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ORGANOANTIMONY COMPOUNDS

V.*. STUDIES ON TRIMETHYL- AND TRIPHENYLANTIMONY(V) DERIVATIVES OF HALOACETIC ACIDS

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SUMMARY

Trimethyl- and triphenylantimony(V) derivatives of fluoro-, chloro-, bromo-, and cyanoacetic acids have been synthesized. Molecular weight, conductance and infrared spectroscopic studies show that these derivatives are pentacoordinated molecular compounds. The carbonyl stretching frequency for these compounds shows a linear dependence upon the pK or the Taft constant σ^* for the parent acid. A linear relationship is also observed between the antimony-methyl proton chemical shift and the strength of the parent acid.

INTRODUCTION

Recent IR spectroscopic studies on tetraphenylantimony carboxyates[1], $Ph_4Sb(OCOR')$, where $R'=CH_3$, CCl_3 or CF_3, showed that in the solid state tetraphenylantimony acetate has a hexacoordinate structure but the trichloro- and trifluoroacetates are pentacoordinated. In solution all the three derivatives appear to possess a pentacoordinate structure. Conductance studies also showed that the acetate and the trichloroacetate do not ionize in nitromethane but the trifluoracetate behaves as a 1/1 electrolyte in this solvent. To further investigate the substituent effects on the Sb–OCOR' bond we have prepared and studied trimethyl- and triphenylantimony(V) derivatives of fluoro-, chloro-, bromo-, and cyanoacetic acids. Triorganoantimony derivatives of formic[2,3], acetic[2-4], propionic[2] and benzoic[2] acids have been studied previously. For comparison trimethyl- and triphenylantimony diacetates have also been included in the present study.

RESULTS AND DISCUSSION

Analytical data and melting points for the compounds prepared for this study are recorded in Table 1. All the compounds are white crystalline solids. They are stable at room temperature and are unaffected by atmospheric moisture. All are

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* For Part IV see ref. 19.

TABLE 1

ANALYTICAL, MOLECULAR WEIGHT AND MELTING POINT DATA FOR $R_3Sb(OCOR')_2$ DERIVATIVES

Compound	*C (%)*		*H (%)*		*Mol. wt.*		*M.p.* (°C)
	Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*	
$Me_3Sb(OCOCF_3)_2$	21.35	21.38	2.51	2.37	393	398	105–106
$Me_3Sb(OCOCF_2H)_2$	23.55	23.39	3.11	3.12	357	355	68–69
$Me_3Sb(OCOCFH_2)_2$	26.19	26.15	4.09	3.94	321	324	131–132
$Me_3Sb(OCOCCl_3)_2$	17.11	17.29	2.01	1.91	492	502	138.5–139.5
$Me_3Sb(OCOCCl_2H)_2$	19.88	20.23	2.63	2.56	423	423	89.5–90
$Me_3Sb(OCOCClH_2)_2$	23.76	23.64	3.71	3.76	354	359	90–91
$Me_3Sb(OCOCBr_2H)_2$	14.00	14.21	1.85	1.75	601	588	102–103
$Me_3Sb(OCOCBrH_2)_2$	18.99	19.09	2.96	2.92	443	430	86–87
$Me_3Sb(OCOCH_3)_2$	29.50	29.63	5.32	5.34	285	284	79.5–80
$Me_3Sb(OCOCD_3)_2$	28.90	28.95	5.06	4.98	291	290	81–81.5
$Me_3Sb(OCOCH_2CN)_2$	32.27	32.16	3.92	4.00	335	[a]	120–121
$Ph_3Sb(OCOCF_3)_2$	45.62	45.97	2.62	2.60	579	577	108–109
$Ph_3Sb(OCOCF_2H)_2$	48.65	48.60	3.16	3.07	543	537	96–96.5
$Ph_3Sb(OCOCFH_2)_2$	52.10	52.09	3.78	3.87	507	510	161–162
$Ph_3Sb(OCOCCl_3)_2$	38.92	38.74	2.23	2.20	678	673	139–140
$Ph_3Sb(OCOCCl_2H)_2$	43.39	43.21	2.82	2.62	609	618	147–148
$Ph_3Sb(OCOCClH_2)_2$	48.92	49.13	3.55	3.46	540	548	132–133
$Ph_3Sb(OCOCBr_2H)_2$	33.58	33.57	2.18	2.22	787	767	154–155
$Ph_3Sb(OCOCBrH_2)_2$	42.01	41.99	3.05	2.96	629	612	133–134
$Ph_3Sb(OCOCH_3)_2$	56.08	56.13	4.50	4.72	471	485	211–212
$Ph_3Sb(OCOCD_3)_2$	55.37	55.34	4.48	4.46	477	483	212–214

[a] Insufficiently soluble for determination.

soluble in polar as well as non-polar solvents. The trimethylantimony(V) derivatives are also soluble in water.

Molecular weight and conductance

Molecular weight determinations by vapor osmometry show that all the derivatives included in this investigation are monomeric, molecular compounds in benzene. Molecular weight data are shown in Table 1. In order to study the substituent effects on the donor property of the $R'OCO^-$ ion, electrical conductances for these compounds were examined in pyridine, which is a reasonably good donor solvent[5]. Observed equivalent conductances at 25°, in the concentration range 1.0×10^{-3} to 2.5×10^{-4} *M*, are recorded in Table 2. The conductance data show, that with the exception of the bis(trifluoroacetates), these compounds do not ionize in pyridine. For the bis(trifluoroacetates) a slight ionization is indicated, but, the observed conductances are much lower than those reported[5] for ionic compounds. It, therefore appears, that the donor property of $R'OCO^-$ ions is not significantly changed except when $R'=CF_3$. The derivatives of trichloro-, monochloro- and monobromoacetic acids decomposed in pyridine during conductance measurements. However, the initially observed conductances for these solutions did not indicate any ionic dissociation.

TABLE 2

CONDUCTANCE DATA FOR $R_3Sb(OCOR')_2$ DERIVATIVES

Compound	Λ_e *(ohm^{-1}·cm^2·eq^{-1})*[a]			
	2×10^{-3} *M*	1×10^{-3} *M*	5×10^{-4} *M*	2.5×10^{-4} *M*
$Me_3Sb(OCOCF_3)_2$	3.08	4.80	7.00	9.20
$Me_3Sb(OCOCF_2H)_2$	0.86	1.52	2.34	3.26
$Me_3Sb(OCOCFH_2)_2$	0.06	0.12	0.20	0.26
$Me_3Sb(OCOCCl_2H)_2$	1.16	1.95	2.88	3.90
$Me_3Sb(OCOCBr_2H)_2$	0.78	1.10	1.42	1.88
$Me_3Sb(OCOCH_3)_2$	0.11	0.15	0.17	0.18
$Me_3Sb(OCOCD_3)_2$	0.0	0.0	0.0	0.0
$Me_3Sb(OCOCH_2CN)_2$	0.21	0.28	0.38	0.52
$Ph_3Sb(OCOCF_3)_2$	3.21	4.90	7.88	12.35
$Ph_3Sb(OCOCF_2H)_2$	0.32	0.66	1.19	1.84
$Ph_3Sb(OCOCFH_2)_2$	0.10	0.12	0.18	0.24
$Ph_3Sb(OCOCCl_2H)_2$	1.25	1.85	2.69	3.78
$Ph_3Sb(OCOCBr_2H)_2$	0.45	0.78	1.24	1.68
$Ph_3Sb(OCOCH_3)_2$	0.07	0.09	0.10	0.14
$Ph_3Sb(OCOCD_3)_2$	0.0	0.0	0.0	0.0

[a] In pyridine at 25°; specific conductance of the solvent 2×10^{-7} ohm^{-1}·cm^{-1}.

Infrared spectra

Infrared spectra of all the compounds were examined in the solid state in the region 4000 to 200 cm^{-1}. The carbon–oxygen stretching frequencies for each compound were also determined in carbon tetrachloride or chloroform solution. The spectra can be interpreted in terms of absorption frequencies due to the internal vibrations of the R_3Sb and R'OCO groups. The bands due to the Me_3Sb or Ph_3Sb group are almost identical to those observed for the triorganoantimony dihalides[4]. The bands due to the R'OCO group were identified by comparison with those for the haloacetic[7-9] acids and their sodium salts[10]. The assignments for the ν(C=O) and ν(C–O) frequencies of the diacetate derivatives were confirmed by deuteration studies.

The observed carbon–oxygen and antimony–carbon stretching frequencies are recorded in Table 3. On comparing the data in Table 3 with those for the sodium salts[10] and other metal derivatives[11-15] of haloacetic acids, it is evident that all the compounds included in this study contain ester-like R'COO groups. No significant shifts in the ν(C=O) and ν(C–O) frequencies between solid state and solution are observed. Significant structural changes are therefore not expected between the solid state and solution. For the derivatives of mono- and dihaloacetic acids conformational isomerism of the type discussed for organotin haloacetates[16] is expected. The appearance of a doublet for the ν(C=O) frequency for these derivatives can therefore be attributed to the conformational effect.

Previous studies[10] on the sodium salts of α-substituted acetic acids show that the asymmetric CO_2 stretching frequency is markedly affected by the electron-withdrawing effects of the substituents. The symmetric CO_2 stretching frequency, however, does not appear to be affected by such effects. Instead, it shows a marked mass

TABLE 3

CARBON-OXYGEN AND ANTIMONY-CARBON STRETCHING FREQUENCIES (cm^{-1}) FOR $R_3Sb(OCOR')_2$ DERIVATIVES

Compound	*R*	*ν(C=O)*				*ν(C–O)*		*$ν_{as}$(Sb–C)*
		Solid		*Solution*[a]		*Solid*	*Solution*	*Solid*
$R_3Sb(OCOCF_3)_2$	CH_3	1725		1724		1406	1398	586
	C_6H_5	1725		1734		1392	1388	
$R_3Sb(OCOCF_2H)_2$	CH_3	1692		1695		1420	1403	588
	C_6H_5	1689	1672(sh)	1709		1318	1318	
$R_3Sb(OCOCFH_2)_2$	CH_3	1688	1650	1676[b]		1405	1403	584[c]
	C_6H_5	1678	1656	1698[b]		1348	1338	
$R_3Sb(OCOCCl_3)_2$	CH_3	1699		1708		1292	1285	584
	C_6H_5	1715		1721		1280	1279	
$R_3Sb(OCOCCl_2H)_2$	CH_3	1692	1680	1704	1682	1334	1318	589
	C_6H_5	1701(sh)	1682	1704(sh)	1689	1304	1302	
$R_3Sb(OCOCClH_2)_2$	CH_3	1669	1638(sh)	1694	1666	1344	1328	588
	C_6H_5	1676	1654	1680		1337	1328	
$R_3Sb(OCOCBr_2H)_2$	CH_3	1691	1678	1695	1674	1320	1310	568
	C_6H_5	1684		1687		1296	1298	
$R_3Sb(OCOCBrH_2)_2$	CH_3	1680	1668	1668	1618	1318	1318	584
	C_6H_5	1673	1655	1678		1319	1315	
$R_3Sb(OCOCH_3)_2$	CH_3	1655	1648	1658		1302	1291	584[c]
	C_6H_5	1633		1651[b]		1320	1310	
$R_3Sb(OCOCD_3)_2$	CH_3	1655	1638	1655		1315	1310	578
	C_6H_5	1624		1649[b]		1332	1320	
$R_3Sb(OCOCH_2CN)_2$	CH_3	1680(sh)	1667	1682[b]		1318	1318	580

[a] In CCl_4 unless stated otherwise. [b] In $CHCl_3$. [c] Observed as a shoulder on an acid band

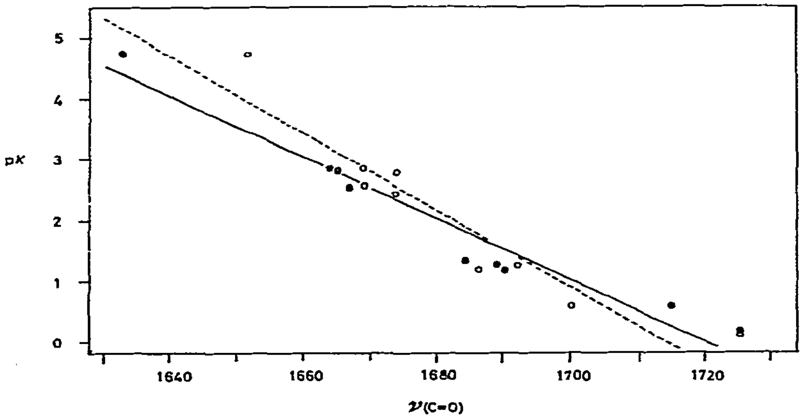

Fig. 1. The p*K* of the parent acid *vs.* the ν(C=O) of the triphenylantimony (●) and the trimethylantimony (○) carboxylic acid derivatives.

effect. Similar trends have also been observed[10] for the carbonyl and carboxyl frequencies of α-substituted acetic acids. For the triorganoantimony dicarboxylates we find that the ν(C=O) frequency shows a linear dependence upon the p*K* or the Taft constant σ^* for the parent acid. The plot of ν(C=O) against pK values[17] for the parent acids is shown in Fig. 1. No correlation is observed between the ν(C–O) frequency and the inductive effects of R′.

A recent far-infrared and Raman spectroscopic study[4,18] shows that the spectra of trimethyl- and triphenylantimony derivatives, R_3SbX_2, are best interpreted in terms of a trigonal bipyramidal structure, containing a planar R_3Sb moiety. For the trimethylantimony(V) derivatives the observation of only the asymmetric Sb–C IR stretching frequency is indicative of the planarity of the Me_3Sb group. However, due to the coupling between the metal–phenyl stretching vibrations and the phenyl ring vibrations, the above criterion cannot be used to determine the symmetry of the Ph_3Sb group. The infrared spectra of all the trimethylantimony dicarboxylates included in this study show only the asymmetric Sb–C stretching frequency (at ca. 570–585 cm^{-1}). Therefore, a trigonal bipyramidal structure can be assigned for these compounds. For the trimethyl- and triphenylantimony diacetates the Sb–O asymmetric stretching frequency is observed[4] at 279 and 287 cm^{-1}, respectively. Due to the presence of several ligand bands in the low frequency region, it is not possible to assign the Sb–O stretching frequency for the dihaloacetates.

Proton magnetic resonance spectra

Proton magnetic resonance spectra for these compounds are similar to those observed for the corresponding dihalides. For the trimethylantimony(V) dicarboxylates a single resonance with a line width of ca. 1 Hz is observed for the Me_3Sb protons. For the triphenylantimony(V) group a complex spectrum consisting of a quartet and a triplet is observed. The integrated intensities for the quartet and the triplet are in the ratio 2/3. Therefore, the quartet can be attributed to the ortho hydrogens and the triplet to the *meta* and *para* hydrogens.

TABLE 4

PROTON CHEMICAL SHIFTS[a] FOR $Me_3Sb(OCOR')_2$ DERIVATIVES

Compound	δ	*Compound*	δ
$Me_3Sb(OCOCF_3)_2$	2.08	$Me_3Sb(OCOCClH_2)_2$	1.95
$Me_3Sb(OCOCF_2H)_2$	2.03	$Me_3Sb(OCOCBr_2H)_2$	2.03
$Me_3Sb(OCOCFH_2)_2$	1.98	$Me_3Sb(OCOCBrH_2)_2$	1.94
$Me_3Sb(OCOCCl_3)_2$	2.10	$Me_3Sb(OCOCH_2CN)_2$	1.98
$Me_3Sb(OCOCCl_2H)_2$	2.03	$Me_3Sb(OCOCH_3)_2$	1.85

[a] In $CDCl_3$, downfield from TMS (internal).

Since the acid strengths of the parent acids occur in a wide range, variations are anticipated in the polarity of the Sb–OCOR′ bond. That this is indeed the case is shown by the Me_3Sb chemical shifts which are recorded in Table 4. The data in Table 4 show that although the chemical shifts occur in a small range of 2.08 to 1.85 ppm, nevertheless, the Me_3Sb protons are progressively deshielded with an increase in the electronegativity of R′. In fact there is a linear correlation between the chemical shift and the pK or the Taft constant σ^* of the parent acid. A plot of chemical shifts *versus* pK is shown in Fig. 2.

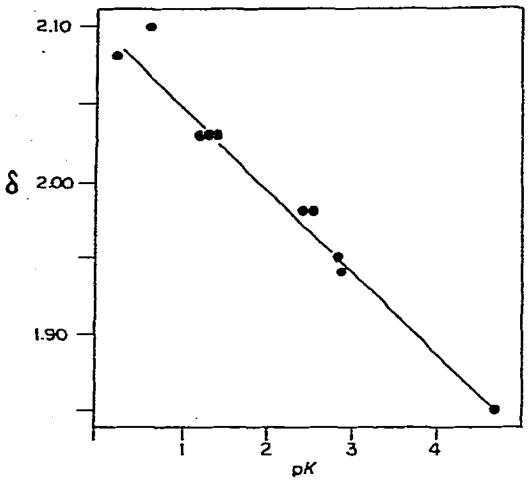

Fig. 2. Chemical shifts of Me_3Sb protons *vs.* the p*K* of the parent acid.

EXPERIMENTAL

General

Silver trifluoroacetate and all the carboxylic acids were obtained from commercial sources and were used without further purification. Pyridine was purified by refluxing with potassium hydroxide and subsequent distillation. Microanalyses were performed in this department or by A. B. Gygli, Microanalytical Laboratory, Toronto.

Preparation of compounds

Trimethyl- and triphenylantimony dihalides, diacetates and their deuterated analogs were prepared as described[4] previously.

Trimethylantimony bis(trifluoroacetate) was prepared by the reaction of triorganoantimony dichloride or dibromide with two equivalents of silver trifluoroacetate in methanol. Other trimethylantimony dicarboxylates were prepared by the reaction of stoichiometric amount of trimethylantimony dihalide with a freshly prepared aqueous solution of silver oxide in the appropriate acid. In each case the product was isolated by concentrating the filtered solution under reduced pressure.

Triphenylantimony(V) derivatives of mono-, di-, and trifluoroacetic acids were prepared by the metathetical reaction of a benzene solution of triphenylantimony dihalide with the silver salt of the appropriate acid. The benzene solution was filtered and the product was isolated by removal of benzene under vacuum. Triphenylantimony(V) derivatives of the chloro- and bromoacetic acids were prepared by adding a benzene solution of triphenylantimony dihalide to an aqueous solution of silver oxide in the desired acid. After filtration the benzene layer was separated from the aqueous layer. It was subsequently dried with molecular sieve and then after filtration benzene was removed under vacuum.

All the compounds were recrystallized from a 1/4 mixture of light petroleum ether and hexane.

Measurements

Molecular weights were determined in benzene with a Hitachi–Perkin–Elmer

Model 115 Vapor osmometer. Electrical conductances were measured with a Beckman Model RC-18A conductivity bridge. The melting points were obtained with a Gallenkamp apparatus. Infrared spectra were recorded on a Beckman Model IR-12 double beam spectrophotometer. Spectra in the solid state were obtained on mulls in Nujol and halocarbon oils, using KRS-5 and polyethylene demountable cells. Solution spectra were measured with 0.1 mm pathlength sodium chloride sealed cells. ^{1}H NMR spectra were obtained on a Varian A-60 spectrometer at ambient temperature.

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