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# Antimony: annual survey covering the year 1992

Leon D. Freedman and G.O. Doak

*Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204 (USA)*

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Only two reviews devoted exclusively to antimony compounds were published in 1992. One of these was our Annual Survey covering the year 1990. The other was an interesting account by Huang of work (mainly from his own laboratory) on synthetic applications of organoantimony compounds [1]. Antimony derivatives have also been mentioned in two annual surveys of organometallic reagents in synthetic chemistry [2] and in reviews on the structure and biological activity of arsenic compounds [3] and on the chemistry of diphosphenes and their heavier congeners [4].

Primary and secondary neopentylstibines have been prepared in 57–58% yields by the lithium aluminum hydride reduction of the corresponding dibromo- and iodostibines, respectively [5]:

$$Me_3CCH_2SbBr_2 \xrightarrow[\text{tetraglyme, } 0^\circ C]{LiAlH_4} Me_3CCH_2SbH_2$$

$$(Me_3CCH_2)_2SbI \xrightarrow[Et_2O,\ -50^\circ C]{LiAlH_4} (Me_3CCH_2)_2SbH$$

The required dibromostibine was obtained in 81% yield by the following redistribution reaction:

$$(Me_3CCH_2)_3Sb + 2SbBr_3 \xrightarrow{140^\circ C} 3Me_3CCH_2SbBr_2$$

Reduction of neopentyldichlorostibine or dineopentylchlorostibine with lithium aluminum hydride yielded little or no isolable primary or secondary stibine. Both of these stibines were colorless, volatile liquids and were soluble in hydrocarbons and ethers. The vapor pressure of the secondary stibine was 0.5 Torr at 24°C, while the vapor pressure of the more volatile primary stibine was 5.5 Torr at 0°C. Both compounds were non-pyrophoric in small quantities but turned to white solids when exposed to air. They exhibited surprising stability at ambient temperatures in the absence of light. Thus, the primary stibine showed no darkening or formation of noncondensable gas when stored under vacuum for two months; the secondary stibine remained unchanged when stored under argon for three months. A blackening of the walls of a tube containing either of the stibines was observed, however, on exposure to fluorescent light for a period of at least two weeks. In the case of the secondary stibine, one photodecomposition product was shown to be tetraneopentyldistibine by NMR and X-ray crystallography. This substance presumably was formed by the following reaction:

$$2(Me_3CCH_2)_2SbH \longrightarrow (Me_3CCH_2)_2SbSb(CH_2CMe_3)_2 + H_2$$

The unusual stability of the primary and secondary stibines was attributed to the presence of large organic substituents that contained no $\beta$-hydrogens. The primary and secondary stibines were characterized by IR and NMR ($^1H$ and $^{13}C$) spectroscopy. The IR spectrum of each compound was dominated by a very intense absorption associated with the Sb–H stretch (1870 $cm^{-1}$ for the primary stibine in the gas phase and 1840 $cm^{-1}$ for the secondary stibine as a neat liquid). The $^1H$ NMR spectrum of the primary stibine exhibited a singlet at $\delta$ 0.86 for the methyl groups, while the methylene protons and the protons bonded to the antimony atom appeared as triplets at $\delta$ 1.62 and $\delta$ 1.70, respectively. The $^1H$ NMR spectrum of the secondary stibine showed a singlet at $\delta$ 0.98 for the methyl groups, while the methylene protons and the antimony proton formed an AA′BB′X system. The signals for the two nonequivalent methylene protons

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Correspondence to: Prof. L.D. Freedman

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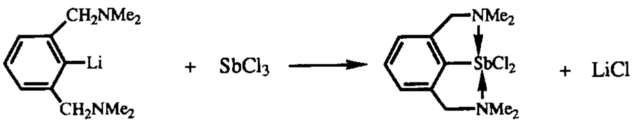
occurred at δ 1.28 and δ 2.03; the antimony proton resonance gave rise to a quintet at δ 2.13. The $^{13}C$ NMR spectra of both compounds showed the expected three resonances. A preliminary evaluation was reported of the potential of these substances as metal organic chemical vapor deposition (MOCVD) precursors. This study showed that both compounds could be used with trimethylindium to deposit thin films of indium antimonide (InSb) at comparatively low temperatures (350°C for the primary stibine and 400°C for the secondary stibine). The primary stibine appeared particularly attractive because of its high volatility and low decomposition temperature. These characteristics were considered of especial importance in growing ternary antimonides and metastable antimony-based materials.

A chelated dichlorostibine has been obtained as a colorless solid in 56% yield by means of the following reaction [6]:



The composition of this substance was established by high-resolution mass spectral data, and its structure was determined by X-ray crystallography. In the solid state, the dichlorostibine was found to consist of individual molecules with no short intermolecular contacts. The geometry at the antimony atom was best described as distorted square-pyramidal. The Cl–Sb–Cl angle (174.0°) was relatively close to the ideal angle of 180°. The N–Sb–N angle, however, was significantly more acute (147.3°), presumably because the nitrogen atoms were incorporated into five-membered rings. The Sb–N distances (2.491 and 2.422 Å) were considerably greater than the sum of the single bond covalent radii (2.16 Å); this fact was believed to be consistent with the idea of internal solvation of the antimony by the amino groups. Further information about this study is given in the Annual Survey of Bismuth for 1992.

The synthesis of (pentamethylcyclopentadienyl)dichlorostibine by the following reaction was first reported in 1990 [7]:

$$\mathrm{Me_5C_5Li + SbCl_3 \xrightarrow[0^\circ C]{Et_2O} Me_5C_5SbCl_2 + LiCl}$$

The solid-state structure of this substance has now been examined by X-ray crystallography [8]. In each $Me_5C_5SbCl_2$ unit, the pentamethylcyclopentadienyl ligand was found to be in a $\eta^3$-bonded state with a short Sb–C bond (2.254 Å) and two longer Sb–C bonds (2.595 and 2.620 Å). It should be noted that even the "short" Sb–C bond was somewhat longer than the normal Sb–C σ-bond distance of 2.169 Å reported for trimethylstibine. The distance from the antimony atom to the center of the ring was 3.36 Å. Menshutkin-type interactions between the $Me_5C_5SbCl_2$ units resulted in additional Sb–ring contacts and were responsible for the fact that the compound crystallized in the form of an asymmetric polydecker sandwich. This additional π-bonding between each ring and a neighboring antimony atom was weaker than the π-bonding within each $Me_5C_5SbCl_2$ unit and was of the $\eta^2$-type. The Sb–C distances associated with the Menshutkin-type interactions ranged from 3.43 to 3.66 Å.

X-ray diffraction at −120°C has been employed to determine the structures of the phenyldihalostibines $PhSbX_2$, where X was Cl, Br, or I [9]. The compounds were prepared by the following reactions:

$$\mathrm{Ph_3Sb + 2SbCl_3 \xrightarrow[reflux]{Et_2O} 3PhSbCl_2}$$

$$\mathrm{3PhSbCl_2 + 2PBr_3 \longrightarrow 3PhSbBr_2 + 2PCl_3}$$

$$\mathrm{PhSbCl_2 + 2NaI \xrightarrow{HCl} PhSbI_2 + 2NaCl}$$

If intermolecular interactions were ignored, the antimony atoms in the three dihalostibines could be considered trigonal-pyramidally coordinated with bond angles ranging from 93° to 98°. The C–Sb distances were 215 pm for $PhSbCl_2$, 216 pm for $PhSbBr_2$, and 214 pm for $PhSbI_2$; the Sb–Cl distances were 241 and 238 pm, the Sb–Br distances were 256 and 253 pm, and the Sb–I distances were 275 and 274 pm. The molecules of each dihalostibine were associated two-dimensionally by a moderately eccentric $\eta^3$-Sb ··· phenyl interaction and two Sb ··· X contacts per molecule. The coordination geometry of each antimony atom could be described as distorted octahedral when these intermolecular interactions were taken into account. The crystal structures were said to represent a variant of the bismuth(III) iodide type.

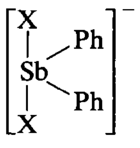
Four phenylhaloantimonates(III) have been prepared by the following types of reactions [10]:

$$\mathrm{Ph_2SbX + [Ph_4P]X \xrightarrow{EtOH} [Ph_4P][Ph_2SbX_2]}$$

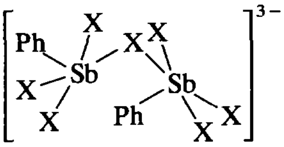
$$\mathrm{2PhSbX_2 + 3[Me_3NH]X \xrightarrow{EtOH} [Me_3NH]_3[Ph_2Sb_2X_7]}$$

(where X was Cl or Br)

The structures of these substances were established by single crystal X-ray diffraction. The $Ph_2SbX_2^-$ anions were shown to display Ψ-trigonal-bipyramidal structures with axial Sb–Cl distances of 2.618 and 2.601 Å and Sb–Br distances of 2.779 and 2.794 Å:



Each $Ph_2Sb_2X_7^{3-}$ anion contained two square-pyramidal coordination polyhedra, which were linked to one another via an Sb–Cl–Sb angle of 152.9° or an Sb–Br–Sb angle of 152.3°:



The $Ph_2Sb_2Br_7^{3-}$ anion was found to exhibit crystallographic $C_2$ symmetry. In both trinegative anions, the Sb–X distance involving the bridging halogen atom was much longer (by 0.59 Å for $Ph_2Sb_2Cl_7^{3-}$ and 0.50 Å for $Ph_2Sb_2Br_7^{3-}$) than the Sb–X distance involving the halogens *trans* to the bridging atom.

A study has been made of the preparation and properties of a number of new organoantimony compounds containing three or more Sb–Sb bonds [11]. The dehalogenation of isopropyldibromostibine with magnesium in THF was found to give a yellow solution that contained (according to PMR and mass spectral studies) pentaisopropylpentastibolane together with a much smaller amount of tetraisopropyltetrastibetane:

$$Me_2CHSbBr_2 + Mg \longrightarrow 1/n(Me_2CHSb)_n + MgBr_2$$

(where $n$ was 4 or 5)

Although air-sensitive, the cyclic compounds in solution were stable in an inert atmosphere at room temperature for several days. At higher temperatures or at room temperature after a long time, they decomposed to form tetraisopropyldistibine, triisopropylstibine, and antimony. Attempts to crystallize the cyclic compounds led to polymerization, and a black solid $(Me_2CHSb)_x$ was obtained. $^1H$ NMR data suggested that the isopropyl substituents in both cyclic compounds adopted a maximum of *trans* positions. The dibromostibine required for the above synthesis was obtained in quantitative yield by the following reaction:

$$(Me_2CH)_2SbBr + SbBr_3 \longrightarrow 2Me_2CHSbBr_2$$

A second tetrastibetane was also prepared by the dehalogenation of a dihalostibine in THF:

$$4(Me_3Si)_2CHSbCl_2 + 4Mg \longrightarrow [(Me_3Si)_2CHSb]_4 + 4MgCl_2$$

The crude product was crystallized from a mixture of petroleum ether and benzene to yield red-orange crystals melting at 130–133°C. These crystals were soluble in hydrocarbons, stable in air for a short time, and very sensitive to oxygen in solution. The tetrastibetane exhibited a remarkable thermal stability. Thus, no decomposition was observed after the compound was heated in benzene for 2 days at 100°C in a sealed glass tube or in the melt at 160°C. The PMR spectrum in $C_6D_6$ at 360 MHz suggested that the compound had an all-*trans* configuration in which all the substituents on the ring were equivalent. The structure of the substance was shown by single-crystal X-ray diffractometry to possess a strongly folded four-membered ring with an all-*trans* configuration. The Sb–Sb bonds alternated between short (2.82 Å) and long (2.87 Å) distances, and the molecule on the whole approximated $C_2$ symmetry. The molecules were isolated from one another, and the shortest intermolecular distance between antimony atoms was 8.20 Å. A $^1H$ NMR study was conducted in $C_6D_6$ of the reactions of the pentastibolanes $(EtSb)_5$ and $(PrSb)_5$ and the tetrastibetanes $(Me_3CSb)_4$, $[(Me_3Si)_2CHSb]_4$ and $(2,4,6\text{-}Me_3C_6H_2Sb)_4$ with the distibines $Me_2SbSbMe_2$, $Et_2SbSbEt_2$, and $Ph_2SbSbPh_2$. The following types of equilibria were observed:

$$5Me_2SbSbMe_2 + (RSb)_5 \rightleftharpoons 5Me_2SbSb(R)SbMe_2$$

(where R was Et or Pr)

$$4Me_2SbSbMe_2 + (RSb)_4 \rightleftharpoons 4Me_2SbSb(R)SbMe_2$$

(where R was $Me_3C$, $(Me_3Si)_2CH$, or $2,4,6\text{-}Me_3C_6H_2$)

$$5Et_2SbSbEt_2 + (RSb)_5 \rightleftharpoons 5Et_2SbSb(R)SbEt_2$$

(where R was Et or Pr)

$$2Ph_2SbSbPh_2 + 3/5(EtSb)_5 \rightleftharpoons Ph_2SbSb(Et)SbPh_2 + Ph_2SbSb(Et)Sb(Et)SbPh_2$$

Attempts to isolate any of the products formed in these reactions were unsuccessful even at low temperatures. In the presence of an excess of the corresponding distibines, however, the tristibines formed stable yellow solutions in benzene or other organic solvents and could be easily handled in an inert atmosphere. The following equilibrium constants were determined from the intensities of the $^1H$ NMR signals:

$$K = \frac{[Me_2SbSb(R)SbMe_2]^5}{[Me_2SbSbMe_2]^5[(RSb)_5]}$$

(where R was Et, $K$ was 120; where R was Pr, $K$ was 46)

$$K = \frac{[Me_2SbSb(R)SbMe_2]^4}{[Me_2SbSbMe_2]^4[(RSb)_4]}$$

(where R was $Me_2CH$, $K$ was 3; where R was $(Me_2Si)_2$-CH, $K$ was 1)

It seemed clear that tristibine formation was favored by sterically less demanding groups. Pentamethyltristibine was formed by the reduction of a mixture of dimethylbromostibine and methyldibromostibine with magnesium in THF:

$$2Me_2SbBr + MeSbBr_2 + 2Mg \longrightarrow Me_2SbSb(Me)SbMe_2 + 2MgBr_2$$

This reaction had to be carried out in the presence of a large excess of dimethylbromostibine and magnesium. These conditions led to the concomitant formation of tetramethyldistibine, the presence of which was necessary to stabilize the tristibine. Removal of the distibine from the reaction product resulted in the formation of the black solid polymer $(MeSb)_x$ even at low temperatures. Attempts were made to prepare pentaphenyltristibine by the following type of reaction in liquid ammonia:

$$2Ph_2SbM + PhSbCl_2 \longrightarrow Ph_2SbSb(Ph)SbPh_2 + 2MCl$$

(where M was Li or Na)

A brown powder containing this tristibine was obtained, but it decomposed to yield tetraphenyldistibine and polymeric $(PhSb)_x$.

The interaction of the cyclic compounds $(EtSb)_n$ and $(PrSb)_n$, where $n$ was 4 or 5, in benzene at room temperature has been found to yield mixed species [12]:

$$(EtSb)_n + (PrSb)_n \rightleftharpoons Et_{n-m}Pr_mSb_n$$

(where $n$ was 4 and $m$ was 1, 2, or 3; or where $n$ was 5 and $m$ was 1, 2, 3 or 4)

The mixed species in the reaction mixture were detected both by $^1H$ NMR and mass spectroscopy. The $^1H$ NMR spectra in $C_6D_6$ showed additional sharp multiplet signals immediately after solutions of the reactants were mixed, but these signals were too complex for a detailed analysis. The mixed species were, however, easily detected in the mass spectra of the reaction mixture and included the trimers $Pr_2EtSb_3$ and $PrEt_2Sb_3$, the tetramers $Pr_3EtSb_4$, $Pr_2Et_2Sb_4$, and $PrEt_3Sb_4$, and the pentamers $Pr_4EtSb_5$, $Pr_3Et_2Sb_5$, $Pr_2Et_3Sb_5$, and $PrEt_4Sb_5$. $^1H$ NMR spectroscopy was used to determine the equilibrium constant of the following reaction in $C_6D_6$ at room temperature:

$$4(EtSb)_5 \rightleftharpoons 5(EtSb)_4$$

The relative intensities of the $^1H$ NMR signals of the tetramer and the pentamer showed that $K = 9 \times 10^{-8}$ mol/l. A mixture of cyclic compounds corresponding to the formula $(4\text{-}MeC_6H_4Sb)_n$ has been obtained by the following sequence of reactions:

$$4\text{-}MeC_6H_4SbCl_2 + 2Mg + 2Me_3SiCl \longrightarrow 4\text{-}MeC_6H_4Sb(SiMe_3)_2 + 2MgCl_2$$

$$4\text{-}MeC_6H_4Sb(SiMe_3)_2 + 1/2O_2 \longrightarrow 1/n(4\text{-}MeC_6H_4Sb)_n + (Me_3Si)_2O$$

The silylstibine was obtained as a yellow oil that ignited spontaneously on paper. The oxidation of this substance was best carried out in THF or toluene by allowing a very slow access of air during the course of several days. Under these conditions, the cyclic material was formed in a 26% yield as yellow air-stable crystals of empirical formula $C_7H_7Sb$. The crystals were too small to be analyzed by X-ray crystallography. The molecular ion of the pentamer $(4\text{-}MeC_6H_4Sb)_5$ appeared at highest mass in the mass spectrum. In addition, signals of fragments of the pentamer as well as signals of the tetramer and trimer were also present. Further information was obtained from the $^1H$ NMR spectra of the yellow benzene solutions of carefully purified samples of the crystalline material. It was concluded that a saturated solution contained 88% of the $4\text{-}MeC_6H_4Sb$ groups in the pentameric form and only 12% in other ring forms. Presumably, there existed equilibria in benzene solution between several cyclic compounds.

A study has been made of the interaction of diselenides or ditellurides with tetramesityltetrastibetane, the polymeric $(EtSb)_x$, tetramethyldistibine, or tetraethyldistibine [13]. The reaction of tetramesityltetrastibetane with di-4-tolyl ditelluride yielded the ditelluro compound as the major product:

$$1/4(MesSb)_4 + (4\text{-}MeC_6H_4Te)_2 \xrightarrow{C_6D_6} (4\text{-}MeC_6H_4Te)_2SbMes$$

(where Mes was $2,4,6\text{-}Me_3C_6H_2$)

This conclusion was based on the PMR and mass spectral analysis of the reaction mixture. The formation of compounds of the type $MesSb(ER)_2$ was not observed, however, when E was Se and R was Me or when E was Te and R was Me or Ph. Preparatively useful results could be obtained with the polymeric $(EtSb)_x$:

$$1/x(EtSb)_x + REER \xrightarrow{C_6D_6} EtSb(ER)_2$$

(where ER was SeMe, SePh, TeMe, TePh,
or $TeC_6H_4Me\text{-}4$)

The above two selenium-containing products were identified by comparison with authentic samples. For the ditellurostibines, the identification was based mainly on $^1H$ NMR spectral data. The phenyltelluro compound was isolated in 78% yield as red-orange crystals, which were air-sensitive in solution. Solutions in cyclohexane were orange or yellow. Diffuse reflection spectra showed an 80 nm red shift of the absorption edge from the saturated solution in cyclohexane (maxima at 374 and 430 nm) to the solid (maxima at 324, 438, and 510 nm). Similar shifts have previously been observed in the spectra of thermochromic distibines. Tetramethyldistibine and tetraethyldistibine reacted as neat liquids with diphenylditelluride in the following manner:

$$R_2SbSbR_2 + PhTeTePh \longrightarrow 2R_2SbTePh$$

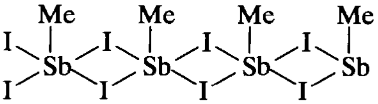
(where R was Me or Et)

The products were obtained as orange-yellow liquids in quantitative yield. They were characterized by $^1$H NMR and mass spectroscopy.

A yellow adduct previously obtained by the interaction of two mol of tetramethylstibonium iodide and one mol of methyldiiodostibine has been shown by X-ray crystallography to be bis(tetramethylstibonium)-tetraiodomethylantimonate(III) [14]:

$$2Me_4SbI + MeSbI_2 \longrightarrow [Me_4Sb]_2[MeSbI_4]$$

This substance was found to contain tetrahedral cations and square-pyramidal anions with Sb–I distances ranging from 290 to 320 pm. The methyl group of the anion was at the apex of the pyramid, and the antimony atom was near the center of the square base. The coordination around the antimony could therefore be described as pseudo-octahedral. Methyldiiodostibine, like other compounds containing covalent Sb–I bonds, was also yellow. X-ray crystallography showed that it contained $MeSbI_2$ units that were associated via iodine bridges to form linear chains with alternating short (276–280 pm) and long (340–347 pm) Sb–I distances:



The coordination around the antimony was distorted tetragonal-pyramidal. Tetramethylstibonium iodide, which was colorless, was shown by X-ray crystallography to contain tetrahedral cations in a wurtzite-type structure with Sb ··· I contacts of 406 and 435 pm. When a solution of dimethyliodostibine in petroleum ether was sealed in a glass ampule and allowed to stand at −18°C for 3 days, the following sequence of reactions appeared to take place:

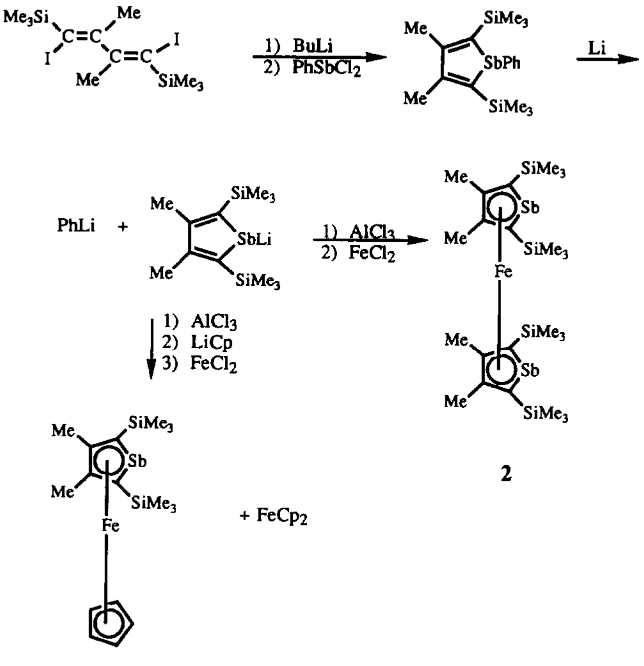
$$2Me_2SbI \longrightarrow Me_3Sb + MeSbI_2 \longrightarrow Me_3Sb \cdot MeSbI_2$$

The adduct was obtained in 30% yield as yellow crystals. Its composition was deduced from its elemental analysis and its mass spectrum, which exhibited molecular ions for trimethylstibine and methyldiiodostibine. PMR signals for the latter two substances were also detected in freshly prepared benzene solutions of the adduct. In a short time, however, it underwent a redox disproportionation to trimethylantimony diiodide and metallic antimony. The poor crystal quality of the adduct prevented the determination of its structure. It was suggested that the adduct was a donor-acceptor complex that was dimerized by iodine bridges. Another unstable adduct was prepared as a red liquid by the interaction of tetramethyldistibine and dimethylbromostibine:

$$Me_4Sb_2 + Me_2SbBr \longrightarrow Me_4Sb_2 \cdot Me_2SbBr$$

The red liquid slowly yielded yellow, needle-like crystals at room temperature. These crystals were thermochromic and (reversibly) became black when cooled with liquid nitrogen. The adduct readily decomposed in the solid state or in solution to yield trimethylstibine, trimethylantimony dibromide, and metallic antimony. The identity of the adduct was established by its synthesis and its mass spectrum, which showed the molecular ions of tetramethyldistibine and dimethylbromostibine. The PMR spectrum did not show sharp signals for the latter two substances but instead exhibited a very broad signal with a maximum at δ 0.9. This result suggested a rapid exchange of $Me_2Sb$ groups between the components of the adduct.

The monostibaferrocene **1** and the highly substituted distibaferrocene **2** have been prepared by the following scheme [15]:



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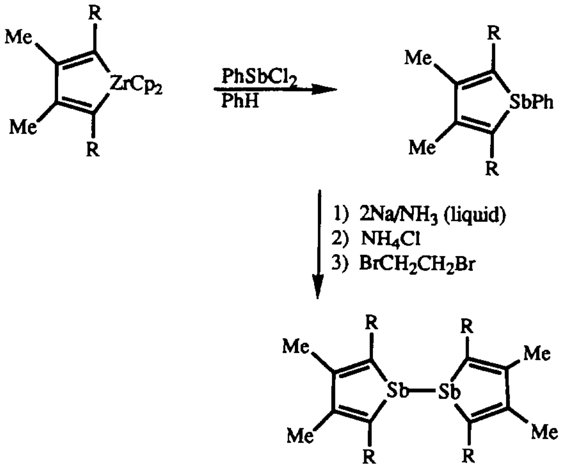
The monostibaferrocene **1** was obtained in 30% yield as dark red crystals, mp 132°C, after removal of the more volatile ferrocene $FeCp_2$ by sublimation (0.05 Torr, 60°C). The UV and PMR spectra of **1** were reported, and its exact mass was verified by electron-impact MS. The distibaferrocene **2** was obtained in 20% yield as dark red crystals, and its exact mass was also verified by electron-impact MS. X-ray diffraction of **2** showed that the molecule had a ferrocene-like structure in which the iron atom was sandwiched between two $\eta^5$-stibolyl rings. Each ring was rotated relative to the other so that its antimony atom eclipsed a carbon atom adjacent to the antimony atom of the second ring. This arrangement allowed the four bulky $Me_3Si$ groups to interlock in what was described as a gear-like manner. The four carbon atoms of each stibolyl ring lay in parallel planes 3.27 Å apart, while the antimony atoms were displaced out of these planes by 0.23 Å away from the iron atom. The inter-annular separation of the antimony atoms was 4.29 Å, a value comparable to the sum of the van der Waals radii (4.4 Å). A closer approach of the antimony atoms to one another was prevented by the bulky $Me_3Si$ groups, and there thus appeared to be no possibility of inter-annular Sb ··· Sb bonding. The conformational properties of **2** were further investigated by a study of its temperature dependent PMR spectrum in $CDCl_3$ or $CD_2Cl_2$ solution. At 30°C the PMR spectrum (300 MHz) of **2** consisted of a single $Me_3Si$ resonance ($\delta = 0.233$) and a single ring methyl resonance ($\delta = 2.061$). This result indicated that there was rapid ring rotation on the NMR time scale. At −40°C, however, two $Me_3Si$ signals ($\delta = 0.180$ and 0.265) and two ring methyl signals ($\delta = 2.103$ and 1.986) were obtained. Coalescence of both sets of signals occurred at −5°C; this observation allowed the $\Delta G^\ddagger$ for the ring rotation process to be estimated as $13.3 \pm 0.5$ kcal $mol^{-1}$. Further information about this study is given in the Annual Survey of Bismuth for 1992.

Two distibines have been synthesized by the following type of reaction sequence [16]:



(where R was Me or $Me_3Si$)

Both compounds exhibited the colors and behavior typical of nonthermochromic distibines. Thus, they were orange solids that melted to identically colored liquids and gave orange-yellow solutions. They were characterized by NMR ($^1H$ and $^{13}C$) and IR spectroscopy. Their bismuth analogs were also prepared and found to be thermochromic. This observation demonstrated for the first time that antimony and bismuth dipnictogen analogs could behave differently with regard to thermochromicity. Further information about this study is given in the Annual Survey of Bismuth for 1992.

The reaction of methylenebis(dichlorostibine) with sodium dithiocarbamates, xanthates, or dithiophosphates has been employed to prepare six new methylene-bridged organoantimony(III) compounds [17]:

$$CH_2(SbCl_2)_2 + 4NaL \xrightarrow[\text{r.t.}]{\text{MeOH}} CH_2(SbL_2)_2 + 4NaCl$$

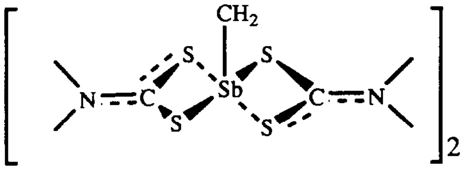
(where L was $S_2CNMe_2$, $S_2CNEt_2$, $S_2COEt$, $S_2CO\text{-}CHMe_2$, $S_2P(OMe)_2$, or $S_2P(OCHMe_2)_2$)

The dithiocarbamato and xanthato derivatives precipitated from the reaction mixtures in almost quantitative yield as white and yellow solids, respectively. The dithiophosphato derivatives were isolated after a series of purification steps as beige powders. All of the compounds were only slightly sensitive to hydrolysis and could therefore be handled in the air for a short time. Although they were almost insoluble at room temperature in polar solvents such as acetonitrile, acetone, and ethanol, they dissolved as monomers in dichloromethane and chloroform. The decomposition points ranged from 57°C, where L was $S_2P(OCHMe_2)_2$, to 197°C, where L was $S_2CNEt_2$. The dithiocarbamato and xanthato derivatives decomposed in accordance with the following equation:

$$CH_2[Sb(S_2CZ)_2]_2 \xrightarrow{\Delta} 2S[C(S)Z]_2 + 1/n[CH_2(Sb{=}S)_2]_n$$

(where Z was $NMe_2$, $NEt_2$, OEt, or $OCHMe_2$)

All six compounds were studied by IR, PMR, and $^{13}C$ NMR spectroscopy; in addition, $^{31}P$ NMR spectroscopy was used with the dithiophosphato derivatives. It was proposed that all of the ligands were bidentate. For example, the following type of structure was suggested for the dithiocarbamato derivatives:



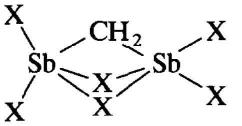
The spectral data and thermal stability of the compounds in this investigation were compared with the corresponding properties of monomethylstibines of the type $MeSbL_2$.

Complex onium salts have been obtained by the reaction of methylenebis(dichlorostibine) with quaternary compounds of nitrogen, phosphorus, arsenic, and antimony [18]:

$$CH_2(SbCl_2)_2 + 2R_4EBr \xrightarrow[\text{r.t. 2–3 h}]{CH_2Cl_2} [R_4E]_2[CH_2(SbBrCl_2)_2]$$

(where $R_4E$ was $Et_4N$, $Ph_4P$, $Ph_4As$, or $Ph_4Sb$)

The products precipitated as colorless, air-stable powders, which were quite soluble in polar organic solvents. Their thermal stability was relatively high; decomposition temperatures ranged from 115°C to 226°C. Conductivities in acetonitrile were in the range of 190–250 $cm^2\ \Omega^{-1}\ mol^{-1}$ and indicated that these salts were 1:2 electrolytes in this solvent. A study of their IR spectra suggested the following type of structure:

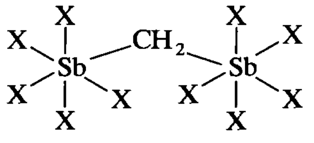


(where X was Br or Cl)

The spectral data, however, did not unequivocally show whether bromine atoms occupied bridge positions and led to a mixture of halogen bridges or a mixture of constitutional isomers. Even an X-ray structural analysis of the arsonium salt $[Ph_4As]_2[CH_2(SbBrCl_2)_2] \cdot MeCN$ did not allow the assignment of definite positions for the halogen atoms, but it did establish the triple-bridged structure of the complex anion. Oxidation of the four complex onium salts with bromine led to the formation of yellow or orange organoantimony (V) derivatives:

$$[R_4E]_2[CH_2(SbBrCl_2)_2] + 2Br_2 \xrightarrow[CH_2Cl_2/-78°C]{\text{exclusion of light}} [R_4E]_2[CH_2(SbBr_3Cl_2)_2]$$

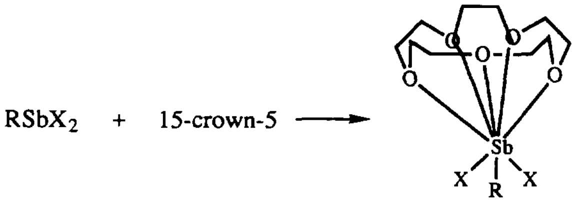
As solids, these substances could be handled in the air for a short time, but in solution they decomposed even at 0°C with loss of color. The IR spectra of these solids showed the absence of chlorine bridges and suggested the following octahedral type of structure:



(where X was Br or Cl)

No information was obtained about the specific positions of the bromine or chlorine atoms.

The interactions of 15-crown-5 and methyldibromostibine, methyldichlorostibine, or phenyldibromostibine in toluene solution at −40°C has been found to give almost quantitative yields of 1:1 adducts [19]:



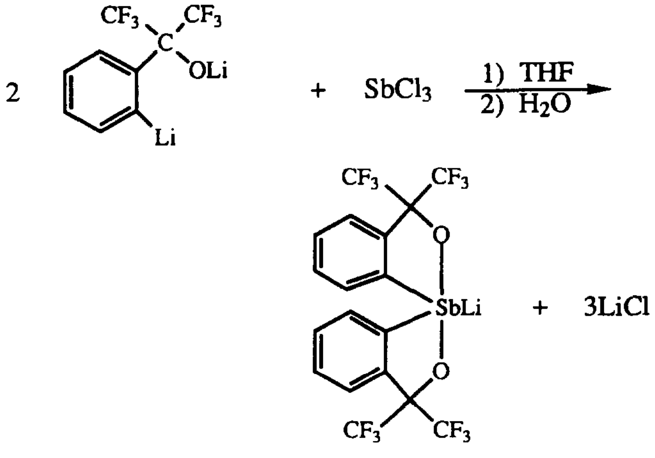
(where R was Me and X was Cl or Br; or where R was Ph and X was Br)

The adducts were colorless, moisture-sensitive crystals. The interaction of 15-crown-5 with the dihalostibines in acetonitrile led to the following type of exchange reaction:

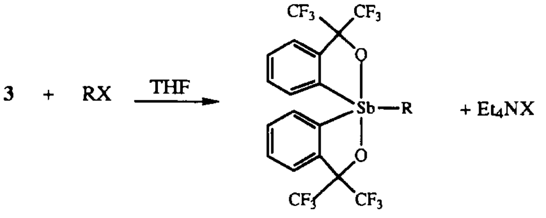
$$3RSbX_2 + 2\ \text{15-crown-5} \longrightarrow 2[SbX_3(\text{15-crown-5})] + R_3Sb$$

It was also noted that neither the tertiary stibines $R_3Sb$ nor the halostibines $R_2SbX$ formed isolable complexes with the crown ether. All three dihalostibine adducts were characterized by IR and $^{121}Sb$ Mössbauer spectroscopy. The two dibromostibine adducts were also studied by X-ray diffraction and were shown to possess molecular structures in which the antimony atoms were surrounded by eight ligands including the five oxygen atoms of the crown ether molecules. The Sb–O distances ranged from 281 to 335 pm and were thus significantly greater than the sum of the covalent radii (207 pm). The Sb–Br and Sb–C distances, however, were not unusual. The Mössbauer spectra of the three adducts exhibited isomers shifts that were distinctly more negative than those observed in the uncomplexed dihalostibines. This effect was attributed to the electron-donating ability of the crown ether and to a decrease in the X–Sb–X and the C–Sb–X angles on complexation.

An organoantimony ate complex of the 10 Sb-4 type has been obtained as a lithium salt in 41% yield by the following reaction [20]:



The corresponding tetraethylammonium salt (**3**) was prepared in 88% yield by reaction of the lithium salt with tetraethylammonium bromide in acetone, subsequent aqueous workup, and recrystallization from a mixture of acetone and ether. The ate complex was found to be remarkably stable towards both air and water. The room temperature $^{19}$F NMR spectrum of **3** exhibited a pair of quartets for the anisochronous pairs of trifluoromethyl groups. Furthermore, variable temperature $^{19}$F NMR measurements showed essentially no change in the band shape of the signals up to 150°C in DMSO-$d_6$. This result suggested high configurational rigidity for the anion, although it could be regarded as a five ligand system susceptible to Berry-type pseudorotation. X-ray structural analysis of **3** demonstrated that the anion had a distorted pseudo trigonal-bipyramidal structure with the oxygen atoms in the apical positions. In contrast, preliminary X-ray structural data on an analogous neutral 10-Sb-5 species (in which there was a chlorine in place of the lone pair) showed a structure much closer to the ideal trigonal-bipyramidal geometry. The reaction of **3** with various alkyl halides in THF was found to give high yields of the neutral 10-Sb-5 compounds **4**:



**4**

(where RX was MeI, $PhCH_2Br$, $CH_2{=}CHCH_2Br$, BuBr, or $EtO_2CCH_2Br$)

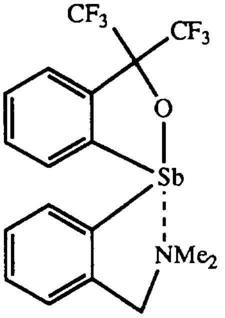
In the case of methyl iodide, the reaction took place instantaneously at room temperature; with the other alkyl halides, longer reaction times or higher temperatures were required. The pentavalent compounds also showed high configurational rigidity on the $^{19}$F NMR time scale. Surprisingly, the reaction of the ate complex **3** with organolithium reagents also gave, after workup, 10-Sb-5 compounds:

$$\mathbf{3} + RLi \xrightarrow{THF} \mathbf{4}$$

(where R was Me, Bu, 4-$MeC_6H_4$, or 4-$CF_3C_6H_4$)

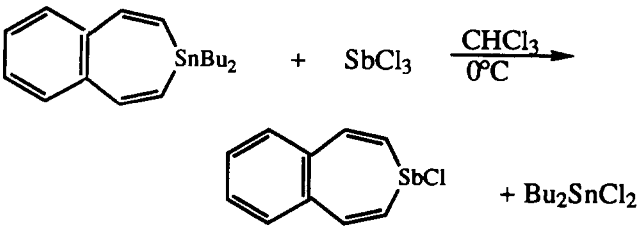
Although the stoichiometry of this type of reaction was not elucidated, it was suggested that an alkylated dianion was first formed and that this species was probably air oxidized on exposure to the atmosphere.

In a paper largely devoted to intramolecularly coordinated organobismuth compounds, a brief reference was made to the following compound [21]:

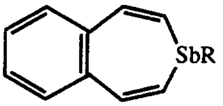


Coalescence of the two $^{10}$F NMR signals for the $CF_3$ groups could not be observed, and the inversion barrier was found to be higher than 20 kcal mol$^{-1}$ (at 150°C in DMSO-$d_6$). This result was said to be consistent with the prediction based on the theory of edge inversion. Further information about this subject is given in the Annual Survey of Bismuth for 1992.

The first synthesis of a stibepine has been accomplished by the following reaction [22]:



After recrystallization from a mixture of diethyl ether and dichloromethane, the chlorostibine was obtained as well-formed yellow crystals, which decomposed above 30°C. Treatment with methyl- or butyllithium in diethyl ether at −10°C gave the corresponding tertiary stibines:



(where R was Me or Bu)

The mps of the methyl and butyl derivatives were 35°C and −10°C, respectively. The three benzo[*d*] stibepines described in this study were characterized by NMR ($^1$H and $^{13}$C) and high-resolution mass spectrometry. All three compounds were thermally labile and readily decomposed to naphthalene and unidentified antimony-containing products. The conversion of the methyl and butyl derivatives to naphthalene in deuterated chloroform was monitored by PMR spectroscopy and exhibited first-order kinetics with half lives of 370 and 660 min, respectively. An X-ray determination of the structure of the chlorostibine showed a boat-like stibepine ring. The bond angles about the antimony atom were close to 90° as had previously been found in other heterocyclic derivatives of antimony. The marked alternation between single and double C–C bond lengths in the seven-membered ring was consistent with the conclusion that there was little conjugation in the stibepine moiety.

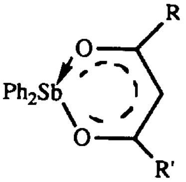
The interaction of diphenylchlorostibine or diphenylacetatostibine and the sodium salts of $\beta$-diketones in a 1:1 molar ratio has been found to proceed in the following manner [23]:

$$Ph_2SbCl + Na[RCOCHCOR'] \xrightarrow[\text{reflux}]{CHCl_3} Ph_2Sb(RCOCHCOR') + NaCl$$

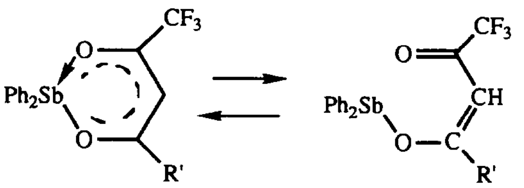
$$Ph_2SbO_2CMe + Na[RCOCHCOR'] \xrightarrow[\text{reflux}]{CHCl_3} Ph_2Sb(RCOCHCOR') + NaO_2CMe$$

(where both R and R′ were Me, $Me_3C$, or Ph; where R was Me and R′ was Ph; and where R was $CF_3$ and R′ was $Me_2CHCH_2$, $Me_2CHCH_2CH_2$, $C_4H_3S$, or Ph)

The organoantimony compounds thus obtained were moisture sensitive, viscous, and soluble in common organic solvents. Osmometric measurements in chloroform at 45°C and cryoscopic measurements in benzene showed that the substances were monomeric in these solvents. Their IR and NMR ($^1H$, $^{13}C$, and $^{19}F$) spectra led to the conclusion that the non-fluorinated derivatives had the following tetracoordinated type of structure:



The fluorine-containing substances, however, appeared to exist (in chloroform solution) as equilibrium mixtures of tri- and tetracoordinated species:



A number of hitherto unreported carboxylic acid derivatives of antimony(III) have been obtained by one of the following types of reactions [24]:

$$Ar_2SbCl + RCO_2H + Et_3N \xrightarrow{PhH} Ar_2SbO_2CR + Et_3N \cdot HCl$$

$$Ar_2SbCl + RCO_2M \xrightarrow{MeOH} Ar_2SbO_2CR + MCl$$

(where Ar was Ph or $4\text{-}MeC_6H_4$, R was $CF_3$, $CH_2Cl$, $CH_2I$, $\beta\text{-}C_5H_4N$, $\beta\text{-}C_4H_3O$, $4\text{-}MeC_6H_4$, $2\text{-}O_2NC_6H_4$, $3\text{-}O_2NC_6H_4$, $4\text{-}O_2NC_6H_4$, $2\text{-}ClC_6H_4$, $4\text{-}ClC_6H_4$, $3\text{-}NH_2C_6H_4$, or $4\text{-}NH_2C_6H_4$, and M was Na or Ag)

All of the reactions were found to proceed under mild conditions (40–80°C). The products were soluble in acetonitrile, chloroform, and to a lesser extent, in carbon tetrachloride. Conductance values of $10^{-3}$ M solutions in acetonitrile ranged from 10 to 20 $ohm^{-1}cm^2mol^{-1}$, values that indicated that the substances were non-electrolytes. Their monomeric nature in benzene was established by cryoscopic molecular weight determinations. The IR spectra of the compounds in the solid state exhibited frequencies that were consistent with bridging or chelating carboxylate groups. In carbon tetrachloride, however, the IR spectra indicated the presence of both unidentate and bidentate carboxylate groups, while in chloroform the IR spectra showed only frequencies characteristic of unidentate carboxylate groups. The IR data suggested that these compounds had a polymeric structure with bridging carboxylate groups and that this type of structure was partially broken down in carbon tetrachloride and was completely destroyed in chloroform. It was concluded that the coordination about each antimony atom in the solid state was pseudo trigonal-bipyramidal, with two aryl groups and the antimony lone pair occupying the equatorial positions and oxygen atoms of two carboxylate groups occupying the axial positions. Attempts to prepare carboxylic acid derivatives of the $ArSb(O_2CR)_2$ type by the interaction of an aryldichlorostibine and the sodium salt of an acid were unsuccessful and invariably resulted in the formation of diarylantimony(III) compounds of the type $Ar_2SbO_2CR$. These results supported an earlier conclusion from another laboratory that phenyldiacetatostibine was unstable.

Four compounds containing Sb–S bonds have been prepared by the interaction of diphenylacetatostibine and a phosphorodithioic acid or an ammonium phosphorodithioate [25]:

$$Ph_2SbO_2CMe + (RO)_2PS_2H \xrightarrow[\text{reflux}]{PhH} Ph_2SbS_2P(OR)_2 + MeCO_2H$$

(where R was Me, Et, or Ph)

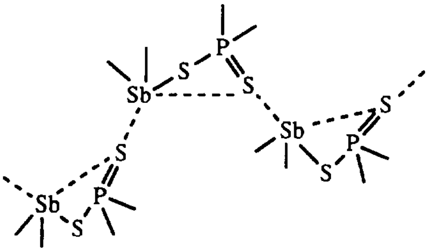
$$Ph_2SbO_2CMe + (RO)_2PS_2NH_4 \xrightarrow[\text{reflux}]{PhH} Ph_2SbS_2P(OR)_2 + MeCO_2NH_4$$

(where R was $Me_2CH$)

In some cases, the compounds could also be formed by the following type of oxidation-reduction reaction:

$$Ph_2SbCl_3 + 3(RO)_2PS_2NH_4 \longrightarrow Ph_2SbS_2P(OR)_2 + [(RO)_2PS_2]_2 + 3NH_4Cl$$

The methyl and ispropyl derivatives were obtained as pale yellow crystals, while the other two compounds were viscuous, yellow liquids. All four compounds were characterized by IR and PMR spectroscopy. The isopropyl derivative was also studied by mass spectrometry and X-ray diffraction. If only interactions of less than 3.0 Å had been considered, it would have seemed that the molecules were discrete monomers with unidentate phosphorodithioate ligands. On the other hand, when Sb · · · S contacts of up to 4.0 Å (the sum of the van der Waals radii) were taken into account, the ligand was best described as tridentate, since it not only chelated the antimony atoms but also linked the molecules into infinite zig-zag chains:



The antimony atoms thus became five coordinate with distorted square-pyramidal geometry.

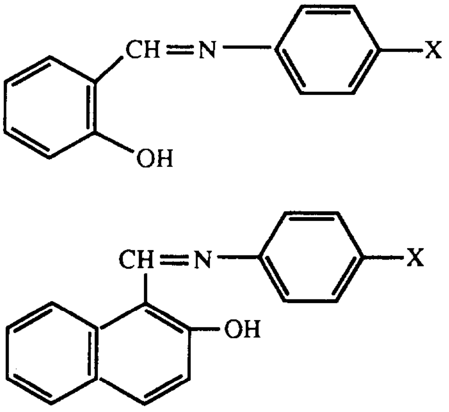
The dithiophosphinate $Ph_2SbS_2PPh_2$ and the dithiophosphate $Ph_2SbS_2P(OCHMe_2)_2$ have been tested against Ehrlich ascites tumor cells both *in vitro* and *in vivo* in mice [26]. *In vitro*, both compounds were about equally effective in inhibiting cell proliferation, cell viability, and protein synthesis and in stimulating respiration and Ca-ATPase activity. In mice bearing Ehrlich ascites tumor cells, the dithiophosphate was more active than the dithiophosphinate in inhibiting the growth of the tumor. On intraperitoneal administration of 5 mg $kg^{-1}$ on days 1, 3, and 5 after inoculation with the tumor cells, the dithiophosphate produced an increase in life span of 83% and a cure rate of 30%.

Two papers published in 1992 described the synthesis and properties of a number of diphenylstibino derivatives containing the azomethine linkage. Six of these compounds were prepared by the interaction of diphenylchlorostibine and the potassium salt of an aldimine in dry methanol [27]:

$$Ph_2SbCl + KL \xrightarrow[6-7\text{ h}]{\text{reflux}} Ph_2SbL + KCl$$

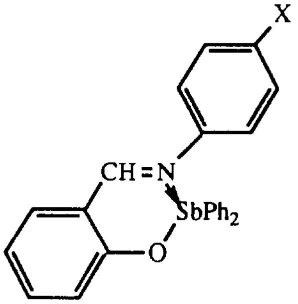
(where L was the anion of the aldimine)

The aldimines employed in this study were of the following types:



(where X was F, Cl, or Br)

The diphenylstibino derivatives were obtained in good yields in the form of colored solids. They were soluble in common organic solvents and were shown to be monomeric in camphor by the Rast method. Their IR and NMR ($^1H$ and $^{13}C$) spectra suggested that the ligands were chelating and that the antimony atom had a coordination number of four. The following type of structure was proposed:



The antifungal activity of the six ligands and the corresponding diphenylstibino derivatives was evaluated against various fungi. The results showed that the antimony compounds were more fungitoxic than the parent ligands and that the naphthaldimines were more active than the benzaldimines.

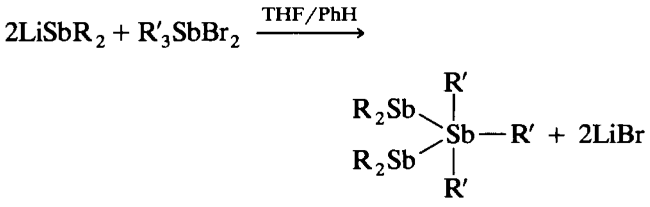
Another series of diphenylstibino derivatives containing the azomethine linkage has been obtained in good yield by the interaction of diphenylchlorostibine and the potassium salt of a thiosemicarbazone in dry methanol [28]:

$$Pb_2SbCl + KL \xrightarrow[6-7\text{ h}]{\text{reflux}} Ph_2SbL + KCl$$

(where L was the anion of the thiosemicarbazone)

The semicarbazones were derived from the following aldehydes and ketones: furfuraldehyde, 2-thiophenecarboxaldehyde, 2-pyridinecarboxaldehyde. 3-indolecarboxaldehyde, 2-acetylfuran, 2-acetylthiophene, 2-acetylpyridine, and 3-acetylindole. The diphenylstibino derivatives were found to be solids, which were partially soluble in common organic solvents. They were also said to be monomers and non-electrolytes. Their IR and NMR ($^1H$ and $^{13}C$) spectra were consistent with the presence of the C=N bond, the involvement of both azomethine nitrogen and thiolic sulfur in a chelate ring, and a tetracoordinated state for the antimony atom. Three of the diphenylstibino derivatives and their corresponding free ligands were screened against some pathogenic fungi. In each case, the presence of the diphenylstibino group enhanced the fungitoxicity.

Trinuclear organoantimony compounds containing both $Sb^{III}$ and $Sb^{V}$ have been prepared by the following type of reaction [29]:



$$2LiSbR_2 + R'_3SbBr_2 \xrightarrow{THF/PhH} (R_2Sb)_2SbR'_3 + 2LiBr$$

(where R was Ph or $MeC_6H_4$ and R′ was Me, Ph, or $MeC_6H_4$)

The products were yellow microcrystalline solids, which were moisture- and air-sensitive. They were soluble in THF and benzene and moderately soluble in dichloromethane and chloroform. They were characterized by UV-Vis, IR, far-IR, PMR, and $^{13}C$ NMR spectral studies. Vapor pressure osmometry measurements showed that the compounds were monomeric in benzene. Thermogravimetric analyses were carried out in a nitrogen atmosphere from room temperature to 540°C; the end product in each case consisted only of antimony. The far-IR spectra exhibited a strong peak at 170–185 $cm^{-1}$, which was attributed to the Sb–Sb bond. UV-Vis spectra were recorded both in the solid phase as diffuse reflectance spectra and in ethanolic solution as absorption spectra. A single maximum around 315–330 nm was observed, and there was no appreciable difference between the solid state and the solution spectra. This observation showed that these compounds were not thermochromic. The PMR spectrum of $(MeC_6H_4)_3Sb(SbPh_2)_2$ in $C_6D_6$ exhibited two peaks at $\delta$ 1.98 and 2.05 in the ratio of 2:1 for the methyl peaks of the tolyl groups; this result demonstrated that two of the tolyl groups were in a different environment from the third one. Similarly, two peaks were observed at $\delta$ 1.37 and 1.39 for the methyl groups in $Me_3Sb(SbPh_2)_2$. Conversely, the PMR spectrum of $Ph_3Sb[Sb(C_6H_4Me)_2]_2$ exhibited only one methyl peak at $\delta$ 2.27, a fact that showed that the tolyl groups were all in the same environment. The conclusions obtained by the PMR spectra were confirmed by the $^{13}C$ NMR spectra. Assuming that the compounds had trigonal-bipyramidal structures, it seemed clear that the two $SbR_2$ groups were in equatorial positions, while one of the three R′ groups occupied an equatorial position and the other two R′ groups occupied the axial positions.

The crystal structures of tetramesityldistibine and trimesitylstibine have been determined by X-ray crystallography [30]. Yellow, plate-like crystals of the distibine were obtained by cooling a solution of this substance in a mixture of equal parts of ether and petroleum ether to 5°C. The crystals were found to consist of isolated molecules exhibiting a distorted antiperiplanar conformation. The Sb–Sb distance of 284.9 pm and the average Sb–C distance of 219 pm were not unusual and were only very slightly larger than the corresponding distances in tetraphenyldistibine. The bulky mesityl groups did, however, appear to influence some of the bond angles. Thus, the two mesityl groups bonded to one of the antimony atoms displayed C–Sb–Sb angles of only 90.0° and 92.2°, while the other two C–Sb–Sb angles were much larger, *viz.* 108.7° and 109.5°. Both C–Sb–C angles (97.5° and 100.9°) were significantly larger than the corresponding angles in tetraphenyldistibine. The shortest intermolecular distance between antimony atoms was 638 pm, a value that far exceeded the sum of the van der Waals radii (440 pm) and thus precluded the type of extended bonding between the antimony atoms of neighboring molecules that has been found in thermochromic distibines. The structural results obtained in this investigation of tetramesityldistibine agreed closely with those reported earlier by a different group of workers [31]. Trimesitylstibine was obtained as colorless needles by cooling an ethanolic solution of this substance. The structure consisted of isolated trigonal-pyramidal molecules, *i.e.*, there was approximately pseudo-tetrahedral coordination about the antimony. Each asymmetric unit consisted of two independent molecules with similar bond angles and distances. The mesityl groups were arranged in a propeller-like fashion and were approximately perpendicular to one another. The average C–Sb–C angle (105.3°) and the average Sb–C distance (218.3 pm) were clearly larger than the corresponding values in triphenylstibine and tri-4-tolylstibine; they were quite similar, however, to the values in tris(2,6-dimethylphenyl)stibine. No close intermolecular Sb···Sb contacts in trimesitylstibine were observed. The PMR spectra of both tetramesityldistibine and trimesitylstibine in $C_6D_6$ were determined at 360 MHz. Three sharp singlets were observed in each case. Accordingly, in solution all mesityl groups in each compound were equivalent on the NMR time scale.

Trineopentylstibine and tris[(trimethylsilyl)methyl] stibine have been prepared by the Grignard reaction [32]:

$$3RMgCl + SbCl_3 \xrightarrow[2)\ \text{reflux 18 h}]{1)\ Et_2O,\ 0°C} R_3Sb + 3MgCl_2$$

(where R was $Me_3CCH_2$ or $Me_3SiCH_2$)

The tertiary stibines thus obtained were white, air-sensitive solids that sublimed slowly at $10^{-5}$ to $10^{-6}$ Torr at ambient temperature and were quite soluble in ethers and in aliphatic and aromatic hydrocarbons. They were characterized by spectroscopy (IR, $^1H$ NMR, and $^{13}C$ NMR) and single-crystal X-ray diffraction. The compounds were isomorphous and adopted a pyramidal geometry about the antimony, which lay on a crystallographic 3-fold axis. The C–Sb distances and the C–Sb–C angles were comparable to the corresponding distances and angles previously reported for trimethylstibine. There were few close contacts, and the intermolecular ones were greater than van der Waals separations. Both compounds oxidatively added iodine to give the expected five-coordinate diiodides:

$$R_3Sb + I_2 \xrightarrow{\text{pentane/toluene}} R_3SbI_2$$

The products were pale yellow, air-sensitive solids that were markedly less soluble than the corresponding tertiary stibines. They were also examined by spectroscopy (IR, $^1H$ NMR, and $^{13}C$ NMR) and single-crystal X-ray diffraction. Both compounds were isomorphous and deviated only slightly from ideal trigonal-bipyramidal geometry. Thus, the axial I–Sb–I bond angle was 179° in both cases. There were a number of intermolecular contacts ($H \cdots I$) in the ranges 3.20–3.42 Å for the neopentyl compound and 3.38–3.44 Å for the (trimethylsilyl)methyl compounds. Both diiodides decomposed cleanly at 270°C to yield iodostibines:

$$R_3SbI_2 \longrightarrow R_2SbI + RI$$

The iodostibines were yellow, slightly air-sensitive oils that were very soluble in ethers and in aliphatic and aromatic hydrocarbons. They were characterized by IR, PMR, and $^{13}C$ NMR spectroscopy. Reaction of the iodostibines with iodine at −78°C yielded five-coordinate triiodides:

$$R_2SbI + I_2 \xrightarrow{Et_2O} R_2SbI_3$$

The latter substances were dark orange, air-sensitive solids. The neopentyl compound was characterized by $^1H$ NMR, while the (trimethylsilyl)methyl derivative was characterized by both PMR and $^{13}C$ NMR. Although both triiodides were indefinitely stable in the dark at −20°C in an inert atmosphere, they slowly underwent reductive elimination at ambient temperature to give diiodostibines:

$$R_2SbI_3 \longrightarrow RSbI_2 + RI$$

These substances were bright yellow, highly viscous, air-sensitive oils. They were characterized by IR, $^1H$ NMR, and $^{13}C$ NMR.

tert-Butyldimethylstibine (**5**) has been prepared by the following "one-pot" procedure [33]:

$$Me_3CMgCl + SbCl_3 \xrightarrow[-50°C]{Et_2O} [Me_3CSbCl_2] \xrightarrow[Et_2O,\ 0°C]{2MeMgBr}$$

$$\underset{\substack{64\%\ \text{yield} \\ \mathbf{5}}}{Me_3CSbMe_2} + \underset{6\%\ \text{yield}}{(Me_3C)_2SbMe} + MgClBr$$

This synthetic methodology avoided the necessity for isolating the intermediate, highly reactive tert-butyldichlorostibine. The tertiary stibine **5** was isolated by fractional distillation (63°C at 30 Torr). It had a mp of 12–13°C and a vapor pressure of 3.6 Torr at 25°C. It was characterized by $^1H$ and $^{13}C$ NMR.

The tertiary stibine **5** has also been synthesized by the following reaction sequence [34]:

$$\begin{tikzcd}
Me_3Sb + 2Na \arrow[r, "\text{liquid}", "NH_3"'] & Me_2SbNa + MeNa \arrow[d, "Me_3CBr"] \\
& \underset{\mathbf{5}}{Me_3CSbMe_2} + NaBr
\end{tikzcd}$$

The colorless, air-sensitive liquid thus obtained was found to have a mp of approximately 8°C; its vapor pressure was 4.5 Torr at 12°C, 7.3 Torr at 23°C, 8.1 Torr at 26°C, and 50 Torr at 56°C. The stibine was characterized by IR, NMR ($^1H$ and $^{13}C$) and gas chromatography/mass spectroscopy. Its 50% decomposition temperature in either helium or deuterium was 300°C in a flow tube reactor with a residence time of approximately 3.2 s at 300°C. The overall decomposition process was shown to be homogeneous and first order. The principal decomposition products in both carrier gases were $C_4H_{10}$, $C_4H_8$, trimethylstibine, and antimony. In helium, a small amount of tetramethyldistibine was also detected. The first step of the decomposition mechanism was believed to be a homolysis that produced $C_4H_9$ and $Me_2Sb$ radicals. The fact that the stibine **5** decomposed at lower temperatures than required for trimethylstibine was ascribed to the relative weakness of the $Me_3C$–Sb bond (33.1 kcal $mol^{-1}$). The addition of trimethylgallium to the stibine **5** did not result in the formation of an adduct. Furthermore, the presence of the gallium compound had no measurable effect on either the pyrolysis rate of the stibine or the products formed in its decomposition. It was concluded that the stibine was worth exploring as an antimony source for the organometallic vapor-phase epitaxy (OMVPE) of antimony-containing semiconductor materials.

Several publications have described the use of tert-butyldimethylstibine (**5**) as an antimony source for the low temperature OMVPE growth of indium antimonide, InSb [35–38]. In two of these studies, good surface morphology of layers of InSb was obtained with growth temperatures from 450 to as low as 325°C [35,36]. The growth temperature was lower by more than 100°C compared to using trimethylstibine and about 50°C compared to using triisopropylstibine. When trimethylindium and the stibine **5** were employed, the growth efficiency of InSb was about $1 \times 10^4$ $\mu$m mol$^{-1}$. This high value indicated that there were negligble parasitic reactions between the organoindium compound and the stibine. The results obtained in these two investigations suggested that the stibine **5** was superior to both trimethylstibine and triisopropylstibine for the OMVPE growth of InSb at temperatures lower than 400°C. It should be noted, however, that trimethylstibine [38–40], triisopropylstibine [37], as well as triethylstibine [41], have continued to be employed for the epitaxial growth of InSb.

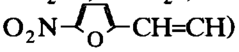
Trimethylstibine [42–44] and triethylstibine [41] have also been the antimony sources for the epitaxial growth of gallium antimonide, GaSb. In addition, both of these stibines have been employed for the reproducible growth of InAsSb/InSb strained-layer superlattice photodiodes by low pressure metalorganic chemical vapor deposition (MOCVD) [45]. Trimethylstibine has also been used in the production of GaAsSb by MOVPE [44], InGaSb/GaSb photodiodes by MOCVD [46] and strained quantum well structures by both MOCVD [47,48] and MOVPE [49], and InGaAsSb/InPSb diode lasers by MOVPE [50]. Triethylstibine has been the antimony source for the lattice-matched low pressure growth of InPSb/InAs [51] and the metalorganic molecular beam epitaxy (MOMBE) of InAsSb and GaAsSb [52]. Triisopropylstibine has been the antimony source for the *p*-type doping of HgCdTe grown by MOCVD [53]. Diethyl(ethyltelluro)stibine, $Et_2SbTeEt$, has been mentioned as an antimony source in a patent application on the preparation of *n*-doped IIIA pnictides grown by MOCVD [54].

The importance of tertiary stibines as antimony sources in vapor-phase epitaxy and chemical vapor deposition has prompted a study of the gas-phase pyrolysis reactions of trimethylstibine under vacuum conditions [55]. The experimental method involved introducing the stibine from either a high-speed molecular beam type pulse valve or a continuous feed source into a fixed-bed microreactor under high vacuum and then measuring the transient response or the steady-state performance with a quadrupole mass spectrometer. The results obtained showed that the onset of pyrolysis occurred near 475°C and that the process was more than 90% complete at 630°C. Methane and ethane were the principal stable gas-phase products. The transient response data showed that the pyrolysis proceeded via a first-order unimolecular reaction in which the activation energy was 41.1 kcal mol$^{-1}$. The initial step of the pyrolysis probably involved the following free-radical process:

$$Me_3Sb \longrightarrow Me_2Sb\cdot + Me\cdot$$

Triphenylstibine and tri-4-tolylstibine have been oxidized to organoantimony(V) derivatives by the following type of reaction [56]:

$$Ar_3Sb + 2RCO_2H \longrightarrow Ar_3Sb(O_2CR)_2 + H_2$$

(where Ar was Ph or 4-$MeC_6H_4$ and R was $CH_2Cl$, $CH_2Br$, $CH_2I$, $CCl_3$, $CF_3$, 3,5-$(O_2N)_2C_6H_3$, or )

The reactions with trichloroacetic acid and trifluoroacetic acid were carried out in dichloromethane at 0°C; the other reactions took place in benzene at about 100°C. Most of the reactions gave high yields, but the reactions with chloroacetic acid and bromoacetic acid were said to be sluggish. Acetic acid, benzoic acid, 4-chlorobenzoic acid, and phenylacetic acid did not react at all. Tri-4-tolylantimony diacetate was obtained by the following metathetical reaction:

$$(4\text{-}MeC_6H_4)_3SbBr_2 + 2AgO_2CMe \xrightarrow[6\ h]{PhH} (4\text{-}MeC_6H_4)_3Sb(O_2CMe)_2 + 2AgBr$$

The dicarboxylates that had not previously been prepared were characterized by elemental analysis, IR, and $^1H$ NMR spectroscopy. No evidence of Ar–Sb cleavage was noted in any of the redox reactions studied in this investigation.

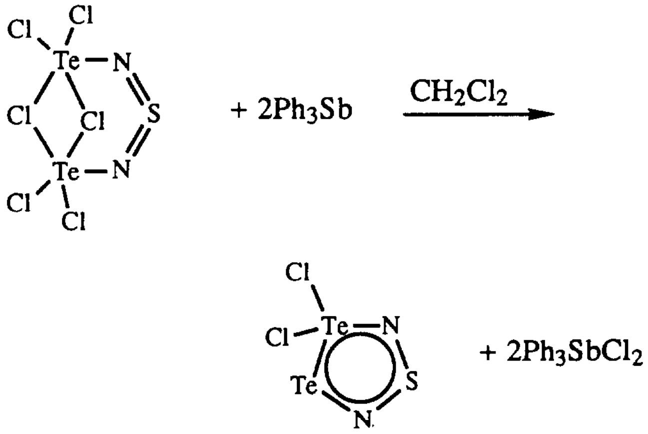
The interaction of 0.5 mol of triphenylstibine or triphenylbismuthine and 1.0 mol of iron(III) chloride or iron (III) isothiocyanate has been found to lead to complexes in which only one-third of the iron(III) was reduced to iron(II) [57]:

$$Ph_3E + 6FeX_3 + 12MeCN \xrightarrow[RT]{MeCN} Ph_3EX_2 + [Fe(MeCN)_6][FeX_4]_2$$

(where E was Sb or Bi and X was Cl or NCS)

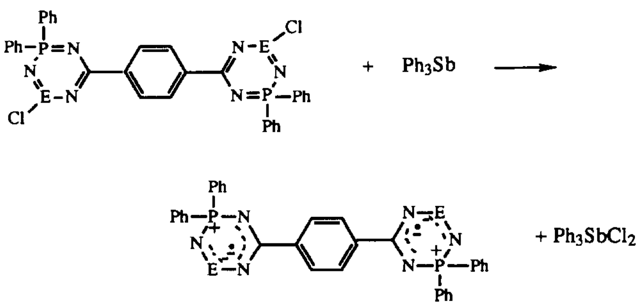
The pentavalent antimony and bismuth compounds formed in these reactions were isolated and then identified by elemental analyses. The iron complexes were studied by IR and electronic spectroscopy. It was concluded that the isothiocyanate group was bonded to iron through the nitrogen atom. Further information about this study is given in the Annual Survey of Bismuth for 1992.

Dechlorination with triphenylstibine has been used for the synthesis of the first five-membered chalcogen-nitrogen ring system containing two tellurium atoms [58]:



The heterocyclic compound was obtained as a dark-red crystalline substance in yields greater than 95%. It was air-sensitive, insoluble in dichloromethane or sulfur dioxide, and did not explode on mechanical shock or on heating. It melted at 250°C with decomposition. The results of a vibrational spectroscopic study were in good agreement with the proposed five-membered ring structure.

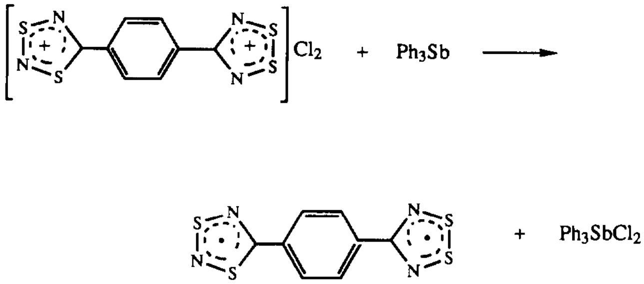
Triphenylstibine has also been employed as a reducing agent in the following type of reaction [59]:



(where E was S or Se)

Triphenylantimony dichloride was presumably formed in these reactions, but it was apparently not identified. ESR and $^{31}$P NMR evidence suggested a pronounced association of the diradicals in solution. The X-ray structure of the selenium-containing diradical revealed association through Se $\cdots$ N interactions to form a centrosymmetric dimer.

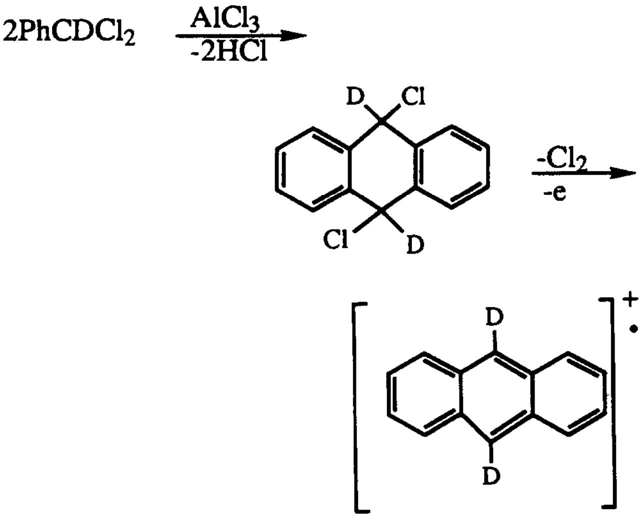
Another diradical has been prepared by the dechlorination of a dithiadiazolylium dication with triphenylstibine [60]:



The diradical, which was described as an insoluble black powder, was studied by ESR spectroscopy.

ESR studies have demonstrated the generation of the 9,10-dideuterioanthracene radical cation via the reaction of a 0.001 M solution of triphenylstibine in deuteriochloroform in the presence of an excess of aluminum chloride [61]. The following series of reactions was suggested:

$$Ph_3Sb \quad + \quad CDCl_3 \xrightarrow{AlCl_3} Ph_2SbCl \quad + \quad PhCDCl_2$$



The ESR spectrum of the radical cation was well resolved, and the hyperfine coupling constants of this species were reported.

The interaction of triphenylstibine and butyl alcohol at 110°C in the presence of cupric pelargonate, $Cu[O_2C(CH_2)_7Me]_2$, has been found to give butyl phenyl ether in a yield of 1 mol of ether per 1 mol of the stibine [62]. Atmospheric oxygen promoted this reaction and increased the yield of the ether to almost

2.8 mol. In the presence of small amounts of cupric acetate, triphenylstibine underwent alcoholysis at 110°C:

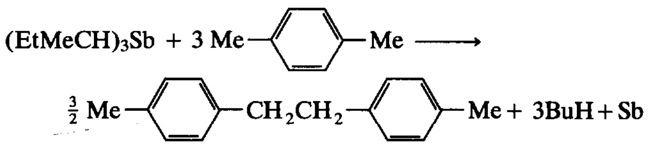
$Ph_3Sb + 3ROH \longrightarrow Sb(OR)_3 + 3PhH$

(where R was Me, $Me_2CH$, or Bu)

The yields of the products were nearly quantitative in the presence of 2,2′-dipyridyl (0.04 mol). Atmospheric oxygen, water, or halides almost completely inhibited the catalytic alcoholysis of triphenylstibine.

A complex of the $(Sb_3)^{3-}$ trianion has been prepared by the interaction of decamethylsamarocene and tributylstibine in toluene [63]. The reaction was accompanied by an immediate color change from dark-green to red-brown. Dark-red single crystals of the complex were obtained by recrystallization of the crude reaction product from benzene in the presence of tetrahydrofuran (THF). An X-ray diffraction study showed that the crystals were the triantimony species $[(C_5Me_5)_2Sm]_3(\mu\text{-}\eta^2:\eta^2:\eta^1\text{-}Sb_3)$ (THF). The $(Sb_3)^{3-}$ ion in this substance had indistinguishable Sb–Sb distances of 2.689 and 2.686 Å, values significantly less than the normal Sb–Sb single bond distance and comparable to species in which the Sb–Sb bond order was 1.25 to 1.5. The observed Sb–Sb–Sb angle of 114° was larger than those in the $(Sb_6)^{8-}$ and $(Ph_4Sb_3)^-$ ions. The structural parameters of each of the three unique $(C_5Me_5)_2Sm$ units in the complex were in the normal range for eight-coordinate trivalent organosamarium species.

Tri-*sec*-butylstibine has been included in an investigation largely devoted to an unusual selective α-fission of the C–In bond in tri-*sec*-alkylindium compounds [64]. Unlike the latter substances, the stibine was so thermally stable that 90% could be recovered after being heated in 1,4-xylene at 140°C for 9 h. A 6% yield of 4,4′-dimethylbibenzyl was also isolated. This substance was presumably formed by the following reaction, which was mediated by the *sec*-butyl radical:



Previous work has shown that triethylstibine in concentrations as low as $5 \times 10^{-8}$ M inhibited the corrosion of iron exposed to 1 N HCl, 1 N $H_2SO_4$, or 1 N $HClO_4$. A new investigation has now been undertaken in an effort to elucidate the mechanism of this protective effect [65]. The study employed polarization and impedance measurements, cyclic voltammetry, X-ray photoelectron spectroscopy (XPS), and surface-enhanced Raman scattering spectroscopy. It was concluded that triethylstibine was cathodically decomposed on the iron surface to form metallic antimony and ethane:

$Et_3Sb + 3H^+ + 3e^- \longrightarrow Sb + 3EtH$

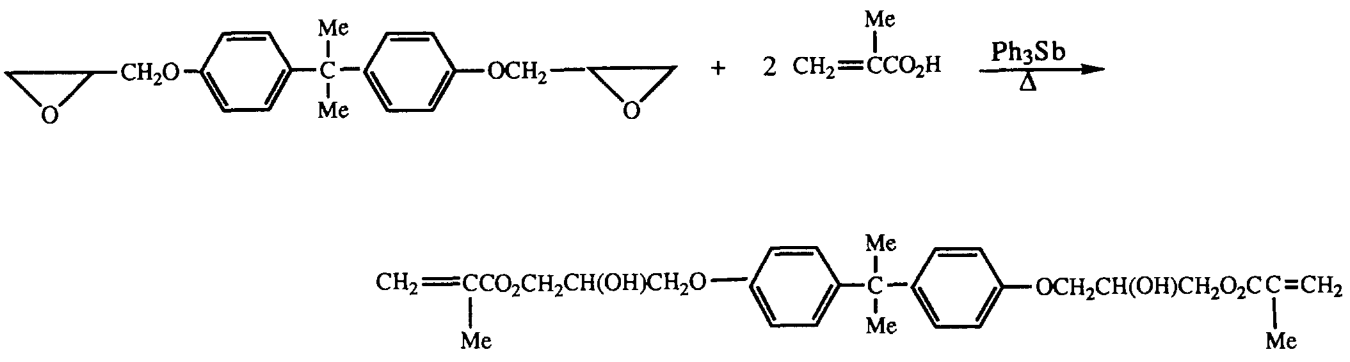
This process resulted in the iron surface being completely covered with an inner layer of antimony. The iron surface and a part of the deposited antimony were then converted by anodic reactions to an outer layer consisting of $Fe^{II}$ and $Sb^{III}$ oxides. An XPS study of the protective film formed by treatment of iron with triphenylstibine in 1 N $HClO_4$ showed a similar film structure, although the film was much thinner than when triethylstibine was used. A thin film was also formed when nickel was exposed to triethylstibine in 1 N $HClO_4$, but this film was thinner and less protective than the films formed by triethylstibine on iron surfaces. The film on the nickel surface was composed of nickelous oxide together with a small amount of antimonous oxide and a trace of metallic antimony. Further information about this study is given in the Annual Survey of Bismuth for 1992.

The triphenyl derivatives of nitrogen, phosphorus, arsenic, antimony, and bismuth have been found to adsorb from solution onto gold or copper [66]. The adsorption was established by reflection IR spectroscopy at grazing incidence, ellipsometry, contact angle measurements, and in the case of triphenylstibine and -bismuthine, by X-ray photoelectron spectroscopy. After immersion of gold or copper slides for 6 h in 1 mM ethanolic solutions of triphenylstibine, the surface layer thickness of this compound was on the order of one monolayer. The thickness on copper increased slightly (albeit significantly) after immersion for another 54 h but did not exceed two monolayer units. On gold, however, no difference in surface layer thickness was found between a 6 h and a 60 h immersion period. Monolayers of triphenylstibine on gold or copper did not desorb at reduced pressure (about $10^{-9}$ mbar). Complete desorption in pure ethanol, however, took place from copper in 1 h or less and within several days from gold. The adsorption process was therefore considered reversible. Further information about this work is discussed in the Annual Survey of Bismuth for 1992.

A study has been reported of the kinetics of the following triphenylstibine-catalyzed reaction [67]. The variables that affected the reaction rate were explored, and a plausible mechanism was reported.

A Japanese patent has claimed that tertiary stibines were effective as catalysts in the manufacture of polycarbonates by the interaction of dialkyl carbonates and bisphenols [68], while a European patent application has described the preparation of xylylene diisocyanate by the thermal decomposition of xylylene dicarbamate in the presence of triphenylstibine in a high boiling inert solvent [69].

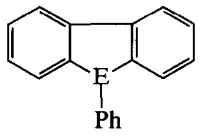
Triphenylstibine has been included in an investigation of the effect of various organic and organometallic



substances on the catalysis of the polymerization of trimethyl[3-(1-propynyl)phenyl]silane, 3-$Me_3SiC_6H_4C \equiv CMe$, by niobium(V) chloride or tantalum(V) chloride [70]. The yield of the polymer was increased when triphenylstibine was added to the niobium compound, and the polymer thus obtained was found to be partially insoluble in chloroform. The presence of the stibine increased both the yield and the molecular weight of the polymer when tantalum(V) chloride was used as the catalyst. In a study mainly devoted to X-ray contrast polymers containing miscible organobismuth compounds, triphenylstibine in admixture with poly(methyl methylacrylate) has been employed as a radiopacifying agent [71]. Further information about both of these studies is given in the Annual Survey of Bismuth for 1992.

The $^{121}Sb$ Mössbauer spectra of a number of triarylstibines $Ar_3Sb$ (where Ar was Ph, 4-$MeC_6H_4$, 4-$FC_6H_4$, 4-$ClC_6H_4$, 2-$MeC_6H_4$, 2-$ClC_6H_4$, or 2-$MeOC_6H_4$) have been studied with a view to elucidating the effect of the ring substituents on the isomer shifts (IS) and the quadrupole coupling constants ($e^2q_zQ$) [72]. The Mössbauer parameters of the stibines were observed at 20 K both in the crystalline state and in frozen cumene solutions. In the crystalline state, the IS values for the *para* substituted compounds were less negative than that for triphenylstibine, while the IS values for the *ortho* substituted compounds were more negative. In the frozen cumene solutions, the IS values decrease and the quadrupole coupling constants increase with an increase in the Hammett substituent constants of the *para* substituents. The results obtained were interpreted in terms of the effect of a substituent on the electron density of the carbon atom bonded to the antimony.

The CNDO/S-CI method has been employed in a study of the effect of the nature of the heteroatom on the electronic structure and the spectral luminescence characteristics of three compounds of the following type [73]:



(where E was P, As, or Sb)

The changes in the nature of the molecular orbitals, of the ground and the electronically excited states, of the spin-orbit interactions, and of the energies and intensities of the $S_1 \rightarrow S_0$ and the $T_1 \rightarrow S_0$ transitions were analyzed. The fluorescence and phosphorescence quantum yields were also discussed. It was concluded that the calculated and the experimental rate constants of the radiative $S_1 \rightarrow S_0$ and the $T_1 \rightarrow S_0$ transitions of the three molecules correctly reflect the general rule that $k_{S_1 \rightarrow S_0} \gg k_{T_1 \rightarrow S_0}$.

Calculations employing the coupled electron-pair approximation (CEPA) procedure have been reported for compounds of the type R–C≡E, where R was H, F, Me, or Ph, and E was N, P, As, or Sb [74]. Bond lengths, force constants, and dipole moments were estimated and compared with any available experimental values. None of the antimony compounds considered in this investigation has yet been prepared.

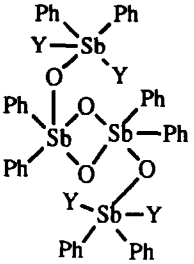
There have been numerous recent publications that mentioned the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these compounds included copper [75], gold [76], iridium [77], iron [78], molybdenum [79], platinum [80], rhodium [81–83], and ruthenium [84–86].

Raman spectroscopy at 77 K has been employed to study the 2:1 Menshutkin complexes of antimony trichloride with benzene, biphenyl, or phenanthrene [87]. The experimentally observed spectra made it possible to perform a group theoretical analysis and a normal coordinate analysis of the antimony trichloride vibrations in the complexes. The interpretation of the observed vibrational frequencies in both the intramolecular vibration region and in the lattice mode region was accomplished without the use of polarization measurements. The method of frequency calculation that was used to interpret the lattice modes did not require a knowledge of the intermolecular potential in an explicit form.

The 1:1 Menshutkin complex of antimony trichloride with hexaethylbenzene has been included in a study of intramolecular rotational barriers in organometallic complexes [88]. In the conformation of lowest energy, the methyl groups alternated above and below the plane of the ring. It was also noted that the antimony atom was located 2.962 Å from the benzene ring plane and that in the complex the methylene carbons of two of the three proximal ethyl groups were forced to the distal side.

In continuation of previously published work on the crystal and molecular structure of organoantimony(V) compounds, Zaitseva and co-workers [89] have reported X-ray diffraction studies on hepta(diphenyl sulfoxide)calcium bis(pentachlorophenylantimonate), [Ca-$(DPSO)_7][PhSbCl_5]_2$. The geometry of the antimony atom in the anion was octahedral. There were two crystallographically independent $[PhSbCl_5]^-$ anions, which differed somewhat in some bond lengths and bond angles. Thus, the *trans* Cl–Sb–Cl angles in one anion were 174.4° and 175.6° and in the other anion were 174.5° and 176.2°, respectively. The *trans* C–Sb–Cl angles were 176.9° and 179.7°, respectively. The lengths of the *trans* Sb–Cl bonds in the two anions differed by 0.022 Å. The average lengths of the Sb–Cl bonds *cis* to the phenyl group in the two anions were identical. The geometry of the anion was not affected by interanion or cation–anion interactions. The authors compared the *cis* Sb–Cl and *trans* Sb–Cl distances in this compound with the same distances in a number of other compounds containing anions of the type $[RSbCl_5]^-$ and found these lengths significantly shorter in their compound, $[Ca(DPSO)_7][PhSbCl_5]_2$. The authors suggested that anions in the latter compound were loosely fixed in the crystal lattice and participated in libration movements to some degree. By analyzing the thermal motion of the anions and correcting the bond lengths for libration, the differences with other anions disappeared.

A number of organoantimony compounds containing the $Sb_2O_2$ 4-membered ring system are known. Several new compounds containing this ring system have been described in a report from Sowerby's laboratory [90]. This paper was among a number of contributed papers from the Sixth International Symposium on Inorganic Ring Systems, and only summarized the work done without experimental details. Both diphenylfluorostibine and diphenylthiocyanatostibine were oxidized by tert-butyl hydroperoxide in toluene solution. The resulting products possessed similar structures corresponding to the formulas $(Ph_2SbO_2)_2$ $(Ph_2SbY_2)_2$, where Y was F or SCN. X-ray diffraction studies of the two compounds revealed that they possessed the following structures:

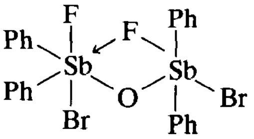


(where Y was F or SCN)

In addition to the above two compounds, the ionic compound obtained from silver oxalate and bis(bromo-$\mu$-oxodiphenylantimony), $(Ph_2SbBrO)_2$, was described. The preparation and molecular structure of this compound have been previously reported [91].

A paper from Sowerby's laboratory has described the preparation of several diphenylantimony trihalides in which the halogens were fluorine and bromine [92]. An attempt to prepare $Ph_2SbFCl_2$ by the oxidative chlorination of $Ph_2SbF$ with the stoichiometric amount of chlorine in dichloromethane at −97°C gave only $Ph_2SbCl_3$. Attempts to isolate mixed fluorine chlorine compounds from the mother liquor were unsuccessful. When a similar reaction was carried out with bromine, $Ph_2SbBr_3$ was obtained by concentrating and cooling the solution. By repeatedly concentrating the mother liquors, five further crystalline fractions were obtained. These showed increasing carbon and hydrogen content and decreasing bromine content with increasing solubility in dichloromethane. Fraction 1 appeared to be principally $Ph_2SbBr_3$ with small amounts of fraction 2, as judged by the IR spectral reports. Fraction 2 gave absorption bands in the IR spectrum in the region expected for Sb–F ··· Sb stretching (533 and 510 $cm^{-1}$) and for Sb–F deformation (*ca.* 360 $cm^{-1}$). The IR spectrum of fraction 3 showed absorption bands at 584 and 552 $cm^{-1}$ assigned to the Sb–F stretching. The IR spectrum of fraction 4 was similar to that of fraction 3, but that of fraction 5 was more complex. Fractions 3, 4, and 5 showed stretching bands at *ca.* 220 $cm^{-1}$, assigned to the Sb–Br stretching mode. The mass spectra of the five fractions gave similar fragments, but there was considerable variations in their relative intensities. All five fractions gave ions containing bromine. The $^{19}F$ NMR spectra of the various fractions did not prove useful in identifying their structures. On the basis of the IR spectral results and of X-ray diffraction studies on fractions 2 and 3, the following formulas were assigned to fractions 2-5, respectively: $Ph_4Sb_2Br_5F$, $Ph_2SbBr_2F$, $Ph_4Sb_2Br_3F_3$, and $Ph_2SbBrF_2$. Recrystallization of fractions 2 and 3 from dichloromethane gave crystals suitable for X-ray diffraction, but suitable crystals were not obtained from fractions 4 and 5. Fraction 2 proved to have the formula $Ph_2SbBr_2F \cdot Ph_2SbBr_3$ in which the two molecules were connected by a Sb–F · · · Sb bridge. The antimony atom of the $Ph_2SbBr_2F$ portion possessed trigonal-bipyramidal geometry with one bromine and the fluorine atom in axial position. The antimony atom of the $Ph_2SbBr_3$ portion showed distorted octahedral geometry with the fluorine atom from the $Ph_2SbBr_2F$ coordinated to the antimony atom of the $Ph_2SbBr_3$. In addition, there is a weak Sb–Br · · · · Sb intermolecular bond linking a bromine atom of $Ph_2SbBr_3$ to the antimony atom of the $Ph_2SbBr_2F$ molecule.

Fraction 3 was shown to consist of two independent molecules of an oxygen bridged diantimony compound, $(Ph_2SbBrF)_2O$. Presumably, the compound $Ph_2SbBr_2F$ was formed initially and then underwent hydrolysis during the recrystallization procedure. The two independent molecules possessed similar structures but differed in some bond angles and bond distances. The closest intermolecular distance between the independent molecules was 5.5 Å. In each molecule there were two different antimony atoms: one possessed trigonal-bipyramidal geometry, and the other, distorted octahedral geometry. The antimony atom with trigonal-bipyramidal geometry possessed a fluorine atom and a bromine atom in the axial position. The fluorine atom was coordinated to the other antimony atom leading to the distorted octahedral geometry. The two antimony atoms, an oxygen atom, and a fluorine atom formed a 4-membered ring with Sb–O–Sb and Sb–F · · · Sb bonds. This molecule thus possessed the following structure:



In addition to experiments involving the chlorination and bromination of $Ph_2SbF$, attempts were made to fluorinate $Ph_2SbCl_3$. Only starting materials were recovered from the reaction of the trichloride with anhydrous potassium fluoride in methanol or with silver fluoride in acetonitrile. However, reaction of the trichloride with arsenic trifluoride gave a product, mp 103°C, the microanalytical data of which were close to the values for $Ph_3SbCl_2$, mp 142°C. The IR spectrum of this product suggested the presence of fluorine, and indeed the mass spectrum gave ion peaks for $Ph_3SbF_2$ and $Ph_3SbFCl$, as well as for $Ph_3SbCl_2$. The analytical results suggested the replacement of about 10% of the chlorine by fluorine. Repeated crystallizations failed to change these results. An X-ray diffraction study of the material showed the presence of two independent molecules of $Ph_3SbCl_2$ which differed somewhat in bond distances and bond angles. In both molecules the geometry of the antimony atoms was trigonal-bipyramidal with two axial chlorine atoms in each molecule. The electron densities at one chlorine atom in each molecule, however, were lower than for the other chlorine atom. It was concluded from the occupation factors that the results implied a random distribution of 74% $Ph_3SbCl_2$ and 26% $Ph_3SbClF$ for one molecule and 85% $Ph_3SbCl_2$ and 15% $Ph_3SbClF$ for the other molecule, giving a molecular formula of $Ph_3SbCl_{1.8}F_{0.2}$ in agreement with the analytical figures. Although the mass spectrum of the material showed peaks for the $Ph_3SbF_2^+$ ion, there was no indication of the presence of this material from the X-ray diffraction results, and the authors suggested it was formed by rearrangement in the ion source of the mass spectrometer. The authors commented on the formation of $Ph_3SbCl_2$ from the starting material $Ph_2SbCl_3$ and suggested it may have been formed according to the following reactions:

$$3Ph_2SbCl_3 + AsF_3 \longrightarrow 3Ph_2SbCl_2F + AsCl_3$$

$$Ph_2SbCl_2F + Ph_2SbCl_3 \longrightarrow Ph_3SbCl_2 + PhSbCl_3F$$

$$Ph_2SbCl_2F + Ph_2SbCl_3 \longrightarrow Ph_3SbClF + PhSbCl_4$$

$$2PhSbCl_4 \longrightarrow Ph_2SbCl_3 + SbCl_5$$

$$2PhSbCl_3F \longrightarrow Ph_2SbCl_3 + SbCl_3F_2$$

Chaturvedi and coworkers [93] have prepared a number of interesting compounds of the type $Ph_3SiOSbPh_3(OL)$, where LOH was a Schiff base derived from either salicylaldehyde or 2-hydroxy-1-naphthaldehyde, and a 4-substituted aniline ($4\text{-}XC_6H_4NH_2$, where X was F, Cl, Br, or $NO_2$). The lithium salt of triphenylsilanol and the lithium salts of the Schiff bases were prepared *in situ* in methanol solution. The compounds were prepared in the following manner:

$$Ph_3SiOLi + Ph_3SbCl_2 \xrightarrow{MeOH} Ph_3SiOSbClPh_3$$

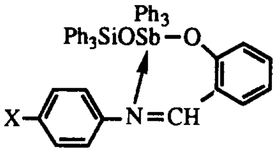
$$Ph_3SiOSbClPh_3 + LiOL \longrightarrow Ph_3SiOSbPh_3(OL)$$

Thus, the following complexes were prepared from salicylaldehyde:

$Ph_3SiOSbPh_3(2\text{-}OC_6H_4CH{=}NC_6H_4X\text{-}4)$

(where X was F, Cl, Br, or $NO_2$)

The compounds were characterized by elemental analyses, molecular weight determinations by the Rast method, IR, and $^1H$ NMR spectroscopy. On the basis of the spectral results it was concluded that the Schiff base acted as a bidentate ligand, and that the complexes obtained from salicylaldehyde, therefore, possessed the following type of structure:



In papers devoted to the copolymerization of acrylonitrile with a number of both electron-donor and electron-acceptor monomers (vinyl acetate, styrene, cyclohexene, 1-hexene, methyl methacrylate, acrylic acid, and methacrylic acid), triisobutylboron and a number of radical initiators were used as initiators of the polymerization [94]. Two antimony(V) compounds, tert-butylperoxytetraphenylantimony and di(tert-butylperoxy)triphenylantimony, were among the radical initiators. In a second paper from the same group, the copolymerization of vinyl chloride with various vinyl monomers, initiated by triisobutylboron and di(tert-butylperoxy)triphenylantimony, was investigated [95].

In a related paper by Grishin and coworkers [96], the copolymerization of acrylic or methacrylic acid with vinyl monomers was described. The catalysts were triisobutylboron and various organometallic peroxides including tert-butylperoxytetraphenylantimony. In another paper from the same laboratory, the effect of a number of organometallic peroxides (combined with tributylboron) on the polymerization of vinylidene chloride was compared [97]. The activity of the organometallic peroxides decreased in the order $(Me_3COO)_2SbPh_3 > Me_3COOSbPh_4 > Me_3COOSnEt_3 > Me_3COOGeEt_3 > Me_3COOSiEt_3$. The copolymerization of vinylidene chloride with vinyl acetate or acrylonitrile varied considerably with different catalysts, but the copolymerization of vinylidene chloride with styrene or methyl methacrylate was less dependent on the nature of the catalyst. The copolymerization of ethylene and vinyl chloride by triisobutylboron and di(tert-butylperoxy)triphenylantimony was the subject of a Russian patent [98].

Raj and Aggarwal [99] have prepared a large number of cationic antimony(V) compounds of the type $[R_3SbL_2][Y]_2$ where R was Me, Ph, or 4-$MeC_6H_4$, L was a neutral mondentate ligand (DMSO, triphenylarsine oxide, or triphenylphosphine oxide) or a bidentate ligand (ethylenediamine or 2,2′-bipyridine), and Y was $BPh_4^-$, or $BF_4^-$. The compounds were prepared from the corresponding trialkyl- or triarylantimony dichlorides or dibromides (1 molar equivalent) and the desired ligand (two molar equivalents of the monodentate ligand or one molar equivalent of the bidentate ligand) in benzene. To this solution was added a methanol solution of sodium tetraphenylborate or sodium tetrafluoroborate:

$$R_3SbX_2 + 2L + 2NaY \longrightarrow [R_3SbL_2][Y]_2 + 2NaX$$

After removal of the sodium halide, the product was recovered from the filtrate by concentration and was recrystallized from petroleum ether. The compounds were characterized by elemental analyses (C, H, and, for most of the compounds containing ethylenediamine or bipyridine ligands, N), IR, and for many of the products, PMR spectroscopy. A total of thirty new compounds was reported. Molar conductances for these compounds in nitromethane or dichloromethane were reported. The values were in accord with a 1 : 2 electrolyte structure. Since the PMR spectra reported for the methyl protons in those compounds containing $Me_3Sb$ or $(4\text{-}MeC_6H_4)_3Sb$ groups and monodentate ligands gave only a single resonance signal, the authors suggested that such compounds possessed a trigonal-bipyramidal structure with two oxygen atoms of the ligands in axial positions. Two methyl signals were found for two compounds containing bidentate ligands, $[Me_3Sb(\text{ethylenediamine})_2][BF_4]_2$ and $[Me_3Sb(2,2'\text{-bipyridine})_2][BF_4]_2$. Accordingly, the authors suggested that such compounds possessed trigonal-bipyramidal structures with two nitrogens of the bidentate ligand and one methyl group in equatorial positions.

In a second paper from Raj's laboratory, a number of antimony-containing cations of the type $[R_3SbL_2]^{2+}$, where R was methyl, phenyl, or a substituted phenyl (4-$MeC_6H_4$, 4-$ClC_6H_4$, 4-$FC_6H_4$, or $C_6F_5$), and L was a monodentate ligand such as thiourea, hexamethylphosphoramide, triphenylarsine oxide, triphenylphosphine oxide, or dimethyl sulfoxide, were prepared [100]. Bidentate ligands L′ were also used (where L′ was 2,2′-bipyridine or ethylenediamine) to yield cations of the type $[R_3SbL']^{2+}$. In all cases the anion was $[ClO_4]^-$. The compounds were prepared by means of the following procedures:

$$R_3SbX_2 + 2L + 2AgClO_4 \xrightarrow[\text{r.t.}]{\text{PhH}} [R_3SbL_2][ClO_4]_2 + 2AgX$$

$$R_3SbX_2 + L' + 2AgClO_4 \xrightarrow[\text{r.t.}]{\text{PhH}} [R_3SbL'][ClO_4]_2 + 2AgX$$

The reactions were carried out in a nitrogen atmosphere under anhydrous conditions. The resulting compounds were susceptible to hydrolysis by atmospheric moisture to give the oxygen-bridged complexes $[(R_3SbL)_2O][ClO_4]_2$. When L was pyridine *N*-oxide, only the oxygen-bridged compounds could be isolated (where R was Me, Ph, 4-$MeC_6H_4$, 4-$ClC_6H_4$, 4-

$FC_6H_4$, or $C_6F_5$). In another reaction, the compounds $[R_3Sbacac][ClO_4]$ were prepared as follows:

$$R_3Sb(OMe)Cl + Hacac + AgClO_4 \xrightarrow{PhH} [R_3Sbacac][ClO_4] + AgCl + MeOH$$

(where Hacac was acetylacetone and R was Ph or 4-$MeC_6H_4$)

Conductance measurements were carried out in dichloromethane or nitromethane and the reported values were in good agreement with reported values for 1:2 electrolytes (except, of course, for the compounds of the type $[R_3Sbacac][ClO_4]$, which were 1:1 electrolytes). The new compounds were characterized by IR and PMR spectroscopy and by elemental analyses. On the basis of these spectral results, it was concluded that the cations of the type $[R_3SbL_2]^{2+}$ possessed trigonal-bipyramidal antimony atoms with the ligands L in axial positions. By contrast, the IR and PMR spectral results suggested that the cations containing the bidentate ligands 2,2′-bipyridine or ethylenediamine were asymmetrical with the bidentate group bonded to the antimony in either two equatorial positions or in one equatorial and one axial position. With the cations $[R_3SbL]^+$, where L was acac, the absence of a free carbonyl absorption band around 1720–1660 $cm^{-1}$ and the presence of a coordinated carbonyl absorption band in the region 1580–1560 $cm^{-1}$ indicated that the acetylacetonato group was chelated to the antimony.

In continuation of previously reported work on hexacoordinated organoantimony(V) compounds, Singhal, Aggarwal, and Raj [101] have reported the synthesis and chemical properties of a number of compounds of the type $R_3Sb(X)L$ and $R_4SbL$, where R was Ph or 4-$MeC_6H_4$, X was I, Cl, or Br, and LH was a $\beta$-diketone (acetylacetone or $Me_3CC(O)CH_2C(O)CMe_3$), ethyl acetoacetate, or diethyl malonate. Several different methods were used for preparing these compounds. When the dihalides, $R_3SbX_2$ (where X was Cl or Br) were refluxed with the sodium salt of the $\beta$-diketone or $\beta$-diketo ester in benzene solution, only one halogen was displaced to give the compounds $R_3Sb(X)L$, even though either one or two molar equivalents of the sodium salt of the ligand were used. It was suggested that this result was due to a steric factor. Thus, compounds of the type $R_3Sb(L')L$ (where L′ was $O_2CMe$ or OMe) could be prepared from $R_3Sb(X)L$ and sodium acetate or sodium methoxide, respectively. The structure of compounds of the type $R_3Sb(L')L$ was based only on IR spectroscopic evidence; neither analytical data nor chemical properties for these compounds were given. Compounds of the type $R_3Sb(I)L$ were prepared from the mixed halogen compounds $R_3Sb(Cl)I$ or $R_3Sb(Br)I$. It was found that only the Cl or Br was displaced when the mixed halogen compounds were refluxed with the sodium salts of the ligands. Only one compound of the type $Ph_4SbL$, namely, $Ph_4SbOC(Me_3C)=CHC(O)CMe_3$, was prepared. The new compounds were characterized by elemental analysis and by IR and PMR spectroscopy. On the basis of the IR spectra, it was concluded that the ligands were bonded to antimony through a C–O $\sigma$-bond and a $\pi$-bonded carbonyl oxygen, *i.e.*, the ligands were bidentate so that the antimony atom was hexacoordinate.

Wirringa, Roesky, and coworkers [102] have reported the preparation of two new compounds containing $Sb^V$–O–Re bonds as well as one compound containing an Sn–O–Re bond and one containing an Sn–N–Re bond. The first compound $Ph_3Sb(OReO_3)_2$ was prepared from triphenylstibine oxide and $Re_2O_7$ in acetonitrile:

$$(Ph_3SbO)_2 + 2Re_2O_7 \xrightarrow[14\ h,\ RT]{MeCN} 2Ph_3Sb(OReO_3)_2$$

Suitable crystals for X-ray diffraction were obtained by recrystallization from acetonitrile. The geometry of the antimony atom was trigonal-bipyramidal with the phenyl groups in equatorial positions. The Re-O-Sb angle was 177.9° and the two perrhenate groups were in axial positions. The second antimony-rhenium compound was obtained from 1 molar equivalent of $(Ph_3SbO)_2$ and 1 molar equivalent of $Re_2O_7$:

$$(Ph_3SbO)_2 + Re_2O_7 \xrightarrow[80^\circ C,\ 6\ h]{MeCN} O_3ReOSb(Ph_3)OSb(Ph_3)OReO_3$$

All of the new compounds were characterized by elemental analyses, IR, $^1H$ and $^{13}C$ NMR, and mass spectroscopy.

The detection and quantification of biomethylated arsenic compounds in seawater have been well documented. Successful assay methods are dependent on the availability of well characterized methylarsenic(V) compounds that can be reduced to volatile arsines, which are then assayed by atomic absorption. Although attempts have been made to apply the same techniques to antimony compounds, the lack of well characterized methylantimony(V) compounds has called such attempts into question. The present paper by Dodd and coworkers [103] describes attempts to prepare such compounds and to test their use by atomic absorption studies.

Trimethylantimony dichloride was reduced to trimethylstibine with $KBH_4$ in aqueous solution and the volatile stibine collected in a cold trap. Oxidation with mercuric oxide in acetone solution led to the formation of trimethylantimony dihydroxide, $Me_3Sb(OH)_2$, in 51% yield. This compound was then treated with trifluoroacetic acid to give trimethylantimony bis(trifluoroacetate). An X-ray diffraction study of the latter compound revealed that the geometry of the antimony atom was that of a trigonal bipyramid with the three methyl groups in equatorial positions. If, instead of using trifluoroacetic acid, the trimethylstibine was treated in ether solution with 30% hydrogen peroxide, the product was $Me_3Sb(O_2H)_2$. This material exploded violently when heated with a heat gun *in vacuo*. In addition to the above compounds containing three methyl groups, several organoantimony compounds with two methyl groups were prepared. Thermolysis of $Me_3SbCl_2$ yielded $Me_2SbCl$ which, after trap-to-trap distillation, was treated with hydrogen peroxide in aqueous acetone and the solution refluxed for 16 h. The product obtained, after removal of the solvents, was $Me_2SbCl(O_2H)_2$. The corresponding bromo compound, $Me_2SbBr(O_2H)_2$, was obtained from $Me_3SbBr_2$ in the same manner. If the reflux step in the reaction of $Me_2SbCl$ with hydrogen peroxide was omitted, the product was $(Me_2Sb)_2O$ rather than $Me_2SbCl(O_2H)_2$. The authors were unable to prepare dimethylstibinic acid, $Me_2SbO(OH)$, by methods described in the literature. Nor were they successful in preparing any well characterized monomethylantimony(V) compounds. Thus, the oxidation of the known but unstable hydride $MeSbH_2$ with a variety of oxidizing agents did not lead to the isolation of any pure compounds. Similar failures were reported for the oxidation of $MeSbCl_2$. Insoluble polymeric products were obtained by the hydrolysis of $MeSb(OMe)_4$. The authors were apparently unaware of the recent paper by Wieber and coworkers [104] describing the preparation and thorough characterization of methylstibonic acid and its sodium salt.

All of the compounds described in the present paper were characterized by elemental analyses, PMR, and IR spectroscopy. Having obtained pure compounds containing either two or three (but not one) methyl groups, the authors treated dilute solutions of the compounds $Me_3SbCl_2$, $Me_3Sb(OH)_2$, and $Me_2SbCl(O_2H)_2$with sodium borohydride and passed the reaction products through a gas chromatograph fitted with an atomic absorption spectrometer detector. Instead of the expected single peak, four peaks were obtained with each compound. The authors suggested that the four peaks were produced by the antimony compounds $SbH_3$, $MeSbH_2$,$Me_2SbH$, and $Me_3Sb$, resulting from molecular rearrangement of the initially produced stibines. These results cast doubt on published reports of speciation of antimony compounds in sea water.

Kraft and Wieber [105] have prepared several compounds of the type $(Me_3SbL)_2O$, where L was a dithiocarbamate ($S_2CNMe_2$ or $S_2CNEt_2$), a xanthate ($S_2COMe$ or $S_2COEt$), or a dithiophosphate ($S_2P(OMe)_2$ or $S_2P(OEt)_2$). The compounds were obtained by the reaction of $\mu$-oxobis(bromotrimethylantimony) with the sodium salt of the ligand:

$$(Me_3SbBr)_2O + 2NaL \xrightarrow{CH_2Cl_2} (Me_3SbL)_2O + 2NaBr$$

The known starting bromo compound was obtained from trimethylantimony dihydroxide and trimethylantimony dibromide:

$$Me_3Sb(OH)_2 + Me_3SbBr_2 \longrightarrow (Me_3SbBr)_2O + H_2O$$

The new compounds were colorless (dithiocarbamates and dithiophosphates) or pale yellow (xanthates) solids, all of which decomposed at fairly low temperatures when heated. They were stable at room temperature for many weeks in an inert atmosphere. Molecular-weight determinations in benzene showed them to be monomolecular. They were characterized by elemental analyses, $^1H$ and $^{13}C$ NMR, and IR spectroscopy. They were soluble in such organic solvents as dichloromethane, chloroform, and benzene, and in solution they were easily hydrolysed:

$$(Me_3SbL)_2O + H_2O \rightleftharpoons Me_3SbL_2 + Me_3Sb(OH)_2$$

In dilute solution the equilibrium was shifted to the left, but in concentrated solution the dihydroxide precipitated from solution, and it was possible to obtain compounds of the type $Me_3SbL_2$ from the mother liquors. However, because of the close similarity of their physical properties, it was difficult to separate the compounds of the type $Me_3SbL_2$ from the $(Me_3SbL)_2O$ type compounds. The IR spectra of the two types of compounds differed only in the presence of bands at 700–740 $cm^{-1}$, due to the Sb–O–Sb bonding in the anhydride type compounds. However, the $^1H$ and $^{13}C$ NMR spectra of the Sb–Me hydrogens and carbons were at 0.3–0.4 ppm ($^1H$) or 1–2 ppm ($^{13}C$) higher fields in the $Me_3SbL_2$ type compounds. An X-ray diffraction study [106] of the compound $Me_3Sb(S_2CNMe_2)_2$ had previously shown that the geometry of the Sb atom was that of a slightly distorted trigonal bipyramid with the three methyl groups in equatorial positions and two unidentate dithiocarbamate groups in axial positions. Since the compounds of the type $(Me_3SbL)_2O$ and $Me_3SbL_2$, described in the present paper, have similar IR spectra (except for the Sb–O–Sb bands in the $(Me_3SbL)_2O$ compounds), it would seem that the structures of the two types of compounds were similar to the structure of the dithiocarbamate.

Bis(2,4,6-tribromophenoxy)triphenylantimony was prepared in 70–80% yield from a dihalotriphenylantimony and 2,4,6-tribromophenol [107]. The product was effective as a flame retardant for polyethylene with no adverse effects on the mechanical properties of the polymer.

A mixture of dimethyltin diiodide and triphenylantimony diiodide in dichloromethane was used as the catalyst for the formation of thermosetting resins derived from mixtures of polyepoxides, polyisocyanates, and vinyl monomers [108].

In several papers, Nomura and coworkers have described the use of triphenylstibine oxide and tetraphosphorus decasulfide as a catalytic mixture for a variety of reactions such as the conversion of carboxylic acids to the corresponding thiolic acids, carboxylic esters, or amides. Thus, *N*-hexylacetamide was prepared in 90% yield from acetic acid, hexylamine, and the catalytic mixture [109]. In a new paper from Nomura's laboratory, the use of this catalytic mixture to prepare substituted ureas from primary amines and carbon dioxide was described [110]:

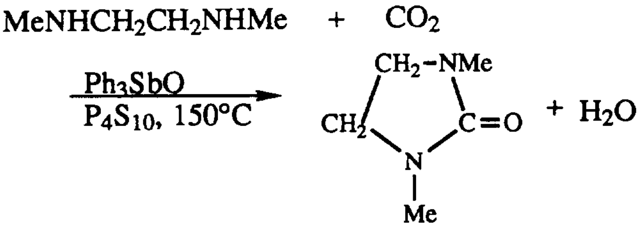
$$2RNH_2 + CO_2 \xrightarrow[P_4S_{10},\ 80°C]{Ph_3SbO} (RNH)_2CO + H_2O$$

Thus, butylamine (4 mmol) in benzene, when heated with carbon dioxide under pressure at 80°C for 24 h in the presence of 1 mmol of $Ph_3SbO$ and 2 mmol of $P_4S_{10}$, gave *N,N′*-dibutylurea in 87% yield. Benzene appeared to be the only successful solvent for this reaction. With other solvents (toluene, dichloromethane, acetonitrile, THF, and pyridine) the yields of *N,N′*-dibutylurea were much smaller. In the absence of catalyst, only butylammonium *N*-butylcarbamate was formed. In addition to butylamine, excellent yields of the corresponding *N,N′*-dialkylureas were obtained from propylamine, isopropylamine, isobutylamine, sec-butylamine, and cyclohexylamine. Tert-butylamine, allylamine, and aniline, however, gave yields of only 27, 21, and 21%, respectively.

The reaction of secondary amines with carbon dioxide was unsatisfactory. At temperatures lower than 150°C, the amines were recovered unchanged, while at 160°C, thioureas were obtained:

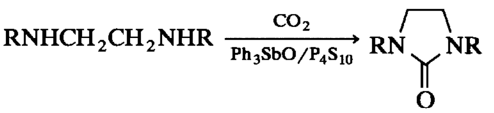
$$2Et_2NH + CO_2 \xrightarrow[P_4S_{10},\ 160°C]{Ph_3SbO} (Et_2N)_2CS$$

Thus, with diethylamine, *N,N,N′,N′*-tetraethylthiourea was obtained in 21% yield. However, *N,N′*-dimethylethylenediamine gave 1,3-dimethylimidazolidin-2-one in 60% yield under the same reaction conditions:



In a later paper from Nomura's laboratory, the carbonylation of amines to produce substituted ureas, using triphenylstibine oxide and tetraphosphorus decasulfide as catalysts, was described in greater detail [111]. In addition to monoamines, the work was expanded to include diamines. The usual reaction conditions (using primary aliphatic amines) was to heat the amine, $Ph_3SbO$, and $P_4S_{10}$ in a ratio of 40:1:2 in benzene in a $CO_2$ atmosphere (4.9 MPa) for 12 h at 80°C. The isolated yields of *N,N′*-dialkylureas, $CO(NHR)_2$, were as follows: R = Bu, 88%; iso-Bu, 89%; sec-Bu, 73%; tert-Bu, 30%; allyl, 62%. When allylamine was used, the amount of catalyst was doubled. Aniline gave a 48% yield of *N,N′*-diphenylurea, but the temperature was increased to 120°C, and the amount of catalyst was doubled. Under similar conditions (except that the reaction was heated for only 3 h) dimethylamine gave a 33% yield of tetramethylurea. The course of the reaction was followed by $^{13}C$ NMR spectroscopy at four different temperatures (15, 30, 60, and 80°C). The amine used was butylamine. At 15° butylammonium butylcarbamate was formed. This was actually isolated and characterized by $^{13}C$ NMR spectroscopy. Other intermediates in the reaction were suggested based on the NMR spectral changes as the reaction proceeded at the different temperatures.

In addition to the reaction with monoamines, the carbonylation of diamines to yield imidazolidin-2-ones was investigated:



With ethylenediamine at 150°C for 12 h, the yield of the cyclic urea (where R was H) was 85%, but the yield was only 17% after heating for 24 h at 80°C. No product was obtained in the absence of the catalytic mixture. Other diamines used to prepare imidazolidin-2-ones were the following: $RNHCH_2CH_2NH_2$, where R was Me, Ph, $HOCH_2CH_2$, or $HOCH(Me)CH_2$, as well as $MeNHCH_2CH_2NHMe$. The carbonylation of a mixture of primary and secondary amines was also investigated. Thus, when butylamine and diethylamine, in a 1:1 ratio in benzene solution, were heated together for 24 h, two products $BuNHCONEt_2$ (**6**) and BuNHCONHBu (**7**) were obtained. However, the ratio between the two products could be varied by controlling the reaction conditions. Thus, at 120°C for 24 h, the yields of **6** and **7** were 39 and 55%, respectively. At 100°C, the yields were 34 and 32%, respectively. By increasing the molar ratio of diethylamine to 2:1 still at 100°C for 24 h, the yields of **6** and **7** were 31 and 3%, respectively. At 80°C for 48 h, the yields of the two products were 42 and 1%, respectively. The carbonylation of a mixture of butylamine and *N,N′*-dimethylethylenediamine was also investigated. In this case, four products, namely (**7**), $\mathrm{BuNHCON(Me)CH_2CH_2NHMe}$ (**8**). $\mathrm{BuNHCON(Me)CH_2CH_2N(Me)CONHBu}$ (**9**), and *N,N'*-dimethylimidazolidin-2-one (**10**) were obtained. As in the previous examples ($\mathrm{BuNH_2}$ and $\mathrm{Et_2NH}$), the yields of the various products could be varied by varying the reaction conditions. Thus, at 150°C the yields of **7** and **10** were 66 and 94%, respectively, with no **8** or **9** formed. At 120°C, the yields of **7** and **10** were 44 and 87%, respectively. At 100°C, the yields of these two products were reduced to 34 and 65%, and a 16% yield of **9** was also obtained. Finally, at 80°C, varying yields of **8**, **9**, and **10** were obtained.

The majority of the products described in this paper were known compounds and were identified by comparison of their mps with those described in the chemical literature. The new compounds were characterized by $^1$H and $^{13}$C NMR and IR spectroscopy, and by elemental analyses.

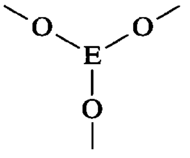
Feher and coworkers have written extensively on condensed silsesquioxanes. A number of antimony(V)-containing derivatives of these silicon compounds have been previously described. Among the synthetic methods the authors contemplated for further syntheses was the reaction of silsesquioxane anions with metal halide complexes. Such reactions were known to be hindered, however, by the susceptibility of the silsesquioxane framework towards cleavage and/or polymerization by moderately nucleophilic reagents. In an attempt to avoid this difficulty, the authors prepared four silsesquioxanes containing $\mathrm{SiOSbMe_4}$ groupings, knowing that such compounds were latent sources of siloxide anions and $\mathrm{Me_4Sb^+}$ cations [112]. Of the four incompletely condensed silsesquioxane precursors chosen, one contained three silanol groups, two contained two silanol groups, and one contained one silanol group. Other silicon atoms in the silsesquioxane framework were bonded to trimethylsilyl groups and/or cyclohexyl groups. The silsesquioxanes were then treated with excess pentamethylantimony which resulted in the formation of compounds containing one, two, or three $\mathrm{SiOSbMe_4}$ groups:

$$\geqslant\!\mathrm{SiOH} + \mathrm{Me_5Sb} \longrightarrow \geqslant\!\mathrm{SiOSbMe_4} + \mathrm{MeH}$$

It was found that replacement of the first hydrogen of the silsesquioxane containing three OH groups occurred at a much faster rate than replacement of the second or third hydrogen. Thus, it was necessary to heat the reaction mixtures to 50–60°C and/or for a prolonged reaction time, in order to replace the second or third hydrogen. The replacement reaction was followed by means of $^1$H and $^{13}$C NMR. It was found that the reaction of the compound containing three silanol groups with less than one equivalent of $\mathrm{Me_5Sb}$ led to a product in which there was a rapid exchange of $\mathrm{Me_4Sb}$ groups with remaining hydrogens on OH groups. In further proof of this rapid exchange, it was found that a mixture of two equivalents of the compound containing three silanol groups plus one equivalent of the silsesquioxane with three $\mathrm{OSbMe_4}$ groups yielded a substance whose NMRspectrum was identical with the product obtained when the silsesquioxane with three silanol groups reacted with one equivalent of $\mathrm{Me_5Sb}$. An X-ray diffraction study of the silsesquioxane with three $\mathrm{OSbMe_4}$ groups was carried out. The structure of each antimony atom was that of a trigonal bipyramid with the oxygen and one methyl group in apical positions. It was also apparent that the $\mathrm{Si_7O_9}$ framework of the silsesquioxane would easily accommodate the three bulky $\mathrm{OSbMe_4}$ groups.

Among the various reactions studied in the present paper was that between the silsesquioxane with three silanol groups (2 equiv) and the silsesquioxane with three $\mathrm{OSbMe_4}$ groups (1 equiv). When these two materials were heated together in PhH at 65°C for 4 h, the resulting product (which contained one $\mathrm{OSbMe_4}$ group) could only have been formed by cyclodehydration of two of the silanol groups. Since the starting compound with three silanol groups does not undergo dehydration when heated as high as 150°C, the formation of the dehydration product was unexpected. It was known from previous work, however, that dehydration of silsesquioxanes was catalyzed by bases. The only possible base present would be $\mathrm{Me_4SbOH}$, which could have been formed from $\mathrm{Me_5Sb}$ by traces of water. Accordingly, the authors added small amounts of $\mathrm{Me_4SbOH}$ ($\sim 3$ mol%) to incompletely condensed silsesquioxanes containing silanol groups and found, indeed, that this base catalyzed cyclodehydration when the silsesquioxane was heated in PhH to 80°C.

Since the original purpose of the present research was to prepare silsesquioxanes which would react with strong nucleophiles without cleavage and/or polymerization of the silsesquioxane framework, the authors treated their silsesquioxanes, containing one, two, or three $\mathrm{OSbMe_4}$ groups, with the powerful nucleophile $\mathrm{Me_3SiCl}$ in hexane at 25°C. In each case the $\mathrm{SbMe_4}$ group was replaced quantitatively with an $\mathrm{Me_3Si}$ group. Finally, the silsesquioxane with three $\mathrm{OSbMe_4}$ groups was treated with the following nucleophiles: $\mathrm{SbCl_3}$, $\mathrm{CpTiCl_3}$ (where Cp was cyclopentadienyl), $\mathrm{MeGeCl_3}$, $\mathrm{MeSnCl_3}$, and $\mathrm{PCl_3}$. In each case all three $\mathrm{SbMe_4}$ groups were replaced to form completely condensed silsesquioxanes containing the following linkage:



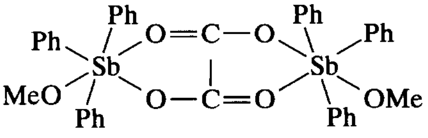
(where E was Sb, Ti, Ge, Sn, or P)

In the previous paper, Feher and coworkers described the reaction of incompletely condensed silsesquioxanes containing one, two, or three silanol groups with pentamethylantimony to yield derivatives containing Si–O–$SbMe_4$ groups. The authors have now described the reaction of one of these silanols (the compound containing three silanol groups) with $BI_3$ to yield a silsesquioxane in which the boron was bonded to three silicon atoms by Si–O–B bonds, *i.e.*, a borate ester [113]. This ester was inert to a number of Lewis bases, but did react with $Me_3SiOSbMe_4$ to give an amorphous white foam. Although the PMR spectrum of this product showed a new resonance for the $Me_3SiO$ group, the $^{13}C$ NMR spectrum revealed at least seven sharp resonances in the methine region indicating that a mixture of products was formed. Variable temperature NMR studies also showed that the composition of this mixture was temperature dependent. None of the various products of the mixture could be identified spectroscopically.

In a third paper in 1992 from Feher's laboratory (a short Communication to the Editor), the synthesis of an antimony(V)-containing aluminosilsesquioxane that violated Loewenstein's Rule was described [114]. Loewenstein's Rule states that whenever two $MO_4$ (where M was Al or Si) tetrahedra are linked by one oxygen bridge, the center of only one of these tetrahedra can be occupied by aluminum; the other center must be occupied by silicon. This rule has been used to dismiss the possibility that $O_3AlOAlO_3$ groups play a role in the chemistry of aluminosilicates and zeolites. Feher and coworkers have synthesized, in a number of steps, an aluminosilsesquioxane dianion containing an AlOAl linkage. The two cations in this complex were $Me_4Sb^+$ and $Me_4P^+$ and several of the intermediate compounds in the synthesis contained either $Me_4Sb^+$ ions or $AlOSbPh_4$ groups.

In the majority of organoantimony(V) compounds the configuration of the antimony atom is trigonal-bipyramidal, although in pentaphenylantimony itself it is square-pyramidal. In a new paper from Sowerby's laboratory, the authors noted that dioxo chelating groups attached to antimony favored square-pyramidal geometry for the antimony atom [115]. Accordingly, they investigated the molecular structure of organoantimony(V) compounds containing oxalato groups. Triphenylantimony oxalate had previously been reported by Goel and coworkers [116] who, solely on the basis of its IR spectrum, concluded that the compound possessed a structure in which the oxalate group bridged two antimony atoms. The present authors refluxed silver oxalate with triphenylantimony dichloride and obtained a crystalline solid (**11**), mp 198–199°C, which was about 40°C higher than the mp reported by Goel and coworkers. Furthermore, the IR spectrum of **11** differed from Goel's compound, and the mass spectrum suggested the presence of the $[Ph_4Sb]^+$ cation. When triphenylantimony dichloride and silver oxalate were shaken together in methanol, the IR spectrum of the initial reaction product was the same as that reported by Goel. When this was recrystallized from methanol, however, a different product (**12**) was obtained. The IR spectrum of **12** suggested the presence of a methyl group, and the mass spectrum showed peaks assigned to $Ph_3Sb(OMe)$, $Ph_2Sb(OMe)$, and PhSb(OMe). Finally, bis(tetraphenylantimony) oxalate (**13**), also previously reported by Goel [117], was prepared by shaking tetraphenylantimony bromide and silver oxalate in toluene.

All of these compounds (**11**, **12**, and **13**) were characterized by elemental analyses and IR spectroscopy. The crystal and molecular structure of all three compounds was obtained by means of X-ray diffraction. Compound **11** was ionic and possessed the structure $[Ph_4Sb][Ph_2Sb(Ox)_2]$ (where Ox was $O_2CCO_2$). The Sb–C distances in the cation were all essentially equal, but the C–Sb–C angles varied from 106.8° to 121°. The anion contained a distorted octahedral antimony atom with two *cis* phenyl groups and two bidentate oxalato groups in which there were two longer *cis* oxygen atoms and two shorter *trans* oxygen atoms.Compound **12** possessed the structure $[Ph_3Sb(OMe)]_2Ox$ with two distorted octahedral antimony atoms. The oxalato group was quadridentate and formed two five-membered rings. The three phenyl groups and the three oxygen atoms occupied meridional positions around the antimony atom:



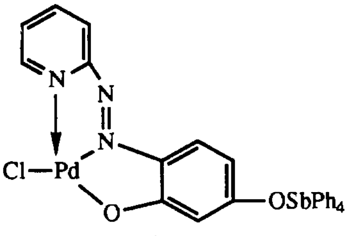
**12**

Compound **13** possessed the structure $(Ph_4Sb)_2Ox$, similar to that of compound **12** with the methoxy group replaced by a phenyl group. There were two independent centrosymmetric molecules in the unit cell, with small differences in the coordination of the two oxalato groups between the two molecules. In the synthesis of compound **11** there was a redistribution of phenyl groups. The authors considered, but could find no evidence for the following:

$$2Ph_3SbCl_2 \longrightarrow [Ph_4Sb][Ph_2SbCl_4]$$

They speculated extensively on several other mechanisms for the redistribution without offering clear evidence for any particular pathway.

A tetraphenylantimony 4-(2-pyridylazo)resorcinolate complex with palladium chloride has been prepared, and the following structure has been assigned on the basis of elemental analysis, IR, and $^1$H NMR spectra [118]:



In an earlier paper from Huang's laboratory, it was reported that pentaorganoantimony compounds reacted with aldehydes to give addition products which could then be hydrolysed to alcohols. Thus, from tetrabutylbenzylantimony and any of a number of aldehydes, homobenzylic alcohols were obtained:

$$\mathrm{Bu_4SbCH_2Ph + RCHO \longrightarrow [RCH(CH_2Ph)OSbBu_4] \xrightarrow{H_2O} RCH(CH_2Ph)OH + Bu_4SbOH}$$

The reaction was later extended to the preparation of homoallylic alcohols, hydroxyesters, and hydroxynitriles. It was also reported that the pentaorganoantimony compounds did not react with ketones. The reaction has now been extended to the reaction of pentaorganoantimony compounds with acyl chlorides to yield ketones in (with a few exceptions) excellent yields [119]. The pentaorganoantimony compound was prepared in several steps, starting with tributylstibine. This was converted to an antimony(V) compound by treatment with an alkyl bromide RBr (where R was benzyl, crotyl, or allyl). Further treatment with butylmagnesium bromide gave the pentaorganoantimony coupound, which, without isolation, reacted with the acyl chloride to yield the ketone:

$$\mathrm{Bu_3Sb + RBr \xrightarrow{RT} [Bu_3RSbBr] \xrightarrow[THF,\,-78°C]{BuMgBr} [Bu_4RSb] \xrightarrow{R'COCl} RCOR' + Bu_4SbCl}$$

Thus, from benzyltetrabutylantimony and aroyl chlorides ($\mathrm{RC_6H_4COCl}$, where R was H, 4-Me, 4-Cl, or 4-Br), or with alkyl or alkenyl acyl chlorides (PhCH=CHCOCl, $\mathrm{Me(CH_2)_4COCl}$, and $\mathrm{Me(CH_2)_9COCl}$), the corresponding ketones (in yields of 66–90%) were obtained. With tetrabutylcrotylantimony and several acyl chlorides, $\alpha$-methylallyl ketones were obtained:

$$\mathrm{Bu_4SbCH_2CH{=}CHMe + RCOCl \longrightarrow RCOCH(Me)CH{=}CH_2 + Bu_4SbCl}$$

(where R was Ph, 4-$\mathrm{MeC_6H_4}$, 4-$\mathrm{ClC_6H_4}$, 4-$\mathrm{O_2NC_6H_4}$, $\mathrm{PhCH_2C_6H_4}$, or $\mathrm{Me(CH_2)_6}$)

None of the crotyl ketone, $\mathrm{RCOCH_2CH = CHMe}$, was obtained from this reaction. Although the benzyl and $\alpha$-methylallyl ketones were obtained in excellent yields, allyltetrabutylantimony reacted with aroyl chlorides to give allyl aryl ketones in poor yields ($\mathrm{PhCOCH_2CH{=}CH_2}$, 15%; 4-$\mathrm{ClC_6H_4COCH_2CH{=}CH_2}$, 40%).

In addition to tetrabutylallyl-, tetrabutylcrotyl-, and tetrabutylbenzylantimony, a number of other pentaorganoantimony compounds were treated with benzoyl chloride. Thus, from the following antimony compounds, the following ketones, in the reported yields, were obtained: $\mathrm{Bu_5Sb}$, PhCOBu, 92%; $\mathrm{Bu_3SbPh_2}$, PhCOPh, 88%; $\mathrm{Bu_3SbMe_2}$, PhCOMe, 79%; $\mathrm{Ph_3SbMe_2}$, PhCOPh, 88%; $\mathrm{Bu_3SbEt_2}$, PhCOEt, 62% and PhCOBu, 25%; $\mathrm{Bu_3Sb(Ph)CH_2Ph}$, PhCOPh, 54% and $\mathrm{PhCOCH_2Ph}$, 36%; $\mathrm{Bu_3Sb(Ph)CH_2CH{=}CHMe}$, $\mathrm{PhCOCH(Me)CH{=}CH_2}$, 44% and PhCOPh, 32%. From these results the following order of transfer of the alkyl or aryl group was demonstrated: $\mathrm{MeCH{=}CHCH_2 > Ph > PhCH_2 > Me > Et > Bu}$. It was also shown that neither ethyl benzoate nor benzyl cyanide reacted with the pentaorganoantimony compounds. Thus, the authors suggested that the reaction of the antimony compounds with acyl chlorides was an excellent method for preparing ketones containing other functional groups such as an ester, nitro, nitrile, or halo group. It was also obvious that the pentaorganoantimony compounds did not react with ketones. The authors found, however, that such a reaction did occur in the presence of aluminum chloride:

$$\mathrm{Bu_4SbCH_2CH{=}CHR + R^1R^2CO \xrightarrow[-78°C,\,THF]{AlCl_3\cdot Et_2O} R^1R^2C(OH)CHRCH{=}CH_2}$$

(where R was H or Me)

Thus, from tetrabutylallylantimony and the following ketones, the corresponding alcohols were obtained in the stated yields: acetophenone, 85%; cyclohexanone, 88%; cyclopentanone, 88%; 3-pentanone, 63%. Similarly, tetrabutylcrotylantimony reacted with cyclohexanone or 3-pentanone to give the corresponding alcohols in 85 and 75% yields, respectively. The majority of the ketones and all of the alcohols were known compounds, and their identity was established either by comparison with authentic samples or by comparison with published data on such compounds. Two of the ketones, 2-methyl-1-(4-tolyl)-3-buten-1-one and 3-methyl-1-phenyl-4-penten-2-one, were characterized by elemental analyses, and by $^1$H NMR, IR, and mass spectrometry. Two different methods were used for the preparation of the pentaorganoantimony compounds. By one method tributylstibine was quaternized with benzyl, allyl, or crotyl bromide and the resulting quaternary compound treated with butyl- or phenylmagnesium bromide. By the other method, tributylstibine was brominated and the resulting dibromide was treated with methyl-, ethyl-, or phenylmagnesium bromide.

In another paper from Huang's laboratory, the attempted preparation of some tetrabutylpropargylantimony compounds was described [120]. It was found that tributylstibine reacted with propargyl bromide to yield allenyltributylantimony bromide:

$$Bu_3Sb + HC{\equiv}CCH_2Br \xrightarrow{RT} Bu_3Sb(Br)CH{=}C{=}CH_2$$

The allenyl compound was characterized by $^1H$ NMR and IR spectroscopy. It was a stable compound and did not react with aldehydes even when heated to 120°C. When treated with butylmagnesium bromide, it was converted to allenyltetrabutylantimony which did react with a variety of aldehydes to yield homopropargylic alcohols:

$$Bu_4SbCH{=}C{=}CH_2 + RCHO \longrightarrow$$
$$RCH(CH{=}C{=}CH_2)OSbBu_4 \xrightarrow{H_2O}$$
$$RCH(OH)CH_2C{\equiv}CH + Bu_4SbOH$$

(where R was Ph, $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $PhCH{=}CH$, or $Me(CH_2)_8$)

The yields varied from 78–92%. No reaction occurred when the allylenic compound was treated with cyclohexanone. When tributylstibine was treated with 1-bromo-2-butyne, the acetylenic compound was formed (rather than the allylenic compound):

$$Bu_3Sb + MeC{\equiv}CCH_2Br \longrightarrow Bu_3Sb(Br)CH_2C{\equiv}CMe$$

This bromo product reacted with aldehydes to give only low yields of homopropargylic and allylenic alcohols. However, the tetrabutyl compound $Bu_4SbCH_2C{\equiv}CMe$, obtained from the bromo compound and butylmagnesium bromide, gave mixtures of homopropargylic and allylenic alcohols:

$$Bu_4SbCH_2C{\equiv}CMe + RCHO \longrightarrow$$
$$RCH(CH_2C{\equiv}CMe)OSbBu_4 \xrightarrow{H_2O}$$
$$RCH(OH)CH_2C{\equiv}CMe + RCH(OH)CH{=}C{=}CHMe$$

(where R was Ph, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $C_6H_{11}$, $Me(CH_2)_7$, or PhC(Me)H)

The total yields of alcohols varied from 80–89%. With aromatic aldehydes the allylenic alcohols predominated (with the homopropargylic alcohols being obtained in less than 3% yields), but with the aliphatic aldehydes the homopropargylic alcohols constituted a significant portion of the product.

The molecular motions of solid $[Me_4Sb][PF_6]$ have been determined over a broad temperature range [121]. The NMR spin lattice relaxation time $T_1$, and the NMR second moments of $^1H$ and $^{19}F$ nuclei were determined in the range $8.6 \leq T/K \leq 332.3$. The cation undergoes isotropic tumbling for $T > 260$ K and thermally activated methyl group rotation in the temperature range $T < 196$ K. Two crystallographically inequivalent methyl groups were found by X-ray diffraction.

Pulham and coworkers [122] have reported the gas-phase electron diffraction determination of the structures of pentamethylantimony and pentamethyltantalum. This work was the first structural determination of any pentaalkyl compound. The geometry of the pentamethylantimony compound was trigonal-bipyramidal ($D_{3h}$ symmetry). $Sb\text{–}C_{axial}$ and $Sb\text{–}C_{equatorial}$ bond lengths were listed, together with the Sb–C–H mean bond angle. Calculated and experimental radial distribution curves were compared diagramatically. In addition to the structure determinations, the $^{13}C$ NMR spectrum of the antimony compound in $CD_2Cl_2$ was determined down to −90°C, and found to consist only of a sharp single line. An *ab initio* molecular orbital calculation for this compound found that the energy of an optimized $C_{4v}$ (square pyramidal) structure was only 12.1 kJ $mol^{-1}$ higher than the optimized $D_{3h}$ model.

Kraft and Wieber have described the reaction of pentaphenylantimony or (in a few cases) methoxytetraphenylantimony with certain dicarboxylic acids or diols [123]. Thus, pentaphenylantimony reacted with thiodiacetic acid or thiodipropionic acid in the following manner:

$$2Ph_5Sb + S(RCO_2H)_2 \xrightarrow[RT,\ 20\ h]{Et_2O}$$
$$(RCO_2SbPh_4)_2 + 2PhH$$

(where R was $CH_2$ or $CH_2CH_4$)

In a somewhat similar manner iminodiacetic acid or nitrolotriacetic acid underwent reaction with methoxytetraphenylantimony:

$$nPH_4SbOMe + Y(CH_2CO_2H)_n \xrightarrow[RT,\ 1\ h]{MeOH}$$
$$Y(CH_2CO_2SbPh_4)_n + 2MeOH$$

(where Y was NH, $n$ was 2; where Y was N, $n$ was 3)

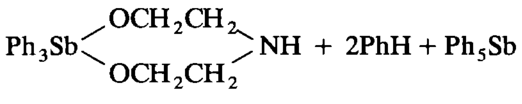
The methoxytetraphenylantimony was prepared by refluxing pentaphenylantimony in methanol. The crude products of the above reactions were sticky residues which retained methanol. They were dissolved in methylene dichloride and the solvents removed by vacuum distillation to yield the pure products as powders. In addition to the reaction of pentaphenylantimony with carboxylic acids, its reaction with several glycols was also investigated:

$$nPh_5Sb + Y(C_2H_4OH)_n \xrightarrow[reflux,\ 3\ h]{PhH}$$
$$Y(C_2H_4OSbPh_4)_n + nPhH$$

(where Y was O or S, *n* was 2; where Y was N, *n* was 3)

The reaction of pentaphenylantimony with diethanolamine took a somewhat different course:

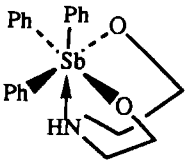
$$2Ph_5Sb + HN(C_2H_4OH)_2 \xrightarrow[\text{reflux, 3 h}]{\text{PhH}}$$



$$Ph_3Sb\genfrac{<}{}{0pt}{}{OCH_2CH_2}{OCH_2CH_2}NH + 2PhH + Ph_5Sb$$

**14**

The crystal and molecular structure of compound **14** was determined by X-ray diffraction. The structure of the antimony atom was octahedral with two phenyl groups and two oxygen atoms in *cis* positions, and a short Sb–N distance (235 pm):



All of the compounds were characterized by elemental analyses, $^1H$ and $^{13}C$ NMR, and IR spectroscopy, and by molecular weight determinations. Melting points and decomposition points were determined by differential thermal analysis. The $^{13}C$ NMR spectrum of compound **14** showed the presence of two different phenyl groups.

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