethers with triarylantimony acetates are summarized in Table 1. The 1-[(trimethylsilyloxy)cyclopentene (**1a**) reacted with triphenylantimony diacetate (**2a**) in the presence of  $\text{PdCl}_2$  (5 mol %) in DME- $\text{CH}_3\text{CN}$  (1 : 1) and  $\text{H}_2\text{O}$  (10% v/v) at room temperature for 6 h to afford the 2-phenylcyclopentanone (**3a**) in 68% yield (entry 1 in Table 1). Of the catalysts  $\text{PdCl}_2$ ,  $\text{Pd}(\text{OAc})_2$ ,  $\text{Pd}_2(\text{dba})_3$ ,  $\text{Pd}(\text{PPh}_3)_4$  tested,  $\text{PdCl}_2$  was the best choice. The solvent system DME- $\text{CH}_3\text{CN}$  (1 : 1) in the presence of a catalytic amount of  $\text{H}_2\text{O}$  (10% v/v) was most suitable among the solvents DMF, DME,  $\text{CH}_3\text{CN}$ , DME- $\text{CH}_3\text{CN}$  (1 : 1), NMP tested. The role of water is not clear. Triarylantimony(v) diacetates **2a** and **2b** were prepared by reaction of triarylantimony(III) with  $\text{PhI}(\text{OAc})_2$  by stirring in  $\text{CH}_2\text{Cl}_2$  at room temperature for 6–7 h (Scheme 2).<sup>9</sup>

Under the same conditions triphenylantimony dichloride (**2c**) was treated with **1a** to give the phenylated cyclopentanone **3a** in 63% yield (entry 2). For the (cyclohexa-1,5-dienyloxy)-trimethylsilane (**1b**) with **2a**, the 6-phenylcyclohex-2-enone (**3b**)



Scheme 2

was afforded in the presence of  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  in DME- $\text{CH}_3\text{CN}$  (1 : 1) and  $\text{H}_2\text{O}$  (10% v/v) in 78% yield (entry 3). Under the same conditions tri-*p*-tolylantimony diacetate (**2b**) reacted with **1b** to give 6-*p*-tolylcyclohex-2-enone (**3c**) in 77% yield (entry 4). The presence of  $\text{H}_2\text{O}$  (10% v/v) is critical in this coupling. Without a small amount of  $\text{H}_2\text{O}$ , we could get the product **3c** in rather low (35%) yield. When the 2-furyloxytrimethylsilane (**1c**) was employed as ketene silyl acetal to react with **2a**, the thermodynamically more stable 5-phenylfuran-2(3*H*)-one (**3d**) was afforded in 82% yield (entry 5). The 2-furyloxysilane **1c** was readily coupled with **2c** and **2b** to provide **3d** and **3e** in 77 and 78% yields, respectively (entries 6 and 7). The regioselectivity of **3d** could be explained by the isomerization of the  $\alpha,\beta$ -unsaturated lactone under the reaction conditions. For the [(1-ethoxycyclopropyl)oxy]-trimethylsilane (**1d**), the reaction with triphenylantimony diacetate (**2a**) in the presence of  $\text{PdCl}_2$  (5 mol%) in DME- $\text{CH}_3\text{CN}$  (1 : 1) at room temperature for 6 h afforded the 3-phenylacrylic acid ethyl ester (**3f**) in 78% yield (entry 8). It is presumed that under these conditions the intermediate ethyl acrylate is formed by  $\beta$ -elimination of the homoenolate  $[\text{Ph}_3(\text{OAc})\text{SbPdCH}_2\text{CH}_2\text{CO}_2\text{Et}]$  followed by Heck reaction with  $\text{Ph}_3\text{Sb}(\text{OAc})_2$ . Under the same conditions triphenylantimony dichloride (**2c**) and tri-*p*-tolylantimony diacetate (**2b**) were treated with **1d** to give the ester **3f** and **3g** in 75 and 68% yields, respectively (entries 9 and 10).





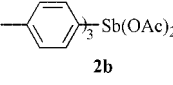
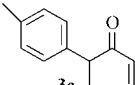
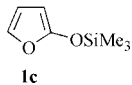
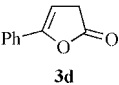
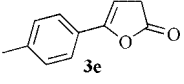
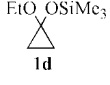
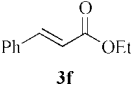
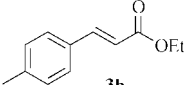
In summary the silyl enol ether, silyl dienol ethers, and silyloxycyclopropane were arylated in the presence of a palladium catalyst with triarylantimony(v) diacetates under mild conditions. This method has the advantage of mild conditions involving the use of  $\text{PdCl}_2$  at room temperature even in the presence of water.

## Experimental

### Typical procedure

To a mixture of tri-*p*-tolylantimony diacetate (**2b**) (454 mg, 1.00 mmol) and  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  (13 mg, 5 mol%) was added (cyclohexa-1,5-dienyloxy)trimethylsilane (**1b**) (168 mg, 1.00 mmol) under an  $\text{N}_2$  atmosphere at room temperature in DME- $\text{CH}_3\text{CN}$  (1 : 1, 20 mL) and  $\text{H}_2\text{O}$  (2 mL, 10% v/v). The reaction mixture was stirred at room temperature for 8 h, extracted with ether (20 mL  $\times$  3), and washed with water (20 mL  $\times$  3). The organic layer was dried over anhydrous  $\text{MgSO}_4$  and evaporated *in vacuo*. The crude product was separated by  $\text{SiO}_2$  column chromatography (EtOAc-hexanes 1 : 10,  $R_f = 0.38$ ) to afford the coupled product 5-*p*-tolylcyclohex-2-enone (**3c**) (143.4 mg,

**Table 1** Palladium-catalyzed regioselective arylation of silyloxy compounds with triarylantimony diacetates

Entry	Silyloxy compounds	Triarylantimony diacetates	Product	Isolated yield (%)
1	 <b>1a</b>	$\text{Ph}_3\text{Sb}(\text{OAc})_2$ <b>2a</b>	 <b>3a</b>	68
2	<b>1a</b>	$\text{Ph}_3\text{SbCl}_2$ <b>2c</b>	<b>3a</b>	63
3	 <b>1b</b>	<b>2a</b>	 <b>3b</b>	78 <sup>a</sup>
4	<b>1b</b>	 <b>2b</b>	 <b>3c</b>	77 <sup>a</sup>
5	 <b>1c</b>	<b>2a</b>	 <b>3d</b>	82 <sup>b</sup>
6	<b>1c</b>	<b>2c</b>	<b>3d</b>	77 <sup>b</sup>
7	<b>1c</b>	<b>2b</b>	 <b>3e</b>	78 <sup>b</sup>
8	 <b>1d</b>	<b>2a</b>	 <b>3f</b>	78 <sup>b</sup>
9	<b>1d</b>	<b>2c</b>	<b>3f</b>	75 <sup>b</sup>
10	<b>1d</b>	<b>2b</b>	 <b>3b</b>	68 <sup>b</sup>

<sup>a</sup>  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  was used as catalyst instead of  $\text{PdCl}_2$ . <sup>b</sup> The reaction was carried out under non-aqueous conditions.

77%);  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 2.27 (m, 2 H), 2.38 (s, 3 H), 2.47 (m, 2 H), 3.57 (t, 1 H,  $J = 9.5$  Hz), 6.15 (m, 1 H), 7.01 (m, 3 H), 7.14 (d, 2 H,  $J = 8.0$  Hz);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3055, 2915, 2880, 1731;  $m/z$  186 (27), 117 (100), 91 (6), 68 (4).

To a mixture of triphenylantimony diacetate (**2a**) (412 mg, 1.00 mmol) and  $\text{PdCl}_2$  (8.9 mg, 5 mol%) was added (furan-2-yloxy)trimethylsilane (**1c**) (156 mg, 1.00 mmol) under an  $\text{N}_2$  atmosphere at room temperature in DME- $\text{CH}_3\text{CN}$  (1:1, 20 mL). The reaction mixture was stirred at room temperature for 8 h, extracted with ether (20 mL  $\times$  3), and washed with water (20 mL  $\times$  3). The organic layer was dried over anhydrous  $\text{MgSO}_4$  and evaporated *in vacuo*. The crude product was separated by  $\text{SiO}_2$  column chromatography (EtOAc-hexanes 1:3,  $R_f = 0.26$ ) to afford the coupled product 5-phenylfuran-2(3H)-one (**3d**) (132 mg, 82%);  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 3.42 (d, 2 H,  $J = 2.7$  Hz), 5.78 (t, 1 H,  $J = 2.7$  Hz), 7.39 (m, 3 H), 7.60 (m, 2 H);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3055, 1804, 1265;  $m/z$  162, 161, 160 (100), 131, 105, 77.

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