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THE PREPARATION OF PENTAFLUOROPHENYL ANTIMONY(III) AND ANTIMONY(V) HALIDES AND MIXED HALIDES

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SUMMARY

$(C_6F_5)_3Sb$ (I) has been found to undergo redistribution reactions with $SbCl_3$ in 2/1 and 1/2 molar ratios to give quantitative yields of $(C_6F_5)_2SbCl$ (II) $(C_6F_5)SbCl_2$ (III), respectively. Oxidative chlorination of ice cold solutions of (II) and (III) gave $(C_6F_5)_2SbCl_3$ (IV) and $(C_6F_5)SbCl_4$ (V), respectively. Bromination of (II) and (III) at - 178°C yielded mixed halides, $(C_6F_5)_nSbCl_{3-n}Br_2$ (n = 1 & 2).

INTRODUCTION

In sharp contrast to well documented organo-substituted antimony(III), R_nSbCl_{3-n} and antimony(V) halides, R_nSbCl_{5-n} (n = 1 or 2) based on hydrocarbon ligands [1-3], those containing pentafluorophenyl groups are virtually unknown and are restricted to tris(pentafluorophenyl)antimony(V) compounds eg. $(C_6F_5)_3SbX_2$ (X=Cl,Br,NO_3,ClO_4,OCH_3)[4,5] and $C_6F_5)_3SbIY$ (Y = Cl,Br,N_3, NCO etc) [6] This is probably because the various methods employed in the preparation of parallel phenyl antimony(III) halides are not easy and the reactions proceed in low yield [1,2]. Our interest in the synthesis and chemical behaviour of pentafluorophenylantimony(V) derivatives led us to develop a rapid and facile route for pentafluorophenyl antimony(III), $(C_6F_5)_nSbCl_{(3-n)}$ (n = 1 & 2) and antimony(V) chlorides $(C_6F_5)_nSbCl_{5-n}$ (n = 1 & 2) and mixed halides, $(C_6F_5)_nSbCl_{3-n}Br_2$ in high yield and high purity.

RESULTS AND DISCUSSION

Pentafluorophenyl antimony(III) and antimony(V) chlorides and mixed halides

In the absence of solvent, tris (pentafluorophenyl) antimony(III) undergoes a facile redistribution reaction with antimony trichloride in 2/1 and 1/2 molar ratios under oxygen free dry atmospheres.

$$2(C_6F_5)_3Sb + SbCl_3 \longrightarrow \underset{\text{(II)}}{3(C_6F_5)_2SbCl} \qquad (1)$$

$$(C_6F_5)_3Sb + 2SbCl_3 \longrightarrow \underset{\text{(III)}}{3(C_6F_5)SbCl_2} \qquad (2)$$

The redistribution is complete in <u>ca.</u> 3h. The resulting $(C_6F_5)_nSbCl_{3-n}$ derivatives are viscous oils which solidify on standing.

Pentafluorophenylantimony chlorides serve as useful intermediates for obtaining pentafluorophenylantimony(V) chlorides or mixed halides. Thus bis(pentafluorophenyl) antimony trichloride, $(C_6F_5)_2SbCl_3$ can be prepared, as a white crystalline solid on treatment of $(C_6F_5)_2SbCl$ with dry chlorine in cold dichloromethane.

$$(C_6F_5)_2SbCl + Cl_2 \longrightarrow \underset{(IV)}{(C_6F_5)_2SbCl_3} \qquad (3)$$

Similarly, $(C_6F_5)SbCl_2$ is readily converted to the Sb(V) derivative, $(C_6F_5)SbCl_4$.

$$(C_6F_5)SbCl_2 + Cl_2 \longrightarrow \underset{(V)}{(C_6F_5)SbCl_4} \qquad (4)$$

Unlike $PhSbCl_4$ which is hygroscopic, $(C_6F_5)SbCl_4$ is remarkably stable at room temperature and not affected by oxygen.

Oxidative bromination of $(C_6F_5)_nSbCl_{3-n}$ leads to the formation of $(C_6F_5)_nSb(V)Cl_{3-n}Br_2$

$$(C_6F_5)_2SbCl + Br_2 \longrightarrow \underset{(VI)}{(C_6F_5)_2SbClBr_2} \qquad (5)$$

$$(C_6F_5)SbCl_2 + Br_2 \longrightarrow \underset{(VII)}{(C_6F_5)SbCl_2Br_2} \qquad (6)$$

In view of the reported low stability of antimony(V) derivatives $(C_6F_5)_3SbBr_2$[4], which tend to decompose at room temperature with the elimination of bromine in solution, reactions of (pentafluorophenyl)antimony(III) chlorides with bromine were carried out at low temperature, -178°C (to prevent the possibility of decomposition of bromo derivative). However, on allowing the reaction mixture to come to room temperature, no decomposition of $(C_6F_5)_2SbClBr_2$ or $(C_6F_5)SbCl_2Br_2$ was observed. Both the halides were obtained in high yield.

IR spectroscopy

All the isolated compounds (II-VII) exhibit characteristic IR absorptions due to C_6F_5 groups attached to an Sb atom and are in conformity with the reported literature values [4,6]. The IR spectra of tris(pentafluorophenyl)antimony and its dihalides have previously been described[5]. The comparison of these data with phenyl analogues has enabled identification of prominent IR absorption for the compounds (II) to (VII) which are listed in Table 1.

The stretching vibrations of the (Sb-X) groups occurs at higher frequencies than for the corresponding phenyl derivatives. The replacement of the hydrocarbon groups by the highly electron withdrawing pentafluorophenyl groups leads to an increase in the partial positive charge on the antimony atom. This in turn could result in a contraction of the orbital used by antimony to bond to the halogen, leading to a stronger bond and higher vibrational frequency.

TABLE 1

Relevant infrared frequencies of (Pentafluorophenyl)antimony (III) &(V) derivatives in cm^{-1})*

R_2SbCl	$RSbCl_2$	R_2SbCl_3	$RSbCl_4$	$R_2SbClBr_2$	$RSbCl_2Br_2$	Assignments
219(ms)	220(w)	225(ms)	228(s) 230(m)	222(m)	224(m)	d,t
-	-	-	-	235(vs)	231(vs)	Sb-Br
290(w)	287(w)	287(w)	288(mw)	287(mw)	285(w)	t
340(m)	339(ms)	325(s)	335(vs)	322(m)	323(ms)	Sb-Cl
448(w)	450(vw)	447(vw)	445(vvw)	446(w)	446(vw)	y
595(m) 591(m)	593(mw)	594(w)	596(mw)	595(w) 599(w)	596(w)	p
604(m)	606(m)	620(ms)	625(ms)	621(ms)	615(ms)	r
713(m)	715(m)	725(m)	729(ms)	728(m)	722(ms)	s
778(m)	779(ms)	761(m)	762(mw) 759(mw)	749(mw) 751(mw)	750(mw)	v
956(vs)	955(vvs)	975(vvs)	980(vvs)	990(vvs)	988(vvs)	q

* s=strong, m=medium, w=weak, v=very

The spectra of all the chlorides show a band between 320-340 cm^{-1} increasing in intensity with increasing chlorine content, which can be attributed to one of the antimony chlorine stretching modes. In the case of $(C_6F_5)_2SbClBr_2$ and $(C_6F_5)SbCl_2Br_2$ a strong band at 235 ± 5 cm^{-1} may be assigned to antimony-bromine stretching vibrations.

EXPERIMENTAL

Pentafluorobromobenzene (Imperial Smelting Company, Bristol) was used as received. Antimony trichloride (Fluka) was dried over P_4O_{10} and sublimed before use. Tris (Pentafluorophenyl)antimony was prepared as described previously [7].

All the solvents were purified and dried by standard procedures and the reactions carried out under anhydrous conditions.

Infrared spectra were recorded in the range 4000-200 cm^{-1} by using KBr/CsI pellets on a Perkin-Elmer-577 spectrophotometer. Antimony and chlorine were determined as reported earlier [4,6].

Typical experimental details of the reactions are described below. Analytical data are given in Table 2.

Bis(pentafluorophenyl)antimony(III)chloride Antimony trichloride (2.28 g, 10 mmol) and tris(pentafluorophenyl) antimony (12.45 gm, 20 mmol) were heated at 60-70°C in absence of solvent for about 3 hrs. Cooling yielded white

TABLE 2

Analytical data for Pentafluorophenylantimony(III) & (V) derivatives

Compound	Molecular formula	M.p. (°C)	Analysis Calcd (Found) in %		
			C	Sb	Cl
II	$C_{12}F_{10}SbCl$	79-80	29.50 (29.31)	24.35 (24.77)	7.1 (7.22)
III	$C_6F_5SbCl_2$	80-81	20.35 (20.01)	33.41 (33.83)	19.33 (19.73)
IV	$C_{12}F_{10}SbCl_3$	248	25.82 (25.61)	21.10 (21.64)	18.65 (18.94)
V	$C_6F_5SbCl_4$	236-7	16.96 (16.71)	28.05 (28.25)	32.50 (32.96)
VI	$C_{12}F_{10}SbBr_2Cl$	206	21.90 (22.11)	18.20 (18 68)	-
VII	$C_6F_5SbBr_2Cl_2$	214	13.56 (13.85)	23.00 (23.41)	-

crystals, which on recrystallisation from dichloromethane gave the pure compound (yield 11.78 gm, 80%).

<u>(Pentafluorophenyl)antimony(III)dichloride</u> Antimony trichloride (4.56 gm, 20 mmol), and tris(pentafluorophenyl) antimony (6.22 gm, 10 mmol) were heated at about 60-70°C in absence of solvent for about 3 hrs. Cooling yielded white crystals, which on recrystallisation from dichloromethane gave the pure compound, (yield = 8.0 gm, 75%).

<u>Bis(pentafluorophenyl)antimony(V)trichloride</u> Bis (pentafluorophenyl)antimony(III)chloride (4.9 gm, 10 mmol) was dissolved in dichloromethane (100 cm^3) and cooled to 0°C in ice. Dry chlorine (0.71 g, 10 mmol) was then added from a weighed trap and the temperature was allowed to rise slowly to room temperature On concentration of solution, white crystals were obtained which on recrystallisation from dichloromethane or petroleum ether (40-60°C) gave the pure compound. (Yield 3.9 gm, 70%).

<u>(Pentafluorophenyl)antimony(V)tetrachloride</u> Pentafluorophenyl antimony(III) dichloride (3.6 gm, 10 mmol) dissolved in dichloromethane (100 cm^3) was ice cooled with ice. Dry chlorine (0.71 gm, 10 mmol) was then added from a weighed trap and the temperature was then added rise slowly to room temperature. On concentration of the

solution white crystals were obtained which on recrystallisation from dichloromethane/petroleum ether (40-60°) gave the pure compound (Yield 3 gm, 70%).

Bis(pentafluorophenyl)antimony chloride dibromide

Anhydrous Br_2 (1.6 gm, 10 mmol) was condensed at -178°C into a solution of bis(pentafluorophenyl)antimony(III) chloride (4.9 gm, 10 mmol) in dichloromethane (100 cm^3). After allowing the temperature to rise slowly on concentrating the solution the compound separated on cooling. Recrystallisation from dichloromethane afforded the pure product (Yield 5.5 gm, 85%).

(Pentafluorophenyl)antimony(V)dichloridedibromide

Anhydrous bromine (1.6 gm, 10 mmol) was condensed at -178°C into a solution of (pentafluorophenyl)antimony(III) dichloride (3.6 gm, 10 mmol) in dichloromethane (100 cm^3). After allowing the temperature to rise slowly on concentrating the solution the compound separated on cooling Recrystallisation from dichloromethane produced the pure product (Yield 4.3 gm, 83%).

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