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Synthesis and Spectroscopic Studies of Trialkyl Bis(iminoxy)stibines

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Monomeric trialkyl bis(iminoxy)stibines, $R_3Sb(ONCR'R'')_2$ *[R = Me and R', R'' = Me, Me; Me, Et; Me, Pr; Me, Ph; Et, Et;* NH_2*, Ph. R = Et and R', R'' = Me, Me; Me, Et; Me, Ph], have been synthesized by the reactions of trialkylstibine dibromides with sodium oximates. On the basis of spectroscopic studies, a trigonal bipyramidal geometry has been suggested for all these derivatives, except* $Me_3Sb(ONCNH_2Ph)_2$ *which appears to become hexacoordinated in the solid state.*

Introduction

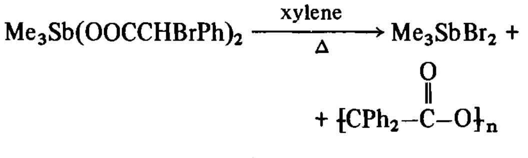
Recently a number of triorganoantimony(V) compounds have been reported [1–5] in which antimony atom has a choice between penta-[1, 5] and hexa-[2–4] coordination. From the studies on the thermal behaviour of some penta-coordinated antimony compounds, interesting results have been observed, *e.g.*,

$$R_3SbX_2 \xrightarrow{\Delta} R_2SbX + RX \qquad [6]$$

$$R_3Sb(OR')_2 \xrightarrow{\Delta} \text{Volatile}$$

(R = alkyl or aryl group, X = halogen, R' = alkyl group)

$$Ph_3Sb(OAc)_2 \xrightarrow{\Delta} Ph_3Sb + AcOH \qquad [7]$$



$$Me_3Sb(OOCCHBrPh)_2 \xrightarrow[\Delta]{\text{xylene}} Me_3SbBr_2 + {+}\!\left[CPh_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O\right]_n \qquad [8]$$

$$Ph_3Sb(ONCR'R'')_2 \xrightarrow{\Delta} Ph_3Sb + HONCR'R'' + \text{+ other products} \qquad [5]$$

(R' and R'' = alkyl or phenyl)

In a previous communication from our laboratories, synthesis and structural studies of triphenyl bis(iminoxy)stibines [5] have been reported. Pyrolysis of these derivatives under reduced pressure yields the oxime and triphenylantimony. In order to throw more light on the stereochemistry and thermal behaviour of triorganoantimony(V) compounds, we have now extended this work to the corresponding trialkyl bis(iminoxy)stibines.

Results and Discussion

Trialkyl bis(iminoxy)stibines have been prepared by the reactions of the trialkylstibine dibromides with sodium salts of the oximes in 1:2 molar ratio in refluxing benzene:

$$R_3SbBr_2 + 2NaONCR'R'' \xrightarrow{\text{Benzene}} R_3Sb(ONCR'R'')_2 + 2NaBr$$

(R = Me and R', R'' = Me, Me; Me, Et; Me, Pr; Me, Ph; Et, Et; NH_2, Ph. R = Et and R', R'' = Me, Me; Me, Et; Me, Ph).

These compounds are colourless (to cream coloured) liquids or white solids [Table II] soluble in common organic solvents and susceptible to hydrolysis. Cryoscopic molecular weight determinations of some typical compounds indicate their monomeric nature in benzene. $Me_3Sb(ONCNH_2Ph)_2$ has been purified by recrystallization from benzene while all other derivatives have been purified by distillation in quantitative yields under reduced pressure. For contrast, it is relevant to mention here that the corresponding triphenyl bis(iminoxy)stibines decompose into triphenylstibine and oximes under similar conditions [5] and triorganostibine dihalides yield diorganostibine halides when subjected to distillation [6].

A weak broad band in the region 3000–3380 cm^{-1} (due to the intramolecularly hydrogen bonded OH group in the free oximes [9]) disappears in the IR spectra of these compounds indicating the formation of Sb–O bond. A weak to medium intensity band in the region 1585–1615 cm^{-1} in the spectra of the newly synthesized trialkyl bis(iminoxy)stibines

TABLE I. PMR Spectral Data of Triorgano bis(iminoxy)stibines at Ambient Temperatures.

Compound	Solvent	Chemical Shift δ							
		Me╲C=N–O	Et╲C=N–O		NH_2╲C=N–O	Me–Sb	Et–Sb		Aromatic
			-CH_3	-CH_2			-CH_3	-CH_2	
$Me_3Sb(ONCMe_2)_2$ [a]	CCl_4	2.07, 2.17	–	–	–	1.87	–	–	–
$Et_3Sb(ONCMe_2)_2$ [b]	$CDCl_3$	1.72, 1.76	–	–	–	–	1.27–1.45 (triplet)	2.00–2.26 (tetraplet)	–
$Ph_3Sb(ONCMe_2)_2$ [a]	$CDCl_3$	1.96, 2.25	–	–	–	–	–	–	7.55–8.40
$Me_3Sb(ONCEt_2)_2$ [b]	$CDCl_3$	–	0.89–1.12 (sextet)	2.02–2.38 (octet)	–	1.55	–	–	–
$Ph_3Sb(ONCEt_2)_2$ [a]	$CDCl_3$	–	0.90–1.47 (sextet)	2.06–2.88 (octet)	–	–	–	–	7.46–8.33
$Me_3Sb(ONCMePh)_2$ [a]	CCl_4	2.25	–	–	–	1.82	–	–	7.25–7.80
$Et_3Sb(ONCMePh)_2$ [c]	CCl_4	2.17[d]	–	–	–	–	1.40–1.65 (triplet)	2.17–2.44 (tetraplet)	7.22–7.80
$Ph_3Sb(ONCMePh)_2$ [a]	$CDCl_3$	2.52	–	–	–	–	–	–	7.40–8.38
$Me_3Sb(ONCNH_2Ph)_2$ [c]	$CDCl_3$	–	–	–	4.88	1.75	–	–	7.35–7.84
$Ph_3Sb(ONCNH_2Ph)_2$ [a]	$CDCl_3$	–	–	–	5.05	–	–	–	7.39–8.41

[a] External standard & 60 MHz. [b] Internal standard & 60 MHz. [c] Internal standard & 90 MHz. [d] Me peak merged in -CH_2.

has been assigned to νC = N vibrations [10–12]. In case of νC = N absorption, a lowering of about 45 ± 10 cm^{-1} has been observed compared to the corresponding free oximes. Out of the possible reasons for this lowering [13–18], the most plausible appears to be the mass effect [17, 18].

In the nujol mull IR spectrum of $Me_3Sb(ONCNH_2Ph)_2$, three bands of almost equal intensity have been observed at 3405, 3300 and 3250 cm^{-1}, in the region in which absorptions due to the amino group are generally observed. The vibration due to νC = N appears as a doublet of equal intensity at 1615 and 1600 cm^{-1}. This indicates two types of bonding by benzamidoximate moieties; one of them behaving as unidentate and the other, bidentate. This conclusion is further supported from the appearance of a weak band at 275 cm^{-1}, which may be assigned to νSb–N. However, this band disappears in the IR spectrum of the compound in chloroform solution. Two bands in NH_2 region at 3480 and 3360 cm^{-1}, which are slightly shifted to lower wave numbers as compared to the free ligand, along with only one absorption due to νC = N at 1610 cm^{-1} have been observed in the solution spectrum. Since the band at 275 cm^{-1} does not appear in the spectrum of the free ligand, Me_3SbBr_2 and also in the corresponding triphenyl derivative, $Ph_3Sb(ONCNH_2Ph)_2$, and appears only in the solid state spectrum of $Me_3Sb(ONCNH_2Ph)_2$, it suggests that in solid state, one of the benzamidoxime ligands is coordinated through the nitrogen of the amino group making the central antimony atom hexacoordinate, but in $CHCl_3$ solution the Sb–N bond reptures and both benzamidoxime ligands become unidentate, bringing antimony back in pentacoordinate state. Interestingly in the corresponding triphenylantimony derivative, both the benzamidoxime ligands behave as unidentate moieties even in solid state.

In all these derivatives a very intense band in the region 905–935 cm^{-1} is attributed to N–O stretching mode. The Sb–C asymmetric stretching absorption has been observed in the regions 570–580 and 535–550 cm^{-1} in the spectra of $Me_3Sb(V)$ and $Et_3Sb(V)$ derivatives respectively; this indicates a triangular bipyramidal geometry for these derivatives containing planar $R_3Sb(V)$ moieties [19–23]. The band in the region 290–335 cm^{-1} has been assigned due to ν_{as} Sb–O vibrations [22–24].

The PMR spectra of these compounds are recorded in CCl_4 or $CDCl_3$ and spectral data are given in Table I together with triphenylantimony(V) derivatives. Earlier PMR studies on oximes [14, 25, 26] and O-organometal oximes [12, 27] indicated separation of the resonances for the protons on the carbon atoms next to the >C = N–O group when an aromatic solvent was present or when the oxime molecule contained an aromatic substituent. However, the PMR spectra of the compounds prepared during the

TABLE II. Reactions of Trialkylstibine Dibromides with Sodium Oximates in 1:2 Molar Ratio.

Reactants (g)					Product and its nature	B. P. °C/mm (% yield recovered) [M.P. °C]	% Analysis Found (calcd)				n_D^{31}
R_3SbBr_2 R =		$\begin{matrix}R' \\ R''\end{matrix}\!\!>CNOH$ R' & R'' =		Sodium			C	H	N	Sb	
Me	1.07	Me, Me	0.48	0.16	$Me_3Sb(ONCMe_2)_2$ white crystalline solid	91–93/2.5 (81) [40]	35.6 (34.75)	6.5 (6.8)	8.6 (9.0)	38.9 (39.1)	–
Me	1.28	Me, Et	0.68	0.18	$Me_3Sb(ONCMeEt)_2$ colourless liquid	81/1.0 (91)	37.6 (39.0)	8.05 (7.4)	–	–	1.4879
Me	1.33	Me, Pr	0.84	0.18	$Me_3Sb(ONCMePr)_2$ colourless liquid	104/0.5 (95)	42.9 (42.5)	8.5 (7.95)	–	–	1.4844
Me	1.51	Me, Ph	1.25	0.22	$Me_3Sb(ONCMePh)_2$ white solid	215–220/2.5 (76) [100–101]	53.75 (52.4)	6.0 (5.8)	6.3 (6.4)	27.8 (28.0)	–
Me	1.62	Et, Et	1.01	0.26	$Me_3Sb(ONCEt_2)_2$ colourless liquid	94/0.2 (95)	–	–	7.7 (7.6)	33.45 (33.2)	1.4810
Me	1.53	$\begin{matrix}NH_2 \\ Ph\end{matrix}\!\!>C{=}N{-}ONa$	1.56	–	$Me_3Sb(ONCNH_2Ph)_2$ white needle shape crystal	[110–111]	–	–	12.1 (12.8)	27.5 (27.85)	–
Et	1.94	Me_2CNONa	1.12	–	$Et_3Sb(ONCMe_2)_2$ colourless liquid	76–77/0.08 (86)	40.85 (40.8)	7.7 (7.7)	–	–	1.4927
Et	1.75	Me, Et	0.83	0.22	$Et_3Sb(ONCMeEt)_2$ colourless liquid	104–105/1.0 (66)	41.7 (44.1)	8.3 (8.2)	–	–	1.4898
Et	2.05	Me, Ph	1.51	0.27	$Et_3Sb(ONCMePh)_2$ cream coloured liquid	210–220/0.1 (88)	54.9 (55.4)	6.8 (6.5)	–	–	1.5916

course of the present investigations show the separation of the lines (in doublets of equal intensity) for the methylene and/or methyl protons of the alkyl groups attached to the imino carbon atom (R′ = R″ = Me or Et) even in non-aromatic solvents (Table I). This indicates non-equivalence of the two radicals bound to the iminoxy group. This may arise from the non-linearity of the >C = N–O group [14, 25, 26]. The magnitude of separation of alkyl proton resonances is larger in triphenylantimony(V) compounds compared to the trialkylantimony(V) derivatives which might be due to the presence of phenyl groups.

On the basis of IR and PMR spectral studies, a trigonal bipyramidal geometry with two oxygen atoms occupying apical positions may be proposed for these derivatives. However, $Me_3Sb(ONCNH_2Ph)_2$ appears to attain an octahedral structure in solid state.

Experimental

Rigorous precautions were taken to exclude moisture during the course of the present investigations, benzene and isopropanol were dried by usual methods. Trimethyl- [28] and triethyl- [19] stibine dibromides were prepared by the literature methods. Oximes were prepared by standard methods. Benzamidoxime was prepared by the method reported by Eloy and Lenaers [29] and was crystallized from water, m.p. 80 °C.

Nitrogen was estimated by Kjeldahls method and antimony was estimated iodometrically. Carbon and hydrogen were analysed with a Colmen-Carbon-Hydrogen Analyser.

IR spectra were recorded as liquid films, nujol mulls or in chloroform solutions on a Perkin-Elmer model 577 spectrophotometer in the range 4000–200 cm^{-1} using CsI optics. PMR spectra were recorded on Perkin-Elmer R12B (60 MHz), Perkin-Elmer R32 (90 MHz) and Varian (60 MHz) spectrometers in CCl_4 or $CDCl_3$ solutions using TMS as an external or internal standard. Molecular weights were determined cryoscopically in benzene. Refrective indices were measured by an Abbe's refractometer under Na-D line.

Reaction of Trimethylstibine Dibromide with Sodium Acetoximate

To the suspension of sodium acetoximate (prepared from 0.16 g sodium and 0.48 g acetoxime) in benzene, solution of trimethylstibine dibromide (1.07 g) was added and reaction mixture was refluxed for 2 hours. Sodium bromide formed during the reaction was filtered off. Filtrate was evaporated under vacuum giving a pasty mass which on distillation gave colourless solid, b.p. 91–93°/2.5 mm; m.p. 40 °C (yield 81%). *Anal.* Found: C, 35.6; H, 6.5; N, 8.6; Sb, 38.9%. Calcd. for $Me_3Sb(ONCMe_2)_2$: C, 34.75; H, 6.8; N, 9.0; Sb, 39.15%.

Other compounds were also prepared similarly and pertinent data are given in Table II.

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