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Mendeleev Commun., 2022, **32**, 109–110

Mendeleev Communications

Stoichiometry-dependent oxidation of tris(2-methoxyphenyl)antimony with diiodine

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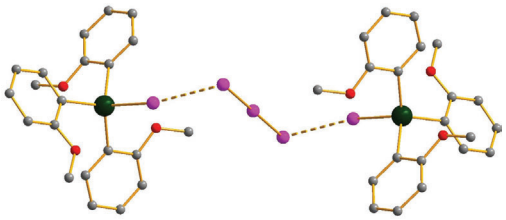
DOI: 10.1016/j.mencom.2022.01.035

The reaction of 2-methoxyphenyllithium with $SbCl_3$ affords tris(2-methoxyphenyl)antimony. Its treatment with equimolar amount of I_2 results in stiborane $(2\text{-}MeOC_6H_4)_3SbI_2$, while heating with 2 equivalents of I_2 leads to iodotris(2-methoxyphenyl)stibonium triiodide $[(2\text{-}MeOC_6H_4)_3SbI]^+ [I_3]^-$ featuring halogen bonding in solid state.



Keywords: antimony, organometallic compounds, non-covalent interactions, crystal structure, organoantimony compounds, iodine.

Among the great variety of organometallic compounds, triarylantimony derivatives represent one of the oldest and best-studied classes (to date, dozens of compounds were prepared and reported).[1–5] One of the general features of Ar_3Sb is their ability to be oxidized into the corresponding Sb^V compounds. In the reactions with Cl_2 or Br_2, stibines Ar_3Sb usually transform[6] into Ar_3SbX_2 (few exceptions were reported[7] yet). With I_2, the diversity of possible reaction outcomes is greater; very recently, we showed that either Ar_3SbI_2 (Ar = 4-MeC_6H_4, 3-MeC_6H_4, 4-FC_6H_4)[8] or triiodide salts of $[Ar_3SbI]^+$ (Ar = 2-MeO-5-BrC_6H_3)[8] could be isolated. We assumed[8] that the difference in reactivity could be related to the substituents at Ar moiety which, on the one hand, affected the electronic structure of $\{Ar_3Sb\}$ reactant in general and, on the other hand, could affect the stabilization of $\{Ar_3SbI\}^+$ species due to the non-covalent interactions. Continuing these studies, we decided to perform in-depth investigation of reaction between Ar_3Sb and I_2 using new stibine $(2\text{-}MeOC_6H_4)_3Sb$ **1** as the precursor. Our choice was based on the fact that structure of **1** is similar to that of $(2\text{-MeO-5-}BrC_6H_3)_3Sb$ which, as mentioned above, oxidized into $(2\text{-MeO-5-}BrC_6H_3)_3SbI^+$ salt. The absence of 5-Br substituent should disable formation of additional I···Br halogen bonding (XB[9–17]) in the solid state (it was observed[8] in the structure of $[(2\text{-MeO-5-}BrC_6H_3)_3SbI]^+I_3^-$ so that the influence of this factor could be eliminated.

Compound **1** was prepared *via* the method general for Ar_3Sb (Scheme 1, for details, see Online Supplementary Materials). *o*-Bromoanisole was treated with PhLi to give $2\text{-}MeOC_6H_4Li$ which was then involved in the reaction with $SbCl_3$. According to XRD [Figure 1(*a*)],† **1** crystallizes as solvate with benzene. There are two crystallographically independent $(2\text{-}MeOC_6H_4)_3Sb$ molecules; one of those is disordered over two positions with 0.92 : 0.08 ratio. The Sb–C bond lengths in non-disordered unit are 2.151(2) Å, being comparable with those in other Ar_3Sb. Interestingly, the methoxy substituents are oriented towards Sb so that the Sb···O distances are 3.054(2) Å, being therefore significantly less than the sum of the corresponding van der Waals radii (3.58 Å[18,19]). Compound **1** is well soluble in arene solvents, chloroform, CCl_4 and DMSO. Its ^1H NMR spectrum ($CDCl_3$) contains signals at 6.84 [3H, Ph, H(3)], 6.90 [3H, Ph, H(5)] and 7.34 [6H, Ph, H(4,6)] ppm corresponding to arene protons and at 3.78 ppm for OMe group.

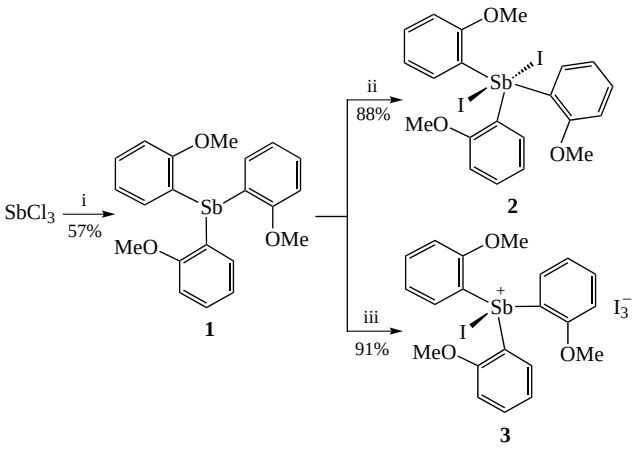
† *Crystal data for* **1**. $C_{522}H_{522}O_{72}Sb_{24}$ ($24C_{21}H_{21}O_3Sb \cdot 3C_6H_6$, M = 10869.37), trigonal, space group $P\bar{3}$, at 293 K: a = 23.266(7), b = 23.480(9) and c = 25.480(9) Å, V = 11944(8) Å^3, Z = 1, d_{calc} = 1.511 g cm^{-3}, μ(MoKα) = 1.40 mm^{-1}, F(000) = 5454. Total of 77674 reflections were collected, and 6699 independent reflections (R_{int} = 0.043) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$]: R_1 = 0.0315, wR_2 = 0.0667.

Crystal data for **2**. $C_{21}H_{21}O_3I_2Sb$ (M = 696.93), triclinic, space group $P\bar{1}$, at 293 K: a = 9.192(8), b = 9.415(7) and c = 15.254(11) Å, α = 81.42(4), β = 80.42(4) and γ = 63.30(4)°, V = 1158.7(16) Å^3, Z = 2, d_{calc} = 1.998 g cm^{-3}, μ(MoKα) = 5.53 mm^{-1}, F(000) = 868. Total of 73387 reflections were collected, and 8464 independent reflections (R_{int} = 0.036) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$]: R_1 = 0.0404, wR_2 = 0.0972.

Crystal data for **3**. $C_{21}H_{21}I_4O_3Sb$ (M = 970.73), triclinic, space group $P\bar{1}$, at 293 K: a = 11.192(9), b = 11.665(13) and c = 12.320(15) Å, α = 63.87(5), β = 77.39(5) and γ = 72.58(4)°, V = 1371(3) Å^3, Z = 2, d_{calc} = 2.304 g cm^{-3}, μ(MoKα) = 3.87 mm^{-1}, F(000) = 656. Total of 63334 reflections were collected, and 6918 independent reflections (R_{int} = 0.0385) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$]: R_1 = 0.0322, wR_2 = 0.0743.

The data were collected on D8 QUEST Bruker diffractometer (MoKα, λ = 0.71073 Å, graphite monochromator). Collection, editing of data and refinement of the unit cell parameters, as well as accounting for absorption, were carried out using the SMART and SAINT-Plus programs. All calculations were performed using the SHELXTL/PC, OLEX2 software. The structure was solved by the direct method and refined by the method of least squares in the anisotropic approximation for non-hydrogen atoms.

CCDC 2070413, 2070393 and 2070385 (**1**, **2** and **3**, respectively) contain the supplementary crystallographic data for this paper. They can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.



Scheme 1 *Reagents and conditions*: i, 2-MeOC$_6$H$_4$Li, Et$_2$O, room temperature, 30 min; ii, I$_2$ (1.0 equiv.), C$_6$H$_6$, room temperature, 1 h; iii, I$_2$ (2.0 equiv.), C$_6$H$_6$, 80 °C, 1 h.

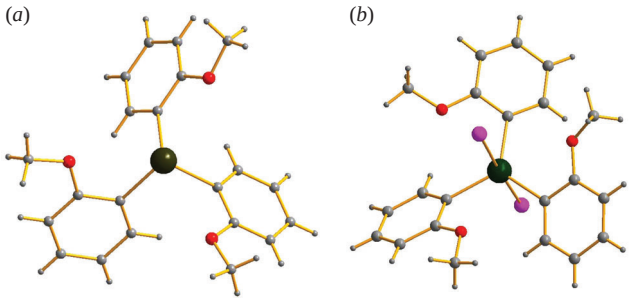


Figure 1 Structures of (*a*) compound **1**·0.125 C$_6$H$_6$ (solvate benzene molecule is omitted) and (*b*) compound **2**.

Reaction of stibine **1** with I$_2$ in 1 : 1 ratio resulted in formation of (2-MeOC$_6$H$_4$)$_3$SbI$_2$ **2** with very good (88%) yield. Coordination environment of Sb in stiborane **2** is trigonal bipyramidal [see Figure 1(*b*)]. The Sb–C distances [2.105(5)–2.117(3) Å] are very similar to those in stibine **1**; the Sb–I bond lengths are 2.851(2)–2.890(2) Å. Compound **2** reveals lower solubility in CDCl$_3$ than **1**, being, however, sufficient for recording ^{1}H NMR spectrum {δ 3.78 (9H, s, O–Me), 6.94 [3H, Ph, H(3), 7.18 (3H, Ph, H(5)] and 7.40 [6H, Ph, H(4,6)] ppm, respectively}.

Performing the reaction between **1** and I$_2$ with other reactant ratio (1 : 2), we isolated dark brown substance which was recrystallized from chloroform to give single crystals of [(2-MeOC$_6$H$_4$)$_3$SbI]$^+$I$_3^-$ **3**, the product which belongs to the same type as [(2-MeO-5-BrC$_6$H$_3$)$_3$SbI]$^+$I$_3^-$. The Sb–C bonds are only slightly shorter than in compound **2** [2.084(4)–2.094(6) Å]; the Sb–I distance is 2.656(2) Å. The triiodide anions are symmetric [I–I = 2.904(2) Å]; the main feature of this structure is the presence of halogen bonding between iodine atom of Ar$_3$SbI$^+$ and terminal iodine atoms of I$_3^-$ (Figure 2) so that supramolecular dimers {(Ar$_3$SbI)$_2$(I$_3$)} [I···I = 3.814(3) Å, I–I–I = 74.5(3)°] are formed.

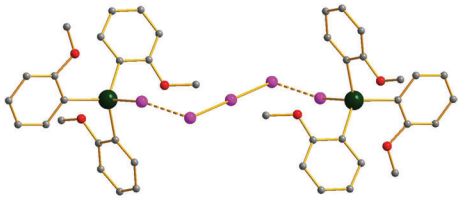


Figure 2 Supramolecular dimers in the structure of **3**. H atoms are omitted.

In IR spectra of compounds **1**–**3**, the bands corresponding to stretching vibrations of Sb–C bonds appear at 441, 441 and 432 cm^{-1}, respectively. The intense peaks at 1234 (**1**), 1234 (**2**) and 1244 (**3**) cm^{-1} are related to C–O bonds (valent vibrations), while bands at 1571, 1462, 1429 (**1**), 1571, 1462, 1429 (**2**), 1573, 1471, 1433 cm^{-1} (**3**) are related to C–C bonds in aryl fragments.

In summary, the reactions between R$_3$Sb and I$_2$ can lead to both types of compounds, namely, R$_3$SbI$_2$ and (R$_3$SbI)I$_3$. Unlike the earlier report,[8] in this case the outcome of the reaction is controlled by stoichiometry rather than the nature of substituents in Ar units. This observation confirms the crucial role of non-covalent interactions which can govern the pathway of such reactions. In our opinion, this finding deserves being investigated further; corresponding experiments are underway.

This work was partially supported by the Ministry of Science and Higher Education of the Russian Federation (spectral characterization of the samples, no. 121031700313-8).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.035.

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Received: 1st June 2021; Com. 21/6575