

# SYNTHESIS AND STRUCTURE OF TRI- AND TETRAPHENYLANTIMONY AROXIDES: Ph<sub>3</sub>Sb[OC<sub>6</sub>H<sub>3</sub>(Br<sub>2</sub>-2,6)(Me-4)]<sub>2</sub> AND Ph<sub>4</sub>SbOC<sub>6</sub>H<sub>3</sub>Br<sub>2</sub>-2,6, Me-4

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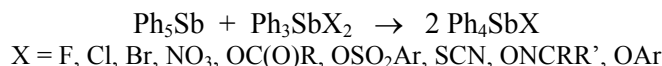
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Interaction of pentaphenylantimony with 2,6-dibromo,4-methylphenol or with *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony (**1**) leads to formation of 2,6-dibromo,4-methylphenoxytetraphenylantimony (**2**). In molecules of compounds **1** and **2** the antimony atoms have distorted trigonal-bipyramidal coordination with the oxygen atoms in axial positions (OSbO 179.20(15)° (**1**), OSbC 179.7(9)° (**2**)). The bond lengths Sb–C and Sb–O equal 2.090(5), 2.101(5), 2.110(5) and 2.088(4), 2.088(4) Å (**1**), 2.11(2), 2.11(2), 2.11(2), 2.17(3) and 2.234(18), 2.234(18) Å (**2**), respectively.

*Keywords:* pentaphenylantimony, triphenylantimony, 2,6-dibromo,4-methylphenol, *tert*-butyl hydroperoxide, *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony, (2,6-dibromo,4-methylphenoxy)tetraphenylantimony, molecular structure, X-ray diffraction analysis.

## Introduction

It is known that redistribution of organic radicals between pentaphenylantimony and symmetrical derivatives of antimony with the general formula Ph<sub>3</sub>SbX<sub>2</sub> leads to formation of the single organoantimony compound with the general formula Ph<sub>4</sub>SbX, yielding up to 99 % [1–6].



This reaction is of universal character, since it is valid for compounds containing substituents (X) of various nature, but for tetraphenylantimony aroxides it has been demonstrated by one example only [5].

In the course of research on characteristic features of ligand redistribution we have studied the reactions of pentaphenylantimony with *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony (**1**) and 2,6-dibromo,4-methylphenol. The structures of the products have been established by X-ray diffraction analysis.

## Experimental

**Synthesis of *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony (**1**).** The mixture of 0.353 g (1.00 mmol) triphenylantimony, 0.532 g (2.00 mmol) 2,6-dibromo,4-methylphenol and 0.129 g 70% solution of *tert*-butyl hydroperoxide in 10 mL ether stood for 18 h at 24 °C. After slow evaporation of the solvent, large crystals **1** with melting point 214 °C were formed to yield 0.786 g (89%). Found, %: C 43.37; H 2.99. Calculated for C<sub>32</sub>H<sub>25</sub>O<sub>2</sub>Br<sub>4</sub>Sb, %: C 43.49; H 2.83.

**Interaction of pentaphenylantimony with *bis*(2,6-dibromo,4-methylphenoxy) triphenylantimony.** The mixture of 0.250 g (0.50 mmol) pentaphenylantimony, 0.441 g (0.50 mmol) *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony and 2 mL toluene in glass ampoule was heated in boiling water bath for 1 hour. The progress of the reaction was controlled by thin-layer chromatography. The solution was decanted from the crystals, and the solvent was evaporated. Formation of large crystals **2** with decomposition temperature 224 °C was observed. IR spectrum (ν, cm<sup>-1</sup>): 3048, 2917, 2361, 2342, 1577, 1447, 1434, 1302, 1291, 1240, 1176, 1069, 1020, 996, 849, 799, 730, 692, 570, 563, 491, 467, 458, 447. Found, %: C 54.43; H 3.71. Calculated for C<sub>31</sub>H<sub>25</sub>OBr<sub>2</sub>Sb, %: C 53.54, H 3.60.

**Interaction of pentaphenylantimony with 2,6-dibromo,4-methylphenol.** The mixture of 0.25 g (0.49 mmol) pentaphenylantimony, 0.131 g (0.49 mmol) 2,6-dibromo-4-methylphenol and 2 mL toluene

in glass ampoule was heated in boiling water bath for 1 hour. The solution was decanted from the crystals, the solvent was evaporated. Colorless crystals with decomposition temperature 224 °C were formed to yield 0.274 g (80%). IR spectrum is identical to the IR spectrum of the compound obtained by the abovementioned procedure.

**IR spectra** were recorded on the Fourier-transform spectrometer Bruker Tensor 27 in KBr pellets.

**The X-ray diffraction analyses** of crystals **1** and **2** were performed on the Bruker D8 Quest diffractometer (Mo  $K_{\alpha}$ -emission,  $\lambda = 0.71073$  Å, graphite monochromator). The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the SMART and SAINT-Plus programs [7]. All calculations for structure determination and refinement were performed using the SHELXL/PC [8] and OLEX2 programs [9]. The structures were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and refinement results for the structures are listed in Table 1, the selected bond lengths and bond angles are given in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1043497, 1009712; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Table 1  
Crystallographic data and the experimental and structure refinement parameters for compounds **1**, **2**

Parameter	Value	
	<b>1</b>	<b>2</b>
Empirical formula	C <sub>32</sub> H <sub>25</sub> O <sub>2</sub> Br <sub>4</sub> Sb	C <sub>31</sub> H <sub>25</sub> OBr <sub>2</sub> Sb
Formula weight	882.91	695.08
<i>T</i> , K	273.15	273.15
Crystal system	triclinic	orthorhombic
Space group	P-1	Pnma
<i>a</i> , Å	10.1942(6)	16.3869(9)
<i>b</i> , Å	11.0622(6)	11.6579(6)
<i>c</i> , Å	15.3136(8)	14.5305(7)
$\alpha$ , deg	87.547(3)	90.00
$\beta$ , deg	78.460(3)	90.00
$\gamma$ , deg	69.703(3)	90.00
<i>V</i> , Å <sup>3</sup>	1586.28(15)	2775.9(2)
<i>Z</i>	2	4
$\rho$ (calcd.), g/cm <sup>3</sup>	1.848	1.663
$\mu$ , mm <sup>-1</sup>	5.934	3.894
<i>F</i> (000)	848.0	1360.0
Crystal size, mm	0.35 × 0.18 × 0.09	0.68 × 0.45 × 0.43
2 $\theta$ Range of data collection, deg	5.56 – 53.02°	6.08 – 52.9°
Range of refraction indices	-12 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 13, -19 ≤ <i>l</i> ≤ 19	-20 ≤ <i>h</i> ≤ 20, -14 ≤ <i>k</i> ≤ 14, -18 ≤ <i>l</i> ≤ 18
Measured reflections	31896	67786
Independent reflections	6504	2998
<i>R</i> <sub>int</sub>	0.0801	0.0474
Refinement variables	354	184
<i>GOOF</i>	1.018	1.050
<i>R</i> factors for $F^2 > 2\sigma(F^2)$	<i>R</i> <sub>1</sub> = 0.0477, <i>wR</i> <sub>2</sub> = 0.1073	<i>R</i> <sub>1</sub> = 0.0324, <i>wR</i> <sub>2</sub> = 0.0785
<i>R</i> factors for all reflections	<i>R</i> <sub>1</sub> = 0.0857, <i>wR</i> <sub>2</sub> = 0.1236	<i>R</i> <sub>1</sub> = 0.0419, <i>wR</i> <sub>2</sub> = 0.0881
Residual electron density (min/max), e/Å <sup>3</sup>	1.35/-0.91	0.60/-0.83

Selected bond lengths and bond angles in the structure of compounds 1, 2

Bond	<i>d</i> , Å	Angle	$\omega$ , deg
<b>1</b>			
Sb(1)–O(1)	2.088(4)	O(1)Sb(1)O(2)	179.20(15)
Sb(1)–O(2)	2.089(4)	O(1)Sb(1)C(1)	89.6(2)
Sb(1)–C(1)	2.110(5)	O(1)Sb(1)C(11)	89.39(18)
Sb(1)–C(11)	2.101(5)	O(1)Sb(1)C(21)	92.17(19)
Sb(1)–C(21)	2.090(5)	O(2)Sb(1)C(1)	89.6(2)
Br(1)–C(32)	1.892(6)	O(2)Sb(1)C(11)	91.17(19)
Br(2)–C(36)	1.892(6)	O(2)Sb(1)C(21)	88.0(2)
Br(3)–C(46)	1.886(7)	C(11)Sb(1)C(1)	121.3(2)
Br(4)–C(42)	1.894(6)	C(21)Sb(1)C(1)	116.9(2)
O(1)–C(31)	1.338(7)	C(21)Sb(1)C(11)	121.8(2)
O(2)–C(41)	1.339(7)	C(31)O(1)Sb(1)	130.1(3)
Sb(1)···Br(4)	3.914(4)	C(41)O(2)Sb(1)	130.3(3)
Sb(1)···Br(2)	3.984(4)	C(2)C(1)Sb(1)	119.2(4)
<b>2</b>			
Sb(1)–O(1)	2.234(18)	C(1)Sb(1)O1	179.7(9)
Sb(1)–C(1)	2.17(3)	C(31)Sb(1)O1	85.0(6)
Sb(1)–C(31 <sup>1</sup> )	2.11(2)	C(31)Sb(1)C1	95.2(7)
Sb(1)–C(31)	2.11(2)	C(31)Sb(1)C21	122.7(6)
Sb(1)–C(21)	2.11(3)	C(31 <sup>1</sup> )Sb(1)C21	122.7(6)
Br(1)–C(12)	1.90(2)	C(21)Sb(1)O1	84.2(9)
O(1)–C(11)	1.31(3)	C(21)Sb(1)C1	95.4(11)

Symmetry operations: <sup>1</sup>+x, 1/2–y, +z

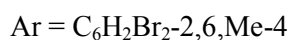
### Results and Discussion

The way of synthesis of antimony compounds with the general formula  $\text{Ph}_4\text{SbX}$  by ligand redistribution reaction is particularly attractive due to easy isolation and high yield of the target product, the amount of which reaches two moles for one mole of initial pentaphenylantimony amount. The similar reaction with the use of pentaphenylantimony and triphenylantimony diarsenides was previously studied on the single example of tetraphenylantimony 4-nitrophenoxide [5].

It has been suggested that this disproportionation reaction proceeds through formation of the intermediate labile complex of ionic structure with tetraphenylstibonium cation and an anion containing two electronegative groups X, apart from four phenyl ligands. The following transition of electronegative group X to tetraphenylstibonium cation is accompanied by formation of the target product  $\text{Ar}_4\text{SbX}$ . It is obvious that aryl compounds of antimony easily enter into disproportionation reactions with groups X, whose electronegativity is high enough.

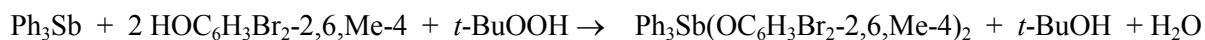
We have studied the possibility of radical redistribution reaction between pentaphenylantimony and *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony (**1**).

The reaction was carried out in toluene solution (1 h, 100 °C). The progress of the reaction was controlled by thin-layer chromatography (Silufol UV-254, *o*-xylene as eluent). The reaction was considered completed after the disappearance of the spot peculiar to pentaphenylantimony. It has been established that the interaction between the abovementioned reactants proceeds with formation of (2,6-dibromo,4-methylphenoxy)tetraphenylantimony (**2**).



Tetraphenylantimony aroxide **2**, obtained by the radical redistribution reaction, was identical in its characteristics (melting point, IR spectrum) to the compound synthesized from pentaphenylantimony and 2,6-dibromo,4-methylphenol.

The parent antimony compound **1** was obtained by triphenylantimony oxidation with the use of *tert*-butyl hydroperoxide in the presence of 2,6-dibromo,4-methylphenol, according to the procedure described in [6]:



From the X-ray analysis data it follows that in molecule **1** the antimony atoms have distorted trigonal-bipyramidal coordination with aroxyl ligands in axial positions (Fig. 1).

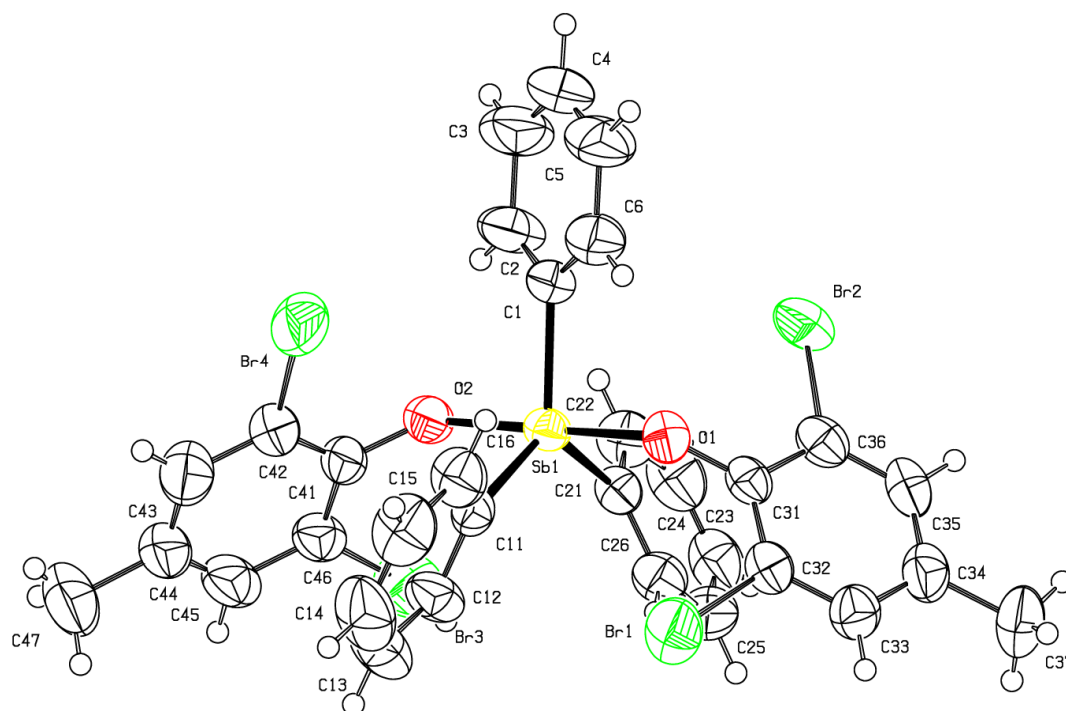


Fig. 1. The structure of compound **1**

The axial angle OSbO measures 179.20(15)°, the sum of angles CSbC in equatorial plane equals 360°. The angles between axial and equatorial bonds OSbC vary in the range 88.0(2)–92.17(19)°. The lengths of equatorial bonds Sb–C (2.090(5), 2.101(5), 2.110(5) Å) exceed the values of axial distances Sb–O (2.088(4), 2.089(4) Å) and the sum of antimony and oxygen covalent radii (2.07 Å [10]). In **1** the close intermolecular contacts between the central atom and one of bromine atoms of aroxyl ligand are observed (Sb⋯Br(2) 3.984(6), Sb⋯Br(4) 3.914(6) Å, while the sum of Van der Waals radii of antimony and bromine is 4.15 Å [10]). The structural organization of the crystal is formed with the participation of weak hydrogen bonds of the type H⋯O (2.61 Å) and H⋯Br (3.02–3.03 Å).

Geometrical characteristics of compound **2** (Fig. 2) differ from those found in **1**, obviously because of the presence of different ligands in axial positions.

For example, the axial angle OSbC equals 179.7(9)°, while the sum of angles CSbC in equatorial plane (357.5°) differs from the ideal value of 360°. The lengths of equatorial bonds Sb–C (2.11(2), 2.11(2), 2.11(3) Å) are less than the values of axial distances Sb–O (2.234(18) Å) and Sb–C (2.17(3) Å). Intra- and intermolecular interactions H⋯Br in crystal **2** are nonexistent, though the structure-forming contacts H⋯O (2.53 Å) are stronger than in **1**.

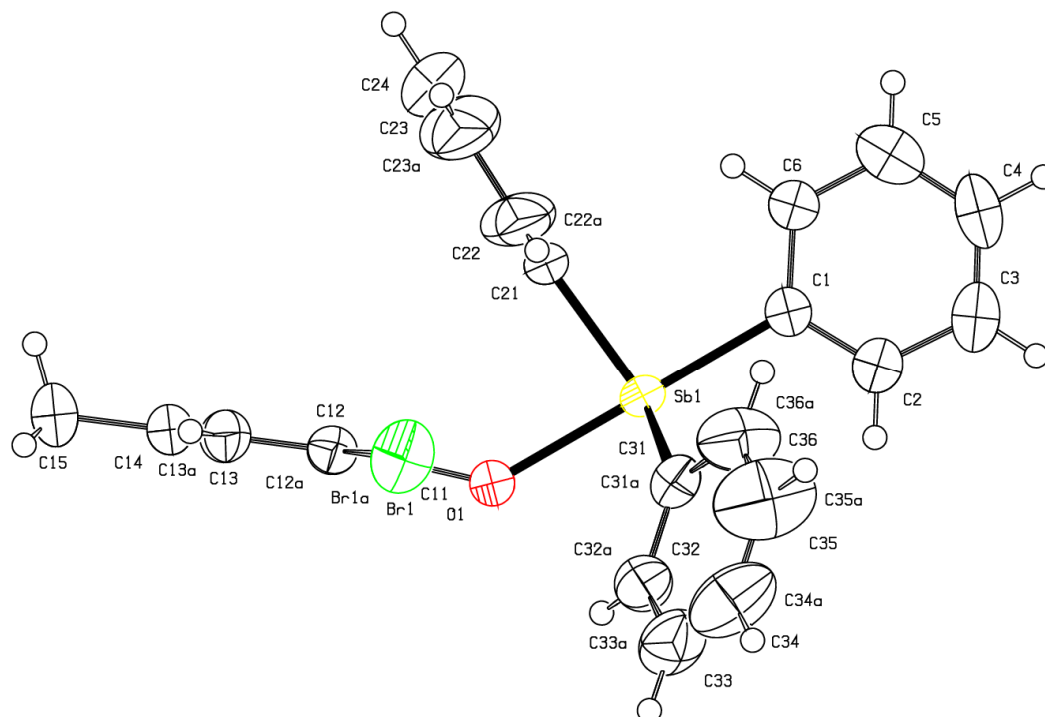


Fig. 2. The structure of compound 2

## Conclusions

To summarize, the ligand redistribution reaction with participation of pentaphenylantimony and *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony, leading to formation of (2,6-dibromo,4-methylphenoxy)tetraphenylantimony, confirms the general character of the abovementioned reaction. In the molecules of *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony and (2,6-dibromo,4-methylphenoxy)tetraphenylantimony the antimony atoms have distorted trigonal-bipyramidal coordination with aroxyl ligands in axial positions. The compound 1 is characterized by short axial bonds Sb–O (2.088(4), 2.089(4) Å), intramolecular contacts Sb⋯Br (3.914(6), 3.984(6) Å).

## References

1. Sharutin V.V., Senchurin V.S., Sharutina O.K., Pakusina A.P., Panova L.P. [Synthesis Method of Tetraphenylstibonium Salts with the General Formula Ph<sub>4</sub>SbX [X=Cl, Br, OC(O)Ph, SCN]. *Russian Journal of General Chemistry*, 1996, vol. 66, no. 10, pp. 1755–1756. (in Russ.)
2. Sharutin V.V., Sharutina O.K., Panova L.P., Bel'skii V.K. [Tetra- and Triphenylantimony Sulfoxides]. *Russian Journal of General Chemistry*, 1997, vol. 67, no. 9, pp. 1438–1442.
3. Sharutin V.V., Sharutina O.K., Pakusina A.P., Belskii V.K. [Reactions of Pentaarylantimony with Triarylantimony Diacylates]. *Russian Journal of General Chemistry*, 1997, vol. 67, no. 9, pp. 1538–1543.
4. Sharutin V.V., Sharutina O.K., Molokova O.V., Etenko E.N., Krivolapov D.B., Gubaydul-lin A.T., Litvinov I.A. [Synthesis and Structure of Tetra- and Triarylantimony Oximates]. *Russian Journal of General Chemistry*, 2001, vol. 71, no. 8, pp. 1243–1247. DOI:10.1023/A:1013220911661
5. Sharutin V.V., Sharutina O.K., Osipov P.E., Subacheva O.V. [New Method for Preparing Aroxy-tetraaryl Derivatives of Antimony]. *Russian Journal of General Chemistry*, 2001, vol. 71, no. 6, pp. 983–984. DOI:10.1023/A:1012368510207
6. Sharutin V.V., Senchurin V.S. *Imennye reaktsii v khimii elementoorganicheskikh soedineniy* [Name Reactions in Chemistry of Organoelemental Compounds]. Chelyabinsk, South Ural St. Univ. Publ., 2011. 426 p. (in Russ.)
7. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.

8. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
9. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.*, 2009, vol. 42, pp. 339–341.
10. Batsanov S.S. [Atomic radiuses of the elements]. *Russian Journal of Inorganic Chemistry*, 1991, vol. 36, no. 12, pp. 3015–3037. (in Russ.)

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## СИНТЕЗ И СТРОЕНИЕ АРОКСИДОВ ТРИ- И ТЕТРАФЕНИЛСУРЬМЫ: $Ph_3Sb[OC_6H_3(Br_{2-2,6})(Me-4)]_2$ И $Ph_4SbOC_6H_3Br_{2-2,6}, Me-4$

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Взаимодействием пентафенилсурьмы с 2,6-дибром,4-метилфенолом или с бис(2,6-дибром,4-метилфенокси)трифенилсурьмой (1) получена 2,6-дибром,4-метилфенокси-тетрафенилсурьма (2). В молекулах 1 и 2 атомы сурьмы имеют искаженную тригонально-бипирамидальную координацию с атомами кислорода в аксиальных положениях ( $OSbO$  179.20(15)° (1),  $OSbC$  179.7(9)° (2)). Длины связей  $Sb-C$  и  $Sb-O$  составляют 2.090(5), 2.101(5), 2.110(5) и 2.088(4), 2.088(4) Å (1), 2.11(2), 2.11(2), 2.11(2), 2.17(3) и 2.234(18), 2.234(18) Å (2) соответственно.

*Ключевые слова:* пентафенилсурьма, трифенилсурьма, 2,6-дибром,4-метилфенол, третбутилгидропероксид, бис(2,6-дибром,4-метилфенокси)три-фенилсурьма, (2,6-дибром, 4-метилфенокси)тетрафенилсурьма, молекулярная структура, рентгено-структурный анализ.

### Литература

1. Способ получения солей тетрафенилстибония общей формулы  $Ph_4SbX$  [ $X=Cl, Br, OC(O)Ph, SCN$ ] / В.В. Шарутин, В.С. Сенчурин, О.К. Шарутина и др. // Журн. общ. химии. – 1996. – Т. 66, № 10. – С. 1755–1756.
2. Сульфонаты тетра- и триарилсурьмы / В.В. Шарутин, О.К. Шарутина, Л.П. Панова, В.К. Бельский // Журн. общ. химии. – 1997. – Т. 67, № 9. – С. 1531–1535.
3. Реакции пентаарилсурьмы с диацилатами триарилсурьмы / В.В. Шарутин, О.К. Шарутина, А.П. Пакузина В.К. Бельский // Журн. общ. химии. – 1997. – Т. 67. – № 9. – С. 1536–1541.
4. Шарутин, В.В. Синтез и строение оксиматов тетра- и триарилсурьмы / В.В. Шарутин, О.К. Шарутина, О.В. Молокова и др. // Журн. общ. химии. – 2001. – Т. 71, № 8. – С. 1317–1321.
5. Новый метод синтеза арокситетраарильных соединений сурьмы / В.В. Шарутин, О.К. Шарутина, П.Е. Осипов, О.В. Субачева // Журн. общ. химии. – 2001. – Т. 71, № 6. – С. 1045–1046.
6. Шарутин, В.В. Именные реакции в химии элементоорганических соединений: справочник / В.В. Шарутин, В.С. Сенчурин. – Челябинск: Издательский центр ЮУрГУ, 2011. – 427 с.
7. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.
8. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
9. OLEX2: a Complete Structure Solution, Refinement and Analysis Program / O.V. Dolomanov, L.J. Bourhis, R.J. Gildea et al. // J. Appl. Cryst. – 2009. – V. 42. – P. 339–341.
10. Бацанов, С.С. Атомные радиусы элементов / С.С. Бацанов // Журн. неорган. химии. – 1991. – Т. 36. – № 12. – С. 3015–3037.

## Organometallic chemistry

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### ОБРАЗЕЦ ЦИТИРОВАНИЯ

Sharutin, V.V. Synthesis and structure of synthesis and structure of tri- and tetraphenylantimony aroxides:  $\text{Ph}_3\text{Sb}[\text{OC}_6\text{H}_3(\text{Br}_{2-2,6})(\text{Me-4})_2]$  and  $\text{Ph}_4\text{SbOC}_6\text{H}_3\text{Br}_{2-2,6}$ , Me-4 / V.V. Sharutin, O.K. Sharutina, V.S. Senchurin // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 4. – С. 86–92. DOI: 10.14529/chem150411

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