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Palladium-Catalyzed Reaction of Some Triphenylbismuth(V) Sulfonates and Phenolates with Methyl Acrylate

A. V. Gushchin[a], Yu. B. Malysheva[a], D. Yu. Kosov[a], and V. V. Sharutin[b]

[a] *Lobachevsky Nizhni Novgorod State University,*
pr. Gagarina 23, Nizhni Novgorod, 603950 Russia
e-mail: gushchin@mail.nnov.ru
[b] *Blagoveshchensk State Pedagogical University, Blagoveshchensk, Russia*

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Abstract—Triphenylbismuth(V) derivatives Ph_3BiX_2 [X = $OC_6H_2(NO_2)_3$-2,4,6, $OC_6H_2(NO_2$-4)Br_2-2,6, OTs, $OSO_2C_6H_4OH$-4] react with methyl acrylate and $PdCl_2$ (1 : 3 : 0.04 molar ratio) in acetonitrile at 20°C to form the cross-coupling products, methyl cinnamate (0.26–0.51 mol mol^{-1} starting bismuth compound) and methyl hydrocinnamate (0–0.17 mol mol^{-1}); diphenyl, the homocoupling product (0–0.13 mol mol^{-1}); and benzene (0.02–0.15 mol mol^{-1}). The reaction of $Ph_3Bi(OSO_2C_6H_4OH\text{-}4)_2$ is characterized by the selective formation of methyl cinnamate, but the reagent activity is low. $Ph_3Bi(OTs)_2$ exhibits the highest activity among the derivatives studied, but the reaction selectivity is low. The mechanisms of the palladium-catalyzed formation of homo- and cross-coupling products are proposed.

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Organometallic bismuth derivatives can be used as mild reagents for C-phenylation of unsaturated compounds. Ph_3Bi was first used for C-phenylation of styrene in the presence of stoichiometric amounts of palladium [1]. The same system was later used for the phenylation of 1-octene, ethyl acrylate [2], and methyl acrylate [3]. C-Phenylation in the presence of catalytic amounts of palladium was carried out with bismuthonium salts [4] and diphenylbismuth chloride [5]. In all the coupling reactions, diphenyl formed in significant amounts as by-product. The homocoupling of organobismuth(III,V) compounds to diaryls in the presence of palladium salts was specially studied in [6, 7].

Triphenylbismuth dicarboxylates were studied as mild reagents for C-phenylation of methyl acrylate **I** at 20–50°C. The reaction gave methyl cinnamate, diphenyl, and benzene. The yields of these products and their ratio significantly depend on the structure of the acid residue [8–10].

In this study we examined the phenylating power of a series of triphenylbismuth phenolates and sulfonates in a model reaction with ester **I**. $Ph_3Bi[OC_6H_2\cdot(NO_2)_3\text{-}2,4,6]_2$, $Ph_3Bi[OC_6H_2(NO_2\text{-}4)Br_2\text{-}2,6]_2$, $Ph_3Bi(OTs)_2$, and $Ph_3Bi(OSO_2C_6H_4OH\text{-}4)_2$ were used as starting organometallic compounds. The typical reaction conditions (Ph_3BiX_2 : **I** : $PdCl_2$ ratio 1 : 3 : 0.04, acetonitrile, 20°C, 24 h) were similar to those of the reactions of triphenylbismuth(V) dicarboxylates, thoroughly studied previously [8, 10].

In the reaction of triphenylbismuth picrate with **I** in the presence of $PdCl_2$ (see table), the main cross-coupling product was methyl cinnamate (yield 0.40 mol mol^{-1} starting Ph_3BiX_2). Also we isolated the second cross-coupling product, methyl hydrocinnamate **III** (yield 0.02 mol mol^{-1}), the homocoupling product, diphenyl **IV** (yield 0.13 mol mol^{-1}), and benzene **V** (yield 0.09 mol mol^{-1}). The total consumption of phenyl groups (this value characterizes the extent of the reaction) was 0.77 mol mol^{-1} (see table, run no. 1).

$$\mathrm{Ph_3BiX_2} + \underset{\textbf{I}}{\mathrm{CH_2{=}CHCO_2Me}}$$

$$\xrightarrow[\mathrm{CH_3CN}]{0.04\ \mathrm{mol\ PdCl_2},\ 20^\circ\mathrm{C},\ 24\ \mathrm{h}} \underset{\textbf{II}}{\mathrm{PhCH{=}CHCO_2Me}}$$

$$+ \underset{\textbf{III}}{\mathrm{PhCH_2CH_2CO_2Me}} + \underset{\textbf{IV}}{\mathrm{Ph_2}} + \underset{\textbf{V}}{\mathrm{PhH}},$$

X = $OC_6H_2(NO_2)_3$-2,4,6, $OC_6H_2(NO_2$-4)Br_2-2,6, OTs, $OSO_2C_6H_4OH$-4.

Replacement of two nitro groups in thiphenylbismuth picrate by less electron-withdrawing bromine atoms led to a certain decrease in the total activity of the organometallic compound (total Ph group con-

Effect of the organobismuth compound structure on the yields of the products of methyl acrylate phenylation with the Ph_3BiX_2–$PdCl_2$ (1 : 0.04) system[a]

Exp. no.	Organobismuth compound	Yield, mol mol^{-1} Ph_3BiX_2				
		II	**III**	**IV**	**V**	ΣPh[b]
1	$Ph_3Bi[OC_6H_2(NO_2)_3\text{-}2,4,6]_2$	0.40	0.02	0.13	0.09	0.77
2	$Ph_3Bi[OC_6H_2(NO_2\text{-}4)Br_2\text{-}2,6]_2$	0.36	0.02	0.07	0.02	0.52
3	$Ph_3Bi(OSO_2C_6H_4Me\text{-}4)_2$	0.51	0.17	0.12	0.15	1.07
4	$Ph_3Bi(OSO_2C_6H_4OH\text{-}4)_2$	0.26	0	0	0.05	0.31

[a] The reactions were carried out in CH_3CN at 20°C for 24 h in air. [b] (ΣPh) Total consumption of phenyl groups.

sumption was 0.52 mol mol^{-1}), mainly at the expense of decreased yield of **IV** and **V** (see table, run no. 2).

Triphenylbismuth tosylate showed the highest activity. The phenyl group consumption was 1.07 mol mol^{-1}. As compared to phenolates, the yields of target product **II** (0.51 mol mol^{-1}), compound **III** (0.17 mol mol^{-1}), and benzene **V** (0.15 mol mol^{-1}) increased (see table, run no 3). C-Phenylation of **I** remained the major reaction pathway.

Replacement of the methyl group in the phenyl residue by a stronger electron-donor substituent, hydroxy group, leads to a twofold decrease in the yield of **II** (to 0.26 mol mol^{-1}) and to a strong decrease in the yield of **V** (to 0.05 mol mol^{-1}). Diphenyl and methyl hydrocinnamate were not detected at all (see table, run no 4). Thus, the latter system appeared to be most selective with respect to methyl acrylate phenylation, but the total consumption of phenyl groups was as low as 0.31 mol mol^{-1}.

Thus, ester **II** is the main C-phenylation product of acrylate with triphenylbismuth(V). Its yield reaches 0.51 mol mol^{-1}.

We believe that product **II** is formed by a chain of transformations involving Pd(0) $\rightleftarrows$ Pd(II) cyclic transformations, as it was established for Bi(V) dicarboxylates [9]. In the first step of the process the starting organometallic compound undergoes transmetallation with the formation of active phenylpalladium intermediate PhPdX [Eq. (1)]. The latter is known [11] to act as a C-phenylation agent of ester **I** with the exclusive formation of the energetically more favorable *trans* isomer of **II** [Eq. (2)]. In the process, palladium is reduced to a Pd(0) complex stabilized in solution with such electron-donating ligands as acetonitrile and organometallic and unsaturated compounds. Then, in the redox transmetallation with Ph_3BiX_2, the Pd(0) complex is converted back to PhPdX [Eq. (3)]. Partial symmetrization of Ph_2BiX gives Ph_3Bi which was found among the reaction products. The overall C-phenylation process of **I** is described by Eq. (4).

$$Ph_3BiX_2 + PdX_2 \longrightarrow Ph_2BiX_3 + PhPdX, \quad (1)$$

$$PhPdX + CH_2{=}CHCO_2Me \longrightarrow PhCH{=}CHCO_2Me + HX + Pd(0), \quad (2)$$

$$Ph_3BiX_2 + Pd(0) \longrightarrow PhPdX + Ph_2BiX, \quad (3)$$

$$Ph_3BiX_2 + CH_2{=}CHCO_2Me \xrightarrow{PdX_2} PhCH{=}CHCO_2Me + Ph_2BiX + HX, \quad (4)$$

X = $OC_6H_2(NO_2)_3$-2,4,6, $OC_6H_2(NO_2$-4$)Br_2$-2,6, OTs, $OSO_2C_6H_4OH$-4.

The activity of triphenylbismuth sulfonates and phenolates used in this study for C-phenylation of ester **I** is similar to that of the previously studied triphenylbismuth carboxylates and halides. The yields of **II** with these reagents were 0.20–0.90 mol mol^{-1} [8, 9].

Formation of diaryls in the reactions of organobismuth compounds with palladium salts has been thoroughly studied [6, 7]. It proceeds via formation and reductive decomposition of the diarylpalladium intermediate. We have shown that the transfer of two phenyl groups from bismuth to palladium occurs not simultaneously but in two consecutive steps [9].

We believe that the PhPdX intermediate formed by Eq. (2) reacts with tri- and pentavalent bismuth phenyl derivatives to form unstable Ph_2Pd giving Ph_2 and Pd(0) [Eqs. (5), (6)]. The latter returns into the catalytic cycle by reaction (3).

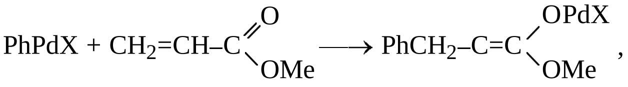
$$PhPdX + Ph\text{–}[Bi(III, V)] \longrightarrow Ph_2Pd + BiX_3 + [Bi(III, V)]\text{–}X, \quad (5)$$

$$Ph_2Pd \longrightarrow Ph_2 + Pd(0). \quad (6)$$

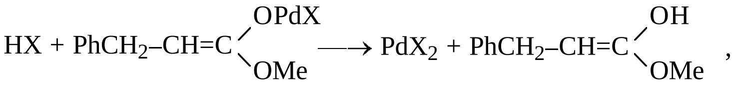
It is important that, in the reactions with triphenylbismuth sulfonate and phenolate, the yields of **II** in all cases were 3–6 times higher than the yields of **IV** (see table). This feature distinguishes the organometallic compounds in question from triphenylbismuth carboxylates and halides, for which the ratio of **II** and **IV** was in the range 0.32–1.4 [8, 9].

The table shows that, along with **II** and **IV**, the hydrophenylation product **III** is formed in most cases. With the most active triphenylbismuth tosylate, its yield reaches 0.17 mol $\mathrm{mol^{-1}}$. The hydrophenylation involves simultaneous hydrogenation and phenylation of the substrate unsaturated group and is therefore of special interest for organic synthesis. Up to now, only hydrophenylation of α,β-unsaturated aldehydes and ketones with a complex system consisting of an organoantimony compound, AgOAc, and $\mathrm{Pd(OAc)_2}$ in 1 : 1 : 0.04 ratio was carried out under mild conditions at 20°C [11]. A simple system based on benzene and Ir(*acac*)$_2$ effects hydrophenylation of any alkenes, but under harsh conditions (180°C) [12]. Recently we examined the $\mathrm{Ph_4SbCl + PdCl_2}$ system (1 : 0.04) in hydrophenylation of ester **I** at 50°C and discussed the possible reaction pathways. The yield of **III** reached 0.32 mol $\mathrm{mol^{-1}}$ organometallic compound [13, 14].

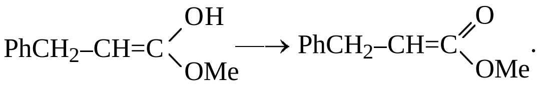
Here we suggest that the scheme of methyl acrylate hydrophenylation with triphenylbismuth tosylate and phenolate is similar to that presented in [13, 14]. The intermediate PhPdX formed by reaction (2) enters the 1,4-addition with **I** [Eq. (7)]. The HX released in the course of phenylation of **I** according to Eq. (2) causes the acidolysis of palladium alkoxide [Eq. (8)]. The released ketene hemiacetal undergoes proton transfer, transforming into stable product **III** [Eq. (9)].



$$\mathrm{PhPdX + CH_2{=}CH{-}C({=}O)OMe \longrightarrow PhCH_2{-}C{=}C(OPdX)OMe}, \qquad (7)$$



$$\mathrm{HX + PhCH_2{-}CH{=}C(OPdX)OMe \longrightarrow PdX_2 + PhCH_2{-}CH{=}C(OH)OMe}, \qquad (8)$$



$$\mathrm{PhCH_2{-}CH{=}C(OH)OMe \longrightarrow PhCH_2{-}CH{=}C({=}O)OMe}. \qquad (9)$$

Thus, methyl hydrocinnamate **III** is formed in parallel to the phenylation product **II**. We never observed formation of **III** without formation of **II** (see table).

Benzene **V** is the secondary product of the reaction of bismuth(II) phenyl derivatives with the acids released in the phenylation reactions [Eq. (2)].

$$\mathrm{HX + Ph_2BiX \longrightarrow 2PhH + BiX_3}.$$

It is known that the rate of this reaction strongly depends on temperature and on the strength of the HX acid [15]. In this connection, it should be noted that, under the conditions studied ($\mathrm{CH_3CN}$, 20°C, 24 h), the yields of benzene were low (0.02–0.15 mol $\mathrm{mol^{-1}}$) and did not differ strongly. This result was explained by the approximately equal strength of acids released in the course of phenylation and the leveling effect of acetonitrile exhibiting weak base properties [16].

Thus, we found that triphenylbismuth phenolates and tosylates, similarly to the previously studied carboxylates, readily enter the $\mathrm{PdCl_2}$-catalyzed reaction with unsaturated substrate **I** at room temperature to form simultaneously products **II**, **IV**, and **V**, but the yield of **IV** is several times lower compared to bismuth carboxylates. Also, the hydrophenylation product **III**, absent in the case of bismuth carboxylates, was detected.

EXPERIMENTAL

Volatile reaction products was analyzed by GLC on a Tsvet-580 chromatograph equipped by flame ionization detector. Argon was used as a carrier gas. For methyl hydrocinnamate, methyl cinnamate, and diphenyl, we used a 2000 × 3-mm column, stationary phase 15% Apiezon L on Chromaton N-AW-DMCS, column temperature 230°C. Benzene was determined on the same column at 130°C.

Reaction of $\mathbf{Ph_3Bi[OC_6H_2(NO_2)_3\text{-}2,4,6]_2}$ with methyl acrylate and $\mathbf{PdCl_2}$ (1 : 3 : 0.04). A mixture of 0.448 g of $\mathrm{Ph_3Bi[OC_6H_2(NO_3)_3\text{-}2,4,6]_2}$, 0.0036 g of $\mathrm{PdCl_2}$, 0.135 ml of methyl acrylate, and 6 ml of acetonitrile was left for 24 h at room temperature in air. Then the mixture was evaporated at reduced pressure. The residue was passed through a silica gel column, elution with 4 : 1 hexane–ethyl acetate. The content of volatile products in the condensate and filtrate was determined by GLC. Phenylation with the other organometallic compounds was carried out similarly.

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