Organometallic Chemistry

Synthesis and structures of triphenylantimony oximates

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The reactions of triphenylantimony or trimethylantimony with *tert*-butyl hydroperoxide in the presence of acetone oxime, acetophenone oxime, cyclohexanone oxime, or benzaldehyde oxime afforded monomeric triorganoantimony oximates $Ph_3Sb(ON{=}CMe_2)_2$, $Ph_3Sb(ON{=}CMePh)_2$, $Ph_3Sb[ON{=}C(CH_2)_5]_2$, $Ph_3Sb(ON{=}CHPh)_2$, and $Me_3Sb(ON{=}CMe_2)_2$ in 87—96% yields. X-ray diffraction analysis demonstrated that $Ph_3Sb(ON{=}CMe_2)_2$ and $Ph_3Sb(ON{=}CHPh)_2$ have trigonal-bipyramidal structures. An analogous reaction with dimethylglyoxime gave rise to polymeric triphenylantimony dioximate in 96% yield. The reaction with butane-2,3-dione monoxime yielded chelate cyclic bis(triphenylantimony) oxides.

Key words: triphenylantimony oximates, trimethylantimony oximates, oximes, acetone oxime, acetophenone oxime, cyclohexanone oxime, benzaldoxime, butane-2,3-dione oxime, dimethylglyoxime, *tert*-butyl hydroperoxide, molecular structure, X-ray diffraction analysis.

The structural chemistry of the triorganoantimony derivatives R_3SbX_2 with oxygen-containing functional groups has been extensively developed in recent years.

Antimony compounds with derivatives of monobasic OH-acids (*viz.*, monohydric alcohols and phenols, monocarboxylic acids, hydroperoxides, and sulfonic acids) have a trigonal-bipyramidal configuration with the monodentate ligands X in the axial positions.[1,2] The structures of derivatives of dibasic OH-acids (*viz.*, glycols, dihydroxybenzenes, dicarboxylic acids, and dibasic inorganic acids) are determined by the mutual arrangement of the OH groups in dibasic acid HO—Y—OH. Polymeric or cyclic oligomeric molecular structures of the general formula $(—R_3Sb—OYO—)_n$ are most commonly occurring. The trigonal-bipyramidal fragments are linked to each other, apparently, through the axial Sb—O bonds.[1,3,4]

However, in the case of α-glycols and pyrocatechol, the OH groups in dibasic OH-acids are located in close proximity, which prevents both O ligands from occupy-

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ing axial positions. As a result, both these ligands are located in the equatorial plane and the configuration of the Sb atom changes from a trigonal bipyramid to an octahedron. The vacant axial position is occupied by a molecule of the solvent or an electron-donating additive. These compounds exist as monomers.[5]

Triorganoantimony derivatives with β-diketones in which the Sb atom has a distorted octahedral configuration and the ligand is bidentate or even tridentate have attracted the particular attention.[6]

As part of continuing studies in this field, it was of interest to study the structures of triphenylantimony derivatives with oximes of mono- and dicarbonyl compounds serving as mono- and bidentate O-ligands of penta- and hexacoordinated antimony.

Results and Discussion

Triorganoantimony(v) oximates are synthesized by the reactions of sodium salts of oximes with triorganoantimony(v) dihalides (reaction (1)), which are preliminarily prepared by halogenation of triorganoantimony(III).[7]

$$R_3SbX_2 + 2\ NaON{=}CR'R'' \rightarrow$$
$$\rightarrow R_3Sb(ON{=}CR'R'')_2 + 2\ NaX. \qquad (1)$$

R = Me, Et, Ph; X = Cl, Br;
R′, R″ = Me, Et, Pr, Ph, *cyclo*-C_6H_{10}

Previously, the following three-step scheme of the synthesis through intermediate antimony alkoxides has been employed:[1]

$$R_3Sb \rightarrow R_3SbCl_2 \rightarrow R_3Sb(OR)_2 \rightarrow$$
$$\rightarrow R_3Sb(ON{=}CR'R'')_2. \qquad (2)$$

We synthesized these compounds with the use of a one-step oxidative procedure, which allows one to prepare different functional antimony(v) derivatives in high yields at room temperature starting directly from triorganoantimony.[8] The reactions of Ph_3Sb with aldehyde and ketone oximes were carried out in the presence of *tert*-butyl hydroperoxide taken in a molar ratio of 1 : 2 : 1, respectively,[9] according to the following scheme

$$R_3Sb + 2\ HON{=}CR'R'' + Bu^tOOH \rightarrow$$
$$\rightarrow R_3Sb(ON{=}CR'R'')_2 + Bu^tOH + H_2O. \qquad (3)$$

R = Ph, Me; R′, R″ = H, Alk, Ph

Bis(acetone oximato)triphenylantimony (**1**), bis(benzaldoximato)triphenylantimony (**2**), bis(cyclohexanone oximato)triphenylantimony (**3**), bis(acetophenone oximato)triphenylantimony (**4**), and bis(acetone oximato)trimethylantimony (**5**) were prepared based on oximes of monocarbonyl compounds, *viz*., acetone, benzaldehyde, acetophenone, and cyclohexanone, respectively. Products **1—5** were obtained in 87—96% yields (Table 1).

These compounds were isolated as colorless crystalline compounds stable to atmospheric air and moisture. All compounds are readily soluble in chloroform and ether. Oximates **1** and **3** are also soluble in alcohols and aromatic hydrocarbons. Oximate **5** is soluble in all usual solvents. The molecular weights, which were determined by the cryoscopic method in benzene, and the results of analysis for the metal content, are in good agreement with the calculated values (see Table 1).

The structures of the compounds were studied by IR spectroscopy, ^1H and ^{13}C NMR spectroscopy, and X-ray diffraction analysis.

The IR spectra of oximates **1—4** have a Sb—Ph stretching absorption band at 450—430 cm^{-1}. The IR spectrum of compound **5** shows a Sb—Me stretching absorption band at 580 cm^{-1}.[10] In the spectra of all oximates **1—5**, the C=N stretching absorption bands are observed in the region of 1615—1570 cm^{-1}, *i.e.*, they are shifted to the low-frequency region by 40—50 cm^{-1} as compared to the corresponding bands for free oximes.[7] In the region of 3400—3000 cm^{-1}, broad absorption bands of the OH groups of free oximes are lacking.

The ^1H NMR spectrum of oximate **4** has a singlet (δ 2.36) of the Me group (Table 2). Consequently, the acetophenone oximate ligands exist only in one of the two possible (*Z* or *E*) forms. The spectrum of acetone oximate **1** shows two singlets for the protons of the Me

Table 1. Characteristics of triorganoantimony oximates $R_3Sb(ON{=}CR'R'')_2$ (**1—5**)

Compound	R	R′	R″	Yield (%)	M.p.* /°C	Found/Calculated	
						Sb (%)	M
1	Ph	Me	Me	87	115 (88—90)[1]	24.3/24.5	492/497
2	Ph	H	Ph	98	188	20.6/20.5	471/469
3	Ph	$(CH_2)_5$		89	121	21.3/21.1	574/577
4	Ph	Me	Ph	92	157	19.7/19.6	627/621
5	Me	Me	Me	96	40 (40)[7]	39.6/39.2	308/311

* The literature data are given in parentheses.

Table 2. ^{1}H and ^{13}C NMR spectra of triorganoantimony oximates **1—5** (27 °C)*

Compound	δ						
	^{1}H				^{13}C		
	H—C=	Me—C=N	Me—Sb	*cyclo*-C_6H_{10}	C—Sb	C=N	C—(C=N)
1	7.10—8.20	1.52, 1.90	—	—	—	—	—
2	7.15—8.20	—	—	—	—	—	—
3	7.15—8.20	—	—	1.25—2.70	—	—	—
4	7.10—8.22	2.36	—	—	—	—	—
5	—	1.77, 1.82	1.58	—	5.11	154.20	21.85, 14.70

* The spectra of compounds **1—4** were recorded on a Tesla BS-567 A spectrometer. The spectrum of compound **5** was measured on a Bruker CXP-200 spectrometer.

groups with equal intensities, which is indicative of the nonequivalence of the Me groups at the C=N bond. This is confirmed by the fact that the integral intensity ratio of the signals for the protons of two methyl and three phenyl groups is 6 : 15. An analogous nonequivalence of the Me groups, though less pronounced, is observed in the spectrum of oximate **5**. The nonequivalence of the alkyl groups in free oximes and their metal derivatives has been noted previously, the splitting of the NMR signals being dependent on the composition of the compound and the conditions of the measurements of the NMR spectra.[7] In the region δ 7.10—8.22, the signals for the protons of all phenyl groups bound to the Sb atom or involved in the oximate ligands are observed.

The ^{13}C NMR spectrum of trimethylantimony acetone oximate **5** confirmed the nonequivalence of the Me groups of the acetone oximate fragment (see Table 2).

According to the results of X-ray diffraction analysis, the pentacoordinated Sb atom in molecules **1** and **2**

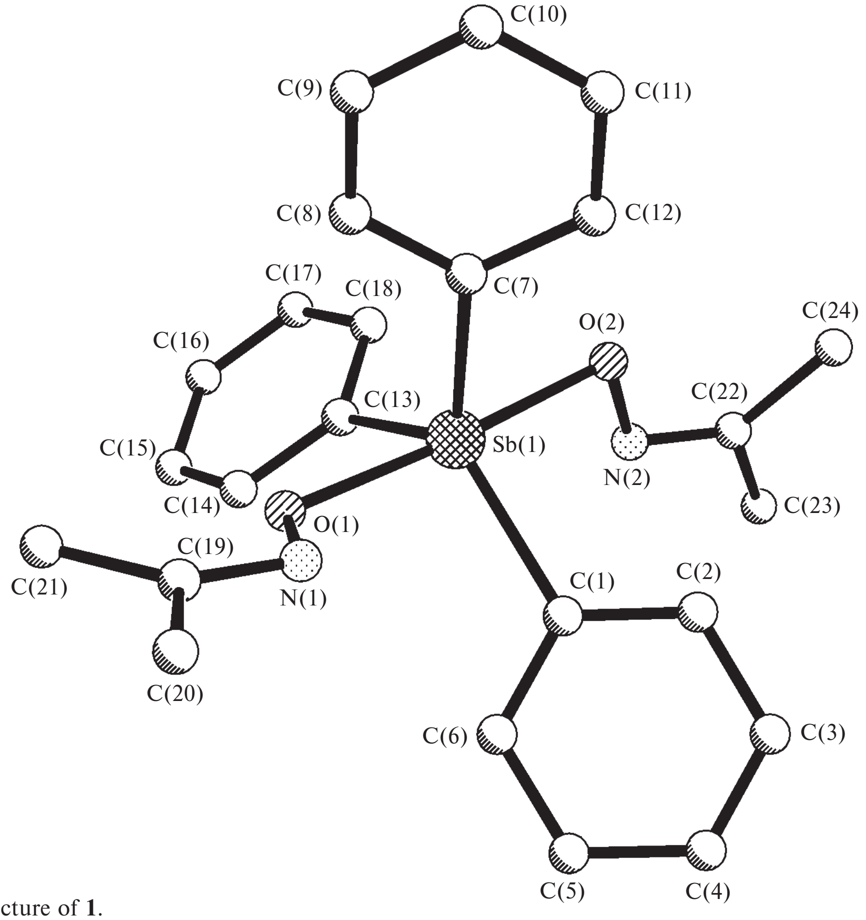


Fig. 1. Molecular structure of **1**.

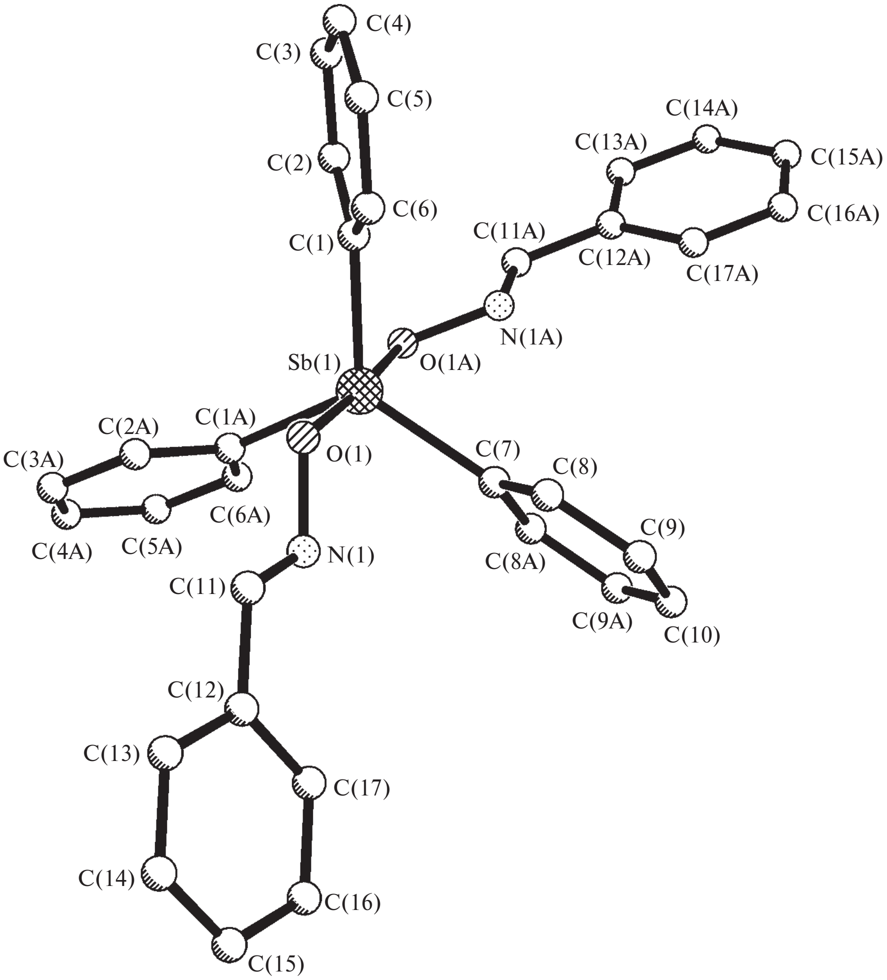


Fig. 2. Molecular structure of **2**.

(Figs. 1 and 2) has a distorted trigonal-bipyramidal coordination with three Ph groups in the equatorial positions and two monodentate iminoxy groups in the axial positions. In the crystal structures, molecules **1** are located in general positions, whereas molecules **2** have the symmetry C_2 and are located on twofold axes passing through the Sb(1) and C(7) atoms. The axial O(1)—Sb(1)—O(2) (176.0(2)°) and O(1)—Sb(1)—O(1A) (176.5(1)°) angles are close to 180°. In both compounds (**1** and **2**), the sum of the equatorial C(Ph)—Sb—C(Ph) angles is 360°. The Sb—C(Ph) distances in molecules **1** and **2** are in the ranges of 2.113(6)—2.120(6) and 2.106(3)—2.108(4) Å, respectively (Tables 3 and 4). The benzene rings are noncoplanar. The Sb—O(1) and Sb—O(2) distances in molecule **1** (2.044(4) and 2.050(4) Å, respectively) are somewhat smaller than the corresponding distances in molecule **2** (2.065(2) Å) and are substantially smaller than those in furfurol oximate (2.150(3) Å)[11] and, particularly, in tetraphenylantimony cyane oximates (2.226(4)—2.259(1) Å)[12] studied previously. Apparently, this is associated with a more covalent character of the bond between the iminoxy group and the metal atom in oximates **1** and **2** and, on the contrary, with a more ionic character of tetraphenylantimony oximates.[11,12]

Table 3. Selected bond lengths (*d*) and bond angles (ω) in molecule **1**

Bond	*d*/Å	Angle	ω/deg
Sb(1)—O(1)	2.044(4)	O(1)—Sb(1)—O(2)	176.0(2)
Sb(1)—O(2)	2.050(4)	O(1)—Sb(1)—C(7)	91.3(2)
Sb(1)—C(7)	2.113(6)	O(2)—Sb(1)—C(7)	87.8(2)
Sb(1)—C(13)	2.119(7)	O(1)—Sb(1)—C(13)	84.8(2)
Sb(1)—C(1)	2.120(6)	O(2)—Sb(1)—C(13)	92.2(2)
O(1)—N(1)	1.410(7)	C(7)—Sb(1)—C(13)	117.5(2)
O(2)—N(2)	1.418(6)	O(1)—Sb(1)—C(1)	93.4(2)
N(1)—C(19)	1.269(9)	O(2)—Sb(1)—C(1)	90.5(2)
N(2)—C(22)	1.249(8)	C(7)—Sb(1)—C(1)	120.8(2)
C(19)—C(21)	1.497(12)	C(13)—Sb(1)—C(1)	121.7(2)
C(19)—C(20)	1.504(11)	N(1)—O(1)—Sb(1)	113.1(4)
C(22)—C(23)	1.493(9)	N(2)—O(2)—Sb(1)	106.8(3)
C(22)—C(24)	1.500(10)	C(19)—N(1)—O(1)	111.5(6)
		C(22)—N(2)—O(2)	113.6(5)

Table 4. Selected bond lengths (d) and bond angles (ω) in molecule **2**

Bond	d/Å	Angle	ω/deg
Sb(1)—O(1)	2.065(2)	O(1)—Sb(1)—O(1A)	176.46(11)
Sb(1)—C(1)	2.106(3)	O(1)—Sb(1)—C(1)	86.30(9)
Sb(1)—C(7)	2.108(4)	O(1A)—Sb(1)—C(1)	91.87(9)
O(1)—N(1)	1.399(3)	C(1)—Sb(1)—C(1A)	117.97(13)
N(1)—C(11)	1.259(4)	O(1)—Sb(1)—C(7)	91.77(5)
C(11)—C(12)	1.460(4)	C(1)—Sb(1)—C(7)	121.02(7)
		N(1)—O(1)—Sb(1)	110.9(2)
		C(11)—N(1)—O(1)	112.2(2)

In molecule **1**, the dimethyliminoxy groups O(1)N(1)C(19)C(20)C(21) and O(2)N(2)C(22)C(23)C(24) are planar (the average deviations of the atoms from the planes are 0.02 and 0.007 Å, respectively) and the dihedral angle between their mean planes is 63.5°. The phenyliminoxy groups in molecule **2** are also planar (to within ±0.026 Å) and the dihedral angle between the mean planes of these groups is 70.1°.

The O—N distances in molecules **1** and **2** have close values (1.410(7) and 1.418(6) Å in **1** and 1.399(3) Å in **2**). Like the O—N distances, the C—N distances in molecules **1** and **2** vary within a narrow range of 1.249(8)—1.269(9) Å.

The Sb(1)—O(1)—N(1) (Sb(1)—O(2)—N(2)) and O(1)—N(1)—C(19) (O(2)—N(2)—C(22)) angles in molecule **1** are 113.1(4)° (106.8(3)°) and 111.5(6)° (113.6(5)°), respectively, and are close to the corresponding angles in molecule **2** (Sb(1)—O(1)—N(1), 110.9(2)°; O(1)—N(1)—C(11), 112.2(2)°).

We believe that monomeric antimony derivatives with oximes of other monocarbonyl compounds also have trigonal-bipyramidal structures.

In line with the goal to be sought, we synthesized the Sb^V derivative with dimethylglyoxime. In the reactions with equimolar amounts of Ph_3Sb and Bu^tOOH at room temperature, dimethylglyoxime acts as a dibasic OH-acid to form triphenylantimony dimethylglyoximate (**6**) in 96% yield (reaction (4)).

$$n\,Ph_3Sb + n\,Bu^tOOH + n\,HON{=}C(Me)C(Me){=}NOH \to$$
$$\to \underset{\mathbf{6}}{[-Ph_3SbON{=}C(Me)C(Me){=}NO-]_n} +$$
$$+\, n\,Bu^tOH + n\,H_2O. \qquad (4)$$

Compound **6** is a colorless noncrystalline solid compound, which is insoluble in organic solvents and decomposes without melting at 230—240 °C. Under the action of concentrated HCl, compound **6** underwent acidolysis to eliminate Ph_3SbCl_2 in *ca.* 100% yield:

$$\underset{\mathbf{6}}{[-Ph_3SbON{=}C(Me)C(Me){=}NO-]_n} + 2n\,HCl \to$$
$$\to n\,Ph_3SbCl_2 + n\,HON{=}C(Me)C(Me){=}NOH. \qquad (5)$$

The IR spectrum of compound **6** has absorption bands at 1550 and 470 cm^{-1} assigned to the stretching vibrations of the C=N and Sb—Ph groups, respectively, whereas the absorption band of the free OH group is not observed.

Based on the results obtained, we assume that, unlike the well-known transition metal dimethylglyoximates, triphenylantimony dimethylglyoximate has a polymeric structure. The cobalt(II) and nickel(II) complexes with dimethylglyoxime are brightly colored mononuclear chelates in which both ligands are bound to one transition metal atom through four N atoms.[13] In addition, the metal atom in cobalt(II) and nickel(II) complexes with 1,2-diphenylethane-1,2-dione dioxime can be coordinated by one ligand through one N atom and one O atom.[14]

In our opinion, the preparation of the iminoxy derivative of triphenylantimony with diacetyl (butane-2,3-dione) monoxime was of particular interest. In this case, unlike the above-considered triphenylantimony derivatives with oximes of monocarbonyl compounds **1—5**, one would expect the formation of a hexacoordinated antimony derivative *via* chelation of the ligand to the central metal atom or the formation of a heptacoordinated antimony compound of the R_3SbX_2 type.

The synthesis was carried out by the reaction of diacetyl monoxime with Ph_3Sb in the presence of Bu^tOOH taken in a molar ratio of 1 : 1 : 1 in a 1 : 2 hexane—isopropyl alcohol mixture. A colorless compound thus obtained is readily soluble in ether, chloroform, and aromatic hydrocarbons. This compound melted with decomposition in an open tube at 146—161 °C (depending on the rate of heating). The molecular weight (cryoscopy, benzene) is 954. The data obtained are indicative of the formation of bis(iminoxytriphenylantimony) oxide in 86% yield according to reactions (6) and (7).

$$Ph_3Sb + Bu^tOOH + HX \to Bu^tOH + Ph_3Sb(OH)X \qquad (6)$$
$$HX = Me{-}C(NOH){-}C(O){-}Me$$

$$2\,Ph_3Sb(OH)X \to (Ph_3SbX)_2O + H_2O \qquad (7)$$

The calculated molecular weight is 922. Under the action of concentrated HCl, Ph_3SbCl_2 was obtained in *ca.* 100% yield with respect to the starting $(Ph_3SbX)_2O$.

According to the literature data, triphenylantimony(v) monohydroxides $Ph_3Sb(OH)X$, which contain not only the OH group but also halide,[1] carboxylate, β-diketonate,[10] or other groups, are unstable and readily undergo intermolecular dehydration to form the bridging Sb—O—Sb bond.

The IR spectrum of the resulting compound has an absorption band at 440 cm^{-1} (ν(Sb—Ph)). The absorption band at 1660 cm^{-1} belongs to vibrations of the carbonyl group, which is involved in conjugation with the

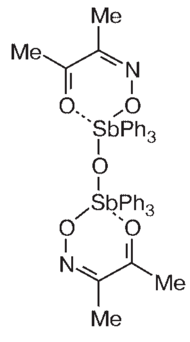
C=N group and coordinated to the Sb atom. Its frequency is close to the corresponding value (1680 cm^{-1}) for individual diacetyl monoxime in which conjugation occurs. The absorption band of the free OH group is not observed in the spectrum.

The ^{1}H NMR spectrum shows six singlets of the Me-groups (δ 1.62—1.97) along with a multiplet for the protons of the Ph groups (δ 7.2—8.1). The ratio between the overall integral intensities of the signals for the protons of the Ph and Me groups is 15 : 6, which counts in favor of the proposed general formula $(Ph_3SbX)_2O$. The above-mentioned six signals of the Me groups can be easily divided into three pairs (δ 1.62 and 1.71; 1.75 and 1.97; 1.79 and 1.95). The integral intensities of the signals within each pair are equal, whereas the intensities for the pairs differ from each other. Hence, it can be concluded that there are three types of binding of the ketoximate ligands MeC(NO)—C(O)Me to the Ph_3Sb groups. Each type includes one Me group bound to the stronger electron-withdrawing carbonyl C=O fragment and one Me group bound to the weaker electron-withdrawing azomethine fragment C=N.

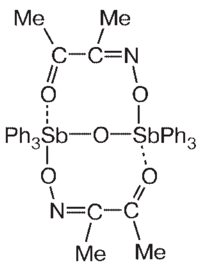
The ^{13}C NMR spectrum of this compound shows three signals for the nonequivalent azomethine C atoms (δ 156.2, 157.0, and 157.7), three signals for the nonequivalent carbonyl C atoms (δ 199.6, 199.7, and 199.8), and a group of signals for the nonequivalent methyl C atoms (δ 8.07, 8.40, 24.48, 24.67, and 24.77).

Based on the molecular weights and the data from IR and NMR spectroscopy, three types of bis-triphenylantimony oxide ketoximates (**A**—**C**) can be proposed.

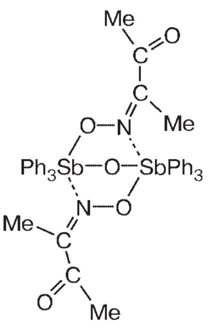
First, the oximate ligand can close the six-membered chelate ring at each Sb atom (**A**), as has been proved previously[6] for triorganoantimony β-diketonates. Second, the ligand can form bridging bonds between the Sb atoms through both the O atoms of the iminoxy group and the carbonyl group (**B**), which is accompanied by the closure of the bicycle. Third, bridging bonds between the Sb atoms can be formed with the participation of the O atom and the N atom of the iminoxy group without the involvement of the carbonyl group (**C**). Recently, the latter structural type has been found[15] in μ-oxobis[(furfuraldoximato)triphenylantimony] studied by X-ray diffraction analysis. For all these types of coordination, the intensities of the signals for the protons of the Me substituent at the C=O group must be equal to the intensities of the signals for the protons of the Me substituent at the imine group. Actually, this situations is observed in the ^{1}H NMR spectrum. At the moment, the reliable assignment of all signals in the NMR spectra is difficult to make. The calculated molecular weight for the complexes **A**—**C** (922) is close to the experimental value (954).



A



B



C

Probably, the above-considered oxidative procedure afforded a mixture of chelate cyclic bis(triphenylantimony) oxide ketoximates. One would expect that a twofold increase in the amount of the starting diacetyl oxime in the course of the synthesis will give rise to triphenylantimony bis(oximate) of the Ph_3SbX_2 type. However, contrary to the expectations, we isolated the same bis(triphenylantimony) oxide $(Ph_3SbX)_2O$. This fact supports the conclusion that this structure is more favorable. Previously, we have demonstrated[6,10] that the oxidative one-step synthesis of β-diketonate derivatives of triphenyl- and trialkylantimony always yielded antimony(v) monodiketonates (independently of the amount of the starting diketone).

Experimental

The IR spectra were recorded on a Specord IR-75 spectrometer in Nujol mulls in the region of 4000—400 cm^{-1}. The ^{1}H and ^{13}C NMR spectra were measured on Bruker CXP-200 (200 MHz) and Tesla BS-567 A (100 MHz) spectrometers using HMDS as the internal standard and $CDCl_3$ as the solvent.

Triphenylantimony,[2] *tert*-butyl hydroperoxide,[16] benzaldehyde oxime, acetone oxime, acetophenone oxime,[17] diacetyl monoxime, and dimethylglyoxime[18] were synthesized according to known procedures.

Bis(acetone oximato)triphenylantimony (1). A solution of *tert*-butyl hydroperoxide (2 mmol) in hexane (5 mL) was added with continuous stirring to a solution of Ph_3Sb (2 mmol) and acetone oxime (4 mmol) in hexane (20 mL) during 20 min. The mixture was kept at ~20 °C for 2 h. The precipitate that formed was separated, washed with hexane, and dried. Compound **1** was obtained in 86% yield. The physicochemical parameters and the NMR spectroscopic data for compound **1** are given in Tables 1 and 2, respectively.

Triphenylantimony derivatives with aldehyde and ketone oximes **2—4** were prepared analogously in a benzene solution. The derivatives with dimethylglyoxime and diacetyl monoxime were prepared in a 1 : 2 mixture of hexane and isopropyl alcohol.

Bis(acetone oximato)trimethylantimony (5). *tert*-Butylhydroperoxide (2 mmol) and acetone oxime (4 mmol) were placed in a tube and dissolved in hexane (20 mL). Then calcined Na_2SO_4 was added. The resulting mixture was degassed and Me_3Sb (2 mmol) was recondensed into this tube under reduced pressure. Then the mixture was kept at ~20 °C for 2 h and the liquid components were distilled off after which the residue slowly crystallized. Compound **5** was obtained in 96% yield.

X-ray structure study of the crystals of the compounds $Ph_3Sb(ONCMe_2)_2$ (**1**) and $Ph_3Sb(ONCHPh)_2$ (**2**) was carried out on a four-circle Siemens P3/PC diffratometer (graphite monochromator, Mo-Kα radiation, $\theta/2\theta$ scanning technique). The crystals of **1** and **2** are monoclinic and tetragonal, respectively, at 20 °C a = 9.332(2) and 16.731(5) Å, b = 16.008(3) and 16.731(5) Å, c = 15.743(3) and 19.867(6) Å, β = 99.78(2)°, V = 2318(1) and 5562(3) Å^3, space groups $P2_1/n$ (Z = 4) and $I4_1/a$ (Z = 8), d_{calc} = 1.425 and 1.417 g cm^{-3} for compounds **1** and **2**, respectively. The structures of complexes **1** and **2** were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The positions of the H atoms of the Ph groups in molecule **1** and all H atoms in molecule **2** were revealed from difference electron density syntheses and refined with isotropic thermal parameters. The positions of the H atoms of the Me groups in molecule **1** were calculated from geometric considerations (C—H 0.96 Å) and refined using the riding model. The final R factors for complexes **1** and **2** were R = 0.056 and 0.032, R_w = 0.107 and 0.073, S = 1.04 and 1.06 based on 4091 and 3160 reflections with $I > 2\sigma(I)$, respectively. All calculations were carried out with the use of the SHELX-97 program packages.[19] The selected bond lengths and bond angles in molecules **1** and **2** are given in Tables 3 and 4, respectively. The atomic coordinates were deposited with the Cambridge Structural Database.

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