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Organometallic Chemistry

Catalytic *C*-phenylation of methyl acrylate with triphenylantimony(V) dicarboxylates

A. V. Gushchin,* D. V. Moiseev, and V. A. Dodonov

N. I. Lobachevsky State University of Nizhnii Novgorod,
23 prosp. Gagarina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 65 8592. E-mail: guav3@uic.nnov.ru

Triphenylantimony dicarboxylates $Ph_3Sb(OAc)_2$ and $Ph_3Sb(O_2CEt)_2$ are efficient *C*-phenylating agents for methyl acrylate. In the presence of the $Pd(OAc)_2$, Li_2PdCl_4 or $Pd_2(dba)_3(CHCl_3)$ catalysts in MeCN at 50 °C, methyl cinnamate forms in 70—150% yield with respect to Sb^V. Copper(II) salts do not increase the reaction yield.

Key words: phenylation, methyl acrylate, methyl cinnamate, triphenylantimony diacetate, triphenylantimony dipropionate, palladium compounds.

It is known that triphenylantimony is used in the Heck reaction for the *C*-phenylation of unsaturated compounds in the presence of equimolar amounts of palladium(II) acetate.[1—4] Triphenylantimony as phenylating agent have advantages over aryl halides (*e.g.*, PhI or PhBr), which, in most cases, require heating to 80—140 °C. A disadvantage of the triphenylantimony application is a high consumption of the Pd^{II} salt, which is reduced in the process to inactive Pd^0.

This work is aimed at studying the antimony derivatives Ph_3SbX_2 (X = OAc, O_2CEt, Cl) as *C*-phenylating agents for methyl acrylate. The chosen Sb^V compounds, unlike Sb^{III} compounds, are capable of Pd^0 re-oxidation to Pd^{II}, and this allowed palladium compounds to be used in catalytic quantities. Methyl acrylate transforms into only one *C*-phenylation product, methyl cinnamate.

Results and Discussion

The reaction of $Ph_3Sb(O_2CEt)_2$ with methyl acrylate in the presence of $Pd(OAc)_2$ in a molar ratio of 1 : 10 : 0.04 in MeCN at 50 °C for 1 h in air afforded methyl cinnamate in 104% yield based on the initial organometallic compound (OMC). In addition, propionic acid (110%), Sb^{III} propionates and biphenyl (2%) (Table 1, entry *1*) were found in the reaction products. The reaction occurred according to the equation

$$\mathrm{Ph_3Sb(O_2CEt)_2 + CH_2{=}CHCO_2Me \xrightarrow{Pd^{II}}}$$
$$\mathrm{\longrightarrow PhCH{=}CHCO_2Me + Ph_2SbO_2CEt + EtCO_2H.} \tag{1}$$

The methyl acrylate phenylation and catalysis with the palladium salt can be presented by the equations

$$\mathrm{Ph_3Sb(O_2CEt)_2 + Pd(OAc)_2} + m\,\mathrm{L} \longrightarrow$$
$$\longrightarrow \mathrm{Ph_2Sb(O_2CEt)_2(OAc) + PhPd(OAc)L}_m, \tag{2}$$

$$\mathrm{CH_2{=}CHCO_2Me + PhPd(OAc)L_m} + (n - m)\,\mathrm{L} \longrightarrow$$
$$\longrightarrow \mathrm{PhCH{=}CHCO_2Me + Pd^0L}_n + \mathrm{AcOH}, \tag{3}$$

$$\mathrm{Ph_3Sb(O_2CEt)_2 + Pd^0L}_n \longrightarrow$$
$$\longrightarrow \mathrm{Ph_2SbO_2CEt + PhPd(O_2CEt)L}_m + (n - m)\,\mathrm{L}, \tag{4}$$

where L = >C=C<, OMC of antimony.

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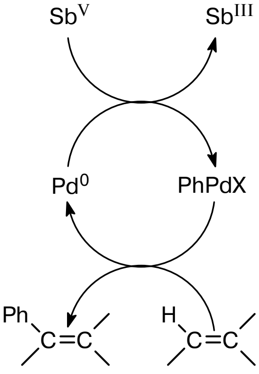
Table 1. Yields of the products of *C*-phenylation of methyl acrylate with the Ph_3SbX_2—PdY_2 (1 : 0.04) system in acetonitrile at 50 °C for 1 h in air

Entry	Ph_3SbX_2	PdY_2	Yield (% per OMC)	
			Methyl cinnamate	Biphenyl
1	$Ph_3Sb(O_2CEt)_2$	$Pd(OAc)_2$	104	2
2	$Ph_3Sb(OAc)_2$	$Pd(OAc)_2$	71	25
3	$Ph_3Sb(OAc)_2$	Li_2PdCl_4	64	15
4	Ph_3SbCl_2	Li_2PdCl_4	1	20
5	$Ph_3Sb(O_2CEt)_2$	$Pd_2(dba)_3(CHCl_3)$*	85	2
6	$Ph_3Sb(O_2CEt)_2$	Pd^0	62	9

* Dibenzylideneacetone is designated as dba.

Transmetallation occurs at the first stage to form the phenylpalladium derivative (Eq. (2)), which arylates methyl acrylate to methyl cinnamate. In this reaction, the carboxylic acid and Pd^0 complex are also formed (Eq. (3)). The latter enters into the redox reaction with the initial $Ph_3Sb(O_2CEt)_2$, which is reduced to the Sb^{III} compound according to Eq. (4). The Pd^{II} complex that formed further phenylates methyl acrylate.

The general scheme of this process demonstrates a catalytic role of palladium, which performs the catalytic transition $Pd^0 \rightleftarrows Pd^{II}$ (Eq. (5)). The reaction ceases when the organoantimony oxidant is completely consumed.

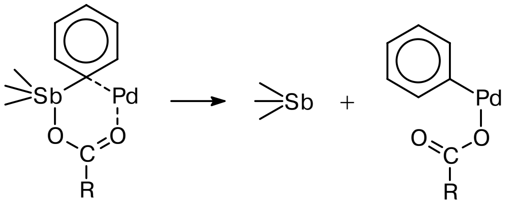


(5)

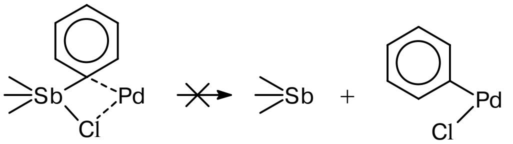
Thus, triphenylantimony(v) dicarboxylates are unique because they are simultaneously the sources of phenyl groups for phenylation and oxidizing agents for Pd^0.

When $Pd(OAc)_2$ was used as catalyst, the yield of methyl cinnamate decreased in the following order of OMC: $Ph_3Sb(O_2CEt)_2 \geq Ph_3Sb(OAc)_2 \gg Ph_3SbCl_2$. An insignificant difference between Sb^V propionate and acetate can be explained by a lower solubility of the latter in acetonitrile.

Unlike Sb^V carboxylates, Sb^V chloride is inefficient in *C*-phenylation. The yield of methyl cinnamate was 1% (see Table 1, entry *4*). This is due, as we believe, to a higher oxidation potential of triphenylantimony(v) dicarboxylates with respect to Pd^0, and on the other hand, to a more favorable structure of the transition state of the redox stage. From this point of view, the transfer of the phenyl and carboxylate groups from the Sb^V atom to Pd^0 through the six-membered cyclic transition state is easier than the transfer of the phenyl and chloride groups through the four-membered transition state (Eqs. (6) and (7)).



(6)



(7)

It has previously[4] been shown that when triphenylantimony is used as a phenylating agent for methyl acrylate the oxidation state of palladium plays a determining role and the Pd^0 complexes are inactive. Unlike this, when antimony(v) dicarboxylates are used, the oxidation degree of palladium is not substantial, and the yields of methyl cinnamate remain high in the presence of both Pd^0 and Pd^{II} (see Table 1, entry *5*). The Pd^0 complex obtained *in situ* by the reduction of $Pd(OAc)_2$ with triethylamine[5] was also used (entry *6*). Various Pd^{II} salts, such as $Pd(OAc)_2$ and Li_2PdCl_4, possess the same activity when $Ph_3Sb(OAc)_2$ is used as phenylating agent (see Table 1, entries *2* and *3*).

It should be emphasized that biphenyl is a byproduct of the *C*-phenylation of methyl acrylate. The yield reached 60—80% when the Ph_3Sb—$Pd(OAc)_2$ (1 : 1) system was used.[4] The application of triphenylantimony dicarboxylates decreased the yield of biphenyl to 2—25% (see Table 1). Biphenyl is formed in the reaction of the σ-phenyl palladium derivative with OMC or without the latter according to Eqs. (8) and (9).[6,7] These stages occur much more slowly than the alternative reaction with an unsaturated compound.[8]

$$PhPd(OAc)L_m + Ph_3Sb(OAc)_2 + (n-m)\,L \longrightarrow$$
$$\longrightarrow Ph_2 + Pd^0L_n + Ph_2Sb(OAc)_3 \qquad (8)$$

$$2\,PhPd(OAc)L_m + (n-m)\,L \longrightarrow$$
$$\longrightarrow Ph_2 + Pd^0L_n + Pd(OAc)_2L_m \qquad (9)$$

We have shown[4] that the air oxygen has a substantial effect on the *C*-phenylation of methyl acrylate with triphenylantimony in the presence of $Pd(OAc)_2$. In all cases of using $Ph_3Sb(OAc)_2$ and $Ph_3Sb(O_2CEt)_2$ as

Table 2. Influence of oxygen on the yield of phenylation products of methyl acrylate with the $Ph_3Sb(O_2CEt)_2$—$Pd(OAc)_2$ (1 : 0.04) phenylating system in acetonitrile at 50 °C

Atmosphere	Time /h	Yield (% per OMC)	
		Methyl cinnamate	Biphenyl
In the absence of air	1	80	25
	3	92	6
	9	92	3
Air	1	104	2
	3	121	3
	9	135	1
Air*	1	71	25
	3	114	5
	9	130	3
Dioxygen	1	115	9
	3	129	7
	9	153	3

* Reactions with $Ph_3Sb(OAc)_2$.

phenylating agents, dioxygen increases the yield of target methyl cinnamate, which reaches 153% with an increase in the time of heating (Table 2). Dioxygen can affect both Pd^0 and Sb^{III} (Eqs. (10) and (11)). The free radical scheme without changing the valences of antimony and palladium (Eq. (12)), proposed[9] for the reaction of diphenylchlorostibine, cannot either be excluded.

$$\mathrm{Pd^0L}_n + \mathrm{O_2} \longrightarrow \mathrm{Pd^{II}L}_{n-2} \xrightarrow{\mathrm{OMC}} [\mathrm{PhPdX}] \tag{10}$$

$$[\mathrm{Sb^{III}\cdot Pd}] + \mathrm{O_2} \longrightarrow \mathrm{Sb^V} \xrightarrow{\mathrm{Pd}} [\mathrm{PhPdX}] \tag{11}$$

$$[\mathrm{HPdX\cdot Ph_2SbX}] + \mathrm{O_2} \longrightarrow [\mathrm{PhPdX}] \tag{12}$$

It is of interest that in these experiments the biphenyl yield decreased with time in all cases (see Table 2).

A solvent plays a noticeable role in the *C*-phenylation of methyl acrylate. When the $Ph_3Sb(O_2CEt)_2$—$Pd(OAc)_2$ (1 : 0.04) phenylating system in acetonitrile (ε = 37.5)[10] is used at 50 °C, the yield of methyl cinnamate was 104% for 1 h for reaction in air. The replacement of acetonitrile by acetic acid (ε = 6.15) decreased the product yield to 67%, and that for methanol (ε = 32.63) decreased to 44%. Such a low yield in methanol having a high dielectric constant can be explained by the capability of methanol of reducing Pd^{II} to Pd^0.[11] Note that the yield of biphenyl was at most 1—2% in all cases.

In the reaction of $Ph_3Sb(O_2CEt)_2$ with methyl acrylate in the presence of minor amounts of palladium compounds, only one of three phenyl groups at the Sb atom participated in phenylation. Dioxygen facilitated the involvement of the second Ph group but only when the time of heating increased. Therefore, it was reasonable to study the influence of copper salt additives, which are capable of oxidizing Pd^0 to Pd^{II} and acting as mediators of the oxygen effect on Pd^0 (Wacker process).

Table 3. Influence of copper salt additives on the yield of *C*-phenylation products of methyl acrylate with the $Ph_3Sb(O_2CR)_2$—Pd^{II}—Cu^{II} (1 : 0.04 : *x*) system at 50 °C for 1 h in air

R	Pd^{II}	Cu^{II}	*x*	Solvent	Yield*	
					Methyl cinnamate	Biphenyl
Me	Li_2PdCl_4	—	—	MeCN	64	14
	Li_2PdCl_4	$CuCl_2$	0.4	MeCN	1	19
	Li_2PdCl_4	$CuCl_2$	2	MeCN	0	2
	Li_2PdCl_4	Li_2CuCl_4	0.4	MeCN	1	6
	Li_2PdCl_4	Li_2CuCl_4	0.4	AcOH	64	5
Et	$Pd(OAc)_2$	$Cu(OAc)_2$	0.4	MeCN	105	1
	$Pd(OAc)_2$	$Cu(OAc)_2$	0.4	AcOH	64	0
	$Pd(OAc)_2$	$Cu(OAc)_2$	0.4	MeOH	64	2

* In % per OMC.

Moreover, a mild oxidation of Sb^{III} to Sb^V with copper(II) halides could be expected, as it is known for Ph_3Sb [12]:

$$\mathrm{Ph_2SbOAc} + 2\,\mathrm{CuCl_2} \longrightarrow \mathrm{Ph_2Sb(OAc)Cl_2} + 2\,\mathrm{CuCl}. \tag{13}$$

$CuCl_2$ additives in different amounts and Li_2CuCl_4 did not increase (Table 3) and even decreased sharply the yield of methyl acrylate upon *C*-phenylation with the $Ph_3Sb(OAc)_2$—Li_2PdCl_4 (1 : 0.04) system. We assumed that the inhibition effect of copper halides is explained by the reversible transformation of reactive Sb^V carboxylates into nonreactive Sb^V halides (see above). In this case, the addition of AcOH should impede this reaction. Indeed, when AcOH was used as solvent instead of acetonitrile, the inhibition effect was eliminated and the yield of methyl cinnamate remained as high as it was in the absence of copper salts.

In this connection, we decided to replace the copper and palladium chloro-containing compounds by acetate compounds. $Ph_3Sb(O_2CEt)_2$ was used as phenylating agent. It turned out that, in this case, the copper salt does not prevent the formation of methyl cinnamate, whose yield in acetonitrile was 105%. The efficient phenylation was also observed in solutions of AcOH and MeOH (see Table 3).

Thus, copper salts cannot act as oxidants in methyl acrylate *C*-phenylation with triphenylantimony dicarboxylates. Depending on the structure and reaction conditions, they either suppress the process or have no effect on it.

It should specially be mentioned that the main process, *C*-phenylation was slightly impeded by the side reaction of biphenyl formation in the presented reactions of triphenylantimony diacetate and especially dipropionate with methyl acrylate in the presence of catalytic quantities of palladium. The yield of biphenyl was, as a rule, 1—5% (see Tables 1—3). Therefore, the selectivity of the phenylating system is much higher than that of the earlier studied $Ph_3Sb—Pd(OAc)_2$ system where the biphenyl yield was[2,4] 10—70%.

Thus, we proposed a new catalytic system for the mild and selective *C*-phenylation of methyl acrylate to methyl cinnamate. The system is based on triphenylantimony dicarboxylates and palladium compounds. The organic compound of antimony(v) is both the source of phenyl groups and oxidizing agent for conversion of Pd^0 to Pd^{II}.

Experimental

The reaction volatile products were analyzed by GLC on an LKhM-80 (DIP) chromatograph using helium as the carrier gas, column 100 cm length, 15% Apieson-L on the Chromaton N-AW support at 220 °C.

Compounds $Ph_3Sb(OAc)_2$, $Ph_3Sb(O_2CEt)_2$, and Ph_3SbCl_2 were synthesized by the reaction of Ph_3Sb [13] with hydrogen peroxide and the corresponding acids in a ratio of 1 : 1 : 2 in an ether—Pr^iOH (1 : 4 v/v) mixture in 85, 78, and 94% yields, respectively.[14] Li_2PdCl_4 was prepared in ~100% yield from $PdCl_2$ and LiCl in an aqueous medium.[15] $Pd(OAc)_2$ was synthesized by the oxidation of palladium black with nitric acid in AcOH for 30 h in 80% yield after recrystallization from AcOH.[16] $Pd_2(dba)_3(CHCl_3)$ was prepared by the reduction of $PdCl_2$ with methanol in the presence of dibenzylideneacetone[10] in 66% yield. Methyl acrylate was washed with an alkali solution until the yellow color disappeared, dried with Na_2SO_4, and distilled.

Reaction of $Ph_3Sb(OAc)_2$ with methyl acrylate and $Pd(OAc)_2$ in the absence of air. $Ph_3Sb(OAc)_2$ (0.50 mmol) and $Pd(OAc)_2$ (0.02 mmol) were placed into one finger of an H-like ampule. Anhydrous acetonitrile[17] (4 mL) and methyl acrylate (5.00 mmol) were poured into another finger, the ampule was degassed and sealed, the reactants were mixed, and the mixture was heated for 1 h at 50 °C. Then the ampule was open, and the liquid was recondensed into a trap cooled with liquid nitrogen. AcOH (0.45 mmol) was found in the condensate by titration of an aliquot with an alkali, and methyl cinnamate (0.001 mmol) was detected by GLC. The solid residue contained the main amount of poorly volatile methyl cinnamate and biphenyl. The residue was liberated from the palladium compounds and antimony carboxylates by treatment with H_2S. With this purpose, MeCN (6 mL) was added to the solid residue in the ampule, the mixture was stirred, an H_2S flow was passed through the solution, and the latter was centrifuged. A transparent solution was separated, and acetonitrile (2 mL) was poured to the remaining black precipitate containing palladium and antimony sulfides. The mixture was centrifuged. Extracts were combined, and the concentrations of methyl cinnamate (0.345 mmol) and biphenyl (0.125 mmol) were determined by GLC.

The reactions in oxygen were conducted similarly in standard sealed 50-mL ampules without degassing of a solution.

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