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Reactions of pentaphenylantimony with dicarboxylic acids

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Abstract

Interaction of pentaphenylantimony with dicarboxylic acids (mole ratio 1:1 or 2:1) in toluene or dioxane leads to formation of acyloxytetraphenyl derivatives of antimony(V) with 87–99% yield. The studies of two of the products, tetraphenylantimonium maleinate and bis(tetraphenyl) antimonium maleinate, were determined by an X-ray diffraction study. © 1997 Elsevier Science S.A.

Keywords: Antimony; Dicarboxylic acids; Crystal structure

1. Introduction

To date, among acyloxytetraphenylantimony derivatives [1–5] those of dicarbonic acids are rare. To fill the gap we carried out reactions of pentaphenylantimony (PPA) with maleic, tartaric and adipic acids. It was shown that the interaction of these reagents with mole ratio 1:1 in toluene or dioxane solutions leads to the formation of acyloxyderivatives of Sb(V):

$$Ph_5Sb + HOC(O)-R-C(O)OH = Ph_4Sb-O-C(O)-R-C(O)OH + PhH$$

Such reactions, as a rule, occur at room temperature for several hours. Compounds obtained after recrystallization from a benzene–isopropyl alcohol mixture (3:1) are crystalline substances easily soluble in polar organic solvents. They are also hydrolyzed in solutions by air moisture, and easily and quantitatively convert into tetraphenylantimonium chloride and dicarbonic acid with diluted hydrochloric acid. IR spectra of these tetraphenylantimonium derivatives contain two characteristic bands in the region of valence vibrations of carbonyl groups and also of monocarboxylic acids.

A 2:1 mole ratio of reagents leads to carboxylic hydrogen substitution in both groups:

$$2Ph_5Sb + HOC(O)-R-C(O)OH = Ph_4SbOC(O)-R-OC(O)SbPh_4 + 2PhH$$

The same products were detected when Ph_5Sb reacted with monosalt:

$$SbPh_5 + HOC(O)-R-C(O)OSbPh_4 = Ph_4SbOC(O)-R-OC(O)SbPh_4 + PhH$$

The latter two reactions require heating in dioxane solution to go to completion.

2. Experimental

^1H and ^{13}C NMR spectra were detected using a Jeol FX 900 spectrometer with $CDCl_3$ as a solvent and TMS as internal standard. IR spectra were recorded on a Hitachi-215 spectrometer (suspension in vaseline oil).

The synthesis of antimony acyloxytetraphenyl derivatives was carried out in evacuated glass ampoules according to following methods.

2.1. Tetraphenylantimonium maleinate (I)

2.50 g (4.9 mmol) of PPA and 0.57 g (4.9 mmol) of maleic acid were dissolved in benzene–dioxane (5:1) mixture and kept at room temperature for 24 h. After

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Table 1
Yield, melting point (MP) and elemental analysis data for compounds $Ph_4SbOC(O)R^1$ obtained from PPA and dicarbonic acids

No.	Compound		Found (Calc.) (%)		MP (°C)	Yield (%)
	R^1	Formula	C	H		
I	CH=CHCOOH	$C_{28}H_{23}O_4Sb$			165	87
II	CH=CHCOOSbPh$_4$	$C_{52}H_{42}O_4Sb_2$			232 [a]	99
III	CH(OH)—CH(OH)COOSbPh$_4$	$C_{52}H_{44}O_6Sb_2$	61.73 (61.90)	4.50 (4.36)	190	93
IV	$(CH2)_4COOSbPh_4$	$C_{54}H_{48}O_4Sb_2$	64.76 (64.54)	4.98 (4.78)	214	96
V	CH_2COOH	$C_{27}H_{23}O_4Sb$	60.54 (60.79)	4.22 (4.31)	183 [a]	91
VI	$(CH_2)_2COOH$	$C_{28}H_{25}O_4Sb$	60.75 (61.43)	4.44 (4.57)	91	94
VII	$CH(OH)CH_2COOH$	$C_{28}H_{25}O_5Sb$	59.39 (59.68)	4.38 (4.44)	93	96
VIII	$(CH_2)_4COOH$	$C_{30}H_{29}O_4Sb$	62.31 (62.61)	5.14 (5.04)	185	97
IX	$C_6H_4COOSbPh_4$	$C_{56}H_{44}O_4Sb_2$	65.31 (65.63)	4.28 (4.30)	240	94
X	$CH_2COOSbPh_4$	$C_{51}H_{42}O_4Sb_2$	63.11 (63.62)	4.41 (4.37)	186	95
XI	$(CH_2)_2COOSbPh_4$	$C_{52}H_{44}O_4Sb_2$	63.86 (63.93)	4.55 (4.51)	197	98
XII	$CH_2CHCOOSbPh_4OH$	$C_{52}H_{44}O_5Sb_2$	62.92 (62.90)	4.40 (4.44)	71	92

[a] Decomposes.

Table 2
Crystal data and structure refinement

	I	II
Empirical formula	$C_{28}H_{23}O_4Sb$	$C_{52}H_{42}O_4Sb_2$
Formula weight	545.21	974.36
Crystal system	Monoclinic	
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	9.498(1)	10.199(2)
b (Å)	25.846(5)	26.391(5)
c (Å)	10.140(1)	16.078(4)
β (deg)	99.64(1)	92.78(2)
Volume (Å^3)	2454.1(6)	4323(2)
Z	4	4
Density (calc) (Mg m^{-3})	1.476	1.497
Absorption coefficient (mm^{-1})	0.619	0.693
F(000)	1096	1952
Crystal size (mm^3)	0.35 × 0.32 × 0.19	0.45 × 0.38 × 0.30
Θ range for data collection (deg)	1.72 to 16.97	1.58 to 16.98
Index ranges	$-9 \le h \le 9, 0 \le k \le 26, 0 \le l \le 10$	$0 \le h \le 10, 0 \le k \le 27, -16 \le l \le 16$
Reflections collected	3280	3456
Independent reflections	1955 (R(int) = 0.021)	3236 (R(int) = 0.017)
Data/restraints/parameters	1955/0/391	3236/0/692
Goodness-of-fit on F^2	1.039	1.036
R indices (all data)	$R1 = 0.0224$, $wR2 = 0.0598$	$R1 = 0.0184$, $wR2 = 0.0524$
Largest diff. peak and hole (e Å^{-3})	0.401 and −0.468	0.417 and −0.165

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

I					II				
	x	y	z	U_{eq} [a]		x	y	z	U_{eq} [a]
Sb	6196(1)	6412(1)	3566(1)	42(1)	Sb(1)	1635(1)	7014(1)	4738(1)	44(1)
O(1)	7748(4)	5664(1)	3156(4)	68(1)	Sb(2)	3618(1)	4807(1)	7930(1)	45(1)
O(2)	6487(4)	4961(2)	3261(5)	89(1)	O(1)	410(3)	6704(1)	5711(2)	53(1)
O(3)	6893(4)	4038(2)	3654(5)	94(1)	O(2)	2051(3)	6250(1)	6303(2)	69(1)
O(4)	8717(5)	3513(2)	3875(6)	108(2)	O(3)	1913(3)	5206(1)	7324(2)	49(1)
C(1)	7800(4)	6734(2)	2639(4)	41(1)	O(4)	1891(4)	5817(1)	8282(2)	67(1)
C(2)	9161(6)	6805(2)	3328(6)	58(1)	C(1)	−83(4)	7433(2)	4381(3)	46(1)
C(3)	10145(7)	7071(3)	2702(9)	83(2)	C(2)	−1265(5)	7372(2)	4754(4)	63(2)
C(4)	9787(7)	7257(2)	1446(8)	81(2)	C(3)	−2342(6)	7647(2)	4481(4)	73(2)
C(5)	8448(6)	7174(2)	737(6)	67(1)	C(4)	−2268(5)	7992(2)	3856(4)	62(1)
C(6)	7454(6)	6919(2)	1353(5)	53(1)	C(5)	−1112(6)	8061(2)	3486(4)	66(2)
C(7)	4570(5)	6040(2)	2231(4)	48(1)	C(6)	−25(6)	7781(2)	3749(3)	57(1)
C(8)	4823(7)	5791(2)	1102(5)	60(1)	C(7)	2831(5)	7344(2)	5702(3)	47(1)
C(9)	3750(8)	5593(2)	174(6)	75(2)	C(8)	2300(7)	7623(2)	6324(4)	70(2)
C(10)	2387(8)	5633(2)	404(7)	81(2)	C(9)	3115(10)	7857(3)	6929(4)	89(2)
C(11)	2090(7)	5875(3)	1519(7)	78(2)	C(10)	4435(9)	7817(3)	6908(4)	88(2)
C(12)	3175(6)	6084(2)	2450(6)	62(1)	C(11)	4967(7)	7535(3)	6303(4)	78(2)
C(13)	5098(4)	7097(2)	3978(4)	41(1)	C(12)	4176(6)	7306(2)	5702(4)	63(2)
C(14)	5206(6)	7557(2)	3310(5)	54(1)	C(13)	2843(4)	7295(2)	3762(3)	46(1)
C(15)	4427(7)	7985(2)	3556(6)	67(2)	C(14)	3455(5)	7762(2)	3829(3)	54(1)
C(16)	3525(6)	7958(2)	4459(6)	67(2)	C(15)	4161(5)	7956(3)	3192(4)	62(2)
C(17)	3411(5)	7512(2)	5153(5)	64(1)	C(16)	4255(6)	7685(2)	2470(4)	73(2)
C(18)	4188(5)	7078(2)	4910(5)	54(1)	C(17)	3663(7)	7228(3)	2395(4)	75(2)
C(19)	6766(4)	6135(2)	5532(4)	43(1)	C(18)	2959(5)	7032(2)	3030(3)	59(1)
C(20)	6356(6)	5662(2)	5914(6)	64(2)	C(19)	1735(5)	6251(2)	4353(3)	48(1)
C(21)	6687(7)	5493(3)	7207(7)	86(2)	C(20)	2895(6)	5991(2)	4431(4)	64(2)
C(22)	7459(8)	5805(3)	8135(7)	85(2)	C(21)	2996(7)	5498(2)	4171(4)	73(2)
C(23)	7879(8)	6281(3)	7794(6)	83(2)	C(22)	1927(8)	5266(3)	3818(4)	81(2)
C(24)	7516(7)	6455(2)	6464(5)	66(2)	C(23)	769(8)	5510(3)	3726(5)	93(2)
C(25)	7645(5)	5195(2)	3247(5)	59(1)	C(24)	667(6)	6007(2)	4000(4)	75(2)
C(26)	8986(6)	4884(2)	3329(7)	70(2)	C(25)	4740(5)	5463(2)	7724(3)	49(1)
C(27)	9214(6)	4390(2)	3534(6)	68(2)	C(26)	4564(6)	5725(2)	6993(4)	58(1)
C(28)	8248(6)	3949(2)	3723(6)	72(2)	C(27)	5382(6)	6118(2)	6816(4)	70(2)
					C(28)	6378(6)	6260(2)	7382(4)	70(2)
					C(29)	6544(6)	6003(2)	8114(4)	69(2)
					C(30)	5744(6)	5605(2)	8284(4)	62(2)
					C(31)	3427(4)	4346(2)	6859(3)	47(1)
					C(32)	2892(6)	4523(2)	6098(3)	63(1)
					C(33)	2857(7)	4206(3)	5412(4)	75(2)
					C(34)	3291(6)	3719(3)	5477(4)	75(2)
					C(35)	3805(6)	3541(2)	6211(4)	70(2)
					C(36)	3896(5)	3852(2)	6901(4)	59(1)
					C(37)	5228(5)	4383(2)	8521(3)	52(1)
					C(38)	6423(6)	4358(2)	8160(4)	63(2)
					C(39)	7467(7)	4089(2)	8520(5)	74(2)
					C(40)	7310(7)	3837(3)	9246(5)	87(2)
					C(41)	6141(7)	3851(3)	9606(5)	96(2)
					C(42)	5128(7)	4120(2)	9251(4)	70(2)
					C(43)	2306(4)	4623(2)	8863(3)	47(1)
					C(44)	2209(6)	4901(2)	9585(3)	63(2)
					C(45)	1458(6)	4717(3)	0219(4)	71(2)
					C(46)	815(6)	4271(3)	0132(4)	72(2)
					C(47)	914(6)	3990(3)	9426(4)	75(2)
					C(48)	1655(5)	4169(2)	8789(4)	64(1)
					C(49)	896(5)	6352(2)	6208(3)	49(1)
					C(50)	−124(5)	6082(2)	6672(3)	49(1)
					C(51)	119(5)	5761(2)	7288(3)	49(1)
					C(52)	1425(5)	5601(2)	7660(3)	49(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

solvent evaporation and recrystallization from benzene–chloroform–isopropyl alcohol (5:5:1), 2.34 g of bulky colorless crystals were obtained. IR (ν, cm^{-1}): 1700, 1620 (C=O).

2.2. Bis(tetraphenylantimonium) maleinate (II)

2.07 g (4.08 mmol) of PPA and 0.28 g (2.04 mmol) of maleic acid were dissolved in 20 ml of dioxane and kept at 60 °C for 1 h and then at room temperature for 12 h. Recrystallization from benzene–isopropyl alcohol (4:1) mixture yielded 1.97 g of colorless crystals. IR (ν, cm^{-1}): 1640, 1620 (C=O).

2.3. Bis(tetraphenylantimonium) tartrate (III)

A mixture of 2.50 g (4.9 mmol) of PPA and 0.37 g (2.45 mmol) tartaric acid in 10 ml of dioxane was heated at 60 °C for 15 min and then kept at room temperature for 12 h. The material obtained was recrystallized from benzene–isopropyl alcohol 3:1 mixture. The yield was 2.31 g. IR (ν, cm^{-1}): 1660, 1640 (C=O). ^{1}H NMR (δ, m.d.): 3.14 (s, CH, 2H); 4.04 (s, OH, 2H); 7.35 (*m*- and

Table 4
Selected bond lengths (Å) and angles (deg)

I		II	
Sb–C(1)	2.092(4)	Sb(1)–C(19)	2.111(4)
Sb–C(19)	2.102(4)	Sb(1)–C(7)	2.114(5)
Sb–C(7)	2.108(4)	Sb(1)–C(1)	2.127(4)
Sb–C(13)	2.130(4)	Sb(1)–C(13)	2.172(4)
Sb–O(1)	2.509(3)	Sb(1)–O(1)	2.207(3)
O(1)–C(25)	1.219(6)	Sb(2)–C(31)	2.109(4)
O(2)–C(25)	1.258(6)	Sb(2)–C(25)	2.111(5)
O(3)–C(28)	1.298(6)	Sb(2)–C(43)	2.114(5)
O(4)–C(28)	1.213(6)	Sb(2)–C(37)	2.168(5)
C(25)–C(26)	1.498(7)	Sb(2)–O(3)	2.217(3)
C(26)–C(27)	1.305(7)	O(1)–C(49)	1.306(5)
C(27)–C(28)	1.496(8)	O(2)–C(49)	1.211(5)
		O(3)–C(52)	1.286(5)
		O(4)–C(52)	1.226(5)
		C(49)–C(50)	1.492(7)
		C(50)–C(51)	1.317(6)
		C(51)–C(52)	1.494(7)
C(1)–Sb–C(19)	118.1(2)	C(19)–Sb(1)–C(7)	125.1(2)
C(1)–Sb–C(7)	113.8(2)	C(19)–Sb(1)–C(1)	117.9(2)
C(19)–Sb–C(7)	119.8(2)	C(7)–Sb(1)–C(1)	115.0(2)
C(1)–Sb–C(13)	100.1(2)	C(19)–Sb(1)–C(13)	94.4(2)
C(19)–Sb–C(13)	98.8(2)	C(7)–Sb(1)–C(13)	93.5(2)
C(7)–Sb–C(13)	100.1(2)	C(1)–Sb(1)–C(13)	96.7(2)
C(1)–Sb–O(1)	74.95(1)	C(19)–Sb(1)–O(1)	83.73(1)
C(19)–Sb–O(1)	80.16(1)	C(7)–Sb(1)–O(1)	87.71(1)
C(7)–Sb–O(1)	85.90(1)	C(1)–Sb(1)–O(1)	84.09(1)
C(13)–Sb–O(1)	173.46(1)	C(13)–Sb(1)–O(1)	178.1(2)
C(25)–O(1)–Sb	134.2(3)	C(31)–Sb(2)–C(25)	111.9(2)
O(1)–C(25)–O(2)	124.1(5)	C(31)–Sb(2)–C(43)	114.3(2)
O(1)–C(25)–C(26)	117.4(5)	C(25)–Sb(2)–C(43)	131.8(2)
O(2)–C(25)–C(26)	118.6(5)	C(31)–Sb(2)–C(37)	95.6(2)
C(27)–C(26)–C(25)	130.6(6)	C(25)–Sb(2)–C(37)	95.0(2)
C(26)–C(27)–C(28)	132.6(6)	C(43)–Sb(2)–C(37)	93.6(2)
O(4)–C(28)–O(3)	120.8(5)	C(31)–Sb(2)–O(3)	82.9(2)
O(4)–C(28)–C(27)	120.4(5)	C(25)–Sb(2)–O(3)	87.8(2)
O(3)–C(28)–C(27)	118.8(5)	C(43)–Sb(2)–O(3)	84.88(1)
		C(37)–Sb(2)–O(3)	177.2(2)
		C(49)–O(1)–Sb(1)	119.1(3)
		C(52)–O(3)–Sb(2)	120.8(3)
		O(2)–C(49)–O(1)	125.0(4)
		O(2)–C(49)–C(50)	121.9(4)
		O(1)–C(49)–C(50)	113.1(4)
		C(51)–C(50)–C(49)	125.0(5)
		C(50)–C(51)–C(52)	127.9(5)

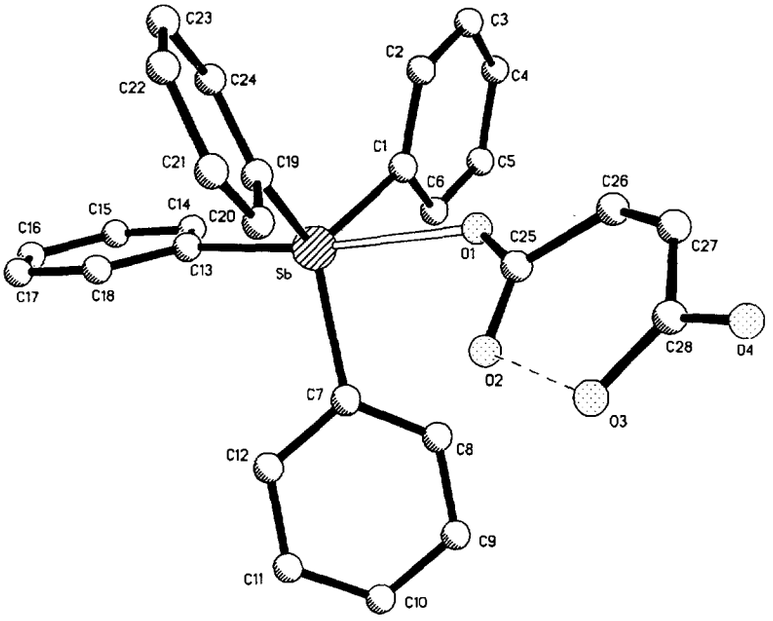

Fig. 1. Molecular conformation of **I**.

p-protons Ph, 24H); 7.63 (*o*-protons Ph, 16H). ^{13}C NMR: 73.32 (CH); 128.99 (*m*-Ph); 130.43 (*p*-Ph); 135.30 (*p*-Ph); 136.47 (*i*-Ph); 174.97 (C=O).

2.4. Bis(tetraphenylantimonium) adipinate (IV)

A mixture of 2.50 g (4.9 mmol) of PPA and 2.87 g (4.9 mmol) of tetraphenyl antimonium adipinate was dissolved at 60 °C in 20 ml of dioxane and was kept at room temperature for 12 h. After solvent removal and recrystallization from benzene–isopropyl alcohol (4:1) mixture, the yield was 4.80 g. IR (ν, cm^{-1}): 1635, 1570 (C=O). ^{1}H NMR: 1.12 (m, $C-CH_2-CH_2C$, 4H), 1.82 (m, 2 $CH_2-C(O)-O$, 4H), 7.29 (m, *m*- and *p*-protons Ph, 24H), 7.56 (m, *o*-protons Ph, 16H). ^{13}C NMR: 25.08 ($C-CH_2-CH_2-C$), 35.87 ($CH_2C(O)O$), 128.73 (*m*-Ph), 129.91 (*p*-Ph), 135.04 (*o*-Ph), 139.20 (*i*-Ph), 177.77 (C=O).

Table 1 gives the elemental analysis data and melting points of the compounds synthesized.

2.5. X-ray data collection and refinement

An automated Enraf–Nonius CAD-4 diffractometer was used both for unit cell parameter determinations and data collection (Θ–2Θ scan method, λ Ag Kα (0.56083 Å), three standard reflections monitored every 60 min showed no decay). Absorption corrections were

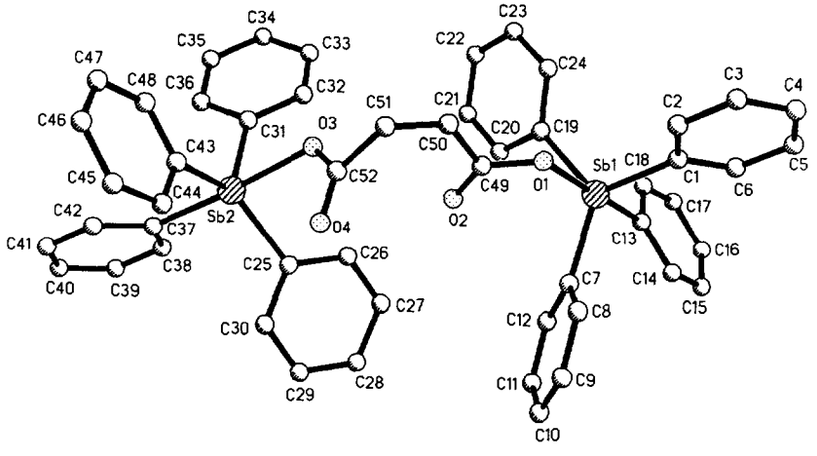

Fig. 2. Molecular conformation of **II**.

not applied. The structures **I** and **II** were solved by Patterson methods and were refined anisotropically (non-hydrogen atoms). Hydrogen atom coordinates were found from difference syntheses and their positional and thermal parameters were refined isotropically. Table 2 gives the crystal data and structure refinement results. Atomic coordinates are given in Table 3, selected bond lengths and angles are shown in Table 4. All calculations were performed using the SHELXL-93 program package [6]. Complete lists of bond lengths and angles, and tables of anisotropic displacement parameters and of hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

3. Discussion

Figs. 1 and 2 illustrate molecular conformation and atomic numbering schemes. In both molecules the Sb atoms have trigonal-bipyramidal coordination with oxygens in apical positions. The main difference is in Sb–O bond lengths. In **II** they are similar (2.207 and 2.217 Å) and close to those found in alkoxy- and aryloxy-derivatives of tetraphenylantimony (2.063–2.167 Å) [7–10], whereas in **I** this distance (2.509 Å) is substantially more than the sum of the covalent radii. Nevertheless, the Sb–O interaction still cannot be considered as ionic, because the coordination polyhedron of Sb (trigonal pyramid) corresponds to d^2sp^2 hybridization. In **I** the maleic acid residue exhibits planar conformation due to an intramolecular H-bond O(2) · · · O(3) 2.439 Å; the plane of carbon atoms makes angles of 5.3 and 3.7° with the carboxy groups. A similar situation exists in the pure maleic acid structure [11]. In **II**, the acid residue is far from planarity; the carbon atoms plane makes angles of 9.6 and 88.0° with the carboxy groups. The corresponding O · · · O distance is 3.392 Å. The distances between Sb and carbon atoms in both structures are in the limits 2.092–2.172 Å, which is quite close to those found in PPA structures [12–14].

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