Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 667 (2003) 176–184
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Pd-catalyzed C-arylation of unsaturated compounds with pentavalent triarylantimony dicarboxylates

Dmitry V. Moiseev [a], Aleksey V. Gushchin [a,*], Andrey S. Shavirin [b], Yury A. Kursky [b], Viktor A. Dodonov [a]

[a] Department of Organic Chemistry, Nizhnii Novgorod State University, 23 Gagarin Avenue, 603950 Nizhnii Novgorod, Russia
[b] G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, GSP-445, 49 Tropinin Street, 603600 Nizhnii Novgorod, Russia

Received 13 December 2002; received in revised form 13 December 2002; accepted 14 December 2002

Abstract

Triarylantimony(V) derivatives Ar_3SbX_2 (X = Hal or acyloxy) were prepared by reaction of Ar_3Sb with equimolar amounts of a peroxide ROOH (R = *t*-Bu, H) in the presence of an acid or an anhydride in good to excellent yields. $Ar_3Sb(O_2CR)_2$ are mild and efficient C-arylation reagents of unsaturated compounds (methyl acrylate, styrene, 2-phenylpropene and acrylonitrile) under palladium catalysis at 50 °C, with $PdCl_2$ being the most effective catalyst. Ar_3SbHal_2 do not react under these conditions.

Keywords: Alkenes; Antimony(V); Arylation; Cross-coupling; Palladium-catalyzed

1. Introduction

Organoantimony compounds have been used in organic synthesis either as reagents or as catalysts for a number of years [1]. However, it is only in the last few years that their application in palladium catalyzed cross-coupling reactions has been described. In the presence of catalytic amounts of $Pd(PPh_3)_4$ or $Pd(OAc)_2$, pentaphenylantimony Ph_5Sb reacted with allyl acetate or allyl phenyl ether to afford allylbenzene [2]. Organoantimony(V) derivatives Ar_3SbX_2 (X = Cl, OAc) gave cross-coupling products with silyloxy alkenes [3] and organotin compounds [4] under palladium catalysis. $Ar_3Sb(OAc)_2$ were used in Pd(0)–Cu(I)-catalyzed cross-coupling reactions with alkynylsilanes [5]. We have recently reported that $Ph_3Sb(OAc)_2$ behaves not only as a phenyl group donor but also as a Pd(0) reoxidant in the Pd catalyzed C-phenylation reaction of methyl acrylate [6]. When trivalent arylantimony compounds are used, the Pd-catalyzed cross-coupling reactions takes place only in the presence of an additional oxidant such as oxygen [7], AgOAc [8] or $(NH_4)_2Ce(NO_3)_6$ [9]. In the course of our studies on the synthesis and reactivity of organoantimony compounds, we decided to prepare a series of triarylantimony compounds Ar_3SbX_2 and to compare their activity in the Pd-catalyzed C-arylation reaction of unsaturated compounds.

2. Results and discussion

2.1. Synthesis of Ar_3SbX_2

The organoantimony derivatives Ar_3SbX_2 were obtained in good yields by the one-step reaction of the appropriate triarylantimony with an acid in the presence of equimolar amounts of peroxide (Scheme 1) [10]:

In the synthesis of triarylantimony dicarboxylates, the anhydride can be used instead of the carboxylic acid (Scheme 2). However in this case, the reaction proceeded more slowly to afford slightly reduced yields of the diacylates.

* Corresponding author. Tel.: +7-831-233-7865; fax: +7-831-265-8592.
E-mail address: gushchin@mail.nnov.ru (A.V. Gushchin).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(02)02179-4

$Ar_3Sb + 2\,HX + ROOH \xrightarrow[24\,h]{rt} Ar_3SbX_2 + ROH + H_2O$

Substrate	Product	Yield with R = *t*-Bu	Yield with R = H
1 Ar = Ph	**1a** X = OAc	90 %	85 %
	1b X = O_2CEt	76 %	78 %
	1c X = O_2CH	58 %	
	1d X = O_2CCF_3	85 %	
	1e X = O_2CPh	80 %	77 %
	1f X = F	90 %	75 %
	1g X = Cl	95 %	94 %
	1h X = Br	75 %	
2 Ar = 4-MeC_6H_4	**2a** X = OAc		80 %
3 Ar = 3-MeC_6H_4	**3a** X = OAc		68 %
4 Ar = 2-MeC_6H_4	**4a** X = OAc	71 %	
5 Ar = 2,4,6-$Me_3C_6H_2$	**5a** X = OAc	48 %	
6 Ar = 4-$MeOC_6H_4$	**6a** X = OAc	84 %	

Scheme 1.

$Ar_3Sb + RC(O)OC(O)R + t\text{-}BuOOH \xrightarrow[90\,h]{rt} Ar_3Sb(O_2CR)_2 + t\text{-}BuOH$

1 Ar = Ph	**1a** R = Me	70 %
	1b R = Et	55 %
	1e R = Ph	44 %

Scheme 2.

2.2. Reaction of Ar_3SbX_2 with methyl acrylate

The different organoantimony(V) compounds were then tested in the Heck-type C-arylation reaction of methyl acrylate **7**, which was used as a model unsaturated substrate. Compound 7 was treated with Ar_3SbX_2 in the presence of catalytic amounts of various palladium species to give only the *trans*-arylation products, the cinnamic acid derivatives **8a–f** under mild conditions. In some instances, besides the main product of C-arylation, a biaryl derivative was isolated as a by-product resulting from a competing homocoupling reaction of the organometallic compound (Scheme 3).

In a preliminary report, we have shown that $Ph_3Sb(O_2CEt)_2$ (**1b**) reacts efficiently with a tenfold molar excess of methyl acrylate **7** in the presence of 4 mol% of $Pd(OAc)_2$ in acetonitrile at 50 °C to give the derived methyl cinnamate [6]. However, a large excess of the substrate **7** is not necessary for the reaction to proceed in good to high yields. In a series of reactions, **1b** was treated with various amounts of methyl acrylate **7** in acetonitrile at 50 °C in the presence of 2 mol% of $Pd_2(dba)_3$. The yields of methyl cinnamate **8a** decreased only slowly from 83% with ten equivalents of **7** to 35% with one equivalent of **7** (the yields being based on the

$CH_2{=}CH{-}CO_2Me \xrightarrow[[Pd],\,50^{\circ}C]{Ar_3SbX_2} Ar{-}CH{=}CH{-}CO_2Me + Ar{-}Ar$

7	**8a** Ar = Ph	**9a** Ar = Ph
	8b Ar = 4-MeC_6H_4	
	8c Ar = 3-MeC_6H_4	
	8d Ar = 2-MeC_6H_4	
	8e Ar = 2,4,6-$Me_3C_6H_2$	
	8f Ar = 4-$MeOC_6H_4$	

Scheme 3.

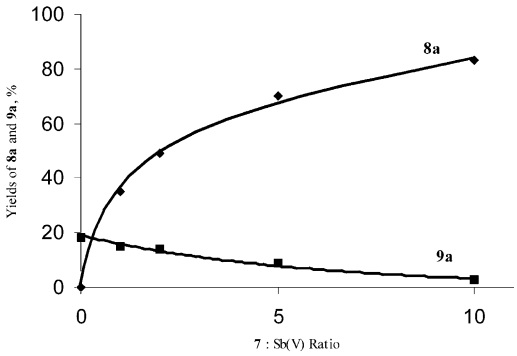


Fig. 1. Effect of the molar ratio **7**:$Ph_3Sb(OAc)_2$ on the yields of **8a** and **9a** in the C-phenylation reaction with **1b**+0.02$Pd_2(dba)_3$ system in CH_3CN, 50 °C, 3 h.

initial organoantimony reagent) (Fig. 1). Concomitantly the biphenyl **9a**, resulting from a homocoupling reaction of **1b**, was formed in yields increasing from a few percent in the reaction with ten equivalents of **7** to 18% in the absence of the acrylate **7**. Similar results were also obtained when $Pd(OAc)_2$ was used as the catalyst. In Fig. 1 representing the yields of product versus the reagent ratios, it appears that the influence of the amount of methyl acrylate is more pronounced in the range 0–4 molar equivalents. In fact, it can be considered that all the phenyl groups present in the original organoantimony reagent can be transferred. Therefore, a 1:3 ratio between [Sb(V)] and **7** was employed in the subsequent investigations.

The nature of the palladium catalyst as well as the presence of additional ligands plays a role on the yields of methyl cinnamate **8a** and of the by-product **9a** (Table 1). The two palladium catalysts, $PdCl_2$ and Li_2PdCl_4,

Table 1
Pd-catalyzed reaction of $Ph_3Sb(O_2CEt)_2$ (**1b**) with methyl acrylate **7**: influence of the nature of the catalyst [a]

Run	[Pd]	Yields (%)	
		8a	**9a**
1	$PdCl_2$	93	–
2	Li_2PdCl_4 [b]	83	–
3	$Pd(OAc)_2$	76	6
4	$Pd_2(dba)_3$	71	8
5	$Pd(PPh_3)_2Cl_2$	–	–
6	$Pd(OAc)_2$+2Ph_3P	–	Trace
7	$Pd(dppf)Cl_2$	9	1
8	$Pd_2(dba)_3$+2Ph_3P	–	–
9	$PdCl_2$+2Ph_3As	57	Trace
10	$PdCl_2$+2Ph_3Sb	61	Trace
11	$PdCl_2$+2Ph_3As [c]	–	–
12	$PdCl_2$+2Ph_3Sb [c]	24	–

[a] The reactions were performed in CH_3CN at 50 °C for 6 h, under air with ratio between **1b**, **7** and [Pd] of 1:3:0.04 unless otherwise stated.
[b] 3 mol% of Li_2PdCl_4 were used.
[c] AcOH was used as solvent.

proved to be the most active as they led only to the C-phenylated product **8a** in 93 and 83%, respectively (Table 1, entries 1 and 2). $Pd(OAc)_2$ and $Pd_2(dba)_3$ were slightly less efficient and less selective, as the by-product **9a** was also formed in 6–8% yields (Table 1, entries 3 and 4). The presence of additional phosphines, Ph_3P or dppf, inhibited the catalytic activity (Table 1, entries 5–8). Under these conditions, the phosphine ligands bind too strongly to the palladium metallic center to allow the exchange reaction with either the solvent, the olefin or the arylantimony compound. When less strongly binding ligands such as Ph_3As and Ph_3Sb were added to the reaction system with $PdCl_2$, the phenylation reaction took place although with a reduced efficiency [57 and 61%, respectively, in CH_3CN (Table 1, entries 9 and 10)]. However, the inhibiting effect of these two ligands was strongly enhanced when AcOH, a less donor solvent, was used. In this case, no reaction product was detected when Ph_3As was added while only 24% of **8a** were obtained in the presence of Ph_3Sb (Table 1, entries 11 and 12). Thus, $PdCl_2$, employed alone, appears to be the most efficient catalytic species for this arylation reaction. It was therefore used in the subsequent studies, for which a ratio between the reagents [Sb]:[alkene]:$PdCl_2$ of 1:3:0.04 was selected as the preferred conditions.

The solvent has a determinant effect on the yield of the products of the C-phenylation. Compared to methylene dichloride or methanol which led to the lowest yields (43 and 51%, respectively), the more donating solvents THF and DMF [11] afforded the highest yields of **8a**, 118 and 116%, respectively, in the reactions of **7** with **1b**, but the by-product **9a** was formed in significant amounts, 18 and 15%, respectively. AcOH and especially CH_3CN showed an excellent selectivity (no formation of the by-product **9a** under these conditions) together with a good activity (92 and 96% yields of **8a**). Therefore, CH_3CN and AcOH were considered to be the solvents of choice for the complementary studies of the reaction.

The outcome of the reaction is also dependent upon the structure of the organoantimony reagent Ar_3SbX_2, the X substituant and the aryl group both influencing the yield of the reaction. In our preliminary studies, we had already noted that Ph_3SbCl_2 was completely inactive in the palladium catalyzed C-phenylation reaction, in contrast to $Ph_3Sb(OAc)_2$ and $Ph_3Sb(O_2CEt)_2$ [6]. Under the conditions of the present study, all triphenylantimony halides were again inactive in the C-phenylation reaction (Table 2, entries 6–8) and the by-product **9a** was not found in any of these reactions. On the other hand, all triphenylantimony dicarboxylates were active phenylating agents (Table 2, entries 1–5). The best yield of **8a** (130%) was obtained with the least bulky formate group (Table 2, entry 1). The strength of the acyl group had little influence, 101% with the acetate and 96% with the trifluoroacetate (Table 2, entries 2 and 4).

Table 2
$PdCl_2$ catalyzed reaction of Ph_3SbX_2 with methyl acrylate **7**: influence of the nature of the substituent X

Entry	X	Yields (%)
		8a
1	O_2CH	130
2	O_2CCH_3	101
3	$O_2CC_2H_5$	96
4	O_2CCF_3	93
5	O_2CPh	68
6	F	4
7	Cl	Trace
8	Br	–

The reactions were performed in CH_3CN at 50 °C for 6 h, under air with ratio between [Sb], **7** and $PdCl_2$ of 1:3:0.04.

Concerning the aryl group, it was supposed that the presence of electron-donating groups in the aromatic ring would decrease the polarity of the C–M bond and reduce the arylating potential of the organometallic reagent. Indeed, in the sequence Ph > *p*-tolyl > *p*-anisyl, the arylating activity decreased (Table 3, entries 1, 2 and 6). The anisyl compound **6a** gave 105% of the product **8f** after 12 h, compared to 186% of **8a** when the phenylantimony reagent **1a** was employed and 163% of **8b** with the *p*-tolylantimony reagent **2a**. After 24 h, the yield of **8f** rose only to 120%. In the methyl substituted series of antimony reagents, the influence of the steric hindrance can be easily observed with the most bulky mesityl derivative being absolutely inactive: 4-MeC_6H_4 > 3-MeC_6H_4 > 2-MeC_6H_4 ≫ 2,4,6-$Me_3C_6H_2$ (Table 3, entries 2–5).

The nature of the reaction atmosphere is also an important factor interfering with the yield of the C-arylation products. For example, when the $PdCl_2$ catalyzed reaction of **7** with **1a** was performed in acetic acid under an atmosphere of argon, the yield of **8a** nearly reached 100% after 12 h and did not evolve

Table 3
$PdCl_2$ catalyzed reaction of $Ar_3Sb(OAc)_2$ with methyl acrylate **7** [a]: influence of the nature of the aryl group Ar

Entry	Ar	Product	Yields (%) [b]
1	Ph	**8a**	186 [c]
2	4-MeC_6H_4	**8b**	163
3	3-MeC_6H_4	**8c**	135
4	2-MeC_6H_4	**8d**	79
5	2,4,6-$Me_3C_6H_2$	**8e**	–
6	4-$MeOC_6H_4$	**8f**	105

[a] The reactions were performed in AcOH at 50 °C for 12 h, under air with ratio between [Sb], **7** and $PdCl_2$ of 1:3:0.04.
[b] Yields of isolated products.
[c] Yield determined by GLC.

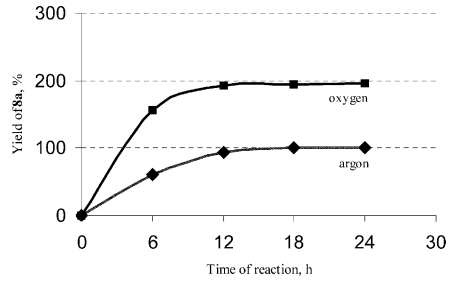


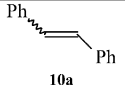
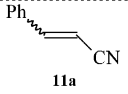
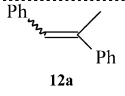
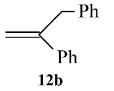
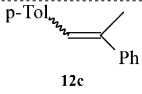
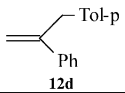
Fig. 2. Effect of the reaction atmosphere on the $PdCl_2$ catalyzed reaction of $Ph_3Sb(O_2CEt)_2$ with methyl acrylate. The reactions were performed in AcOH at 50 °C with the ratio **1a**:**7**:$PdCl_2$ (1:3:0.04).

noticeably with longer reaction times (Fig. 2). Under these conditions, only one phenyl group is transferred completely from the initial organometallic compound. However, under an atmosphere of oxygen, the yield of **8a** rose to nearly 200% after 12 h. This means that the transfer of the second phenyl group from the organometallic compound **1a** occurs. Thus, the C-arylation reactions with triarylantimony dicarboxylates should be preferentially carried out either under air or under oxygen, as they favour a considerable increase of the efficiency of organoantimony phenylating reagents when acetic acid is used as the solvent. By contrast, when the C-phenylation of **7** by the $PdCl_2$ catalyzed reaction with **1a** was performed in acetonitrile, the nature of the atmosphere had a less remarkable influence and the amount of the alkene played a more important role. For example, with a ratio of 1:3 between **1a** and **7**, a 100% yield of **8a** was obtained after 6 h in acetonitrile and was not improved by longer reaction time. But with a 1:10 ratio, the yield of **8a** reached 184% after 12 h.

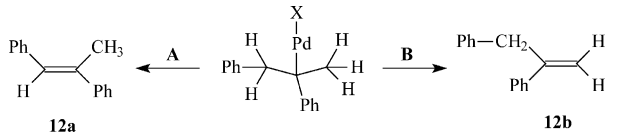
2.3. Reaction of Ar_3SbX_2 with other ethylene derivatives

After the initial optimization studies with methyl acrylate used as the model unsaturated substrate, the Pd-catalyzed reactions with Ar_3SbX_2 reagents were extended to the arylation of other unsaturated compounds. Two monosubstituted ethylene derivatives containing either an electron-withdrawing cyano group (acrylonitrile), or an electron-donating phenyl group (styrene) and also a disubstituted ethylene derivative, α-methylstyrene, were selected as representative substrates. Styrene **10** containing a donor phenyl group on the double bond was the most active among the monosubstituted ethylene derivatives (Table 4). Stilbene **10a** was isolated in a 167% yield with an *E*:*Z* ratio of 80:20. Unlike **10**, acrylonitrile **11** showed a lower reactivity, as the yield of cinnamonitrile **11a** was only 100%. In contrast with the stereoselectivity observed in the arylation of methyl acrylate affording only the *trans* isomer, the stereoselectivity in the case of acrylonitrile

Table 4
Influence of the alkene structure on the $PdCl_2$ catalyzed reaction of $Ar_3Sb(OAc)_2$ [a]

Entry	Substrate	Organoantimony compounds	Product	Yields, % [b]
1	 **10**	**1a**	 **10a**	167 (*E* : *Z* = 80 : 20)[c]
2	 **11**	**1a**	 **11a**	100 (*E* : *Z* = 83 : 17)
3	 **12**	**1a**	 **12a**	83 (*E* : *Z* = 97 : 3)
			 **12b**	12
4	**12**	**2a**	 **12c**	44 (*E* : *Z* = 97 : 3)
			 **12d**	6

[a] The reactions were performed in AcOH at 50°C for 12 h, under air with ratio between [Sb], [alkene] and $PdCl_2$ of 1 : 3 : 0.04
[b] Yields of isolated products.
[c] *E* : *Z* ratio determined by ^{1}H NMR.



Scheme 4.

was quite similar (E:Z = 83:17) to that observed with styrene. In the case of α-methylstyrene **12**, two isomeric products **12a** and **12b** were isolated in 83 and 12% yields, respectively (Table 4, entry 3). This fact can be explained by the occurrence of competitive β-elimination reactions (Scheme 4). The normal Heck product is formed via route A and the alternative route B gives the phenylation product **12b** with the shifted C=C double bond. When the *p*-tolylantimony derivative **2a** was used instead of the phenyl derivative **1a**, the analogous products **12c** and **12d** were obtained in lower yields but with the same selectivity (Table 4, entry 4).

2.4. Possible reaction pathways

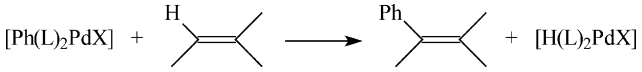
Several key facts can be singled out for their mechanistic implications: (i) only triarylantimony dicarboxylates participate in the arylation reaction while dihalides are ineffective; (ii) phosphine ligands inhibit palladium catalysis; (iii) the steric hindrance of the aromatic rings of the organoantimony compounds leads to a decrease in the reaction yields; (iv) the presence of oxygen is mandatory for the transfer of a second phenyl group from the organoantimony reagent.

The general mechanism of the Heck-type palladium catalyzed C-arylation reaction of alkenes is now well established [12,13]. The catalytic cycle includes four main steps: activation of the catalyst, oxidative addition, migratory insertion and palladium hydride elimination [13]. In the case of the palladium catalyzed C-arylation with Ar_3SbX_2, the mechanistic pathways depend on the reaction atmosphere.

2.4.1. Under inert atmosphere

Recently, Amatore and Jutand have demonstrated that $L_2Pd(0)$ complexes are the active species in the classical Heck reaction [14,15]. In our arylating system, the formation of the $L_2Pd(0)$ complexes proceeds most probably through the following steps described in Eqs. (1)–(4). With Pd(II) salts used as the catalyst, it can be considered that, in the first stage, transmetallation takes place to yield a phenylpalladium intermediate (Eq. (1)). This intermediate participates directly in the arylation reaction with formation of a palladium hydride (Eq. (2)). The palladium hydride complex is known to decompose by reductive elimination to an acid and the active species $L_2Pd(0)$ (Eq. (3)). Molecules of solvent, olefins or organoantimony(III) derivatives can play the role of ligands. Thus, the activation of the catalyst involves the reactions (1)–(3).

$$Ph_3SbX_2 + (L)_2PdX_2 \rightarrow [Ph(L)_2PdX] + Ph_2SbX_3 \quad (1)$$



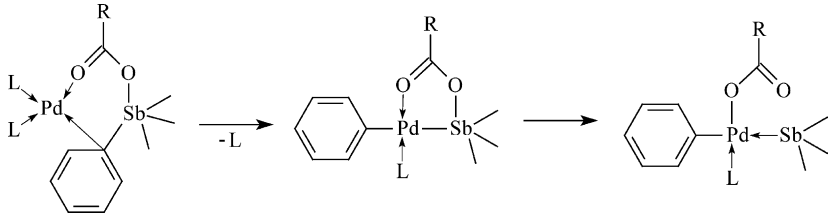
(2)

$$[H(L)_2PdX] \rightarrow (L)_2Pd + HX \quad (3)$$

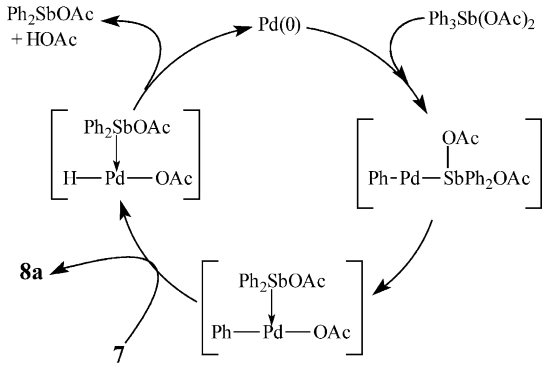
$$Ph_3SbX_2 + (L)_2Pd \rightarrow [Ph(L)_2PdX] + Ph_2SbX \quad (4)$$

The active palladium catalytic species $L_2Pd(0)$ then undergoes an oxidative addition step by reaction with the initial organoantimony(V) compound to give again the phenylpalladium intermediate (Eq. (4)). The nature of the X group in Ar_3SbX_2 is important for this reaction. Palladium insertion along a Ph–Sb bond of triarylantimony dicarboxylates occurs with the participation of a carboxylic group. This favors the preliminary coordination of $L_2Pd(0)$ on the organometallic compound and the redistribution of electrons in a five- or a six-member cycle (Scheme 5). As a result, the phenylpalladium intermediate is formed and the initial antimony(V) is reduced to antimony(III), which can serve as a ligand of the Pd atom [16,17]. Kawamura et al. suggested a similar mechanism of AcO group participation in the stoichiometric reaction of $Pd(OAc)_2$ with Ph_3M (M = P, As, Sb, Se or Te) and octene-1 [18]. They showed also that $PdCl_2$ is active in these reactions only in the presence of NaOAc additive. This mechanism is not realizable for triarylantimony dihalides for which the formation of the same cyclic transition state is not possible. In the mild reaction conditions used in this study, all Ph_3SbHal_2 showed a very low or no activity.

The presence of strongly binding ligands such as Ph_3P in the coordination sphere of the palladium metal center induces a substantial steric hindrance both in the



Scheme 5.



Scheme 6.

transmetallation reaction (Eq. (1)) and in the oxidative addition process (Scheme 5). Also bulky aromatic groups, especially *ortho*-substituted ones, cause a significant steric hindrance for all reactions occuring either in the palladium or in the antimony coordination spheres (Eqs. (1), (2) and (4)). The mesityl derivative **5a** is not reactive at all. In the case of the three isomeric tritolylantimony derivatives **2a**, **3a** and **4a**, the position of the methyl group influences significantly the reaction. Between the freely rotating *p*-tolyl derivative **2a** and the hindered *ortho*-substituted tolyl and mesityl derivatives **2a** and **5a**, the dihedral angles formed between the equatorial plane (containing the antimony center and the three *ipso* carbon atoms) and the plane of each aromatic rings are expected to become more important, making the approach of the palladium catalyst towards the *ipso* carbon atoms more difficult.

It should be noted that, according to this mechanism (Eqs. (1)–(4)), as soon as the initial organoantimony(V) compound is totally consumed the catalytic cycle should stop. Therefore the yield of **8a** cannot be higher than 100%, and this is indeed the case when the reaction is performed under an atmosphere of argon (Fig. 2). Thus, the complete catalytic process of the Pd-catalyzed C-phenylation of alkenes under argon can be represented by the cycle shown in Scheme 6, where Pd(0) is the active catalytic form.

2.4.2. Under air or an atmosphere of oxygen

In the presence of oxygen, the reaction pathway changes (Scheme 7). Oxygen reacts with the Pd–Sb complex **13**, [HPdOAc–Ph_2SbOAc], which is formed as described in Scheme 6.

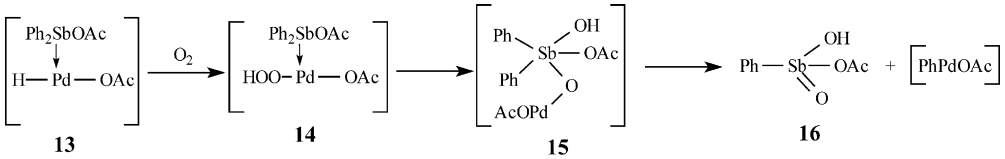
Oxygen inserts into the H–Pd bond to give the Sb(III)–palladium hydroperoxide complex **14**. The formation of such palladium hydroperoxide complexes was suggested by Yoshimoto et al. [19] and by Bregeault et al. [20]. Moreover, the complex $[CF_3COOPdOOBu\text{-}t]_4$ was isolated and characterized by Mimoun et al. [21]. As hydroperoxides are able to oxidize organoantimony(III) derivatives [10,22], the hydroperoxide **14** can undergo an internal redox process leading to the μ-oxo Sb–O–Pd intermediate **15** which subsequently rearranges intramolecularly to give the phenylpalladium acetate intermediate and a pentavalent phenylantimony compound **16**.

The effect of oxygen appears more clearly when the reaction is performed in AcOH. AcOH being a less donating solvent than acetonitrile, the antimony(III) derivative Ph_2SbO_2CR can remain longer in the coordination sphere of the palladium atom. On the other hand, Ph_3Sb is a more strongly donating ligand of palladium than Ph_2SbOAc, so that it impedes the coordination of oxygen with palladium and therefore behaves as an inhibitor of the reaction. Matoba et al. have shown that Ph_2SbCl phenylates unsaturated compounds in the presence of catalytic amounts of Pd(II) salts in acetonitrile under air or an atmosphere of oxygen [7]. But this reaction does not occur under an inert atmosphere. They suggested a free radical mechanism to explain this interaction. However, another possible explanation for the oxygen effect can be suggested. Oxygen could oxidize Pd(0) to Pd(II) in the presence of an acid (Eq. (5)) [23]. Then the Pd(II) species will accept a phenyl group from Sb(III) reagent by transmetallation (Eq. (6)).

$$Pd^0 + O_2 + 4H^+ \rightarrow Pd^{2+} + 2H_2O \quad (5)$$

$$Ph_2SbX + PdX_2 \rightarrow PhSbX_2 + PhPdX \quad (6)$$

This conclusion is confirmed by the greater efficiency of oxygen in AcOH solution (Fig. 2). However, the inhibition effect of Ph_3Sb is surprising since it reacts rather quickly with PdX_2 [24], and as we [25] and others [18] have observed that Ph_3Sb can be used as phenylating agent in the presence of stoichiometric amounts of $PdCl_2$. Moreover, Cho et al. have observed that Ph_3Sb reacts with methyl acrylate in acetic acid in the presence of a catalytic amount of palladium acetate and of silver acetate acting as a reoxydant [8]. The inhibition of the reaction described in our present work can be explained by the insufficient oxidizing power of oxygen towards



Scheme 7.

Pd(0), when this one is relatively strongly coordinated with Ph_3Sb.

Further studies are now underway to better understand the various intertwined mechanistic facets of the catalytic reaction reported in this work.

3. Conclusion

The Heck-type Pd-catalyzed C-arylation reaction of unsaturated compounds by triarylantimony(V) dicarboxylates can be easily performed at 50 °C in CH_3CN and AcOH as the best solvents, with $PdCl_2$ (4 mol%) as the most effective catalyst. One or two aryl groups of the organometallic compound can participate in the C-arylation reaction depending on the reaction conditions. The transfer of one aryl group occurs under inert atmosphere. Two aryl groups participate only when the reaction is performed in air or in an atmosphere of oxygen. In the case of ArI (as C-arylating reagents) the analogous C-arylation reaction occurs at 100–120 °C with the yield of **8a** 97% based on ArI [26]. The C-arylation reaction with $Ar_3Sb(O_2CR)_2$ reagents is inhibited by the presence of strong palladium ligands such as Ph_3P, and also by the steric hindrance in the aromatic groups. Moreover, we have found that all triarylantimony dihalides are inactive in the reaction.

4. Experimental

4.1. General methods

Gas chromatographic analyses were performed with a LKhM-80 chromatograph using helium as the carrier gas, column 100 cm length, 15%-Apiezon-L on the Chromaton N-AW at 220 °C. ^{1}H NMR spectra were measured on a Bruker Avance DPX-200 spectrometer for solutions in $CDCl_3$ with Me_4Si as the internal standard. Column chromatographies were performed with silica gel 60 Merck.

The triarylantimony compounds **1**–**5** were prepared as described previously [27]. *t*-BuOOH was prepared by the method of Milas and Surgenor [28]. Commercial methyl acrylate was washed with an alkali solution until the yellow color disappeared, then dried with Na_2SO_4 and distilled. Commercial styrene, α-methyl styrene and acrylonitrile were dried with Na_2SO_4 and distilled. All solvents were distilled prior to use. Li_2PdCl_4 [29], $Pd(OAc)_2$ [30], $Pd_2(dba)_3$ [31], $Pd(Ph_3P)_2Cl_2$ [32] were prepared by the reported methods, and $PdCl_2$ or $Pd(dppf)Cl_2$ were commercially available.

4.2. Synthesis of $Ph_3Sb(OAc)_2$ (**1a**) using AcOH and *t*-BuOOH

t-BuOOH (0.58 ml 97%, 5.7 mmol) was added dropwise to a stirred cold (5–10 °C) solution of Ph_3Sb (2 g, 5.7 mmol) and AcOH (0.98 ml, 17.1 mmol) in Et_2O (10 ml). The reaction mixture was kept in the dark for 24 h at room temperature. The solvent was distilled off under reduced pressure and the solid residue was purified by recrystallization (chloroform/hexane) to afford **1a** (2.4 g, 90%) as a white solid, m.p. 213 °C (lit. [33] 215 °C).

Other organoantimony compounds were prepared by the same procedure.

Triphenylantimony dipropionate (**1b**): m.p. 140 °C (lit. [34] 139–140 °C).

Triphenylantimony diformate (**1c**): m.p. 160 °C (lit. [33] 159–160 °C).

Triphenylantimony bis(trifluoroacetate) (**1d**): m.p. 109 °C (lit. [35] 109 °C).

Triphenylantimony dibenzoate (**1e**): m.p. 181 °C (lit. [33] 177 °C).

Triphenylantimony difluoride (**1f**): m.p. 113 °C (lit. [36] 115 °C).

Triphenylantimony dichloride (**1g**): m.p. 142 °C (lit. [34] 139–142 °C).

Triphenylantimony dibromide (**1h**): m.p. 218 °C (lit. [36] 214 °C).

Tris(*p*-tolyl)antimony diacetate (**2a**): m.p. 168 °C (lit. [4] 157–159 °C).

Tris(*m*-tolyl)antimony diacetate (**3a**): m.p. 140 °C; ^{1}H-NMR: δ 7.82–7.75 (m, 6H), 7.43–7.23 (m, 6H), 2.41 (s, 9H) and 1.84 (s, 6H). Anal. Found: C, 58.5; H, 5.4. $C_{25}H_{27}O_4Sb$ calc.: C, 58.5; H, 5.3%.

Tris(*o*-tolyl)antimony diacetate (**4a**): m.p. 178 °C; ^{1}H-NMR: δ 8.21 (d, 3H), 7.49–7.28 (m, 9H), 2.52 (s, 9H), 1.73 (s, 6H). Anal. Found: C, 58.2; H, 5.1. $C_{25}H_{27}O_4Sb$ calc.: C, 58.5; H, 5.3%.

Trimesitylantimony diacetate (**5a**): m.p. 98–101 °C; ^{1}H-NMR: δ 6.96 (s, 6H), 2.52 (s, 18H), 2.31 (s, 9H), 1.88 (s, 6H). Anal. Found: C, 62.5: H, 6.8. $C_{31}H_{39}O_4Sb$ calc.: C, 62.3: H, 6.6%.

Tris(*p*-anisyl)antimony diacetate (**6a**): m.p. 153 °C; ^{1}H-NMR: δ 7.92 (d, $J = 9$ Hz, 6H), 7.0 (d, $J = 9$ Hz, 6H), 3.83 (s, 9H), 1.81 (s, 6H). Anal. Found: C, 53.1; H, 5.1. $C_{25}H_{27}O_7Sb$ calc.: C, 53.5; H, 4.9%.

4.3. Synthesis of $Ph_3Sb(OAc)_2$ (**1a**) using AcOH and H_2O_2

H_2O_2 (1.05 ml 29.6%, 10.5 mmol) was added dropwise over 10 min to a stirred cold (5–10 °C) solution of Ph_3Sb (3.53 g, 10 mmol) and AcOH (30 mmol) in Et_2O (3 ml) and *i*-PrOH (20 ml). The reaction mixture was kept in the dark for 3 h at room temperature (r.t.). The solid was filtered and washed with *i*-PrOH and recrys-

talled (chloroform–hexane) to afford **1a** as white crystals (3.77 g, 85%).

4.4. Synthesis of $Ph_3Sb(OAc)_2$ (**1a**) using $(CH_3CO)_2O$ and t-BuOOH

t-BuOOH (0.58 ml 97%, 5.7 mmol) was added dropwise to a stirred cold (5–10 °C) solution of Ph_3Sb (2 g, 5.7 mmol) and $(CH_3CO)_2O$ (2.15 ml, 22.8 mmol) in Et_2O (10 ml). The reaction mixture was kept in the dark for 90 h at r.t. The solvent was distilled off under reduced pressure and the solid residue was purified by recrystallization (chloroform–hexane) to afford **1a** (1.87 g, 70%).

4.5. Typical procedure for the C-phenylation reaction

A mixture of $Ph_3Sb(OAc)_2$ (0.236 g, 0.5 mmol), $PdCl_2$ (3.6 mg, 0.02 mmol), methyl acrylate (0.135 ml, 1.5 mmol) in acetic acid (4 ml) was placed in a 50 ml tube. The tube was sealed and the reaction mixture was kept at 50 °C for 12 h. The solvent was then evaporated under reduced pressure. The solid residue was purified from inorganic products by elution through a short column on silica gel using a mixture of hexane–diethyl ether (v/v 4:1) as the eluant. The filtrate was analyzed by GLC. Methyl cinnamate (0.151 g) was isolated after distillation of the solvents under reduced pressure.

In the reactions with the antimony compounds **2a**, **3a**, **4a** and **6a**, the arylated products were isolated by column chromatography on silica gel eluting with hexane–diethyl ether (v/v 4:1) mixture. Distillation of the solvents afforded the arylated products.

8c ^{1}H-NMR: δ 7.67 (d, $J = 16$ Hz, 1H), 7.37–7.13 (m, 4H), 6.43 (d, $J = 16$ Hz, 1H), 3.80 (s, 3H), 2.36 (s, 3H). Anal. Found: C, 74.6; H, 7.1. $C_{11}H_{12}O_2$ calc.: C, 75.0; H, 6.9%.

8d ^{1}H-NMR: δ 8.00 (d, $J = 16$ Hz, 1H), 7.58–7.16 (m, 4H), 6.36 (d, $J = 16$ Hz, 1H), 3.81 (s, 3H), 2.44 (s, 3H). Anal. Found: C, 75.1; H, 7.1. $C_{11}H_{12}O_2$ calc.: C, 75.0; H, 6.9%.

8f ^{1}H-NMR: δ 7.65 (d, $J = 16$ Hz, 1H), 7.48 (d, $J = 9$ Hz, 2H), 6.90 (d, $J = 9$ Hz, 2H), 6.31 (d, $J = 16$ Hz, 1H), 3.85 (s, 3H), 3.78 (s, 3H). Anal. Found: C, 68.7; H, 6.1. $C_{11}H_{12}O_2$ calc.: C, 68.7; H, 6.3%.

In the reactions with the other unsaturated substrates **10**, **11** and **12**, the procedure was the same as above. All products are known compounds and were identified only by ^{1}H-NMR.

(*E*)-Stilbene and (*Z*)-stilbene were isolated as an *E*:*Z*-mixture **10a**. (*E*)-**10a**: δ 7.67–7.30 (m, 10H), 7.22 (s, 2H). (*Z*)-**10a**: δ 7.52–7.30 (m, 10H), 5.58 (s, 2H).

(*E*)-Cinnamonitrile and (*Z*)-cinnamonitrile were isolated as an *E*:*Z*-mixture **11a**. (*E*)-**11a**: δ 7.50–7.38 (m, 5H), 7.39 (d, $J = 16.6$ Hz, 1H), 5.87 (d, $J = 16.6$ Hz, 1H). (*Z*)-**11a**: δ 7.50–7.38 (m, 5H), 7.13 (d, $J = 12.3$ Hz, 1H), 5.44 (d, $J = 12.3$ Hz, 1H)

(*E*:*Z*)-α-Methylstilbene (**12a**) and 2,3-diphenyl-1-propene (**12b**) were identified by the ^{1}H-NMR spectrum of their mixture. (*E*)-**12a**: δ 7.69–7.21 (m, 10H), 6.90 (s, 1H), 2.34 (s, 3H). (*Z*)-**12a**: δ 7.69–7.21 (m, 10H), 6.52 (s, 1H), 2.25 (s, 3H). **12b**: δ 7.69–7.21 (m, 10H), 5.55 (s, 1H), 5.07 (s, 1H), 3.88 (s. 2H).

(*E*:*Z*)-1-*para*-Tolyl-2-phenyl-1-propene (**12c**) and 3-*para*-tolyl-2-phenyl-1-propene (**12d**) were identified by the ^{1}H-NMR spectrum of their mixture. (*E*)-**12c**: δ 7.60–7.11 (m, 9H), 6.86 (s, 1H), 2.41 (s, 3H), 2.33 (d, $J = 1.3$ Hz, 3H). (*Z*)-**12c**: δ 7.60–7.11 (m, 9H), 6.48 (s, 1H), 2.43 (s, 3H), 2.37 (s, 3H). **12d**: δ 7.60–7.11 (m, 9H), 5.52 (s, 1H), 5.05 (m, 1H), 3.84 (s, 2H), 2.34 (s, 3H).

4.6. C-phenylation reaction under argon or oxygen

A mixture of $Ph_3Sb(OAc)_2$ (0.236 g, 0.5 mmol), $PdCl_2$ (3.6 mg, 0.02 mmol), methyl acrylate (0.135 ml, 1.5 mmol) in acetic acid (4 ml) was placed in a 50 ml tube. The reaction mixture was degassed by repeated freeze–pump–thaw cycles and the tube was filled with argon (or oxygen). The following procedure was the same as described above.

Acknowledgements

The spectral studies were carried out in the Analytical Center of the G.A. Razuvaev Institute of Organometallic Chemistry (Russian Academy of Sciences) with the financial support of the Russian Foundation for Basic Research (project no. 00-03-40116). We thank Dr. Jean-Pierre Finet (Universite de Provence, Marseille, France) for fruitful discussions.

References

[1] (a) Y.Z. Huang, Acc. Chem. Res. 25 (1992) 182;
(b) W.I. Cross, S.M. Godfrey, C.A. McAuliffe, A.G. Mackie, R.G. Pritchard, in: N.C. Norman (Ed.), Chemistry of Arsenic, Antimony and Bismuth, Ch. 5, Blackie Academic and Professional, London, 1998.
[2] M. Fujiwara, M. Tanaka, A. Baba, H. Ando, Y. Souma, J. Organomet. Chem. 525 (1996) 39.
[3] S.-K. Kang, H.-C. Ryu, Y.-T. Hong, J. Chem. Soc. Perkin Trans. 1 (2000) 3350.
[4] S.-K. Kang, H.-C. Ryu, S.-W. Lee, J. Organomet. Chem. 610 (2000) 38.
[5] S.-K. Kang, H.-C. Ryu, Y.-T. Hong, J. Chem. Soc. Perkin Trans. 1 (2001) 736.
[6] A.V. Gushchin, D.V. Moiseev, V.A. Dodonov, Russ. Chem. Bull. 50 (2001) 1291.
[7] K. Matoba, S. Motofusa, C.S. Cho, K. Ohe, S. Uemura, J. Organomet. Chem. 574 (1999) 3.
[8] (a) C.S. Cho, K. Tanabe, S. Uemura, Tetrahedron Lett. 55 (1994) 1275;

(b) C.S. Cho, S. Motofusa, K. Ohe, S. Uemura, Bull. Chem. Soc. Jpn. 69 (1996) 2341.
[9] C.S. Cho, K. Tanabe, O. Itoh, S. Uemura, J. Org. Chem. 60 (1995) 274.
[10] V.A. Dodonov, T.I. Zinov'eva, Metalloorg. Khim. 5 (1992) 1265 (Engl. Transl.).
[11] V. Gutman, Khimiya koordinacionnych soedinenii v nevodnych rastvorach [Chemistry of coordination compounds in nonaqueous solutions], Mir, Moscow, 1971, 220 pp. (in Russian).
[12] A. de Meijere, F.E. Meyer, Angew. Chem. Int. Ed. Engl. 33 (1994) 2379.
[13] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.
[14] C. Amatore, A. Jutand, Acc. Chem. Res. 33 (2000) 314.
[15] C. Amatore, A. Jutand, M.J. Medeiros, L. Mottier, J. Electroanal. Chem. 422 (1997) 125.
[16] D.H.R. Barton, J. Khamsi, N. Ozbalik, J. Reibenspies, Tetrahedron 46 (1990) 3111.
[17] A. Mentes, R.D.W. Kemmitt, J. Fawcett, D.R. Russell, J. Organomet. Chem. 528 (1997) 59.
[18] T. Kawamura, K. Kikukawa, M. Takagi, T. Matsuda, Bull. Chem. Soc. Jpn. 50 (1977) 2021.
[19] H. Yoshimoto, H. Itatani, Bull. Chem. Soc. Jpn. 46 (1973) 2490.
[20] J.-M. Bregeault, M. Faraj, J. Martin, C. Martin, New J. Chem. 11 (1987) 337.
[21] H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, R. Weiss, J. Am. Chem. Soc. 102 (1980) 1047.
[22] R. Hiatt, C. McColeman, G.R. Howe, Can. J. Chem. 53 (1975) 559.
[23] I.V. Kozhevnikov, K.I. Matveev, Uspekhi Khim. 47 (1978) 1231.
[24] R. Asano, I. Moritani, Y. Fujiwara, S. Teranishi, Bull. Chem. Soc. Jpn. 46 (1973) 2910.
[25] A.V. Gushchin, D.V. Moiseev, V.A. Dodonov, Zh. Obshch. Khim. 72 (2002) 1669 (Engl. Transl.).
[26] T. Mizoriki, K. Mori, A. Ozaki, Bull. Chem. Soc. Jpn. 44 (1971) 581.
[27] I.E. Pokrovskaya, V.A. Dodonov, Z.A. Starikova, E.N. Kanunnikova, T.M. Shchegoleva, G.P. Lebedeva, Zh. Obshch. Khim. 51 (1981) 1247 (Engl. Transl.).
[28] N. Milas, D. Surgenor, J. Am. Chem. Soc. 68 (1946) 205.
[29] R.F. Heck, J. Am. Chem. Soc. 90 (1968) 5518.
[30] T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer, G. Wilkinson, J. Chem. Soc. (1965) 3632.
[31] T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet, J.A. Ibers, J. Organomet. Chem. 65 (1974) 253.
[32] H. Itatani, J.C. Bailar, J. Am. Oil Chem. Soc. 44 (1967) 147.
[33] J. Havranek, J. Mleziva, A. Lycka, J. Organomet. Chem. 157 (1978) 163.
[34] K.A. Kocheshkov, A.P. Skoldinov, N.N. Zemlyanskii, Metody elementoorganicheskoi khimii. Sur'ma, vismut [Methods of Organoelement Chemistry. Antimony, Bismuth], Nauka, Moscow, 1976, 483 pp. (in Russian).
[35] R.G. Goel, D.R. Ridley, J. Organomet. Chem. 38 (1972) 83.
[36] G.O. Doak, G.G. Long, L.D. Freedman, J. Organomet. Chem. 4 (1965) 82.