Organometallic Chemistry

One-step synthesis of the chelate oxides of bis(trialkylantimony) by an oxidative method

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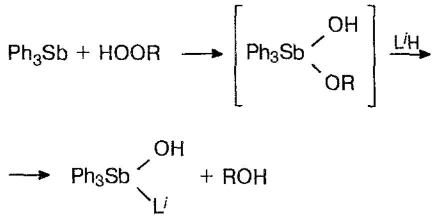
The chelate oxides of bis(trimethylantimony) $(Me_3SbL^i)_2O$ (i = 1 or 2, L^1 — acetylacetonate, L^2 — trifluoroacetylacetonate) and bis(triethylantimony) $(Et_3SbL^1)_2O$ have been obtained in 79—85 % yields by a one-step oxidation of trialkylantimony with *tert*-butylhydroperoxide in the presence of β-diketones in benzene at 20 °C.

Key words: trimethylantimony, triethylantimony, *tert*-butylhydroperoxide, oxidation; β-diketones, acetylacetone, trifluoroacetylacetone, ligands; chelates, synthesis.

A method based on the oxidation of antimony(III) compounds with *tert*-butylhydroperoxide or hydrogen peroxide makes it possible to synthesize various functional derivatives of antimony(V) with the general molecular formula Ph_3SbX_2, where X = Cl, Br, F (see Ref. 1), OB(Ph)O—, $OSiR_2O$—, $OSiR_2OSiR_2O$— (see Ref. 2), OCR_2—R_2CO— (see Ref. 3), and —OOCR, —$OOBu^t$ (see Ref. 4).

In the previous work,[5] we reported that the oxidative method allows one chelate group to be introduced into a triphenylantimony molecule to form hydroxychelate antimony derivatives in high yields (reaction (1)).



$$Ph_3Sb + HOOR \longrightarrow \left[Ph_3Sb\begin{matrix}OH\\OR\end{matrix}\right] \xrightarrow{L^iH} Ph_3Sb\begin{matrix}OH\\L^i\end{matrix} + ROH \qquad (1)$$

R = H, Bu^t; i = 1...3; L^1 is acetylacetonate, L^2 is trifluoroacetylacetonate, and L^3 is pivaloyltrifluoroacetonate

In a continuation of our investigations in the use of the oxidative method in the synthesis of alkyl antimony(III) derivatives, we have studied the reactions of trimethyl- and triethylantimony with *tert*-butylhydroperoxide in the presence of equimolar amounts of acetylacetone and trifluoroacetylacetone. However, instead of the hydroxy derivatives that were expected to form, bis(acetylacetonatotrimethylantimony)oxide, $(Me_3SbL^1)_2O$ (**1**), bis(acetylacetonatotriethylantimony)oxide, $(Et_3SbL^1)_2O$ (**2**), and bis(trifluoroacetylacetonatotrimethylantimony)oxide, $(Me_3SbL^2)_2O$ (**3**), were isolated in 79—85 % yields (reaction (2)).

$$2\,R_3Sb + 2\,Bu^tOOH + 2\,LH \longrightarrow$$
$$\longrightarrow (R_3SbL)_2O + 2\,Bu^tOH + H_2O \qquad (2)$$

R = Me, L = L^1 and L^2; R = Et, L = L^1

The reactions occur in one stage in benzene or ether at room temperature. The yields of the *tert*-butyl alcohol and water are 0.94—0.98 and 0.42—0.47 mol per mol of the starting trialkylantimony, respectively. Traces of

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trialkylantimony oxides, R_3SbO, were found as side-products. It was found that the highest yield of the target products can be achieved by increasing the content of the starting Bu^tOOH and β-diketone 1.5-fold.

The compounds obtained are viscous yellow liquids readily soluble in organic solvents (hexane, benzene, toluene, dioxane, chloroform, THF). They slowly hydrolyze in air and decompose at 124—128 °C under reduced pressure.

The composition and molecular structure of the synthesized chelate oxides of bis(trialkylantimony) **1—3** were confirmed by their molecular weights, elemental analysis (Table 1), and IR spectroscopy data.

The IR spectra exhibit the following absorption bands (cm^{-1}): 560 (ν(Sb—C)); 760—750 (ν(Sb—O—Sb)); 1640, 1600, 1490 (ν(C$\overset{-}{-}$O, C$\overset{-}{-}$C)); 3050—2860 ($\nu_{as}CH_3$); 1410—1390 (δCH_3); 1300 (δCF_3).

To confirm the molecular structure of the obtained compounds, acidolysis with glacial acetic acid was carried out. The reaction was performed in toluene and THF at 60—80 °C (reaction (3)).

$$\begin{aligned}(R_3SbL)_2O + 4\ AcOH \longrightarrow{}& 2\ R_3Sb(OAc)_2 + \\ &+ 2\ LH + H_2O\end{aligned} \qquad (3)$$

Trimethylantimony diacetate (1.86 mol per mol of the starting organometallic compound) and triethylantimony diacetate (1.91 mol) were isolated. Acetylacetone (1.90 mol), trifluoroacetylacetone (1.80 mol), and water (0.94 mol) were determined by chromatography.

Experimental

The IR spectra were recorded on a Specord instrument in a thin layer in the 4000—400 cm^{-1} range.

Bis(acetylacetonatotrimethylantimony)oxide. A mixture of trimethylantimony (5 mmol), *tert*-butylhydroperoxide (5 mmol), and acetylacetone (5 mmol) in benzene was stored for 20 h at 20 °C. Then the tube was opened, and the liquid part was condensed at reduced pressure. In the condensate, *tert*-butyl alcohol and water were determined by GLC. The remaining viscous liquid was washed with hexane. The yield of $(Me_3SbL^1)_2O$ was 80 %.

The other chelate oxides of bis(trialkylantimony) were synthesized analogously. The data of the elemental analysis are given in Table 1.

Table 1. Synthesis of the chelate oxides of bis(trialkylantimony) (20 °C, 20 h)

Compound	Yield (%)	Mol. weight, found / calculated	Found / Calculated (%)		
			C	H	Sb
1	85	556	34.86	6.02	44.22
		548	35.04	5.84	44.53
2	81	621	41.77	9.17	38.19
		632	41.61	9.05	38.61
3	79	624	31.57	4.56	—
		602	31.81	4.32	40.53

Reaction of the chelate oxides of bis(trialkylantimony) with acetic acid. A solution of the chelate oxide of bis(trialkylantimony) (1 mmol) and glacial acetic acid (5 mL) in THF (5 mL) was heated for 15 min over a water bath. Then the liquid part was condensed. The water, acetylacetone, and trifluoroacetylacetone were determined by GLC. After recrystallization, the yield of trimethylantimony diacetate was 90 %.

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