Syntheses of antimony(v) derivatives from trimethyl and triphenylantimony(III), dihydric phenols, and *tert*-butyl hydroperoxide

V. A. Dodonov,* A. Yu. Fedorov, R. I. Usyatinsky, S. N. Zaburdyaeva, and A. V. Gushchin

N. I. Lobachevsky State University, Nizhnii Novgorod, 23 prosp. Gagarina, 603600 Nizhnii Novgorod, Russian Federation. Fax: +7 (831 2) 658 592

Trimethyl and triphenylantimony *o*-phenylene dioxides were obtained by the reaction of trimethyl- and triphenylantimony with pyrocatechol in the presence of *tert*-butyl hydroper-oxide in 68 and 81 % yields, respectively. 7,7,7,15,15,15-Hexamethyl-(and phenyl)-6,8,14,16-tetraoxa-7,15-distibatricyclo[11.3.1.1^{9,13}]octadeca-1,3,5,9,11,13-hexaenes were synthesized analogously by the reaction with resorcinol (in 79 and 93 % yields, respectively). The use of hydroquinone resulted in polymeric trimethyl- and triphenylantimony hydroquinolates.

Key words: triphenylantimony, trimethylantimony; *tert*-butyl hydroperoxide, oxidation; pyrocatechol, resorcinol, hydroquinone, synthesis.

The one-step synthesis of antimony(v) phenyl derivatives, Ph_3SbX_2 , has made it possible to obtain the corresponding dihalides, diacylates, glycolates, and other compounds.¹ The method is based on the hypothesis that at the first stage triphenylantimony is oxidized by a hydroperoxide to form adduct (A) (Eq. (1)). The stability of the latter is determined by the structure of the hydroperoxide.

$$Ph_{3}Sb + HOOR \longrightarrow \begin{bmatrix} Ph_{3}Sb \\ OR \end{bmatrix}$$
(1)

 $R = Bu^{t}$, Me₃Si, Ph₃Si, Ph₃Ge

In the case of *tert*-butyl hydroperoxide, adduct A easily splits of an alcohol to yield the triphenylantimony oxide, while in the case of the silicon and germanium analogs, a molecule of water is eliminated to form a bisoxiderivative.¹ Many examples have been used to confirm that in the presence of compounds containing an active hydrogen atom, adduct A is converted to various stable compounds depending on the concentration of the organic substrate and the reaction conditions.

Thus, reaction (2) occurs at a 1:1 molar ratio between the triphenylantimony and hydroperoxide starting reagents. When the triphenylantimony : hydroperoxide ratio is 1 : 3, di(*tert*-butylperoxi)triphenylantimony (70 %) is obtained according to reaction (3) and bis(*tert*butylperoxitriphenylantimony) oxide (30 %) is obtained according to reaction (4).^{2,3} In excess hydroperoxide at a 1:5 molar ratio, the process is described by reaction (3).⁴ When the reaction mixture contains triphenylantimony, hydroperoxide, and a carboxylic acid, reaction (3) takes place to form triphenylantimony diacetate in a high yield.¹ Under analogous conditions, in the presence of some β -diketones, triphenylantimony hydroxychelates were obtained in high yields according to reaction (5),⁵ whereas reaction (6) proceeds in the presence of α -dioles to form the corresponding dioxostibolates.⁶

→
$$Ph_3SbO + ROH$$
 (2)

$$\xrightarrow{HX} Ph_3Sb \overset{\wedge}{\underset{X}{\leftarrow}} + H_2O + ROH$$
(3)

$$\begin{array}{c|c} Ph_3Sb & & HX \\ OR & & Ph_3Sb & O \\ & & & X & X \\ & & & X \\ & & & X \\ & & & X \end{array} + H_2O + 2ROH (4)$$

$$\stackrel{\text{IL}}{\longrightarrow} \text{Ph}_3\text{Sb} \stackrel{\text{OH}}{\longleftarrow} \text{Ph}_3 \text{FOH}$$
(5)

$$\begin{array}{c} \text{HOR'OH} \\ \text{Ph}_{3}\text{Sb} < \begin{array}{c} 0 \\ 0 \end{array} \\ \begin{array}{c} R' + ROH + H_{2}O \end{array} (6) \end{array}$$

 $R = Bu^{t}$; X = tert-butyl peroxi, acyloxi; HO---R'---OH = α -diols; HL = β -diketones

OH]

The purpose of the present work was to continue the investigation of possible applications of the oxidative method using the reactions of phenyl and methyl antimony(III) derivatives with dihydric phenols (pyrocatechol, resorcinol, hydroquinone) in the presence of

occurs in 81 % yield.

tert-butyl hydroperoxide as examples. The syntheses were carried out as follows. A solution of hydroperoxide was added with cooling (5-10 °C) and stirring to a solution of triphenylantimony and dihydric phenol (using equimolar amounts of the reagents). When the reaction was completed, the volatile products were removed to a trap under reduced pressure. Thus, the reaction of triphenylantimony with pyrocatechol in the presence of *tert*-butyl hydroperoxide resulted in a condensate that contained 0.92 mol of *tert*-butyl alcohol and 0.9 mol of water per one mol of triphenylantimony. Reaction (7)



Compound 1 is a yellow crystalline substance readily soluble in organic solvents. Its structure was confirmed by IR spectral data.

The reaction of triphenylantimony with resorcinol in the presence of *tert*-butyl hydroperoxide was performed under analogous conditions. The condensate was found to contain 0.96 mol of *tert*-butyl alcohol and 0.80 mol of water per one mol of triphenylantimony. Product **2** has m.p. 112 °C (benzene—hexane). There are no adsorbtion bands of the hydroxyl groups in the IR spectra. The data obtained attest to the fact that adduct **A** reacts with resorcinol to form unstable hydroxyphenolate (**B**) according to reaction (8), and the dimerization of the latter (Eq. (9)) gives 7,7,7,15,15,15-hexaphenyl-6,8,14,16-tetraoxa-7,15-distibatricyclo[11.3.1.1^{9,13}]octadeca-1,3,5,9,11,13-hexaene (**2**).



To confirm the structure of 2, reaction (10) was performed using an alcohol solution of HCl to obtain triphenylantimony dichloride and resorcinol in high yields.

The products obtained were separated using their different solubilities in benzene.

For the reaction of hydroquinone with triphenylantimony under the conditions of the oxidative method, similarly to the previous case of resorcinol, *tert*-butyl alcohol and water were determined quantitatively. The IR spectra of the solid residue exhibits no absorbtion bands of hydroxyl groups. The solid product is virtually insoluble in organic solvents, and, therefore, the Sb^v hydroxyphenolates that are formed at the intermediate stage and resemble adduct **B** react with each other to split off the water and yield polymeric triphenylantimony hydroxyphenolate (3).



Like in the previous case, the reaction of compound 3 with an alcoholic solution of HCl was performed and triphenylantimony dichloride and hydroquinone were isolated in high yields.

Unlike triphenylantimony, trimethylantimony is easily oxidized by atmospheric oxygen. In view of this, the reactions of trimethylantimony were carried out under reduced pressure in the absence of atmospheric oxygen. Organic solvents (benzene, toluene, ether, dioxane) were used, and the ratio between the reagents was as follows: trimethylantimony : hydroperoxide : phenol = 1.1 : 1.1 :1.0.

Thus, in the case of the reaction of trimethylantimony with pyrocatechol in the presence of *tert*-butyl hydroperoxide, trimethylantimony *o*-phenylenedioxide (4) was isolated in 68 % yield. M.p. 105 °C (*cf.* Ref. 7: m.p. 114 °C, yield 55 %). The structure of 4 was confirmed by the IR spectral data and by the molecular weight determined.

7,7,7,15,15,15-Hexamethyl-6,8,14,16-tetraoxa-7,15distibatricyclo[11.3.1.1^{9,13}]octadeca-1,3,5,9,11,13-hexaene (5) was prepared in 79 % yield (m.p. 34 °C) by the reaction of trimethylantimony with resorcinol.

Trimethylantimony hydroquinoneate (6) (m.p. $155 \, ^{\circ}$ C, decomp.) was obtained in 80 % yield by the

reaction of trimethylantimony with hydroquinone in the presence of *tert*-butyl hydroperoxide.

Compounds 4 and 5 are readily soluble in aromatic hydrocarbons, ether, and dioxane, while compound 6, similarly to compound 3, is virtually insoluble in these solvents.

It should be noted that water and *tert*-butanol were quantitatively detected in all of the reactions.

In order to confirm the structures of compounds 4, 5, and 6, we treated them with an excess of alcoholic HCl. As a result, trimethylantimony dichloride and the corresponding dihydric phenols were isolated in high yields.

The performed reactions indicate that the route of the synthesis is controlled by the disposition of the hydroxyl groups in dihydric phenol: pyrocatechol gives products containing a five-membered cycle, resorcinol gives rise to heteroanalogs of [3.3]metacyclophane, and in the case of hydroquinone, antimony(v) poly(oligo)hydroquinoneates are formed. Phenyl and methyl substituents at the antimony atom have virtually no effect on the course of the reaction.

Experimental

Triphenylantimony *o*-phenylenedioxide (1). 0.45 g (5 mmol) of *tert*-butyl hydroperoxide in 10 mL of benzene was slowly added over a period of 40 min with cooling (an ice bath) and stirring to a mixture of 1.76 g (5 mmol) of triphenylantimony⁸ and 0.5 g (5 mmol) of pyrocatechol in 20 mL of benzene. When the reaction was completed, the volatile products were refrozen in a trap. The condensate contained 0.34 g (4.6 mmol) of *tert*-butyl alcohol and 0.08 g (4.5 mmol) of water. The solid residue was recrystallized from a benzene—hexane mixture. Compound 1 was isolated in 81 % (1.86 g) yield, m.p. 144 °C (benzene—hexane) (compare m.p. 142–143 °C reported in Ref. 7). The IR spectra exhibits no adsorbtion bands of hydroxyl groups.

7,7,7,15,15,15-Hexaphenyl-6,8,14,16-tetraoxa-7,15-distibatricyclo[11.3.1.1^{9,13}]octadeca-1,3,5,9,11,13-hexaene (2). Compound 2 was synthesized by an analogous procedure from 1.76 g (5 mmol) of triphenylantimony, 0.55 g (5 mmol) of resorcinol, and 0.45 g (5 mmol) of hydroperoxide. 0.36 g (4.8 mmol) of *tert*-butyl alcohol and 0.07 g (4.0 mmol) of water were found in the condensate. 2.1 g (93 %) of compound 2 was isolated, m.p. 112 °C (decomp.) (benzene—hexane). Found (%): C, 62.47; H, 5.16. Mol. weight 900 (cryoscopy, benzene). $C_{24}H_{18}O_4Sb_2$. Calculated (%): C, 62.47; H, 4.12. Mol. weight 922.

Triphenylantimony hydroquinoneate (3). The reaction was carried out as described above using 1.76 g (5 mmol) of triphenylantimony, 0.55 g (5 mmol) of hydroquinone, and 0.45 g (5 mmol) of *tert*-butyl hydroperoxide. 0.34 g (4.6 mmol) of *tert*-butyl alcohol and 0.08 g (4.4 mmol) of water were found in the condensate. The obtained compound was washed with hot dioxane. 2.11 g (95 %) of the product **3** was isolated, m.p. 205 °C (decomp.). Found(%): C, 62.35; H, 4.50. $(C_{24}H_{19}O_2Sb)_n$. Calculated (%): C, 62.47; H, 4.12.

A general procedure for the reactions of trimethylantimony with dihydric phenols. A solution of a dihydric phenol and *tert*butyl hydroperoxide in an organic solvent was poured into a tube, which was then evacuated. A fixed amount of trimethylantimony was refrozen in the tube.⁸ The ratio of the starting compounds was trimethylantimony : *tert*-butyl hydroper-oxide : phenol = 1.1 : 1.1 : 1. After 20 h, the volatile products were refrozen in a trap.

Trimethylantimony *o*-phenylenedioxide (4) was prepared from 0.6 g (5.5 mmol) of pyrocatechol, 0.54 g (6.0 mmol) of hydroperoxide in 30 mL of benzene (toluene), and 1.0 g (6.0 mmol) of trimethylantimony. 0.42 g (5.6 mmol) of *tert*-butyl alcohol and 0.09 g (5.2 mmol) of water were found in the condensate. The product was purified by recrystallization from a mixture of benzene and hexane to yield 1.0 g (68 %) of compound 4, m.p. 105 °C (decomp.) (compare Ref. 7, m.p. 114 °C). Found, mol. weight 282. $C_9H_{13}O_2Sb$. Calculated, mol. weight 275.

7,7,7,15,15,15-Hexamethyl-6,8,14,16-tetraoxa-7,15-distibatricyclo[11.3.1.1^{9,13}]octadeca-1,3,5,9,11,13-hexaene (5). Compound 5 was obtained from 0.55 g (5 mmol) of resorcinol, 0.46 g (5.1 mmol) of *tert*-butyl hydroperoxide, and 0.85 g (5.1 mmol) of trimethylantimony. The synthesis was carried out in dioxane. 0.35 g (4.7 mmol) of *tert*-butyl alcohol and 0.09 g (5.0 mmol) were found in the condensate. The solid residue was purified by recrystallization from a benzene—hexane mixture to give 1.1 g (79 %) of compound 5, m.p. 34 °C (benzene hexane). Found, mol. weight 587. $C_{18}H_{26}O_4Sb_2$. Calculated, mol. weight 550.

Trimethylantimony hydroquinolate was obtained from 0.67 g (6.1 mmol) of hydroquinone, 0.6 g (6.7 mmol) of hydroperoxide, and 1.1 g (6.7 mmol) of trimethylantimony. The reaction was carried out in dioxane (or in ether). 0.46 g (6.2 mmol) of *tert*-butanol and 0.10 g (5.5 mmol) of water were found in the condensate. The solid residue was insoluble in organic solvents. It was washed with hot dioxane. 1.3 g (80 %) of the product (m.p. 155 °C) was isolated.

The reactions of the derivatives of dihydric phenols and trimethyl- and triphenylantimony with an alcohol solution of HCl. An excess of a saturated alcoholic solution of HCl was added to a known amount of a trimethyl- or triphenylantimony derivative. The mixture was heated for 3 h with a reflux condenser over a water bath, and then the solution was poured into a Petri dish. The solid products were separated using the different solubilities of the antimony(v) dichlorides and phenols in benzene (antimony(v) dichlorides are readily soluble in benzene). In the case of compounds 2 and 3, 85 and 87 % triphenylantimony dichloride and 85 and 86 % resorcinol and hydroquinone were isolated, respectively. In the case of the reactions of compounds 4, 5, and 6 with an alcohol solution of HCl, 65, 70, and 82 % trimethylantimony dichloride, and 62 % pyrocatechol, 69 % resorcinol, and 74 % hydroquinone were isolated, respectively.

This work was carried out with financial support from the Russian Foundation for Basic Research (Project No 94-03-08846).

References

- 1. V. A. Dodonov and T. I. Zinov'eva, Metalloorg. Khim., 1992, 5, 1265 [Organomet. Chem. USSR, 1992, 5 (Engl. Transl.)].
- G. A. Rasuvaev, T. G. Brilkina, A. I. Filimonov, E. V. Krasilnikova, and T. I. Zinovyeva, J. Organomet. Chem., 1972, 151.
- 3. E. I. Pokrovskaya, V. A. Dodonov, E. A. Starikova, E. N. Kapustina, and T. M. Shchegoleva, *Zh. Obshch. Khim.*, 1981, **51**, 1247 [*J. Gen. Chem. USSR*, 1981, **51** (Engl. Transl.)].

- 4. Patent 1567584 USSR, Byul. Izobret., 1990, 89 (in Russian).
- 5. 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.)].
- V. A. Dodonov, S. N. Zaburdyaeva, and N. N. Nevkina, Metalloorg. Khim., 1989, 2, 1286 [Organomet. Chem. USSR,

1989, 2 (Engl. Transl.)].

- 7. M. Shindo and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 1969, 5, 77.
- K. A. Kocheshkov, A. P. Skoldinov, and N. N. Zemlyanskii, Metody elementoorganicheskoi khimii. Sur'ma, vismut [Methods of Organometal Chemistry. Antimony, Bismuth], Nauka, Moscow, 1976 (in Russian).

Received July 18, 1994; in revised form December 30, 1994