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New Preparation Method of Chlorotriphenylantimony Aryloxides $Ph_3SbCl(OAr)$

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Abstract—The reaction of bis(2,6-dichlorophenoxo)triphenylantimony with triphenylantimony dichloride gave chloro(2,6-dichlorophenoxo)triphenylantimony $Ph_3SbCl(OC_6H_3Cl_2\text{-}2,6)$ (**I**). 2,6-Dichlorophenoxotetraphenylantimony $Ph_4Sb(OC_6H_3Cl_2\text{-}2,6)$ (**II**) was prepared from pentaphenylantimony and bis(2,6-dichlorophenoxo)triphenylantimony. According to X-ray diffraction data, the antimony atoms in **I** and **II** have a distorted trigonal-bipyramidal coordination with the following axial: OSbCl, 179.59(5)° (**I**); CSbO, 178.20(14)° (**II**); the equatorial angles are 115.72(9)°–124.87(10)° (**I**) and 111.43(18)°–123.18(19)° (**II**); the equatorial bond lengths are Sb–C, 2.099(3)–2.111(2) Å (**I**), 2.111(4)–2.122(5) Å (**II**); and the axial bond lengths are Sb–Cl, 2.4740(7) Å; Sb–O, 2.0802(16) Å (**I**); Sb–O, 2.237(3) Å; and Sb–C, 2.167(4) Å (**II**) (CIF files CCDC no. 998625 for **I** and no. 1010553 for **II**).

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INTRODUCTION

Despite the large structural diversity of organic compounds of antimony, some types are presented in the literature as only few examples, in particular, mixed-ligand antimony(V) derivatives Ar_3SbXY (X and Y are electronegative groups). Only one aryloxohalotriphenylantimony was reported, namely, $Ph_3SbCl(OC_6H_2Br_3\text{-}2,4,6)$, prepared from μ-oxo-bis(chlorotriphenylantimony) and 2,4,6-tribromophenol [1]. Our attempts to prepare other antimony compounds of this type according to the same path did not always give the target product; therefore, to study the properties and especially the structure of aryloxohalotriphenylantimony, a more reliable method of synthesis was required.

A known efficient method of synthesis of heteroorganic compounds is based on the ligand redistribution reaction [2]. These reactions are successfully used to prepare organic antimony derivatives and involve equimolar amounts of pentaarylantimony Ar_5Sb and Ar_3SbX_2, which react under mild conditions to give Ar_4SbX (X = Br, Cl, SCN [3], OAr' [4], OC(O)R [5], OSO_2R [6], F, NO_3 [7], ON = CRR' [8]) in high yields. The reactions occur in solutions of aromatic hydrocarbon at room temperature, unlike, for example, organic silicon, germanium, and tin derivatives, which are synthesized upon long-term heating of the reaction mixture above 150°C [2].

As follows from published data, numerous attempts were made to prepare the antimony derivatives of the type R_3SbYX from R_3SbY_2 and R_3SbX_2 via redistribution of electronegative substituents [9–13]. However, only in a single case, was the target product, acetophenonoximatochlorotriphenylantimony, reliably identified by X-ray diffraction [13].

This communication describes the first ligand redistribution synthesis and X-ray diffraction study of chloro(2,6-dichlorophenoxo)triphenylantimony (**I**) and 2,6-dichlorophenoxotetraphenylantimony (**II**).

EXPERIMENTAL

Synthesis of $Ph_3SbCl(OC_6H_3Cl_2\text{-}2,6)$ (I). A mixture of bis(2,6-dichlorophenoxo)triphenylantimony (0.150 g, 0.25 mmol), triphenylantimony dichloride (0.107 g, 0.25 mmol), and toluene (2 mL) was placed into an evacuated glass ampoule, which was heated on a water bath for 1 h. Then the ampoule was cooled and opened, the solvent was evaporated to a volume of 0.5 mL, and the crystals thus formed were filtered off and dried. The yield of the colorless crystals was 0.229 g (89%), mp = 162°C.

For $C_{24}H_{18}OCl_3Sb$		
anal. calcd., %:	C, 52.34;	H, 3.27.
Found, %:	C, 52.23;	H, 3.36.

IR (ν, cm^{-1}): 3064, 3055, 1574, 1553, 1477, 1437, 1335, 1289, 1274, 1263, 1198, 1182, 1160, 1142, 1071, 1061, 1019, 997, 951, 921, 855, 780, 761, 745, 733, 691, 629, 613, 559, 542, 460, 451.

Table 1. Crystal data and X-ray experiment and structure refinement details for **I** and **II**

Parameter	Value	
	I	**II**
T, K	296(2)	296(2)
M	550.48	592.13
System	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	9.6571(4)	11.3986(6)
b, Å	10.3155(4)	14.0914(7)
c, Å	13.1891(6)	16.7490(9)
α, deg	94.133(2)	90.00
β, deg	110.192(2)	95.444(2)
γ, deg	107.315(2)	90.00
V, Å^3	1154.62(8)	2678.1(2)
Z	2	4
ρ(calcd.), g/cm^3	1.583	1.469
μ, mm^{-1}	1.554	1.250
T, K	296(2)	296(2)
F(000)	544.0	1184.0
Crystal size, mm	0.50 × 0.40 × 0.20	0.72 × 0.68 × 0.40
Range of θ angles, deg	4.66–52	6.28–52.82
Ranges of reflection indices	$-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-9 \leqslant l \leqslant 16$	$-14 \leqslant h \leqslant 14$, $-17 \leqslant k \leqslant 17$, $-20 \leqslant l \leqslant 20$
Number of measured reflections	9988	32902
Number of independent reflections (R_{int})	4457 (0.0233)	5458 (0.0225)
Number of refinement parameters	262	307
GOOF	1.043	1.226
R-factors ($F^2 > 2\sigma(F^2)$)	$R_1 = 0.0260$, $wR_2 = 0.0580$	$R_1 = 0.0395$, $wR_2 = 0.1078$
R-factors (all reflections)	$R_1 = 0.0314$, $wR_2 = 0.0600$	$R_1 = 0.0452$, $wR_2 = 0.1115$
Residual electron density (max/min), e/Å^3	0.49/–0.28	0.70/–0.66

Synthesis of $Ph_4Sb(OC_6H_3Cl_2$-2,6) (II). A mixture of pentaphenylantimony (0.250 g, 0.49 mmol), bis(2,6-dichlorophenoxo)triphenylantimony (0.332 g, 0.49 mmol), and toluene (2 mL) was placed into an evacuated glass ampoule, which was heated on a water bath for 1 h. Then the ampoule was cooled and opened, and the solvent was evaporated. The yield of the colorless crystals was 0.280 g (96%), mp = 230°C.

For $C_{30}H_{23}OCl_2Sb$		
anal. calcd., %:	C, 60.84;	H, 3.89.
Found, %:	C, 60.75;	H, 3.94.

IR (ν, cm^{-1}): 3045, 1570, 1478, 1434, 1290, 1186, 1069, 996, 852, 770, 761, 742, 730, 693, 616, 457, 448.

The IR spectra were recorded on a BrukerTensor 27 IR spectrometer in KBr pellets.

X-ray diffraction study of the crystals of **I** and **II** was carried out on a D8 Quest Bruker diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The data were collected and edited, the unit cell parameters were refined, and the absorption corrections were applied using the SMART and SAINT-Plus program packages [14]. All calculations on the structure solution and refinement were performed using the SHELXL/PC [15] and OLEX2 [16] program packages. The structures of **I** and **II** were solved by the direct method and refined by least squares method in the anisotropic approximation for non-hydrogen atoms. The key crystallographic data and structure refinement details for **I** and **II** are summarized in Table 1 and selected bond lengths and angles are in Table 2.

The full lists of atom coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (no. 998625 for **I**, 1010553 for **II**; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The exchange of electronegative substituents between triphenylantimony dichloride and triphenylantimony diaroxide gave compound I:

$$Ph_3SbCl_2 + Ph_3Sb(OC_6H_3Cl_2\text{-}2,6)_2 \rightarrow 2Ph_3SbCl(OC_6H_3Cl_2\text{-}2,6). \qquad \textbf{(I)}$$

The reaction of pentaphenylantimony and bis(2,6-dichlorophenoxo)triphenylantimony afforded compound **II**:

$$Ph_5Sb + Ph_3Sb(OC_6H_3Cl_2\text{-}2,6)_2 \rightarrow 2Ph_4Sb(OC_6H_3Cl_2\text{-}2,6). \qquad \textbf{(II)}$$

The initial bis(2,6-dichlorophenoxo)triphenylantimony was prepared from triphenylantimony, 2,6-dichlorophenol, and *tert*-butyl hydroperoxide by a procedure reported previously [17].

The IR spectra of compounds **I** and **II** exhibit absorption bands at 460 and 457 cm^{-1} corresponding to the Sb–C(Ph) mode of the SbC_3 moiety [18]. The spectra also exhibit absorption bands due to the C–O bonds (1263 and 1290 cm^{-1} in **I** and **II**, respectively) and the full set of bands (in the 3100–950 cm^{-1} range) corresponding to bond vibrations in aryl substituents.

Table 2. Selected bond lengths and bond angles in **I** and **II**

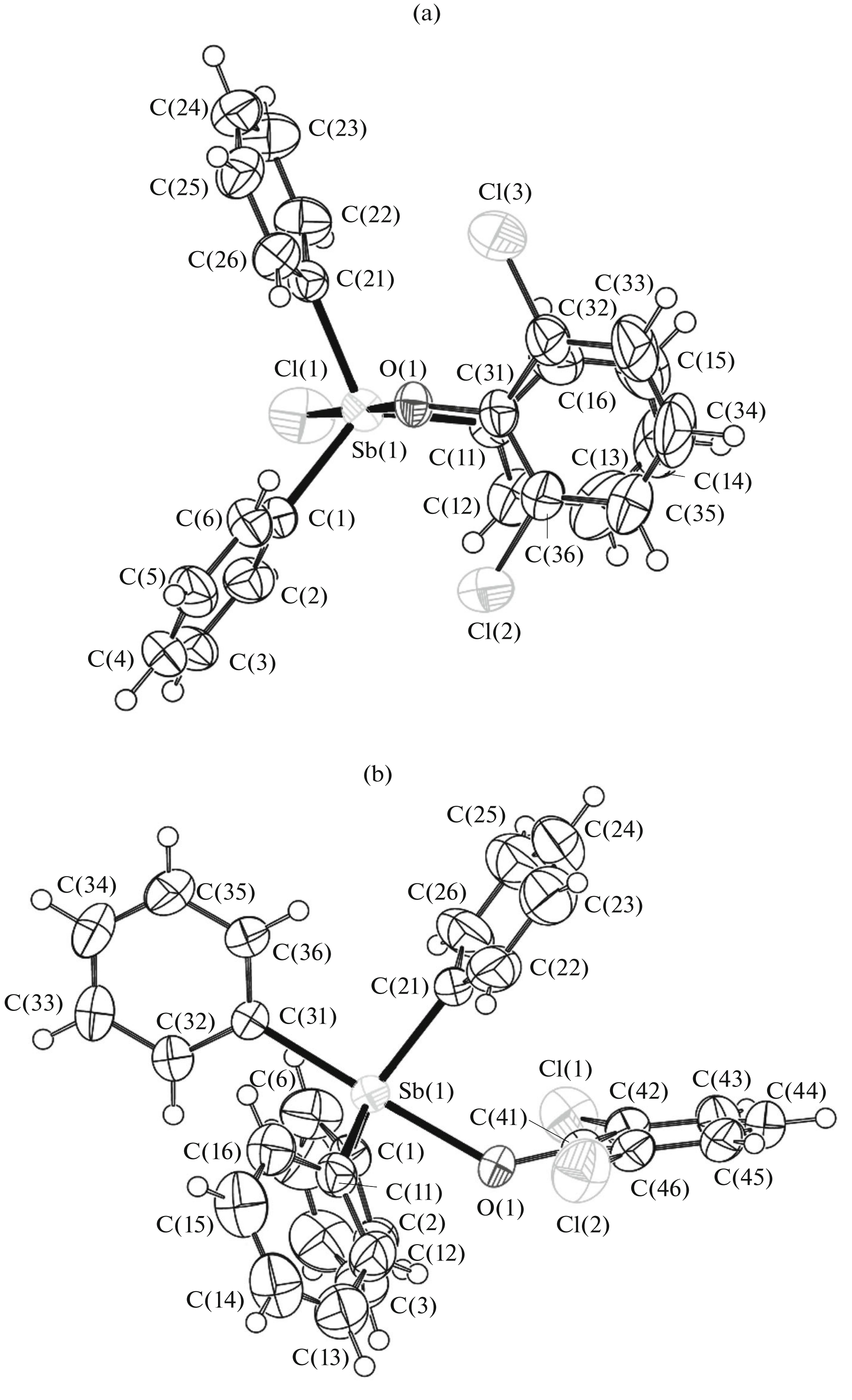
Bond	*d*, Å	Angle	ω, deg
		I	
Sb(1)–Cl(1)	2.4740(7)	O(1)Sb(1)Cl(1)	179.59(5)
Sb(1)–O(1)	2.0802(16)	O(1)Sb(1)C(21)	88.59(8)
Sb(1)–C(21)	2.107(2)	O(1)Sb(1)C(1)	89.61(8)
Sb(1)–C(1)	2.111(2)	O(1)Sb(1)C(11)	91.81(9)
Sb(1)–C(11)	2.099(3)	C(21)Sb(1)Cl(1)	91.01(7)
Cl(2)–C(36)	1.724(3)	C(21)Sb(1)C(1)	115.72(9)
Cl(3)–C(32)	1.731(3)	C(1)Sb(1)Cl(1)	90.64(7)
O(1)–C(31)	1.335(3)	C(11)Sb(1)Cl(1)	88.32(8)
C(21)–C(26)	1.377(4)	C(11)Sb(1)C(21)	119.41(10)
C(21)–C(22)	1.382(4)	C(11)Sb(1)C(1)	124.87(10)
		II	
Sb(1)–O(1)	2.237(3)	C(31)Sb(1)O(1)	178.20(14)
Sb(1)–C(31)	2.167(4)	C(1)Sb(1)O(1)	84.37(15)
Sb(1)–C(1)	2.115(5)	C(1)Sb(1)C(31)	96.67(18)
Sb(1)–C(21)	2.111(4)	C(1)Sb(1)C(11)	111.43(18)
Sb(1)–C(11)	2.122(5)	C(21)Sb(1)O(1)	83.03(14)
C(41)–O(1)	1.317(5)	C(21)Sb(1)C(31)	95.18(17)
C(41)–C(46)	1.399(7)	C(21)Sb(1)C(1)	122.05(19)
C(41)–C(42)	1.406(7)	C(21)Sb(1)C(11)	123.18(19)
Cl(2)–C(46)	1.739(6)	C(11)Sb(1)O(1)	84.47(15)
Cl(1)–C(42)	1.739(5)	C(11)Sb(1)C(31)	96.49(17)
C(31)–C(32)	1.388(7)	O(1)C(41)C(46)	122.6(4)

According to X-ray diffraction data, the antimony atoms in **I** and **II** have a trigonal-bipyramidal coordination distorted to a different extents with heteroatoms in the axial positions (figures).

The axial angles, OSbCl in **I** and CSbO in **II**, are 179.59(5)° and 178.20(14)°, respectively. The sum of the CSbC bond angles in the equatorial plane are 360° (**I**) and 356.26° (**II**). The equatorial angles vary in the ranges of 115.72(9)°–124.87(10)° (**I**) and 111.43(18)°–123.18(19)° (**II**). The phenyl ring conformations in **I** and **II** with respect to the equatorial plane are similar, as indicated by the dihedral angles between the phenyl ring planes and the C_3 equatorial plane: 29.92°, 53.37°, and 60.77° in **I** and 18.08°, 52.41°, and 65.01° in **II**.

The antimony atom in **I** lies nearly in the equatorial plane. In **II**, the antimony atom deviates from this plane towards the axial phenyl substituent by 0.224 Å. The angles between the axial and equatorial bonds in **I** vary in the range of 88.32(8)°–91.81(9)°. In **II**, the OSbC angles (83.0(2)°–84.5(1)°) are smaller than the $C_{ax}SbC_{eq}$ angles (95.2(2)°–96.7(2)°). The Sb–C_{ax} distance in **II** (2.167(4) Å) exceeds the average Sb–C_{eq} bond length (2.116(5) Å). In **I**, the lengths of the equatorial Sb–C bonds are 2.099(3)–2.111(2) Å. The Sb–O bond in **II** (2.237(3) Å) is much longer than in **I** (2.080(2) Å). The Sb–Cl distance in **I** (2.4740(7) Å) is shorter than the average Sb–Cl length in the triphenylantimony dichloride (2.4810(6) Å [19]). In **II**, the O–C bond (1.317(5) Å) is shorter than in **I** (1.335(3) Å). The plane of the aryloxy group in **I** forms a dihedral angle of 45.40° with the equatorial plane; in **II**, this angle is 52.71°.

The molecular packing in the crystals of **I** and **II** is determined by weak intermolecular contacts, C(Ph)–H···Cl of 2.84 Å in **I**; 2.93 Å in **II**; and C(Ph)–H···O of 2.70 Å in **I** and 2.67 Å in **II**.



Molecular structure of compounds (a) **I** and (b) **II**.

Thus, using the synthesis of chloro-2,6-dichlorophenoxotriphenylantimony as an example, we proposed a new method for the preparation of chloroaryloxotriphenylantimony compounds by the ligand redistribution reaction between the triphenylantimony dichloride and triphenylantimony diaroxide, which gives different-ligand derivatives of pentavalent antimony in one step.

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