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Reactions of Tri-*p*-tolylantimony with Carboxylic and Arylsulfonic Acids and Phenols

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Abstract—The tri-*p*-tolylantimony dicarboxylates were synthesized by the reaction of tri-*p*-tolylantimony with trifluoroacetic, trichloroacetic, and iodoacetic acids in the absence of oxygen. The amount of the corresponding compound in the reaction product is defined by the nature of the reacting acid. The reaction of tri-*p*-tolylantimony with toluenesulfonic acid and 2,4,6-trinitrophenol under similar conditions leads to the formation of tri-*p*-tolylantimony bis(toluenesulfonate) and bis(2,4,6-trinitrophenoxide) respectively with the yield reaching 82% . According to X-ray diffraction data, in the two crystallographically independent molecules of tri-*p*-tolylantimony bis(trifluoroacetate) the Sb atoms have distorted trigonal–bipyramidal coordination.

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It is known that dephenylation of triphenylantimony with carboxylic acids depends on the nature of the solvent and the organic residue in the starting acid, and affords diphenylantimony carboxylates, phenylantimony dicarboxylates and antimony tricarboxylates [1]. At the same time, in the reaction of halocarboxylic acids with triphenylantimony triphenylantimony dicarboxylates are formed. The formation of these compounds was ascribed to the following redox reactions [2, 3]:

$$\mathrm{Ph_3Sb + 2\,HOOCR \rightarrow Ph_3Sb(OOCR)_2 + H_2\uparrow},$$

$$\mathrm{R = CH_2Cl, CH_2Br, CH_2F, CCl_3, CF_3}.$$

In the present work we have studied the reaction of tri-*p*-tolylantimony with trifluoroacetic, trichloroacetic, iodoacetic, and toluenesulfonic acid and with 2,4,6-trinitrophenol in toluene in the presence or absence of oxygen.

We found that reaction of trifluoroacetic acid with tri-*p*-tolylantimony in an evacuated glass ampule in toluene at 100°C (8 h) leads to tri-*p*-tolylantimony bis (trifluoroacetate) **I** (28%):

$$p\text{-}\mathrm{Tol_3Sb + 2\,HOC(O)CF_3 \rightarrow} \underset{\textbf{I}}{p\text{-}\mathrm{Tol_3Sb[OC(O)CF_3]_2}} + \mathrm{H_2}.$$

Reaction in air atmosphere also led to formation of tri-*p*-tolylantimony bis(trifluoroacetate) in 42% yield. The increase in the yield of triarylantimony dicarboxylate in this case can obviously be attributed to the occurrence of parallel reactions:

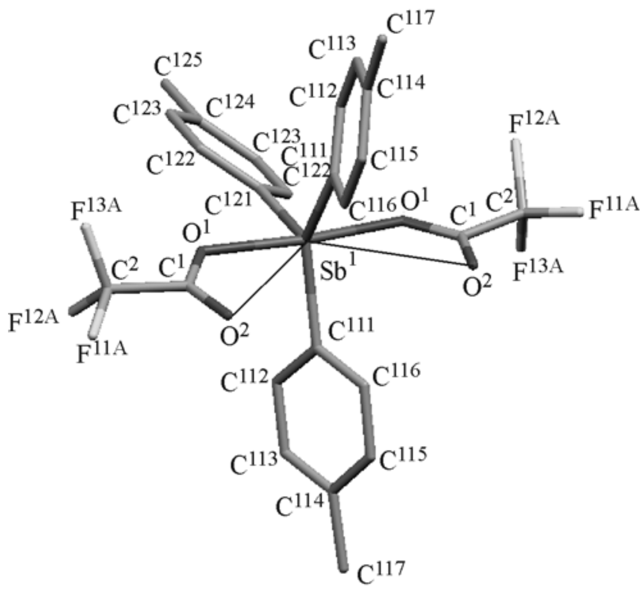
$$p\text{-}\mathrm{Tol_3Sb + 2\,HOC(O)CF_3 + 1/2O_2 \rightarrow \textbf{I} + H_2O}.$$

Reaction of tri-*p*-tolylantimony with trichloroacetic acid resulted in the formation of tri-*p*-tolylantimony bis(trichloroacetate), which was isolated in 14% yield. In air the yield increased to 26%, which indicates the oxidative addition of tri-*p*-tolylantimony with involvement of the air oxygen.

The interaction of tri-*p*-tolylantimony with toluenesulfonic acid at the lack of oxygen resulted in the formation of tri-*p*-tolylantimony bis(toluenesulfonate) in 7% yield, while in the presence of oxygen the yield of tri-*p*-tolylantimony disulfonate increased to 48%.

However, iodoacetic acid and 2,4,6-trinitrophenol react with tri-*p*-tolylantimony both in the absence and in the presence of oxygen with an almost quantitative formation of tri-*p*-tolylantimony bis(iodacetate) and bis(2,4,6-trinitrophenoxide) respectively. The synthesis, apparently, corresponds to the first of the two schemes described above.

Thus, the reaction of the tri-*p*-tolylantimony with carboxylic and toluenesulfonic acids and with 2,4,6-trinitrophenol proceeds in two competing directions with the formation of pentavalent antimony derivatives



Molecular structure of tri-*p*-tolylantimony bis(trifluoroacetate).

of general formula *p*-Tol_3SbX_2 (X is the residue of carboxylic or toluenesulfonic acid, or 2,4,6-trinitrophenol).

According to X-ray diffraction (XRD), the crystal of compound **I** contains crystallographically independent symmetric molecules of two types (**A** and **B**) having a second order rotation axis. One of the trifluoromethyl groups is disordered over two positions. In the **A** and **B** molecules the Sb atoms have a somewhat distorted trigonal–bipyramidal coordination with O atoms of the carboxylate ligands in axial positions (see the figure). The axial OSbO angles in the **A** and **B** molecules and the sum of the angles in the equatorial plane are 172.18°, 174.65°, and 360°, respectively. The Sb atoms are located in the equatorial plane. Planar phenyl rings in the structures of **A** and **B** are turned around the Sb–C bonds to minimize the intra- and intermolecular contacts.

Geometric parameters of molecules **A** and **B** slightly differ by the Sb–C and Sb–O bond lengths. The Sb–C distances in **B** [2.102(3), 2.093(3), and 2.093(3) Å] are larger than in **A** [2.083(3), 2.090(2), and 2.090(2) Å]. The Sb–O bond lengths in molecules **A** and **B** are 2.136(2) and 2.135(2) Å, respectively, which is comparable with similar bonds in the known structurally characterized triphenylantimony dicarboxylates [2.095(2)–2.185(2) Å].

As in the other triphenylantimony dicarboxylates, in **A** and **B** there are intramolecular Sb···O(=C) interactions. The corresponding distances 3.298(2) and 3.212(2) Å are longer than the similar distances in $Ph_3Sb[OC(O)CH_3]_2$ (2.779 Å [4]), $Ph_3Sb[OC(O)C_6H_5]_2$ (2.70 and 2.81 Å [5]), and $Ph_3Sb[OC(O)C_4H_3S\text{-}2]_2$ (2.744 and 2.949 Å [6]). The average values of Sb···O(=C) distances in triarylantimony dicarboxylates are 2.664–3.219 Å. Since the carboxylate ligands in **A** and **B** are in *cis* orientation relatively to the equatorial fragment Ar_3Sb and lie almost in the same plane (the dihedral angles between the planes of the carboxyl groups are less than 10°), one of the equatorial angles CSbC is slightly increased [128.2(1)° and 133.5(1)° in **A** and **B**] at the side of Sb···O(=C) contacts, which leads to a decrease in the other two angles [115.9(1)° and 113.3(2)° in **A** and **B**, respectively] (Table 1).

Thus, the configuration of molecules of compound **I** is characterized by a slight deviation from the ideal trigonal bipyramid, which for the most triarilantimony dicarboxylates is manifested in a significant distortion of the equatorial angles due to stronger intramolecular interactions in them than in compound **I**.

EXPERIMENTAL

IR spectra were recorded on a FTIR 1201 spectrometer from KBr tablets. The tri-*p*-tolylantimony dicarboxylates, bis(arensulfonates), and diaryloxides obtained in this work were identified by melting point and IR spectra of compounds synthesized from tri-*p*-tolylantimony by the reaction of oxidative addition [3].

XRD of compound **I** was taken on a Bruker AXS Smart Apex diffractometer (MoK_α-radiation, λ 0.71073 Å, graphite monochromator). Data acquisition and editing, and refinement of the unit cell parameters and accounting for the extinction were carried out with the programs SMART and SAINT-Plus [7]. All calculations to determine and refine the structure were executed with the SHELXL/PC program [8].

The structure was solved by the direct method and refined by least-squares procedure anisotropically for nonhydrogen atoms.

The main crystallographic data and structure refinement are given in Table 2.

Tri-*p*-tolylantimony bis(trifluoroacetate). A mixture of 0.50 g (1.27 mmol) of tri-*p*-tolylantimony, 0.29 g (2.54 mmol) of trifluoroacetic acid, and 10 ml of toluene was heated in an evacuated glass ampule for 8 h at 100°C. The precipitate formed was filtered off, treated with toluene, and dried. Yield 0.22 g (28%) mp

Table 1. Bond lengths and bond angles in the structure **I**[a]

Bond *d*, Å	
Sb^1–O^{1a}	2.1363(17)
Sb^1–O^1	2.1364(17)
Sb^1–C^{111a}	2.090(2)
Sb^1–C^{111}	2.090(2)
Sb^1–C^{121}	2.083(3)
Sb^2–O^{3б}	2.1355(17)
Sb^2–O^3	2.1355(17)
Sb^2–C^{211}	2.093(3)
Sb^2–C^{211б}	2.093(3)
Sb^2–C^{221}	2.102(3)
O^1–C^1	1.276(3)
O^2–C^1	1.207(3)
O^3–C^3	1.274(3)
O^4–C^3	1.210(3)
Angle ω, deg	
O^{1a}Sb^{1}O^1	172.18(9)
C^{111a}Sb^{1}O^{1a}	91.69(8)
C^{111}Sb^{1}O^{1a}	91.72(8)
C^{111a}Sb^{1}O^1	91.72(8)
C^{111}Sb^{1}O^1	91.69(8)
C^{111a}Sb^{1}C^{111}	128.22(12)
C^{121}Sb^{1}O^{1a}	86.09(4)
C^{121}Sb^{1}O^1	86.09(4)
C^{121}Sb^{1}C^{111a}	115.89(6)
C^{121}Sb^{1}C^{111}	115.89(6)
O^{3б}Sb^{2}O^3	174.65(9)
C^{211}Sb^{2}O^{3б}	92.10(9)
C^{211б}Sb^{2}O^{3б}	90.01(9)
C^{211}Sb^{2}O^3	90.01(9)
C^{211б}Sb^{2}O^3	92.10(9)
C^{211}Sb^{2}C^{211б}	133.48(14)
C^{211}Sb^{2}C^{221}	113.26(7)
C^{211б}Sb^{2}C^{221}	113.26(7)
C^{221}Sb^{2}O^{3б}	87.32(4)
C^{221}Sb^{2}O^3	87.33(4)

[a] Symmetry transformations: # 1) $-x + 1/2, y, -z + 3/2$, #2) $-x + 1/2, y, -z + 1/2$.

Table 2. Crystallographic data, experimental parameters, and structure refinement.

Parameter	Value
Formula	$C_{25}H_{21}F_6O_4Sb$
M	621.17
T, K	293 K
Crystal system	Monoclinic
Space group	*P*2/n
a, Å	12.2346(4)
b, Å	11.8079(4)
c, Å	18.7055(7)
β, deg	103.5170(10)
V, Å^3	2627.44(16)
Z	4
d_{calc}, g cm^{-3}	1.570
μ, mm^{-1}	1.120
F(000)	1232
Crystal shape (size, mm)	Plates (0.22×0.13×0.05)
Scope of data collection θ, deg	2.24–31.60
Intervals of reflection indices	$-14 \le h \le 17$, $-16 \le k \le 15$, $-26 \le l \le 25$
Measured reflections	32008
Independent reflections	7484
Number of variables for refining	386
GOOF	1.036
R-factors over $F^2 > 2\sigma(F^2)$	R_1 0.0329 wR_2 0.0712
R-factors over all reflections	R_1 0.0649 wR_2 0.0831
Residual electron density (min / max), *e* A^{-3}	1.748/–0.418

190°C. IR spectrum (ν, cm^{-1}): 2923, 1722, 1495, 1398, 1171, 1070, 1014, 847, 800, 789, 726, 483. Found, %: C 48.02, H 2.98. $C_{25}H_{21}O_4F_6Sb$. Calculated, %: C 48.33, H 3.38.

Tri-*p*-tolylantimony bis(trichloroacetate) was prepared similarly from 0.40 g (1.00 mmol) of tri-*p*-tolylantimony and 0.33 g (2.00 mmol) of trichloroacetic acid. Yield 0.10 g (14%), mp 200°C. IR spectrum (ν, cm^{-1}): 2926, 2856, 1650, 1327, 846, 837, 746, 680, 566, 484. Found, %: C 41.28, H 2.83. $C_{25}H_{21}O_4Cl_6Sb$. Calculated, %: C 41.68, H 2.92.

Tri-*p*-tolylantimony bis(iodoacetate) was prepared similarly from 0.40 g (1.00 mmol) of tri-*p*-tolylantimony and 0.37 g (2.00 mmol) of iodoacetic acid. Yield 0.66 g (86%), mp 126°C. IR spectrum (ν, cm^{-1}): 3036, 2973, 2919, 2861, 1649, 1489, 1419, 1318, 1310, 1194, 1190, 1079, 1011, 034, 797, 674, 488. Found, %: C 38.89, H 3.38. $C_{25}H_{25}O_4I_2Sb$. Calculated, %: C 39.24, H 3.27.

Tri-*p*-tolylantimony bis(2,4,6-trinitrophenoxide) was prepared similarly from 0.40 g (1.00 mmol) of tri-*p*-tolylantimony and 0.46 g (2.00 mmol) of 2,4,6-trinitrophenol. Yield 0.72 g (84%), mp 251°C. IR spectrum (ν, cm^{-1}): 3080, 2923, 2861, 1646, 1609, 1576, 1533, 1491, 1349, 1330, 1277, 802, 482. Found, %: C 46.37, H 2.98. $C_{33}H_{25}N_6O_{14}Sb$. Calculated, %: C 46.55, H 2.94.

Tri-*p*-tolylantimony bis(4-methybenzenesulfonate) was prepared similarly from 0.40 g (1.00 mmol) of tri-*p*-tolylantimony and 0.34 g (2.00 mmol) 4-methylbenzenesulfonate acid. Yield 0.05 g (7%), mp 201°C. IR spectrum (ν, cm^{-1}): 3033, 3020, 2952, 2921, 2066, 1589, 1494, 1446, 1396, 1293, 1275, 1212, 1190, 1162, 1099, 1073, 1039, 1023, 1017, 977, 822, 801, 737, 699, 679, 634, 616, 590, 576, 564, 533, 481. Found, %: C 57.72, H 4.98. $C_{35}H_{35}S_2O_6Sb$. Calculated, %: C 57.01, H 4.75.

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