Tetraphenylantimony carboxylates in the cascade Pd-catalyzed C-phenylation reaction of methyl acrylate in the presence of peroxide

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Abstract

Tetraphenylantimony(V) carboxylates have been used in the palladium-catalyzed C-phenylation reaction of methyl acrylate in the presence of $(PhCO_2)_2$ or t-BuOOH under mild conditions (50 °C). The peroxides promote a cascade participation of the organoantimony compound and result in the transfer of three phenyl groups. Organoantimony intermediates have been isolated from the reaction.
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1. Introduction

Organoantimony compounds have been used in organic synthesis either as reagents or as catalysts for a number of years [1]. The catalysis of these reactions using palladium has been reported [2]. We have recently reported that triarylantimony dicarboxylates were efficient reagents in the palladium-catalyzed C-arylation reactions of unsaturated compounds with the involvement of two aryl groups [3]. Triarylstibines Ar_3Sb can also be used as reagents in the C-arylation reaction via formation of $Ar_3Sb(OAc)_2$ in situ in the presence of peroxides [4]. Tetraphenylantimony derivatives Ph_4SbX have shown lower activities in comparison with $Ar_3Sb(OAc)_2$. Only one phenyl group was involved in the C-phenylation reaction [5].

The aim of the present work is to increase the efficiency of tetraphenylantimony derivatives in the C-phenylation reaction using organic peroxides.

2. Results and discussion

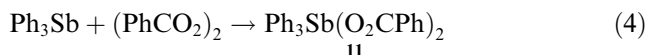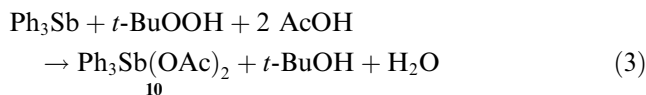### 2.1. Ph₄SbX + peroxide system in the palladium-catalyzed C-phenylation reaction

The tetraphenylantimony compounds are involved in the palladium-catalyzed phenylation reaction of methyl acrylate to give Ph_3Sb, which is inactive in a catalytic C-phenylation [5]. Moreover, Ph_3Sb can deactivate a palladium catalyst [3]. We assumed that an addition of organic peroxide in the reaction mixture in the presence of a carboxylic acid could convert Ph_3Sb into triphenylantimony dicarboxylate in situ [4]. The latter is an active phenylating agent [3,4].

We investigated the model C-phenylation reaction of methyl acrylate **1** with tetraphenylantimony hydroxide Ph_4SbOH **2** (**1**:**2** = 4:1) in AcOH in the presence of t-BuOOH **3** (1.2 equivalent per **2**) and Li_2PdCl_4 (4 mol%). Compound **2** was selected for the following reasons. It is one of the most accessible compounds of this type and can easy give tetraphenylantimony acetate Ph_4SbOAc **4** in AcOH solution [6,7] (Scheme 1). Peroxide **3** is the best oxidant for antimony(III) derivatives [4]. Li_2PdCl_4 is the optimum precatalyst for the C-phenylation in the presence of the peroxide [4]. Methyl acrylate **1** was taken in

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$$\text{1} \xrightarrow[\text{AcOH, 50 }^{\circ}\text{C}]{\text{Ph}_4\text{SbOH}/t\text{-BuOOH}/\text{Li}_2\text{PdCl}_4} \text{5}$$

$$\text{Ph}_4\text{SbOH} + \text{AcOH} \longrightarrow \text{Ph}_4\text{SbOAc} + \text{H}_2\text{O}$$
$$\quad\quad\quad\text{2} \quad\quad\quad\quad\quad\quad\quad\quad\quad\text{4}$$

Scheme 1.

molar excess to **2** (4:1), one molecule of **1** per one phenyl group of **2**.

The C-phenylation reaction of **1** with the (**2** + **3**) system gives methyl cinnamate **5** (Scheme 1) in a 247% yield for 24 h (the yield being based on the initial organoantimony reagent, the yield of 100% corresponds to the transfer of only one phenyl group) (Table 1, entry 1). The yield of **5** is not changed significantly in the presence of an excess of **3** (Table 1, entries 2 and 3). In the absence of the peroxide the product yield is only 30% (Table 1, entry 5). Tetraphenylantimony propionate $\text{Ph}_4\text{SbO}_2\text{CEt}$ **6** being used instead of **2** shows the same activity, the yield of **5** is 254% (Table 1, entry 4). The high yield of **5** corresponds to the transfer of almost three phenyl groups.

The substitution of **3** for benzoyl peroxide $(\text{PhCO}_2)_2$ **7** gives rise to the yield of **5**. It is 240% and 300% in the case of 12 and 24 h duration of the reaction, respectively (Table 1, entries 6 and 7). This yield corresponds to the full involvement of three phenyl groups of **2**. It is known that peroxide **7** in contrast with **3** can oxidize Sb(III) into active Sb(V) without involvement of carboxylic acid [4,8]. This allows the new system based on tetraphenylantimony derivatives to be used in a neutral solvent,

Table 1
Pd-catalyzed reaction of Ph_4SbOH with methyl acrylate **1** in the presence of a peroxide: influence of the nature and the amount of the peroxide[a]

Entry	Peroxide	Ph_4SbOH: peroxide	Yields of **5** (%)[b]
1	t-BuOOH	1:1.2	247
2	t-BuOOH	1:1.5	257
3	t-BuOOH	1:2	240
4[c]	t-BuOOH	1:1.2	254
5	–	–	30
6[d]	$(\text{PhCO}_2)_2$	1:1.5	240
7	$(\text{PhCO}_2)_2$	1:1.5	300
8[e]	$(\text{PhCO}_2)_2$	1:1.5	300

[a] The reactions were performed in AcOH at 50 °C for 24 h, under air with ratio between **1**, [Sb] and Li_2PdCl_4 of 4:1:0.04.
[b] Yields were determined by GLC, the yield of 100% corresponds to the involvement of one phenyl group.
[c] $\text{Ph}_4\text{SbO}_2\text{CEt}$ was used as a phenylating agent.
[d] Reaction duration was 12 h.
[e] $\text{Ph}_4\text{SbO}_2\text{CEt}$ was used as a phenylating agent and CH_3CN was used as a solvent.

e.g. CH_3CN. However Ph_4SbOH is not effective in acetonitrile where it gives mainly a homo-coupling product, namely, biphenyl [5]. Therefore, propionate **6** was used as a phenylating agent. The reaction of **1** with the (**6** + **7**) system (1:1.5) gives **5**, as expected, in a 300% yield (CH_3CN, 50 °C, 24 h) (Table 1, entry 8). When **7** is heated in the absence of organoantimony compound under the same conditions the phenylated product **5** is not formed.

Thus, the tetraphenylantimony derivatives can be effective cross-coupling agents. In the presence of $(\text{PhCO}_2)_2$ they phenylate methyl acrylate under mild conditions (50 °C) to provide a transfer of three phenyl groups. It was found that Ph_4SbOH was the preferable agent in AcOH, and $\text{Ph}_4\text{SbO}_2\text{CEt}$ in CH_3CN, respectively.

2.2. Mechanistic aspects of the organoantimony(V) involvement in the palladium-catalyzed C-phenylation reaction

To understand the mechanism of the tetraphenylantimony compounds participation in the investigated reaction we isolated three key stages, within each stage only one phenyl group is transferred. The catalytic cycle consists of the consecutive redox reactions of the antimony atom, which are caused by the presence of peroxide and palladium in the system.

2.2.1. Transfer of the first phenyl group
At the first stage of the catalytic cycle tetraphenylantimony carboxylate **4** reacts with the active Pd(0) species formed on the activation stage. As a result, the phenylpalladium intermediate **8** and Ph_3Sb **9** are formed (Eq. (1)). The intermediate **8** interacts with **1** to give the phenylation product **5** (Eq. (2)). At this stage the yield of **5** could reach a value of 100%. In reality, in the absence of peroxide the yield is only 30% (Table 1, entry 5) because of the inhibiting effect of Ph_3Sb [3].

$$\text{Ph}_4\text{SbOAc} + \text{Pd(0)} \longrightarrow \text{PhPdOAc} + \text{Ph}_3\text{Sb} \quad\quad (1)$$
$$\quad\text{4} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\text{8} \quad\quad\quad\text{9}$$

$$\underset{\text{CO}_2\text{Me}}{\diagdown} + \text{PhPdOAc} \longrightarrow \underset{\text{CO}_2\text{Me}}{\overset{\text{Ph}}{\diagdown}} + \text{Pd(0)} + \text{HOAc}$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (2)$$

2.2.2. Transfer of the second phenyl group
At the second stage the peroxide oxidizes **9** into the active pentavalent state [3,4]. The mechanism of the oxidation has been reported [9,10]. Ph_3Sb forms either triphenylantimony diacetate $\text{Ph}_3\text{Sb}(\text{OAc})_2$ **10** in the AcOH solution in the presence of hydroperoxide **3** (Eq. (3)) or triphenylantimony dibenzoate $\text{Ph}_3\text{Sb}(\text{O}_2\text{CPh})_2$ **11** in CH_3CN in the presence of benzoyl peroxide **9**

(Eq. (4)). The triphenylantimony dicarboxylates oxidize Pd(0) into PhPdOAc **8** (Eq. (5)), which phenylates methyl acrylate according to Eq. (2).

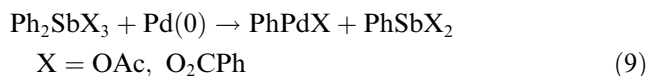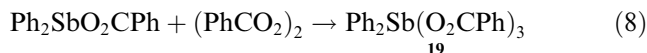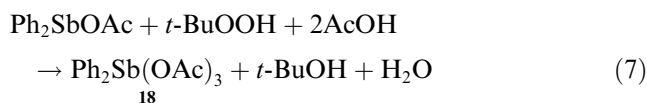$$Ph_3Sb + t\text{-}BuOOH + 2\,AcOH$$
$$\rightarrow \underset{\mathbf{10}}{Ph_3Sb(OAc)_2} + t\text{-}BuOH + H_2O \qquad (3)$$

$$Ph_3Sb + (PhCO_2)_2 \rightarrow \underset{\mathbf{11}}{Ph_3Sb(O_2CPh)_2} \qquad (4)$$

$$Ph_3Sb(OAc)_2 + Pd(0) \rightarrow PhPdOAc + \underset{\mathbf{12}}{Ph_2SbOAc} \qquad (5)$$

To prove the existence of the reaction (5) we made a special investigation of the C-arylation reaction of **1** with tris(*para*-tolyl)antimony diacetate *p*-Tol$_3$Sb(OAc)$_2$ **13** by ^{1}H NMR. This system was selected for the following reasons. The initial compounds as well as the arylation products such as methyl 3-(*para*-tolyl)propionate **14** and bis(*para*-tolyl)antimony acetate **15** had clear and easy identifiable NMR signals (Scheme 2). D$_3$CCOOD was used as a solvent. The reaction was carried out under argon atmosphere.

The initial ^{1}H NMR spectrum of the reaction mixture contained the resolved signals of **13** at 7.88 (d, *ortho*-protons), 7.36 (d, *meta*-protons), 2.39 (s, CH$_3$), 2.06 (s, OAc) ppm and **1** at 6.41, 6.16, 5.86 (d, protons at the double bond), 3.74 (s, OMe) ppm (Fig. 1(a)). In the second spectrum, recorded after 3 h, two new sets of signals appeared (Fig. 1(b)). They corresponded to the expected products **14** at 7.71 (d), 7.48 (d, *ortho*-protons), 7.20 (d, *meta*-protons), 6.48 (d), 3.79 (s, OMe), 2.35 (s, CH$_3$) ppm and **15** at 7.55 (d, *ortho*-protons), 7.24 (d, *meta*-protons), 2.33 (s, CH$_3$), 2.06 (s, OAc) ppm. The **14**:**15** ratio was 1:1. An amount of **14** corresponded to an amount of consumed organoantimony compound **13**. Spectra, recorded for 12 and 24 h of the reaction duration (Fig. 1(c)), confirmed that the product formation and the consumption of **13** occurred in equivalent amounts. However, the new signals appeared at 7.66 (d), 7.29 (d), 2.33 (s), 2.06 (s) ppm were associated with mono(*para*-tolyl)antimony diacetate *p*-TolSb(OAc)$_2$ **16** and signals at 7.31 (d), 7.13 (d), 2.31 (s) ppm were associated with tris(*para*-tolyl)antimony *p*-Tol$_3$Sb **17**. These compounds are the products of the ligand exchange reaction of **15** according to Eq. 6. Thus, we confirmed that triarylantimony dicarboxylates were involved in the arylation according to Eq. (5). The total catalytic process (Eqs. (1)–(3), (5)) can give 200% of phenylation product **5** with respect to the initial Ph$_4$SbOAc.

$$2p\text{-}Tol_2SbOAc \rightleftharpoons \underset{\mathbf{16}}{p\text{-}TolSb(OAc)_2} + \underset{\mathbf{17}}{p\text{-}Tol_3Sb} \qquad (6)$$
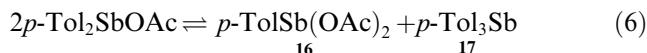
2.2.3. Transfer of the third phenyl group

Organoantimony(III) derivatives Ph$_2$SbX (X = OAc, O$_2$CPh) are involved in the third stage of the phenylation reaction. Like in the case of Ph$_3$Sb, a peroxide oxidizes Ph$_2$SbX to give an active antimony(V) derivative, diphenylantimony triacetate Ph$_2$Sb(OAc)$_3$ **18** (Eq. 7) or diphenylantimony tribenzoate Ph$_2$Sb(O$_2$CPh)$_3$ **19** (Eq. 8). These compounds react with Pd(0) to give the phenylpalladium intermediate **8** (Eq. 9), which phenylates the third molecule of **1** (Eq. (2)). Antimony(V) is reduced to the phenylantimony(III) dicarboxylate. Thus, peroxide is consumed in oxidation of both triphenyl- and diphenylantimony(III) derivatives.

$$Ph_2SbOAc + t\text{-}BuOOH + 2\,AcOH$$
$$\rightarrow \underset{\mathbf{18}}{Ph_2Sb(OAc)_3} + t\text{-}BuOH + H_2O \qquad (7)$$

$$Ph_2SbO_2CPh + (PhCO_2)_2 \rightarrow \underset{\mathbf{19}}{Ph_2Sb(O_2CPh)_3} \qquad (8)$$

$$Ph_2SbX_3 + Pd(0) \rightarrow PhPdX + PhSbX_2$$
$$X = OAc,\ O_2CPh \qquad (9)$$

Another route of Ph$_2$SbX involvement can occur in the presence of oxygen. Matoba et al. [2e] suggested a radical mechanism of this process. In previous work [3] we suggested the speculative mechanism of the oxygen involvement via formation of a palladium hydroperoxide XPdOOH, which oxidized antimony(III) into antimony(V).

We investigated the arylation reaction of **1** with *p*-Tol$_3$Sb(OAc)$_2$ **13** (Scheme 2) in the presence of oxygen by ^{1}H NMR. Under oxygen conditions, comparable to argon, products **14-17** were registered. However, in the presence of oxygen the rate of formation of the arylation product, **14**, was observed to be greater than rate of consumption of **13**. The organoantimony(III) compound *p*-Tol$_2$Sb(OAc)$_2$ **16** was the main product. It was found that oxygen is absorbed at the rate of 0.5 mol per 1 mol of **5**. Thus, the following scheme of oxygen involvement in the transfer of the third phenyl group is realized (Scheme 3). The scheme could be explained by concerted oxidation of two molecules of **12** with an oxygen molecule in the coordination sphere of palladium like in the homogeneous oxidation of phosphines with oxygen on Rh, Co, Pt catalysts [11–13] (Scheme 4).
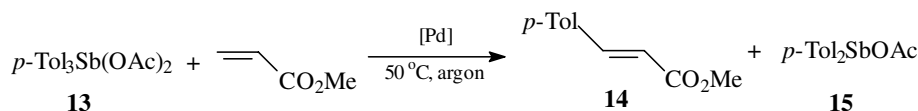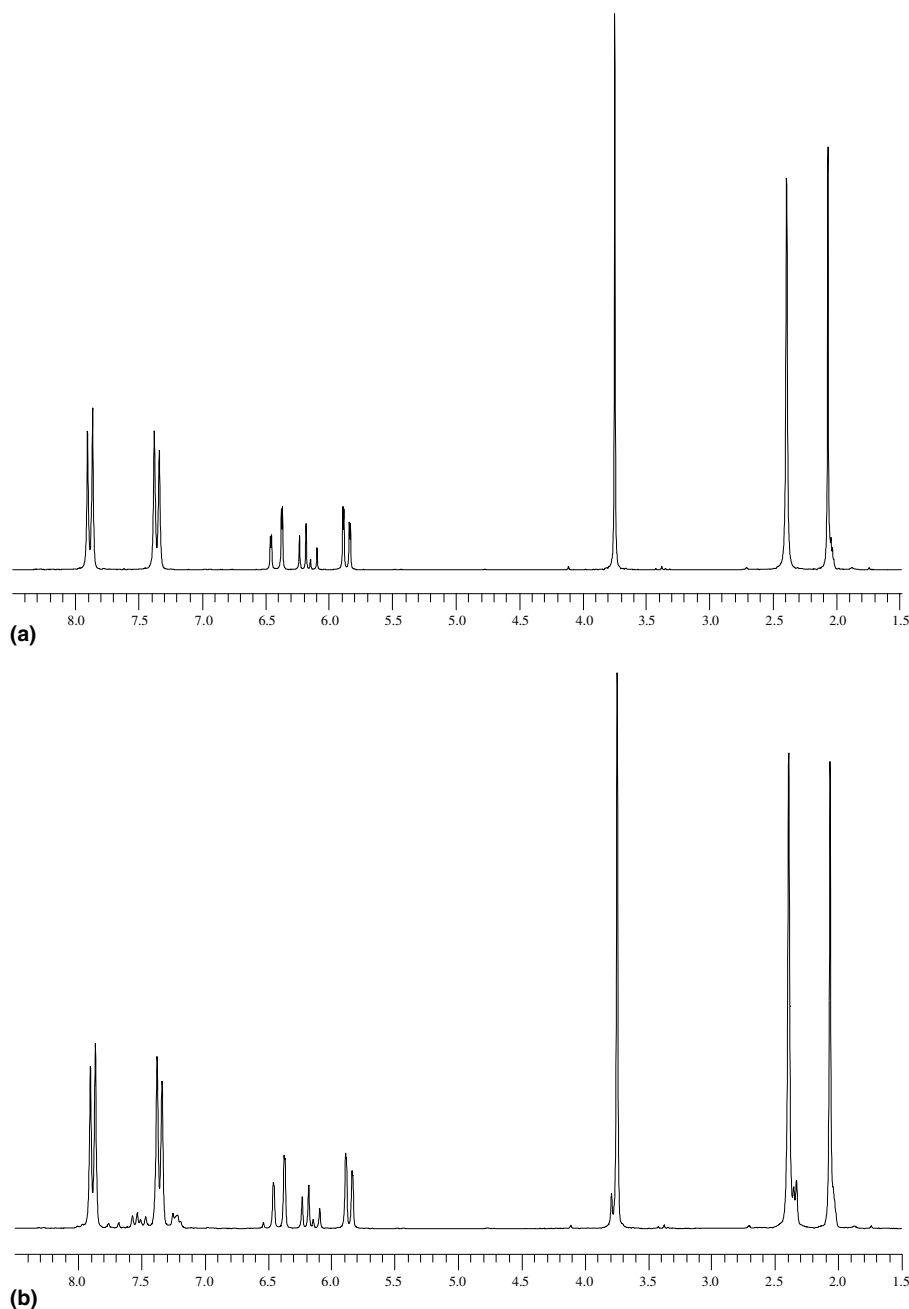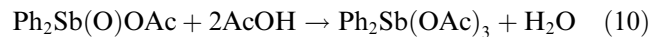
Scheme 2.

Fig. 1. ^{1}H NMR spectra of the reaction mixture: *p*-Tol$_3$Sb(OAc)$_2$ + **1** (1:2), PdCl$_2$ (4 mol%), D$_3$CCOOD, argon, 50 °C: (a) at the start of the reaction; (b) after 3 h; (c) after 24 h.

The compound **20** in AcOH forms **18** (Eq. 10), which acts with Pd(0) (Eq. 9). Thus, diphenylantimony(V) tricarboxylates are preliminarily formed in the both routes of transfer of the third phenyl group at the third stage of the catalytic cycle. To prove the Eq. 9 we used diphenylstibine acid Ph$_2$Sb(O)OH as a phenylating agent. In this reaction the yield of **5** was 92% (50 °C, 12 h, AcOH) (Scheme 5). This fact confirms the mechanism via diphenylantimony tricarboxylates. This is the final stage and the yield of **5** can reach a value of 300%.

$$Ph_2Sb(O)OAc + 2AcOH \rightarrow Ph_2Sb(OAc)_3 + H_2O \quad (10)$$

The total catalytic cycle is shown on Scheme 6. The active Pd(0) species interact with the initial tetraphenylantimony compound to give phenylpalladium intermediate, which phenylates **1**. Triphenylstibine is oxidized by a peroxide to give antimony(V), which reacts with Pd(0) giving PhPdX. As a result, the second molecule of **5** and antimony(III) derivative are formed. Oxygen (or peroxide in excess) oxidizes the latter into antimony(V), which transfers the third phenyl group to methyl acry-
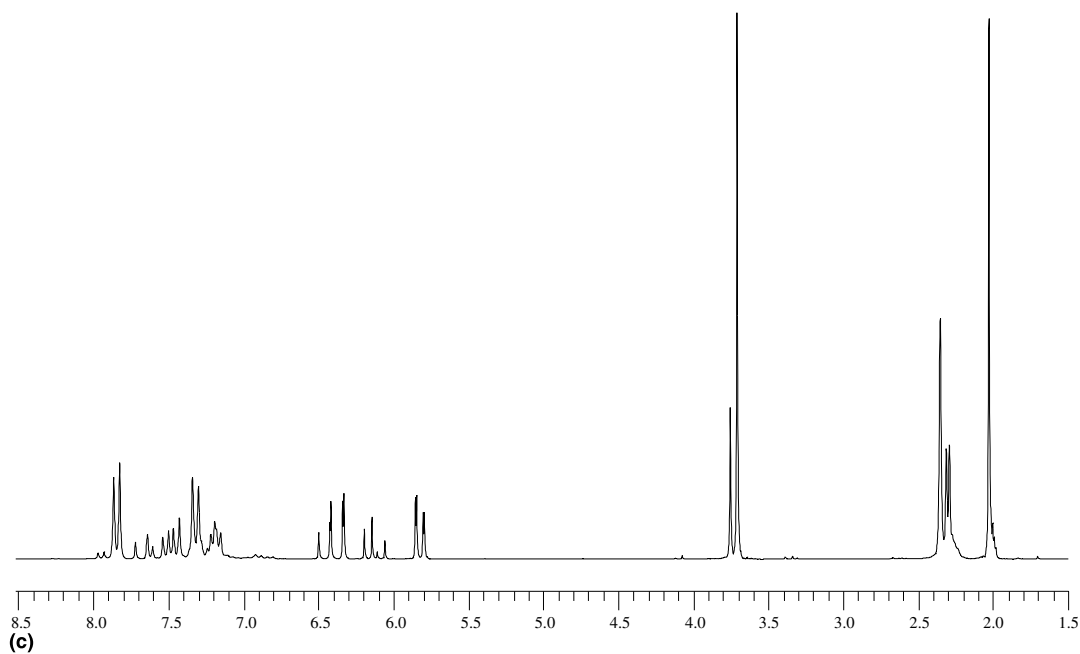
Fig. 1. (*continued*)
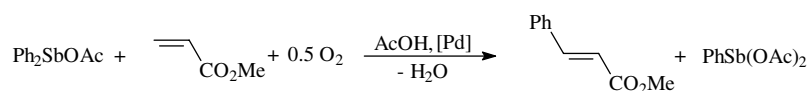
Scheme 3.
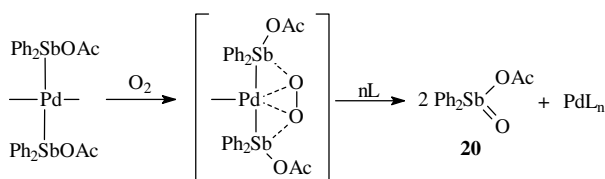
Scheme 4.
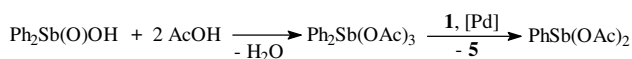
Scheme 5.

late. $PhSbX_2$ ($X = OAc$, O_2CPh), the final product of transformation, is not involved in the C-phenylation reaction in these conditions. The total yield of **5** is 300% in respect to the initial tetraphenylantimony derivative.

3. Conclusion

Thus, the addition of peroxide increases the activity of tetraphenylantimony derivatives in the C-phenylation reaction. The presence of the peroxide provides the involvement of three phenyl groups from the initial or-

ganoantimony compound via consecutive redox stages. We found that $(PhCO_2)_2$ is the optimum peroxide for this system. The reactions can be performed both in AcOH and in CH_3CN. It was established that the initial Ph_4SbX derivative transforms in this cascade reaction in the following range: $Ph_4SbX \rightarrow Ph_3Sb \rightarrow Ph_3SbX_2 \rightarrow Ph_2SbX \rightarrow Ph_2SbX_3 \rightarrow PhSbX_2$. The final $PhSbX_2$ derivative is inactive in the C-phenylation under these conditions. The key role of peroxides is oxidation of inactive Ph_3Sb or Ph_2SbX compounds into an active pentavalent state.

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 D_3CCOOD. Column chromatographies were performed with silica gel 60 Merck.

The tetraphenylantimony compounds Ph_4SbOH, Ph_4SbO_2CEt and $Ph_2Sb(O)OH$ were prepared as
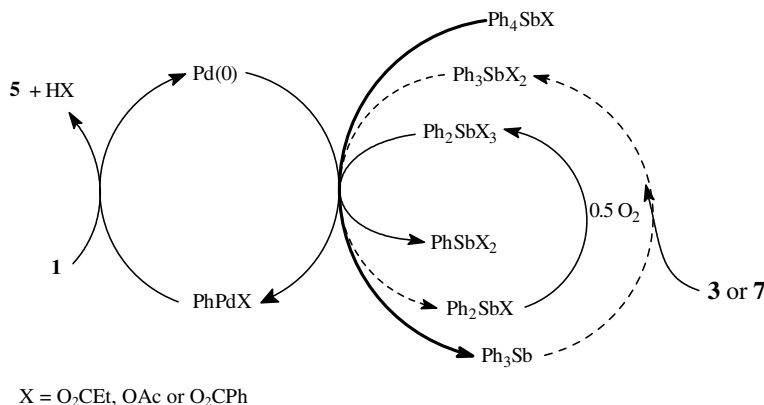
Scheme 6.

described [6]. The triarylantimony compounds *p*-Tol$_3$Sb(OAc)$_2$ and Ph$_3$Sb(OAc)$_2$ were prepared as described [3]. *t*-BuOOH was prepared by the method of Milas and Surgenor [14]. Commercial (PhCO$_2$)$_2$ was purified by recrystallization from methanol. Commercial methyl acrylate was washed with an alkali solution until the yellow color disappeared, then dried with Na$_2$SO$_4$ and distilled. All solvents were distilled prior to use. PdCl$_2$ was commercially available. Li$_2$PdCl$_4$ [15] was prepared by the reported methods.

4.2. Typical procedure for the C-phenylation reaction

Ph$_4$SbOH (0.224 g, 0.5 mmol) was dissolved in AcOH (1 ml) in a 50 ml tube. A mixture of *t*-BuOOH (0.075 ml, 0.75 mmol), Li$_2$PdCl$_4$ (5.2 mg, 0.02 mmol) and methyl acrylate (0.18 ml, 2 mmol) in acetic acid (3 ml) was added to Ph$_4$SbOH solution. The tube was sealed and the reaction mixture was kept at 50 °C for 24 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 (0.208 g) was found.

4.3. Procedure for measurement of oxygen consumption in C-phenylation of methyl acrylate with Ph$_3$Sb(OAc)$_2$

A mixture of Ph$_3$Sb(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) under air was placed in the 10 ml tube being the reflux condenser. The tube was connected with a gas burette filled by the brine and was placed into the thermostat at 50 °C. After equating the pressure in the tube and the burette with atmosphere pressure, the tube was locked on the gas burette by the three-way cock. The reaction mixture was kept at 50 °C. After 12 h, the 0.21 mmol of oxygen was consumed. The yield of methyl cinnamate was 0.88 mmol. The same

reaction under argon yielded 0.44 mmol of methyl innamate.

4.4. Procedure for ^{1}H NMR spectroscopic study

PdCl$_2$ (0.9 mg, 0.005 mmol) and *p*-Tol$_3$Sb(OAc)$_2$ (64.1 mg, 0.125 mmol) were placed into NMR tube under argon. Air-free D$_3$CCOOD (1 ml) and methyl acrylate (0.034 ml, 0.375 mmol) were placed into the tube under argon. The tube was sealed and ^{1}H NMR analysis was carried out. The reaction mixture was heated at 50 °C. The ^{1}H NMR spectra were recorded in 3, 12, and 24 h.

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