# **Organometallic Chemistry**

## Synthesis of triphenylantimony (hydroxo)diketonates by oxidative methods

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Triphenylantimony (hydroxo)acetylacetonate, (hydroxo)trifluoroacetylacetonate, and (hydroxo)pivaloyltrifluoroacetonate were prepared in 85-98 % yields by oxidation of triphenylantimony with hydrogen peroxide or *tert*-butyl hydroperoxide in the presence of  $\beta$ -diketones.

Key words: triphenylantimony; oxidation with peroxides; antimony complexes.

Halides, acylates, glycolates, and other  $Sb^V$  derivatives of the general formula  $Ph_3SbX_2$  have been prepared previously<sup>1-3</sup> by oxidative methods under mild conditions.

The reaction between triphenylantimony, *tert*-butyl hydroperoxide, and a compound containing an active hydrogen (acids, glycols, *etc.*) occurs in one step (at 20 °C in ether or in a hydrocarbon) to give  $Ph_3SbX_2$  in 70–100 % yield.

It was of interest to use this method for the preparation of novel hydroxo(diketonate) complexes of  $Sb^{V}$ .

A number of  $Sb^V$  acetylacetonates were prepared by the substitution of an acetylacetonate group for a halide atom or an alkoxy group, which occurs throuh the action of acetylacetone or its sodium derivative on  $Sb^V$ compounds, according to the following equation:

 $R_nSbCl_{5-n} + LH \rightarrow R_nSbCl_{4-n}L + HCI.$ 

A this time, the following compounds of the general formula  $R_nSbCl_{4-n}L$  have been synthesized:

R	n	LH*	Reference
Me, Et, Ph	4	$L^{1}H$	4
Ph	3	$L^{1}H$	5
Ph	3	$L^2H$	6
Alk, Ph	2	$L^{1}H$	6
Me, Ph	1	$L^{1}H$	4
<sup>′</sup>	0	$L^{1}H$	4

 $*L^{1}H = MeCOCH_{2}COMe$ ,  $L^{2}H = MeCOCH_{2}COEt$ .

In addition, triphenylantimony (chloro)acetylacetonate and triphenylantimony (hydroxo)acetylacetonate have been prepared by the cleavage of the Sb—O—Sb bond in bis(chlorotriphenylantimony) oxide and in the polymeric triphenylantimony oxide by the action of acetylacetone.<sup>7</sup>

A study of the interaction of triarylantimony and triarylbismuth with organic and organometallic hydroperoxides<sup>8</sup> provided strong evidence that the first step of the process involves the formation of an organoantimony adduct (A).

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One might expect that the reaction of the adduct with enol forms of diketones would make it possible to synthesize chelate-type complexes of  $Sb^{V}$ .

#### **Results and Discussion**

The reaction of triphenylantimony with *tert*-butyl hydroperoxide and acetylacetone (at a 1 : 1 : 1 ratio) was carried out at room temperature in benzene or ether.

 $\begin{array}{rl} \mbox{Ph}_3 \mbox{Sb} + \mbox{Bu}^t \mbox{OOH} + \mbox{LH} \rightarrow \mbox{Ph}_3 \mbox{Sb}(\mbox{OH})\mbox{L} + \mbox{Bu}^t \mbox{OH} \\ & \mbox{1a-c} & \mbox{2a-c} \\ \mbox{1,2: LH} = \mbox{MeC}(\mbox{O})\mbox{CH}_2 \mbox{COMe} (\mbox{a}); \\ \mbox{CF}_3 \mbox{C}(\mbox{O})\mbox{CH}_2 \mbox{COMe} (\mbox{b}); \\ \mbox{CF}_3 \mbox{C}(\mbox{O})\mbox{CH}_2 \mbox{C}(\mbox{O})\mbox{Et} (\mbox{c}) \\ \mbox{CH}_2 \mbox{C}(\mbox{O})\mbox{CH}_2 \mbox{C}(\mbox{O})\mbox{CH}_2 \mbox{C}(\mbox{O})\mbox{C} \mbox{H}_2 \mbox{C} \mbox{O}); \\ \mbox{CF}_3 \mbox{C}(\mbox{O})\mbox{CH}_2 \mbox{C}(\mbox{O})\mbox{Et} (\mbox{c}); \\ \mbox{CF}_3 \mbox{C}(\mbox{O})\mbox{CH}_2 \mbox{C}(\mbox{O})\mbox{Et} \mbox{Et} \mbox{C}); \\ \mbox{CF}_3 \mbox{C}(\mbox{O})\mbox{CH}_2 \mbox{C}(\mbox{O})\mbox{Et} \mbox{Et} \mbox{C}); \\ \mbox{CF}_3 \mbox{C}(\mbox{O})\mbox{C} \mbox{Et} \mbox{C} \mbox{Et} \mbox{C}); \\ \mbox{CF}_3 \mbox{C}(\mbox{O})\mbox{Et} \mbox{Et} \$ 

When the reaction was carried out in the presence of **1a**, triphenylantimony (hydroxo)acetylacetonate (**2a**, yield 90 %) and *tert*-butyl alcohol (89 %) were isolated. No starting triphenylantimony, peroxide, or acetylacetone were found among the reaction products. When ether was used as the solvent, the yields of **2a** and the alcohol were also high (90 and 98 %, respectively), however, some triphenylantimony (6 %) remained unchanged. No benzene was present in the reaction products.

Compound 2a is a colorless crystalline solid, m.p. 169 °C (dec.); the melting point may vary over several degrees depending on the rate of heating. This is in agreement with the data<sup>4</sup> on the decomposition of other Sb<sup>V</sup> acetylacetonates. The IR spectrum of the product coincided with the spectrum of compound 2a prepared by us from triphenylantimony oxide and acetylacetone in a 75 % yield.

In contrast to earlier investigations,<sup>7</sup> we carried out the reaction in THF (20 °C, 20 h) at a stoichiometric ratio between the reactants using soluble dimeric triphenylantimony oxide (mol. weight 688 in benzene) with m.p. 214–216 °C, which had been prepared from triphenylantimony and *tert*-butyl hydroperoxide in THF.

The chelate structure of compound 2a is confirmed by the fact that it does not react with hydroxylamine hydrochloride with evolution of HCl. The IR spectrum (a pellet with KBr) exhibits intense absorption bands of conjugated C--C and C-O bonds of the chelate ring (1575, 1550, 1495, and 1350 cm<sup>-1</sup>), while the band at 1715 cm<sup>-1</sup> typical<sup>4</sup> of an unchelated acetylacetonate group at a Sb<sup>V</sup> atom is absent from the spectrum. These data are somewhat different from those reported for suspensions in vaseline oil.<sup>7</sup>

Fluorinated diketones 1b and 1c afford under similar conditions (toluene, 2–24 h) the corresponding fluorine-containing triphenylantimony (hydroxo)diketonates 2b and 2c in 85–93 % yields (Table 1).

**Table 1.** Characteristics of (hydroxo)chelates of triphenylantimony prepared by the oxidation of triphenylantimony with *tert*-butyl hydroperoxide or hydrogen peroxide

Com-	Com- Yield (%)		M.p./°0	C <u>Fou</u>	Found (		Mol. weight	
pound	Bu <sup>t</sup> OOH	H <sub>2</sub> O <sub>2</sub>	(dec.)	Calculated		(70)	<u>Found</u>	
				С	Н	Sb	Calculated	
2a	90	98	169	<u>57.26</u>	<u>4.90</u>	24.97	<u>461</u>	
				58.88	4.94	25.95	469	
2b	93	92	150	<u>50.82</u>	<u>4.10</u>		<u>505</u>	
				52.80	3.85	23.27	523	
2c	85	96	116	<u>55.19</u>	<u>4.78</u>	<u>20.05</u>	<u>557</u>	
				55.25	4.64	21.54	564	

Vibrations of the C—C and C—O bonds are responsible for the IR absorption bands at 1670, 1615 cm<sup>-1</sup> (2b) and 1700, 1660 cm<sup>-1</sup> (2c) that are shifted to higher frequencies with respect to those in the spectrum of  $Ph_3Sb(OH)L^1$  due to the effect of the electron-withdrawing trifluoromethyl groups.<sup>9</sup>

All of the Sb<sup>V</sup> compounds obtained are stable when stored for 2 h in acetone or THF containing 5 % water. After this, the melting points of the compounds did not change.

In special runs we showed that triphenylantimony does not react with diketones in the absence of *tert*-butyl hydroperoxide, and diketones do not react with *tert*-butyl hydroperoxide without triphenylantimony.

Hydroxo chelates of triphenylantimony 2a-c were also prepared by oxidation of triphenylantimony with hydrogen peroxide in the presence of  $\beta$ -diketones. The reaction was carried out in an ether—THF solvent mixture, 1 : 1, v/v (20 °C, 20 h). The products were obtained in 92–98 % yields and did not differ from those prepared using *tert*-butyl hydroperoxide, according to their melting points, IR spectra, and molecular weights (see Table 1).

Thus, stable triphenylantimony(v) (hydroxo)diketonates were synthesized by the oxidative method. We believe that the fact that these  $Sb^V$  hydroxo chelates are stable, in contrast to adduct **A** and other hydroxo derivatives of  $Sb^V$ , is due to the stability of the six-coordinate state of the  $Sb^V$  atom.

The attempts to introduce a second acetylacetonate group were unsuccessful, apparently due to the instability of seven-coordinate chelates of  $Sb^{V}$ .

We studied acylation of the resulting  $Sb^{V}$  (hydroxo)diketonates. One might expect that the reaction would involve both the hydroxyl and the diketonate group.



We showed that for the acetylacetonate derivative of  $Sb^V$  both reaction routes are in fact equally probable. For example, treatment of triphenylantimony (hydroxo)acetylacetonate with acetic acid (1 : 1) in benzene (20 °C, 40 h) afforded acetylacetone in a yield of 0.51 mole per mole of the starting  $Sb^V$  compound. The acid was consumed completely (Table 2). Heating triphenylantimony (hydroxo)diketonates with excess acetic or benzoic acid in toluene, benzene, ether, or THF for 10 min at 60–80 °C resulted in the complete replacement of the hydroxyl and diketonate groups and gave triphenylantimony diacylates.

$$2\mathbf{a-c} + 2\mathrm{RCO}_{2}\mathrm{H} \rightarrow \mathrm{Ph}_{3}\mathrm{Sb}(\mathrm{O}_{2}\mathrm{CR})_{2} + \mathrm{LH} + \mathrm{H}_{2}\mathrm{O}$$
$$\mathrm{R} = \mathrm{Me}, \mathrm{Ph} \qquad \mathbf{3a-c}$$

The resulting diacylates 3a-c were identified on the basis of their melting points.<sup>6</sup> Their yields amounted to 0.87-0.95 mole and the yields of diketones were 0.82-0.97 mole (see Table 2). Acetylacetone and trifluoroacetylacetone were determined by chromatography and pivaloyltrifluoroacetone was determined by a method based on its interaction with hydroxylamine hydrochloride.<sup>10</sup>

### Experimental

IR spectra in the region from 4000 to 400  $cm^{-1}$  were recorded on a Specord instrument in KBr pellets.

Preparation of triphenylantimony (hydroxo)acetylacetonate (2a). A solution of 5 mmol of Bu<sup>t</sup>OOH in 2 mL of benzene was added dropwise over a period of 30 min to a vigorously stirred solution of 5 mmol of triphenylantimony and 5 mmol of acetylacetone in 10 mL of benzene cooled with cold water. After 2 h, the volatiles were distilled off, and Bu<sup>t</sup>OH was determined in the condensate by GLC. Its yield was 4.45 mmole (no acetylacetone or Bu<sup>t</sup>OOH were detected). 0.3 mmol of unchanged triphenylantimony was extracted from the solid residue by cold hexane. 2a (4.5 mmol) insoluble in hexane was twice recrystallized from a chloroform—hexane or a toluene—hexane mixture. The elemental analysis data are listed in Table 1.

Compounds 2b and 2c were prepared in a similar way (the reactions were carried out in toluene, see Table 1). In the reactions that involved hydrogen peroxide, the latter was used as an 0.8 M ethereal solution, and the reactions were carried out in a mixture of ether and THF (see Table 1).

Acylation of triphenylantimony (hydroxo)diketonates. A solution of 1 mmol of chelate and 1 g of an acid in 5 mL of a solvent was heated on a hot water bath for 10 min. The volatiles were distilled off, and water, acetylacetone, and trifluoroacetylacetone were determined by GLC (see Table 2). To determine pivaloyltrifluoroacetone, <sup>10</sup> 40 mL of a 0.5 N solution of NH<sub>2</sub>OH · HCl in 60 % aqueous methanol was added to the condensate, the mixture was stirred for 1 h, and its potentiometric titration with a 0.1 N alkali solution was carried out. The resulting triphenylantimony diacylates were

Table 2. Yields	of t	the pro	ducts of	the	react	lions	of
triphenylantimony	(hyd	roxo)dik	tetonates	with	acids	(1 :	10,
60-80 °C, 0.2 h)							

The starting compound	RCO <sub>2</sub> H	Solvent	Yields of the products (mole per mole of the starting compound)			
		-	Ph <sub>3</sub> Sb(O <sub>2</sub> CR) <sub>2</sub>	LH	H <sub>2</sub> O	
2a	PhCO <sub>2</sub> H AcOH AcOH AcOH*	THF Ether Benzene Benzene	0.75 0.95	0.92 0.82 0.97 0.51	1.12	
2b 2c	PhCO <sub>2</sub> H AcOH PhCO <sub>2</sub> H AcOH	THF Toluene THF THF	0.87 	0.86 0.85**	1.12 	

\* A 1 : 1 ratio between  $Ph_3Sb(OH)L^1$  and AcOH, 20 °C, 40 h. \*\* Determined by oximation.

identified from their melting points and the melting point of a mixture with an authentic sample.<sup>6</sup>

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