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Syntheses and Properties of *gem*-Diolatotriarylantimony(V)

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Synopsis. Titled compounds of the general formula $R_3Sb(R'R''CO_2)$ have been prepared, where R=phenyl, *p*-tolyl or *p*-chlorophenyl, R′,R″=CF_3,CF_3; CF_3,H; or CCl_3, H. From the infrared spectra and ^{1}H-NMR data, the *gem*-diolato group appears to bond to the antimony bidentately through two oxygen atoms, as in the 1,1,1-trifluoro-4-oxo-2,2-pentanediolato complex of triarylantimony(V).

Trifluoroacetylacetone reacted with dibromotriarylantimony(V), to give a new type complex, where the *β*-diketone hydrated and acted as a terdentate.[1,2] In that complex, the ligand bonds to the antimony through one keto oxygen near the methyl group, and two *gem*-diolato oxygens of the hydrated carbonyl group next to the trifluoromethyl one. From the X-ray structure analysis, the bond between antimony and the keto-oxygen is weaker than the other two.[1] Consequently *gem*-diols are also expected to form stable complexes with organoantimony(V), working as a bidentate ligands and making four membered ring chelates. This paper reports the reaction between dibromotriarylantimony(V) and some *gem*-diols, such as chloral hydrate.

Experimental

Synthesis of (2,2,2-Trichloroethane-1,1-diolato)triphenylantimony(V). Two grams (4 mmol) of dibromotriphenylantimony(V), which was synthesized by the standard technique,[3] and 2,2,2-trichloro-1,1-ethanediol (Wako Pure Chemical Co., Ltd., G. R. grade) (0.83 g, 5 mmol) were dissolved in benzene (20 ml). To the solution, triethylamine (1.0 g, 10 mmol) was added as a deprotonation reagent. After stirring for 1 h at room temperature, the precipitated triethylammonium bromide was filtered off and the filtrate evaporated to dryness using a rotary evaporator (60 °C, water pump). The residue was recrystallized from acetonitrile, the yield being about 1.5 g (75%) on average after one recrystallization.

Seven other kinds of complex having the same formula, $R_3Sb(R'R''CO_2)$, where R=phenyl, *p*-tolyl, or *p*-chlorophenyl, R′,R″=CF_3, CF_3; CF_3,H; CCl_3,H; were synthesized by the same technique from the reaction between the appropriate dibromotriarylantimony(V) and hydrated hexafluoroacetone, 2,2,2-trifluoro-1-ethoxyethanol, or chloral hydrate. The products thus obtained were very stable in air at room temperature, and kept for several months without any decomposition. Attempts to synthesize this type of compound using dihalogenotrialkyl antimony(V), or a ketone such as hexachloroacetone, acetophenone, benzophenone, or acetone were not successful.

Infrared spectra of the samples were obtained by a JASCO infrared spectrophotometer, type 403G, using Nujol and hexachloro-1,3-butadiene mull, and ^{1}H-NMR by a JEOL JNM-MH-100 (100 MHz) NMR spectrometer using a 20% $CDCl_3$ solution at 26 °C with TMS as the internal standard. The mp and decomposition points were obtained by the simultaneous TG-DTA technique using a Rigaku Denki M-8075 thermal analyser.

Results and Discussion

The analyses of the products, as well as their calculated values from the formula, $R_3Sb(R'R''CO_2)$, are shown as follows. R=C_6H_5, R′=CF_3, R″=CF_3; Found: C, 47.10; H, 2.84%. Calcd: C, 47.14; H, 2.82%. Mp 122 °C. R=C_6H_5, R′=CF_3, R″=H; Found: C, 51.36; H, 3.47%. Calcd: C, 51.43; H, 3.47%. Dec at 134 °C. R=C_6H_5, R′=CCl_3, R″=H; Found: C, 46.50; H, 3.10%. Calcd: C, 46.51; H, 3.21%. Dec. at 130 °C. R=*p*-tolyl, R′=CF_3, R″=CF_3; Found: C, 49.62; H, 3.42%. Calcd: C, 49.95; H, 3.62%. Dec at 132 °C. R=*p*-tolyl, R′=CF_3, R″=H; Found: C, 54.12, H, 4.46%. Calcd: C, 54.26; H, 4.36%. Dec at 115 °C. R=*p*-tolyl, R′=CCl_3, R″=H; Found: C, 49.46; H, 4.03%. Calcd: C, 49.46; H, 3.97%. Dec at 120 °C. R=*p*-chlorophenyl, R′=CF_3, R″=CF_3; Found: C, 39.22; H, 1.88%. Calcd: C, 39.51; H, 1.90%. Dec at 160 °C. R=*p*-chlorophenyl, R′=CCl_3, R″=H; Found: C, 39.54, H, 2.21%. Calcd: C, 38.76; H, 2.11%. Dec at 145 °C.

From the molecular weight measurement by the freezing point depression of the benzene solution, all of these compounds were shown to be monomers. All the products are white crystalline powders, stable at room temperature for several months, soluble in organic solvents such as benzene, acetone, chloroform, and insoluble in water.

The infrared spectra of these compounds were

TABLE 1. ν(C–O)[5] OF THE R_3Sb (R′R″CO_2), R′R″$C(OH)_2$, AND (1,1,1-TRIFLUORO-4-OXO-2,2-PENTANEDIOLATO)TRIPHENYLANTIMONY(V) (shown as $Ph_3Sb(HtfacO)$ in the table) (cm^{-1})

R′	R″	$R_3Sb(R'R''CO_2)$			R′R″$C(OH)_2$
		R=phenyl	R=*p*-tolyl	R=*p*-chlorophenyl	
CF_3	CF_3	1092, 1063	1100, 1064	1090, 1063	1080,
CF_3	H	1110, 1050	1110, 1070		1100, 1075[a]
CCl_3	H	1105, 1065	1110, 1063	1110, 1063	1075
$Ph_3Sb(HtfacO)$		1019, 1089			

a) Ethyl hemiacetal.

Table 2. ^{1}H-NMR spectra (TMS=0, shown by δ ppm)
(J values of AB pattern quartets are shown in parentheses (Hz))

Compd	R							
	Phenyl		p-Tolyl			p-Chlorophenyl		CH
	Ar	CH	Ar	CH	Me	Ar	CH	
$R_3Sb(R'R''CO_2)$								
$R'=CF_3$, $R''=CF_3$	7.70, 7.60 m		7.67, 7.31 q(8)		2.43	7.64, 7.56 q(9)		
$R'=CF_3$, $R''=H$	7.74, 7.55 m	5.48	7.64, 7.35 q(8)	5.41	2.44			
$R'=CCl_3$, $R''=H$	7.75, 7.55 m	5.63	7.63, 7.34 q(7)	5.55	2.44	7.64, 7.48 q(8)	5.54	
$R_3Sb(HtfacO)$	7.65, 7.36 m					7.49, 7.33 q(8)		
R_3SbBr_2	8.17, 7.57 m		8.04, 7.37 q(8)		2.44	8.12, 7.58 q(8)		
R_3Sb	7.39 m		7.34 m		2.44	7.22 m		
$CCl_3CH(OH)_2$								5.38
$CF_3CH(OH)(OCH_3)$								4.85

m: multiplet, q: quartet.

examined. Almost all bands originated from the aryl groups, as well as those from the trihalogenomethyl groups which appeared in the same wave number region as those of the dibromotriarylantimonies, or the *gem*-diols, respectively. However, ν(OH) (about 3400 cm^{-1}),[4] as well as ν(C=O) (about 1700 cm^{-1})[4] were absent in the spectra of these compounds. The wave number of the ν(C=O) band[4,5] of the complexes as well as those of the corresponding *gem*-diols are shown in Table 1. As is evident this band splits into two peaks, likely *sym*- and *antisym*-stretching bands, which are also found in the spectra of the hydrated β-diketonato complex as shown in the Table. This strongly supports bonding between the diolato oxygens and the central metal.

The ^{1}H-NMR spectra of these complexes are shown in Table 2, together with those of related substances.[6] In general, the ^{1}H-NMR of the aryl group of Ar_3SbL_2 type organoantimony(V), shifts to the higher field, when the bonded HL is a weaker acid.[6,7] The lower field shifts of the phenyl peaks of these *gem*-diolato complexes were less than those of the carboxylato or halogeno derivatives.[6,7] Therefore, the *gem*-diolato ligands work as less negative ones than the carboxylato or phenolato derivatives. The hydrated β-diketone complex of triarylantimony(V) gives the same order shift for phenyl peaks. The splitting of each aryl proton peak due to the geometrical arrangement of the groups in the complex was not observed; in the case of the *p*-tolyl, or *p*-chlorophenyl derivatives, one sharp quartet of AB pattern was retained.

These results suggest that the *gem*-diolato ligand works bidentately in these complexes; and the central antimony is a penta coordinated one, probably in the trigonal bipyramidal configuration as in the cases of these type quinquevalent organoantimony compounds. From consideration of bond lengths,[2,8,9] the O–C–O bond of the ligand cannot span the central antimony from the equatorial direction, when there is serious deformation in the complex. Therefore, it may be assumed that the bidentate spans between apical and equatorial directions, although some deformation of the shape is inevitable in this case, too. Three aryl groups bonding to the antimony are thus in a facial array. As in the cases of other trigonal bipyramidal compounds,[10,11] Berry's rotation easily occurs, and the splitting of each aryl proton peak in the ^{1}H-NMR due to their situations was not observed, but only the average recognized.

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