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Organoantimony Derivatives of 2,4,6-Tribromophenol

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Abstract—2,4,6-Tribromophenoxytetraphenylantimony was prepared in 93% yield by the reaction of pentaphenylantimony with bis(2,4,6-tribromophenoxy)triphenylantimony $Ph_3Sb(OC_6H_2Br_3\text{-}2,4,6)_2$ in toluene at 90°C (1 h). Bis(2,4,6-tribromophenoxy)triphenylantimony, in turn, was prepared by oxidation of triphenylstibine with hydrogen peroxide in the presence of 2,4,6-tribromophenol in ether at 20°C (12 h) in 47% yield, with the second reaction product being μ-oxobis[(2,4,6-tribromophenoxy)triphenylantimony] in which the antimony atom, according to single crystal X-ray diffraction, has a trigonal bipyramidal surrounding with the bridging oxygen atom and 2,4,6-tribromophenoxy substituents in the axial positions.

Aroxytetraaryl derivatives of Sb(V), Ar_4SbOAr', are prepared in high yields from pentaarylantimony and phenol [1–3]. No data are available on synthesis of such Sb(V) derivatives by the substituent redistribution reaction from pentaarylantimony and symmetrical compounds Ar_3SbX_2, although numerous other antimony derivatives Ar_4SbX [X = Hlg, SCN, NO_3, OC(O)R, OSO_2R] are prepared by this route in fairly high yields [4–9].

We found that pentaphenylantimony reacts with bis(2,4,6-tribromophenoxy)triphenylantimony in toluene at 90°C (1 h) to give a single product, 2,4,6-tribromophenoxytetraphenylantimony **I**.

$$Ph_5Sb + Ph_3Sb(OC_6H_2Br_3\text{-}2,4,6)_2 \longrightarrow \underset{\mathbf{I}}{2Ph_4SbOC_6H_2Br_3\text{-}2,4,6}.$$

The target product was isolated as a coarsely crystalline colorless compound. The IR spectrum and melting point of this product were identical to those of the same compound prepared from pentaphenylantimony and 2,4,6-tribromophenol:

$$Ph_5Sb + HOC_6H_2Br_3\text{-}2,4,6 \longrightarrow Ph_4SbOC_6H_2Br_3\text{-}2,4,6 + PhH.$$

The starting bis(2,4,6-tribromophenoxy)triphenylantimony **II** was prepared by oxidative addition from triphenylstibine, hydrogen peroxide, and 2,4,6-tribromophenol (molar ratio 1 : 2 : 1) in ether (20°C, 12 h):

$$Ph_3Sb + 2HOC_6H_2Br_3\text{-}2,4,6 + H_2O_2 \longrightarrow \underset{\mathbf{II}}{Ph_3Sb(OC_6H_2Br_3\text{-}2,4,6)_2} + 2H_2O.$$

After removal of the solvent, the target product was washed with warm toluene. The remaining crystalline substance, which was poorly soluble in toluene, was identified by single crystal X-ray diffraction as μ-oxobis[(2,4,6-tribromophenoxy)triphenylantimony] **III**, the hydrolysis product of bis(2,4,6-tribromophenoxy)triphenylantimony. Indeed, hydrolysis of bis(2,4,6-tribromophenoxy)triphenylantimony in acetone yielded μ-oxobis[(2,4,6-tribromophenoxy)triphenylantimony]; this derivative was also prepared in high yield by oxidative addition at equimolar ratio of the reactants.

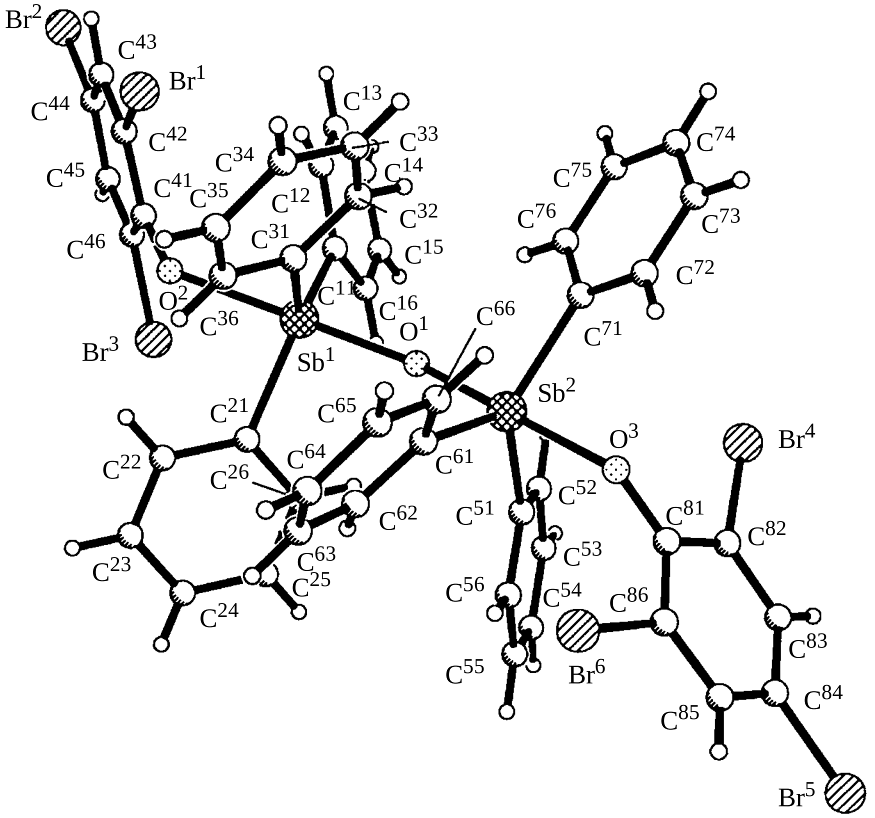
$$2Ph_3Sb(OC_6H_2Br_3)_2 + H_2O \longrightarrow \underset{\mathbf{III}}{[Ph_3Sb(OC_6H_2Br_3)]_2O} + 2HOC_6H_2Br_3,$$

$$2Ph_3Sb + 2HOC_6H_2Br_3\text{-}2,4,6 + 2H_2O_2 \longrightarrow \mathbf{III} + 3H_2O.$$

The single crystal X-ray diffraction study of **III** showed (see figure) that the antimony atom has a trigonal bipyramidal surrounding typical of five-coordinate antimony; the bridging oxygen atom and 2,4,6-tribromophenoxy groups occupy the axial positions.

By now, structural data are available for ~20 compounds $(Ar_3SbX)_2O$ [10–24]. In some of them, the SbOSb moiety is approximately linear [angle ω(SbOSb) ~180°], whereas in the other compounds it is noticeably bent (ω 139.0°–160.0°). Variations in the geometry of the SbOSb moiety may be due to steric and electronic effects of substituents at the Sb atoms or to features of molecular packing in the crystal.

The Sb atom in **III** has a slightly distorted trigonal bipyramidal surrounding: The equatorial CSbC angles range from 115.4(1)° to 123.8(1)°, and the axial



General view of the molecule of μ-oxobis[(2,4,6-tribromophenoxy)triphenylantimony].

$OSbO_{br}$ angles are 178.1(1)° and 176.5(1)° (Table 1). The $Sb^1O^1Sb^2$ angle is 144.0(1)°.

The $Sb–O_{br}$ bond lengths in the molecule of **III** are 1.968(2) and 1.974(2) Å (Table 1) and are somewhat larger than those in related molecules (1.930–1.965 Å) [16, 20]. The Sb–C(Ph) distances range from 2.091(3) to 2.112(3) Å and are typical of organoantimony(V) derivatives. The $Sb–O_{Ar}$ distances [2.185(2) and 2.170(2) Å] are shorter than the distances between the Sb and oxygen atoms of the acid residue in μ-oxobis[(nitrato)triphenylantimony] [23] and μ-oxobis[(2,5-dimethylbenzenesulfonato)tri-*p*-tolylantimony] [24], in which these distances are 2.264(3), 2.295(3), and

Table 1. Selected bond lengths (*d*, Å) and bond angles (ω, deg) in the molecule of **III**

Bond	*d*	Angle	ω	Bond	*d*	Angle	ω
$Sb^1–O^1$	1.968(2)	$O^1Sb^1C^{11}$	90.7(1)	$Br^3–C^{46}$	1.892(3)	$C^{51}Sb^2C^{71}$	123.8(1)
$Sb^1–C^{11}$	2.091(3)	$O^1Sb^1C^{31}$	96.2(1)	$Br^4–C^{82}$	1.886(3)	$O^1Sb^2C^{61}$	98.0(1)
$Sb^1–C^{31}$	2.094(3)	$C^{11}Sb^1C^{31}$	118.8(1)	$Br^5–C^{84}$	1.895(3)	$C^{51}Sb^2C^{61}$	115.4(1)
$Sb^1–C^{21}$	2.112(3)	$O^1Sb^1C^{21}$	93.5(1)	$Br^6–C^{86}$	1.880(3)	$C^{71}Sb^2C^{61}$	120.0(1)
$Sb^1–O^2$	2.185(2)	$C^{11}Sb^1C^{21}$	118.4(1)	$O^2–C^{41}$	1.312(4)	$O^1Sb^2O^3$	176.5(1)
$Sb^2–O^1$	1.974(2)	$C^{31}Sb^1C^{21}$	121.7(1)	$O^3–C^{81}$	1.320(3)	$C^{51}Sb^2O^3$	88.9(1)
$Sb^2–C^{51}$	2.108(3)	$O^1Sb^1O^2$	178.1(1)	$C^{11}–C^{12}$	1.373(4)	$C^{71}Sb^2O^3$	87.1(1)
$Sb^2–C^{71}$	2.111(3)	$C^{11}Sb^1O^2$	88.1(1)	$C^{11}–C^{16}$	1.378(4)	$C^{61}Sb^2O^3$	85.2(1)
$Sb^2–C^{61}$	2.117(3)	$C^{31}Sb^1O^2$	85.7(1)	$C^{12}–C^{13}$	1.383(5)	$Sb^1O^1Sb^2$	144.0(1)
$Sb^2–O^3$	2.170(2)	$C^{21}Sb^1O^2$	85.9(1)	$C^{13}–C^{14}$	1.364(5)	$C^{41}O^2Sb^1$	130.0(2)
$Br^1–C^{42}$	1.896(3)	$O^1Sb^2C^{51}$	88.6(1)	$C^{14}–C^{15}$	1.374(5)	$C^{81}O^3Sb^2$	131.3(2)
$Br^2–C^{44}$	1.901(4)	$O^1Sb^2C^{71}$	92.5(1)				

Table 2. Atomic coordinates and their isotropic equivalent thermal parameters in the molecule of **III**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Sb^1	0.88703(2)	0.66049(2)	0.27515(1)	0.03799(6)
Sb^2	1.01290(2)	0.86929(2)	0.27620(2)	0.04231(6)
Br^1	0.58357(3)	0.60843(4)	0.46810(3)	0.0794(1)
Br^2	0.44114(3)	0.45665(4)	0.21954(4)	0.1065(2)
Br^3	0.91251(3)	0.42312(3)	0.11591(3)	0.0660(1)
Br^4	1.05424(3)	1.11343(3)	0.14972(3)	0.0856(1)
Br^5	1.51637(3)	1.07418(3)	0.10053(3)	0.0736(1)
Br^6	1.28120(3)	0.88575(3)	0.39117(3)	0.0731(1)
O^1	0.9481(2)	0.7753(2)	0.2380(1)	0.0505(6)
O^2	0.8204(2)	0.5317(2)	0.3117(1)	0.0453(6)
O^3	1.0865(2)	0.9758(2)	0.3100(1)	0.0487(6)
C^{11}	0.7815(2)	0.7124(2)	0.1946(2)	0.0369(8)
C^{12}	0.6619(3)	0.7368(2)	0.2287(2)	0.048(1)
C^{13}	0.5984(3)	0.7582(3)	0.1707(3)	0.062(1)
C^{14}	0.6541(3)	0.7568(3)	0.0794(3)	0.072(1)
C^{15}	0.7731(3)	0.7360(3)	0.0449(2)	0.075(1)
C^{16}	0.8353(3)	0.7136(3)	0.1024(2)	0.056(1)
C^{21}	1.0556(2)	0.5359(2)	0.2192(2)	0.043(1)
C^{22}	1.0814(3)	0.4359(3)	0.2507(2)	0.055(1)
C^{23}	1.1905(3)	0.3554(3)	0.2108(2)	0.069(1)
C^{24}	1.2742(3)	0.3752(3)	0.1394(3)	0.076(1)
C^{25}	1.2491(3)	0.4752(3)	0.1065(3)	0.075(1)
C^{26}	1.1394(3)	0.5563(3)	0.1473(2)	0.055(1)
C^{31}	0.8106(2)	0.7112(2)	0.4144(2)	0.043(1)
C^{32}	0.7293(3)	0.8156(3)	0.4420(2)	0.062(1)
C^{33}	0.6731(3)	0.8493(3)	0.5339(3)	0.078(1)
C^{34}	0.6994(3)	0.7788(3)	0.5970(3)	0.079(1)
C^{35}	0.7811(3)	0.6758(3)	0.5692(2)	0.076(1)
C^{36}	0.8370(3)	0.6418(3)	0.4781(2)	0.058(1)
C^{41}	0.7397(2)	0.5127(2)	0.2908(2)	0.041(1)
C^{42}	0.6241(3)	0.5390(2)	0.3524(2)	0.050(1)
C^{43}	0.5358(3)	0.5246(3)	0.3325(2)	0.059(1)
C^{44}	0.5617(3)	0.4781(3)	0.2488(3)	0.062(1)
C^{45}	0.6739(3)	0.4468(3)	0.1840(2)	0.057(1)
C^{46}	0.7603(2)	0.4642(2)	0.2064(2)	0.045(1)
C^{51}	1.1531(3)	0.8233(3)	0.1499(2)	0.058(1)
C^{52}	1.1251(4)	0.8393(3)	0.0704(3)	0.088(2)
C^{53}	1.2147(4)	0.8048(4)	–0.0144(3)	0.127(2)
C^{54}	1.3275(4)	0.7547(4)	–0.0186(4)	0.140(2)
C^{55}	1.3553(4)	0.7391(3)	0.0579(4)	0.117(2)
C^{56}	1.2657(3)	0.7732(3)	0.1450(3)	0.073(1)
C^{61}	1.0507(2)	0.7854(2)	0.3862(2)	0.044(1)
C^{62}	1.1330(3)	0.6819(2)	0.3688(2)	0.054(1)
C^{63}	1.1636(3)	0.6272(3)	0.4379(3)	0.064(1)
C^{64}	1.1091(3)	0.6752(3)	0.5258(2)	0.065(1)
C^{65}	1.0241(3)	0.7777(3)	0.5435(2)	0.063(1)
C^{66}	0.9960(3)	0.8336(3)	0.4738(2)	0.052(1)
C^{71}	0.8545(2)	1.0058(2)	0.3007(2)	0.045(1)
C^{72}	0.8280(3)	1.0936(3)	0.3580(2)	0.059(1)
C^{73}	0.7253(3)	1.1826(3)	0.3715(3)	0.076(1)
C^{74}	0.6476(4)	1.1832(3)	0.3300(3)	0.094(2)
C^{75}	0.6738(3)	1.0965(3)	0.2736(3)	0.084(1)
C^{76}	0.7770(3)	1.0059(3)	0.2591(2)	0.065(1)
C^{81}	1.1802(2)	0.9974(2)	0.2632(2)	0.041(1)
C^{82}	1.1868(2)	1.0555(2)	0.1865(2)	0.050(1)
C^{83}	1.2870(3)	1.0769(2)	0.1371(2)	0.055(1)
C^{84}	1.3806(2)	1.0444(2)	0.1664(2)	0.048(1)
C^{85}	1.3772(3)	0.9908(2)	0.2433(2)	0.051(1)
C^{86}	1.2795(2)	0.9661(2)	0.2900(2)	0.042(1)

2.258(5) Å, respectively. Thus, the higher the electronegativity of the terminal ligand X, the longer the Sb–X bond and the shorter the Sb–O$_{br}$ bonds. This trend is characteristic for the whole class of antimony compounds under consideration.

With the aim to reveal factors responsible for the wide variation of SbOSb angles in the compounds $(Ar_3SbX)_2O$, we have considered the following series of compounds: (1) $(Ph_3SbX)_2O$, X = Cl [15, 19], Br [16, 20], I [17, 18], and (2) $(Ar_3SbBr)_2O$, Ar = Ph [16], *o*-Tol [20], *p*-Tol [20]. In the series $(Ph_3SbX)_2O$, the SbOSb angle ranges from 139.0° to 180.0° irrespective of atom X {X = Cl (ω 139.0° [15], 173.1° [19]), Br (ω 170.3° [16]), I (ω 180.0° [17, 18], 144.6° [17])}. A similar pattern is observed with the compounds $(Ar_3SbBr)_2O$ in which the SbOSb angle is in the range 161.0°–180.0° and is independent of the structure of the aryl group {Ar = Ph (ω 170.3° [16]), *o*-Tol (ω 161.0° [20]), *p*-Tol (ω 180.0° [20])}.

Replacement of an electronegative terminal ligand (Hlg, NO_3, OSO_2Ar, etc.) by a less electronegative group (OAr) in the compounds $(Ph_3SbX)_2O$, as we noticed, leads to smaller SbOSb angles; however, available experimental data are insufficient to speak about the effect of the electron-acceptor properties of ligands X on the SbOSb angle.

EXPERIMENTAL

The IR spectra were recorded on a Hitachi-215 spectrometer (mull in mineral oil, NaCl plates).

Single crystal X-ray diffraction study of μ-oxobis[(2,4,6-tribromophenoxy)triphenylantimony] III. $C_{48}H_{34}Br_6O_3Sb_2$. The unit cell parameters and intensities of 5065 unique reflections with $I > 2\sigma(I)$ were measured on a Bruker SMART-1000CCD automatic diffractometer (graphite monochromator, MoK_α radiation, θ/2θ scanning). The data were collected as groups of 906 images at angles φ 0°, 90°, 180°, and 270°. ω-Scanning was performed with a 0.2° step and 10 s exposure per image; the crystal–detector distance was 45 mm. The X-ray absorption in the sample was considered taking into account indices of faces. The crystals are triclinic; at 20°C *a* 13.028(2), *b* 13.451(2), *c* 15.722(2) Å; α 87.161(2)°, β 69.888(2)°, γ 67.972(2)°; *V* 2388.3(5) Å^3; space group $P\bar{1}$; *Z* 2; d_{calc} 1.921 g cm^{-3}. The structure was solved by the direct method and refined by the least-squares method in the anisotropic approximation for nonhydrogen atoms (isotropic for hydrogen atoms) to *R* 0.0277, R_W 0.0571. The positions of hydrogen atoms were calculated geometrically and included in refinement using the rider model (C–H distance 0.93 Å).

The data collection and editing and the refinement of the unit cell parameters were performed with the SMART and SAINT Plus programs [25]. All the calculations for the structure determination and refinement were performed using the SHELXTL/PC program package [26]. The perspective view of the molecule is shown in the figure, and the atomic coordinates are listed in Table 2.

2,4,6-Tribromophenoxytetraphenylantimony I. *a*. A mixture of 1.00 g of pentaphenylantimony, 0.65 g of 2,4,6-tribromophenol, and 10 ml of toluene was kept at 90°C for 1 h, after which it was cooled to –18°C. The precipitated crystals were filtered off and dried. Yield of 2,4,6-tribromophenoxytetraphenylantimony 1.40 g (93%), mp 253°C.

b. A mixture of 0.50 g of pentaphenylantimony, 1.00 g of bis[(2,4,6-tribromophenoxy)triphenylantimony], and 10 ml of toluene was kept at 90°C for 1 h, after which it was cooled to –18°C. The precipitated crystals were filtered off and dried. Yield of 2,4,6-tribromophenoxytetraphenylantimony 1.42 g (95%), mp 253°C.

Bis(2,4,6-tribromophenoxy)triphenylantimony II. To a mixture of 1.00 g of triphenylstibine and 1.88 g of 2,4,6-tribromophenol in 10 ml of ether, we added 0.32 ml of 30% aqueous hydrogen peroxide. The mixture was allowed to stand for 12 h, after which the solvent was evaporated, and the residue was recrystallized from toluene and dried. Yield of bis(2,4,6-tribromophenoxy)triphenylantimony 1.35 g (47%),[1] mp 168°C. IR spectrum, ν, cm^{-1}: 1265 vs, 1182 s, 995 s, 845 vs.

μ-Oxobis[(2,4,6-tribromophenoxy)triphenylantimony] III. To a mixture of 1.00 g of triphenylstibine and 0.94 g of 2,4,6-tribromophenol in 10 ml of ether, we added 0.32 ml of 30% aqueous hydrogen peroxide. The mixture was allowed to stand for 12 h, after which the solvent was evaporated, and the residue was washed with 10 ml of benzene and dried. Yield of **III** 1.92 g (98%), mp 238°C. IR spectrum, ν, cm^{-1}: 1528 s, 1438 vs, 1285 vs, 1180 s, 998 s, 850 vs.

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[1] The yield of crystalline compound **III** (mp 238°C), insoluble in toluene, was 0.92 g (23%).

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