Phenyl Derivatives of Antimony(III, V) and Bismuth(III, V) in the Presence of Palladium Salts, as C-Phenylating Agents for Methyl Acrylate

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Received December 22, 2000

Abstract — The C-phenylation of methyl acrylate to methyl cynnamate with Ph_3Sb , Ph_3SbX_2 (X = Cl, OAc), Ph_3Bi , and Ph_3BiX_2 (X = OAc, O_2CEt) in the presence of $PdCl_2$, $Pd(OAc)_2$, Li_2PdCl_4 , $NaPd(OAc)Cl_2$, and $Na_2Pd(OAc)_2Cl_2$ was studied to show that the reactions with Ph_3Sb and $Ph_3Sb(OAc)_2$ are more selective and give higher yields of the target product than those with Ph_3Bi and $Ph_3Bi(OAc)_2$, while $Ph_3M(OAc)_2$ are preferred over Ph_3M . Copper(II) alkanecarboxylate additives have no effect on the yield of methyl cynnamate in the reactions with Ph_3Sb .

Antimony- and bismuth-containing reagents are finding increasing use in organic synthesis. Previously unknown copper(I)-catalyzed O- and N-phenylation reactions of alcohols, primary and secondary amines, and amino acids have been discovered [1, 2]. These reactions occur in mild conditions and feature high yields and selectivity. Of particular interest is the use of triphenylantimony and triphenylbismuth in the C-phenylations of styrene [3], 1-octene and ethyl acrylate [4], vinylsilanes [5], allyl alcohols and ethers, and other alkenes [6] by the C–H bond in the presence of palladium(II) compounds (Heck reaction) at 20– 50°C.

The aim of the present work was to study C-phenylation of methyl acrylate (I) with triphenylantimony and triphenylbismuth in the presence of palladium(II) compounds. The choice of methyl acrylate as the model unsaturated compound was motivated by its high reactivity and selectivity in the Heck reaction [4]. We planned to examine the effects of the structure of the palladium compound, of the central atom of the organometallic reagent, of atmospheric air, and copper(II) salt additives on the yield of methyl cynnamate (II).

It was shown that $Ph_3Sb + Pd(OAc)_2$ completely reacts with methyl acrylate (1:1:1) in acetonitrile at 50°C within 1 h. The solution completely decolorizes, which suggests the consumption of the strongly colored starting Pd(II) acetate [scheme (1)].

$$CH_2 = CHCO_2Me \xrightarrow{Ph_3SB + Pd(OAc)_2} PhCH = CHCO_2Me$$

$$I \qquad II$$

$$+ Ph_2SbOAc + Pd + AcOH. (1)$$

The yield of ester II is 94% (per Ph_3Sb). In addition, acetic acid (156%), phenyl acetate (8%), and biphenyl (III) (76%) are formed. The black mixture of insoluble reaction products contains Pd(0) and antimony hydroxides and acetates. With excess ester I (10 mol per mole Ph_3Sb), the yield of ester II is slightly higher (110%), the yield of acetic acid does not change (154%), while phenyl acetate in completely lacking. Further experiments were performed with a 1:10 organometallic compound:ester I ratio.

The yield of ester **II** is much affected by the amount and composition of the starting Pd(II) salt. Thus, when the amount of $Pd(OAc)_2$ is reduced from 1 to 0.3, 0.1, and 0.03 mol per 1 mol of Ph_3Sb , the yield of ester II is reduced from 110 to 24, 8, and 2%, respectively. Simultaneously, the yields of compound **III** are reduced from 61 to 3, 2, and 4% and of AcOH, from 154 to 54, 20, 3%, respectively. In the absence of the palladium salt, triphenylantimony fails to react with ester I. The proportionality of the yield of ester II to the amount of $Pd(OAc)_2$ provide evidence for the known classical scheme of the Heck reaction involving phenyl derivatives of main group metals and Pd(II) salts [4, 7]. The metal-exchange reaction initially forms a σ -phenyl Pd(II) derivative which undergoes cis addition to the unsaturated compound involving π -bond cleavage in the latter, followed by syn elimination of palladium(II) acetate hydride and its reductive decomposition to give Pd(0) [schemes (2)–(4)]. Recently palladium σ complexes PhPdX (X = OAc, Cl, Br) with triphenylantimony, triphenylphosphine, and other donor neutral ligands have been isolated and characterized [8–10].

Table 1. Effect of Pd(II) salt on the yield of phenylation of ester I with the system $Ph_3Sb + Pd(II)$ (1:x) in MeCN at 50°C in air

Exp. no.	Palladium compound	x	Time, h	Yield, % ^a		
				Π	III	PhCl
1	PdCl ₂	0.3	1	32	3	_
2	$Na_2PdCl_2(OAc)_2$	0.3	1	30	2	_
3	Li ₂ PdCl ₄	0.3	1	86	7	_
4 ^b	$NaPdCl_{2}(OAc)$	1.0	3	65	2	0.2
5 ^b	$NaPdCl_{2}(OAc)$	1.0	5	76	3	0.3
6 ^b	NaPdCl ₂ (OAc)	1.0	200 ^c	110	1	1.9
7	$Pd_2(dba)_3(CHCl_3)$	0.15	3	0	20	_
8	Pd-black	0.2	50	0	0	_
		I I				

^a Per Ph₃Sb. ^b Solvent AcOH. ^c 20°C.

$$Ph_{3}Sb + Pd(OAc)_{2} + mL \longrightarrow Ph_{2}SbOAc$$
$$+ [PhPd(OAc)L_{m}], \qquad (2)$$

 $[PhPd(OAc)L_m] + CH_2 = CHCO_2Me$

$$\longrightarrow$$
 [HPd(OAc)L_m] + PhCH=CHCO₂Me, (3)

$$[\mathrm{HPd}(\mathrm{OAc})\mathrm{L}_m] + (n - m)\mathrm{L} \longrightarrow \mathrm{Pd}(0)\mathrm{L}_n + \mathrm{AcOH}, \quad (4)$$

 $L = Ph_3Sb, >C=C<, MeCN.$

Palladium(II) compounds strongly affect the yield of phenylation of ester **I** with triphenylantimony. Along with $Pd(OAc)_2$, we also tried $PdCl_2$ and other Pd(II) salts (Table 1). They all, especially Li_2PdCl_4 , proved to be more active than $Pd(OAc)_2$. The yield of ester **II** in comparable conditions is 30–86%. The reaction with NaPdCl₂(OAc) gave PhCl in an yield of up to 2% (Table 1, exp. nos 4–6). With palladium black and the complex of Pd(0) with dibenzylideneacetone $Pd_2(dba)_3(CHCl_3)$, unlike Pd(II) acetates and chlorides, no C-phenylation products are formed (Table 1, exp. nos. 7 and 8).

With the most active Li_2PdCl_4 (Table 1, exp. no. 3), the yield of ester **II** is as high as 3 mol per mole Pd(II), which is inconsistent with the above stoichiometric scheme [Eqs. (2)–(4)].

Deviation from the stoichiometry, while not so strong, takes place with $Pd(OAc)_2$ if the heating time in air is prolonged to 50 h. Therewith, the yield of ether **II** is 48%, i.e. 1.6 mol per mole Pd(II) (Table 2, exp. no. 1). The effect of atmospheric oxygen showed up faster in exp. nos. 3–5 (Table 2), where high concentrations of the starting Pd(OAc)₂ (1 mol per mole Ph₃Sb) were used: Aready after 1 h the yields of ester **II** were 96 (without air), 110 (in air), and 140% (in

Table 2. Effect of oxygen on the yield of phenylation of ester I with the system $Ph_3Sb + Pd(OAc)_2(1:x)$ in MeCN at 50°C

Exp.	x	Conditions	Time,	Yield, % ^a	
no.		Conditions	h	П	Ш
1	0.30	Air	50	48	5
2	0.30	In the absence	50	25	2
		of air			
3	1.00	The same	1	96	64
4	1.00	Air	1	110	61
5	1.00	Oxygen	1	140	80

^a Per Ph₃Sb.

oxygen) per Pd(II). The yield of compound **III** was almost invariable. Consequently, PhPdOAc is regenerated from Pd(0) with atmospheric oxygen and takes part in further transformations by Eqs. (2) and (3).

It would appear reasonable that oxygen oxidizes the inactive Pd(0) to the active Pd(II) in the presence of AcOH by Eq. (5), and, therewith, in the latter experiments this effect is more pronounced owing to the higher acid concentration (Table 2, exp. nos. 3-5).

$$2\mathrm{Pd}(0)\mathrm{L}_{n} + \mathrm{O}_{2} + 4\mathrm{HX} \longrightarrow 2 \mathrm{PdX}_{2}\mathrm{L}_{m} + 2\mathrm{H}_{2}\mathrm{O}$$
$$+ (2n - 2m)\mathrm{L}.$$
(5)

To confirm this scheme, we accomplished Pd(II) acetate–catalyzed C-phenylation of ester I with triphenylantimony in the presence of and acetic or perchloric acids $[Ph_3Sb:Pd(OAc)_2:HX = 1:0.03:2]$. The reactions were performed in acetonitrile (50°C, 1 h) in air. It was found that acid additives did not improve the yield of ester II: It was low both with acetic and with perchloric acid (3% per triphenylantimony). It was also showed in the presence of water (20 mol per mole organometallic compound) the yield of ester II in the C-phenylation of ester I with triphenylantimony in the presence of Pd(OAc)₂ or Li₂PdCl₄ in acetonitrile at a 1:0.3 organometallic compound: Pd(II) salt ratio remains almost the same. This result is further evidence against scheme (5).

Probably, oxygen reacts with the intermediate palladium hydride complex by a scheme proposed earlier [6] for the reaction with chlorodiphenylstibine [scheme (6)].

 $[HPdX \cdot Ph_2SbX] + O_2 \longrightarrow [PhPdX] + PhSbO_2 + HX. (6)$

Table 3. Yields of phenylation of ester **I** with the system $Ph_3Sb + Pd(OAc)_2 + Cu(O_2CR)_2$ (1:x:y) in MeCN at 50°C for 1 h in air

Exp.	R	x	у	Yield, % ^a		
no.				II	III	
1	-	0.03	0	2	4	
2	Me	0.02	0.1	0.7	1	
3	Et	0.02	0.1	0.5	1	
4	Oct	0.04	0.06	2	1	
5	Oct	0.04	0.20	1	3	
6	Oct	0.04	1.00	2	2	
7 ^b	Æ	0.02	0.1	0.1	3	
8^{b}	Me	0.02	0.1	1.1	3	
9 ^b	Et	0.02	0.1	1	4	
10 ^b	Oct	0.02	0.1	1	7	

^a Per Ph₃Sb. ^b In the presence of pyridine (0.2 mol).

We assessed the effect of copper(II) additives on C-phenylation of ester I with the system $Ph_3Sb + Pd(II)$. As known, copper(II) can oxidize Pd(0) by scheme (7). Taking this into account, we proposed a catalytic system for alkene phenylation, including Ph_2Hg , Li_2PdCl_4 , and $CuCl_2$ (1:0.02:0.1) in the presence of atmospheric oxygen for reoxidizing copper and palladium; by this scheme, the phenylation yield was up to 60% per organometallic compound [7].

$$Pd(0) + 2Cu(II) \longrightarrow Pd(II) + 2Cu(I).$$
 (7)

We performed C-phenylation of ester I with triphenylantimony in the presence of $Pd(OAc)_2$ and copper(II) alkanecarboxylates, such as copper(II) acetate, formate, propionate, and pelargonate, at 50°C in acetonitrile in air. As seen from Table 3, copper(II) acetate, propionate, and pelargonate do not reoxidize palladium in the reaction of interest and do not improve the yield of ester II compared with the reactions in the absence of copper (Table 3, exp. nos. 1–4). With increased or reduced amounts of the starting Cu(O₂CR)₂ (Table 3, exp. nos. 4–6) and in the presence of pyridine which forms water-soluble copper complexes (Table 3, exp. nos. 7–10), the phenylation yield is still too low (<2%).

It should be noted that the inactive copper alkanecarboxylates $Cu(O_2CR)_2$ in our case, unlike the situation in [7], can not be replaced by the active $CuCl_2$, since the latter is immediately reduced with triphenylantimony to CuCl [11], which is incharacteristic of diphenylmercury.

It was found that the reactivity of Bi(III, V) and

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Table 4. Effect of organometallic compound on the yield of phenylation of ester I with the system $MOC + Pd(OAs)_2$ (1:1) in MeCN at 50°C in air

Exp.	Organometallic compound	Time, h	Yield, % ^a		
no.			II	III	
1	Ph ₃ Sb	1	110	61	
2 ^b	$Ph_3Sb(OAc)_2$	1	258	20	
3 ^c	Ph ₃ SbCl ₂	14	59	47	
4	Ph ₃ Bi	14	17	129	
5 ^d	Ph ₃ Bi	1	16	110	
6	$Ph_3Bi(OAc)_2$	14	87	107	
7	$Ph_3Bi(O_2CEt)_2$	14	87	76	

 ^a Per organometallic compound. ^b PhOAc was found (2%).
 ^c PhCl was found (1%). ^d Na₂PdCl₂(OAc)₂ instead of Pd(OAc)₂; PhH (1%) and PhCl (1%) were found.

Sb(III, V) phenyl derivatives toward ester I strongly depends on their structure. Among the Sb(V) derivatives used, $Ph_3Sb(OAc)_2$ provided the highest yield of ester II, 25% per organometallic compound (Table 4, exp. no. 2). In this case, the three phenyl groups are involved in the target C-phenylation. This result can be explained by that Sb(V) here acts not only as a donor of phenyl groups, but also, along with atmospheric oxygen, as a reoxidant for Pd(0) [schemes (8) and (9)].

$$Ph_{3}Sb(OAc)_{2} + Pd(OAc)_{2}L_{m} + CH_{2}=CHCO_{2}Me + (n - m)L$$

$$\longrightarrow Ph_{2}Sb(OAc)_{3} + Pd(0)L_{n} + AcOH$$

$$+ PhCH=CHCO_{2}Me, \qquad (8)$$

$$Ph_{2}Sb(OAc)_{3} + Pd(0)L_{n} \longrightarrow PhSb(OAc)_{2}$$

+ PhPdOAcL_m +
$$(n - m)$$
L. (9)

It is interesting that Ph_3SbCl_2 is less active not only compared with $Ph_3Sb(OAc)_2$, but also with Ph_3Sb . Even when the reaction time is prolonged to 14 h, the yield of ester **II** is as low as 59% (Table 4, exp. no. 3).

Triphenylbismuth, unlike Ph_3Sb , proved to be an inactive C-phenylating agent. The yield of ester II is no higher than 16–17% with various Pd(II) salts (Table 4, exp. nos. 4 and 5). In going from triphenylbismuth to triphenylbismuth(V) diacylates $Ph_3Bi \cdot (OAc)_2$ and $Ph_3Bi(O_2CEt)_2$, the yield of ester II increases to 87% (Table 4, exp. nos. 6 and 7).

Special experiments were performed to find out whether ester I can be arylated with ester II and bi-

phenyl (III). The latter two compounds are always isolated in the C-phenylation reactions of ester I and organic derivatives of antimony and bismuth. They contain phenyl groups and, therefore, are themselves able to effect arylation of ester I, involving Pd(II), and thus to compete with Bi- and Sb-containing phenylating agents. Danno *et al.* [12, 13] have studied in detail such olefin arylation with arenes at $80-110^{\circ}$ C.

We found that ester II, compound III, as well as benzene and chlorobenzene have almost no effect on arylation in the conditions chosen. Thus, upon heating of benzene with $Pd(OAc)_2$ and ester I (1:1:10) in MeCN at 50°C for 5 h in air, the yield of ester II is as low as 0.2%, and 98.8% of benzene remains unreacted. Similarly, ester II, chlorobenzene, and compound III were recovered (98, 97, and ca. 100%, respectively) upon heating with $Pd(OAc)_2$ and ester I.

In the above consideration of the results of phenylation of ester **I** with systems including organic derivatives of antimony(III, V), bismuth(III, V), and palladium(II) we did not dwell on the formation of compound **III**. This side reaction involves homocoupling of the organometallic substrates in the presence of palladium(II) complexes [scheme (10)].

$$2Ph_{3}M \xrightarrow{Pd(0)_{n}} 2M + 3Ph-Ph,$$
(10)
III

M = Sb, Bi.

Such reactions have been reported for derivatives of antimony(III, V) and bismuth(III, V) in different coordination states [8, 14, 15] and for other organometallic compounds [16]. In the phenylation reactions in question, the yield of compound **III** is 1–10%, but sometimes attains 80 [with antimony(III, V) derivatives] and 80–130% [with bismuth(III, V) derivatives]. The **II/III** yield ratio which measures the selectivity of C-phenylation of ester **I** for Sb(III, V) derivatives is always higher than for Bi(III, V) derivatives. Pentavalent antimony and bismuth derivatives $Ph_3M(OAc)_2$ are always preferred over corresponding trivalent derivatives Ph_3M .

EXPERIMENTAL

Volatile products were analyzed by GLC on an LKhM-80 chromatograph, flame-ionization detector, column 100 cm, packing 15% Apieson-L on Chromaton N-AW, oven temperature 120–220°C, carrier gas helium.

 Ph_3Bi and Ph_3Sb were prepared as described in [11, 17]. $Ph_3Bi(OAc)_2$ and $Ph_3Bi(O_2CEt)_2$ were pre-

pared by reactions of Ph₃Bi with t-BuO₂H and carboxylic acids in 90 and 80% yields, respectively [1]. $Ph_3Sb(OAc)_2$ and Ph_3SbCl_2 were prepared by reactions of Ph₃Sb with hydrogen peroxide and acids in 85 and 94% yields, respectively [18]. Palladium black was prepared in 90% yield by reduction of PdCl₂ with formic acid [19]. Li₂PdCl₄ was prepared in nearly quantitative yield from PdCl₂ and LiCl in water [7]. $Na_2Pd(OAc)_2Cl_2$ and $NaPd(OAc)Cl_2$ were prepared in situ from $PdCl_2$ and NaOAc in acetic acid. $Pd(OAc)_2$ was synthesized by oxidation of palladium black with nitric acid in AcOH for 30 h in 80% yield (after recrystallization from AcOH [20]). Pd₂(dba)₃(CHCl₃) was prepared by reduction of PdCl₂ with methanol in the presence of dibenzylideneacetone [21] in 66% yield. Ester I was washed with aqueous alkali, dried with Na₂SO₄, and distilled. Acetonitrile was allowed to stand over K₂SO₃ and twice distilled over phosphoric anhydride [22].

Reaction of triphenylantimony with palladium(II) acetate and ester I in the absence of air. One neck of an H-shaped ampule was charged with 0.177 g of Ph₃Sb and 0.05 g Pd(OAc)₂, and the other, with 4 ml of acetonitrile, 0.45 ml of ester I. The ampule was degassed, sealed, the reagents were mixed, and the mixture was heated for 50 h at 50°C. The ampule was then unsealed, and the liquid was recondensed into a liquid nitrogen trap and analyzed. Acetic acid (0.015 g) was determined by alkaline titration, and ester II (0.004 g), by GLC. The solid residue was treated with benzene (2 × 7 ml). The benzene extract was centrifuged and analyzed by GLC to find ester II (0.016 g) and compound III (0.002 g).

The reactions in oxygen were performed in a similar way. The reactions in air were performed in plugged ampules, and the solutions were not degassed.

ACKNOWLEDGMENTS

The work was financially supported by the Universitety Rossii Program (project no. 992839) and the Integratsiya Federal Program (State Contract A 0047).

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