Organoantimony Oxides: Preparation and Crystal Structures of $[(2\text{-PhOC}_6H_4)O(C_6H_4)_2Sb]_2O_2$ and $(o\text{-Tol}_2Sb)_4O_6$☆

Hans Joachim Breunig*[a], **Joachim Probst**[a], **Klaus Heinz Ebert**[a], **Enno Lork**[a], **Raymundo Cea-Olivares***[b], **and José-Guadalupe Alvarado-Rodríguez**[b]

Fachbereich 2, Universität Bremen[a],
P.O. Box 330440, D-28334 Bremen, Germany

Instituto de Quimica, Universidad Nacional Autónoma de México[b],
04510 México, D.F., México

Received January 22, 1997

Keywords: Phenoxystibanes / Organoantimony oxides / Antimony / Main group elements

Air oxidation of (Oxydi-2,1-phenylene)(2-phenoxyphenyl)stibane (**1**) gives the phenoxystibane oxide $[(2\text{-PhOC}_6H_4)O(C_6H_4)_2Sb]_2O_2$ (**2**). Single crystals of $(o\text{-Tol}_2Sb)_4O_4(O_2)_2$ (**3**) were obtained by air oxidation of $o\text{-TolSb}(SiMe_3)_2$. Crystal structures of **2** and **3** are reported.

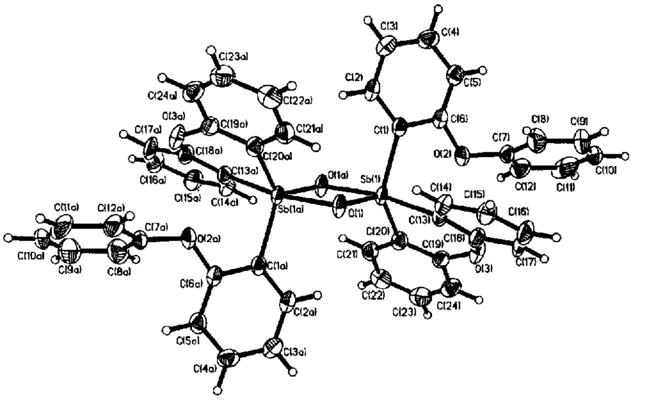
Triarylstibanes are air-stable[1], in contrast to trialkylstibanes which are very sensitive towards oxygen in the air. Powerful oxidizing agents such as alkyl peroxides or H_2O_2 are required for the oxidation of Ph_3Sb to $(Ph_3Sb)_2O_2$[2]. We report here the air oxidation of (Oxydi-2,1-phenylene)(2-phenoxyphenyl)stibane (**1**)[3], a cyclic compound with aryl substituents. The present study of the phenoxystibane oxide $[R\{O(C_6H_4)_2\}Sb]_2O_2$ [$R = 2\text{-PhOC}_6H_4$; (**2**)] continues structural investigations[4,5] of phenoxy group-15 element compounds with an emphasis on the dihedral angles between the planes of the phenylene rings of the phenoxy–element moiety.

A side product of the reaction of Ph_3Sb with H_2O_2 is $(Ph_2Sb)_4O_6$[2]. This antimony–oxygen cage is the dimeric form of phenylstibinic anhydride, $Ph_2Sb(O)O(O)SbPh_2$, and may be considered as a product of the insertion and addition of oxygen atoms to tetraphenyldistibane. Following these lines we have recently investigated the reaction of the analogous *o*-tolyl derivative, $(o\text{-Tol}_2Sb)_2$, with atmospheric oxygen and found that $(o\text{-Tol}_2Sb)_4O_6$ (**3**) was formed[6]. However, samples obtained by this synthetic pathway were powders; attempts at crystallisation failed because of the low solubility in organic solvents. We report here the formation of single crystals of **3** by air oxidation of $o\text{-TolSb}(SiMe_3)_2$ and the crystallographic characterisation of this cluster.

Air Oxidation of the Phenoxystibane $R\{O(C_6H_4)_2\}Sb$ (1) and the Structure of $[R\{O(C_6H_4)_2\}Sb]_2O_2$ (2) ($R = 2\text{-PhOC}_6H_4$)

The synthesis of **1** was achieved by reaction of $SbCl_3$ with $(2\text{-LiC}_6H_4)_2O$ and $2\text{-LiC}_6H_4OC_6H_5$ in tetrahydrofuran/petroleum ether. The lithium reagents were prepared by reaction of diphenyl ether with *n*-butyllithium[7]. The reaction of a solution of **1** in dichloromethane with atmospheric oxygen gave the novel oxide **2** as a colorless crystalline solid (m.p. 220 °C), soluble in chloroform and other organic solvents. Mass spectra show that the molecular ion and fragments possess an Sb_2O_2 group. The structure of **2** in the crystalline state is depicted in Figure 1.

Figure 1. Molecular structure of **2** in the crystalline phase[a]



[a] Selected distances [pm] and angles [°]: Sb(1)–O(1) 194.3(3), Sb(1)–O(1a) 206.0(2), Sb–C(1) 211.3(4), Sb(1)–C(20) 209.9(4), Sb(1)–C(13) 212.8(4); O–Sb–O 78.21(11), Sb–O–Sb 101.79(11), C(13)–Sb–C(20) 90.7(2), C(1)–Sb–C(13) 98.68(14), C(1)–Sb–C(20) 117.76(14), O(1)–Sb–C(1) 113.51(13), O(1a)–Sb–C(1) 91.29(12), O(1)–Sb–C(13) 91.41(13), O(1)–Sb–C(20) 127.69(13), O(1a)–Sb–C(20) 90.74(13).

The centrosymmetric molecules contain a planar 1,3,2,4-dioxadistibetane unit where the organo substituents occupy *trans* positions. The distances and angles in the central ring and the distorted square pyramidal environment of the antimony atoms compare well with the structure of $(Ph_3Sb)_2O_2$[2]. The dihedral angle between the planes of the phenylene rings is 160.2°. The adduct $O(C_6H_4)_2\text{-}As(O)ClSbCl_4$[8], the only other compound containing the phenoxy moiety coordinated to a heavy group-15 element in the oxidation state (V), displays a larger dihedral angle of 167.7°. A folded $S(C_6H_4)_2Sb$ arrangement with a di-

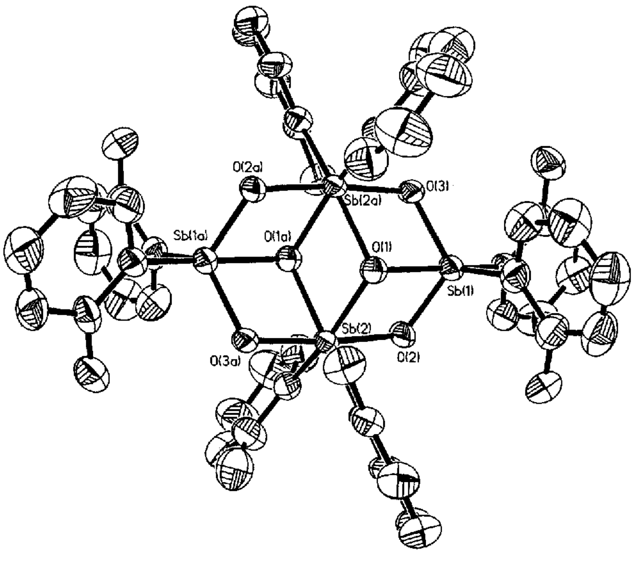
0009–2940/97/0707–0959 $ 17.50+.50/0

hedral angle of 112° has been found in the structure of $S(C_6H_4)_2$ SbCl[9].

Formation and Structure of (o-$Tol_2Sb)_4O_6$ (3)

Single crystals of **3** suitable for X-ray analysis were formed when a solution of o-TolSb$(SiMe_3)_2$ in tetrahydrofuran was exposed to atmospheric oxygen in a glass ampoule for several weeks. Under these conditions the access of air is slow but leads finally to excess oxygen in the reaction mixture. The formation of **3** represents a novel aspect of the chemistry displayed by arylbis(trimethylsilyl)stibanes in the presence of air. Known oxidation products are hexaarylhexastibanes, $(ArSb)_6$, which form when an excess of the silylantimony component is maintained during the oxidation[10]. Air oxidation in solution in an open flask leads to rearrangement products of the type $Ar_2SbOSiMe_3$[11] and $Sb(OSiMe_3)_3$. It is evident that migrations of the o-tolyl groups also occur during the formation of **3**. A possible reaction path could begin with a rearrangement of the substituents during the first step of the oxidation of o-TolSb$(SiMe_3)_2$ giving o-$Tol_2SbOSiMe_3$ as one of the products. Subsequent elimination of $(Me_3Si)_2O$ from this intermediate could lead to (o-$Tol_2Sb)_2O$ which gives **3** when oxygen is present. The molecular structure of **3** in the crystalline phase is shown in Figure 2.

Figure 2. Molecular structure of **3** in the crystalline phase[a]



[a] Selected distances [pm] and angles [°]: O(1)−Sb(2) 207.6(5), O(1)−Sb(1) 227.6(5), O(2)−Sb(2) 204.1(5), O(3)−Sb(2a) 202.8(5), O(1)−Sb(2a) 208.7(5), O(2)−Sb(1) 190.7(5), O(3)−Sb(1) 189.9(5); O(3)−Sb(1)−O(2) 111.7(2), O(3)−Sb(1)−O(1) 76.5(2), O(3a)−Sb(2)−O(2) 174.6(2), O(1)−Sb(2)−O(1a) 73.5(2).

The structure contains a central Sb_4O_6 cage surrounded by o-tolyl substituents. The cage consists of a puckered $(Sb-O)_4$ ring with Sb−O bond lengths of 189.9(5) pm and 204.1(5) pm. Two additional oxygen atoms, O(1) and O(1a), occupy triple-binding positions and have shorter bonds to the six-coordinate antimony atoms, O(1)−Sb(2a) 208.7(5) pm and O(1)−Sb(2) 207.6(5) pm, and relatively long separations to the five-coordinate antimony atoms, O(1)−Sb(1) 227.6(5) pm. The structure of **3** compares well with the analogous phenyl derivative $(Ph_2Sb)_4O_6$[2].

We gratefully acknowledge financial support by the *Fonds der Chemischen Industrie* and by the *Universität Bremen*. J.-G. A.-R. thanks the *UNAM Foundation* for a fellowship.

Experimental Section

General: ^{1}H NMR: Bruker WH 360. − MS: Finnigan MAT 8222; the pattern of antimony-containing ions was compared with theoretical values. − Elemental analyses: Beller Mikroanalytisches Laboratorium, Göttingen.

X-Ray Crystallographic Study[12]: Diffractometer: Siemens P4, Mo-K_α radiation, graphite monochromator, T = 173 K, 2Θ-ω scans, 3 reference reflections (every 197 reflections). − Solution by direct methods and refinement with full-matrix least squares (Sb and C anisotropic, H atoms fixed with isotropic temperature factors on calculated positions). − Systems used: SHELXTL-PLUS[13], SHELXL-93[14].

$[(2\text{-}PhOC_6H_4)O(C_6H_4)_2Sb]_2O_2$: $C_{48}H_{34}O_6Sb_2$ (950.25), crystal size 0.6 × 0.2 × 0.2 mm, monoclinic space group $P2_1/n$, a = 951.8(1), b = 2016.1(2), c = 1017.7(2) pm, β = 104.35(1)°, V = 1.8920(5) nm^3, Z = 2, $D_{calcd.}$ = 1.668 Mg/m^3, μ (Mo-K_α) = 1.481 mm^{-1}, 9310 reflections measured (Θ_{max} = 27.50°), 4341 independent reflections (R_{int} = 6.26%), R_1 = 4.06%, parameters 254, wR_2 = 9.50%, residual electron density 1444 and −1752 e nm^{-3}.

$(o\text{-}Tol_2Sb)_4O_6$: $C_{56}H_{56}O_6Sb_4$ (1312.00); crystal size 0.8 × 0.4 × 0.1 mm, triclinic space group $P\bar{1}$, a = 1114.8(2), b = 1116.3(2), c = 1219.5(2) pm, α = 92.65(3), β = 111.67(3), γ = 113.59(3)°, V = 1.25854(4) nm^3, Z = 1, $D_{calcd.}$ = 1.731 Mg/m^3, μ (Mo-K_α) = 2.174 mm^{-1}, 6725 reflections measured (Θ_{max} = 27.5°), 5740 independent reflections (R_{int} = 5.9%), R_1 = 6.54%, parameters 305, wR_2 = 18.08%, residual electron density 2574 and −2557 e nm^{-3}.

(Oxydi-2,1-phenylene)(2-phenoxyphenyl)stibane (**1**): A solution of 1.856 g (29 mmol) of nBuLi in a mixture of 18 ml of petroleum ether and 10 ml of ether was added dropwise to a solution of 2.14 g (12.6 mmol) of diphenyl ether in 20 ml of THF. During the addition the solution was stirred and cooled with an ice/salt bath. The mixture was stirred for 14 h at room temperature. This solution and a solution of 2.29 g (12.6 mmol) of $SbCl_3$ in 10 ml of THF in separate dropping funnels were added dropwise at the same rate into a flask cooled with an ice/salt bath. After the addition, the mixture was refluxed for 1 h, cooled with an ice bath and hydrolysed with water. The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure leaving a pale yellow oil, which after addition of 20 ml of petroleum ether gave 0.33 g of **1** as a colorless solid (m.p. 122−125°C; ref.[3] 122−128°C). − MS (70 eV); m/z (%): 458 (27) $[M^+]$, 381 (8) $[M^+ - C_6H_5]$, 365 (11) $[M^+ - OC_6H_5]$, 289 (24) $[O(C_6H_4)_2Sb]$, 168 (100) $[O(C_6H_4)_2]$.

Di(oxydi-2,1-phenylene)(2-phenoxyphenyl)stibane Dioxide (**2**): Exposure of **1** to the atmosphere in a dichloromethane/petroleum ether system gave colorless crystals of **2** (m.p. 261−264°C). − MS (70 eV); m/z (%): 949 (5) $[M^+]$, 857 (10) $[M^+ - OC_6H_5]$, 781 (12) $[M^+ - C_6H_4OC_6H_5]$, 289 (24) $[O(C_6H_4)_2Sb]$, 168 (100) $[O(C_6H_4)_2]$. − $C_{48}H_{34}O_6Sb_2$ (950.3): calcd. C 60.67, H 3.61; found C 62.45, H 3.85.

Tetrakis(di-o-tolylstibane) Hexaoxide (**3**): Colorless crystals suitable for X-ray crystallography (m.p. 266°C) were obtained by exposing to the atmosphere a solution of 0.06 g (0.166 mmol) of o-TolSb$(SiMe_3)_2$[10] in 1.5 ml tetrahydrofuran in a glass ampoule covered with a plastic foil (para film) for three months. − MS (DCI pos., NH_3, 8 mA/s); *m/z* (%): 1313 (16) [M^+ + H], 395 (76), 320 (100), 230 (80).

☆ Dedicated to Prof. Dr. *Gottfried Huttner* on the occasion of his 60th birthday.

[1] M. Wieber, *Gmelin Handbook of Inorganic Chemistry*, 8th ed., Sb, Organoantimony Compounds, part 1, Springer Verlag, Berlin, **1980**, p. 51.

[2] J. Bordner, G. O. Doak, T. S. Everett, *J. Am. Chem. Soc.* **1986**, *108*, 4206–4213.

[3] D. Hellwinkel, M. Bach, *J. Organomet. Chem.* **1969**, *17*, 389–403.

[4] R. Cea-Olivares, R.-A. Toscano, M. Estrada, C. Silvestru, P. Garcia y Garcia, M. Lopez-Cardoso, G. Blass-Amador, *Appl. Organomet. Chem.* **1995**, *9*, 133–140.

[5] R. Cea-Olivares, J. G. Alvarado-Rodríguez, G. Espinosa-Perez, *Inorg. Chim. Acta*, accepted for publication.

[6] H. J. Breunig, T. Krüger, E. Lork, *Angew. Chem.* **1997**, *109*, 654–655; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 615–617.

[7] H. Gilman, W. J. Trepka, *J. Org. Chem.* **1961**, *26*, 5202–5203.

[8] A. W. Cordes, R. J. Holliday, R. W. Broach, L. B. Handy, L. Thomas, *Inorg. Chem.* **1972**, *11*, 1849–1851.

[9] A. W. Cordes, W. T. Pennington, J. C. Graham, Y. W. Jung, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 709–711.

[10] H. J. Breunig, K. H. Ebert, S. Gülec, J. Probst, *Chem. Ber.* **1995**, *128*, 599–603.

[11] H. J. Breunig, A. Soltani-Neshan, K. Häberle, M. Dräger, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 327–333.

[12] Crystallogrpahic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallogrphaic Data Centre as supplementary publication no. CCDC-100138. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ. UK (fax: int. code +44(1223) 336-033, e-mail: deposit@chemcrys.cam.ac.uk).

[13] G. M. Sheldrick, *SHELXLTL-PLUS*, revision 4.11 V, SHELXTL-PLUS users manual, Siemens Analytical X-ray Inst. Inc., Madison, Wisconsin, U.S.A.

[14] G. M. Sheldrick, Universität Göttingen, **1993**.

[97012]