ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 8, pp. 1253–1255. © Pleiades Publishing, Inc., 2006.
Original Russian Text © A.V. Gushchin, Yu.B. Malysheva, D.Yu. Kosov, V.V. Sharutin, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 8, pp. 1305–1308.

Palladium-Catalyzed Coupling of Tetraphenylbismuth(V) Derivatives with Methyl Acrylate

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Received September 2, 2005

Abstract — Tetraphenylbismuth(V) derivatives of the general formula Ph_4BiX [X = $OSO_2C_6H_4Me$-4, $OC_6H_2(NO_2)_3$-2,4,6, $OC_6H_2(NO_2$-4)$(Br_2$-2,6), $OSO_2C_6H_3(OH)(COOH)$] react with methyl acrylate in the presence of palladium dichloride (1 : 3 : 0.04 molar ratio) in acetonitrile at 20°C to form the cross-coupling products, methyl cinnamate (0.17–0.54 mol mol^{-1} starting bismuth compound) and methylhydrocinnamate (0.10–0.73 mol mol^{-1}), diphenyl (0.06–0.80 mol mol^{-1}), and benzene (0.02–0.36 mol mol^{-1}). The highest C-phenylating activity is shown by $Ph_4BiOSO_2C_6H_4Me$-4. The mechanisms with the palladium-catalyzed cross-coupling reactions are suggested.

DOI: 10.1134/S1070363206080147

Organobismuth compounds always attract the researchers' attention in connection with the development of the organic synthesis. They are highly reactive because of the low Bi–C bond energy; under mild conditions, they can enter the coupling reactions with organic substrates to form new C–O, C–N, and C–C bonds. The catalytic coupling reactions of bismuth compounds with unsaturated organic substrates are being actively studied. C-Phenylation of unsaturated compounds with triphenylbismuth in the presence of stoichiometric amounts of $Pd(OAc)_2$ was reported for the first time in [1]. Later a similar system was studied as applied to other substrates [2, 3]. C-phenylation with a trivalent bismuth derivative (Ph_2BiCl) in the presence of catalytic amounts of palladium was described in [4].

Triphenylbismuth carboxylates, halides, phenolates, and sulfonates were studied as reagents for mild C-phenylation of methyl acrylate **I** at 20–50°C. Two cross-coupling products, methyl cinnamate **II** and methyl hydrocinnamate **III**, and also diphenyl **IV** and benzene **V** were detected. The yields and ratio of the products significantly depend on the structure of acid residue [5–7]. With an alkenyltriphenylbismuthonium salt taken as a C-phenylating agent for ethyl acrylate, a series of products were obtained, including the product of coupling of alkenyl and phenyl groups of the starting organobismuth compound, the products of coupling of both groups with ethyl acrylate, and also diphenyl and benzene [8].

In this study we examined the coupling reaction of unsaturated substrate **I** with tetraphenylbismuth compounds Ph_4BiX and compared the product yields and selectivity with the known data for alkenyl (R_4BiX) and phenyl (Ph_3BiX_2) bismuth derivatives.

Tetraphenylbismuth halides and carboxylates cannot be used as starting organobismuth compounds because they are unstable at room temperature. Therefore, we chose more stable tetraphenylbismuth phenolates and sulfonates. The reactions were carried out under typical conditions previously chosen for studying triphenylbismuth carboxylates (Ph_4 : **I** : $PdCl_2$ ratio 1 : 3 : 0.04, acetonitrile, 20°C, 24 h).

$$Ph_4BiX_2 + \underset{\mathbf{I}}{CH_2{=}CHCO_2Me} \xrightarrow[CH_3CN]{0.04\ mol\ PdCl_2,\ 20°C,\ 24\ h} \underset{\mathbf{II}}{PhCH{=}CHCO_2Me} + \underset{\mathbf{III}}{PhCH_2CH_2CO_2Me} + \underset{\mathbf{IV}}{Ph_2} + \underset{\mathbf{V}}{PhH},$$

X = $OSO_2C_6H_4Me$-4, $OC_6H_2(NO_2)_3$-2,4,6, $OC_6H_2(NO_2$-4)Br_2-2,6, $OSO_2C_6H_3(OH)(COOH)$.

C-Phenylation of ester **I** with tetraphenylbismuth tosylate leads to the formation of the coupling products in high yields. The yield of **II** was 0.54 mol mol^{-1} starting organobismuth compound; that of **III**, 0.73 mol mol^{-1}; and that of **IV**, 0.68 mol mol^{-1} (see table, run no. 1). Benzene was

Influence of the structure of organobismuth compounds on the yield of the products of methyl acrylate phenylation with the $Ph_4BiX + PdCl_2$ (3 : 1 : 0.04) system[a]

Exp. no.	Organobismuth compound	Yield, mol mol^{-1} Ph_4BiX				
		II	**III**	**IV**	**V**	ΣPh[b]
1	$Ph_4BiOSO_2C_6H_4Me$-4	0.54	0.73	0.68	0.02	2.65
2	$Ph_4BiOC_6H_2(NO_2)_3$-2,4,6	0.30	0.63	0.49	0.14	2.05
3[c]	$Ph_4BiOC_6H_2(NO_2$-4)$(Br_2$-2,6)	0.22	0.15	0.80	0.36	2.33
4	$Ph_4BiOSO_2C_6H_3(OH)(COOH)$	0.17	0.10	0.06	0.08	0.47
5	$[(Ph_4Bi)_2OSO_2C_6H_3Me_2$-2,5$]_2^+[Ph_2Bi_2I_6]^{2-}$	0.89	0.21	0.29	0.12	1.80

[a] Reactions were carried out in CH_3CN at 20°C for 24 h in air. [b] (ΣPh) Total consumption of phenyl groups. [c] Organobismuth compound : methyl acrylate ratio 1 : 30.

obtained in a low yield (0.02 mol mol^{-1}). The use of tetraphenylbismuth phenolates instead of tosylate decreases the yields of the cross-coupling products **II** and **III** to 0.22–0.30 and 0.15–0.63 mol mol^{-1}, respectively, and the yield of **V** increases to 0.14–0.36 mol mol^{-1} (see table, run nos. 2, 3). Thus, tetraphenylbismuth tosylate and phenolate readily react with ester **I**; the consumption of phenyl groups is 2.05–2.65 mol mol^{-1} (see table, run nos. 1–3). On the contrary, tetraphenylbismuth salicylsulfonate showed very low activity (consumption of phenyl groups was 0.47 mol mol^{-1}) in formation of all the phenylation products. In this case, the yield of methyl cinnamate **II** was 0.17 mol mol^{-1}; that of methyl hydrocinnamate **III**, 0.10 mol mol^{-1}; that of diphenyl **IV**, 0.06 mol mol^{-1}; and that of benzene, 0.08 mol mol^{-1} (see table, run no. 4). In the reaction with $[(Ph_4Bi)_2 \cdot OSO_2C_6H_3Me_3$-2,5$]_2^+[Ph_2Bi_2I_6]^{2-}$, the yield of methyl cinnamate **II** was 0.89 mol mol^{-1}; that of methyl hydrocinnamate **III**, 0.21 mol mol^{-1}; that of diphenyl **IV**, 0.29 mol mol^{-1}; and that of benzene **V**, 0.12 mol mol^{-1} (see table, run no. 5).

We suggested a scheme of this reaction based on the previously studied reaction of tetraphenylantimony chloride with methyl acrylate [9, 11]. In the first step, the organobismuth compound undergoes transmetallation with $PdCl_2$ to form the active phenylpalladium intermediate PhPdCl [Eq. (1)]. The latter C-phenylates ester **I** to give product **II** [Eq. (2)]. In the course of this process, Pd(II) is reduced to Pd(0). Further redox transmetallation with Ph_4BiX converts the Pd(0) complex again to PhPdX [Eq. (3)]. The overall C-phenylation of **I** is described by Eq. (4).

$$Ph_4BiX + PdCl_2 \longrightarrow Ph_3BiXCl + PhPdCl, \quad (1)$$

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

$$Ph_4BiX + Pd(0) \longrightarrow Ph_3Bi + PhPdX, \quad (3)$$

$$Ph_4BiX + CH_2{=}CHCO_2Me \xrightarrow{PdCl_2} PhCH{=}CHCO_2Me + Ph_3Bi + HX. \quad (4)$$

As mentioned previously, the phenylation of methyl acrylate **I** with the formation of **II** was always accompanied by hydrogenation–phenylation of **I** yielding methyl hydrocinnamate **III**. Its yield in all the experiments with tetraphenylbismuth tosylate and picrate was 1.5–2 times higher than the yield of methyl cinnamate (see table, run nos. 1, 2). The highest yield of **III** was 0.73 mol mol^{-1} with tetraphenylbismuth tosylate (see table, run no. 1). In the previously described reactions with methyl acrylate, methyl hydrocinnamate was never isolated as the prevalent product. For example, in the reactions with Ph_3BiX_2, its highest yield was 17% with X = OTs [7], and in the reactions with Ph_4SbX it was 31% with X = Cl [9, 11].

The suggested scheme of the hydrogenation–phenylation of methyl acrylate with Ph_4BiX is based on the previously studied reaction with Ph_4SbCl [10]. The phehylpalladium intermediate formed according to Eq. (1) enters into the 1,4-cycloaddition reaction with ester **I** [Eq. (5)]. The acid released in the course of phenylation of **I** to **II** effects the acidolysis of palladium alkoxide [Eq. (6)], yielding $PdCl_2$ and product **III**.

$$PhPdX + CH_2{=}CHC(=O)OMe \longrightarrow PhCH_2CH{=}C(OPdCl)OMe, \quad (5)$$

$$HCl + PhCH_2CH{=}C(OPdCl)OMe \rightarrow PdCl_2 + PhCH_2CH_2CO_2Me. \quad (6)$$

Diphenyl is formed in the processes studied by the reaction of PhPdX with bismuth derivatives containing phenyl group via intermediate Ph_2Pd [Eq. (7)].

$$PhPdX + Ph–[Bi(III, V)] \longrightarrow Ph_2 + Pd(0) + [Bi(III, V)]–X. \quad (7)$$

Benzene **V** is a secondary product in the reactions under study. It is formed by the reactions of Bi(III) phenyl derivatives with acids released in the phenylation reactions [Eq. (2)]:

$$HX + Ph_3Bi \longrightarrow BiX_3 + 3PhH. \quad (8)$$

The benzene yields are low, and this reaction does not significantly contribute to the catalytic reaction of organobismuth compounds with methyl acrylate.

Thus, we found that Ph_4BiX compounds undergo $PdCl_2$-catalyzed coupling with methyl acrylate at room temperature. The major reaction products are diphenyl **IV** and the cross-coupling products: methyl cinnamate **II** and methyl hydrocinnamate **III**.

A significant feature of the reactions of tetraphenylbismuth picrate and tosylate (Ph_4BiX), as compared to the recently described reactions of triphenylbismuth picrate and tosylate [7], is a significant increase in the yields of diphenyl **IV** and methyl hydrocinnamate **III** at a constant yield of methyl cinnamate **II**. Higher total activity of Ph_2BiX compared to Ph_3BiX_2 is confirmed by a 2.5–3 times higher total consumption of phenyl groups, reaching 2.05–2.65 mol mol^{-1} starting organobismuth compound. We failed to involve all the four phenyl groups in the reaction under so mild conditions. Contrary to the above-described tetraphenylbismuth sulfonates and phenolates, C-phenylation with alkenyltriphenylbismuthonium salt gives no hydrophenylation products [8]. As compared to tetraphenylantimony halides, the bismuth derivatives studied exibit higher activity toward methyl acrylate, which leads to formation of not only products **II** and **III**, but also diphenyl **IV** and benzene **V**. In the case of tetraphenylbismuth picrate and tosylate, the yield of hydrophenylation product **III** exceeds the yield of phenylation product **II**, whereas in the case of antimony derivatives methyl cinnamate **II** is the major product [9–11].

EXPERIMENTAL

GLC analysis of volatile products was carried out on a Tsvet-580 chromatograph equipped with a flame ionization detector (carrier gas Ar). Methyl hydrocinnamate, methyl cinnamate, and diphenyl were determined on 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 80°C.

Reaction of $Ph_4BiOSO_2C_6H_3(OH)(COOH)$ with methyl acrylate and $PdCl_2$ (1 : 3 : 0.04). A mixture of 0.448 g of $Ph_4BiOSO_2C_6H_3(OH)(COOH)$, 0.0036 g of $PdCl_2$, 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, and the residue was passed trough a column packed with silica gel, elution with 4 : 1 hexane–ethyl acetate. The volatile products in the condensate and filtrate were determined by GLC.

Phenylation with other organobismuth compounds was performed similarly.

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