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Dephenylation of triphenylbismuth(v) and antimony(v) derivatives in a methyl acrylate—methanol system in the presence of copper and palladium salts

A. V. Gushchin, M. V. Korotkova, Yu. B. Malysheva, V. A. Morugova, and D. V. Moiseev*

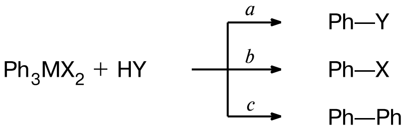
N. I. Lobachevsky Nizhnii Novgorod State University,
23 prosp. Gagarina, 603950 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 65 8592. E-mail: gushchin@mail.nnov.ru

The influence of the central metal atom and acid residue in a molecule of organometallic compound Ph_3MX_2 (M = Bi, Sb; X = Cl, Br, OAc, O_2CEt) on the direction and yield of dephenylation products in a methyl acrylate—methanol system in the presence of $Cu(OAc)_2$ and $Na_2PdCl_2(OAc)_2$ was studied at 50 °C in acetonitrile. The main product of dephenylation of the antimony compounds is methyl cinnamate (yield 0.31—1.59 moles per mole of the starting Ph_3SbX_2), while anisole (0.55—0.97 mol) and halobenzene (0.67—1.04 mol) are those for compounds $Ph_3Bi(O_2CR)_2$ and Ph_3BiHal_2, respectively.

Key words: organobismuth(v) compounds, organoantimony(v) compounds, catalysis, copper, palladium, methyl acrylate, methanol.

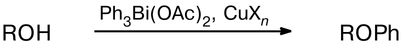
Organic compounds of antimony(v) and bismuth(v) of the Ph_3MX_2 type are known[1] to be dephenylated by various inorganic and organic reagents due to a low energy of the M—Ph bond (see Ref. 2). The majority of the known reactions of these organometallic compounds (OMC) with reactants containing an active hydrogen atom proceed according to Scheme 1.

Scheme 1



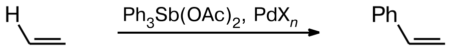
Routes *a* and *b* afford non-symmetric coupling products. Molecules of these products contain the Ph group bonded to the functional Y group, which enters the reactant composition (route *a*), or with the X group, which is a constituent of the starting OMC (route *b*). The third route (*c*) includes the formation of diphenyl, and the Ph groups can be originated from one or two OMC molecules. All coupling reactions are accompanied by a decrease in the oxidation state of the central metal atom from V to III. Numerous examples of the coupling reactions of the bismuth OMC involving alcohols, glycols, phenols, ketones, ketoesters, indoles, thiols, and others and their mechanism and stereochemical features are described in a monograph.[1] In the recent time, the coupling reactions of the bismuth and antimony OMC catalyzed by copper and palladium compounds evoke special interest. These reactions occur under mild conditions (20—50 °C) and afford coupling products through the step of intermediate formation of copper and palladium σ-phenyl derivatives. For instance, triphenylbismuth diacetate undergoes cross-coupling with alcohols, phenols, and diols in the presence of copper salts to form phenyl ethers[1,3] (Scheme 2).

Scheme 2



It has recently[4—6] been found that $Ph_3Sb(OAc)_2$ can be cross-coupled with alkene functional derivatives in the presence of palladium salts (Scheme 3).

Scheme 3



Triphenylbismuth dicarboxylates can also undergo similar reactions but the process is not selective in this case.[4]

The present work is aimed at studying the behavior of the antimony and bismuth Ph derivatives under the conditions when both *O*- and *C*-phenylations of organic sub-

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strates can occur simultaneously. For this purpose, we studied the interaction in the Ph_3MX_2—$Cu(OAc)_2$—$Na_2PdCl_2(OAc)_2$—$H_2C{=}CHCO_2Me$—MeOH (1 : 0.3 : 0.3 : 10 : 10) system at 50 °C in acetonitrile for 1 h. Triphenylbismuth(V) and triphenylantimony(V) dihalides (chloride, bromide) and dicarboxylates (acetate, propionate) were used as phenylating agents, because the difference in their properties in the reactions catalyzed by palladium and copper has been observed earlier.[6]

Results and Discussion

Methyl acrylate is a convenient model compound for *C*-phenylation. In the presence of palladium, it is selectively phenylated into the *trans*-position[4—7] and, at the same time, does not react with copper salts. Methanol is a convenient model for copper-catalyzed *O*-phenylation.[1,8—10] Acetonitrile is used because it is a convenient polar solvent and simultaneously can act as an electron-donor ligand for palladium and copper ions. The reaction was carried out in sealed ampules in the presence of air. The dephenylation products and their yields based on the starting OMC are given in Table 1.

The Pd-catalyzed reaction of the antimony derivatives with methyl acrylate results in selective *C*-phenylation to form methyl cinnamate (Scheme 4). Triphenylantimony dicarboxylates exhibit the highest reactivity in this reaction, where the yield of methyl cinnamate reaches 1.40—1.59 moles per mole of the starting antimony OMC (see Table 1, entries *1* and *2*). We believe that one mole of the product is formed in this process due to the dephenylation of Ph_3SbX_2, which is reduced to Ph_2SbX. The latter can also react with methyl acrylate in the presence of air oxygen to form other 0.4—0.6 moles of methyl cinnamate. This assumption is confirmed by the known data[6,11] on the reactions of triphenylantimony(V) dicarboxylates and diphenylantimony(III) acetate with methyl acrylate catalyzed by the palladium salts in the presence of air.

Scheme 4

$$Ph_3Sb(OAc)_2 + H_2C{=}CHCO_2Me \xrightarrow{[Pd]}$$

$$\longrightarrow PhCH{=}CHCO_2Me + Ph_2SbOAc + AcOH$$

$$2\ Ph_2SbOAc + O_2 + 2\ H_2C{=}CHCO_2Me + 2\ AcOH \xrightarrow{[Pd]}$$

$$\longrightarrow 2\ PhCH{=}CHCO_2Me + 2\ PhSb(OAc)_2 + 2\ H_2O$$

On going from triphenylantimony(V) dicarboxylates to dichloride, the yield of the cross-coupling product decreases sharply but high selectivity is retained. In this case, the yield of methyl cinnamate was 0.31 mol, and no other products were observed (see Table 1, entry *3*). We believe that $Ph_3Sb(OAc)_2$ or $Ph_3Sb(OAc)Cl$, which is formed by ligand exchange between antimony(V) chloride and copper(II) or palladium(II) acetate, acts as phenylating agent rather than Ph_3SbCl_2. We have previously[4,6] shown that Ph_3SbCl_2 cannot phenylate methyl acrylate in the presence of catalytic amounts of $PdCl_2$ and Li_2PdCl_4 containing no carboxylate groups.

Thus, the antimony compounds Ph_3SbX_2 used undergo selective cross-coupling reactions with methyl acrylate with catalytic participation of palladium. The role of $Cu(OAc)_2$ is restricted only by donating of the acetate groups in the exchange reaction.

The bismuth compounds, unlike the antimony OMC, afford the whole series of dephenylation products. For $Ph_3Bi(O_2CEt)_2$, the copper-catalyzed *O*-phenylation of methanol to anisole is prevailing (Scheme 5, see Table 1, entry *5*). The reaction of triphenylbismuth dicarboxylates occurs easily at room temperature,[1,3,8—10] although similar antimony compounds can react with alcohols only in the presence of equimolar amounts of the copper salts at 80 °C.[12]

When $Ph_3Bi(O_2CEt)_2$ is used in the catalytic decomposition of triphenylbismuth dichloride, chlorobenzene (0.26 mol) is formed (Scheme 6). The latter is formed *in situ* due to the exchange reaction of $Ph_3Bi(O_2CEt)_2$ with $Na_2Pd(OAc)_2Cl_2$.

Table 1. Yields of the organic products of OMC dephenylation in the Ph_3MX_2—$Cu(OAc)_2$—$Na_2PdCl_2(OAc)_2$—$H_2C{=}CHCO_2Me$—MeOH (1 : 0.3 : 0.3 : 10 : 10) system (acetonitrile, 50 °C, reaction duration 1 h)

Entry	Ph_3MX_2	Yield (mole per mole of OMC)				
		$PhCH{=}CHCO_2Me$	Ph_2	MeOPh	PhHal	PhH
1	$Ph_3Sb(OAc)_2$	1.40	0.01	0	0	0
2	$Ph_3Sb(O_2CEt)_2$	1.59	0.03	0	0	0
3	Ph_3SbCl_2	0.31	0	0	0	0
4	$Ph_3Bi(OAc)_2$	0.15	0.53	0.55	0.32	0.27
5	$Ph_3Bi(O_2CEt)_2$	0.14	0.51	0.97	0.26	0.37
6	Ph_3BiCl_2	0.13	0.37	0	1.04	0.23
7	Ph_3BiBr_2	0.17	0.59	0	0.67	0.13

Scheme 5

$$Ph_3Bi(O_2CEt)_2 + MeOH \xrightarrow{[Cu]} MeOPh + Ph_2BiO_2CEt + EtCO_2H$$

Scheme 6

$$Ph_3BiCl_2 \xrightarrow{[Cu],\ [Pd]} PhCl + Ph_2BiCl$$

Examples for the formation of halobenzenes by the reaction of $Ph_3Bi(OAc)_2$ with $Cu(OAc)_2$ in the presence of calcium and ammonium halides and for the reaction of Ph_3BiCl_2 with $PdCl_2$ have been described.[9,13]

In the case of $Ph_3Bi(O_2CEt)_2$, two compounds involving palladium are formed along with anisole and chlorobenzene. For instance, methyl cinnamate, being the product of cross-coupling of $Ph_3Bi(O_2CEt)_2$ with methyl acrylate, was isolated in a yield of 0.14 mol (Scheme 7, see Table 1, entry *5*). This reaction occurs readily in the presence of the palladium salts[5] but does not occur when they are replaced by the copper salts.

Scheme 7

$$Ph_3Bi(O_2CEt)_2 + H_2C{=}CHCO_2Me \xrightarrow{[Pd]} PhCH{=}CHCO_2Me + Ph_2BiO_2CEt + EtCO_2H$$

The palladium-catalyzed formation of diphenyl is more pronounced (0.51 mol, Scheme 8, see Table 1, entry *5*). Similar mild dephenylation of compounds Ph_3Bi and Ph_3BiX_2 is described.[14,15]

Scheme 8

$$\mathbf{A} \xrightarrow{[Pd]} Ph_2$$

A is $Bi^{III(V)}$-OMC.

Benzene (0.37 mol) was also isolated along with the mentioned coupling products. It is formed, most likely, through the dephenylation of the bismuth OMC with acid $EtCO_2H$ in the steps of formation of anisole and methyl cinnamate (Scheme 9).

Scheme 9

$$Ph_nBiX_{3-n} + HX \longrightarrow PhH + Ph_{n-1}BiX_{4-n}$$

$X = O_2CEt$; $n = 1, 2, 3$

This reaction is characteristic of all bismuth(III) compounds.[16] The copper salts can accelerate this process.[17]

Triphenylbismuth diacetate exhibits similar reactivity (see Table 1, entry *4*).

The catalytic effect of the copper salt is observed when Ph_3BiCl_2 is used, as well as in the case of Ph_3SbCl_2. The reaction products contained chlorobenzene, whose yield was 1.04 mol (see Table 1, entry *6*). This process suppresses completely methanol *O*-phenylation, which prevails in the case of triphenylbismuth dicarboxylates. This effect has been described previously.[9] In addition to chlorobenzene, the reaction products contained diphenyl and methyl cinnamate, whose formation is caused by catalytic participation of palladium. When Ph_3BiBr_2 is used, the reaction proceeds similarly to the case of Ph_3BiCl_2 (see Table 1, entry *7*).

The bismuth(V) compounds undergo deeper dephenylation compared to similar antimony(V) compounds. The total amount of the Ph groups detached from bismuth is 2.10—2.76 moles per mole of OMC (see Table 1, entries *4—7*), while that for the detachment from antimony is 0.31—1.65 mol (see Table 1, entries *1—3*). This is related to a lower strength of the Bi—C bond compared to the Sb—C bond.[2]

Thus, all processes studied involving the bismuth(V) compounds are lowly selective. For copper catalysis, bismuth(V) halides form only halobenzene, while carboxylates give predominantly anisole. The catalytic participation of palladium is also substantial. However, the main process in the presence of Pd is the decomposition of the bismuth OMC to form diphenyl rather than the cross-coupling of Ph_3BiX_2 with methyl acrylate. This sharply distinguishes the bismuth compounds from the antimony compounds Ph_3SbX_2.

Experimental

Volatile reaction products were analyzed by GLC on an LKhM-80 chromatograph using a flame-ionization detector and helium as carrier gas. To determine the benzene content, a column 300 cm long with 15% dinonyl phthalate on Chromaton N-AW-DMCS at 80 °C was used. The contents of methyl cinnamate and diphenyl were determined on a 240-cm column with 15%-Apieson L on Chromaton N-AW-DMCS at 220 °C. Anisole, chlorobenzene, bromobenzene, and phenyl acetate were determined on the same column at 130 °C.

The syntheses of $Ph_3Sb(OAc)_2$, $Ph_3Sb(O_2CEt)_2$, Ph_3SbCl_2,[6] $Ph_3Bi(OAc)_2$, $Ph_3Bi(O_2CEt)_2$, Ph_3BiCl_2, and Ph_3BiBr_2 [16,18] were carried out according to known procedures; $Cu(OAc)_2$ was prepared from monohydrate,[10] and $Na_2Pd(OAc)_2Cl_2$ was obtained from $PdCl_2$ and NaOAc. Methanol was used as received.

Dephenylation of $Ph_3Bi(OAc)_2$. A mixture of $Ph_3Bi(OAc)_2$ (0.5 mmol), $Cu(OAc)_2$ (0.15 mmol), $Na_2Pd(OAc)_2Cl_2$ (0.15 mmol), $CH_2{=}CHCO_2Me$ (5 mmol), MeOH (5 mmol), and acetonitrile (4 mL) were placed in a 50-mL ampule in air. The ampule was sealed and heated for 1 h at 50 °C, and then the liquid fraction was distilled off under reduced pressure. Acetonitrile (4 mL) was added to the solid residue, and H_2S was purged for 1 min to bind dissolved metal compounds. The transparent solution obtained after centrifugation and the resulting condensate were analyzed by GLC to determine the contents of methyl cinnamate, diphenyl, anisole, chlorobenzene, and benzene. No phenyl acetate was found in the products. The reactions with other OMC were carried out similarly.

References

1. J.-P. Finet, *Ligand Coupling Reactions with Heteroatomic Compounds*, Pergamon Press, Oxford, 1998, 291 pp.
2. I. B. Rabinovich, V. P. Nistratov, V. I. Tel´noi, and M. S. Sheiman, *Termodinamika metalloorganicheskikh soedinenii* [*Thermodynamics of Organometallic Compounds*], Izd-vo Nizhnii Novgorod Gos. Univ., Nizhnii Novgorod, 1996, 297 pp. (in Russian).
3. H. Suzuki and Y. Matano, *Organobismuth Chemistry*, Elsevier, New York, 2001, 619 pp.
4. A. V. Gushchin, D. V. Moiseev, and V. A. Dodonov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1230 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1291].
5. A. V. Gushchin, D. V. Moiseev, and V. A. Dodonov, *Zh. Obshch. Khim.*, 2002, **72**, 1669 [*Russ. J. Gen. Chem.*, 2002, **72**, 1571 (Engl. Transl.)].
6. D. V. Moiseev, A. V. Gushchin, A. S. Shavirin, Yu. A. Kursky, and V. A. Dodonov, *J. Organomet. Chem.*, 2003, **667**, 176.
7. D. V. Moiseev, V. A. Morugova, A. V. Gushchin, and V. A. Dodonov, *J. Organomet. Chem.*, 2004, **689**, 731.
8. V. A. Dodonov, A. V. Gushchin, and T. G. Brilkina, *Zh. Obshch. Khim.*, 1984, **54**, 2157 [*J. Gen. Chem. USSR*, 1984, **54** (Engl. Transl.)].
9. V. A. Dodonov, A. V. Gushchin, and T. G. Brilkina, *Zh. Obshch. Khim.*, 1985, **55**, 2514 [*J. Gen. Chem. USSR*, 1985, **55** (Engl. Transl.)].
10. V. A. Dodonov, T. I. Starostina, Yu. L. Kuznetsova, and A. V. Gushchin, *Izv. Akad. Nauk*, *Ser. Khim.*, 1995, 156 [*Russ. Chem. Bull.*, 1995, **44**, 151 (Engl. Transl.)].
11. K. Matoba, S. Motofusa, C. S. Cho, K. Ohe, and S. Uemura, *J. Organomet. Chem.*, 1999, **574**, 3.
12. A. V. Gushchin, Doct. Sci. (Chem.) Thesis, Nizhnii Novgorod Gos. Univ., Nizhnii Novgorod, 1998, 283 pp. (in Russian).
13. D. V. Moiseev, Yu. B. Malysheva, A. S. Shavyrin, Yu. A. Kurskii, and A. V. Gushchin, *J. Organomet. Chem.*, 2005, **690**, 3652.
14. D. H. R. Barton, N. Ozbalik, and M. Ramesh, *Tetrahedron*, 1988, **44**, 5661.
15. T. Ohe, T. Tanaka, M. Kuroda, C. S. Cho, K. Ohe, and S. Uemura, *Bull. Chem. Soc. Jpn*, 1999, **72,** 1851.
16. K. A. Kocheshkov, A. P. Skoldinov, and N. N. Zemlyanskii, *Metody elementoorganicheskoi khimii. Sur´ma, vismut* [*Methods of Organoelement Chemistry. Antimony, Bismuth*], Nauka, Moscow, 1976, 483 pp. (in Russian).
17. V. A. Dodonov, A. V. Gushchin, and O. P. Bolotova, *Zh. Obshch. Khim.*, 1990, **60**, 2083 [*J. Gen. Chem. USSR*, 1990, **60** (Engl. Transl.)].
18. V. A. Dodonov and A. V. Gushchin, *Izv. Akad. Nauk*, *Ser. Khim.*, 1993, 2043 [*Russ. Chem. Bull.*, 1993, **42**, 1955 (Engl. Transl.)].

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