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A Method for the Synthesis of Tetra(*para*-tolyl)stibonium Benzenesulfonate from Tetra(*para*-tolyl)stibonium Chloride and Benzenesulfonic Acid

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Abstract—The reaction of tetra(*para*-tolyl)stibonium chloride *p*-Tol_4SbCl (**I**) with benzenesulfonic acid in water affords tetra(*para*-tolyl)stibonium benzenesulfonate *p*-Tol_4SbOSO_2Ph (**II**). According to the X-ray diffraction (XRD) data (CIF files CCDC nos. 2167562 and 2126493, respectively), compounds **I** and **II** have molecular structures with the distorted trigonal bipyramidal coordination of the antimony atom. The geometric characteristics for molecules of compound **I**: angles CSbC 96.12(8)°–124.83(8)°, axial angle CSbCl 174.91(6)°, distances Sb–C and Sb–Cl 2.107(2)–2.170(2) and 2.7230(13) Å, respectively; for molecules of compound **II** angles CSbC 97.72(14)°–118.77(15)°, axial angle CSbCl 174.91(6)°, distances Sb–C and Sb–Cl 2.107(2)–2.170(2) and 2.7230(13) Å, respectively.

Keywords: chloride, benzenesulfonate, tetra(*para*-tolyl)stibonium, synthesis, structure, XRD

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INTRODUCTION

Increasing interest in organic antimony compounds is caused, in many respects, by a growing potential of their use in diverse areas of practical activity: as drugs, biocides, and fungicides; as reagents and components of catalytic systems of polymerization; in fine organic synthesis; as antioxidants; and others [1]. The phenyl derivatives of pentavalent antimony of the general formula Ph_4SbX (X is an electronegative group) are among the most studied organostibium compounds [2]. Similar tolyl derivatives are studied to less extent [3–24].

The reaction of tetra(*para*-tolyl)stibonium (**I**) with benzenesulfonic acid, the single organostibium product of which was tetra(*para*-tolyl)stibonium benzenesulfonate (**II**), was studied in order to extend an experimental material in this field. The refined XRD results are presented for complexes **I** and **II**.

EXPERIMENTAL

Synthesis of tetra(*para*-tolyl)stibonium benzenesulfonate *p*-Tol_4SbOSO_2Ph (II). A solution of benzenesulfonic acid (79 mg) in water (5 mL) was added with stirring to a solution of compound **I** (261 mg, 0.50 mmol) in water (15 mL). After water was evaporated from the filtrate, colorless crystals of complex **II** with T_m = 146°C were obtained in a yield of 310 mg (97%). IR (ν, cm^{-1}): 1280 m, 1170 vs, 1130 s (SO_2).

For $C_{34}H_{33}O_3SSb$		
Anal. calcd., %	C, 63.45	H, 5.13
Found, %	C, 63.26	H, 5.20

The IR spectrum of compound **II** was recorded on a Shimadzu IRAffinity-1S FT-IR spectrometer for a sample pelleted with KBr in an absorption range of 4000–400 cm^{-1}.

XRD was carried out on a Bruker D8 QUEST automated four-circle diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Data were collected and edited, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [25]. All calculations on structure determination and refinement were performed using the SHELXL/PC [26] and OLEX2 [27] programs. The structures were solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The crystallographic data and structure refinement results are listed in Table 1.

The full tables of atomic coordinates, bond lengths, and bond angles for compounds **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2167562 and 2126493, respec-

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds **I** and **II**

Parameter	**I**	**II**
Empirical formula	$C_{28}H_{28}ClSb$	$C_{34}H_{33}O_3SSb$
FW	521.70	643.41
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pbca*
a, Å	9.786(3)	9.923(8)
b, Å	23.168(8)	18.932(16)
c, Å	12.026(5)	32.72(3)
α, deg	9000	90.00
β, deg	113.689(16)	90.00
γ, deg	90.00	90.00
V, Å^3	2496.6(16)	6146(9)
Z	4	8
ρ_{calc}, g/cm^3	1.388	1.391
μ, mm^{-1}	1.224	0.997
F(000)	1056.0	2624.0
Crystal size, mm	0.47 × 0.32 × 0.1	0.21 × 0.2 × 0.13
Range of data collection over 2θ, deg	6.44–56.72	5.954–56.644
Ranges of reflection indices	$-13 \le h \le 13$, $-30 \le k \le 30$, $-15 \le l \le 15$	$-8 \le h \le 12$, $-25 \le k \le 25$, $-43 \le l \le 43$
Measured reflections	59454	73682
Independent reflections (R_{int})	6189 (0.0394)	7553 (0.0589)
Reflections with $I > 2\sigma(I)$	5133	4775
Refinement variables	275	359
GOOF	1.055	1.076
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0272$, $wR_2 = 0.0581$	$R_1 = 0.0493$, $wR_2 = 0.0981$
R factors for all reflections	$R_1 = 0.0383$, $wR_2 = 0.0620$	$R_1 = 0.0955$, $wR_2 = 0.1148$
Residual electron density (min/max), e/Å^3	−0.52/0.23	−0.58/0.60

tively; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

It is known that the exchange reactions of a halide anion in tetraarylstibonium halides are used for the preparation of various metal complexes [2]. An interesting substitution of the halide anion by the stronger acid residue was described [28]: the reactions of organyltriphenylphosphonium halides with arenesulfonic acids in water lead to the formation of organyltriphenylphosphonium arenesulfonates.

Continuing the studies of the substitution reactions of a halide anion in aryl derivatives of antimony, we studied the reaction of tetra(*para*-tolyl)stibonium chloride (**I**) with benzenesulfonic acid. Tetra(*para*-tolyl)stibonium benzenesulfonate *p*-Tol_4SbOSO_2Ph (**II**) was shown to be the single product of this reaction.

$$p\text{-}Tol_4SbCl + HOSO_2Ph \rightarrow p\text{-}Tol_4SbOSO_2Ph + HCl.$$
(II)

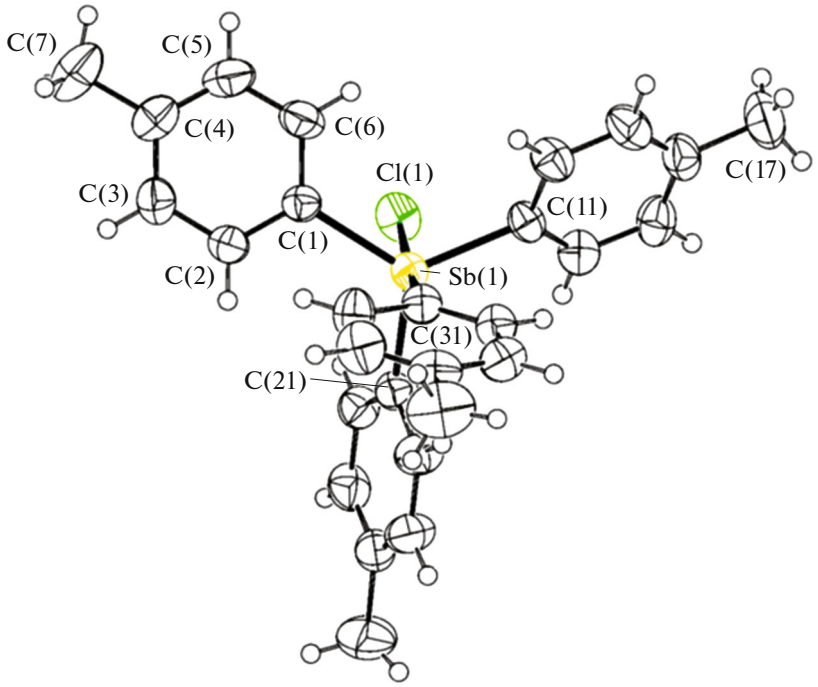

Fig. 1. Structure of tetra(*para*-tolyl)stibonium chloride *p*-Tol_4SbCl.

The structure of compound **I** (Fig. 1) has previously been described [3, 4], and in the present work its structure was refined to $R = 2.7\%$.

The complex has a molecular structure with the distorted trigonal bipyramidal coordination of the antimony atom (the CSbC angles vary in a range of

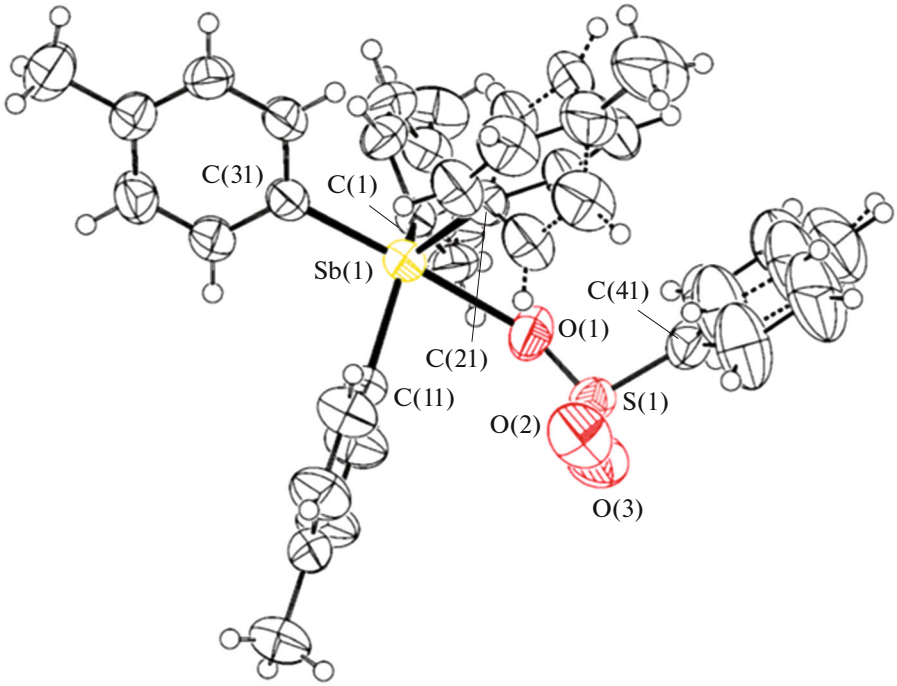

Fig. 2. Structure of tetra(*para*-tolyl)stibonium benzenesulfonate *p*-Tol_4SbOSO_2Ph.

96.12(8)°–124.83(8)°, the axial CSbCl angle is 174.91(6)°, and the Sb–C and Sb–Cl distances are 2.107(2)–2.170(2) and 2.7230(13) Å, respectively).

The structure of complex **II** (Fig. 2) was reported [7, 9]. According to the XRD data, molecules of compound **II** have the trigonal bipyramidal structure. The sulfonate group is in the axial position, which is completely consistent with the theory of repulsion of electron pairs of valence orbitals, and the observed Sb–O bond length (2.409(3) Å) exceeds the sum of covalent radii of the atoms bound to each other (2.14 Å [29]). The CSbC angles vary in a range of 97.72(14)°–118.77(15)°, the axial CSbO angle is 176.44(13)°, and the Sb–C distances are 2.105(4)–2.150(4) Å.

Thus, tetra(*para*-tolyl)stibonium benzenesulfonate (**II**) was synthesized for the first time by the substitution reaction from tetra(*para*-tolyl)stibonium chloride (**I**) and benzenesulfonic acid in a yield of 97%. The structures of complexes **I** and **II** were refined by XRD.

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CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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