ANTIMONY

ANNUAL SURVEY COVERING THE YEAR 1981 *

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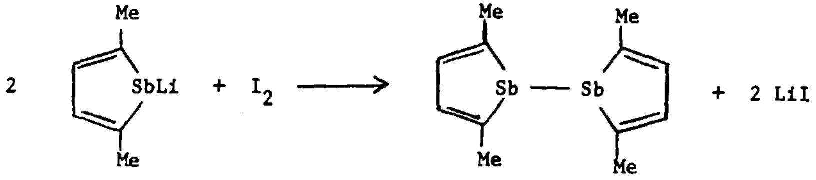
No book or review devoted exclusively to organoantimony chemistry was published in 1981. Information about organoantimony compounds was included, however, in a short survey of recent work on organic derivatives of arsenic, antimony, and bismuth [1] and in a supplement to *Rodd's Chemistry of Carbon Compounds* [2]. A review with 113 references on the crystal structure of antimony(III) compounds has appeared in the Russian literature [3], and organoantimony compounds have been briefly mentioned in surveys of recent work on substitution reactions of metal and organometal carbonyls with Group V and Group VI ligands [4] and on organometallic compounds containing metal-metal bonds [5].

2,2',5,5'-Tetramethyl-1,1'-distibole has been prepared by the following reaction [6]:



Unlike other reported distibines, this compound was air-stable. It crystallized as intensely colored plates which were iridescent purple-blue in reflected light but appeared red to transmitted light. A thin film of these crystals showed a broad absorption maximum centered at 520 nm. Most remarkably, the crystals melted reversibly at 99°C to a pale yellow oil. Solutions of the distibine in toluene or carbon tetrachloride were pale yellow; the UV absorption spectrum showed a shoulder at 346 nm (ε 1900). Since it seemed likely that the intense color of the distibine was a solid-phase effect, an X-ray crystal structure was obtained. It was found that the intramolecular bond distances and angles were not unusual. Thus, the

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*Antimony; Annual Survey covering the year 1980 see J. Organometal. Chem., 227 (1982) 21-50.

Sb-Sb bond length was 283.5 pm and the average Sb-C bond length was 213.8 pm; these values were similar to those recently reported for tetraphenyldistibine. The crystal packing structure of the distibole, however, revealed several remarkable features. All of the antimony atoms were aligned in a collinear chain, and there was a very short intermolecular Sb···Sb separation of 362.5 pm. In contrast, the expected van der Waals radius separation was about 440 pm, and the closest intermolecular Sb···Sb approach in tetraphenyldistibine was 482 pm. It was suggested, therefore, that there was extended bonding along the Sb-Sb···Sb-Sb chain of the distibole and that the solid-phase color was probably due to electronic excitation along this chain. The C-Sb-C bond angles indicated that the antimony used primarily *p* orbitals in bonding and that the lone pair was essentially *s* in character. Since the antimony $5p_z$ orbitals were probably aligned along the chain of antimony atoms, the extended Sb-Sb···Sb-Sb bonding presumably involved partial bonding via *p* orbitals.

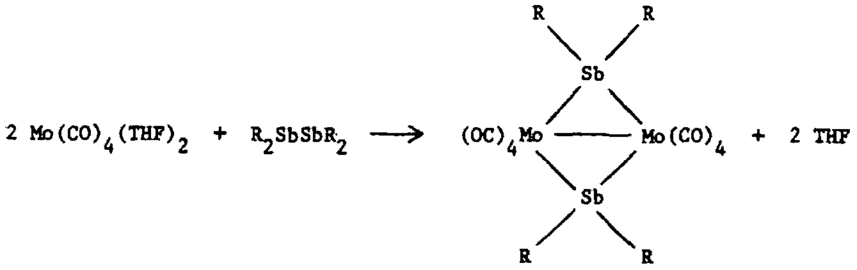
Tetramethyldistibine and tetraphenyldistibine have been found to react with photochemically generated solutions of pentacarbonyl(tetrahydrofuran)molybdenum in THF to yield binuclear complexes [7]:

$$\mathrm{Mo(CO)_6} + \mathrm{THF} \xrightarrow{h\nu} \mathrm{Mo(CO)_5(THF)} + \mathrm{CO}$$

$$2\ \mathrm{Mo(CO)_5(THF)} + \mathrm{R_2SbSbR_2} \longrightarrow \mathrm{(OC)_5MoSbR_2SbR_2Mo(CO)_5} + 2\ \mathrm{THF}$$

(where R was Me or Ph)

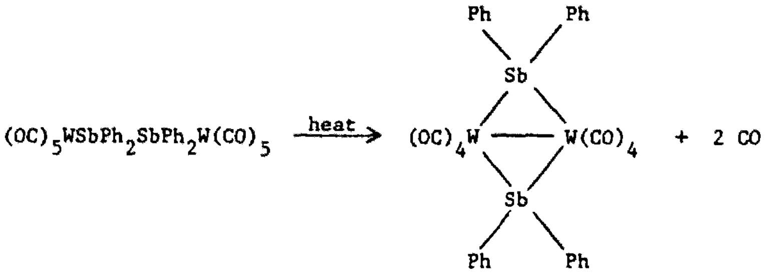
When a vigorous stream of argon was passed through the THF solution of the molybdenum hexacarbonyl during the irradiation, the disubstituted species *cis*-$\mathrm{Mo(CO)_4(THF)_2}$ was also formed and reacted with distibines to give complexes in which the Sb-Sb bond was no longer present:



(where R was Me, Et, or Ph)

The thermal reaction of tungsten hexacarbonyl with tetraphenyldistibine in refluxing diglyme gave similar types of antimony-containing complexes:

$$2\ W(CO)_6 + Ph_2SbSbPh_2 \xrightarrow{heat} (OC)_5WSbPh_2SbPh_2W(CO)_5 + 2\ CO$$



The reaction of bromine with an equimolar quantity of a binuclear complex of tetramethylstibine and chromium (described in an earlier publication) was also found to result in cleavage of the Sb-Sb bond:

$$(OC)_5CrSbMe_2SbMe_2Cr(CO)_5 + Br_2 \longrightarrow 2\ Cr(CO)_5Sb(Br)Me_2$$

The interaction of two moles of enneacarbonyldiiron and one mole of tetraethyldistibine in pentane at room temperature yielded both a mononuclear complex and a diethylstibino-bridged complex [8]:

$$Fe_2(CO)_9 + Et_2SbSbEt_2 \longrightarrow Fe(CO)_4SbEt_2SbEt_2 + Fe(CO)_5$$

$$2\ Fe_2(CO)_9 + Et_2SbSbEt_2 \longrightarrow (OC)_3Fe(SbEt_2)_2Fe(CO)_3 + 2\ Fe(CO)_5 + 2\ CO$$

Under similar conditions tetra-*tert*-butyldistibine appeared to give only a mononuclear complex. In contrast to these results, tetraphenyldistibine did not form a mononuclear complex but yielded a binuclear complex at room temperature:

$$2\ Fe_2(CO)_9 + Ph_2SbSbPh_2 \longrightarrow (OC)_4FeSbPh_2SbPh_2Fe(CO)_4 + 2\ Fe(CO)_5$$

When a solution of this complex in ethylcyclohexane was refluxed for several hours, a diphenylstibino-bridged complex was obtained:

$$(OC)_4FeSbPh_2SbPh_2Fe(CO)_4 \xrightarrow{heat} (OC)_3Fe(SbPh_2)_2Fe(CO)_3 + 2\ CO$$

The interaction of nickel tetracarbonyl and tetramethyldistibine yielded only a binuclear complex:

$$2\ \mathrm{Ni(CO)_4} + \mathrm{Me_2SbSbMe_2} \longrightarrow \mathrm{(OC)_3NiSbMe_2SbMe_2Ni(CO)_3} + 2\ \mathrm{CO}$$

Bis(di-*tert*-butylantimony) oxide has been prepared by the interaction of an ether solution of di-*tert*-butylchlorostibine and an aqueous solution of sodium hydroxide [9]:

$$2\ \mathrm{(Me_3C)_2SbCl} + 2\ \mathrm{OH^-} \longrightarrow \mathrm{(Me_3C)_2SbOSb(CMe_3)_2} + 2\ \mathrm{Cl^-} + \mathrm{H_2O}$$

Treatment of the ether solution with aqueous sodium sulfide gave the corresponding sulfur compound:

$$2\ \mathrm{(Me_3C)_2SbCl} + 2\ \mathrm{HS^-} \longrightarrow \mathrm{(Me_3C)_2SbSSb(CMe_3)_2} + 2\ \mathrm{Cl^-} + \mathrm{H_2S}$$

When *tert*-butyldichlorostibine in ether reacted with aqueous sodium hydroxide, a mixture of polymeric cyclic stiboso compounds was obtained:

$$\mathrm{Me_3CSbCl_2} + 2\ \mathrm{OH^-} \longrightarrow 1/n\ \mathrm{(Me_3CSbO)}_n + 2\ \mathrm{Cl^-} + \mathrm{H_2O}$$

(where n was 3 or 4)

Aqueous sodium sulfide yielded cyclic thiostiboso compounds:

$$\mathrm{Me_3CSbCl_2} + 2\ \mathrm{HS^-} \longrightarrow 1/n\ \mathrm{(Me_3CSbS)}_n + 2\ \mathrm{Cl^-} + \mathrm{H_2S}$$

(where n was 2,3,4, or 5)

The structures of the various substances prepared in this investigation were deduced from elemental analyses and IR, PMR, and mass spectral data.

The ^{121}Sb Mössbauer spectra of the four compounds of type $\mathrm{Me}_n\mathrm{SbCl}_{3-n}$ (where n was 0,1,2, or 3) have been determined at 4.2 K [10]. The quadrupole coupling parameters of all four compounds could be explained qualitatively with a simple point charge model in which the antimony lone-pair electron density was treated as a ligand and the bond angles between the ligands were assumed to be close to 90°. The isomer shift data suggested that the *s*-electron density at the antimony nucleus decreased with an increase in the value of n. This decrease was ascribed to an increase in the *p* character of the lone-pair electrons when a chlorine atom was replaced by a methyl group. It was also concluded in this study that pure dimethylchlorostibine was best prepared by the interaction of equimolar amounts of tetramethyldistibine and sulfuryl chloride in methylene dichloride:

$$Me_2SbSbMe_2 + SO_2Cl_2 \xrightarrow{-78^{\circ}C} 2\ Me_2SbCl + SO_2$$

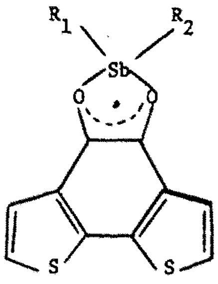
Pure methyldichlorostibine could be obtained by heating dimethylantimony trichloride at 120°C for 10 minutes:

$$Me_2SbCl_3 \longrightarrow MeSbCl_2 + MeCl$$

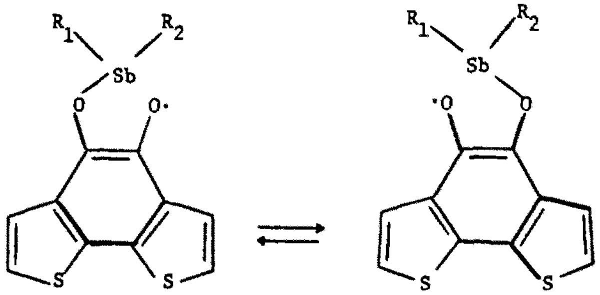
Samples to be used for Mössbauer spectroscopy were stored at liquid-nitrogen temperature immediately after preparation. When pure samples of dimethylchlorostibine or methyldichlorostibine were stored in the dark at room temperature for two months, a black solid (assumed to be metallic antimony) formed. PMR analysis showed that the dimethylchlorostibine had partially decomposed into a mixture that contained trimethylstibine, methyldichlorostibine, and trimethylantimony dichloride. Similarly, the methyldichlorostibine had partially decomposed into a mixture that contained the latter two compounds. Presumably, antimony trichloride was also present in these mixtures, but no attempt was made to determine its amount.

The synthesis and the IR and ^{121}Sb Mössbauer spectra of phenylhaloantimonates(III) of the type $M[PhSbX_3]$, where M was Me_4N or Ph_4As and X was Cl, Br, or I, have been reported [11]. The IR spectra in the 1200–350 cm^{-1} region were very similar to those previously found for the corresponding phenylhaloantimonates(V) of the type $M[PhSbX_5]$. The Sb-Ph and Sb-Cl stretching frequencies, which were found in the 350–250 cm^{-1} region, were somewhat lower in the antimony(III) compounds. This effect was attributed to the tendency of the Sb 5*s* electrons to concentrate in the lone pair orbital and result in a weakening of the Sb-Ph and Sb-Cl bonds. The Mössbauer isomer shifts were in the range observed for other Sb(III) compounds, but were somewhat larger than the shifts for the corresponding SbX_4^- species. This result suggested that the *s*-electron density at the antimony nucleus was lowered when an X was replaced by Ph; it was in accord with some participation of the Sb 5*s* electrons in the Sb-Ph bond. The electric field gradient parameters were characterized by large and positive quadrupole coupling constants, small asymmetry parameters, and a dependence of quadrupole coupling on X in the order Cl>Br>I. It was concluded that both the lone pair and the Sb-Ph bond electron densities made important contributions to the *z* component of the electric field gradient.

ESR spectroscopy has been used to investigate paramagnetic intermediates resulting from the thermal reaction of benzo[2,1-*b*:3,4-*b*']dithiophene-4,5-dione (TQ) with a number of trivalent derivatives of arsenic, antimony, and bismuth [12]. Included in this study were triphenylstibine, phenyldichlorostibine, and diphenylchlorostibine. The reactions were carried out by melting a mixture of the antimony compound, the dione TQ, and biphenyl inside the spectrometer cavity. Under these conditions triphenylstibine gave a radical identified as $[TQSbPh_2]\cdot$. Phenyldichlorostibine gave rise to three overlapping ESR spectra attributed to $[TQSbCl_2]\cdot$, $[TQSbPh_2]\cdot$, and $[TQSb(Cl)Ph]\cdot$. The latter two radicals were also obtained by the interaction of diphenylchlorostibine and TQ. The radicals were depicted as either containing four-coordinate antimony (I) or consisting of rapidly equilibrating three-coordinate structures (II and III):



I



II

III

(where $R_1 = R_2 = Ph$; $R_1 = R_2 = Cl$; or $R_1 = Ph$, $R_2 = Cl$)

A large number of potentially bi-, tri-, and tetradentate ligands containing various combinations of antimony and other donor atoms have been studied in Levason's laboratory. In one paper [13] eleven tertiary stibines containing divalent oxygen or sulfur were described. Three *o*-methoxy-substituted triarylstibines were easily prepared via the Grignard reaction:

$$o\text{-}MeOC_6H_4MgBr + Ph_2SbCl \longrightarrow o\text{-}MeOC_6H_4SbPh_2$$

$$2\ o\text{-}MeOC_6H_4MgBr + PhSbCl_2 \longrightarrow (o\text{-}MeOC_6H_4)_2SbPh$$

$$3\ o\text{-}MeOC_6H_4MgBr + SbCl_3 \longrightarrow (o\text{-}MeOC_6H_4)_3Sb$$

The three stibines were white, air-stable, crystalline solids and were readily soluble in organic solvents. The Grignard reaction was also used to prepare (*o*-methoxyphenyl)dimethylstibine:

$$o\text{-MeOC}_6\text{H}_4\text{MgBr} + \text{Me}_2\text{SbBr} \longrightarrow o\text{-MeOC}_6\text{H}_4\text{SbMe}_2$$

This substance was a colorless, air-sensitive liquid and was readily quaternized by treatment with methyl iodide. The PMR spectra of the tertiary stibines showed sharp singlets at τ 6.0-6.5 due to the methoxy groups. The mass spectra were straightforward; the major fragment ions resulted from successive Sb-C cleavage. Four *o*-methylthiophenylstibines were prepared from an organolithium reagent:

$$o\text{-MeSC}_6\text{H}_4\text{Li} + \text{Ph}_2\text{SbCl} \longrightarrow o\text{-MeSC}_6\text{H}_4\text{SbPh}_2$$

$$2\ o\text{-MeSC}_6\text{H}_4\text{Li} + \text{PhSbCl}_2 \longrightarrow (o\text{-MeSC}_6\text{H}_4)_2\text{SbPh}$$

$$3\ o\text{-MeSC}_6\text{H}_4\text{Li} + \text{SbCl}_3 \longrightarrow (o\text{-MeSC}_6\text{H}_4)_3\text{Sb}$$

$$o\text{-MeSC}_6\text{H}_4\text{Li} + \text{Me}_2\text{SbBr} \longrightarrow o\text{-MeSC}_6\text{H}_4\text{SbMe}_2$$

The three triarylstibines were air-stable, microcrystalline solids, while (*o*-methylthiophenyl)dimethylstibine was an air-sensitive oil which readily gave a monomethiodide. The PMR spectrum of the latter compound showed that quaternization had occurred at antimony since the SbMe_2 resonance at τ 9.2 in the free ligand was shifted to τ 8.0 in the derivative (with the expected increase in relative intensity) while the SMe signal at *ca.* τ 7.5 was unshifted. Two other sulfur-containing tertiary stibines were prepared by the following type of reaction in liquid ammonia:

$$\text{MeSCH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{R}_2\text{SbNa} \longrightarrow \text{MeSCH}_2\text{CH}_2\text{CH}_2\text{SbR}_2$$

(where R was Me or Ph)

The (3-methylthiopropyl)diphenylstibine thus obtained was a non-distillable, viscous oil which was converted to a monomethiodide. The PMR spectrum of this derivative showed no peak due to SbMe^+, but the SMe resonance at τ 8.1 in the free ligand had disappeared and a new signal at τ 7.5 had appeared which was assigned to SMe_2^+. (3-Methylthiopropyl)dimethylstibine was a colorless, air-sensitive liquid that gave a dimethiodide on treatment with excess methyl iodide. A potentially tridentate ligand was prepared by the following reaction in liquid ammonia:

$$(ClCH_2CH_2CH_2)_2S \;+\; 2\;Ph_2SbNa \longrightarrow (Ph_2SbCH_2CH_2CH_2)_2S$$

This compound was a viscous oil which was converted to a monomethiodide. The latter substance was not sufficiently soluble for a PMR spectrum to be obtained. The mass spectra of the sulfur-containing ligands were generally as expected. Attempts to prepare ethylenebis(diphenylstibine) and tridentate ligands of the type $(R_2SbCH_2CH_2)_2S$, where R was Me or Ph, were unsuccessful.

In a second paper [14] from Levason's laboratory, an investigation of nine ligands containing both tertiary antimony and tertiary nitrogen atoms was reported. Three *N*,*N*-dimethylaminophenylstibines were obtained via the Grignard reaction:

$$o\text{-}Me_2NC_6H_4MgBr \;+\; Ph_2SbCl \longrightarrow o\text{-}Me_2NC_6H_4SbPh_2$$

$$3\;o\text{-}Me_2NC_6H_4MgBr \;+\; SbCl_3 \longrightarrow (o\text{-}Me_2NC_6H_4)_3Sb$$

$$o\text{-}Me_2NC_6H_4MgBr \;+\; Me_2SbBr \longrightarrow o\text{-}Me_2NC_6H_4SbMe_2$$

A somewhat higher yield of the second stibine was obtained by the use of *o*-*N*,*N*-dimethylaminophenyllithium. Both triarylstibines were air-stable solids, the mass spectra of which showed ions due to successive Sb-C cleavage. The mass spectral fragmentation of the dimethylstibino compound showed stepwise loss of methyl groups. Two dimethylaminopropyl stibines were prepared in liquid ammonia by the following type of reaction:

$$Me_2NCH_2CH_2CH_2Cl \;+\; R_2SbNa \longrightarrow Me_2NCH_2CH_2CH_2SbR_2$$

(where R was Me or Ph)

The diphenylstibino compound was a fawn-colored, air-stable oil which yielded a white monomethiodide. The PMR spectrum of the latter substance showed that the nitrogen was the alkylated heteroatom. The dimethylstibino compound was a colorless, air-sensitive, distillable oil which gave a diquaternary derivative on treatment with methyl iodide. Two potentially tridentate ligands were prepared in liquid ammonia by the following type of reaction:

$$MeN(CH_2CH_2Cl)_2 \;+\; 2\;R_2SbNa \longrightarrow MeN(CH_2CH_2SbR_2)_2$$

(where R was Me or Ph)

Treatment of the diphenylstibino compound with methyl iodide gave a monomethiodide in which only the nitrogen was quaternized. The dimethylstibino compound was an air-sensitive, fawn-colored, non-distillable oil. A stibine sulfide derivative was easily prepared by the interaction of the ligand and two equivalents of sulfur in refluxing toluene. The PMR spectrum of the sulfide showed a single $Me_2Sb(S)$ resonance at τ 8.45. Two potentially tetradentate ligands were prepared by the reaction of tris(3-chloropropyl)amine with lithium diphenylstibide in THF or with sodium dimethylstibide in liquid ammonia:

$$N(CH_2CH_2CH_2Cl)_3 \quad + \quad 3\ R_2SbM \longrightarrow N(CH_2CH_2CH_2SbR_2)_3$$

(where R was Me or Ph and M was Na or Li)

The diphenylstibino ligand was obtained as a brownish viscous oil which could not be crystallized. The dimethylstibino analog was a mobile, yellowish, air-sensitive liquid which was readily converted to a trisulfide. The latter compound was a brown oil which solidified at *ca.* 10°C. Attempts to prepare (2-dimethylaminoethyl)diphenylstibine and tris(2-diphenylstibinoethyl)amine were unsuccessful.

A third paper [15] from Levason's laboratory described five potentially tetradentate ligands with SbNNSb, SbSSSb, or SbOOSb donor sequences. Two distibino-diamines were prepared by the interaction of *N,N'*-dimethyl-*N,N'*-bis(3-chloropropyl)ethylenediamine and sodium dimethylstibide in liquid ammonia or lithium diphenylstibide in THF:

$$[ClCH_2CH_2CH_2N(CH_3)CH_2]_2 \quad + \quad R_2SbM \longrightarrow [R_2SbCH_2CH_2CH_2N(CH_3)CH_2]_2$$

(where R was Me or Ph and M was Na or Li)

The dimethylstibino compound was a yellow, air-sensitive, non-distillable oil. The diphenylstibino compound could not be isolated in pure form from the reaction mixture. It was therefore converted to a Ni(II) complex, which was decomposed by refluxing with concentrated aqueous ammonia to yield the pure ligand as a white waxy solid melting around room temperature. Two distibino-dithioethers were obtained by a route similar to that used for the distibino-diamines:

$$[ClCH_2CH_2CH_2SCH_2]_2 \quad + \quad R_2SbM \longrightarrow [R_2SbCH_2CH_2CH_2SCH_2]_2$$

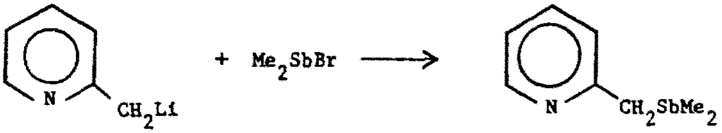
(where R was Me or Ph and M was Na or Li)

These antimony compounds were isolated and purified by essentially the same methods used for the corresponding distibino-diamines. The phenyl-substituted ligands were air-stable oils at room temperature and were most conveniently characterized via their palladium(II) complexes. The methyl-substituted ligands reacted with sulfur in toluene to yield the corresponding stibine sulfides as foul-smelling brown oils, which were characterized by elemental analysis and PMR spectra. A distibino-diether was easily prepared in liquid ammonia by the following reaction:

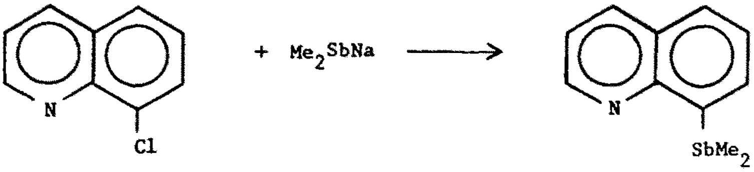
$$[ClCH_2CH_2OCH_2]_2 + Me_2SbNa \longrightarrow [Me_2SbCH_2CH_2OCH_2]_2$$

The product was a colorless, air-sensitive oil which was readily converted by treatment with bromine to a white tetrabromide.

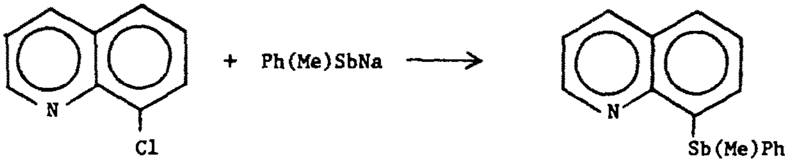
Shewchuk and Wild [16] have described the synthesis and properties of three tertiary stibines containing a heterocylic nitrogen ring. Dimethyl(α-picolyl)stibine was prepared in diethyl ether by the following reaction:



The compound was a pale yellow, air-sensitive liquid that was readily converted to a monomethiodide. The PMR spectrum of the stibine consisted of sharp singlets at δ 0.68 and δ 2.94 for the methyl and methylene protons, respectively, and a broad multiplet at δ 6.74-7.60 assigned to the aromatic protons. The PMR spectrum of the methiodide exhibited a sharp singlet at δ 2.01 due to the Me_3Sb^+ group; there was no evidence of quaternization of the nitrogen atom. A molecular ion was observed in the mass spectrum of the stibine, but the base peak corresponded to the loss of a methyl group from the molecular ion. Dimethyl(8-quinolyl)stibine was prepared in liquid ammonia by the following reaction:

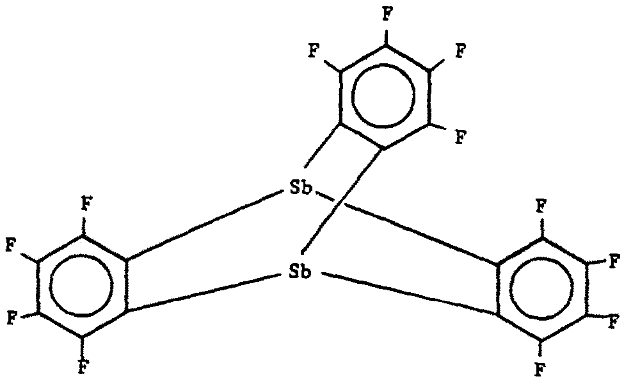


This compound was also a yellow, air-sensitive liquid that was readily quaternized with methyl iodide. The PMR spectrum of the stibine consisted of a sharp singlet at δ 0.96 and a broad multiplet at δ 7.22-8.94. Upon quaternization, the $SbMe_2$ resonance was shifted downfield to δ 2.39. The mass spectrum of the stibine was similar to that of the α-picolyl compound. An asymmetric stibine was obtained by the following reaction in liquid ammonia:



This stibine was a viscous yellow oil that could also be converted to a methiodide. The Me resonance occurred at δ 1.18, and the aromatic protons gave a broad multiplet at δ 7.16-8.92. The methiodide displayed a resonance at δ 2.43 attributed to the Me_2Sb^+ group. Once again the mass spectrum of the stibine exhibited the molecular ion, but the base peak corresponded to the loss of a methyl group. All three stibines readily formed the expected neutral complexes $[MCl_2(\text{bidentate})]$, where M was Pd or Pt. These yielded complexes of the type $[MX_2(\text{bidentate})]$, where X was Br, I, or SCN, upon metathesis with the appropriate sodium salt. Dimethyl-(α-picolyl)stibine and dimethyl(8-quinolyl)stibine were also converted to zerovalent octahedral complexes of the type $[M(CO)_4(\text{bidentate})]$, where M was Cr, Mo, or W, by ultraviolet irradiation of the metal carbonyl with one equivalent of the ligand in THF solution.

Mistry and Massey [17] have reinvestigated and extended previously published work on the following antimony analog of triptycene:



As in an earlier paper [18] from their laboratory they reported that the antimony compound could be prepared in satisfactory yield by simply heating a mixture of 1,2-diiodotetrafluorobenzene and antimony powder at elevated temperatures. It could also be obtained by heating a mixture of antimony and the organomercurial $(HgC_6F_4)_3$. The melting point of the antimony compound was 258-259°C; in contrast Cullen and Wu [19] had reported that the substance melted at 155°C. The mass spectrum exhibited the molecular ion, but the base peak was $C_6F_4Sb^+$. The ^{19}F NMR and IR spectra were exactly as expected for a 1,2-C_6F_4 compound. The antimony compound was very stable thermally. It showed no change on being heated overnight at 350°C; a slow decomposition was observed at 400°C. The C-Sb bonds were not cleaved by heating the antimony compound with water vapor for many hours at 300°C. When heated with selenium at 300°C, a good yield of octafluoroselanthrene, $Se_2(C_6F_4)_2$, was obtained. In a similar reaction sulfur gave a low yield of octafluorothianthrene. No reaction occurred when the antimony compound and methyl iodide were refluxed together. When a mixture of powdered arsenic and antimony was heated at 250°C with 1,2-diiodotetrafluorobenzene, the product had a mass spectrum that exhibited ions corresponding to $(C_6F_4)_3Sb_2^+$, $(C_6F_4)_3As_2^+$, and $(C_6F_4)_3AsSb^+$. No organoantimony compound could be isolated from the reaction mixture obtained by heating antimony powder with 1,2-diiodobenzene. However, when antimony was heated with a mixture of 1,2-diiodobenzene and 1,2-diiodotetrafluorobenzene, a product was formed that exhibited the ions $(C_6F_4)_3Sb_2^+$, $(C_6F_4)_2(C_6H_4)Sb_2^+$, and $(C_6F_4)(C_6H_4)_2Sb_2^+$ in its mass spectrum; no peak corresponding to $(C_6H_4)_3Sb_2^+$ could be detected.

Tri-2,4-cyclopentadien-1-ylstibine has been prepared in quantitative yield by the interaction of tris(dimethylamino)stibine and excess cyclopentadiene [20]:

$$Sb(NMe_2)_3 \ + \ 3\ CpH \ \xrightarrow[-80^{\circ}C]{Et_2O} \ Cp_3Sb \ + \ 3\ Me_2NH$$

(where Cp was cyclopentadienyl)

The analytically pure, yellow crystals thus obtained melted at 53°C and were subjected to X-ray diffraction. The molecular structure determined by this procedure unequivocally showed the existence of σ-bonded cyclopentadienyl rings with approximate tetrahedral angles between the "best planes" of the five-membered rings and the Sb-C bond directions. The non-bonding electron pair at the antimony atom was found to influence the molecular packing. The average Sb-C bond distance was 224.9 pm, and the average C-Sb-C angle was 96.4°. The value for this angle was similar to the 97.3° previously reported for tri-*p*-tolylstibine.

The cleavage of the C-Sb bonds in triphenylstibine has been accomplished by heating it at 140-160°C with $Rh(CO)_2acac$ in the presence of cesium benzoate in tetraethylene glycol-dimethyl ether solution under about 400 atmopheres of an equimolar mixture of carbon monoxide and hydrogen [21]. Under these conditions the antimony was converted in about 3 hours to an anionic species, which was subsequently isolated as a salt of the composition $[Et_4N]_3\ [Rh_{12}Sb(CO)_{27}]$. This substance was characterized via a complete three-dimensional X-ray diffraction study. The structure of the anion was found to consist of twelve rhodium atoms situated at the corners of a distorted icosahedron, an antimony atom within the polyhedral cavity, and the carbonyl groups bonded to the rhodium atoms. Six of the Sb-Rh contacts were 292.2 pm, while the other six were 271.2 pm. The average of these observed values was about equal to the sum of the covalent radii of antimony and rhodium (280 pm).

Trialkylstibines have been found to react readily with sulfur trioxide in methylene dichloride to yield antimony trisulfonates [22]:

$$R_3Sb + 3\ SO_3 \xrightarrow{-50^{\circ}C} Sb(OSO_2R)_3$$

(where R was Me_2CH or Bu)

The ease with which these insertion reactions occurred was attributed to the comparative weakness of the alkyl-antimony bond.

The one-electron oxidation of compounds of the type Ph_3E (where E was N, P, As, Sb, or Bi) by radical cations of the type $(4\text{-}RC_6H_4)_3N^{\dot{+}}$ (where R was MeO, Me, Ph, or Br) has been investigated by ESR and electronic spectroscopy [23]. The reactions were found to obey a second order rate law and to depend strongly on both E and R. The presence of an electron-donating substituent at the *para* position of the radical cation led to a sharp reduction in the rate of the process; this effect was ascribed to a decrease in the oxidizing ability of the radical cation. The ability of the Group V triphenyl derivatives to act as one-electron reducing agents decreased in the order $Ph_3P>Ph_3As\gtrsim Ph_3Sb>>Ph_3N>Ph_3Bi$. This order agreed well with the affinity of these compounds for electrophiles. The radical cations used in this study were obtained by oxidation of the corresponding triarylamines with antimony pentachloride and were isolated as hexachloroantimonates.

The rate of the reaction of triphenylstibine with pyridine *N*-oxide has been reported as part of an investigation of the interaction of the latter compound with trivalent derivatives of Group V elements [24]. The reactivity followed the order: $Ph_3P>>Ph_3Sb\gtrsim Ph_3As$. This result was explained by the combined effect of the electron-accepting ability of the Group V element and the stability of Group V element-oxygen double bonds.

Triphenylarsine, -stibine, and -bismuthine have been included in a study of the cyclic voltammetry redox potentials of several tertiary phosphines [25]. The antimony compound exhibited irreversible redox potentials of + 0.58 and + 0.93 V (vs. the SCE).

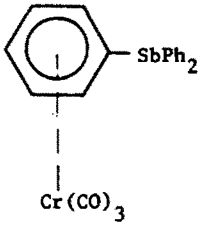
Although triphenylstibine had virtually no effect on the rate of polymerization of methyl methacrylate initiated by 2,2'-azobisisobutyronitrile (AIBN) or lauroyl peroxide, it inhibited oxidative thermal degradation of poly(methyl methacrylate) when introduced either directly into the polymer or into the monomer prior to polymerization [26]. Analysis of the degraded polymer indicated that triphenylstibine was able to terminate the oxidative chain by reacting with peroxy radicals of the polymer to form phenyl radicals and relatively stable macroradicals containing the Ph_2SbO group.

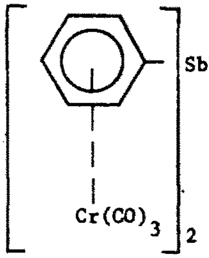
A British patent application [27] has claimed that the presence of a small amount of triphenylstibine was useful in the preparation of bromine-containing, fire-resistent unsaturated polyesters with improved discoloration prevention.

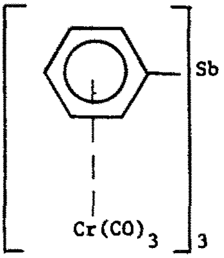
The reaction of triphenylstibine with triamminechromium tricarbonyl in dioxane at 120°C has been found to give a mixture of three σ-bonded complexes [28]:

$$Ph_3Sb + (NH_3)_3Cr(CO)_3 \longrightarrow Ph_3SbCr(CO)_5 + (Ph_3Sb)_2Cr(CO)_4 + (Ph_3Sb)_3Cr(CO)_3$$

In the presence of boric acid, however, the following three π-bonded complexes were formed:







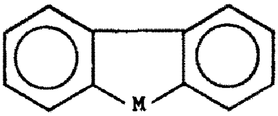
The IR and PMR spectra of the six triphenylstibine complexes were consistent with the assigned structures.

In addition to the paper reviewed in the above paragraph, there have been numerous other recent articles on the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included chromium [16], cobalt [29-35], gold [36], iridium [37,38], iron [39-45], mercury [46], molybdenum [16], nickel [15], palladium [15, 16, 47, 48], platinum [16, 49, 50], rhodium [51], ruthenium [52-57], vanadium [58, 59], and tungsten [16]. A convenient PMR technique for making stereochemical assignments in platinum metal complexes of triphenylphosphine, -arsine, and -stibine has been described [60], but the specific antimony compounds studied were not mentioned. It has also been reported [61] that triphenylstibine did not react with the rhodium(I) complex $[Rh(COD)(4\text{-}MePyO)_2]ClO_4$, where COD was 1,5-cyclooctadiene and 4-MePyO was 4-methylpyridine *N*-oxide.

An X-ray crystal structure of tris(2,6-dimethylphenyl)stibine has shown that the *ortho* methyl groups have a great influence on the shape of the molecule [62]. The mean value of the C-Sb-C bond angle (104.7^{o}) was significantly larger than the 97.3^{o} previously reported for tri-*p*-tolylstibine; and the mean C-Sb bond distance in the 2,6-dimethyl compound was 219.0 pm, a value somewhat longer than the 214.1 pm reported for the corresponding distance in the *p*-tolyl compound. These and other differences found in comparing the structures of the two tertiary stibines were attributed to steric effects of the methyl groups in the *ortho* positions. The electronic spectra in hexane of triphenylstibine, tris(2,6-dimethylphenyl)stibine, and trimesitylstibine were also compared. Triphenylstibine exhibited peaks at 195 nm (log ε, 4.96) and 254 nm (log ε, 4.08). The absorption maxima in the spectra of other two compounds were shifted to longer wavelengths. Thus, the spectrum of tris(2,6-dimethylphenyl)stibine had peaks at 204 nm (log ε, 4.98) and 282 nm (log ε, 4.04), and the spectrum of trimesitylstibine had peaks at 208 nm (log ε, 5.04) and 284 nm (log ε, 4.11). The dipole moment of tris(2,6-dimethylphenyl)stibine in benzene was found to be 0.62 D, while the dipole moment of trimesitylstibine was 1.10 D. This difference was ascribed to the expected effect of the *para* methyl groups in the latter compound.

5-Phenyl-5*H*-dibenzostibole has been included in two spectroscopic investigations of fluorene-like molecules. In one [63] of these studies, the electronically excited states of carbazole, 5-phenyl-5*H*-dibenzophosphole, -arsole, and -stibole were investigated by the CNDO/S-CI method. The contribution of the heteroatom to the formation of the excited state was determined; and the matrix elements of the spin-orbit coupling operator, the oscillator strengths of the $S_o \rightarrow S_1$ and $S_o \rightarrow T_1$ transitions, and the phosphorescence lifetimes were calculated. The effects of planarity or nonplanarity on the luminescence-spectroscopic properties of these molecules were also discussed.

In a second paper [64], singlet and triplet state energies, luminescence properties, and triplet-triplet absorption spectra were compared for twelve compounds of the following type:

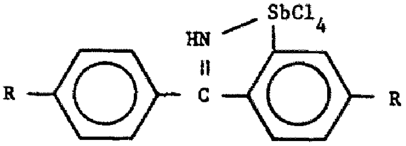


(where M was CMe_2, $SiPh_2$, $GePh_2$, $SnEt_2$, NMe, PPh, AsPh, SbPh, BiPh, O, S, or Se)

It was found that as the atomic number of the heteroatom increased within a group of the periodic table, the fluorescence quantum yield decreased, the quantum yield ratio of phosphorescence to fluorescence increased, and the lifetime of the phosphorescent state decreased.

Thermodynamic functions have been determined for the vaporization of triethylstibine, diethyl ether, and various mixtures of the two substances [65]. The equimolar complex of the stibine and ether was thermally unstable and dissociated during evaporation. The data obtained in this study made it possible to calculate the enthalpy and the entropy of the dissociation.

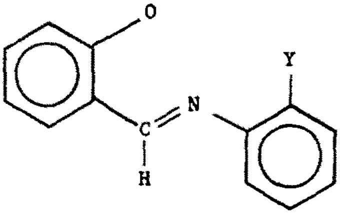
Parish and Parry [66] have reported on the Mössbauer spectra of three series of compounds prepared by the reaction of antimony pentachloride with ketimines or with lithium derivatives of ketimines $R_2C=NLi$. The compounds obtained were divided into three groups on the basis of their IR and Mössbauer spectra. One group, obtained from $SbCl_5$ and the ketimines $Ph_2C=NH$ or $(p\text{-}MeC_6H_4)_2C=NH$, contained inorganic antimony(V) with the structure $[Ar_2C=NH_2]$ $[SbCl_6]$. From $SbCl_5$ and the lithium derivatives, two groups of compounds were obtained. One group contained antimony(III) and possessed the general formula $[Ar_2C=NH_2]$ $[SbCl_4]$. Analytical data for the other group showed that one chlorine of $SbCl_5$ had been displaced. IR spectra for these compounds indicated the presence of a single N-H stretching band. The Mössbauer spectra were compatible with either five or six coordinate antimony. On the basis of these results the authors suggested that *ortho*-metalation had occurred and that the compounds possessed the following molecular structure:



(R = H or Me)

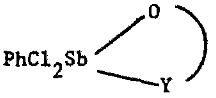
Quadrupole coupling constants (e^2qQg) and isomer shifts ($\delta_{In}Sb$) were given for all of the compounds under study.

Several papers by Di Bianca and coworkers have previously reported on antimony(V) complexes of planar tridentate Schiff bases containing ONO or ONS donor systems. The present paper [67] reported three antimony(V) compounds containing the following two groups:

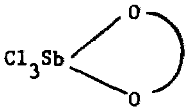


(where Y was O or S)

The three compounds were of the following types:



or



Two of these were obtained by the reaction of $[PhSbCl_5]NH_4$ with the dimethyltin complexes of the above two ligands. The other compound was obtained by the reaction of $SbCl_5$ and the ligand where Y = O. A compound obtained from $SbCl_5$ and the ligand where Y = S was apparently unstable and could not be isolated. Elemental analyses, IR, and PMR spectra and the mass spectrum of the $Cl_3Sb\begin{smallmatrix}O\\O\end{smallmatrix})$ compound were reported. By analogy with similar compounds previously prepared from these two ligands and whose structures had been determined by X-ray diffraction as well as spectroscopy, it was suggested that the three compounds reported in the present paper contained an octahedral antimony atom. The data did not allow a distinction to be made between the *trans*- and *cis*-$PhCl_2Sb$ compounds.

Andreae and coworkers [68] have reported on a method involving atomic absorption spectrometry for the determination of inorganic Sb(III), inorganic Sb(V), and two organic Sb(V) compounds, $MeSbO(OH)_2$ and $Me_2SbO(OH)$, in natural waters. The procedure involved reduction of the various species with sodium borohydride to stibine, methylstibine, and dimethylstibine. The inorganic Sb(III) compounds were reduced at near-neutral pH. Under these conditions inorganic Sb(V) compounds were not reduced. The combined

Sb(III) and Sb(V) inorganic compounds could be reduced in highly acid solution in the presence of iodide ion. The Sb(V) values were then obtained by difference. All of the stibines were collected in cold traps and were separated chromatographically. They were eluted into a quartz cuvette burner or a graphite furnace either of which was mounted in the beam of the atomic absorption spectrophotometer. As standards for the determination of inorganic Sb(III) and Sb(V), potassium antimonyl tartrate and potassium antimonate were used, respectively. As noted below, the methylstibonic and dimethylstibinic acids were obtained from an outside source.

The techniques described above were then used to determine inorganic Sb(III), inorganic Sb(V), methylstibonic acid, and dimethylstibinic acid in natural waters. These waters were obtained from several rivers and river bays in the USA, two heavily polluted rivers in Germany, and the Gulf of Mexico. Inorganic Sb(III) and Sb(V) were found in nanogram amounts in all of the waters tested. Methylstibonic acid was found in all but one of the waters tested but in amounts much smaller than those found for the inorganic antimony species. Dimethylstibinic acid was found in only one of the natural waters investigated.

The results reported in this paper may be misleading with regard to one of the organic antimony compounds reported. The authors stated that they obtained methylstibonic and dimethylstibinic acids (both in very impure forms) from the laboratory of Meinema and Noltes in the Netherlands and cited a reference [69] to these two authors for the preparation of the two compounds. But in this reference only dimethylstibinic acid was described. As far as the authors of the present survey are aware, methylstibonic acid has never been described in the chemical literature. Other compounds containing a single Me-Sb(V) bond are known, and it is possible that one of these was obtained from Meinema and used in this investigation. Alternatively, Meinema and Noltes may have prepared but not reported methylstibonic acid. At any rate it would seem from the results reported in this investigation that compounds containing the Me-Sb bond occur in trace amounts in many natural waters.

Trialkystibine imides have been prepared by the interaction of trialkylstibines and arenesulfonyl azides in diethyl ether [70]:

$$R_3Sb + ArSO_2N_3 \xrightarrow{20^\circ C} R_3Sb{=}NSO_2Ar + N_2$$

(where R was Et or Pr and Ar was Ph or $4\text{-}MeC_6H_4$)

The antimony-nitrogen bonds of the imides were readily cleaved by acids:

$$R_3Sb{=}NSO_2Ar + 2\ HX \longrightarrow R_3SbX_2 + ArSO_2NH_2$$

(where X was Cl, $MeCO_2$, or $PhCO_2$)

The imides reacted in a similar manner with 2,2,3,3,4,4,5,5-octafluoro-1-pentanol:

$$Pr_3Sb{=}NSO_2Ar \;+\; 2\,H(CF_2)_4CH_2OH \longrightarrow Pr_3Sb[OCH_2(CF_2)_4H]_2 \;+\; ArSO_2NH_2$$

Treatment of the imides with aromatic aldehydes yielded trialkylstibine oxides:

$$R_3Sb{=}NSO_2Ph \;+\; 4\text{-}MeOC_6H_4CHO \longrightarrow R_3SbO \;+\; 4\text{-}MeOC_6H_4CH{=}NSO_2Ph$$

The interaction of the imides and tin tetrahalides also resulted in cleavage of the antimony-nitrogen bonds:

$$R_3Sb{=}NSO_2Ar \;+\; SnX_4 \longrightarrow R_3SbX_2 \;+\; ArSO_2N{=}SnX_2$$

(where X was Cl or Br)

Three Sb(V) organoantimony compounds containing peroxide groups have been reported in the Russian chemical literature [71]. The compounds were $Ph_3Sb(OOCMe_3)_2$, $Ph_3Sb(OOCMe_2C_6H_4CHMe_2\text{-}p)_2$, and $[Ph_3Sb(OOCMe_3)]_2O$. The reactions for the preparation of these compounds involved the treatment of triphenylstibine with the appropriate hydroperoxide. Thus, treatment of triphenylstibine with *tert*-butyl hydroperoxide gave $Ph_3Sb(OOCMe_3)_2$; small amounts of the compound $[Ph_3Sb(OOCMe_3)]_2O$ were formed as a by-product. The reaction was carried out under a variety of conditions in order to obtain a maximum yield of the first compound. A mechanism for the reaction was suggested.

The two compounds $Ph_3Sb(OOCMe_3)_2$ and $[Ph_3Sb(OOCMe_3)]_2O$ were quite unstable. The first compound decomposed in the air in a few hours, the the second compound was stable for 2-3 weeks. The chemical structures of the decomposition products were not determined. An X-ray diffraction study of the two reaction products established their structure. The antimony atom in both compounds was that of a distorted trigonal bipyramid. The Sb-O-Sb angle in the second compound was linear, a fact which suggested to the authors that the unshared electrons on the oxygen atom overlapped vacant d-orbitals of the antimony. A shortened Sb-O distance was in agreement with this suggestion.

The reaction of trimethylantimony dibromide with carboxylic acids, amides, or oximes in benzene solution, and in the presence of triethylamine, led to the formation of trimethylantimony dicarboxylates, diamides, or dioximates [72]. The carboxylic acids used in this study were $PhCH_2CO_2H$, $PhCH{=}CHCO_2H$, $MeCH{=}CHCO_2H$, and HCO_2H; the amides included succinimide and three benzimidazole derivatives; the oximes were $RR'C{=}NOH$, where R = R' = Me, R = Me, R' = Et, and R = Me, R' = p-$NO_2C_6H_4$. All of the products were monomeric by cryoscopic molecular weight determinations in benzene and were non-electrolytes in acetonitrile. Both IR and PMR data on the products were reported. Results of studies on the insecticidal and antibacterial properties of the new compounds were also given.

A series of dioximates of the type $R_3Sb(ON{=}CR'R'')_2$, where R = Ph, p-MeC_6H_4, or Me, and R' and R" = H, aryl, alkyl, or similar groups, have been prepared by Bajpai and Srivastava [73]. Several different reactions were employed for the preparation of these compounds. In one case the oxime and a triarylantimony dihalide (bromide or chloride) were refluxed in benzene solution in the presence of triethylamine. For the preparation of the trimethyl compounds $Me_3Sb(ON{=}CR'R'')_2$, trimethylantimony dimethoxide and the oxime were refluxed in benzene. All of the compounds were crystalline solids and possessed definite melting points. They were characterized by elemental analyses, IR, and PMR spectra. The Sb-O bond in these compounds was cleaved by $PhTeCl_3$ or $TeCl_4$ to yield the corresponding dihalides, R_3SbCl_2. The Sb-O bond, however, was not cleaved by methanol or by CS_2.

Similar compounds of the type $R_3Sb(ON{=}CR'R'')_2$ have been reported by Jain and coworkers [74]. In these compounds R was Me or Et and R' and R" were either two alkyl groups or R' was alkyl and R" was an aryl group. One additional compound, $Me_3Sb[ON{=}CPh(NH_2)]_2$, was also prepared. All of the compounds were synthesized from trimethyl- or triethylantimony dibromide and the sodium salt of the oxime:

$$R_3SbBr_2 \;+\; 2\ NaON{=}CR'R'' \longrightarrow R_3Sb(ON{=}CR'R'')_2 \;+\; 2\ NaBr$$

The reactions were carried out in refluxing benzene and, except for the compound $Me_3Sb[ON{=}CPh(NH_2)]_2$, all of the compounds were purified by distillation under reduced pressure. Of the nine compounds prepared three were crystalline solids with sharp melting points, while six of the compounds were liquids at room temperature.

Both PMR and IR spectral data were reported for these compounds. Assignments of bands in the IR spectra were generally similar to those reported in the previous paper with one marked exception. In the present paper ν_{as} Sb-O was assigned to a band in the 290–335 cm^{-1} region, whereas Bajpai and Srivastava [73] assigned this mode to a strong band occuring in the region 430 to 500 cm^{-1}. The IR spectrum of the compound $Me_3Sb[ON{=}CPh(NH_2)]_2$ was of some interest. The solid-state spectrum of this compound gave two bands of equal intensity at 1615 cm^{-1} and 1600 cm^{-1}, assigned to ν C=N. From this observation the authors concluded that the antimony atom was six-coordinate with one nitrogen of an oxime bonded to the antimony. This conclusion was supported by the presence of a weak band at 275 cm^{-1} which was assigned to ν Sb-N. This band, as well as the C=N doublet, was not observed in chloroform solution. In the PMR spectra of the compounds where R' = R" = Me, signals due to the methyl protons occurred as doublets. Similarly in the compounds where R' = R" = Et, signals due to the methyl protons were observed as sextets, and those from the methylene protons as octets. These effects were attributed to the non-linearity of the C=N-O group.

Compounds of the type o-$R'N{=}CRC_6H_4OSb(Cl)Ph_3$ (where R = H, R' = Me, Et, Pr, Bu, Ph, or *p*-tolyl, and R = Me, R' = Me, Bu, or CH_2CHMe_2) have been synthesized by Jain and coworkers [75]. The reaction involved the condensation of one equivalent of Ph_3SbCl_2 with one equivalent of the sodium salt of the *o*-hydroxy Schiff base; o-$NaOC_6H_4CR{=}NR'$. In a similar manner the reaction of one equivalent of $Ph_3Sb(OMe)_2$ with one equivalent of the phenol, o-$HOC_6H_4CR{=}NR'$, gave the corresponding methoxy compound, o-$R'N{=}CRC_6H_4OSb(OMe)Ph_3$, where R = H, R' = Me or R = R' = Me. All of the compounds were yellow crystalline solids which were monomeric by cryoscopic molecular weight determinations in benzene solution. On the basis of IR and PMR spectra, the authors concluded that all of the compounds possessed octahedral geometry around the central atom (*i.e.* the nitrogen of the Schiff base was coordinated to the antimony atom) both in the solid state and in solution. Such geometry would lead to three different configurations of the molecule. A choice between these configurations could not be made on the basis of the spectral data.

Sonsale and coworkers [76] have studied the insertion of SO_2 into a series of chelated organtimony(V) compounds of the type Ph_3SbL_2, where LH was salicylaldehyde, a β-diketone, a 2-hydroxybenzophenone, benzoyl(phenyl)-hydroxylamine, 8-hydroxyquinoline, or dehydroacetic acid. One mole of SO_2 was inserted between a Ph group and the Sb atom to give an *O*-sulfinate of the type $PhSO_2SbPh_2L_2$. The mechanism of the insertion reaction and extrusion of SO_2 from the sulfinate compounds were discussed.

The ^{13}C NMR spectra of a series of pentacovalent antimony compounds of the type Ph_3SbX_2, where X = F, Cl, Br, I, or O_2CR (R = H, Me, Et, CH_2Cl, $CHCl_2$, $CH{=}CH_2$, or $C(Me){=}CH_2$), have been reported [77]. Both chemical shifts and aromatic J_{C-H} coupling constants were given. The largest ^{13}C chemical shift occurred for the C-1 atom. This chemical shift increased with an increase in the electronegativity of the halogen X, or with an increase in the strength of the acid RCO_2H. Also, for the halogen groups X, there was a linear dependence of the ^{13}C chemical shift of the C-2 and C-3 carbon atoms with an increase in the electronegativity of X. For the compound Ph_3SbF_2, the ^{19}F spectrum and J_{C-F} coupling constants were also reported.

Werner and coworkers [78] have investigated the reaction between trimethylantimony dichloride and antimony trichloride and between trimethylantimony dibromide and antimony tribromide. The reactions were carried out by mixing equimolar quantities of the reactants in methylene dichloride solution. On cooling the solutions, crystals of the complexes $Me_3SbX_2 \cdot SbX_3$ were obtained. In contrast to the reaction between Me_3SbCl_2 and $SbCl_5$, where an onium complex $[Me_3SbCl]SbCl_6$ was formed, the complexes formed from SbX_3 were non-ionic. An X-ray diffraction study of the crystals showed that each halogen of the Me_3SbX_2 molecule formed a halogen bridge, Sb-X-Sb, to an antimony of an SbX_3 molecule, and each SbX_3 molecule was thus linked to threee different Me_3SbX_2 molecules. Accordingly, the antimony of the Me_3SbX_2 possessed a coordination number of five, but the antimony of each SbX_3 molecule possessed a coordination number of six. A comparison of the Raman spectra of the complexes in the solid state and in methylene dichloride solution showed that the complexes were dissociated in solution.

Sau, Carpino, and Holmes [79] have reported previously that organic compounds of tin in which the central atom was pentacoordinate gave PMR spectra in which the signals of the *ortho* protons of the phenyl ring occurred at lower field than those of the *meta* and *para* protons. Sau and Holmes [80] have now examined the PMR spectra of a series of phenyl-substituted compounds of Si, Pb, P, As, Sb, S, Te, and I, in which the central atom was pentacoordinate. The organoantimony compounds examined were Ph_3SbCl_2, $Ph_3Sb(O_2CMe)_2$, and $Ph_3Sb(O_2CC_6H_4CO_2Me\text{-}o)_2$. In the PMR spectra of all of the pentacoordinate compounds of the above elements, signals for the *ortho* protons occurred as multiplets at lower fields than the multiplets assigned to the *meta* and *para* protons. These two groups of signals occurred with an intensity ratio of 2:3. The authors suggested, therefore, that this splitting pattern is diagnostic for the presence of the pentacoordinate (or hexacoordinate) state of the main group element in solution. Since many derivatives of Group IIIA, IVA, and VA, nominally exhibiting tri- or tetacoordination, are actually pentacoordinate (as revealed by X-ray analysis), and some Group VA compounds, which might be expected to be pentacoordinate, actually exist as tetracoordinate "onium" salts in solution and in the solid state, this observation of Sau and Holmes is of considerable importance in the chemistry of pentacoordinate compounds of the main group elements.

Making use of IR and Raman spectra reported by other workers for the four triphenylantimony dihalides Ph_3SbX_2, where X was F, Cl, Br, or I, Natarajan and Chockalingam [81] have calculated force constants, mean amplitudes of vibration, generalized mean-square amplitudes of vibration, shrinking constants, Coriolis coupling coefficients, and centrifugal distortion constants for these compounds. The results were given in tabular form. A number of trends were observed. For example, there was a decrease in the force constants in going from Me_3SbF_2 to Me_3SbI_2 due to a variation in the electronegativity of the halogen. A large decrease in the axial stretching force constants, also in going from Me_3SbF_2 to Me_3SbI_2, was attributed to the large differences in the masses of the halogens.

Pentavalent organic compounds of the type Bu_3SbY_2, where Y was the laurate or octyl maleate group, have been used as heat stabilizers for halogen-containing resin compositions [82].

Meyer and coworkers [83] have synthesized $[Me_3SbCH_2CH_2OH]^+$, the antimony analog of choline, for use in biochemical studies. The synthesis involved the reaction between trimethylstibine and 2-iodoethanol in diglyme solution in a sealed tube at 90° for 16 hours. The product (termed Sb-choline iodide) was obtained as colorless crystals (admixed with a small amount of yellow solid). It was purified by extraction with water and subsequent lyophilization of the aqueous solution. Both PMR and IR spectra of the resulting white powder were in accord with the assigned structure. For elemental analysis the iodide was converted to the tetraphenylborate which was recrystallized from acetone. An impurity was tentatively identified as $Me_3Sb(OH)_2$ from its PMR and IR spectra. For further studies on Sb-choline, the iodide was converted to the chloride by means of an ion-exchange column. The acetyl derivative of this was prepared by acetylation with acetic anhydride. Neutron activation of the chloride gave labelled ^{122,124}Sb-choline, but 83% of the starting material was destroyed by the process.

It was found that the Sb-choline was a substrate for choline kinase and that this enzyme could be readily used for the assay of the Sb-choline. The procedure involved incubation of the Sb-choline, choline kinase, and [^{32}P]ATP in a buffered solution containing magnesium chloride. It was concluded that Sb-choline was 100% phosphorylated by this procedure, whereas acetyl Sb-choline was phosphorylated only after hydrolysis. It was predicted that the Sb-choline and the acetylated derivative should be useful, not only as readily assayable cholinergic analogs for biochemical studies, but as excellent substrates for X-ray microanalytical localization in cell structures.

Four organoantimony compounds containing titanium have been prepared by Sharma and coworkers [84]. Tetraphenylstibonium chloride was found to react with titanium tetrachloride to give either $[Ph_4Sb][TiCl_5]$ or $[Ph_4Sb]_2[TiCl_6]$. The former compound was prepared from equimolar quantities of the reactants; the latter compound was obtained with the stibonium chloride in excess. Both reactions were carried out in benzene solution in a nitrogen atmosphere. The first compound was a 1:1

electrolyte with a molar conductance value of 17.7 mhos cm^2 mol^{-1} in nitrobenzene, but the second compound was too insolube in polar solvents for its conductance to be measured. A compound $Ph_3SbCl_2:TiCl_4$ was obtained from Ph_3SbCl_2 and $TiCl_4$ in benzene. Owing to its insolubility in organic solvents, it was believed to be polymeric. The fourth compound prepared was $Ph_3SbCl_2 \cdot TiCl_3$, obtained from triphenylstibine and $TiCl_4$. Magnetic susceptibilities, IR and UV spectra, and elemental analyses were reported for the four compounds.

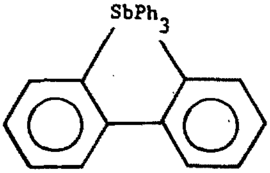
It has been found that $Ph_4SbO_2CCl_3$ decomposed with loss of CO_2 to yield Ph_4SbCCl_3, Ph_4SbCl, and dichlorocarbene [85]. In addition to these decomposition products Ph_4SbOCO_2H was formed. When the latter was treated with MeI or $PhCH_2Cl$, Ph_4SbI or Ph_4SbCl was eliminated with the formation of MeOH or $PhCH_2OH$, respectively. Treatment of Ph_4SbOCO_2H with $BrCH_2CH_2Br$ or $ClCH_2CH_2Cl$ under similar conditions give ethylene carbonate. When $BrCH_2CH_2CH_2Br$ was used, the corresponding six-membered ring was obtained.

Peregudov and coworkers [86] have studied the ^{19}F NMR spectra of mixtures of p-$FC_6H_4CO_2H$ with compounds of the type p-$FC_6H_4CO_2M$, where M was PhHg , Ph_3Pb, Ph_3Sn, Ph_2Sb, and Ph_4Sb. Also studied were mixtures of two such p-$FC_6H_4CO_2M$ compounds. The spectra were determined in $CHCl_3$ or pyridine solution, and only a single ^{19}F signal was found for each mixture. This suggested that exchange of H and an M group or an exchange between two M groups occurred in solution. The ability to exchange increased in the order Ph_3Sn, $Ph_3Pb < Ph_2Sb <$ PhHg, Ph_4Sb.

Onium compounds of the type $[C_6T_5EPh_3]BF_4$ (where E was a Group V element) have been prepared by reaction of the cation $C_6T_5^+$ with Ph_3E [87]. The cation $C_6T_5^+$ was prepared by the β-cleavage of C_6T_6. The yield of $[C_6T_5SbPh_3]BF_4$ was 30.9%.

The gas phase HeI photoelectron spectra of Me_5Sb, Me_3SbCl_2, Me_3SbBr_2, Me_3SbI_2, and $SbCl_5$ have been reported and studied by Elbel and Dieck [88]. They have concluded that all of these compounds possessed a D_{3h} structure by comparison with the photoelectron spectra of Me_3Sb and $SbCl_3$. The highest molecular orbital of Me_5Sb had non-bonding character, and d-orbital participation was excluded. For comparison, the photoelectron spectra of the Group V compounds $TaMe_5$, $TaCl_5$, and $NbCl_5$ were given.

Millington and Sowerby [89] have determined the crystal structure of 5,5-dihydro-5,5,5-triphenyl-5H-dibenzostibole (named biphenyl-2,2'-diyltriphenylantimony by the authors):



The structure of the compound was of interest, since pentaphenylantimony unexpectedly possesses square pyramidal geometry around the antimony atom. The above heterocyclic antimony compound showed slightly distorted trigonal-bipyramidal geometry about the central atom. Two phenyl groups were in equatorial positions and one phenyl group in axial position; the biphenyl group spanned an axial and an equatorial position. The C_{axial}-Sb-C_{axial} angle was 170.8°. The five-membered ring was planar, and hence the sum of its angles was 540°.

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