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Competing Reactions of Hydrophenylation and Phenylation in Tetraphenylantimony Chloride Methyl Acrylate Palladium Chloride System

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Abstract—A new catalytic reaction of the competing phenylation and hydrophenylation in air of methyl acrylate with tetraphenylantimony chloride in the presence of $PdCl_2$ (0.04 mol per 1 mol of organometallic compound) in acetonitrile at 50°C for 6 h was studied. The yields of methyl cynnamate and methyl hydrocynnamate were 0.73 and 0.27 mol mol^{-1} respectively. The products ratio obtained depends slightly on the process duration, the Ph_4SbCl and methyl acrylate ratio, and the structure of Pd salt [$PdCl_2$, $Pd(OAc)_2$, Li_2PdCl_4], but significantly on the nature of a solvent (MeCN > DMF > THF). The use of Ph_4SbCl instead of Ph_4SbBr leads to decrease in the yield of methyl hydrocynnamate to 0.04 mol mol^{-1}. In the reactions of Ph_4SbX (X = F, I, OAc, O_2CEt) the product is not formed at all.

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Triphenylantimony dicarboxylates $Ph_3Sb(O_2CR)_2$ are known to act at 50°C in the presence of the catalytic amounts of Pd(0,II) as a soft C-phenylating agents for methyl acrylate **I**. They play the role simultaneously as a source of phenyl group and as an oxidant of Pd(0) to Pd(II). The methyl cynnamate **II** yield is 1–2 mol mol^{-1} on the starting organometallic compound [1]. The phenylating systems on the basis of Ph_3Sb, Ph_3SbX_2, and Ph_4SbX in the presence of organic peroxides occured to be more effective. The ester **II** yield reaches two, and in the case of tetraphenyl derivatives three mol mol^{-1} on the starting organometallic compound [2–4].

We have recently found that Ph_4SbX as the phenylating agent in the reaction with the ester **I** in the absence of peroxides leads besides the product of phenylation **II** to the product of hydrophenylation, methyl hydrocynnamate **III**. Formation of the latter was confirmed by chromatomass spectrometry [5].

The process of hydrophenylation presents special interest for organic synthesis because the simultaneous hydrogenation and phenylation of unsaturated group of an organic substrate takes place.

Examples of hydrophenylation of methyl acrylate and some other alkenes with benzene at the catalysis with iridium acetylacetonate have been reported. In that case the reaction proceeds at high temperature with low selectivity and a mixture of the esters of 2-phenylpropanoic and 3-phenylpropanoic acids is formed [6]. Participation of benzene in the reaction of hydrophenylation of norbornene and some other non-activated olefines (2-butene, propylene, cyclopentene, cyclohexene) has also been studied [7]. This reaction proceeds in the presence of platinum complexes at the activation by Ag(I) salt in *o*-dichlorobenzene–benzene mixture at 80–115°C. The product yield reaches 90%. Hydrophenylation was also carried out by means of PhX (X = Br, I, OTf) in Et_3N/HCOOH system on the palladium catalysts in the presence of phosphine ligands at room temperature. The products yields reach 50–80%.

Palladium-catalyzed hydophenylation of α,β-unsaturated ketones and aldehydes with the trivalent antimony phenyl derivatives has also been reported [9]. It was shown that the process takes place in the presence of stoichiometric amounts of silver acetate. But with such substrates as methyl acrylate, methyl cynnamate, styrene, acrylonitrile and allyl acetate the hydrophenylation product was not found to form. Reaction does not proceed with another palladium compounds instead of $Pd(OAc)_2$. That is why the authors proposed that the role of silver acetate is to oxidizing of Pd(0) obtained in the course of the process to $Pd(OAc)_2$.

The aim of the present work was to study reaction of hydrophenylation of the ester **I** with tetraphenylantimony derivatives under mild conditions, to es-

Yields of the products of phenylation and hydrophenylation in Ph_4SbX–**I**–$PdCl_2$ system (1 : 3 : 0.04 molar ratio)[a]

Exp. no.	X	Yield, mol per 1 mol Ph_4SbX	
		II	**III**
1	Cl	0.73	0.27
2	Br	0.57	0.04
3	F	0.29	Traces
4	OAc	0.21	0
5	O_2CEt	0.28	0
6	I	0	0

[a] Reactions were carried out in MeCN at 50°C for 6 h in the presence of air.

tablish effect of the nature of organometallic compound, palladium catalyst, solvent, and reagent ratio on the yield of the target product.

We studied reaction of a series of tetraphenylantimony derivatives Ph_4SbX with the ester **I** and $PdCl_2$ (1 : 3 : 0.04 ratio) in acetonitrile at 50°C. The reaction was carried out for 6 h. From the table is seen that tetraphenylantimony chloride exhibits higher activity both in the reaction of hydrophenylation and in phenylation of the ester **I**. The yields of the products **III** and **II** were 0.27 and 0.73 mol mol^{-1} on the starting organometallic compound (see the table, exp. 1). In the case of Ph_4SbBr the yield of the ester **III** sharply falls to 0.04 mol mol^{-1}, and the main product was the ester **II** (0.57 mol mol^{-1}, exp. 2). Tetraphenylantimony fluoride, acetate, and propionate gave the ester **II** in low yield only (0.21–0.29 mol mol^{-1}, exp. 3–5). Tetraphenylantimony iodide was not reactive at all (exp. 6).

Thus, Ph_4SbCl_3 provides the largest yields of the products of hydrophenylation and phenylation according to the following scheme:

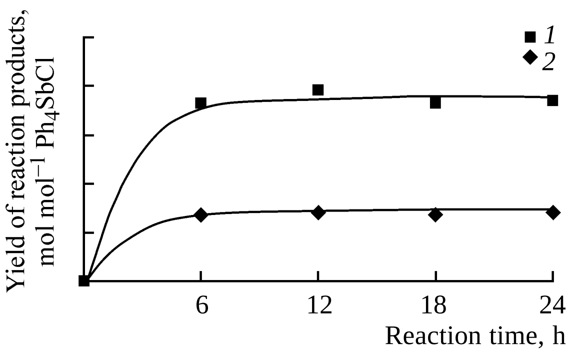
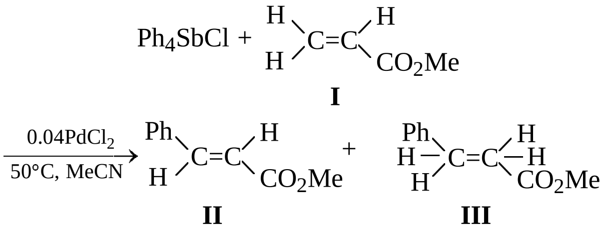


Fig. 1. Yields of the products (*1*) **II** and (*2*) **III** in the reaction of ester **I** with Ph_4SbCl (3 : 1) in the presence of 4 mol% of $PdCl_2$ (MeCN, 50°C).



More thorough investigation of the reaction of C-phenylation of methyl acrylate with the participation of Ph_4SbCl showed that longer reaction duration does not cause alteration in the yield and in the products ratio **II** : **III** (see Fig.1). Total yield of the phenylated products was 1 mol mol^{-1} on Ph_4SbCl what tells about the participation of one phenyl group only in the reaction. Besides, from the Fig. 1 is seen that reaction completes in 6 h. This fact indicates high activity of this reagent.

For the detailed consideration of the initial stage of the reaction we investigated the product yield in time at the smaller concentration of the substrate. The results obtained showed that the process includes an induction period. For 3 h the esters **III** and **II** respectively were formed in the yield 0.02 and 0.05 mol mol^{-1} only. The total rate of the process decreased, but the ratio of the products varied only slightly in the course of the reaction. Thus, after 6, 12, 18, and 24 h the yield of the ester **III** was 0.14, 0.24, 0.27, and 0.29 mol mol^{-1} and of the ester **II** 0.34, 0.64, 0.66, and 0.70 mol mol^{-1}, respectively.

Dependence the products ratio at hydrophenylation and phenylation on the ratio of the starting reagents was also studied. We have previously shown that in the case of $Ph_3Sb(OAc)_2$ decrease in the concentration of the ester **I** leads to the sharp decrease in the yield of the product of phenylation and to formation of the product of homocombination [10]. In the process under investigation we found that varying the ratio of organometallic compound and the ester **I** from 1 : 5 to 1 : 1 leads to the simultaneous decrease in the yield the product **III** from 0.29 to 0.10 mol mol^{-1} and of the compound **II** from 0.71 to 0.24 mol mol^{-1}, but their ratio remains close to 0.4. In all the cases no diphenyl formation was found. The results obtained are listed in the Fig. 2.

We found that the yields of the products **III** and **II** slightly depend on the nature of palladium salt, $PdCl_2$, $LiPdCl_4$ or $Pd(OAc)_2$. For example, in the reaction of Ph_4SbCl with the ester **I** and the palladium salt (1 : 2 : 0.04) in acetonitrile at 50°C for 6 h the yields of the esters **II** and **III** were 0.34 and 0.14 mol mol^{-1}

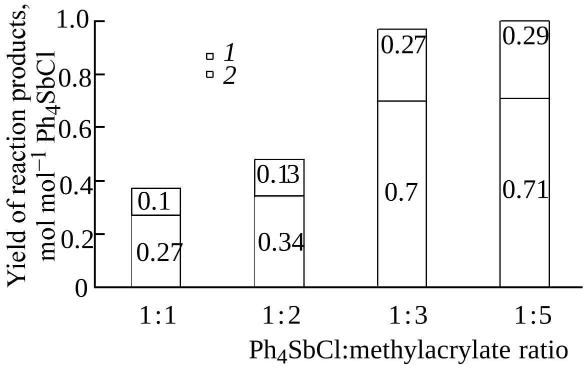


Fig. 2. Yields of the products (*1*) **II** and (*2*) **III** in the reaction of the ester **I** with Ph_4SbCl (4 mol% of $PdCl_2$, MeCN, 50°C) depending on the reagent ratio.

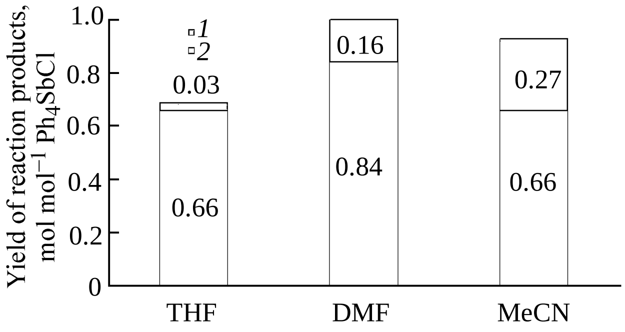


Fig. 3. Yields of compounds (*1*) **II** and (*2*) **III** in the reaction of the ester **I** with Ph_4SbCl (3 : 1) in the presence of 4 mol% of $PdCl_2$ at 50°C in different solvents.

for $PdCl_2$, 0.37 and 0.14 mol mol^{-1} for Li_2PdCl_4, and 0.31 and 0.11 mol mol^{-1} for $Pd(OAc)_2$.

Nature of solvent also plays significant role in the process under investigation. Besides acetonitrile, DMF (N-donor) and THF (O-donor) were chosen. From the Fig.3 is seen that the yield of the ester **III** is the largest in acetonitrile (0.27 mol mol^{-1}), in DMF it is close to the same value, but sharply decreases to 0.03 mol mol^{-1} at the transfer to THF (O-donor). Contrary to the product **III** the yields of the ester **II** in all the cases remain high (0.66–0.84 mol mol^{-1}) and slightly differ with solvent.

It is important to note that the dependence of the yields of the products on the reaction conditions is more expressed when tetraphenylantimony rather than chloride bromide is used. The product **III** is formed in small amount in the reaction with the ester **I** in acetonitrile in the presence of $PdCl_2$ (1–4 mol%). The yield of the product **II** strongly depends on the catalyst [0.57 mol mol^{-1} for $PdCl_2$, 0.33 mol mol^{-1} for $Pd(OAc)_2$, zero for $Pd(dppf)Cl_2$ and $Pd(PPh_3)Cl_2$] as well as on the nature of solvent (0.57 mol mol^{-1} for MeCN, 0.25 mol mol^{-1} for DMF, 0.07 mol mol^{-1} for MeOH, 0.06 mol mol^{-1} for AcOH and THF). In the last case 0.09 mol mol^{-1} of diphenyl was also detected. The above results allow to conclude that the process of hydrophenylation of the starting ester **I** as well as the process of its phenylation is catalytic one. The yield of the product **III** reaches 7 mol mol^{-1} (see the table, exp. no 1), and of the product **II** 18 mol mol^{-1}. Both processes are connected with one another because in almost all the experiments the ester **II** is the single product or is obtained together with the ester **II**. In connection with that we have proposed that the reaction of hydrophenylation of the starting ester **II** is secondary one in relation to the reaction of phenylation. On the first stage the cross-combination of Ph_4SbCl with the substrate **I** takes place with the catalytic participation of palladium salt. Reaction proceeds according to the equation (1). Evolving hydrogen chloride adds to the unreacted ester **I** to form methyl 3-chloropropanoate. The latter reacts with Ph_4SbCl with the participation of $PdCl_2$ to give product **III** and Ph_3SbCl_2.

$$Ph_4SbCl + CH_2{=}CH{-}COOMe \xrightarrow{[Pd]} PhCH{=}CH{-}COOMe + HCl + Ph_3Sb. \qquad (1)$$

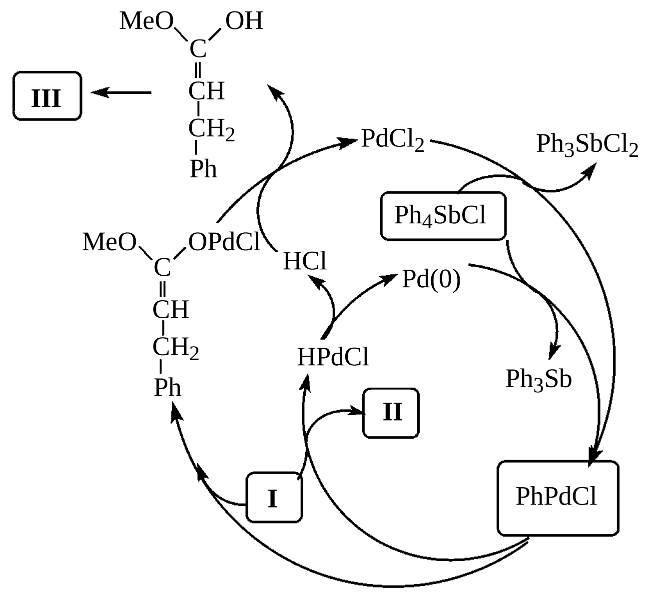
Presence of triphenylantimony in the reaction products was confirmed by TLC.

For checking above scheme we prepared an authentic sample of methyl 3-chloropropanoate by hydrochlorination of the ester **I**. But heating of Ph_4SbCl with methyl 3-chloropropanoate under the common conditions ($Ph_4SbCl : ClCH_2CH_2COOMe : PdCl_2$ = 1 : 3 : 0.04) gave neither the product **II** nor the compound **III**. Alternative scheme of formation of the product **III** in the secondary reaction of triphenylantimony with the ester **I** and HCl evolving on the stage of primary phenylation according to the following equation may be also offered.

$$Ph_3Sb + HCl + CH_2{=}CHCO_2Me \xrightarrow{[Pd]} PhCH_2CH_2CO_2Me + Ph_2SbCl. \qquad (2)$$

The process was carried out under common conditions at the Ph_3Sb : **I** : HCl ratio 1 : 3 : 1. Hydrogen chloride was added to the reaction mixture as a saturated solution in acetonitrile. The expected ester **III** was detected in the reaction mixture in the yield 0.005 mol mol^{-1} only. Hence, though the possibility of formation of ester **III** using Ph_3Sb was established, the above result shows that this process can not be the main source of compound **III** due to low yield.

We suggest that the processes of phenylation and hydrophenylation of the ester **I** proceed in parallel. The source of phenyl groups in both processes is the tetraphenyl derivative of antimony(V). In this case the active form of Pd(0) is oxidized with Ph_4SbX to the phenylpalladium intermediate PhPdX which simultaneously takes part in two catalytic cycles ac0 cording to the scheme (2). It may add to the ester **I** according to the scheme of 1,2- as well as 1,4-addition. In the first case the catalytic cycle proceeds with the formation of the ester **II** and evolution of Ph_3Sb and HCl. Further transformation of Pd(0) to Pd(II) proceeds via redox transmetallation with Ph_4SbCl which is reduced to triphenylantimony. The inner cycle of this scheme has been thoroughly considered by us earlier [4, 5].



Simultaneous 1,4-addition of PhPdCl to the ester **I** forms palladium alkoxide. Acidolysis of the latter under the action of HCl leads to formation of enol which immediately rearranges to the stable product **III**. This reaction regenerates $PdCl_2$ which then enters the reaction of transmetallation with Ph_4SbCl to form PhPdCl and Ph_3SbCl_2.

We established important specific features of participation of HCl in the reaction of hydrophenylation of the ester **I**. On the one hand, addition of Et_3N (1 mol mol^{-1} of organometallic compound) for neutralization of HCl leads to formation of ester **II** only in the yield 0.27 mol mol^{-1}. No formation of the ester **III** under these conditions occurs. On the other hand increase in the concentration of HCl at adding 1 equiv. of HCl causes strong decrease in the yields of the products **III**and **II** to 0.04 and 0.06 mol mol^{-1} respectively. Hence, shortage of HCl brakes the cycle of hydrophenylation due to lack of the stage of acydolysis of palladium alkoxide.

$$\begin{array}{l} PhCH_2CH{=}C(OMe)OPdCl + HCl \\ \longrightarrow [PhCH_2CH{=}C(OMe)OH] + PdCl_2. \end{array}$$

Excess of HCl suppresses reversible ionization of the starting Ph_4SbCl at Sb–Cl bond what leads to desseleration of transmetallation with palladium compounds [10], and hence complifies the formation of PhPdCl occurring in the reactions of phenylation and hydrophenylation. These facts agree with the effect of the increase in the rate of hydrophenylation at the adding of water. In the Ph_4SbCl–**I**–$PdCl_2$–H_2O system (1:3:0:04:1) under the typical conditions (MeCN, 50°C, 6 h) the yield of the ester **III** increases to 0.4 mol mol^{-1} while the yield of the ester **II** remains as high as 0.77 mol mol^{-1}. Obviously, water can decompose palladium alkoxide similarly to HCl but it does not suppress the Ph_4SbCl ionization.

EXPERIMENTAL

GLC analysid of volatile products was carried out on a Tsvet-560 chromatograph with the flame ionization detector and argon as a carrier gas. For the evaluation of methyl hydrocynnamate, methyl cynnamate, and diphenyl 2400 × 3 mm column was used filled with 15% of Apieson L on Chromaton N-AW-DMCS at 230°C.

Ph_4SbCl, Ph_4SbBr, Ph_4SbF, Ph_4SbI, Ph_4SbOAc, and Ph_4ScO_2CEt were prepared according to the procedures [11]. Commercial $PdCl_2$ was used without further purification. $Pd(OAc)_2$ was prepared by oxidation of palladium black with nitric acid in AcOH for 30 h, yield 80% after crystallization from AcOH [12]. Li_2PdCl_4 was prepared by dissolution of $PdCl_2$ and LiCl (1:2) in boiling water, evaporation of water, and drying of the residue by spraying in a vacuum at 100°C [13]. The ester **I** was washed with aqueous alkali solution until the disappearance of yellow coloration, dried over sodium sufate, and distilled at decreased pressure. Methyl 3-chloropropanoate was prepared according to [14] from the ester **I** and HCl in 60% yield, bp 155–157°C; n_D^{20} 1.4263. Organic solvents were purified according to the published procedures [15, 16].

Reaction of Ph_4SbCl with the ester (I) in the presence of 4 mol % of $PfCl_2$. To a mixture of 0.233 g of Ph_4SbCl and 3.6 mg of $PdCl_2$ the freshly prepared solution of 0.135 ml of compound **I** in 4 ml of MeCN was added. The ampule was sealed and thermostated at 50°C for 6 h. The solvent and the unreacted ester **I** were distilled off at reduced pressure. The solid residue was purified from inorganic products by filtration through a short column filled with silica gel, elution with 4 : 1 hexane–ether. Obtained filtrate was analyzed by GLC. Compound **II**, 59 mg, and the ester **III**, 22 mg, were found.

Reaction of Ph_4SbCl with the ester **I** in the presence of another palladium compounds, in another solvents, and also the reactions of organoantimony compounds with another acidic residues were carried out analogously.

Reaction of Ph_3Sb with the ester (I) and 4 mol % of $PdCl_2$ in the presence of the equimolar amount of HCl. To a solution of 0.177 g of Ph_3Sb in 2 ml of MeCN 0.25 ml of 2 M HCl solution in acetonitrile was added. Resulting mixture was treated with a solution of 3.6 mg of $PdCl_2$ and 0.135 ml of compound **I** in 1.75 ml of MeCN. The ampule was sealed and heated at 50°C for 6 h. After that the ampule was opened, the solvent was removed, and the solid residue was treated similarly to the above-described procedure. Formation of 0.4 mg of the ester **III** was established.

Reaction of Ph_4SbCl with the ester (I) in the presence of 4 mol % of $PdCl_2$ with the addition of aqueous HCl solution. To a mixture of 0.233 g of Ph_4SbCl and 3.6 mg of $PdCl_2$ the freshly prepared solution of 0.135 of the ester **I** in 4 ml of MeCN was added. Resulting mixture was treated with 0.04 ml of 11.8 M HCl. The ampule was sealed and thermostated at 50°C for 6 h. Analysis of the reaction products was carried out according to the abovementioned procedure. Compound **II**, 4.5 mg, and 3.5 mg of the ester **III** were found.

Reaction of Ph_4SbCl in the presence of 4 mol % of $PdCl_2$ with the addition of water. To a mixture of 0.233 g of Ph_4SbCl and 3.6 mg of $PdCl_2$ the freshly prepared solution of 0.135 ml of the ester **I** in 4 ml of MeCN was added. Resulting mixture was treated with 9 μl of water. The ampule was sealed and thermostated for 6 h at 50°C. Analysis of the reaction products was carried out according to above-presented procedure. Compound **II**, 63 mg, and 32 mg of the ester **III** were found.

Reaction of Ph_4SbCl with the ester (I) in the presence of 4 mol % of $PdCl_2$ and the addition of triethylamine. To a mixture of 0.233 g of Ph_3SbCl and 3.6 mg of $PdCl_2$ the freshly prepared solution of 0.135 ml of the ester **I** in 4 ml of MeCN was added. Resulting mixture was treated with 69 μl of triethylamine, and the ampule was sealed and thermostated at 50°C for 6 h. Analysis of the reaction products was carried out according to the above-presented procedure. Compound **II**, 22 mg, was found.

Reaction of Ph_4SbCl with methyl 3-chloropropanoate. To a mixture of 0.233 g of Ph_4SbCl and 3.6 mg of $PdCl_2$ the freshly prepared solution of 0.052 ml of $ClCH_2CH_2COOMe$ in 4 ml of NeCN was added. Reaction mixture was degased, the ampule was sealed, and kept for 6 h at 50°C. After that 55 mg of diphenyl was found.

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