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Research Article

Synthesis, characterization and reactions of some Pentafluorophenylantimony(III) Diamides

Ram Nath Prasad Yadav

Department of Chemistry, Tribhuvan University, Thakur Ram Multiple Campus, Birganj, Nepal.
*Corresponding author e-mail: *ramnathy@rocketmail.com*

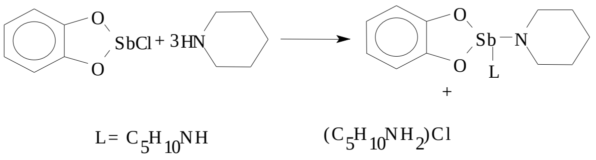
Abstract

A series of some new pentafluorophenylantimony(III) diamides of general formula $R_fSb(NR_2)_2$. Where, $R_f = C_6F_5$ and NR_2 = $-N(CH)NCHCH$, $-N(CH)NC_6H_4$, $-N(CCH_3)NCHCH$, $-NCH_2COCH_2CO$, $-NCOC_6H_4CO$ have been prepared by metathesis reaction of $C_6F_5SbCl_2$ with an amide/imide. The amides derivatives were also obtained by the interaction of $C_6F_5SbCl_2$ with the appropriate metals salts of the organic ligands. The newly synthesized compounds have been characterized by conventional methods. A tentative pyramidal structure is suggested for these compounds. A failure to prepare $R_fSb(OCOCH_3)_2$ by the cleavage of Sb-N bond may be attributed to instability of arylantimony(III) acetate.

Keywords: Pentafluorophenyl, Amide, Imide, Metathesis, Cleavage reaction, Insertion reaction.

Introduction

A persual of literature reveals that the synthesis of reported amido derivatives of antimony could be accomplished via different routes. Reaction of halogen derivatives with an amine is a common synthetic route employed for the preparation of organoantimony(III) amides derivatives are also available by this method.



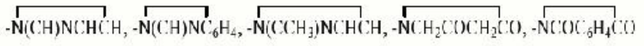
Synthesis of aminostibines, containing Sb(III)-N bonds of the general formula $Ph_nSb(NEt_2)_{3-n}$ (n=1,2) obtained by the reaction of lithium diethylamide with halo or dihalostibine at low temperature (-80°C) has been reported by Meinema and Noltes (Meinema and Noltes 1970). Three coordinated diarylantimony(III) amides of the general, formula Ar_2SbL [Ar = phenyl, pentafluorophenyl; L = $-NR_2$ = $-NCOCH_2CH_2CO$, $-NCOC_6H_4CO$, $-NNNC_6H_4$ etc has been reported from this laboratory (Premraj *et al.*, 1989^b). A series of isatin derivatives of $Ar_nSb(NR_2)_n$ and their reactions with CS_2, PhNCO and other reagents *viz*, H_2O, CH_3OH and $TeCl_4$ has also appeared (Singhal, 1993).

Despite such a varied interest, published data on arylantimony(III) amides are lacking. It is more surprising in the light of the fact that phenylantimony(III) compounds of the type ph_nSbX_{3-n} (n = 1 and 2), X = halide, (Doak and Freedman 1970), alkoxide (Wieber and Baudis

1978), carboxylate (Bone and Sowerby 1980 and Hall *et al.*,1986) thiol (Weiber *et al.,* 1985), dithiophosphate, xanthate (Gupta *et al.,* 1985), etc. are well documented in literature.

It is also worth mentioning that reports on the synthesis and reactivity of organoantimony(III) amides based on hydrocarbon based, ligands *viz*. $Ar_nSb(NR_2)_{3-n}$ and corresponding derivatives of antimony bearing pentafluorophenyl or trifluoromethyl groups have been reported to a limited extent. Pentafluoro group based derivatives are hydrolytically stable but found susceptible to Br_2 and CH_3COOH preferably at Sb-N bond compared to Sb-C bond. Strong dipole like PhNCS and PhNCO were found to add across Sb-N bond. (Premraj *et al.*,1985). Preliminary biological studies on such compounds suggested them to be with significant antimicrobial activity (Yadav, 2013). Presence of pentafluorophenyl group not only enhances the water and lipid solubility but also its reactivity towards MF-7 cancer cell line (Yadav, 2012). Such studies are restricted to simple $(C_6F_5)_nSbX_{3-n}$. The present investigation relates to the synthesis of (R_f) Sb $(NR_2)_2$ compounds where

$R_f = C_6F_5$ and NR_2 = -



$-N(CH)NCHCH, -N(CH)NC_6H_4, -N(CCH_3)NCHCH, -NCH_2COCH_2CO, -NCOC_6H_4CO$

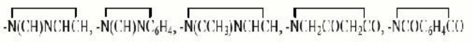
have been isolated for the first time.

Results and Discussion

Under anhydrous oxygen free conditions, pentafluorophenylantimony (III) diamides can readily be synthesised by metathetical reaction of corresponding (pentafluorophenyl)antimony(III) dichloride with an amide/imide moiety in 1:2 molar ratio in the presence of triethylamine as a hydrogen chloride acceptor.

$$R_fSbCl_2 + 2HL \xrightarrow{Et_3N / C_6H_6} R_fSbL_2 + 2Et_3N.HCl$$

where [$R_f = C_6F_5$; L =



$-N(CH)NCHCH, -N(CH)NC_6H_4, -N(CCH_3)NCHCH, -NCH_2COCH_2CO, -NCOC_6H_4CO$

Alternatively, the complexes could also be obtained by the interaction of (pentafluorophenyl) antimony(III) dichloride with corresponding sodium or silver salt of the ligand in an appropriate ratio in benzene / methanol.

$$R_fSbCl_2 + 2ML \xrightarrow{MeOH / C_6H_6} R_fSbL_2 + 2MCl$$

where [$R_f = C_6F_5$; L =

$-N(CH)NCHCH, -N(CH)NC_6H_4, -N(CCH_3)NCHCH, -NCH_2COCH_2CO, -NCOC_6H_4CO$

;M = Na, Ag]

All the reactions were found to proceed under mild conditions. Unlike phenylaminostibines. $Ph_n(NEt_2)_{3-n}$ which are obtained as liquid the newly synthesised pentafluorophenylantimony (III) diamides. $(R_f)Sb(NR_2)_2$ are solids with sharp melting points which are generally on higher sides. The complexes were found to be monomeric, the molar conductance of 10^{-3} M solution in acetonitrile ranges between 12-22 ohm^{-1} mol^{-1} at 30°C which shows that the absence of ionic species in solution.

The complexes are reasonably stable towards air and moisture and the melting point of compound **(1)** did not change even after stirring (1h) with water at room temperature.

Cleavage reaction of pentafluorophenyl antimony(III) diamide derivatives $(R_f)Sb(NR_2)_2$.

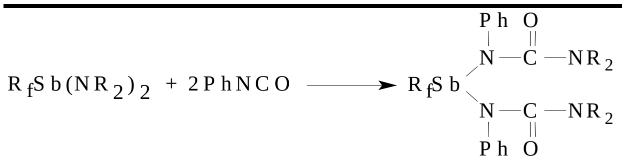
The antimony-nitrogen bond in $(R_f)Sb(NR_2)_2$ was cleaved in preference to the Sb-R_f bond by bromine and acetic acid to give the corresponding bromides.

$$R_fSb(NR_2)_2 + 2Br_2 \longrightarrow R_fSbBr_2 + 2BrNR_2$$

Attempts to prepare $R_fSb(OCOCH_3)_2$ by the cleavage of the Sb-N bond were unsuccessful. This was in conformity with the earlier observation of Hall *et al.* regarding the instability of phenylantimony (III) acetate (Hall *et al.* 1986).

Insertion reaction

It has been reported (Premraj *et al.*1989[b]) that CS_2 readily adds across the Sb-N bonds in $Sb(NMe_2)_3$ to give $Sb(SCSNME_2)_3$. However $R_fSb(NR_2)_2$ failed to react with an excess of CS_2 even after prolonged refluxing. On the other hand, PhNCO added to the Sb-N bonds as shown below.



The formation of the PhNCO adduct was confirmed by the absence of the νNCO band around 2200 cm^{-1} and the appearance of a new medium intensity ν(C=O) band at 1700 cm^{-1}. A medium band at 1600 cm^{-1} may be assigned to ν(C-N). The failure of CS_2 to react with $(R_f)Sb(NR_2)_2$ may partly be attributed to the weak dipole nature of the former, coupled with the presence of the electron withdrawing nature of the pentafluorophenyl group bonded to antimony amide. Reactions of CS_2, RNCS and RNCO with organometal nitrogen compounds have been previously reported to proceed in the same fashion (Premraj *et al.,* 1984, Premraj *et al.,* 1989 and Singhal, 1993).

Infrared spectra

Infrared absorptions inherent to pentafluorophenyl groups appear almost at identical positions due to C_6F_5 group. The pattern position and intensity of these bands do not differ significantly than those reported earlier for $C_6F_5SbCl_2$ derivatives and hence not discussed here (Premraj *et al.*, 1989[a]).

The characteristics IR absorption together with their assignments are given in table 3. Absorption frequencies in amido derivatives, bearing carboxyl group have been assigned as ν_{assy} (CO) and ν_{sym}(CO). The appearance of a strong band ranging between 1720-1770 cm^{-1}, which is clearly suggest that the presence of a 'ester' type CO group.

ν(Sb-C) frequency corresponding to 'y' mode was observed in the range from 445-470 cm^{-1} (Wardell, 1982), ν(Sb-N) band cannot be assigned with certainty due to complex nature of the spectra owing to the presence of absorptions associated with ligands and the pentafluorophenyl group.

^{1}H and ^{19}F NMR Spectra

The ^{1}H NMR spectra of compound $(C_6F_5)Sb(-\overline{NCOCH_2CH_2CO})_2$ **(4)** in $CDCl_3$ at room temperature showed a singlet at δ2.60 ppm (due to -CH_2-CH_2- group). The ^{19}F NMR spectrum was recorded on a Jeol FX 90Q. FT NMR spectrometer at δ 4.26 MHz. The amide derivative was dissolved in 99.8% pure $CDCl_3$. The tri fluoroacetic acid (δ-76.5 ppm) was taken as reference. The characteristic signals of $F_{2,6}$, $F_{3,5}$ and F_4 were observed at δ-122.08,–152.06 and –144.38 ppm respectively. The peak of F_4 was easily recognized due to half intensity compared to $F_{2,6}$ and $F_{3,5}$ peaks. The F_4 signals appeared as triplet of triplet due to spin-spin coupling with $F_{3,5}$.

Similarly, phthalimido derivative $(C_6F_5)Sb(-\overline{NCOC_6H_4CO})_2$ **(5)** showed a complex multiplet centered at δ7.56 ppm due to aromatic protons (8H**).**

The ^{19}F spectra of compound **(4)** showed the characteristic signals due to F_4, $F_{3,5}$ and $F_{2,6}$ appeared at δ-146.08, –152.05 and –122.38 ppm respectively.

On the basis of IR, ^{1}H and ^{19}F NMR spectra and conductance measurements. The newly synthesized amido derivative could be assigned a monomeric non-ionic pyramidal structure.

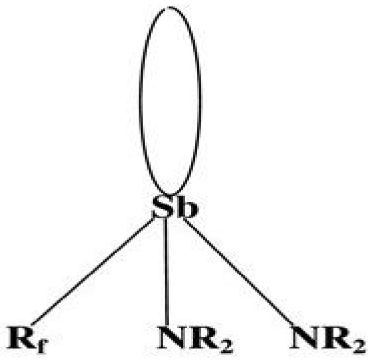


Fig: Suggested structure of $R_fSb(NR_2)_2$.
$R_f = C_6F_5$ and NR_2 =

$-\overline{N(CH)NCHCH}$, $-\overline{N(CH)NC_6H_4}$, $-\overline{N(CCH_3)NCHCH}$, $-\overline{NCH_2COCH_2CO}$, $-\overline{NCOC_6H_4CO}$

Experimental

Arylantimony (III) dichloride, $(ArSbCl_2)$ was prepared by the addition of antimony trichloride to triphenylantimony. Pentafluorophenylantimony(III) dichloride, $C_6F_5SbCl_2$ was prepared by the redistribution reaction of tris(pentafluorophenyl)antimony and antimony trichloride combined in the approximate stoichiometry ratio. The amides/imide moities were procured commercially or prepared by the standard techniques and were purified by crystallization. Conductivity data were obtained in acetonitrile with the aid of Philips magic eye conductivity bridge using a dip type conductivity cell special precautions were taken to exclude moisture all manipulations were done in atmosphere of nitrogen. The melting points of the compounds were determined on the electrically operated melting point apparatus (M/s Toshniwal and Bros, Mumbai India). The stoichiometry of the compounds was established by elemental analysis. Percentage of C, H and N of the compounds was obtained on a semi-microscale (using elemental analyzer Carlo Eaba 1106, Thomas CH and Coleman analyzer. Typical representative experiments are described below, the analytical data, IR assignments and NMR spectra are summarized in tables 1- 4.

Reaction of Pentafluorophenylantimony(III) Dichloride with Imidazole (1)

To a stirring solution of pentafluorophenylantimony (III) dichloride (0.360 g, 1 mmol) in benzene (~25 ml) a solution of imidazole (0.136 g, 2 mmol) in the same solvent (~25 ml) was added drop wise. The contents were stirred together in the presence of triethylamine (~1 ml) at room temperature for 6 h. $Et_3N.HCl$ (m.p. 240^od) thus formed was filtered off. The filtrate on concentration in *vacuo* yielded a crystalline solid and was recrystallised from petroleum ether (40^o-60^oC) to afford pentafluorophenylantimony (III) dimidazole. M.P.: 110°C, Yield: 0.324 g (62%).

Reaction of Pentafluorophenylantimony(III) Dichloride with Sodium Salt of Phthalimide (5)

A solution of pentafluorophenylantimony (III)dichloride (0.360 g, 1 mmol) in benzene (~25 ml) and sodium salt of phthalimide (0.336 g, 2 mmol) in methanol (~ 25 ml) was refluxed for 2h under anhydrous conditions. NaCl thus formed was filtered off. The filtrate an concentration in *vacuo* afforded a crystalline solid which was recrystallised from petroleum-ether (40^o-60^oC) to afford pentafluorophenylantimony(III) diphthalimide. M.P.: 98°C, Yield: 0.421 g (70%).

Reaction of Pentafluorophenylantimony(III) Disuccinimide with Bromine

To a solution of pentafluorophenylantimony(III) disuccinimide (0.485g, 1 mmol) in CCl_4 (20 ml), bromine (2 mmol) in the same solvent (5 ml) was slowly added at -5^oC over 30 min in a N_2 atmosphere. Initially, the colour of bromine disappeared readily after each addition, but at the end light brown colour persisted.

The mixture was allowed to warm to room temperature and then freed from volatiles in *vacuo*. Attempts to separate the mixture were unsuccessful. However, the IR spectrum of the residue and TLC in benzene showed the presence of both pentafluorophenylantimony(III) bromide and succinimide moiety.

Reaction of Pentafluorophenylantimony(III) Diphthalimide with PhNCO

A mixture containing 1:2 molar amounts of pentafluorophenylantimony(III) diphthalimide (0.581 g, 1mmol) and phenylisocyanate (0.119 g, 2 mmol) was refluxed for 3h at 170^o in a nitrogen atmosphere. The resulting brown liquid was treated with diethyl-ether to afford light brown crystals of PhNCO adducts. M.P.: 175°C, Yield: 0.508 g (62%).

Reaction of Pentafluorophenylantimony(III) Diphthalimide with S = C = S

Pentafluorophenylantimony (III) diphthalimide (0581 g, 1 mmol) was refluxed with excess of carbondisulphide (~125 ml) for 3h under nitrogen atmosphere. After removal of volatiles in *vacuo* residue showed no change in the melting point and IR spectra as compared to the parent compound.

Table 1. Preparation and properties of pentafluorophenylantimony(III) Diamides

C. No.	Complex $(R_f)Sb(NR_2)_2$	Ligand (g)	Recrystallization solvent	Molar Ratio	M.P. (^oC)	Colour
	$R_f = C_6F_5$					
1.	$R_fSb(-\overline{N(CH)NCHC}H)_2.$	$H\overline{N(CH)NCHC}H$ (0.136)	Petroleum ether (40-60^{o}C)	1:2	110	Pale yellow
2	$R_fSb(-\overline{N(CH)NC}_6H_4)_2$	$Ag\overline{N(CH)NC}_6H_4$ (0.450)	Petroleum ether (40-60^{o}C)	1:2	80	Pale yellow
3.	$R_fSb(-\overline{N(CCH_3)NCHC}H)_2$	$H\overline{N(CCH_3)NCHC}H$ (0.164)	Petroleum ether (40-60^{o}C)	1:2	120	Off white
4.	$R_fSb(-\overline{NCH_2COCH_2C}O)_2$	$Na\overline{NCH_2COCH_2C}O$ (0.242)	Petroleum ether (40-60^{o}C)	1:2	93-94	White
5.	$R_fSb(-\overline{NCOC_6H_4C}O)_2$	$H\overline{NCOC_6H_4C}O$ (0.336)	Petroleum ether (40-60^{o}C)	1:2	98	White

Table 2. Elemental analysis of Pentafluorophenylantimony(III) Diamides

C. No.	Complex $(R_f)Sb(NR_2)_2$	Empirical formula	Found (Calcd) %		
			C	H	N
	$R_f = C_6F_5$				
1.	$R_fSb(-\overline{N(CH)NCHC}H)_2.$	$C_{12}H_6F_5N_4Sb$	32.06 (34.06)	1.02 (1.42)	11.25 (13.25)
2.	$R_fSb(-\overline{N(CH)NC}_6H_4)_2$	$C_{20}H_{10}F_5N_4Sb$	44.91 (45.91)	1.00 (1.91)	9.71 (10.71)
3.	$R_fSb(-\overline{N(CCH_3)NCHC}H)_2$	$C_{14}H_{10}F_5N_4Sb$	36.27 (37.27)	1.22 (2.22)	11.42 (12.42)
4.	$R_fSb(-\overline{NCH_2COCH_2C}O)_2$	$C_{14}H_8F_5N_2O_4Sb$	33.66 (34.66)	1.00 (1.65)	4.78 (5.78)
5.	$R_fSb(-\overline{NCOC_6H_4C}O)_2$	$C_{22}H_8F_5N_2O_4Sb$	43.46 (45.46)	0.95 (1.38)	3.82 (4.82)

Table 3. Important IR data of pentafluorophenyl antimony(III) Diamides

C. No.	IR (cm^{-1}) ¬$_{asym}$	¬$_{sym}$	
1.	1720	1304	
2.	1720	1312	
3.	–	–	
4.	–	–	
5.	1740	1331	

Table 4. Molar conductance and yield of pentafluorophenylantimony(III) Diamides

Compound No.	Molar conductance data of 10^{-3} M in acetonitrile (Ohm^{-1} cm^{2} mol^{-1})	Yield	
		(g)	(%)
1.	16.22	0.324	62
2.	15.21	0.405	64
3.	17.23	0.322	60
4.	20.10	0.321	58
5.	19.18	0.421	70

Reaction of Pentafluorophenylantimony(III) Diimidazole with Water

A mixture containing pentafluorophenylantimony (III) diimidazole (0.423g, 1 mmol) and excess of water were refluxed for 3h. After removal of the solvent, the residue showed no change in the melting point and IR spectra.

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