Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 3155–3157

TETRAHEDRON LETTERS

Use of triarylstibines in *C*-arylation reactions

Dmitry V. Moiseev, Vera A. Morugova, Alexey V. Gushchin* and Victor A. Dodonov

Organic Chemistry Department, Nizhnii Novgorod State University, Nizhnii Novgorod, 603950, Russian Federation

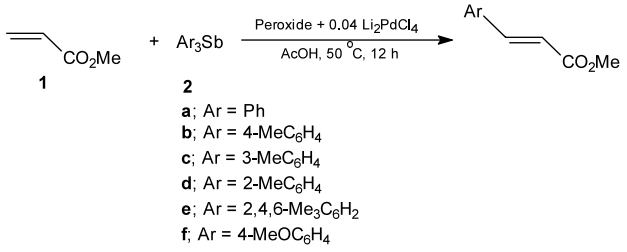
Received 22 January 2003; revised 14 February 2003; accepted 20 February 2003

Abstract—A new catalytic system based on triarylstibines for *C*-arylation of unsaturated compounds is proposed. It was found for a model reaction, the *C*-arylation of methyl acrylate, that in the presence of equimolar amounts of peroxide and catalytic amounts of a palladium compound (4 mol%), triarylstibines can act as mild efficient arylating agents.

Synthetic applications of organoantimony compounds are rapidly increasing. Organoantimony(V) derivatives are efficient reagents in palladium-catalyzed C-C bond formation.[1a–f] The application of organoantimony(III) derivatives is limited since they can give palladium-catalyzed cross-coupling only in the presence of additional oxidants: oxygen, AgOAc, $(NH_4)_2Ce(NO_3)_6$[2a–c] or in the presence of stoichiometric amounts of palladium salts.[3a–d]

In the present work a new catalytic system based on triarylstibines for *C*-arylation of unsaturated compounds is proposed. We have found for a model reaction, the *C*-arylation of methyl acrylate, that in the presence of equimolar amounts of peroxide and catalytic amounts of a palladium compound (4 mol%), triarylstibines can act as mild efficient arylating agents (Scheme 1).

For the reaction of **1** with **2a** (3:1) we tested a number of peroxides H_2O_2 **3**, *t*-BuOOH **4**, $(PhCO_2)_2$ **5**, (cyclo-$C_6H_{11}OCO_2)_2$ **6** in order to choose the best. All reactions proceeded under standard conditions (AcOH, 50°C, 12 h).[4] The results are summarized in Table 1. In all cases a product yield of 100% corresponds to the transfer of only one aryl group from the initial organoantimony compound.



Scheme 1.

Table 1. *C*-phenylation reaction of **1** with Ph_3Sb/Peroxide/Li_2PdCl_4 systems[a]

Entry	Peroxide	Yields of **7**[b] (%)
1	–	2
2	H_2O_2	171
3	*t*-BuOOH	174
4[c]	*t*-BuOOH	189
5	$(PhCO_2)_2$	164
6[d]	$(PhCO_2)_2$	121
7	$(cyclo\text{-}C_6H_{11}OCO_2)_2$	127
8	$PhI(OAc)_2$	26
9[e]	–	186

[a] The reactions were carried out with 0.5 mmol Ph_3Sb, 1.5 mmol methyl acrylate, 0.5 mmol peroxide, 0.02 mmol Li_2PdCl_4 in AcOH (4 ml) for 12 h at 50°C under air.

[b] The yields of methyl cinnamate in all cases were determined by GLC.

[c] The ratio **2a**:*t*-BuOOH = 1:2.

[d] Acetonitrile was used as solvent.

[e] $Ph_3Sb(OAc)_2$ was utilized instead of **2a**.

Keywords: antimony(III); arylation; palladium.

* Corresponding author. Tel.: +7-831-233-7865; fax: +7-831-265-8592; e-mail: gushchin@mail.nnov.ru

0040-4039/03/$ - see front matter
doi:10.1016/S0040-4039(03)00511-2

All the peroxides exhibited high activity. Peroxides **3** and **4** turned out to be the most effective, giving the following yields of the reaction product—methyl cinnamate **7** 171% and 174%, respectively. Peroxide **5** was less efficient (164%). In the case of **6** the yield was minimal (127%). A two-fold excess of hydroperoxide **4** ensured an increase in the product yield but only to a small extent (Table 1, entry 4). The yield of **7** did not exceed the stoichiometric yield based on palladium in the absence of the oxidant (Table 1, entry 1). This fact shows that a catalytic reaction does not occur.

The principal role of the peroxides in this system is the oxidation of Sb(III) to Sb(V) in the form of triarylantimony diacetates (Scheme 2). The mechanism of this interaction has been well studied.[5a,b] Triarylantimony diacetates are known to be effective arylating agents.[1e,f]

$$Ar_3Sb + t\text{-BuOOH} + 2\,AcOH \longrightarrow Ar_3Sb(OAc)_2 + t\text{-BuOH} + H_2O$$

Scheme 2.

With peroxide **5**, the availability of an acid is not obligatory since Ar_3Sb transforms to triarylantimony dibenzoate without participation of an acid. Therefore, reactions with **5** can be carried out in neutral solvents, e.g. acetonitrile, but the rate becomes lower (Table 1, entry 6).

$$Ar_3Sb + (PhCO_2)_2 \rightarrow Ar_3Sb(O_2CPh)_2$$

While comparing the new systems Ph_3Sb/peroxide with the known system based on $Ph_3Sb(OAc)_2$, it is seen that they display similar efficiencies (Table 1, entries 3 and 9). Nevertheless, the former differs advantageously from the latter in that the synthesis, isolation and purification necessary for triphenylantimony diacetate are not needed.

To compare with the peroxides, we used another known oxidant $PhI(OAc)_2$[1c] which gives $Ph_3Sb(OAc)_2$ on interacting with **2a** as well.

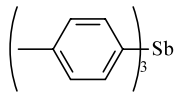
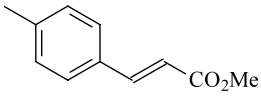
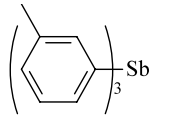
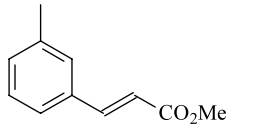
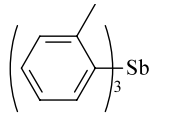
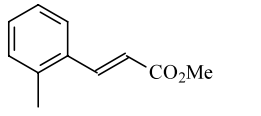
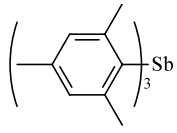
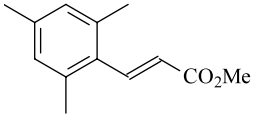
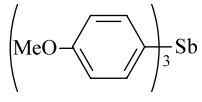
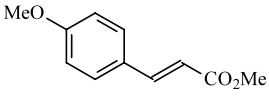
$$Ph_3Sb + PhI(OAc)_2 \rightarrow Ph_3Sb(OAc)_2 + PhI$$

However, as seen from our results, the yield of the target product proved to be low (Table 1, entry 8). Moreover, as it turned out, the addition of an equimolar amount of PhI inexplicably inhibits the phenylation reaction under these conditions.

In this *C*-arylation reaction, other triaryl derivatives of antimony(III) were examined. All reactions were carried out under the standard conditions (AcOH, 50°C, 12 h) using *tert*-butyl hydroperoxide **4**. The results are given in Table 2.

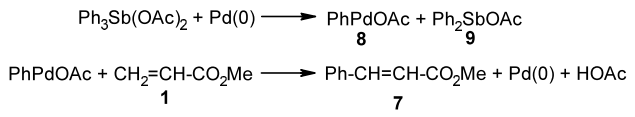
As seen, for **2b** and **2c** the yields of the *C*-arylated products remained high (180 and 192%, respectively). In the case of the *ortho*-substituted derivative of antimony **2d** the product yield decreased sharply to 125%. With the most sterically hindered **2e**, no reaction was observed at all. Thus, the *C*-arylation reaction is sensitive to steric hindrance in the aromatic ring, especially, in the *ortho*-position.

Table 2. *C*-arylation reactions of **1** with Ar_3Sb/t-BuOOH/Li_2PdCl_4 systems[a]

Entry	Triarylstibine	Product	Yields of **7** [b], %
1			180
2			192
3			125
4			-
5			158

[a]The reactions were carried out with 0.5 mmol Ar_3Sb, 1.5 mmol methyl acrylate, 0.5 mmol peroxide, 0.02 mmol Li_2PdCl_4 in AcOH (4 ml) for 12 h at 50 °C under air.

[b]All *C*-arylated products were isolated in pure state by column chromatography on silica gel 60 μm and characterized by ^1H NMR.



Scheme 3.

As should be expected, better donor substituents reduced the rate of the arylation reaction. So, in the case of **2f**, the yield of the product was smaller, compared with **2b** (Table 2, entries 1 and 5).

The catalytic mechanism is represented in Scheme 3. Triphenylantimony diacetate formed during the preliminary stage (Scheme 2) interacts with the active form of the catalyst—Pd(0). As a result, intermediate **8** is formed and it phenylates **1** immediately with formation of the reaction product **7,** the catalyst being transformed again to the active form and the cycle being repeated.

The antimony(III) derivative **9** does not take part later on in the reaction because it is not able to oxidize Pd(0) to Pd(II). The yield of **7** can reach only 100% of initial **2a**. As was shown earlier,[1f,2a] in the presence of oxygen antimony compounds Ph_2SbX can transfer the second phenyl group onto palladium. Then the yield can attain 200% of **2a** corresponding to the transfer of two of the three possible phenyl groups of the starting organometallic compound.

Hence, we offer a new catalytic system for *C*-arylation of unsaturated compounds based on triarylstilbines in the presence of equimolar amounts of a peroxide and a catalytic amount of Li_2PdCl_4 (4 mol%). The role of the peroxides is in the in situ preparation of triarylantimony diacetates without isolation and purification of the latter. H_2O_2 and *t*-BuOOH can be considered as the best peroxides. This system enables the reaction to be conducted at low temperatures with transfer of two of the three possible aryl groups. The new system compares favorably with the earlier proposed system based on triarylantimony dicarboxylates.

References

1. (a) Fujiwara, M.; Tanaka, M.; Baba, A.; Ando, H.; Souma, Y. *J. Organomet. Chem.* **1996**, *525*, 39–42; (b) Kang, S.-K.; Ryu, H.-C.; Hong, Y.-T. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3350–3351; (c) Kang, S.-K.; Ryu, H.-C.; Lee, S.-W. *J. Organomet. Chem.* **2000**, *610*, 38–41; (d) Kang, S.-K.; Ryu, H.-C.; Hong, Y.-T. *J. Chem. Soc., Perkin Trans. 1* **2001**, 736–739; (e) Gushchin, A. V.; Moiseev, D. V.; Dodonov, V. A. *Russ. Chem. Bull.* **2001**, *50*, 1291–1294; (f) Moiseev, D. V.; Gushchin, A. V.; Shavirin, A. S.; Kursky, Yu. A.; Dodonov, V. A. *Organomet. Chem.* **2003**, *667*, 176–184.
2. (a) Matoba, K.; Motofusa, S.; Cho, C. S.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **1999**, *574*, 3–10; (b) Cho, C. S.; Tanabe, K.; Uemura, S. *Tetrahedron Lett.* **1994**, *35*, 1275–1278; (c) Cho, C. S.; Tanabe, K.; Itoh, O.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 274–275.
3. (a) Asano, R.; Moritani, I.; Fujiwara, Y.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2910–2911; (b) Kawamura, K.; Kikukawa, K.; Takagi, M.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2021–2024; (c) Kikukawa, K.; Ikenaga, K.; Wada, F.; Matsuda, T. *Tetrahedron Lett.* **1984**, *25*, 5789–5792; (d) Gushchin, A. V.; Moiseev, D. V.; Dodonov, V. A. *Zh. Obshch. Khim.* **2002**, *72*, 1669–1672 [*Russ. J. Gen. Chem.* **2002**, *72* (Engl. Transl.)].
4. **Typical procedure for *C*-phenylation reaction**: Ph_3Sb (0.177 g, 0.5 mmol), Li_2PdCl_4 (5.2 mg, 0.02 mmol) and methyl acrylate (0.135 ml, 1.5 mmol) in acetic acid (4 ml) were placed in a 50 ml tube. The tube was sealed and the reaction mixture was kept for 12 h at 50°C. The solvent was evaporated under reduced pressure. The solid residue was filtered from inorganic products through a short column on silica gel eluting with hexane–diethyl ether (v/v 4:1) mixture. The filtrate was analyzed by GLC. Methyl cinnamate (0.151 g) was found.
5. (a) Dodonov, V. A.; Zinov'eva, T. I. *Metallorg. Khim.* **1992**, *5*, 1265–1271 [*Organomet. Chem. USSR*, **1992**, 5 (Engl. Transl.)]; (b) Hiatt, R.; McColeman, C.; Howe, G. R. *Can. J. Chem.* **1975**, *53*, 559–563.