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Synthesis and Characterization of Unsymmetrical Tetraarylstibonium Amides, Oximates and Carboxylates

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Several hitherto unreported pentacoordinated unsymmetrical amide, oximate and carboxylate complexes of the general formula $R_3R'SbL$ ($R = R' = C_6H_5$, C_6F_5, C_2H_5 and C_8H_{17}) [$L = —NR_2'' = \overline{NCO(CH)_2CO}$, $—\overline{NCOC_6H_4CO}$, $—\overline{NNNC_6H_4}$, $—\overline{NC_6H_8C_6H_4}$, $—\overline{NCHCNC_6H_4}$, $—\overline{NCOC_6H_4SO_2}$, $L = —ONCR^1R^2$ (R^1, R^2 = Me, Me; Me, Ph; Ph, Ph; $(CH_2)_4CH_2$); $L = —OOCR'''$, $R''' = p\text{-}NH_2C_6H_4$, $p\text{-}ClC_6H_4$, $p\text{-}NO_2C_6H_4$, $m\text{-}NO_2C_6H_4$] have been isolated and characterized by elemental analysis solid state infrared spectra, conductivity and molecular weight measurements. These complexes remain unaffected in the presence of water, methanol and carbon disulfide. However (Sb—O) and (Sb—N) bonds are cleaved in preference to (Sb—Ar) bond(s) by bromine and tellurium(IV) chloride. A few compounds were tested for and found to exhibit moderate to significant biological activity.

Key Words: Unsymmetrical tetrarylstibonium amides, Oximates, Carboxylates, IR, NMR, Conductance, Biological activity.

INTRODUCTION

There has been a considerable volume of research content around the synthesis and bonding of organic derivatives of antimony(III) and antimony(V) in the past three decades. As a result of this variety of compounds including halides, pseudohalides, alkoxides, carboxylates, amides and oximates etc. have been prepared and their physico-chemical properties have been studied. Apart from developing synthetic routes for such compounds they have been studied from their structural and biological points of view.

A few primary screening studies[1–5] on the biological activity organoantimony(V) compounds of the type R_nSbX_{5-n} ($n = 2, 3, 4$) have revealed many compounds active against infections by trypanosomal and leishmanial organisms especially where those organisms resist arsenicals. Organoantimony iminodiacetates can be used as insecticides[6]. Pyrimidine derivatives of phenyl antimony also show antifungal activity[7]. Recently, Burrell investigated fungitoxicity of organoantimony compounds[8].

Reports on biological activity of organoantimony compounds have stated that most of them are toxic when injected in patients, but do not have any reputation

as potential hazards to those preparing them and tested by the pharmaceutical industry as potential drugs[5].

Structure-reactivity relationships have indicated that the nature of the organic group (R = alkyl or aryl) or anions plays an important role while determining their activity. Moreover, from the structural point of view significant changes in bonding and streochemistry have been observed on changing the nature and contents of organic groups bonded to antimony.

In sharp contrast to the well documented symmetrical onium salts of antimony(V), R_4SbX (R = Me, Ph; X = electron withdrawing group), synthetic routes to the corresponding unsymmetrical tetraaryl antimony(V) compounds, $R_3R'SbX$, have not attracted much attention. In view of these observations, we have prepared a series of hitherto unreported unsymmetrical tetraorganoantimony(V) amides, -oximates and -carboxylates ($R_2R'SbX$) reported herein.

EXPERIMENTAL

Unsymmetrical tetraorganostibonium bromide $(R_f)_3R'Sb$ and $R_fR'_3Sb$ ($R_f = C_6F_5$, $R' = C_6H_5$) were prepared by the reported method[9] and the melting points and superimposable IR spectra were reported. Organic moieties, oximes, carboxylic acids and amides were used without further purification. Molecular weights were determined cryoscopically in benezene, conductances were recorded in acetonitrile, methanol and nitrobenzene using a direct reading conductivity meter type 303, SR No. 038 (Systronics). Infrared spectra in the region 4000–400 cm^{-1} were recorded in KBr on a Perkin-Elmer 577 spectrophotometer.

Stringent precautions were taken to avoid moisture. Solvents were distilled and dried before use.

Representative experiments are given below. Further details are given in Table-1.

TABLE-1
ANALYTICAL DATA OF UNSYMMETRICAL TETRAORGANOSTIBONIUM AMIDES, OXIMATES AND CARBOXYLATES

S.No.	Compounds	m.p. (°C)	Yield (%)	Analysis %, Found (Calcd.)		
				C	H	N
NR_2 (Amides)						
1.	$Ph_3(C_6F_5)Sb—\overline{NCOC_6H_4CO}$	128	70	57.61 (57.58)	2.80 (2.85)	2.05 (2.10)
2.	$Ph_3(C_6F_5)Sb—\overline{NCO(CH_2)_2CO}$	180	80	54.35 (54.89)	3.00 (3.07)	2.21 (2.26)
3.	$Ph_3(C_6F_5)Sb—\overline{NCOC_6H_4CO_2}$	122	75	52.06 (53.01)	2.65 (3.70)	1.94 (1.99)
4.	$Ph_3(C_6F_5)Sb—NCHNC_6H_4$	110	60	58.38 (58.42)	3.10 (3.14)	4.34 (4.39)
5.	$Ph_3(C_6F_5)Sb—\overline{NHC_6H_4}$	124	68	48.08 (44.02)	1.06 (1.10)	5.09 (5.73)

S.No.	Compounds	m.p. (°C)	Yield (%)	Analysis %, Found (Calcd.) C	H	N
6.	$(C_6F_5)_3C_2H_5Sb—\overline{NCOC_6H_4CO}$	164	59	45.34 (45.40)	1.00 (1.05)	1.60 (1.65)
7.	$(C_6F_5)_3C_2H_5Sb—\overline{NCOC_6H_4SO_2}$	188	60	42.15 (42.19)	1.00 (1.02)	1.53 (1.58)
8.	$(C_6F_5)_3C_2H_5Sb—\overline{NCHNC_6H_4}$	174	65	45.50 (45.00)	1.18 (1.22)	3.37 (3.42)
9.	$(C_6F_5)_3(C_2H_5)Sb—\overline{NNNC_6H_4}$	126	69	40.48 (40.53)	1.11 (1.16)	5.40 (5.45)
10.	$(C_6F_5)_3(C_2H_5)Sb—\overline{NCOC_6H_4CO}$	128	65	42.08 (42.12)	1.07 (1.12)	1.70 (1.75)
11.	$(C_6F_5)_3(C_2H_5)Sb—\overline{NCOC_6H_4SO_2}$	136	59	38.80 (38.86)	1.02 (1.07)	1.62 (1.67)
12.	$(C_6F_5)_3(C_2H_5)Sb—\overline{NC_6H_8C_6H_4}$	198	53	48.61 (49.67)	1.90 (1.95)	1.55 (1.60)
ONCR′R″ (Oximates)						
13.	$(C_6F_5)_3C_6H_5Sb—ONC(Me)Me$	116	59	41.92 (41.98)	1.40 (1.42)	1.75 (1.81)
14.	$(C_6F_5)_3C_6H_5Sb—ONC(Me)Ph$	132	62	46.00 (46.05)	1.50 (1.55)	1.60 (1.67)
15.	$(C_6F_5)_3C_6H_5Sb—ONC(Ph)Ph$	195	60	49.50 (49.57)	1.61 (1.67)	1.50 (1.56)
16.	$(C_6F_5)_3C_6H_5Sb—ONC(CH_2)_5$	88	58	44.30 (44.35)	1.80 (1.84)	1.68 (1.72)
17.	$(C_6F_5)_3Ph_3SbONC(Me)Me$	108	96	54.70 (54.75)	3.50 (3.54)	2.30 (2.35)
18.	$(C_6F_5)_3Ph_3SbONC(Ph)Ph$	222	70	62.00 (62.03)	3.45 (3.49)	1.90 (1.95)
19.	$(C_6F_5)Ph_3SbONC(Me)Ph$	146	68	58.70 (58.74)	3.45 (3.51)	2.10 (2.14)
20.	$(C_6F_5)Ph_3SbONC(CH_2)_5$	111	68	56.92 (56.98)	3.90 (3.95)	2.16 (2.21)
21.	$(C_6F_5)_3C_2H_5SbONC(Me)Me$	101	59	38.09 (38.13)	1.45 (1.51)	1.87 (1.93)
22.	$(C_6F_5)_3C_2H_5SbONC(Ph)Ph$	230	72	46.65 (46.71)	1.70 (1.74)	1.60 (1.65)
23.	$(C_6F_5)_3C_2H_5SbONC(Et)Ph$	165	70	43.43 (43.51)	1.82 (1.87)	1.70 (1.75)
24.	$(C_6F_5)_3EtSbONC(CH_2)_5$	124	68	40.80 (40.85)	1.90 (1.96)	1.78 (1.83)
25.	$(C_6F_5)_3OctSbONC(Et)Ph$	Viscous mass	–	47.48 (47.52)	3.00 (3.05)	1.51 (1.58)
26.	$(C_6F_5)_3OctSbONC(Ph)Ph$	142	58	50.20 (50.23)	2.82 (2.89)	1.44 (1.50)

S.No.	Compounds	m.p. (°C)	Yield (%)	Analysis %, Found (Calcd.) C	H	N
27.	$(C_6F_5)_3OctSbONC(Me)Ph$	Viscous mass	–	46.82 (46.91)	2.82 (2.87)	1.58 (1.60)
28.	$(C_6F_5)_3OctSbONC(CH_2)_5$	128	59	45.22 (45.29)	3.12 (3.18)	1.60 (1.65)
29.	$(p\text{-}CH_3C_6H_4)_3(C_6F_5)SbONC(Ph)Ph$	130	60	63.29 (63.34)	4.02 (4.09)	1.80 (1.84)
OOCR″ (Carboxylates)						
30.	$(C_6F_5)_3PhSbOOCC_6H_4Cl\text{-}p$	164	68	43.41 (43.47)	1.00 (1.05)	–
31.	$(C_6F_5)_3PhSbOOCC_6H_4NH_2\text{-}p$	120	70	44.45 (44.51)	1.20 (1.31)	1.62 (1.67)
32.	$(C_6F_5)_3PhSbOOCC_6H_4NO_2\text{-}p$	124	72	42.92 (42.97)	1.00 (1.03)	1.57 (1.61)
33.	$(C_6F_5)_3PhSbOOCCH_2C_6H_5$	135	65	45.95 (46.00)	1.40 (1.43)	–
34.	$Ph_3(C_6F_5)SbOOCC_6H_4Cl\text{-}p$	108	58	55.02 (55.09)	2.75 (2.81)	–
35.	$Ph_3(C_6F_5)SbOOCC_6NH_2\text{-}p$	144	57	56.70 (56.73)	3.16 (3.20)	2.10 (2.13)
36.	$Ph_3(C_6F_5)SbOOCC_6H_4NO_2\text{-}p$	155	61	54.20 (54.25)	2.70 (2.77)	2.00 (2.04)
37.	$Ph_3(C_6F_5)SbOOCC_6H_4NO_2\text{-}m$	167	65	54.20 (54.25)	2.72 (2.77)	1.80 (2.04)
38.	$(C_6F_5)_3EtSbOOCC_6H_4Cl\text{-}p$	152	59	40.08 (40.13)	1.07 (1.11)	–
39.	$(C_6F_5)_3EtSbOOCC_6H_4NH_2\text{-}p$	110	62	41.00 (41.13)	1.35 (1.39)	1.71 (1.77)
40.	$(C_6F_5)_3EtSbOOCC_6H_4NO_2\text{-}p$	108	65	39.57 (39.62)	1.06 (1.10)	1.65 (1.71)
41.	$(C_6F_5)_3EtSbOOCCH_2C_6H_5$	162	68	42.65 (42.71)	1.47 (1.52)	–

Reaction of $(C_6H_5)_3(C_6F_5)SbBr$ with succinimide: In a typical reaction triphenyl (pentafluorophenyl) antimony bromide (0.599 g, 1 mmol), succinimide (0.199 g, 1 mmol) and Et_3N (1 mL) were stirred together in benzene (50 mL) at room temperature for 3 h. The reaction mixture was refluxed for 1h more to ensure completion of the reaction. $Et_3N{\cdot}HBr$ (m.p. 248°C) was filtered off. The filtrate on concentration *in vacuo* afforded a white crystalline solid which was recrystallized from acetonitrile/pet-ether (40–60°C) to afford triphenyl (pentafluorophenyl) antimony succinimide (m.p. = 180°C, yield = 80%).

Reaction of $(C_6H_5)_3(C_6F_5)SbBr$ with methyl phenyl ketoxime: Triphenyl (pentafluorophenyl) antimony bromide (0.599 g, 1 mmol) and methylphenyl ketoxime (0.135 g, 1 mmol) and Et_3N (1 mL) were stirred together in benzene (50 mL) at room temperature for 2 h. The reaction mixture was refluxed for 1 h

to ensure completion of the reaction. $Et_3N{\cdot}HBr$ (m.p. 248°C) was filtered off. The filtrate on concentration *in vacuo* afforded a white crystalline solid which was recrystallized from acetonitrile/pentane mixture to afford triphenyl (pentafluorophenyl) antimony methylphenyl ketoxime (m.p. = 146°C, yield = 60%).

Reaction of $(C_6H_5)_3(C_6F_5)SbBr$ with sodium salt of *p*-NO_2-benzoic acid: Tris(pentafluorophenyl) phenyl antimony bromide (0.779 g, 1 mmol) and sodium salt of *p*-nitrobenzoic acid (0.189 g, 1 mmol) were stirred together for 4 h in benzene (50 mL) and NaBr was filtered off. The filtrate was concentrated at reduced pressure followed by addition of pet-ether (40–60°C) to yield a white crystalline compound, tris(pentafluorophenyl) phenyl antimony *p*-nitrobenzoic acid (m.p. = 124°C, yield = 72%).

RESULTS AND DISCUSSION

Amine hydrochloride or salt elimination reaction has been conventionally employed to accomplish the synthesis of the new onium complexes. Thus tetraorganostibonium amides, oximates and carboxylates may be prepared by the equimolar reaction of $R_3R'SbBr$ with an amide, oxime and carboxylic acid in presence of triethylamine as hydrogen halide acceptor or by a metathetical reaction of $R_3R'SbBr$ with the corresponding sodium salt of the ligand (Eq. 1 and 2).

$$R_3R'SbBr + NaL \xrightarrow{\text{Benzene}} R_3R'SbL + NaBr \quad (1)$$

$$R_3R'SbBr + HL \xrightarrow{Et_3N} R_3R'SbL + Et_3N{\cdot}HBr \quad (2)$$

$R' = C_6H_5$, C_6F_5, C_2F_5 and C_8H_{17}

L = —NR''_2, $\overline{NCO(CH)_2CO}$, —$\overline{NCOC_6H_4CO}$,

—$\overline{NNNC_6H_4}$, —$\overline{NC_6H_8C_6H_4}$, —$\overline{NCHCNC_6H_4}$, —$\overline{NCOC_6H_4SO_2}$

L = —$ONCR^1R^2$; [R^1R^2 = Me, Me; Me, Ph; Ph, Ph; $(CH_2)_4CH_2$—]

L = —$OOCR'''$; $R''' = p$-$NH_2C_6H_4$, p-ClC_6H_4, p-$NO_2C_6H_4$, m-$NO_2C_6H_4$]

All the reactions proceed smoothly to give the near quantitative yield of the products except oximes at room temperature. Physical and chemical data are presented in Table-3.

The newly formed compounds are off-white or pale yellow crystalline solids with sharp melting points and are moderately soluble in common organic solvents. The complexes are stable towards air and moisture. The melting points of the compounds do not change even often stirring with water at room temperature.

The molecular weight data in freezing benzene indicates that these amides oximates and carboxylates have molecular monomeric constitution. The molar conductance values of 10^{-3} M solutions of all the three type of complexes at room temperature (30°C) are in the range between 15–30 and 166 ohm^{-1} mol^{-1} cm^2 in

acetonitride and nitrobenzene respectively which shows the absence of ionic species in solutions (Table-2).

TABLE-2
MOLAR CONDUCTIVITY DATA OF TETRAORGANOSTIBONIUM AMIDES, OXIMATES AND CARBOXYLATES

Compd.	Molar conductance of 10^{-3} M solution (ohm^{-1} cm^{-2} mol^{-1})	
	Acetonitrile	Nitrobenzene
1	20.33	4.80
2	22.24	3.20
3	25.66	3.12
4	28.64	4.60
12	30.69	4.36
21	12.56	4.00
26	19.55	3.20
28	13.90	2.12
29	21.32	5.01
37	24.54	6.00
39	26.44	5.82
40	28.32	6.20

Infrared Spectra: The infrared spectra of all the newly synthesized unsymmetrical tetraorganostibonium compounds exhibit absorption bonds due to aryl or alkyl group and do not differ significantly from the literature values[10]. The characteristic frequencies of diagnostic values and their possible assignments for representative complexes are listed in Table-3. As expected the oximate derivatives do not display a weak broad band in the region 3400–3000 cm^{-1} assignable to the intramolecularly hydrogen bonded OH in free oxime[11]. Compound to free oximes ν(C═N) vibrations are considerably lowered and are observed in the 1650–1550 cm^{-1} region[12]. The lowering of ν(C═N) may be attributed to stablization of CN bond by resonance with non-bonding electron pair on the oxygen atom of the imino group. However, this type of lowering may be related to the mass effect as has been reported earlier in the case of group IV elements[13].

The (N—O) stretching vibration of medium to strong intensity appear at 930–915 cm^{-1}, while (Sb—O) stretching is tentatively assigned at[14] 510–470 cm^{-1}.

The solid state infrared spectra of unsymmetrical tetraorganostibonium carboxylates $R_3R'SbOOCR$ exhibit ν_{asym}(COO) and ν_{sym}(COO) at *ca.* 1640 cm^{-1} at 1345–1320 cm^{-1} respectively as strong band and suggest the presence of a

monodentate ester like COO^- group with a pentacoordinated antimony atom. The nonconducting nature of these derivatives and the absence of evidence for carboxylate ions in the IR spectra further rules out the possibility of an ionic structure.

Absorption frequencies due to carbonyl group symmetric as well as asymmetric in amido derivatives are given in Table-3. The ureido derivatives show the presence of a strong band in the region 1750–1700 cm^{-1} indicating the ester type CO group(s).

TABLE-3
KEY IR BANDS (cm^{-1}) OF UNSYMMETRICAL TETRAORGANOSTIBONIUM AMIDES, OXIMATES AND CARBOXYLATES

Compd.	ν(CO)/ν(CN)/ν(COO)		ν(N—O)	ν(Sb—O)
	asym	sym		
1	1710 s	–	–	–
2	1720 s	–	–	–
3	1725 s	–	–	–
6	1740 s	–	–	–
10	1750 s	–	–	–
11	1700 s	–	–	–
13	1615 m	–	915 m	472 w
14	1620 m	–	920 m	492 w
15	1630 m	–	930 m	480 w
21	1625 m	–	925 m	508 w
22	1520 m	–	920 m	485 w
26	1580 m	–	930 m	478 w
30	1646 s	1320 ms	–	475 w
31	1635 s	1318 ms	–	482 w
32	1638 s	1345 ms	–	495 w
34	1642 m	1330 ms	–	476 w
36	1648 s	1332 ms	–	488 w
38	1638 s	1338 ms	–	480 w
40	1639 s	1320 ms	–	492 w

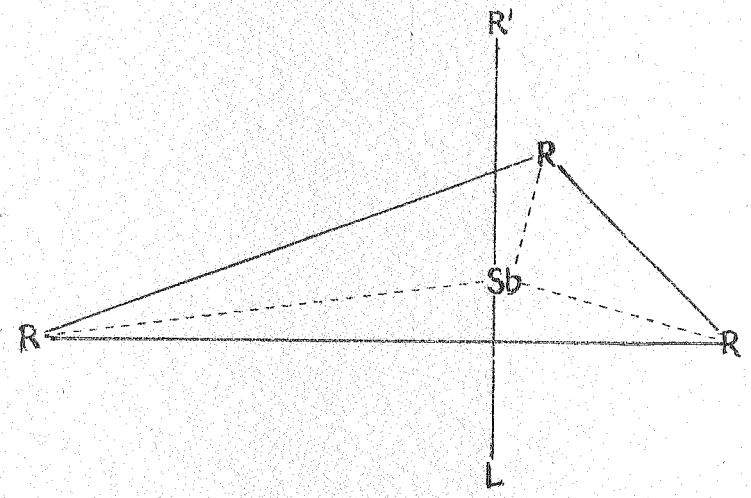
No definite assignment could be made for (Sb—C) stretching vibration due to the presence of phenyl absorption bands in the same region. However, tentatively they are assigned between 470–445 cm^{-1} as medium bands.

^{1}H NMR spectra: The NMR spectra of $(C_6F_5)_3PhSbONC(Me)_2$ in $CDCl_3$ at room temperature showed multiplets centered at δ 7.20 ppm due to phenyl proton and a singlet at δ 2.40 ppm (due to Me 611). Similarly, NMR spectra of (*p*-$CH_3C_6H_4)_3(C_6F_5)Sb(ONC(Ph)Ph)$ displayed two multiplets centered at δ 7.20 and

δ 8.10 due to phenyl protons and a singlet due to CH_3 proton at δ 2.25. This feature of NMR spectra is similar to that of $(p\text{-}MeC_6H_4)_4Sb$—OMe which has been reported by Shen *et al.* to show a single peak of *p*-methyl protons even at 60°C arising due to the equilibrium mixture of trigonal bipyramidal (TBP) and square pyramidal (SP) conformation or to the exclusive presence of later conformation in solution.

However, X-ray diffraction data for Ph_4SbOMe indicate a trigonal bypyramidal (TBP) structure and the same has been observed in case of other R_4SbX salts (X = Cl, Br, NCS, OMe and OH) in solid state using vibrational data.

Thus on the basis of monomeric and non-conducting nature of unsymmetrical tetraorganostibonium compounds and the absence of bridging CO group(s) from IR spectra in case of ureido and carboxylate derivatives, tetraorganostibonium amides oximales and carboxylates are assigned pentacoordinated trigonal bipyramidal structure in solid state in accordance with symmetrical tetraarylstibonium salts.



L = —ONCR^{1}R^2, —NR$''_2$, —OOCR'''; R = C_6H_5; R' = C_6H_5

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