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Reaction of triphenylantimony and triphenylbismuth with *tert*-butyl peracetate

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Triphenylantimony and triphenylbismuth diacetates, $Ph_3M(OAc)_2$ (M = Sb, Bi), were obtained in 50—94 % yields by the reaction of triphenylantimony and triphenylbismuth with *tert*-butyl peracetate in the presence of acetic acid or acetic anhydride (molar ratio 1 : 1 : 1) in toluene. *tert*-Butyl peracetate oxidizes Ph_3M into alkoxides, $Ph_3M(OAc)OBu^t$, which at the instant of formation are acylated with acetic acid or acetic anhydride to give the corresponding derivatives, $Ph_3M(OAc)_2$.

Key words: triphenylantimony, triphenylbismuth, oxidation; *tert*-butyl peracetate; triphenylantimony diacetate, triphenylbismuth diacetate; *tert*-butylhydroperoxide.

At present, organic derivatives of antimony and bismuth, particularly triphenylbismuth diacetate $Ph_3Bi(OAc)_2$, find wide use in organic synthesis as reagents for selective oxidation of alcohols and glycols, phenylation of phenols, enols, and amines, *o*-*C*-phenylation of phenols,[1,2] and for obtaining polyfunctional organic products.[3] Considerable interest is drawn to organometallic compound (OMC)—peroxide systems, *e.g.*, $Bu^tOOH—Ph_3M$ (M = Sb, Bi), which find use both in organometallic syntheses of a number of hydroxy, siloxy, alkoxy, acyloxy, and peroxy derivatives of the type Ph_3MXY[1,4—6] and in organic syntheses of carbonyl compounds.[7,8] All of the above reactions are redox processes and involve one or several valent transitions of antimony or bismuth, $M^{III} \leftrightarrow M^{V}$.

The purpose of the present work was to develop a method for synthesizing $Ph_3Bi(OAc)_2$ (**1**) and $Ph_3Sb(OAc)_2$ (**2**) using a peroxy ester as an oxidant, to estimate the stability of asymmetric antimony and bismuth alkoxyacetates of the type $Ph_3M(OAc)OBu^t$, and to determine the possible ways for their transformation into products **1** and **2**.

Results and Discussion

Preliminary studies showed that the reactions of the peroxy ester with Ph_3M (M = Sb, Bi) in toluene at 70 °C cease almost completely (98—100 %) in 35 h. In the absence of triphenylantimony, the peroxy ester undergoes only a slight decomposition under these conditions (4.4 %) to give *tert*-butanol, *tert*-butyl acetate, and dibenzyl in 2.5 %, 1.9 %, and 1.8 % yields, respectively.

The yields of the products of the reaction of triphenylantimony with *tert*-butyl peracetate are presented in Table 1. *tert*-Butanol was found in an insignificant amount (14 %). However, its yield increased to 72 % in the presence of moist THF. In addition, we isolated triphenylantimony diacetate (43 %), which was identified by the melting point and by the IR spectrum, and antimony(v) hydroxides insoluble in organic solvents. These data show that the first reaction step involves oxidative addition of *tert*-butyl peracetate to triphenylantimony according to Eq. (1). Compound **2** is formed by disproportionation of antimony(v) alkoxyacetate (Eq. (2)).

$$Ph_3Sb + Bu^tOOAc \longrightarrow [Ph_3Sb(OAc)OBu^t] \tag{1}$$

$$2\,[Ph_3Sb(OAc)OBu^t] \rightleftharpoons Ph_3Sb(OAc)_2 + [Ph_3Sb(OBu^t)_2] \tag{2}$$

Table 1. Yields (%) of products of reaction of Ph_3M (M = Sb, Bi) with Bu^tOOAc (1 : 1) without additives and in the presence of AcOH (1 : 1 : 1) or AcOAc (1 : 1 : 1) in toluene at 70 °C

Product	M = Sb			M = Bi		
	without additives	AcOH	AcOAc	without additives	AcOH	AcOAc
Bu^tOH	14	96	23	31	74	16
Bu^tOAc	0	0	65	24	0	72
Bu^tOPh	0	0	0	39	0.4	4.0
PhH	3.0	2.0	2.0	8.0	37	8.0
PhOAc	0	0	0	0	2.0	35
After hydrolysis						
Bu^tOH	72	0	9.0	6.0	0	0
$Ph_3M(OAc)_2$	43	94	94	32	69	59
Ph_3M	7.0	6.0	4.0	36	15	22

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Dialkoxytriphenylantimony is likely to undergo hydrolysis to give the corresponding dihydroxy derivatives of antimony(v) and *tert*-butanol (Eq. (3)).

$$[\mathrm{Ph_3Sb(OBu^t)_2}] + 2\,\mathrm{H_2O} \longrightarrow \mathrm{Ph_3Sb(OH)_2} + 2\,\mathrm{Bu^tOH} \quad (3)$$

It was found that triphenylbismuth reacts with *tert*-butyl peracetate in the same temperature range as triphenylantimony to give compound **1** in 32 % yield (see Table 1). The reaction products, unlike those formed in the reaction with triphenylantimony, contain considerable quantities of triphenylbismuth (36 %), *tert*-butyl acetate (24 %), and *tert*-butyl phenyl ether (39 %). The yield of *tert*-butanol after hydrolysis is as low as 6 %.

In the first step of the reaction involving triphenylbismuth, as in the case of triphenylantimony, the peroxy ester oxidizes the starting OMC into bismuth(v) alkoxyacetate (see Eq. (1)), which disproportionates according to Eq. (2). Mono- and dialkoxides of bismuth(v) are unstable[9,10] and are reduced to give *tert*-butyl phenyl ether and bismuth(III) derivatives, which undergo symmetrization to give triphenylbismuth (Eq. (4)).

$$[\mathrm{Ph_3Bi(X)OBu^t}] \longrightarrow \mathrm{Bu^tOPh} + \mathrm{Ph_2BiX} \quad (4)$$

$$\mathrm{X = OAc, OBu^t}$$

tert-Butyl acetate is formed through an alternative pathway of bismuth(v) alkoxyacetate decomposition according to Eq. (5).

$$[\mathrm{Ph_3Bi(OAc)OBu^t}] \longrightarrow \mathrm{Bu^tOAc} + [\mathrm{Ph_3BiO}] \quad (5)$$

It is known[7,11] that $\mathrm{Ph_3BiO}$ decomposes according to a radical mechanism to give triphenylbismuth and bismuth(III) oxides. It should be noted that $\mathrm{Ph_3PO}$, unlike $\mathrm{Ph_3BiO}$, is a thermodynamically stable compound; hence the reactions of $\mathrm{Ph_3P}$ with peroxy esters gives exclusively $\mathrm{Ph_3PO}$ and esters.[12] In order to confirm the pathways of transformation of unstable *tert*-butoxyacetates of triphenylantimony and -bismuth, we studied the reactions of compounds **1** and **2** with lithium *tert*-butoxide (molar ratio 1 : 1) in toluene in an evacuated tube. These reactions cease in 35 h at 70 °C (Table 2).

$$\mathrm{Ph_3M(OAc)_2} + \mathrm{Bu^tOLi} \longrightarrow [\mathrm{Ph_3M(OAc)OBu^t}] + \mathrm{LiOAc} \quad (6)$$

$$\mathrm{M = Sb, Bi}$$

The reaction of compound **2** followed by hydrolysis gave *tert*-butanol as the main product, while bismuth(v) alkoxides gave *tert*-butyl acetate (3 %) and *tert*-butyl phenyl ether (66 %) according to Eqs. (4) and (5). This was accompanied by partial thermal decomposition of compound **1** to give phenyl acetate (11 %)[13] according to Eq. (7).

$$\mathrm{Ph_3Bi(OAc)_2} \longrightarrow \mathrm{PhOAc} + \mathrm{Ph_2BiOAc} \quad (7)$$

Table 2. Yields (%) of products of reaction of $\mathrm{Ph_3M(OAc)_2}$ with $\mathrm{Bu^tOLi}$ (1 : 1) in toluene at 70 °C

Product	M = Sb	M = Bi
$\mathrm{Bu^tOPh}$	0	66
$\mathrm{Bu^tOAc}$	0	3.0
PhOAc	0	11
$\mathrm{Bu^tOH}$	6.0	15
PhH	0	1.0
	After hydrolysis	
$\mathrm{Bu^tOH}$	69	4.0
$\mathrm{Ph_3M(OAc)_2}$	—	17
$\mathrm{Ph_3M}$	—	37

Based on the data that antimony(v) and bismuth(v) alkoxides are formed on treatment of *tert*-butyl peracetate with triphenylantimony and -bismuth, we studied the possibility of acylating the above alkoxides at the instant of their formation with acetic acid and acetic anhydride to obtain compounds **1** and **2**.

The reaction of triphenylantimony with the peroxy ester and acetic acid (at a molar ratio of 1 : 1 : 1) in toluene in an evacuated tube at 70 °C for 35 h gave product **2** and *tert*-butanol in almost quantitative yields (94 % and 96 %, respectively, see Table 1).

$$\mathrm{Ph_3M} + \mathrm{Bu^tOOAc} \longrightarrow [\mathrm{Ph_3M(OAc)OBu^t}]$$

$$[\mathrm{Ph_3M(OAc)OBu^t}] \xrightarrow{\mathrm{AcOH}} \mathrm{Ph_3M(OAc)_2} + \mathrm{Bu^tOH} \quad (8)$$

$$[\mathrm{Ph_3M(OAc)OBu^t}] \xrightarrow{\mathrm{AcOAc}} \mathrm{Ph_3M(OAc)_2} + \mathrm{Bu^tOAc} \quad (9)$$

$$\mathrm{M = Sb, Bi}$$

The corresponding reaction with triphenylbismuth also occurs according to Eq. (8) but gave product **1** in a lower yield (69 %), since dephenylation of triphenylbismuth with acetic acid occurred in parallel (Eq. (10)). The yield of benzene was up to 37 %.

$$\mathrm{Ph_3Bi} + \mathrm{AcOH} \longrightarrow \mathrm{PhH} + \mathrm{Ph_2BiOAc} \quad (10)$$

The reaction of triphenylantimony with *tert*-butyl peracetate and acetic anhydride under the above conditions (see Eq. (9)) gave compound **2** and *tert*-butyl acetate in 94 % and 65 % yields, respectively (see Table 1). The reaction of triphenylbismuth under similar conditions gave compound **1** in 59 % yield. The decrease in the yield occurred due to thermal decomposition of **1** according to Eq. (7), while the yield of phenyl acetate was 35 %.

Previously,[14] the participation of *tert*-butyl peracetate in one-step syntheses of triphenylbismuth diacylates was reported. These syntheses involved *tert*-butylhydroperoxide as the oxidant used in the presence of anhydrides of carboxylic acids. In order to estimate the oxidative ability of the peroxy ester and hydroperoxide in the syntheses of compounds **1** and **2**, we studied the reactions of Ph_3M (M = Sb, Bi) with Bu^tOOH and AcOAc (1 : 1 : 1 ratio) in ether at 50 °C for 4 h. In the case of triphenylbismuth, the main products included compound **1** (60 %), *tert*-butanol (76 %), and *tert*-butyl peracetate (21 %). The reaction involving triphenylantimony carried out under similar conditions gave **2** in 59 % yield and *tert*-butanol in 87 % yield, while *tert*-butyl peracetate was virtually absent. Based on these data, we assume that acetic anhydride acylates *tert*-butylhydroperoxide under catalysis with bismuth compounds. This reaction gives a peroxy ester and acetic acid, which react with triphenylbismuth according to Eq. (8) to give compound **1**. On the other hand, *tert*-butylhydroperoxide can act as an oxidant, according to Eq. (11).

$$\mathrm{Ph_3M + Bu^tOOH \longrightarrow [Ph_3M(OH)OBu^t] \xrightarrow{AcOAc} Ph_3M(OAc)_2 + Bu^tOH} \qquad (11)$$

M = Sb, Bi

In the case of triphenylantimony, the process occurs predominantly according to Eq. (11).

When evaluating the reactions of Ph_3Sb and Ph_3Bi with Bu^tOOAc in the presence of AcOH and AcOAc and with Bu^tOOH in the presence of AcOAc (see Eqs. (8), (9), and (11)) as one-step oxidative methods for synthesizing compounds **1** and **2**, it should be noted that they are inferior to the method of synthesis from Ph_3M, Bu^tOOH, and AcOH (*cf.* Refs. 1 and 13), judging by the yields of the target products, particularly that of compound **1**. This results from the lower reactivity of Bu^tOOAc (in comparison with Bu^tOOH) toward Ph_3Sb and Ph_3Bi and from the instability of the intermediate bismuth alkoxide, $Ph_3Bi(OAc)OBu^t$.

Experimental

IR spectra were recorded in the range of 3800—400 cm^{-1} on a UR-20 spectrophotometer in an oil using NaCl windows.

GLC analyses of the products were carried out on a LKhM-80 chromatograph equipped with a thermal conductivity detector using helium as the carrier gas. *tert*-Butyl peracetate in toluene and ether was analyzed using a column (1 m length) with 15 % dinonyl phthalate on Chromaton N-AW-HMDS at 100 °C; *tert*-butanol in ether, toluene, and THF, on a 3 m column with the same packing at 80—100 °C; *tert*-butyl acetate and benzene in ether and toluene, on a 1 m column with 15 % Apieson-L on Chromaton N-AW at 80 °C; diphenyl and dibenzyl in hexane, with a similar column and packing at 230 °C; phenyl acetate and *tert*-butyl phenyl ether in ether and toluene, on a 1 m column with 15 % Reoplex-400 on Chromaton N-AW at 140 °C; acetic anhydride, *tert*-butyl acetate, and benzene in ether and toluene, on two successively combined columns: 3 m with 15 % Apieson-L on Chromaton N-AW and 2 m with Carbowax-6000 on Chromaton N-AW at 100 °C.

Reaction of triphenylbismuth with *tert*-butyl peracetate and acetic anhydride. A mixture of Ph_3Bu [11] (1 mmol), Bu^tOOAc [15] (1 mmol), and AcOAc (1 mmol) in toluene (1 mL) was heated at 70 °C for 35 h in an evacuated tube. The liquid fraction was condensed in a cooled trap (liquid nitrogen) and analyzed by GLC (see Table 1). THF (5 mL) containing water (10 %) was added to the solid residue, the liquid fraction was condensed, and the amount of *tert*-butanol after hydrolysis was determined by GLC. Treatment of solid hydrolysis products with hexane (20 mL) gave Ph_3Bi, m.p. 72 °C (*cf.* Ref. 11: m.p. 76—78 °C). Treatment with chloroform (20 mL) gave compound **1** (see Table 1), yield 59 %, m.p. 181 °C, m.p. of a mixture with the pure compound[13] (with m.p. 182 °C) was 182 °C. Found (%): OAc,[16] 20.96. $C_{22}H_{21}BiO_4$. Calculated (%): OAc, 21.15. IR, ν/cm^{-1}: 3040 (C—H); 1580 (C=O); 1330 (C—O); 455 (C—Bi).

Reaction of triphenylantimony with *tert*-butyl peracetate and acetic anhydride. The procedure for performing the reaction involving triphenylantimony[11] and analyzing the products is similar to that described for triphenylbismuth. Treatment of the solid products with hexane after hydrolysis gave Ph_3Sb, and treatment with chloroform gave compound **2** (see Table 1), yield 94 %, m.p. 215 °C (*cf.* Ref. 11: m.p. 215 °C). Found (%): OAc,[16] 21.78. $C_{22}H_{21}O_4Sb$. Calculated (%): OAc, 25.05. IR, ν/cm^{-1}: 3050 (C—H); 1615 (C=O); 1320 (C—O); 465 (C—Sb).

The reactions of triphenylantimony and triphenylbismuth with *tert*-butyl peracetate in toluene in the presence and in the absence of acetic acid (see Table 1) and with *tert*-butylhydroperoxide and acetic anhydride in ether were carried out in a similar way. The reactions of compounds **1** and **2** with lithium *tert*-butoxide were carried out in an H-shaped tube; the components were mixed after evacuating and sealing the tube.

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References

1. V. A. Dodonov and A. V. Gushchin, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 2043 [*Russ. Chem. Bull.*, 1993, **42**, 1955 (Engl. Transl.)].
2. R. A. Abramovitch, D. H. R. Barton, and J. P. Finet, *Tetrahedron*, 1988, **44**, 3039.
3. Y.-Z. Huang, C. Chen, and Y. Shen, *Tetrahedron Lett.*, 1988, **29**, 5275.
4. A. V. Gushchin, V. A. Dodonov, R. I. Usyatinskii, E. R. Koreshkova, and B. B. Tipanov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1302 [*Russ. Chem. Bull.*, 1994, **43**, 1239 (Engl. Transl.)].
5. V. A. Dodonov, S. N. Zaburdyaeva, and N. N. Nevkina, *Metalloorg. Khim.*, 1989, **2**, 1296 [*Organomet. Chem. USSR*, 1989, **2**, 685 (Engl. Transl.)].
6. V. A. Dodonov and T. I. Zinov'eva, *Metalloorg. Khim.*, 1992, **5**, 1265 [*Organomet. Chem. USSR*, 1992, **5**, 616 (Engl. Transl.)].
7. A. V. Gushchin, Ph. D. Thesis (Chemistry), Gor'ky State University, Gor'ky, 1986 (in Russian).
8. V. A. Dodonov, A. V. Gushchin, and T. I. Zinov'eva, in *Karbonil'nye soedineniya v sinteze geterotsiklov* [*Carbonyl Compounds in the Synthesis of Heterocycles*], Saratov, 1989, Ch. 2, 13 (in Russian).

9. A. V. Gushchin and T. G. Brilkina, in *Organicheskie peroksidy i gomoliticheskie reaktsii s ikh uchastiem* [*Organic Peroxides and Homolytic Reactions with Their Participation*], Volgograd, 1987, 81 (in Russian).
10. V. A. Dodonov, A. V. Gushchin, D. F. Grishin, and T. G. Brilkina, *Zh. Obshch. Khim.*, 1984, **54**, 100 [*J. Gen. Chem. USSR*, 1984, **54** (Engl. Transl.)].
11. K. A. Kocheshkov, A. P. Skoldinov, and N. N. Zemlyanskii, in *Metody elementoorganicheskoi khimii. Sur'ma, vismut* [*Methods of Organometallic Chemistry. Antimony, Bismuth*], Nauka, Moscow, 1976, 387 (in Russian).
12. L. Horner and W. Jurgeleit, *Ann. Chem.*, 1955, **591**, 138.
13. V. A. Dodonov, A. V. Gushchin, and T. G. Brilkina, *Zh. Obshch. Khim.*, 1985, **55**, 73 [*J. Gen. Chem. USSR*, 1985, **55** (Engl. Transl.)].
14. V. A. Dodonov, A. V. Gushchin, and M. B. Ezhova, *Zh. Obshch. Khim.*, 1988, **58**, 2170 [*J. Gen. Chem. USSR*, 1988, **58** (Engl. Transl.)].
15. V. L. Antonovsky and O. K. Lyashenko, *Zh. Prikl. Khim.*, 1967, **40**, 243 (in Russian).
16. K. H. Bauer, in *Die Organische Analyse*, Geest&Portig, Leipzig, 1950.

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