Oxidation of triphenylantimony with 4-hydroperoxy-2-hydroxy-3,4,6-triisopropylcyclohexa-2,5-dienone or 3,4,6-triisopropyl-1,2-benzoquinone

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According to the NMR spectroscopic data, the oxidation of triphenylantimony with 4-hydroperoxy-2-hydroxy-3,4,6-triisopropylcyclohexa-2,5-dienone involves three steps. The first step affords the 2,4,10,12-tetraoxa-3,11-distibatricyclo[11.3.1.1^{5,9}]octadecatetraene derivative. The latter is rearranged into benzodioxastibolone derivatives followed by the rearrangement into 4,6,7-triisopropyl-2,2,2-triphenyl-1,3,2-benzodioxastibol-5-ol. The transformation of the latter depends on the presence of oxygen and the mode of its dosing.

Key words: organoantimony compounds, hydroperoxides, quinones, catecholates, oxidation, oxygen, X-ray diffraction study, NMR.

Recently, the unique ability of *o*-amidophenolate[1] and catecholate[2] derivatives of antimony(v) to reversibly bind molecular oxygen has been discovered. This process can proceed only with antimony(v) complexes, which have a relatively low ligand oxidation potential.[2] In this connection, new antimony catecholate complexes containing electron-donating substituents in the aromatic ring of catecholate are of considerable interest. Among these compounds are, in particular, adducts of triphenylantimony(iii) (**1**) with 4-hydroperoxy-2-hydroxy-3,4,6-triisopropylcyclohexa-2,5-dienone (**2**) and 3,4,6-triisopropyl-1,2-benzoquinone (**3**) synthesized in the present study.

Various phenyl derivatives of antimony(v) can be prepared by the oxidative method,[3] to be more precise, by the reaction of triphenylantimony(iii) with hydroperoxide and compounds containing labile hydrogen (RC(O)H, RC(O)OH, *etc*.). The characteristic feature of dienone **2** is that it contains simultaneously the hydroperoxide and hydroxy groups.

The reaction pathway of dihydroxybenzenes with triphenylantimony in the presence of *tert*-butylhydroperoxide depends on the structure of phenol.[4] For example, the reaction of pyrocatechol produces antimony(v) triphenylcatecholate. The reaction of resorcinol gives 3,3,3,11,11,11-hexaphenyl-2,4,10,12-tetraoxa-3,11-distibatricyclo[11.3.1.1^{5,9}]octadeca-1,5,6,8,13,15-hexaene, in which each antimony atom is bound to the oxygen atoms of two different resorcinol fragments. The reaction of hydroquinone affords polymeric triphenylantimony(v) hydroquinolate. Not only hydroperoxides but also quinones can serve as oxidants. For example, **1** is quantitatively oxidized with *o*-quinones to the corresponding antimony(v) catecholates.[5]

The reaction of **1** with **2** (Scheme 1) under consideration is of interest because molecule **2** contains two fragments, quinone and hydroperoxide, with potential oxidative activity. The arrangement of the oxygen atoms in compound **2** allows the formation of catecholate, dimeric, or polymeric derivatives of antimony(v). Apparently, the first step of the reaction involves the insertion of **1** at the peroxide bond of **2** to form the unstable intermediate $HOSbPh_3OR$. Earlier, it has been shown[3,4] that this intermediate rapidly reacts with the hydroxy groups that are present in the system to give the corresponding derivative of antimony and water.

The reaction of **1** with **2** was monitored by NMR spectroscopy. In benzene or toluene, the solution turned turbid at the instant of mixing. Immediately after mixing, the ^{1}H NMR spectrum in C_6D_6 shows the signal of water present as an emulsion (δ 5.4). In $CDCl_3$, the signal of water is observed at δ 1.8. In both solvents, the signals of the starting reagents disappeared within 2—3 min after mixing of compounds **1** and **2** in a ratio of 1 : 1. Taking into account the structure of the known reaction product of **1** with resorcinol[4] and the NMR spectra of the reaction mixture, the reaction most probably produces 1,7,9,15,17,18-hexaisopropyl-3,3,3,11,11,11-hexaphenyl-2,4,10,12-tetraoxa-3,11-distibatri-

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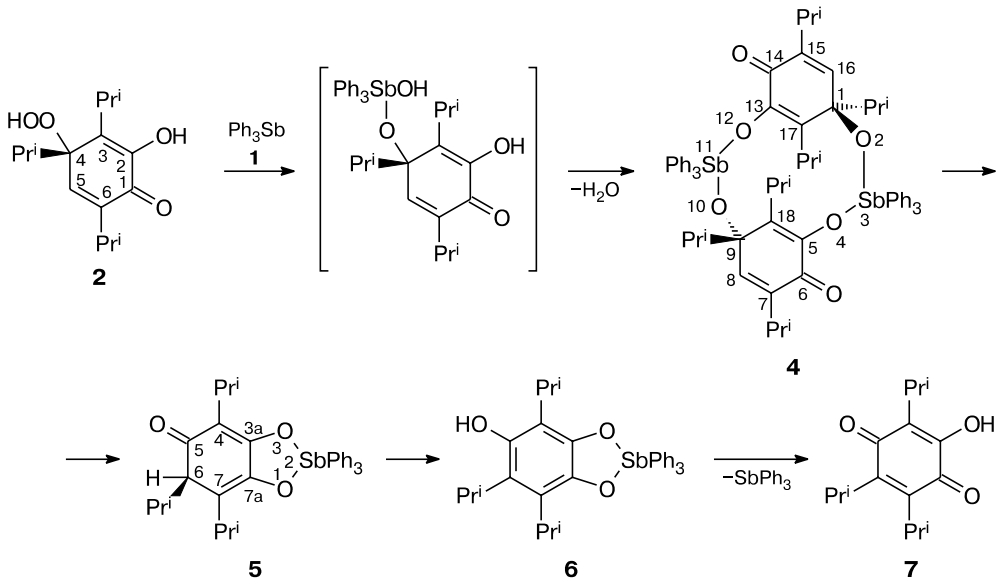
Scheme 1



cyclo[11.3.1.1^{5,9}]octadeca-5,7,13,15-tetraene-6,14-dione (**4**) (see Scheme 1).

The starting hydroperoxide **2** contains the chiral center, resulting in the nonequivalence of the methyl fragments of the isopropyl groups in the NMR spectra.[6] For example, the difference in the chemical shifts of the methyl protons of the Pr^{i}C(4)OOH fragment is 0.39 ppm. Compound **4** is also chiral, the difference in the chemical shifts for the protons of the diastereotopic methyl groups of the Pr^{i}C(1,9) fragments being larger (0.72 ppm). Compound **4** is completely transformed into 4,6,7-triisopropyl-2,2,2-triphenyl-1,3,2-benzodioxastibol-5(6*H*)-one (**5**) within 1 h. The structure of compound **5** was determined by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of compound **5** shows a doublet at δ 2.82 assigned to the HC(6) proton. The difference in the chemical shifts for the protons of the diastereotopic methyl groups of the Pr^{i}C(6) fragment is 0.35 ppm. The transformation **4** → **5** proceeds, apparently, as a result of the migration of the isopropyl groups from positions 1 and 9 to positions 16 and 8, respectively.

After the completion of the induction period (~8 h in $CDCl_3$), compound **5** undergoes the rearrangement into 4,6,7-triisopropyl-2,2,2-triphenyl-1,3,2-benzodioxastibol-5-ol (**6**) (see Scheme 1), which is completed in one day. The structure of catecholate **6** recrystallized from methanol was established by X-ray diffraction (Fig. 1, Tables 1 and 2). According to the X-ray diffraction study, the antimony atom in molecule **6** is in a distorted octahedral environment. In addition to two oxygen atoms of the catecholate ligand and three carbon atoms of the phenyl groups, the antimony atom in the crystal structure of **6** is coordinated by the MeOH molecule. The antimony atom of the complex is in a single plane with the oxygen atoms and the ring of the catecholate ligand. The observed distribution of the C—C, C—O, and Sb—O bond lengths in **6** is characteristic of Sb^V catecholate complexes.[7,8]

In $CDCl_3$ or C_6D_6, catecholate **6** slowly (during 3—4 weeks) decomposes into $SbPh_3$ (**1**) and 2-hydroxy-3,4,6-triisopropyl-1,4-benzoquinone (**7**). Therefore, hydroperoxide **2** is finally decomposed with triphenylantimony into hydroxy-*p*-quinone **7** and water, compound **7** being the only organic product of this transformation of **2**.

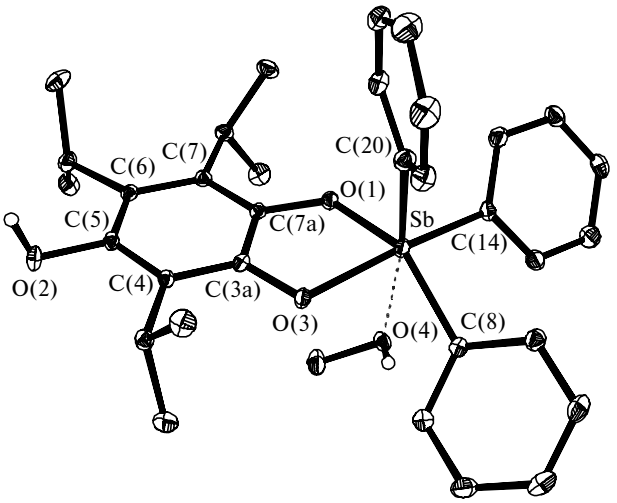


Fig. 1. Molecular structure of catecholate **6**. The hydrogen atoms only at the hydroxy groups are shown. Displacement ellipsoids are drawn at the 30% probability level.

Table 1. Selected bond lengths in compounds **6**, **12**, and **13***

Bond	*d*/Å	Bond	*d*/Å
	6		**12**
Sb—O(3)	2.034(1)	C(57)—C(56)	1.342(6)
Sb—O(1)	2.026(1)	C(56)—C(55)	1.372(6)
O(1)—C(7a)	1.370(2)	C(55)—C(54)	1.520(7)
O(3)—C(3a)	1.356(2)	C(54)—C(53)	1.333(6)
O(2)—C(5)	1.403(2)		**13**
(C—C)**	1.392(2)—1.417(2)	Sb—O(1)	2.109(2)
	12	Sb...O(3)	2.668(3)
Sb(1)—O(1)	2.106(3)	O(1)—C(1)	1.324(3)
Sb(1)...O(2)	2.490(3)	O(2)—C(3)	1.231(3)
Sb(1)—O(4)	1.968(6)	O(3)—C(6)	1.225(3)
O(1)—C(1)	1.334(6)	C(1)—C(2)	1.351(3)
O(2)—C(6)	1.227(5)	C(2)—C(3)	1.468(3)
O(3)—C(3)	1.215(5)	C(3)—C(4)	1.514(3)
C(1)—C(6)	1.483(5)	C(4)—C(5)	1.346(4)
C(6)—C(5)	1.462(4)	C(5)—C(6)	1.482(3)
C(5)—C(4)	1.361(1)	C(6)—C(1)	1.498(3)
C(4)—C(3)	1.629(5)	Sb—O(4)	2.113(2)
C(3)—C(2)	1.368(7)	Sb...O(6)	2.619(3)
C(1)—C(2)	1.377(5)	O(4)—C(16)	1.325(3)
Sb(2)—O(6)	2.139(3)	O(5)—C(18)	1.232(3)
Sb(2)...O(5)	2.543(3)	O(6)—C(21)	1.231(3)
Sb(2)—O(4)	1.937(6)	C(16)—C(17)	1.352(3)
O(6)—C(53)	1.299(5)	C(17)—C(18)	1.463(3)
O(5)—C(52)	1.239(5)	C(18)—C(19)	1.514(3)
O(7)—C(55)	1.223(4)	C(19)—C(20)	1.342(3)
C(52)—C(53)	1.539(6)	C(20)—C(21)	1.478(3)
C(52)—C(57)	1.476(7)	C(21)—C(16)	1.492(3)

* For complex **13**, the geometric characteristics of one independent molecule are given.
** The catecholate fragment.

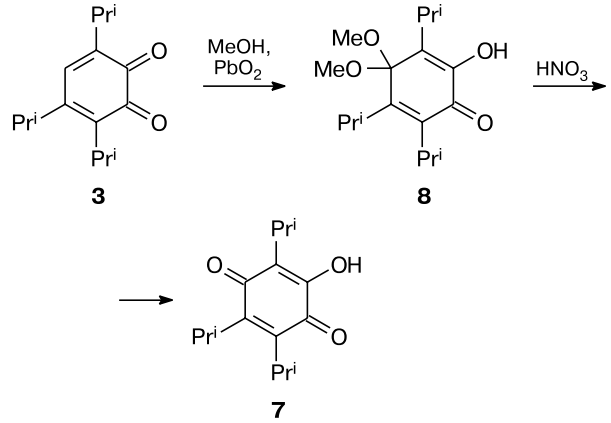
Table 2. Selected bond angles (ω) in compounds **6**, **12**, and **13***

Angle	ω/deg
	6
O(3)—Sb—O(1)	79.39(5)
Sb—O(3)—C(3a)	113.21(10)
Sb—O(1)—C(7a)	113.10(10)
	12
Sb(1)—O(4)—Sb(2)	175.0(4)
Sb(1)—O(1)—C(1)	121.2(2)
Sb(1)—O(2)—C(6)	111.3(2)
Sb(2)—O(6)—C(53)	125.4(3)
Sb(2)—O(5)—C(52)	113.7(3)
O(1)—Sb(1)—O(2)	71.0(1)
O(5)—Sb(2)—O(6)	68.5(1)
	13
O(1)—Sb—O(4)	166.91(6)
O(1)—Sb—O(3)	65.8(1)
O(4)—Sb—O(6)	66.2(1)
Sb—O(1)—C(1)	128.7(1)
Sb—O(3)—C(6)	117.1(1)
Sb—O(4)—C(16)	128.0(1)
Sb—O(6)—C(21)	112.5(1)

* For complex **13**, the geometric characteristics of one independent molecule are given.

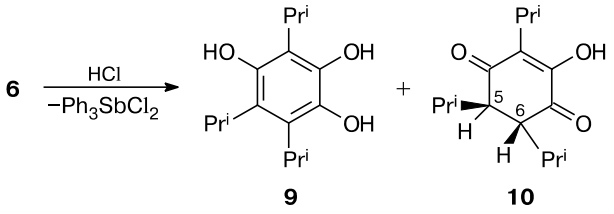
The structure of product **7** was established by IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis. In addition, hydroxy-*p*-quinone **7** was synthesized by the two-step oxidation of *o*-quinone **3** (Scheme 2).

Scheme 2



To confirm the structure of catecholate **6**, we performed its acidolysis (Scheme 3). Unexpectedly, the reaction produced, along with 1,2,4-trihydroxy-3,5,6-triisopropylbenzene (**9**), isomeric nonaromatic 2-hydroxy-3,5,6-triisopropylcyclohex-2-ene-1,4-dione (**10**), the ratio between the products being dependent on the reaction conditions. In the reaction with HCl in methanol, the ratio between products **9** and **10** is 2 : 1, whereas the acidolysis with acetic acid affords predominantly product **10**.

Scheme 3

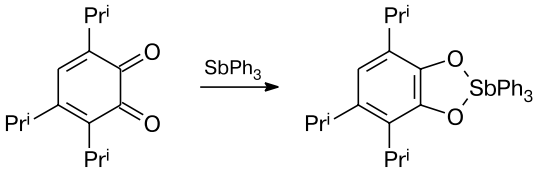


The loss of aromaticity occurs only in the coordination sphere of antimony, because product **10** is not generated upon the treatment of compound **9** with HCl/MeOH or AcOH under an inert atmosphere. Compound **9** is oxidized to hydroxy-*p*-quinone **7** upon the contact with atmospheric oxygen in an acidic medium. Unlike triol **9**, its isomer **10** is stable to oxidation both in the crystalline state and in solution. The structure of compound **10** was determined by one-dimensional and two-dimensional

NMR spectroscopy. The presence of intense cross-peaks in the two-dimensional NOESY spectrum with dipole-dipole coupling between the HC(5) and HC(6) protons is indicative of their spatial proximity. The vicinal spin-spin coupling constants between the protons H—C(5)—C(6)—H is only 0.9 Hz. Consequently, the dihedral angle between these protons is close to 90°, which is possible only if these atoms are in equatorial positions. Consequently, the isopropyl groups bound to the C(5) and C(6) atoms of the cyclohexene ring are in axial positions.

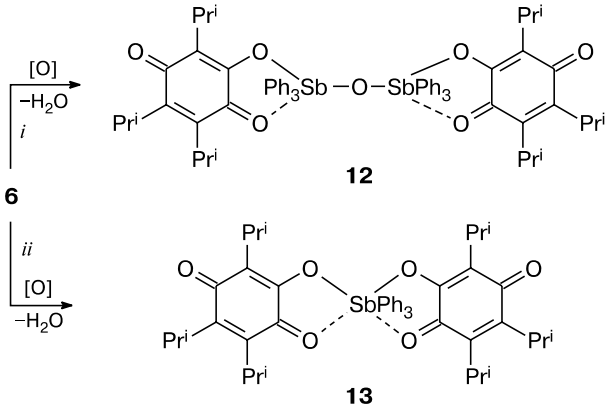
In solution, quinone **3** oxidizes triphenylantimony immediately after mixing (Scheme 4). The oxidation affords 4,5,7-triisopropyl-2,2,2-triphenyl-1,3,2-benzodioxastibole (**11**) as the only product. Compound **11** proved to be stable to atmospheric oxygen both in solution and in the crystalline state.

Scheme 4



Unlike compound **11**, catecholate **6** is readily oxidized in solution with atmospheric oxygen (Scheme 5). The slow dosage of oxygen leads to the predominant formation of 1,3-bis[(20′,4′,5′-triisopropyl-3′,6′-dioxocyclohexa-1′,4′-dien-1′-yl)oxy]-1,1,1,3,3,3-hexaphenyl-1,3-distiboxane (**12**). If a solution is rapidly saturated with oxygen, bis[(2,4,5-triisopropyl-3,6-dioxocyclohexa-1,4-dien-1-yl)oxy](triphenyl)stiborane (**13**) is formed as the major oxidation product. In both cases, the oxidation is irreversible.

Scheme 5



i. Deficiency of O_2. *ii*. Excess of O_2.

The structures of complexes **12** and **13** were established by X-ray diffraction. Product **12** is the dinuclear oxy-*para*-quinoid complex, in which the antimony atoms are oxygen-bridged (Fig. 2, see Tables 1 and 2). Each antimony atom is in a distorted octahedral environment and is bound to three types of oxygen atoms, which is reflected on the Sb—O bond lengths. The rings of the oxy-*p*-quinone ligands and the antimony and oxygen atoms are approximately in a single plane (the O(1)Sb(1)Sb(2)O(6) pseudotorsion angle is 171.1(3)°). The oxy-*p*-quinone fragments are in *trans* positions with respect to the virtually linear SbOSb triad (Sb—O—Sb, 175.0(4)°). The Sb(1)...O(2) and Sb(2)...O(5) distances (2.490(3) and 2.543(3) Å, respectively) are substantially smaller than the sum of the van der Waals radii of these

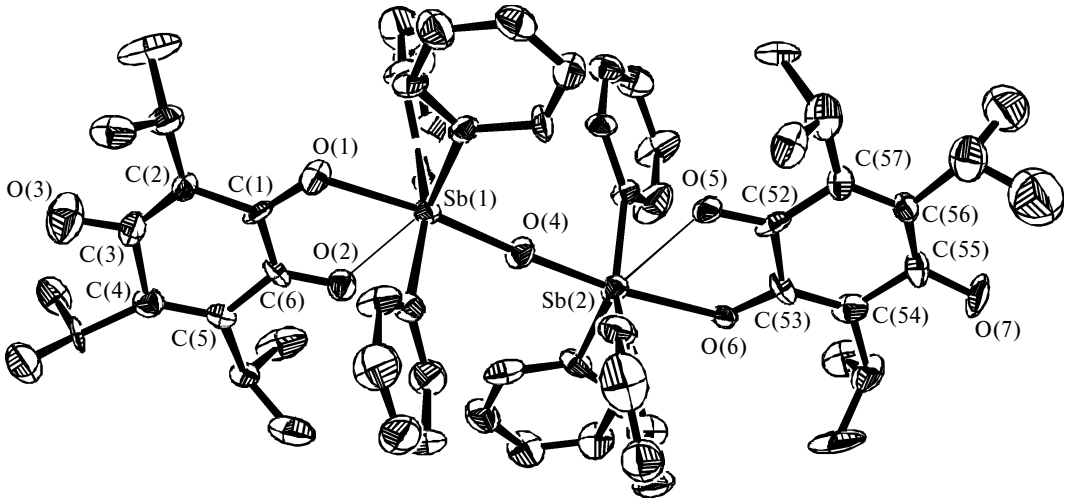


Fig. 2. Molecular structure of product **12**. Displacement ellipsoids are drawn at the 30% probability level.

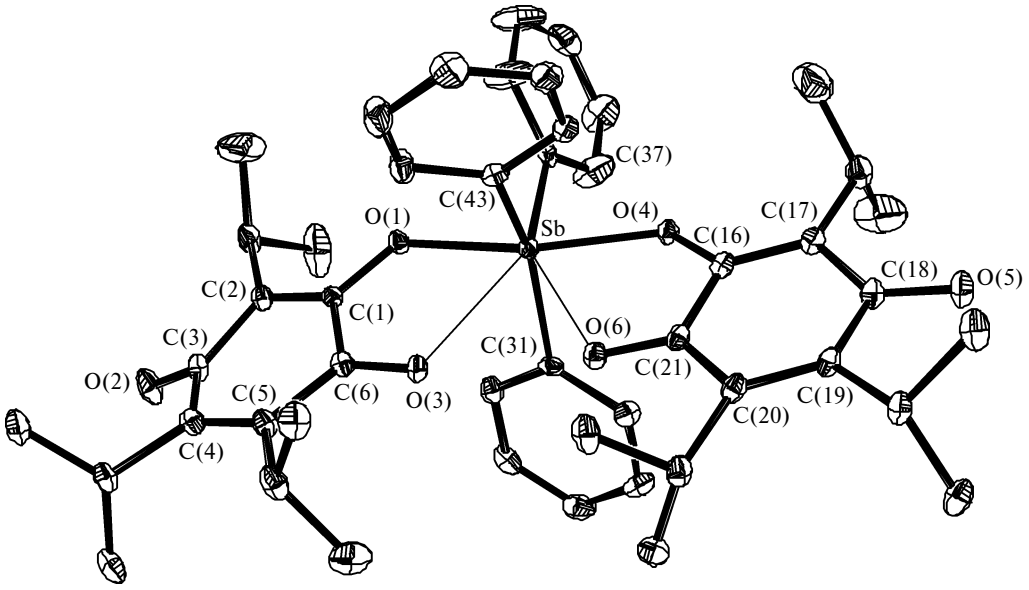


Fig. 3. Molecular structure of **13**. Displacement ellipsoids are drawn at the 30% probability level.

atoms (3.7 Å). This is evidence of the presence of the coordination bond between the antimony atoms and the carbonyl oxygen atoms of the ligands.

Unlike complex **12**, complex **13** is mononuclear. In spite of the fact that the coordination number of the antimony atom is formally 7, its configuration can be considered as a distorted trigonal-bipyramidal (Fig. 3, see Tables 1 and 2). The equatorial positions are occupied by the Ph substituents. The oxy-*p*-quinone groups are in axial positions. The oxy-*p*-quinone rings and the antimony and oxygen atoms in complex **13**, like those in **12**, are approximately in a single plane. The equatorial Ph—Sb—Ph angle from the side of the carbonyl oxygen atoms is substantially larger than the other Ph—Sb—Ph angles, which confirms the presence of interactions between the antimony atom and the carbonyl oxygen atoms of the oxy-*p*-quinone ligands. The Sb...O(3) and Sb...O(6) distances are 2.668(3) and 2.619(3) Å, respectively, and they are substantially longer than the corresponding distances in complex **12**, whereas the Sb—O(1) and Sb—O(4) bond distances (2.109(2) and 2.113(2) Å, respectively) are comparable with the corresponding distances in compound **12**.

The distribution of the C—C, C—O, and Sb—O bond lengths in compounds **12** and **13** (see Tables 1 and 2) differs substantially from that observed in catecholate **6** and is characteristic of quinoid structures. This fact confirms the oxy-*para*-quinone structure of the ligands in complexes **12** and **13**. After the hydrolysis of compounds **12** and **13** with an HCl solution in methanol, hydroxy-*p*-quinone **7** was isolated. The structure of compound **13** was additionally confirmed by its synthesis from Ph_3SbCl_2 and **7**.

To summarize, we synthesized two new triphenylantimony catecholates containing three isopropyl groups in the aromatic ring. Triphenylantimony triisopropylcatecholate does not react with atmospheric oxygen. The catecholate ligand containing an additional hydroxy group is unstable to oxidation, resulting in the irreversible oxidation of this catecholate with molecular oxygen. This is the difference between this compound and the already known antimony(v) catecholate derivatives, which reversibly bind molecular oxygen to form *endo*-peroxides.

Experimental

One-dimensional and two-dimensional NMR spectra were recorded on a Bruker Avance DPX-200 instrument at 200 MHz for ^1H and at 50 MHz for ^{13}C with Me_4Si as the internal standard. The spectra were processed with the use of the XwinNMR 2.1 program. The IR spectra were measured on a Specord M-80 instrument in Nujol mulls. X-ray diffraction data were collected on an automated Smart APEX diffractometer. All structures were solved by direct methods and refined by the least-squares method based on F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. All H atoms in compound **12** were positioned geometrically and refined using a riding model. In compounds **6** and **13**, some H atoms were located in difference Fourier maps and refined isotropically. All calculations were carried out with the use of the SHELXTL v. 6.10 program package.[9] Absorption corrections were applied using the SADABS program.[10] Principal crystallographic characteristics and the X-ray diffraction data collection and refinement statistics are given in Table 3.

Triphenylantimony (1) was synthesized according to a known procedure[11] and purified by recrystallization from methanol, m.p. 52—53 °C. **4-Hydroperoxy-2-hydroxy-3,4,6-triisopropylcyclohexa-2,5-dienone (2)** was synthesized by oxidation of a so-

Table 3. Principal crystallographic characteristics and the X-ray data collection and refinement statistics for compounds **6**, **12**, and **13**

Parameter	**6**	**12**	**13**
Molecular formula	$C_{34}H_{41}O_4Sb$	$C_{66}H_{72}O_7Sb_2$	$C_{48}H_{57}O_6Sb$
Molecular weight	635.42	1220.74	851.69
Temperature/K	100(2)	293(2)	100(2)
Space group	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$
a/Å	9.2210(8)	10.6721(6)	12.3165(6)
b/Å	10.4354(9)	11.0913(7)	18.529(1)
c/Å	31.897(3)	14.5105(9)	29.343(2)
α/deg	90	107.195(1)	93.286(1)
β/deg	97.073(2)	108.147(1)	100.856(1)
γ/deg	90	99.042(1)	101.951(1)
V/Å^3	3046.0(5)	1499.3(26)	6401.8(6)
Z	4	1	6
ρ_{calc}/g cm^{-3}	1.386	1.352	1.325
μ/mm^{-1}	0.941	0.952	0.694
F(000)	1312	626	2664
θ_{max}/deg	29.63	26.0	24.50
hkl Ranges	$-12 \le h \le 12$	$-13 \le h \le 13$	$-14 \le h \le 14$
	$-11 \le k \le 14$	$-13 \le k \le 13$	$-21 \le k \le 21$
	$-41 \le l \le 43$	$-17 \le l \le 17$	$-28 \le l \le 34$
Number of measured/independent reflections (R_{int})	22259/8359 (0.0234)	12947/11108 (0.0187)	34158/21261 (0.0224)
Number of constraints	5	69	0
Number of variables	534	629	2082
GOOF (F^2)	1.138	1.055	1.072
R_1/wR_2 ($I > 2\sigma(I)$)	0.0335/0.0758	0.0467/0.1100	0.0422/0.0948
R_1/wR_2 (based on all reflections)	0.0405/0.0785	0.0607/0.1158	0.0539/0.0994
Absolute structure parameter	?	0.51(3)	?
Residual electron density peaks, max/min, e Å^{-3}	0.791/−0.662	1.116/−0.411	1.489/−0.502

lution of 3,4,6-triisopropylpyrocatechol in hexane with atmospheric oxygen.[6] **3,4,6-Triisopropyl-1,2-benzoquinone (3)** was prepared according to a procedure described earlier.[6]

Reaction of Ph_3Sb (1) with hydroperoxide 2. Hydroperoxide **2** (0.0135 g, 0.05 mmol) and Ph_3Sb (**1**) (0.0175 g, 0.05 mmol) were placed in an NMR tube. Then $CDCl_3$ or C_6D_6 (0.5 mL) was frozen under vacuum into the NMR tube, and the tube was sealed and kept at 77 K. The progress of the reaction was monitored by NMR spectroscopy. Before the measurements, the NMR tube was heated to ~20 °C, and the solution was stirred.

1,7,9,15,17,18-Hexaisopropyl-3,3,3,11,11,11-hexaphenyl-2,4,10,12-tetraoxa-3,11-distibatricyclo[11.3.1.1^{5,9}]octadeca-5,7,13,15-tetraene-6,14-dione (4) was identified in an NMR tube within the first 5—10 min after the beginning of the reaction of **1** with **2**. ^{1}H NMR ($CDCl_3$), δ: 0.12 and 0.84 (both d, 6 H each, $(CH_3)CHC\underline{H}_3$ at C(1) and C(9), J = 6.8 Hz); 0.90 (d, 6 H, $CHC\underline{H}_3$, J = 6.8 Hz); 0.99—1.41 (three d, 6 H each, $CHC\underline{H}_3$); 2.06 (sept, 2 H, $C\underline{H}Me_2$ at C(1) and C(9), J = 6.8 Hz); 2.74 and 2.78 (both sept, 2 H each, $C\underline{H}Me_2$ at C(7), C(15), and C(17), C(18)); 6.49 (s, 2 H, C(8)CH, C(16)CH); 7.42—7.58 and 7.72—7.77 (both m, 18 H, 12 H, $Sb(C_6H_5)_3$). The assignment of the signals for the protons of the isopropyl groups at C(1) and C(9) was made based on the ^{1}H-{^{1}H} NMR spectroscopic data.

4,6,7-Triisopropyl-2,2,2-triphenyl-1,3,2-benzodioxastibol-5(6*H*)-one (5) was identified in an NMR tube in the course of the reaction of **1** with **2** within 1 h after the beginning of the reaction. ^{1}H NMR ($CDCl_3$), δ: 0.72 and 1.07 (both d, 3 H each, $C(6)(C\underline{H}_3)CHC\underline{H}_3$, J = 7.0 Hz); 1.14 and 1.21 (both d, 3 H each, $C(7)(C\underline{H}_3)CHC\underline{H}_3$, J = 7.0 Hz); 1.22 and 1.26 (both d, 3 H each, $C(4)(C\underline{H}_3)CHC\underline{H}_3$, J = 7.0 Hz); 2.12 (sept.d, 1 H, $C(6)HC\underline{H}Me_2$, J = 7.0 Hz, J = 2.8 Hz); 2.44 (sept, 1 H, $C(4)C\underline{H}Me_2$, J = 7.0 Hz); 2.82 (d, 1 H, HC(6), J = 2.8 Hz); 3.21 (sept, 1 H, $C(7)C\underline{H}Me_2$, J = 7.0 Hz); 7.42—7.58 and 7.72—7.77 (both m, 9 H, 6 H, $Sb(C_6H_5)_3$). ^{13}C NMR DEPT ($CDCl_3$), δ: 17.0, 20.26, 20.41, 20.9, and 21.4 (all CH_3); 24.0, 31.5, and 32.8 (all $\underline{C}HMe_2$); 58.6 (C(6)H); 117.1; 129.0, 129.4, 137.7 (C(3a), C(4), C(7), C(7a)); 129.6 (*o*-CH Ph); 131.8 (*p*-CH Ph); 135.2 (*m*-CH Ph); 136.4 (CSb Ph); 200.1 (C(5)=O). The assignment of the signals for the protons of the isopropyl groups was made based on the ^{1}H-{^{1}H} NMR spectroscopic data.

4,6,7-Triisopropyl-2,2,2-triphenyl-1,3,2-benzodioxastibol-5-ol (6). A solution of hydroperoxide **2** (0.27 g, 1 mmol) in toluene (20 mL) was slowly added to a solution of $SbPh_3$ (0.35 g, 1 mmol) in toluene (20 mL) at ~20 °C *in vacuo* (10^{-3} Torr). The colorless components turned bright-yellow upon mixing. The reaction mixture was kept at 20 °C for 1 h, during which the color of the solution changed to bright-orange. Then toluene together with water that was liberated in the course of the reaction were removed *in vacuo*, and the orange-yellow oily precipitate was dissolved in hexane and kept in an evacuated tube at 15 °C for 10—15 h. Pale-orange crystals of catecholate **6**,

which was stable only in the absence of traces of oxygen, were obtained in a yield of 0.41 g (70%). Found (%): C, 65.53; H, 6.37; Sb, 19.56. $C_{33}H_{37}O_3Sb$. Calculated (%): C, 65.69; H, 6.18; Sb, 20.18. IR, ν/cm^{-1}: 3630 (OH hindered); 1160 (C(Ar)O); 690, 730 (Ph); 450, 460 (SbC). ^{1}H NMR ($CDCl_3$), δ: 1.37 (d, 6 H, CH$\underline{Me}_2$, J = 7.0 Hz); 1.43 and 1.44 (both d, 6 H each, CH$\underline{Me}_2$, J = 7.0 Hz); 3.38 (sept, 1 H, C$\underline{H}Me_2$, J = 7.0 Hz); 3.4 and 3.39 (both br.m, 1 H each, C$\underline{H}Me_2$); 4.2 (s, 1 H, OH); 7.5 (m, 9 H, Ph_3Sb); 7.8 (m, 6 H, Ph_3Sb). An analogous NMR spectrum was recorded in a tube in the course of the reaction of **1** with **2** within 1 day after the beginning of the reaction. ^{13}C NMR DEPT ($CDCl_3$), δ: 21.4, 22.1 (CH$\underline{Me}_2$); 25.9, 27.4 (br) and 28.3 ($\underline{C}HMe_2$); 129.1 (*m*-CH); 131.0 (*p*-CH); 135.2 (*o*-CH); 138.2 (CSb). The signals for the carbon atoms of the catecholate ligand were not detected because of their strong broadening. The results of the X-ray diffraction study are presented in Tables 1 and 2. The oxygen atom of the coordinated MeOH molecule is disordered over two positions; the Sb...O(H)Me distances are 2.600(3) and 2.902(3) Å.

2-Hydroxy-4,4-dimethoxy-3,5,6-triisopropylcycloxeha-2,5-dien-1-one (8). Sodium hydroxide (0.1 g) and PbO_2 (1 g) were added to a solution of quinone **3** (0.50 g, 2.1 mmol) in methanol (30 mL). The reaction mixture was magnetically stirred for 1 h. The red-brown color of *o*-quinone disappeared, and the solution turned orange. The liquid phase was separated from the inorganic solid phase and acidified with dilute AcOH. The pale compound that precipitated was filtered off, washed with an aqueous methanolic solution, dried in air, and recrystallized from hexane. White crystals of compound **8** were obtained in a yield of 0.41 g (65%), m.p. 142 °C. Found (%): C, 68.72; H, 9.46. $C_{17}H_{28}O_4$. Calculated (%): C, 68.89; H, 9.52. IR, ν/cm^{-1}: 3325 (OH intermolecular interactions); 1650 (C=O); 1050 (OMe). ^{1}H NMR ($CDCl_3$), δ: 1.25—1.34 (three d, 6 H each, CH(C$\underline{H}_3$)$_2$); 2.72 (sept, 1 H, C$\underline{H}Me_2$, J = 7.0 Hz); 3.05—3.25 (both sept, 1 H each, C$\underline{H}Me_2$); 3.11 (s, 6 H, OMe); 6.84 (s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 19.8, 20.7, and 21.3 (all CH$\underline{Me}_2$); 25.6, 26.6, and 28.9 (all $\underline{C}HMe_2$); 51.9 (OMe); 102.3 ($\underline{C}$(OMe)$_2$); 128.1 (C(3)); 143.2, 146.1 (C(2), C(6)) 160.8 (C(5)); 182.0 (C=O).

2-Hydroxy-3,5,6-triisopropyl-1,4-benzoquinone (7). Compound **8** (0.30 g, 1 mmol) was dissolved in glacial acetic acid (15 mL). Then concentrated HNO_3 (0.5 mL) was added. The solution immediately turned red, and then the color of the solution gradually changed to pale-orange. After 30 min, the reaction solution was diluted with an equal amount of water, and the product was twice extracted with diethyl ether. The ethereal extract was washed with water and dried over $CaCl_2$. Then diethyl ether was removed. Bright-orange crystals of compound **7** were obtained in a yield of 0.24 g (96%), m.p. 45—46 °C. Found (%): C, 72.13; H, 9.06. $C_{15}H_{22}O_3$. Calculated (%): C, 71.97; H, 8.86. IR, ν/cm^{-1}: 3380 (OH); 1650, 1640 (C=O); 1270 (C=CO). ^{1}H NMR ($CDCl_3$), δ: 1.22, 1.27, and 1.28 (all d, 6 H each, CH(C$\underline{H}_3$)$_2$, J = 7.0 Hz); 3.15—3.35 (all sept, 1 H each, C$\underline{H}Me_2$, J = 7.0 Hz); 7.12 (s, OH). ^{13}C NMR ($CDCl_3$), δ: 19.9, 20.8, and 21.3 (all CH$\underline{Me}_2$); 24.3, 27.7, and 27.9 (all $\underline{C}HMe_2$); 124.9 (C(3)); 143.8, 149.7, 151.7 (C); 184.4 and 187.5 (both C=O).

1,2,4-Trihydroxy-3,5,6-triisopropylbenzene (9). Compound **7** (0.252 g, 1 mmol) was dissolved in MeOH (20 mL) containing NaOH (0.1 g). The solution turned dark-violet. Then an aqueous $Na_2S_2O_4$ solution was added to the reaction solution with vigorous shaking until the reaction mixture became colorless. All operations were carried out *in vacuo*. White crystals of reduced product **9** gradually precipitated from an aqueous methanolic solution. After 0.5 h, triol **9** was filtered off, washed three times with water, and dried *in vacuo*. The yield of compound **9** was 0.21 g (80%), m.p. 104—106 °C (from hexane). Found (%): C, 71.58; H, 9.62. $C_{15}H_{24}O_3$. Calculated (%): C, 71.43; H, 9.52. IR, ν/cm^{-1}: 3630 (OH free); 3450, 3425 (OH intermolecular interactions). ^{1}H NMR ($CDCl_3$), δ: 1.32—1.42 (three d, 6 H each, CH(C$\underline{H}_3$)$_2$); 3.35 (sept, 1 H, J = 7.0 Hz, C$\underline{H}Me_2$); 3.30—3.56 (br.m, 2 H, 2 C$\underline{H}Me_2$); 4.44, 4.53, and 5.3 (all s, 1 H each, OH).

2-Hydroxy-3,5,6-triisopropylcyclohex-2-ene-1,4-dione (10). Compound **6** (0.30 g, 0.5 mmol) was dissolved in glacial acetic acid (15 mL) *in vacuo*. The pale-yellow solution was kept at room temperature for 15 min. Then acetic acid was removed *in vacuo*, and hexane was added to the solid residue. Triphenylantimony diacetate insoluble in hexane was separated, and the hexane solution was cooled to −15 °C. After 12 h, pale crystals of compound **10** were isolated in a yield of 0.08 g (63%), m.p. 98—100 °C. Found (%): C, 71.65; H, 9.44. $C_{15}H_{24}O_3$. Calculated (%): C, 71.43; H, 9.52. IR, ν/cm^{-1}: 3250 (OH); 1690, 1670 (C=O); 1630 (C=C). ^{1}H NMR ($CDCl_3$), δ: 0.88 and 0.90 (both d, 3 H each, C(5)(Me)CHC$\underline{H}_3$, J = 6.7 Hz); 0.90 and 0.93 (both d, 3 H each, C(6)(Me)CHC$\underline{H}_3$, J = 6.7 Hz); 1.22 (d, 6 H, C(3)CH(C$\underline{H}_3$)$_2$, J = 7.1 Hz); 1.79 (oct, 1 H, HC(6)C$\underline{H}Me_2$, J = 6.8 Hz); 1.92 (oct, 1 H, HC(5)C$\underline{H}Me_2$, J = 6.7 Hz); 2.55 (dd, 1 H, (6)CH, J = 7.4 Hz, J = 0.9 Hz); 2.67 (dd, 1 H, (5)CH, J = 6.5 Hz, J = 0.9 Hz); 3.19 (sept, 1 H, C(3)C$\underline{H}Me_2$, J = 7.1 Hz); 7.09 (br.s, 1 H, C(2)OH). ^{13}C NMR ($CDCl_3$), δ: 19.3, 19.9 (C(3)(Me)CH$\underline{C}H_3$); 20.4, 20.6, 21.0, 21.2 (MeCH$\underline{C}H_3$ at C(5), C(6)); 25.0 (C(3)$\underline{C}HMe_2$); 33.4 (C(6)$\underline{C}HMe_2$); 33.7 (C(5)$\underline{C}HMe_2$); 54.5 (C(5)H); 58.2 (C(6)H); 131.3 (C(3)); 153.8 (C(2)OH); 198.2 (C(1)=O); 200.6 (C(4)=O). The assignment of the signals in the ^{1}H and ^{13}C NMR spectra was made based on the data from two-dimensional NMR spectroscopy (proton-proton (COSY), proton-carbon (CHCORR), and proton-proton dipole (NOESY) scalar coupling correlations.

4,5,7-Triisopropyl-2,2,2-triphenyl-1,3,2-benzodioxastibole (11). A solution of quinone **3** (0.23 g, 1 mmol) in hexane (20 mL) was added to a solution of Ph_3Sb (0.35 g, 1 mmol) in hexane (30 mL). The dark-red color of the quinone immediately disappeared, and the reaction mixture turned yellow-orange. After cooling, yellow-orange crystals precipitated. The yield of catecholate **11** was 0.43 g (74%), m.p. 137—139 °C. Found (%): C, 68.14; H, 6.34; Sb, 20.20. $C_{33}H_{37}O_2Sb$. Calculated (%): C, 67.47; H, 6.34; Sb, 20.73. IR, ν/cm^{-1}: 690, 740 (Ph); 460, 495 (Sb—C). ^{1}H NMR ($CDCl_3$), δ: 1.23, 1.32, and 1.44 (all d, 6 H each, CH(C$\underline{H}_3$)$_2$); 3.18, 3.3, and 3.34 (all sept, 1 H each, C$\underline{H}Me_2$); 6.51 (s, 1 H, (6)CH); 7.36—7.56, 7.75—7.87 (m, 15 H, Sb(C_6H_5)$_3$). ^{13}C NMR DEPT ($CDCl_3$), δ: 21.3, 22.5, 24.5 (CH($\underline{C}H_3$)$_2$); 27.3, 29.22, 29.24 ($\underline{C}HMe_2$); 111.1 ((6)CH); 126.9, 129.2, 134.5, 142.5, 145.1 (C(1)—C(5)); 129.0 (*m*-CH); 131.0 (*p*-CH); 135.3 (*o*-CH); 138.2 (CSb).

1,3-Bis[(2′,4′,5′-triisopropyl-3′,6′-dioxocyclohexa-1′,4′-dien-1′-yl)oxy]-1,1,1,3,3,3-hexaphenyl-1,3-distiboxane (12). A solution of catecholate **6** (0.22 g, 0.5 mmol) in hexane (30 mL) was kept at room temperature for 3 days in an evacuated tube connected to a rubber pipe fastened with a clamp. Dark-red crystals of the oxidation product were formed on the bottom and walls at the interface with the hexane solution. The oxidation

occurs due to the presence of oxygen that slowly diffuses through the rubber pipe. Crystals of compound **12** were separated in air and washed three times with cold toluene. The yield was 0.09 g (39%). In the solid state, the product is stable in air. Found (%): C, 66.12; H, 6.42; Sb, 19.65. $C_{66}H_{72}O_7Sb_2 \cdot C_6H_{14}$. Calculated (%): C, 65.18; H, 6.63; Sb, 18.63. IR, ν/cm^{-1}: 1625, 1580 (C=O, C=C); 1270 (C=C—O); 690, 760 (Ph); 470, 445 (Sb—C). ^1H NMR ($CDCl_3$), δ: 0.93, 1.12, and 1.13 (all d, 12 H each, 2 $CH(C\underline{H}_3)_2$); 2.90 (sept, 2 H, 2 $C\underline{H}Me_2$); 3.02—3.29 (both m, 2 H each, 2 $C\underline{H}Me_2$); 7.09—7.24 and 7.64—7.69 (both m, 18 H, 12 H, 2 $Sb(C_6H_5)_3$). According to the X-ray diffraction study (see Fig. 2, Tables 1 and 2), the Ph groups occupying the axial positions adopt a nearly eclipsed conformation. In the quinoid ligands of complex **12**, the electron density is delocalized over the C(1)C(2)C(3) and C(55)C(56)C(57) fragments containing both formally single and double bonds. The C(2)—C(3) (1.368(7) Å) and C(55)—C(56) (1.372(6) Å) bonds are similar in length to the C(1)=C(2) (1.377(5) Å) and C(56)=C(57) (1.342(6) Å) double bonds.

Bis[(2,4,5-triisopropyl-3,6-dioxocyclohexa-1,4-dien-1-yl)oxy](triphenyl)stiborane (13). ***A.*** A solution of catecholate **6** in toluene was kept in air. The color of the solution rapidly changed from yellow to bright-red. After 10 h, bright-red crystals of **13** were isolated from the solution.

B. A solution of compound **7** (0.251 g, 1 mmol) in toluene (10 mL) was added to a solution of Ph_3SbCl_2 (0.212 g, 0.5 mmol) and Et_3N (0.14 mL, 1 mmol) in toluene (15 mL) *in vacuo*. A white precipitate of $Et_3N \cdot HCl$ immediately formed, and the solution turned bright-red. The reaction mixture was kept at ~20 °C for 3 h. Then $Et_3N \cdot HCl$ was filtered off, and toluene was replaced with hexane. After cooling, bright-red crystals of **13** precipitated in a yield of 0.32 g (75%). Found (%): C, 67.63; H, 6.72; Sb, 13.54. $C_{48}H_{57}O_6Sb$. Calculated (%): C, 67.69; H, 6.75; Sb, 14.29. IR (Nujol mulls), ν/cm^{-1}: 1635, 1625, 1580 (C=O, C=C); 1260 (C=CO); 730, 690 (Ph); 465, 450 (SbC). ^1H NMR ($CDCl_3$), δ: 1.06, 1.09, and 1.22 (all d, 12 H each, 2 $CH(C\underline{H}_3)_2$); 3.03, 3.19, and 3.3 (all sept, 2 H each, 2 $C\underline{H}Me_2$); 7.27—7.39, 7.48—7.58 (m, 15 H, $Sb(C_6H_5)_3$). ^{13}C NMR DEPT ($CDCl_3$), δ: 19.8, 20.5, 21.5 ($CH(\underline{C}H_3)_2$); 23.8—28.5 ($\underline{C}HMe_2$); 126.4 (C(2)); 141.1, 143.3, 151.1, 155.1 (CSb, C(1), C(4), C(5)); 128.6 (*m*-CH); 129.8 (*p*-CH); 133.2 (*o*-CH); 187.2 and 188.0 (both C=O). According to the X-ray diffraction study of the crystals of **13**, there are three independent molecules having similar geometric parameters per asymmetric unit. The geometric characteristics of only one molecule are given in Tables 1 and 2.

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