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Synthesis and Reaction of tris(*p*-fluorophenyl)antimony(v) Dicarboxylates and Halo-Carboxylates

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ABSTRACT

Several unknown tris(*p*-fluorophenyl)antimony(v) dicarboxylates and tris(*p*-fluorophenyl)antimony(v) halo-carboxylates of the general formula $(p\text{-}FC_6H_4)_3Sb(L)_2$ and $(p\text{-}FC_6H_4)_3SbCl_2$, respectively have been synthesized by the metathetical reactions of tris(*p*-fluorophenyl)antimony dichloride reactions and silver salts of corresponding carboxylic acids in 1:2 and 1:1 ratio [where L= 2-pyrazine carboxylic acid, *p*-methoxymandelic acid, salicylic acid, benzillic acid and *p*-(trifluoromethyl)mandelic acid)]. The newly synthesized antimony derivatives have been characterized on the basis of melting point, elemental analysis, IR ^1H and ^{13}C NMR spectra. The molecular weight and conductivity data indicate the monomeric and non-electrolytic behaviour in solution.

Keywords:tris(*p*-fluorophenyl)antimony(v), carboxylates, halo-carboxylates, tris(*p*-fluorophenyl)antimony dichloride.

INTRODUCTION

The first organoantimony carboxylate, $Ph_3Sb(OOCH_3)_2$ was prepared way back in 1922 by Schmidt [1] by the oxidation of triphenylantimony with hydrogen peroxide and subsequent reaction with acetic acid. Since then, several trioganoantimony(V) dicarboxylate have been prepared by different methods *e.g.*, by dissolving triphenylantimonydihydroxide in hot formic acid. Doak*et al*. [2] obtained triorganoantimonydiformate.Organoantimony(V) compounds of formic, benzoic, acetic, propionic, halo and cyano-acetic acids [3-7] have been prepared by the reaction of antimony halide with (a) the corresponding silver carboxylate or (b) silver oxide and carboxylic acid. The substitution of the Sb-OOCR' bond has been studied with the help of infrared and MNR spectroscopy [4,5]. A few organoantimony(V) dicarboxylates of the type R_2SbL_3, R_3SbL_{-2} (R=*p*-FC_6H_4, *p*-ClC_6H_4) and R_4SbL (R=Ph, *p*-tolyl) have also been synthesized and characterised [8,9,10,11].The biocidal activity of a series of tertiary substituted aryl antimony (V) dicarboxylates has also been reported [12,13].Tertiary substituted arylantimonydipseudohalides of the type R_3SbX_2 (R=*p*-ClC_6H_4, *p*-FC_6H_4; X=N_3, NCO, NCS) have been prepared through replacement reaction between tertiary substituted aryl antomony(V) dihalide and the corresponding metallic salt [12]. As studied above in earlier publication reported from this laboratory, organoantimony carboxylates $R_nSb(OCOR)_{4-n}$ have been found to exhibit significant biologically activity. The activity is further enhanced if the phenyl group is replaced by fully or partially substituted aryl group(s). We have identified certain carboxylates acid salts moieties which are biologically active to react them with substituted

aryl derivative of antimony and to isolate and characterise them. The present work describes the preparation of hitherto unknown *p*-fluoroantimonydicarboxylates of general formula $(p\text{-}C_6H_4)_3Sb(OCOR)_2$. Carboxylic acid = Salicylic acid, Benzoic acid, Mandelic acid, 2-Pyrazine carboxylic acid &Nicotonic acid, Gallic acid

EXPERIMENTAL

Tris (*p*-fluorophenyl) antimony(V) dichloride was prepared by slowly passing chlorine gas ($KMNO_4$ + conc.HCl) through a solution of tri(*p*-fluorophenyl) antimony (III) in petroleum ether (60-80^{o}C) at -5^{o}C.

The carboxylic acids were used in the farm of salts which were obtained by reacting sodium salt with corresponding acid. Special precautions were taken to exclude moisture and oxygen. The reaction of sodium, salts were done under dark condition to avoid decomposition. Details of reactions alongwithanalytial data for the complexes are given in tables 1-3.

I.Reaction of tris-(*p*-fluorophenyl) antimony(V) dichloride with sodium salt of salicyclic acid

Under the dry atmosphere of dry nitrogen, a heterogenous solution of tris-(*p*-fluorophenyl)antimony(V) dichloride (0.480 g, 1 mmol) and sodium salt of salicylic acid (0.320 gm, 2 mmol) in THF (20 ml) was stirred at room temperature for 6 h further it was refluxed for 3 h to ensure the completion of reaction. The white precipitate of NaCl formed was filtered off. On removal of solvent from filtrate under vaccuo the crystalline off white solid was obtained, which was recrystallised from a mixture of THF and n-Hexane (1:3). The compound was characterised as tris(*p*-fluorophenyl) antimony salicylate. M.P.= 150^{o}C Yield= 1.20 g (45%)

II. Reaction of tris(*p*-fluorophenyl)antimony(V)dichloride with sodium salt of 2-pyrazine carboxylic acid

In presence of dry nitrogen atmosphere a solution of tris(*p*-fluorophenyl) antimony(V)dichloride (0.480 g, 1 mmol) and sodium salt of 2-pyrazine carboxy acid (0.292 g, 2 mmol) in THF (30 ml) was stirred at room temperature for 6 h further it was refluxed 3 h to ensure the completion of reaction. The heterogenous solution contain precipitate of NaCl was filtered and filtrate was concentrated in vaccuo (2-3 ml) followed by addition of n-hexane afforded off white crystalline solid characterised as tris(*p*-fluorophenyl) antimony(V) 2-pyrazine carboxylate.

M.P.=120^{o}C Yield =0.614 g (46%)

III. Reaction of tris(*p*-fluorophenyl)antimony(V) dichloride with sodium salt of hippuric acid

In oxygen and moisture free atmosphere, solution of tris(*p*-fluorophenyl) antimony(V)dichloride (0.480 g, 1 mmol) and sodium salt of Hippuric acid (0.402 g, 2 mmol) in THF (20 ml) was stirred at room temperature for 6 hr further it was refluxed 4 h to ensure the completion of reaction. The white precipitate of NaCl thus as formed was filtered off. The filtrate on concentration in vaccuo (2-3 ml) followed by addition of petroleum ether (60-80^{o}C) and n-hexane afforded white

crystalline solid characterised as tris(*p*-fluorophenyl)antimony(V) hipparate. M.P.=130°C Yield =1.2 g (40%)

IV. Reaction of tris(*p*-fluorophenyl)antimony(V)dichloride with sodium salt of naphthyl acetic acid

In oxygen and moisture free atmosphere, a solution of tris(*p*-fluorophenyl)antimony(V)dichloride (0.480 g, 1 mmol) and sodium salt (0.418 g, 2 mmol) of naphthyl acetic acid in Benzene (20 ml) was stirred at room temperature for 6 h further it was refluxed 3 h to ensure the completion of reaction. The white precipitate of NaCl thus as formed was filtered off. The filtrate on concentration in vaccuo (2-3 ml) followed by addition of n-hexane afforded white crystalline solid characterised as tris(*p*-fluorophenyl) antimony(V)naphthyl acetic acid.M.P.=112°C Yield =1.48 g (48%)

V. Reaction of tris(*p*-fluorophenyl)antimony(V) dichloride with sodium salt of ethyl aceto acetate

An solution of tris(*p*-fluorophenyl)antimony(V)dichloride (0.480 g, 1 mmol) and sodium salt of ethyl acetoacetate (0.304 g, 2 mmol) in benzene (20 ml) was stirred at room temperature use for 6 h, further it was refluxed 3 h to ensure the completion of reaction. On filtration of heterogenous, solution containing white precipitate of NaCl, clear solution was obtained which was concentrated in vaccuo (2-3 ml) after adding n-hexane the solid was allowed to stand overnight at 0°C affording a white crystalline solid which was recrystallised from n-hexane. The compound was characterised as tris(*p*-fluorophenyl)antimony(V) ethyl acetoacetate.M.P. = 170°C Yield = 1.10 g (42%)

VI. Reaction of tris(*p*-fluorophenyl)antimony(V)dichloride with sodium salt of 3,5 dinitrobenzoic acid

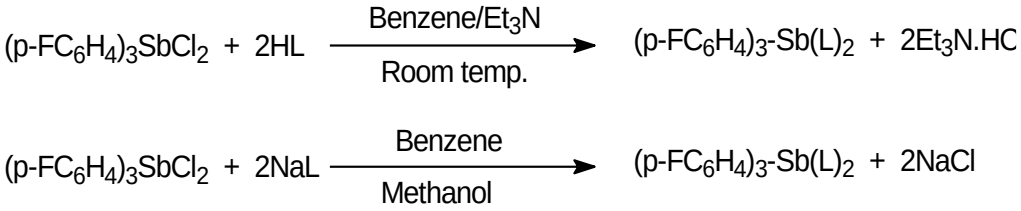
Under dry atmosphere of dry nitrogen, a heterogenous solution of tris(*p*-fluorophenyl)antimony(V)dichloride (0.480 g, 1 mmol) and sodium salt of 3,5 dinitrobenzoic acid (0.668 g, 2 mmol) in 30 ml Benzene was stirred at room temperature for 6 h further it was refluxed 4 h to ensure the completion of reaction. The white precipitate of NaCl has formed was filtered off, on removal of solvent from filtrate was crystallised off white solid was obtained which was recrystallised off white solid was obtained which was recrystallised from a mixture of petroleum ether and n-hexane (1:3). The compound was characterised as tris(*p*-fluorophenyl)antimony(V) 3,5 dinitrobenzoate.

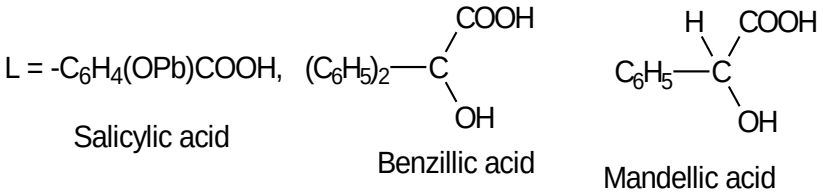
M.P. = 180°C Yield = 0.780 (46%)

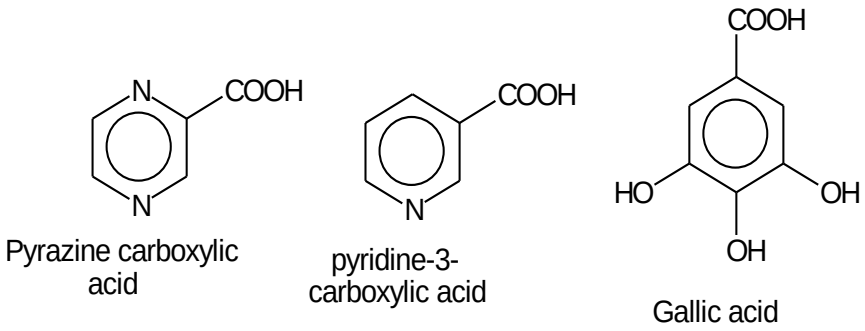
RESULT AND DISCUSSION

In an anhydrous oxygen free atmosphere tris(p-fluorophenyl) antimony (V) dicarboxylate can conveniently be prepared by the interaction of tris(p-fluorophenyl) antimony(V) dichloride $(p\text{-}FC_6H_4)_3\text{-}SbCl_2$, with a carboxylic acid in 1:2 molar ratio in presence of a Lewis base (triethylamine (Et_3N) as hydrogen halide acceptor). Alternatively, these could also be obtained by the simple metathesis of $(p\text{-}FC_6H_4)_3SbCl_2$ with an

appropriate sodium or silver salt of corresponding carboxylic acid.







The reaction was carried out in dried benzene or THF at room temperature (R.T.) with constant stirring for 8 hours. The yield of the products was nearly quantitative except for the losses during work up process. The complexes are soluble in most of the organic solvents except petroleum-ether and n-hexane. They are off white are light brown crystalline solids with sharp melting points. The complexes remain unaffected by air and atmosphere moisture and can be stored for several weeks without decomposition. All these derivatives were found non-electrolytes in acetonitrile. Molecular weight determination by cryoscopic method in benzene showed their monomeric constitution.

IR SPECTRA

The entire complex were characterised by diagnostic infrared absorption data in range 4000-400 cm^{-1}. The diagnostic IR absorption bonds of newly synthesized compounds have been identified and are listed in table-3.

The infrared spectra of all compounds show almost identical absorptions due to *p*-fluoro groups. The Sb-C stretching frequency was observed in the range of 440-480 as a medium to weak band. The antimony halogen frequency in the spectra of the carboxylates was not observed in the range 3000-400 cm^{-1}.The IR absorption due to carboxylate group were observed in the characteristic region [ν_{asym}(OCO) between 1665-1582.6 cm^{-1}, ν_{sym}(OCO) between 1491-1327 cm^{-1}]. On the basis of $\Delta\nu$ (OCO) (Seperation values >250 cm^{-1}). In all the cases, it seems reasonable to conclude that the carboxylate moiety behave as unidentate, easter type – OCO group.

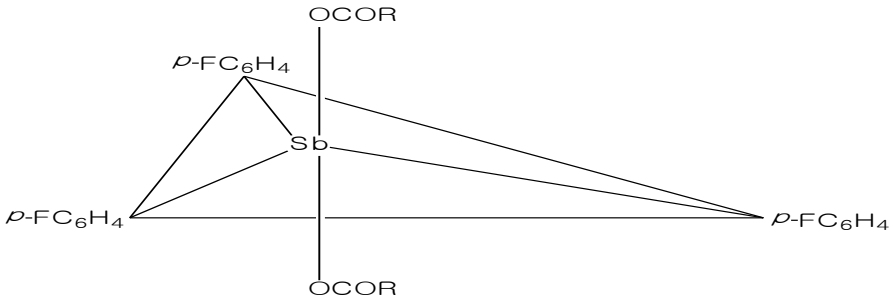
[1]H NMRSpectra

The ^{1}H NMR spectra of representative compounds (4,6,7,8 and 9) was recorded at room temperature in $CDCl_3$. The spectra of all the compounds showed multiplets in the range δ 7 to 8.32 ppm attributed to aromatic proton. The spectra of compound (6) showed a peak at δ 2.50 ppm due to CH_2 proton, while for compound (8) peak due to CH_3 proton appeared at δ 3.40 ppm. The integration of the peaks is consistent with the proposed formulation of the compounds.

*[19]F*NMR Spectra

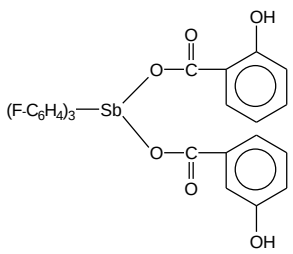
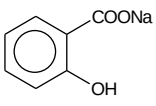
^{19}F spectra of compound ware recorded using CF_3COOH as reference at 85.26 MHz. The characteristics signals of $F_{2,6}$, $F_{3,5}$ and F_4 were observed at 110ppm, ppm and 120ppm respectively. The peak of F_4 was easily recognized due to its intensity compared to $F_{2,6}$ and $F_{3,5}$ peaks. F_4 signals appear at triplet of triplet due to spin-spin coupling. Thus on the basis of spectral data molecular weight and conductance measurement, the newly synthesized compounds are tentatively assigned trigonalbipramidal structure.

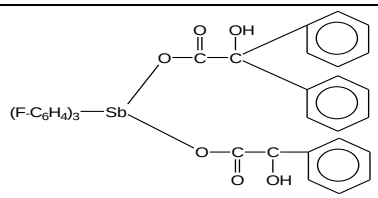
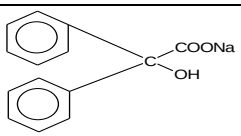
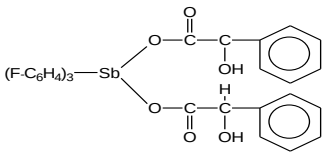
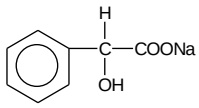
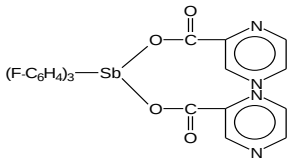
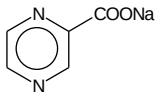
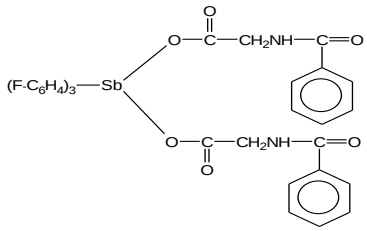
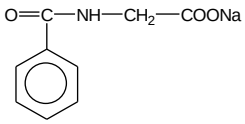
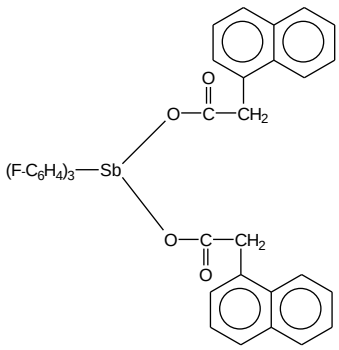
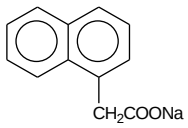
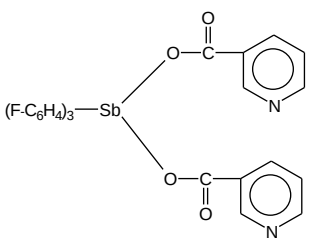
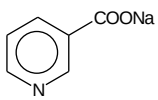
Suggested structures of tris (*p*-fluorophenyl) antimony (v) derivatives



Tris(*p*-fluorophenyl)antimony,dicarboxylates (p-$FC_6H_4)_3Sb(OOCR)_2$

TABLE-1: Preparation and Property of tris(*p*-fluorophenyl) antimony (v) dicarboxylates

S. No.	Complex	Ligand (Sodium salt of)	Molar ratio	Reaction condition		M.P. °C	Yield%	Colour	Recrystallizing solvent
				Temp. (°C)	Time (h)				
1.		 (0.320 g, 2 mmol) salicylic acid	1:2	80	3	150	45% (1.20 gm)	Off white	n-hexane

2.		 (0.50 g, 2 mmol) Benzoic acid	1:2	80	4	195	50% (1.2 gm)	White	n-hexane
3.		 (0.348 g, 2 mmol) Mandelic acid	1:2	80	2.5	115	48% (0.620 gm)	Off white	Pet ether (60°-80°)
4.		 (0.292 g, 2 mmol) 2-pyrazine carboxylic acid	1:2	80	3	120	48% (1.10 gm)	Off White	n-hexane
5.		 (0.402 g, 2 mmol) Hippuric acid	1:2	80	4	130	40% (1.2 gm)	White	Pet ether (60°-80°)
6.		 (0.418 g, 2 mmol) Naphthyl acetic acid	1:2	80	3	112	48% (1.48 gm)	Off White	n-hexane
7.		 (0.290 g, 2 mmol) Nicotinic acid	1:2	80	2	90	47% (0.58 gm)	Dull White	n-hexane

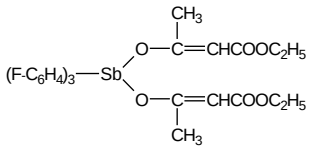
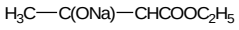
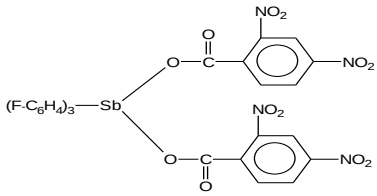
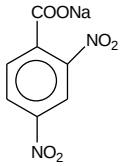
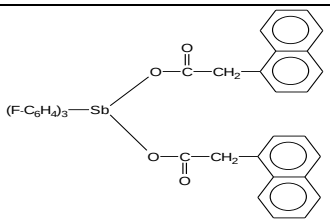
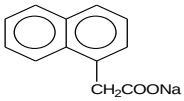
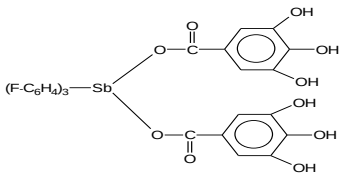
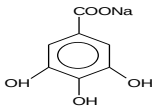
8.		 (0.304 g, 2 mmol) Ethylacetoacetate	1:2	80	3	170	42% (1.10 gm)	White	n-hexane
9.		 (0.668 g, 2 mmol) 3,5 dinitrobenzoic acid	1:2	80	4	180	46% (0.78 gm)	Off White	Pet ether (60°-80°) + n-hexane
10.		 (0.434 gm, 2 mmol) Naphthyl acetic acid	1:2	80	3	112	48% (1.48 gm)	Off White	Pet ether (60°-80°) + n-hexane
11.		 (0.384 g, 2 mmol) Gallic acid	1:2	80	6	120	58% (1.60 gm)	Dull White	n-hexane

TABLE-2: Elemental Analysis of tris(*p*-fluorophenyl) antimony (v) dicarboxylates

S. No.	Molecular formula	Molecular weight	Carbon Found (Calcd.)	Hydrogen Found (Calcd.)	Nitrogen Found (Calcd.)
1.	$C_{32}H_{22}F_3O_6Sb$	681.27	56.25 (56.42)	3.21 (3.32)	–
2.	$C_{46}H_{34}F_3O_6Sb$	861.51	63.90 (64.13)	3.72 (3.98)	–
3.	$C_{34}H_{26}F_3O_6Sb$	709.32	57.40 (57.57)	3.25 (3.69)	–
4.	$C_{28}H_{18}F_3N_4O_4Sb$	653.22	51.25 (51.48)	2.60 (2.78)	8.40 (8.58)
5.	$C_{36}H_{28}F_3N_2O_6Sb$	763.37	56.35 (56.64)	3.56 (3.70)	3.30 (3.67)
6.	$C_{42}H_{30}O_4F_3Sb$	777.44	64.62 (64.89)	3.70 (3.89)	–
7.	$C_{30}H_{20}O_4N_2F_3Sb$	651.25	55.10 (55.33)	3.00 (3.10)	4.10 (4.30)
8.	$C_{30}H_{28}F_3O_6Sb$	663.29	54.18 (54.32)	4.10 (4.25)	–

9.	$C_{32}H_{18}F_3N_4O_{12}Sb$	829.26	46.15 (46.35)	2.10 (2.19)	6.40 (6.76)
10.	$C_{42}H_{38}F_3O_4Sb$	785.50	64.22 (64.57)	4.52 (4.88)	–
11.	$C_{32}H_{22}F_3O_{10}Sb$	745.27	51.20 (51.57)	2.70 (2.98)	–

TABLE-3: Characteristics IR absorption bands (cm^{-1}) for tris(*p*-fluorophenyl) antimony (v) dicarboxylates

S.No.	Compound	γ (OH)	ν (OCO)			ν (Sb-C)
			νasym	νsym	Δν (νasy - νsym)	
1.	$F_3C_{36}H_{28}O_6N_2Sb$	–	1582.6 (S)	1356.4 (m)	226.2	508.3
2.	$F_3C_{42}H_{38}O_4Sb$	–	1652.3 (S)	1491 (m)	161	509
3.	$F_3C_{34}H_{26}O_6b$	3425 (b)	1594 (VS)	1379 (s)	125	489
4.	$F_3C_{46}H_{34}O_6Sb$	3433 (b)	1665 (S)	1490 (s)	175	509
5.	$F_3C_{32}H_{22}O_6Sb$	3456 (s)	1662 (S)	1482 (s)	180	623
6.	$F_3C_{30}H_{28}O_6Sb$	–	1638 (VS)	1491 (s)	147	507
7.	$F_3C_{32}H_{22}O_{10}Sb$	3405 (b)	1588 (S)	1327 (vs)	261	510

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